THE CALCULATION OF THERMODYNAMIC FUNCTIONS FROM SPECTROSCOPIC DATA[1]

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I. INTRODUCTION

Whenever all the energy levels of a system are known all its equilibrium properties may be calculated, including the heat capacity, heat content, entropy, and free energy with which this paper is concerned. The analysis of spectroscopic data is a powerful method of obtaining such energy levels, and within recent years this new thermodynamic tool has been developed rapidly. This review consists of three parts: the first sketches the fundamental theory, the second outlines the more important techniques of numerical calculation, and the third discusses the results that have been obtained by use of the method.

II. FUNDAMENTAL THEORY

Consider an assemblage of N identical systems of one kind and N' of a second kind, where both N and N' are very large numbers. Let the possible energy levels be ϵ_i and ϵ'_j, where i and j represent all the quantum numbers required to specify the condition of a system. Let the number of systems in the various states be N_i, N'_j. The quantum weight of the assemblage in this condition is the number of permutations

$$W = N!\,N'!\left(\prod_i N_i!\right)^{-1}\left(\prod_j N'_j!\right)^{-1} \tag{1}$$

or

$$\log W = N \log N - \sum_i N_i \log N_i + N' \log N' - \sum_j N'_j \log N'_j \tag{2}$$

The most probable state of the assemblage is determined by the conditions

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$$\left.\begin{aligned} -\,\delta \log W &= \sum_i (\log N_i + 1)\,\delta N_i + \sum_j (\log N'_j + 1)\,\delta N'_j = 0 \\ \delta E &= \sum_i \epsilon_i \delta N_i + \sum_j \epsilon'_j\, \delta N'_j = 0 \\ \delta N &= \sum_i \delta N_i = 0 \\ \delta N' &= \sum_j \delta N'_j = 0 \end{aligned}\right\} \tag{3}$$

from which, by Lagrange's method of multipliers,

$$\left.\begin{aligned} N_i/N &= e^{-\mu\epsilon_i}\left(\sum_i e^{-\mu\epsilon_i}\right)^{-1} \\ N'_j/N' &= e^{-\mu\epsilon'_j}\left(\sum_j e^{-\mu\epsilon'_j}\right)^{-1} \end{aligned}\right\} \tag{4}$$

Since appreciable deviations are easily shown to be very improbable, equations 4 are the equilibrium conditions. Then since μ is the same for two substances in equilibrium, it must be a kind of temperature.

In what follows only the unprimed systems are considered. Define

$$S = k \log (W/N!) \tag{5}$$

where k is an as yet undetermined constant. Since this S is an additive property of an assemblage which approaches a maximum as the assemblage approaches equilibrium adiabatically, it must be proportional to the thermodynamic entropy; then by suitable choice of k the two can be made equal.

Define

$$Q = \sum_i e^{-\mu\epsilon_i} \tag{6}$$

The total energy is then

$$E = -\,(N/Q)(\mathrm{d}Q/\mathrm{d}\mu) \tag{7}$$

A kind of specific heat is

$$\mathrm{d}E/\mathrm{d}\mu = (N/Q^2)(\mathrm{d}Q/\mathrm{d}\mu)^2 - (N/Q)(\mathrm{d}^2Q/\mathrm{d}\mu^2) \tag{8}$$

At equilibrium

$$S = Nk \log Q + \mu k E - k \log N! \tag{9}$$

from equations 4 and 5. Define

$$-\,\mu A = N \log Q - \log N! \tag{10}$$

It is clear from equation 9 that A has the properties of maximum work.

The equations 7 to 10 are a complete set and could be used in that form. It is customary, however, to replace the statistical "temperature," μ, by the thermodynamic temperature, T, defined by

$$1/T = \partial S/\partial E = (\partial S/\partial \mu)/(\partial E/\partial \mu) = \mu k \tag{11}$$

When T replaces μ in equation 4 the Maxwell-Boltzmann distribution law is obtained in its familiar form. When T is substituted in equations 7 to 10 the results are

$$E = -Nk(Q'/Q) \tag{12}$$

$$C_v = \mathrm{d}E/\mathrm{d}T = (Nk/T^2)[Q''/Q - (Q'/Q)^2] \tag{13}$$

$$-A/T = Nk \log Q - k \log N! \tag{14}$$

$$S = Nk[\log Q - (1/T)(Q'/Q)] - k \log N! \tag{15}$$

It is evident from the form of the foregoing equations that when the energy of a system splits into several independent parts

$$\epsilon_i = \epsilon_j^{\mathrm{I}} + \epsilon_k^{\mathrm{II}} + \cdots \tag{16}$$

where no quantum number occurs in more than one subscript, then Q is a product of independent factors $Q^{\mathrm{I}}Q^{\mathrm{II}} \cdots$, and the thermodynamic functions are sums, for example $E = E^{\mathrm{I}} + E^{\mathrm{II}} + \cdots$. Now for any system in field-free space the wave equation may be separated to give

$$[\partial^2/\partial x^2 + \partial^2/\partial y^2 + \partial^2/\partial z^2 + (8\pi^2 m/h^2)W]\psi = 0 \tag{17}$$

for the motion of the center of gravity. When the system is confined to a cubical box of edge l the energy levels corresponding to equation 17 are

$$W = (h^2/8ml^2)(n_x^2 + n_y^2 + n_z^2),\ n_u = 0, 1, 2 \cdots \tag{18}$$

Each translational degree of freedom thus makes a separate contribution

$$Q = \sum_0^{\infty} e^{-n^2h^2/8ml^2kT} \tag{19}$$

or

$$\mathbf{Q} = (2\pi mkT/h^2)^{1/2}l + 1/2 \tag{19a}$$

the summation being made by the Euler-Maclaurin expansion formula and becoming asymptotically exact as $h^2/8ml^2kT \rightarrow 0$. Such asymptotic sums and all functions derived from them will be printed in bold-face type throughout this paper. The error in equation 19a as found by direct summation of equation 19 is 1 in 10^3 for $h^2/8ml^2kT = 1.4$ and 1 in 10^6 for $h^2/8ml^2kT = 0.7$. These values are far larger than any of experimental interest; for example, for H_2 at 1°K. with $l = 10^{-2}$ cm., $h^2/8ml^2kT = 10^{-10}$ and the error in equation 19a has become totally insignificant; even when the second term is dropped the error is only 1 in 10^5 in Q, corresponding to 0.00015 cal. per degree in S and rather less in C_v. When this very satisfactory approximation is made, three translational contributions give

$$\mathbf{E} = (3/2)NkT \tag{20}$$

$$\mathbf{C_v} = (3/2)Nk \tag{21}$$

$$\begin{aligned}\mathbf{S} &= Nk[\log (2\pi mk/h^2)^{3/2} + \log V + (3/2) \log T + 5/2 - \log N] \\ &= Nk[\log (2\pi m)^{3/2}k^{5/2}h^{-3} + (5/2) \log T - \log P + 5/2]\end{aligned} \tag{22}$$

$$-\mathbf{F}/T = -A/T - Nk = Nk[\log (2\pi m)^{3/2}k^{5/2}h^{-3} + (5/2) \log T - \log P] \tag{23}$$

$$\mathbf{H} = (5/2)NkT \tag{24}$$

$$\mathbf{C_p} = (5/2)Nk \tag{25}$$

Since the perfect gas law, $PV = NkT$, is used in obtaining equations 22 to 25, it may be well to point out that this law follows at once from equation 20, since for any distribution of velocities $PV = (2/3)E$. The constant k, however, must of course be determined experimentally from equation 21 or 25. When numerical values of the constants are used, the molar entropy and free energy at atmospheric pressure become

$$\mathbf{S} = (5R/2) \log T + (3R/2) \log M - 2.300 \tag{22a}$$

$$-\mathbf{F}/T = (5R/2) \log T + (3R/2) \log M - 7.267 \tag{23a}$$

where M is the molecular weight. This derivation of the Sackur-Tetrode equation is more satisfactory than any that were given before quantum mechanics was developed. It should be noted that the term $-k \log N!$ in equation 9 has been included in the translational contribution to S and $-F/T$; it is not to be used again when the internal energy contributions are evaluated.

III. THE TECHNIQUE OF NUMERICAL CALCULATIONS

The rotational sum for diatomic molecules

For all real molecules the translational energy is the only part that can be separated out as in equation 16. The rotation-vibration energy for a diatomic molecule is represented by some such expression as

$$E = E_0 + hc[\omega_0 v - x\omega_0 v^2 + y\omega_0 v^3 + \cdots] + hc\{B_v[J(J + 1) + \text{const.}] + D_v J^2(J + 1)^2 + \cdots\} \tag{26}$$

where

$$B_v = B_0 - \alpha v + \gamma v^2 + \cdots \tag{26a}$$

$$D_v = D_0 + \beta v + \cdots \tag{26b}$$

The problem of finding Q for an energy of the form in equation 26 is conveniently preceded by finding it for the rotational part

$$E_{\text{rot}} = hc[BJ(J+1) + DJ^2(J+1)^2 + FJ^3(J+1)^3 + \cdots] \tag{27}$$

where for convenience the subscripts v have been dropped.

The wave functions for a rigid rotator are

$$\psi = P_J^M(\cos\theta)e^{iM\varphi} \tag{28}$$

where P_J^M are the associated Legendre polynomials. The corresponding energy levels are

$$E = (h^2/8\pi^2 I)J(J+1) = hcBJ(J+1) \tag{29}$$

The quantum number J measures the total angular momentum and takes values 0, 1, 2 $\cdots$. The quantum number M is the projection of J on a preferred external direction, with allowed values $0, \pm 1, \pm 2 \cdots \pm J$. When there is no preferred direction (absence of external fields) the level J is degenerate with a quantum weight $2J + 1$. For such a rotator

$$Q = \sum_{J=0}^{\infty} (2J+1) \exp.[-(hcB/kT)J(J+1)] \tag{30}$$

When hcB/kT is large, successive terms in equation 30 decrease rapidly, but when it is small direct summation becomes extremely laborious. It is then convenient to replace the sum by an asymptotic expansion[2]

$$\begin{aligned} \mathbf{Q} &= e^{hcB/4kT}[kT/hcB + 1/12 + (7/480)(hcB/kT) \\ &\qquad + (31/8064)(hcB/kT)^2 + (127/92160)(hcB/kT)^3 + \cdots] \qquad (31) \\ &= kT/hcB + 1/3 + (1/15)(hcB/kT) + (4/315)(hcB/kT)^2 \\ &\qquad + (1/315)(hcB/kT)^3 + \cdots \end{aligned}$$

These expressions are never exactly equal to Q, and will in fact always diverge if the series are carried far enough. For small values of hcB/kT, however, the first few terms are an excellent approximation. Thus for $hcB/kT = (1/2) \log 2 = 0.34657$ the first five terms give an error considerably less than 1 in 10^6; the speeds of convergence for the direct and the asymptotic sums are compared in table 1, which gives the fraction contributed to the sum by successive terms. For values of hcB/kT much larger than this, direct summation is the easier process, while for smaller

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[2] This result was first derived by Mulholland (80) from the theory of residues, but, in common with all the asymptotic expansions used in this work, it is obtained most easily by using the Euler-Maclaurin expansion formula.

values the asymptotic summation becomes not only increasingly superior to the direct summation but also easier in an absolute sense.

For an actual molecule which differs from the ideal simplicity of a rigid rotator only in the addition of small correction terms due to stretching, as in equation 27, use of the power series expansion[3]

$$\begin{aligned} \exp.[-(hcD/kT)J^2(J+1)^2 - (hcF/kT)J^3(J+1)^3] &= 1 - (hcD/kT)J^2 \\ \times (J+1)^2 - (hcF/kT)J^3(J+1)^3 + (1/2)(hcD/kT)^2J^4(J+1)^4 + \cdots \end{aligned} \quad (32)$$

and of asymptotic expansions related to equation 31, which have been published elsewhere (63), leads to

$$\begin{aligned} Q = kT/hcB + 1/3 + (1/315)(hc/kT)(21B - 8D - 6F) + \cdots \\ - 2(D/B)(kT/hcB)^2 + [12(D/B)^2 - 6(F/B)](kT/hcB)^3 + \cdots \end{aligned} \quad (33)$$

TABLE 1

Comparison of speeds of convergence

Q	Q FIRST FORM	Q SECOND FORM
0.30833	0.97011	0.88960
0.46249	0.02802	0.10277
0.19270	0.00170	0.00712
0.03372	0.00015	0.00047
0.00271	0.00002	0.00004
0.00005		
1.00000	1.00000	1.00000

The first line converges better for high T, the second for low, but for a wide range of temperature, up to beyond 5000°C., both converge with practical rapidity. D is always negative, and in many cases only B and D are known. The empirical energy level formula then leads to absurd results for $J(J+1) > B/2D$, and the second line of equation 33 eventually diverges. Essentially the same mathematical difficulty is almost always present in a more subtle form. If the empirical energy level formula leads to levels which increase indefinitely with J, the second line of equation 33 will converge; but if there is an upper limit to the levels, as there is for all real molecules, then summation over an infinite number of levels must give an infinite Q. There are actually only a finite number of rotational levels, but this fact does not reduce the pitfalls in a mathematical summation from $J = 0$ to ∞. It can be shown, however, by easy though somewhat

[3] This device was first used by Giauque and Overstreet (30).

inelegant marginal calculations, that whenever the empirical energy-level formula represents the actual levels satisfactorily out to a J such that $(2J + 1)$ exp. $(-\epsilon_J/kT)$ makes a negligible contribution to Q, the successive terms in the second line of equation 33 will decrease, at least until a negligible contribution of similar magnitude is reached. It can be shown further that when the series in equation 33 is broken off at that point, the result is equivalent to breaking off the direct sum at the J value specified above. In practice, this means that the second line of equation 33 can be treated like the first; the successive terms initially decrease, and if they become small enough to be neglected, the series may be broken off without appreciable error; if the terms in either line begin to increase before becoming negligibly small, term-by-term summation is necessary. The second line of equation 33 must always become unsatisfactory for large enough T, but for all molecules for which calculations have as yet been made, the break-down occurs well above the temperature range of interest.

When the molecule is composed of two identical atoms only those states are allowed which have eigenfunctions symmetric for an exchange of nuclei if the nuclei obey the Bose statistics, and only those states which have antisymmetric eigenfunctions if the nuclei obey the Fermi-Dirac statistics. The symmetry of the total eigenfunction depends upon several parts which must be considered separately. All energy levels of diatomic molecules are either positive or negative, according to whether ψ remains constant or changes sign when all positional coordinates (nuclear and electronic) change sign. When $\Lambda > 0$ (Π, Δ $\cdots$ states) each rotational level is a doublet, one member being a positive and the other a negative level. When $\Lambda = 0$ (Σ states) the levels do not have this type of doubling. There are two possibilities here; for Σ^+ states levels with even K are positive and levels with odd K negative, and for Σ^- states levels with even K are negative, levels with odd K positive. For diatomic molecules composed of two chemically identical atoms there is an additional type of symmetry which relates to the electronic eigenfunction alone; when this function is constant on reflection in the origin the state is called even and designated by the subscript g (for German *gerade*); when the function changes sign on reflection the state is odd, designated by u (for *ungerade*). Finally, when the two nuclei are identical, the nuclear spin eigenfunction may be either symmetric or antisymmetric for an exchange of nuclei. Then the total eigenfunction will be symmetric for any of the combinations

even	positive	symmetric spin function
odd	negative	symmetric spin function
even	negative	antisymmetric spin function
odd	positive	antisymmetric spin function

and antisymmetric for the remaining combinations

even	positive	antisymmetric spin function
odd	negative	antisymmetric spin function
even	negative	symmetric spin function
odd	positive	symmetric spin function

Proofs of all these statements have been given in an excellent review by Mulliken (81).

The symmetry properties of the spin eigenfunction are conveniently studied by supposing each spin separately coupled to a strong field. This procedure is permissible, since the number of functions of each type is independent of the coupling scheme. When the spin is zero there is only one atomic spin function, say α, and hence only one molecular spin function, $\alpha(1)\alpha(2)$, which is evidently symmetric. It is very probable that all nuclei with zero spin obey the Bose statistics; when that is so, the allowed combinations are even-positive and odd-negative. Thus, for example, a Σ_u^+ state of a molecule with identical atoms of zero spin must have negative levels and hence can have only odd values of K. For electronic states with $\Lambda > 0$ there are no missing K values, but only one member of each Λ-doublet has the allowed symmetry properties and hence the doubling disappears for homonuclear molecules.

When the nuclear spin is 1/2, its projection on the external field has two eigenvalues, 1/2 and $-1/2$; the corresponding eigenfunctions may be called α and β. It is then possible to construct three symmetric spin functions for the molecule, namely $\alpha(1)\alpha(2)$, $\beta(1)\beta(2)$, and $2^{-1/2}[\alpha(1)\beta(2) + \beta(1)\alpha(2)]$ and one antisymmetric spin function, $2^{-1/2}[\alpha(1)\beta(2) - \beta(1)\alpha(2)]$. In general, when the spin is i, there are $2i + 1$ atomic spin functions. Then there are obviously $2i + 1$ symmetric molecular functions of type $\alpha(1)\alpha(2)$ and $(2i + 1)i$ of type $2^{-1/2}[\alpha(1)\beta(2) + \beta(1)\alpha(2)]$, a total of $(2i + 1)(i + 1)$. There are $(2i + 1)i$ antisymmetric molecular functions, all of type $2^{-1/2} \times [\alpha(1)\beta(2) - \beta(1)\alpha(2)]$.

Under some experimental conditions equilibrium between the states with symmetric and those with antisymmetric spin eigenfunctions is almost completely frozen, and the two states behave as separate chemical species. It is customary to use the term "ortho" for states with symmetric spin functions and "para" for those with antisymmetric spin functions. The normal electron state of H_2 is $^1\Sigma_g^+$; protons obey Fermi-Dirac statistics and have a spin of 1/2; hence for orthohydrogen the spin weight is 3 and only odd J are permitted, while for parahydrogen the spin weight is 1 and even J are required. Deuterons have a spin of 1 and obey Bose statistics; the normal electron state of D_2 is the same as that of H_2; hence orthodeuterium with even J has a spin weight of 6, paradeuterium with odd J a spin weight of 3.

It is evidently necessary to calculate the Q-sum for even J and for odd J separately. It has been shown (63) that for the energy levels of equation 27 and rotational quantum weights $2J + 1$, for unit spin weight

$$\mathbf{Q}(\text{even } J) = \mathbf{Q}(\text{odd } J) = (1/2)\mathbf{Q} \tag{34}$$

Hence for the temperature range to which the asymptotic expansion is applicable, the abundance ratio of ortho and para forms is simply the ratio of their spin weights. For lower temperature, however,

$$Q(\text{odd } J) \rightarrow 0$$
$$Q(\text{even } J) \rightarrow \text{the spin weight}$$

and the equilibrium mixture approaches 100 per cent the form with even J. In this temperature range Q for the equilibrium mixture and for the equilibrium frozen at the high temperature value take entirely different courses. The derived thermodynamic functions likewise differ. The discovery of the ortho and para states of hydrogen was an immediate consequence of Dennison's successful calculation of the specific heat of hydrogen on the assumption of a frozen equilibrium; all previous attempts to reproduce the experimental curve by more or less arbitrary quantum weight assignments had been failures. Phenomena of this sort are of the greatest interest both theoretically and experimentally, but of no interest as a problem in calculation. There is nothing to do with the Q-sum except to add it up term by term; since only four or five terms are needed, this is very easy to do.

The calculation which led to equation 33 applies only to $^1\Sigma$ molecules. The calculations become more complicated when $S > 0$, giving multiplet states. A comparatively simple example is the normal state of O_2, a $^3\Sigma_g^-$ with $S = 1$. In Hund case *b* coupling, which is followed here as in most other Σ states (case *a* being impossible), the orbital angular momentum Λ and the nuclear angular momentum N combine to give a quantum number K, which has values $\Lambda, \Lambda + 1, \cdots$. In this case $\Lambda = 0$ and $K = 0, 1, 2 \cdots$. K then couples with S to give J. It is the different possibilities in this last coupling which give rise to the multiplicity. Thus for O_2 the three components of the triplet are designated F_1, F_2, F_3 according as $J = K + 1$, K, or $K - 1$. The rotational energy is given by $hc[BK(K + 1) + \cdots] + \tau_i(K)$, where $\tau(K)$ is the K–S coupling energy, which depends upon K and which is slightly different for each member of the multiplet. For $K = 0$ the K–S coupling can give only $J = 1$, and hence only the F_1 component exists. For $K > 0$, all three components are present, the quantum weights being $2J + 1$, hence $2K + 3$, $2K + 1$, $2K - 1$, respectively. For $O^{16}O^{16}$, since the nuclei have zero spin and obey the Bose statistics and since the normal state is $^3\Sigma_g^-$, only odd values of K are allowed.

The most interesting effects due to these multiplet terms are rather sharp maxima in the specific heats at temperatures which may lie below 1°C. or above 100°C., depending upon the separations. When, as in O_2, this electronic heat capacity is excited before the rotational heat capacity approaches its equipartition value, the effect can be studied only by direct summation. For the higher temperatures where asymptotic summation is possible, a comparatively rough treatment of the small multiplet separation is allowable. Thus the separations may be approximated by the empirical equations

$$\left.\begin{aligned}\tau_1(K) - \tau_3(K) &= a(2K+3)^{-1} + b + c(2K+1)\\ \tau_2(K) - \tau_3(K) &= d(2K+1)^{-1} + e + f(2K+1)\end{aligned}\right\} \tag{35}$$

the F_3 state being the lowest. Then

$$\begin{aligned}Q = \sum_{K=1}^{\infty}{}^{(2)} \{&(2K-1) + (2K+1)\ \text{exp.}\,[-(kT)^{-1}\{d(2K+1)^{-1}\\ &+ e + f(2K+1)\}] + (2K+3)\ \text{exp.}\,[-(kT)^{-1}\{a(2K+3)^{-1}\\ &+ b + c(2K+1)\}]\}\ e^{-T(K)/kT}\end{aligned} \tag{36}$$

where

$$T(K) = hc[BJ(J+1) + DJ^2(J+1)^2 + \cdots] \tag{37}$$

is the same for all members of the multiplet and the superscript (2) on Σ indicates summation over alternate values of the index, that is, over odd K. When the exponential terms within the braces are expanded and only the first two terms in each expansion retained, equation 36 becomes

$$\begin{aligned}Q = \sum_{K=1}^{\infty}{}^{(2)} [(3-2c)(2K+1) - (a+d)(kT)^{-1}&\\ - (c+f)(kT)^{-1}(2K+1)]\ e^{-T(K)/kT}&\end{aligned} \tag{38}$$

a form very convenient for asymptotic summation.

The normal state of NO is $^2\Pi_{1/2,\,1\,1/2}$, with Hund case a coupling. Here $S = 1/2$ and its projection on the axis, Σ, $= 1/2, -1/2$. Then $\Omega = |\Lambda + \Sigma| = 3/2, 1/2$, measures the total angular momentum parallel to the axis. This combines with the nuclear rotation angular momentum to give J, with allowed values $\Omega, \Omega + 1, \cdots$. Then for $^2\Pi_{1/2}$ the energy is

$$hc\{B_{1/2}[J(J+1) - 1/4] + \cdots\} + \text{const.} \qquad J = 1/2, 3/2 \cdots \tag{39}$$

and for $^2\Pi_{1\,1/2}$

$$hc\{B_{1\,1/2}[J(J+1) - 9/4] + \cdots\} + \text{const.} \qquad J = 3/2, 5/2 \cdots \tag{40}$$

The theoretically interesting terms $-(1/4)hcB_{1/2}$ and $-(9/4)hcB_{1\ 1/2}$ in practice frequently are absorbed in the constants, but can of course always be rescued when they are desired. A very pretty method of summation has been suggested by Witmer (107) for case *a* molecules. The rotational and vibrational constants for all members of the multiplet are assumed equal as a first approximation. Then the summation over J for a single member gives

$$\mathbf{Q}_{\text{rot}} = kT/hcB + 1/3 + (hcB/kT)(1/15 - \Omega_s^2/6) \tag{41}$$

for J integral, as is shown by the argument in the following section where l plays exactly the same mathematical rôle as Ω_s and gives a similar expression with only a feeble dependence on Ω_s for the other possible cases (half-integral J, alternate J values). The multiplet spacing in case *a* is uniform, the positions being given by a term $(s - 1)\Delta$. Then as a first approximation the multiplet structure contributes a factor to **Q**

$$\begin{aligned} Q_{\text{mult}} &= 1 + e^{-hc\Delta/kT} + e^{-2hc\Delta/kT} + \cdots + e^{-(m-1)hc\Delta/kT} \\ &= (1 - e^{-mhc\Delta/kT})/(1 - e^{-hc\Delta/kT}) \end{aligned} \tag{42}$$

This factor is the ratio of two vibrational factors, and the contribution to the thermodynamic functions is thus the difference between two vibrational contributions. The contribution to **C** passes through a maximum the height of which depends only on m, approaching R as m increases. The contribution to **H** reaches a limiting value of $(1/2)(m - 1)\Delta$ and that to **S** and $-\mathbf{F}/T$ a limiting value of $R \log m$ as T increases.

If the rotational and vibrational constants are too greatly different for the various members of the multiplet, the anharmonic term associated with Witmer's calculation would be inconveniently large, and separate treatment of each member would be easier. In any case, formulas for sums over half integral J values are needed. These have been given elsewhere (63).

The rotational sum for polyatomic molecules

The simplest polyatomic molecules are linear, but even these lead to complexities absent in the diatomic case. The linear triatomic molecule has been shown by Dennison (17) to have two stretching vibrations, ω_1 and ω_3, and a double bending vibration ω_2 with a subsidiary azimuthal quantum number l which measures the angular momentum of the bending vibrations parallel to the molecular axis. The allowed values of l are $-v_2, -v_2 + 2, \cdots v_2 - 2, v_2$, where v_2 is the quantum number for the vibration ω_2. The allowed values of J are $J \geqq |l|$. The first approximation to the rotational energy is

$$E = hcB[J(J + 1) - l^2] \tag{43}$$

Then if the molecule is unsymmetrical, so that there are no alternating weights for the rotational levels due to spin and symmetry,

$$\begin{aligned}\mathbf{Q} &= e^{(hcB/kT)(l^2+1/4)}\,[kT/hcB + 1/12 + (7/480)(hcB/kT) + \cdots] \\ &\quad - e^{(hcB/kT)l^2} - 3e^{(hcB/kT)(l^2-2)} - \cdots - (2l-1)\,e^{(hcB/kT)(l^2-l^2-l)} \\ &= e^{(hcB/kT)(l^2+1/4)}[kT/hcB + 1/12 + (7/480)(hcB/kT) + \cdots] \\ &\quad - l^2 - (1/2)(hcB/kT)(l^4 + l^2) - \cdots = kT/hcB + 1/3 \\ &\quad + (hcB/kT)(1/15 - l^2/6) + \cdots\end{aligned} \tag{44}$$

This result is in a form suitable for use in summing over l, a step which is part of the vibrational treatment. The method used here can be applied equally well when the desired sum extends over only alternate J values.

The rotations of non-linear polyatomic molecules are vastly more complicated. The quantum mechanical treatment of a rigid symmetrical top with moments of inertia A, A, C gives the energy levels

$$E = (h^2/8\pi^2A)[K(K+1) + n^2(A/C-1)] \qquad |n| \leqq K \tag{45}$$

with a quantum weight of $2K + 1$ for each pair K, n. (If only positive n are considered, the quantum weight is $2(2K + 1)$ for $n > 0$). Then

$$Q = \sum_{K=0}^{\infty} \sum_{n=-K}^{K} \exp. - (h^2/8\pi^2AkT)[K(K+1) + n^2(A/C-1)] \tag{46}$$

The asymptotic expansion of this double sum has been shown (103, 63, 104) to be

$$\begin{aligned}\mathbf{Q} = \pi^{1/2}\sigma^{-3/2}e^{\sigma/4}(\beta+1)^{-1/2}[1 &+ (1/12)\beta(\beta+1)^{-1}\sigma \\ &+ (7/480)\beta^2(\beta+1)^{-2}\sigma^2 + \cdots]\end{aligned} \tag{47}$$

where

$$\begin{aligned}\sigma &= h^2/8\pi^2AkT \\ \beta &= A/C - 1\end{aligned} \tag{48}$$

Asymptotic formulas have also been given (63) by which stretching effects expressed as higher powers of $K(K + 1)$ and n^2, as well as cross products, can be treated. The asymmetrical top has been solved quantum mechanically, but it is hard to make much use of the results owing to their complicated form. There are still the same quantum numbers K, n and the same weights as before, but there is no closed formula for the energy levels. Instead, when K is even the levels are given as the roots of three algebraic equations of degree $K/2$ and one of degree $K/2 + 1$; when K is odd they are the roots of three equations of degree $(K + 1)/2$ and one of degree

$(K - 1)/2$. The expansion for the symmetrical case, however, may be written

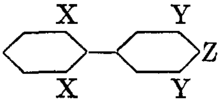
$$\mathbf{Q} = \pi^{1/2}(h^2/8\pi^2kT)^{3/2}(A^2C)^{-1/2} + \cdots \tag{49}$$

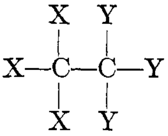
and one might guess that for the asymmetrical top

$$\mathbf{Q} = \pi^{1/2}(h^2/8\pi^2kT)^{3/2}(ABC)^{-1/2} + \cdots \tag{50}$$

Gordon (36) has shown by numerical calculations that this is correct.

Many polyatomic molecules possess internal rotations as well as external. It will be understood readily that little progress has been made in the theoretical treatment of rotation in such cases and *a fortiori* in the calculation of the **Q**-sum. The model of ethane—two identical coaxial symmetrical tops—has been solved both for free rotation (78) and for an assumed potential function (83). The model of tetramethylmethane has been solved for the case of free rotation (68). Asymptotic expansions have been found for **Q** in both cases of free rotation (78, 65). Eidinoff and Aston (19) have obtained the first term in **Q**, corresponding to replacing the summations by integrals, for the more general case of two coaxial asymmetric tops, the common axis being a principal axis for each. Typical molecules are[4]





where X, Y, Z are atoms or linear radicals, such as $-C{\equiv}N$. The general method used by Eidinoff and Aston has been further developed by Kassel (66a), and applied to a number of more complex cases, including propane, butane, isobutane, propylene, 1-butene, *cis*- and *trans*-2-butenes, isobutene, trimethylethylene, tetramethylethylene, butadiene, and all the methyl derivatives of benzene. The assumption of perfectly free rotation cannot be entirely correct in any of these cases; even if there were no real potential energy resisting rotation, there would still be the pseudo-potential energy discovered by Kassel (66), caused by change of vibration frequencies with change of angle. In the case of butane, this pseudo-potential energy amounts to about 50 cal. For most of the molecules listed above the

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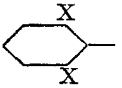
[4] The symmetrically substituted groups such as  have three different moments of inertia, hence are asymmetrical tops; if substitution were unsymmetrical, the tops would not be coaxial. The group CX_3, however, is a symmetrical top.

true potential energy also is likely to be small, and the assumption of free rotation should give fair results. When there are dipole moments, as in ethylene chloride, or large rotating groups, as in triphenylmethane, or long floppy chains whose ends could strike, as in hexane, the assumption of free rotation would not be permissible. In such cases there is no way known by which thermodynamic calculations could be made.

The application of symmetry considerations to polyatomic molecules presents very considerable difficulties. Hund (48) solved the problem for ammonia, and Elert (20) applied his method to methane; but greatly simplified calculations for these molecules, as well as for benzene, trimethylene, ethylene, and several others, have been made by Wilson (106) with the aid of group theory methods. As an example of the procedure which must be used to obtain the Q-sum in such cases, a brief treatment of CH_4 and CD_4 is given here; this calculation has not been published elsewhere.

For the methane framework there are three symmetry types, A, E, and T, which play a rôle similar to the two types S and A (not the same A) for diatomic molecules. When the product of electronic and vibrational eigenfunctions has the symmetry A, as is the case for the non-vibrating normal state, the weights for each symmetry type of nuclear spin eigenfunction are as follows:

ψ_{spin}	$J = 6p$	$J = 6p+1$	$J = 6p+2$	$J = 6p+3$	$J = 6p+4$	$J = 6p+5$
A	$5p+5$	$5p$	$5p$	$5p+5$	$5p+5$	$5p$
E	$2p$	$2p$	$2p+2$	$2p$	$2p+2$	$2p+2$
T	$9p$	$9p+3$	$9p+3$	$9p+6$	$9p+6$	$9p+9$
Total	$16p+5$	$16p+3$	$16p+5$	$16p+11$	$16p+13$	$16p+11$

All the weights in this table must be multiplied by $2J + 1$ to obtain the total quantum weight for a given J and spin symmetry; it should perhaps be mentioned explicitly that since methane is a top with three equal moments the quantum number n effectively disappears. Any weight factors which can be represented by a table of this sort can be expressed analytically by a weight factor

$$G(2ap + 2b + 1)\,[(2ap + 2b + 1) + f(b)]$$

for the level $J = ap + b$, where the constant G depends upon the symmetry type of the nuclear spin function. Then

$$\begin{aligned} Q &= \sum_{b=0}^{a-1} \sum_{p=0}^{\infty} G(2ap + 2b + 1)[(2ap + 2b + 1) + f(b)]\, e^{-J(J+1)\sigma} \\ &= \sum_{J=0}^{\infty} G(2J + 1)^2 e^{-J(J+1)\sigma} + \sum_{b=0}^{a-1} \sum_{p=0}^{\infty} Gf(b)(2ap + 2b + 1) e^{-J(J+1)\sigma} \end{aligned} \tag{51}$$

$$\mathbf{Q} = G\pi^{1/2}e^{\sigma/4}\sigma^{-3/2} + G\sum_{b=0}^{a-1} f(b)X(b) \tag{52}$$

where

$$\begin{aligned} X(b) = e^{-b(b+1)\sigma}\{1/a\sigma + b + 1/2 - a/6 \\ + \sigma\,[(a/12)(2b+1)^2 - a^3/60] + \cdots\} \end{aligned} \tag{53}$$

The first asymptotic expansion has already been given and the second is easily made. Now by the substitution $b = a - 1 - b_0$ in $X(b)$ and expansion of part of the exponential it can be shown that

$$X(a - 1 - b) = X(b) \tag{54}$$

In Wilson's weight tables, partly reproduced above,

$$f(a - 1 - b) = -f(b) \tag{55}$$

for all nuclear spin symmetry types for all electronic-vibrational symmetry types for both CH_4 and CD_4. Hence in all these cases

$$\sum_{b=0}^{a-1} f(b)X(b) = 0 \tag{56}$$

and

$$\mathbf{Q} = G\pi^{1/2}e^{\sigma/4}\sigma^{-3/2} \tag{57}$$

For the particular case being considered, the normal state of methane, $G = 5/12$, $1/6$, and $3/4$ for A, E, T spin symmetries respectively, or $4/3$ for the three together. This same factor $4/3$ is given by the empirical rule that the effective weight is the product of the spin multiplicities for all the atoms divided by the symmetry number of the molecule, here $2^4/12 = 4/3$. For the corresponding states of CD_4 the weights are $5/4$, 1, $9/2$, a total of $27/4 = 3^4/12$. The range of validity of these asymptotic expansions has been tested by direct summation. For $\sigma = 0.11512925$, for CH_4

$$Q = 62.27472 \qquad \mathbf{Q} = 62.26373 \qquad Q/\mathbf{Q} = 1.00018$$

and for CD_4

$$Q = 315.23487 \qquad \mathbf{Q} = 315.21013 \qquad Q/\mathbf{Q} = 1.000078$$

For $\sigma = 0.23025851$, for CH_4

$$Q = 23.12567 \qquad \mathbf{Q} = 22.65636 \qquad Q/\mathbf{Q} = 1.0207$$

The asymptotic expansion thus fails for σ only a little greater than 0.1, very considerably sooner than is the case with the simple symmetrical top, where for $\sigma = 0.2302585092994046$

$$Q = 16.99227012072823 \qquad \mathbf{Q} = 16.99227012072823$$

For CH_4, $\sigma = 0.1$ is at 72°K., $\sigma = 0.23$ at 31.5°K. There is thus little likelihood that any calculations ever will be needed for which Q is not satisfactory for this or any other polyatomic molecule; should such calculations prove necessary, however, they could always be made by direct summation with comparative ease.

The vibrational sum

The next operation to be considered is the summation over vibrational states. Since it is an experimental fact that B_v, D_v, etc. can be represented by rapidly converging power series in v, the result of the rotational summation may be put in the form

$$\mathbf{Q}(v) = K_0 + K_1 v + K_2 v^2 + \cdots \tag{58}$$

for a diatomic molecule, or a similar power series expansion in several variables for a polyatomic molecule. Then

$$\begin{aligned}\mathbf{Q} &= \sum_{v=0}^{\infty} \mathbf{Q}(v) \exp.[-hc(\omega_0 v - x\omega_0 v^2 + \cdots)/kT] \\ &= \sum_{v=0}^{\infty} P(v) \exp. [- hc\omega_0 v/kT]\end{aligned} \tag{59}$$

where $P(v)$ is the product of $\mathbf{Q}(v)$ and the power series expansion of exp. $[- hc(- x\omega_0 v^2 + \cdots)/kT]$. An exact term-by-term evaluation of this sum is possible by means of the following formulas (61), where

$$z = e^{-hc\omega_0/kT} \tag{60}$$

$$(1 - z)^{-1} f_i = \sum_{v=0}^{\infty} v^i z^v \tag{61}$$

$$\begin{aligned}
f_0 &= 1 \\
f_1 &= z(1 - z)^{-1} \\
f_2 &= z(1 + z)(1 - z)^{-2} \\
f_3 &= z(1 + 4z + z^2)(1 - z)^{-3} \\
f_4 &= z(1 + 11z + 11z^2 + z^3)(1 - z)^{-4} \\
f_5 &= z(1 + 26z + 66z^2 + 26z^3 + z^4)(1 - z)^{-5} \\
f_6 &= z(1 + 57z + 302z^2 + 302z^3 + 57z^4 + z^5)(1 - z)^{-6} \\
f_7 &= z(1 + 120z + 1191z^2 + 2416z^3 + 1191z^4 + 120z^5 + z^6)(1 - z)^{-7} \\
f_8 &= z(1 + 247z + 4293z^2 + 15619z^3 + 15619z^4 + 4293z^5 + 247z^6 + z^7) \\
&\quad \times (1 - z)^{-8}
\end{aligned} \tag{62}$$

The result of the vibrational summation with the use of these formulas is then (for a diatomic molecule)

$$\mathbf{Q} = (\mu kT/hcB_0)(1 - z)^{-1} \sum_{i=0}^{\infty} f_i g_i \tag{63}$$

Here the first factor contains the contribution from a rigid rotator with moment of inertia $h/8\pi^2 cB_0$, the constant μ taking care of symmetry and of nuclear spin, the second factor the contribution of a harmonic oscillator of frequency $c\omega_0$, and the third factor all corrections for stretching, anharmonicity, missing levels, etc. In this factor the f_i are the previously given functions and the g_i are power series in T and $1/T$ with numerical coefficients (Laurent series). It is clear from the form of the fundamental equations that each factor in **Q** makes an additive contribution to the thermodynamic functions. The rotational factor gives (per mole)

$$\begin{aligned} \mathbf{H}_{\text{rot}} &= RT \qquad \mathbf{C}_{\text{rot}} = R \\ \mathbf{S}_{\text{rot}} &= R + R \log \mu k/hcB_0 + R \log T \\ -\mathbf{F}_{\text{rot}}/T &= R \log \mu k/hcB_0 + R \log T \end{aligned} \tag{64}$$

The vibrational factor gives

$$\begin{aligned} \mathbf{H}_{\text{vib}} &= R(hc\omega/k)[z/(1-z)] \\ \mathbf{C}_{\text{vib}} &= R(hc\omega/kT)^2[z/(1-z)^2] \\ \mathbf{S}_{\text{vib}} &= R(hc\omega/kT)[z/(1-z)] - R \log (1-z) \\ -\mathbf{F}_{\text{vib}}/T &= -R \log (1-z) \end{aligned} \tag{65}$$

Several convenient tables of these vibrational contributions, often called Einstein functions, are available (69, 82).

The anharmonic factor is

$$h = \sum_i f_i g_i \tag{66}$$

Then

$$h' = \sum_i (f_i g'_i + f'_i g_i) \tag{67}$$

$$h'' = \sum_i (f_i g''_i + 2f'_i g'_i + f''_i g_i) \tag{68}$$

where, as always in this paper, a $'$ means differentiation with respect to $1/T$. The g_i can be differentiated at sight. The derivatives of the f_i, which have not been published previously, are

$$\begin{aligned} f'_0 &= 0 \\ f'_1 &= -(hc\omega/k)z(1-z)^{-2} \\ f'_2 &= -(hc\omega/k)z(1+3z)(1-z)^{-3} \\ f'_3 &= -(hc\omega/k)z(1+10z+7z^2)(1-z)^{-4} \\ f'_4 &= -(hc\omega/k)z(1+25z+55z^2+15z^3)(1-z)^{-5} \\ f'_5 &= -(hc\omega/k)z(1+56z+276z^2+236z^3+31z^4)(1-z)^{-6} \\ f'_6 &= -(hc\omega/k)z(1+119z+1134z^2+2114z^3+889z^4 \\ &\qquad + 63z^5)(1-z)^{-7} \end{aligned} \tag{69}$$

$$\begin{aligned}
f_7' &= -\,(hc\omega/k)z(1 + 246z + 4173z^2 + 14428z^3 + 13203z^4 \\
&\qquad + 3102z^5 + 127z^6)(1 - z)^{-8} \\
f_8' &= -\,(hc\omega/k)z(1 + 501z + 14361z^2 + 83941z^3 + 140571z^4 \\
&\qquad + 72615z^5 + 10315z^6 + 255z^7)(1 - z)^{-9} \\
f_0'' &= 0 \\
f_1'' &= (hc\omega/k)^2z(1 + z)(1 - z)^{-3} \\
f_2'' &= (hc\omega/k)^2z(1 + 8z + 3z^2)(1 - z)^{-4} \\
f_3'' &= (hc\omega/k)^2z(1 + 23z + 41z^2 + 7z^3)(1 - z)^{-5} \\
f_4'' &= (hc\omega/k)^2z(1 + 54z + 240z^2 + 170z^3 + 15z^4)(1 - z)^{-6} \\
f_5'' &= (hc\omega/k)^2z(1 + 117z + 1052z^2 + 1772z^3 + 627z^4 \\
&\qquad + 31z^5)(1 - z)^{-7} \\
f_6'' &= (hc\omega/k)^2z(1 + 244z + 3997z^2 + 12992z^3 + 10787z^4 \\
&\qquad + 2156z^5 + 63z^6)(1 - z)^{-8} \\
f_7'' &= (hc\omega/k)^2z(1 + 499z + 13995z^2 + 78577z^3 + 123727z^4 \\
&\qquad + 58221z^5 + 7093z^6 + 127z^7)(1 - z)^{-9} \\
f_8'' &= (hc\omega/k)^2z(1 + 1010z + 46590z^2 + 421930z^3 + 1122560z^4 \\
&\qquad + 997974z^5 + 290050z^6 + 22670z^7 + 255z^8)(1 - z)^{-10}
\end{aligned} \tag{70}$$

It is convenient to calculate the anharmonic correction at a few widely spaced temperatures, say 250, 500, 750, 1000, 2000, 3000, 4000, and 5000°K., and fit the results by least squares to

$$\mathbf{F}_{\text{anh}}/T = a + b/T + c \log T + dT + eT^2 \tag{71}$$

and the thermodynamically consistent equations for $\mathbf{H}_{\text{anh}}$ and $\mathbf{C}_{\text{anh}}$. Values at intermediate temperatures are given by the resulting equations with an error considerably less than 0.001 cal. per degree when the underlying calculations are made with equal accuracy.

In the case of polyatomic molecules with no two vibrations of the same frequency the procedure is obvious. When there are n identical frequencies the level $vhc\omega$ has a quantum weight $(n + v - 1)!/(n - 1)!v!$, which is a polynomial in v and could be multiplied out into $P(v)$. It is much more convenient to proceed a little differently, however, as indicated by the following example with $n = 4$. The weight factor is then $(1/6)(v + 1)(v + 2)(v + 3)$. Define

$$(1 - z)^{-4}m_i = \sum_{v=0}^{\infty} (1/6)(v + 1)(v + 2)(v + 3)\, v^iz^v \tag{72}$$

so that m_i will play a rôle analogous to the previously used f_i. Then it is easily shown by using the formulas for f_i that

$$\begin{aligned}
m_0 &= 1 \\
m_1 &= 4z(1 - z)^{-1} \\
m^2 &= 4z(1 + 4z)(1 - z)^{-2} \\
m^3 &= 4z(1 + 13z + 16z^2)(1 - z)^{-3} \\
m^4 &= 4z(1 + 32z + 113z^2 + 64z^3)(1 - z)^{-4}
\end{aligned} \tag{73}$$

Tables of the derivatives m_i' and m_i'' can then be prepared and used in exactly the same way as f_i' and f_i''. This procedure has the very great advantage of isolating the complete harmonic factor $(1 - z)^{-4}$ and keeping a relatively small anharmonic contribution.

It is to be expected that the higher levels will be somewhat less degenerate than simple theory indicates. An example is furnished by the linear triatomic molecule which has been shown by Dennison (17) to have two single valence vibrations ω_1 and ω_3 and one double bending vibration ω_2. The energy is

$$E = hc[\omega_1 v_1 + \omega_2 v_2 + \omega_3 v_3 - av_1^2 - b\{v_2^2 - (1/3)l^2\} - cv_2^2 - dv_1 v_2 - ev_1 v_3 - fv_2 v_3 + \text{higher terms}] \tag{74}$$

where l is a subsidiary azimuthal quantum number with values $-v, -v + 2, \cdots v - 2, v$. Then the degeneracy is removed when l is considered, and

$$Q = \sum_{v_1=0}^{\infty} \sum_{v_2=0}^{\infty} \sum_{v_3=0}^{\infty} \sum_{l=-v_2}^{+v_2}{}^{(2)} e^{-E/kT} \tag{75}$$

where $\Sigma^{(2)}$ means summation over alternate values of the index. In handling this summation the first of the following formulas is necessary; if higher anharmonic terms are to be considered, the second one also will be needed.

$$\begin{aligned} \sum_{-v}^{+v}{}^{(2)} l^2 &= (v/3)(v + 1)(v + 2) \\ \sum_{-v}^{+v}{}^{(2)} l^4 &= (v/15)(v + 1)(v + 2)(3v^2 + 6v - 4) \end{aligned} \tag{76}$$

The resulting formula for Q has been published elsewhere (64) and need not be repeated here. It consists of harmonic and anharmonic factors and hence is convenient for computation. Similar methods undoubtedly can be used for more complex polyatomic molecules whenever the spectroscopic data become available.

Another complication which can arise in polyatomic molecules is degeneracy involving unequal frequencies whose ratio is approximately that of two small integers. Thus in carbon dioxide ω_1 is almost exactly $2\omega_2$, and there are as a result perturbations of the order of 50 cm.$^{-1}$ in the positions of the levels from locations based on a simple equation such as equation 74. An exact analysis of the data for carbon dioxide has been given by Adel and Dennison (1), and their equations have made possible exact calculation of **Q** (64). The computations are somewhat lengthy, however, and since rather special methods are needed the details will not be discussed here.

An alternative method of vibrational summation

An alternative method has been developed by Gordon and Barnes (42) and extended by Gordon (38). Consider an unsymmetrical $^1\Sigma$ diatomic molecule with energy levels given by

$$E = hc[(v + 1/2)\omega_e - (v + 1/2)^2\omega_e x + B_v(J + 1/2)^2 + D_v(J + 1/2)^4 + F_v(J + 1/2)^6] \tag{77}$$

Put

$$q_v = kT/B_v hc \qquad d_v = -2(D_v/B_v)q_v \qquad f_v = -6(F_v/B_v)q_v^2 \tag{78}$$

In this notation equation 33 becomes

$$\mathbf{Q}_{\text{rot}} = e^{1/4q_v}q_v(1 + 1/12q_v + d_v + 3d_v^2 + f_v + \ldots) \tag{79}$$

Now use the unconventional representation

$$B_v = B_0/(1 + \beta_1 v + \beta_2 v^2) \tag{80}$$

Then

$$\mathbf{Q}_{\text{rot}} = e^{1/4q_0}q_0(1 + \beta_1 v + \beta_2 v^2)(1 + 1/12q_0 + d_0 + 3d_0^2 + f_0) + \text{higher terms} \tag{81}$$

and

$$\mathbf{Q} = Q_V e^{1/4q_0}q_0(1 + \beta_1\bar{v} + \beta_2\overline{v^2})(1 + 1/12q_0 + d_0 + 3d_0^2 + f_0) \tag{82}$$

where

$$\begin{aligned} Q_V &= \sum_v e^{-\epsilon_v hc/kT} \\ \bar{v} &= (1/Q_V)\sum_v v e^{-\epsilon_v hc/kT} \\ \overline{v^2} &= (1/Q_V)\sum_v v^2 e^{-\epsilon_v hc/kT} \end{aligned} \tag{83}$$

It is at this point that Gordon and Barnes introduce the essential feature of their method. It is evident that log Q_V, $\bar{v}$, and $\bar{v}^2$ are functions of $hc\omega_e/kT$ and x. They give double-entry tables for these three functions as well as for a number of others needed in calculating Q' and Q''. Once these tables have been prepared the thermodynamic functions can be computed somewhat more rapidly than in the purely analytic way. The method is somewhat inflexible, but not to the extent that might be imagined. It lacks the capability of making calculations of unlimited precision, but it has been shown to yield accuracy as great as is aimed at in most current calculations. The account of the method given here is very incomplete; it must not be thought that the space devoted to it is a measure of the utility of the technique.

IV. APPLICATIONS

Methods

Thermodynamic functions obtained by the methods of the foregoing pages may of course be used in exactly the same ways that have now become classical for functions obtained from experimental specific heats, equilibrium constants, electromotive force values, etc. Somewhat different procedures, however, may be used with advantage. Both H and F as given by these calculations are referred to the gas at 0°K., that is, in the non-vibrating, non-rotating, non-translating state of lowest electronic energy. This is frequently indicated by writing $F^0 - E_0^0$ in place of F. It is necessary to correct the purely spectroscopic "ΔF" for a reaction by adding ΔE_0^0. When accurate spectroscopic dissociation energies are known, ΔE_0^0 can be obtained directly; then to calculate equilibrium constants it is necessary to calculate spectroscopic values only for F/T, and hence only Q is needed. When a calorimetric heat of reaction is used, it is necessary to calculate H up to the temperature of the calorimetry to obtain ΔE_0^0, but equilibrium constants for higher temperatures may then be obtained from F/T. Even when all the thermodynamic functions have been computed, the foregoing method is considerably more expeditious than the more conventional procedures that have sometimes been used. Likewise it will be found that H is far more useful than C_p, and the habit of talking about specific heat when only integrated values are actually used should not mislead one into graphical integrations of spectroscopic C_p values.

Historical

The earliest actual calculations seem to be those of Urey (97), Tolman and Badger (95), and Hicks and Mitchell (47), all dealing with HCl. In all these calculations incorrect quantum weights were used. Giauque and Wiebe (31) made the first correct calculation of the entropy of HCl, and Hutchisson (49) the first correct calculation of its specific heat. Meanwhile Dennison (16), assuming a frozen ortho–para equilibrium, had successfully calculated the specific heat of hydrogen. The method was thus well-established in 1928, though the development of convenient mathematical techniques came somewhat later.

Results of calculations

In the following pages there is an attempt to include all but the most trivial calculations that have been made. Compounds are arranged according to the system used in the International Critical Tables; the key-numbers used here are

O	H	Cl	Br	I	S	N	C
1	2	4	5	6	8	11	16

All isotopes of an element are assigned the same key number. Equilibria are discussed under the component of highest key number.

Atomic oxygen, O. Values of $-F/T$ for atomic oxygen have been tabulated by Johnston and Walker (58); a few minor corrections to these values were published later (59).

Molecular oxygen, O_2. Johnston and Walker (57) calculated C_p, S, and $-F/T$ to 5000°K., taking account of the normal $^3\Sigma_g^-$ state and the $^1\Sigma_g^+$ state at 1.62 v. above the normal. They omitted the $^1\Delta$ level, which had been predicted to lie 0.8 v. above the normal state but had not yet been observed. They (58) combined their $-F/T$ values with a spectroscopic heat of dissociation to calculate equilibrium constants for

$$O_2 = 2O$$

Spencer and Justice (93) gave an empirical equation to fit the spectroscopic C_p values. Lewis and von Elbe (71) calculated from the excess observed specific heat of O_2 in O_3 explosions over Johnston and Walker's values that the $^1\Delta$ state lay 0.75 v. above the normal; revision (74) of this calculation, with correction for temperature gradients in the bomb, subsequently gave 0.85 v. Meanwhile Herzberg (46) had observed the 0, 0 band of the system $^3\Sigma_g^-$–$^1\Delta_g^+$ at 7881.6 cm.$^{-1}$, thus definitely fixing the $^1\Delta$ state 0.97 v. above the normal, and Johnston and Walker (60) had recalculated their earlier values of C_p, S, and $-F/T$ for O_2 and of K for the dissociation

$$O_2 = 2O$$

from 1000 to 5000°K. and given a complete table for H from 90.13° to 5000°K. The agreement between the position of the $^1\Delta$ level, as determined by spectroscopy and as estimated by Lewis and von Elbe from experimental specific heats in combination with the incomplete spectroscopic values, is really excellent. This will be realized when it is stated that at 2500°K., slightly above the highest explosion temperatures, a $^1\Delta$ level at 0.97 v. increases H by 160 cal., and one at 0.85 v. by 250 cal. This difference of 90 cal. amounts to a temperature difference of less than 10°C., and is in the direction to be accounted for by a slight heat loss during the explosion.

Molecular oxygen, O_2^{18}. Urey and Greiff (98) calculated the ratio of Q (including the translational part) for O_2^{18} to that for O_2^{16} at 273.1, 293.1, and 600°K.; these values are referred to the non-vibrating state as a zero of energy and are thus immediately applicable to the calculation of equilibrium constants in isotopic exchange reactions. In what follows this somewhat specialized Q will be designated f, following the notation used by Urey and Greiff.

Ozone, O_3. Kassel (62) calculated approximate values of $-F/T$ for ozone up to 5000°K. on the basis of an approximate frequency assignment, and from the thermochemical heat of formation of ozone calculated K for

$$O_3 = O_2 + O$$

and

$$O_3 = \tfrac{3}{2}O_2$$

The results showed that earlier experimental attempts to determine the entropy of ozone by electromotive force measurements and also by the formation of ozone when filaments were heated in liquid oxygen (24) had given wholly incorrect values. The maximum concentration of ozone in the system O–O_2–O_3 at equilibrium at a total pressure of 1 atm. is 10^{-6} atm. at 3500°K.; at all temperatures above 900°K. O is more abundant than O_3. The 1 per cent of ozone formed in liquid oxygen must have been due to the escape of atomic oxygen from the hot region; the mole fraction of O at 2300°K. is about 0.5 per cent, a value of the right order of magnitude to support this interpretation. The same spectroscopic data were used later to calculate H for ozone up to 1000°K.; the values may be found in the useful tabulation of Lewis and von Elbe (73).

Atomic hydrogen, H. Giauque (25) has tabulated $-F/T$ to 5000°K.

Deuterium, D. Johnston and Long (55, 56) have tabulated $-F/T$ to 3000°K.

Molecular hydrogen, H_2. The first successful spectroscopic calculations for hydrogen were the historic specific-heat calculations of Dennison (16), in which a rigid molecule was assumed, and hence no high accuracy was obtained. Giauque (25) used the actual energy levels to calculate the equilibrium ortho–para ratio up to 298.1°K., where the composition is 25.074 per cent para, S at 298.1°K., H and C_p up to 298.1°K. for pure ortho, pure para, the 3:1 mixture, and the true equilibrium composition, and $-F/T$ from 298.1°K. to 5000°K. Using the spectroscopic heat of dissociation given by Richardson and Davidson (85), he calculated also the equilibrium constant for

$$H_2 = 2H$$

obtaining values surprisingly close to the experimental results of Langmuir (70). The calculated entropy agreed with the experimental third law value only when the entropy of mixing of ortho and para states in the solid, $-(R/4)\log 1/4 - (3R/4)\log 1/12$, was added to the observed value. The controversy concerning the legitimacy of this addition has now subsided and need not be revived here. Gordon and Barnes (40) calculated approximate values for C_p and S up to 1200°K. Davis and Johnston (15) subsequently calculated C_p, H and S to 5000°K.; they also gave a corrected table for $-F/T$ which replaces the corresponding values given by Giauque, and gave a few additional corrections to Giauque's calculations. Empirical equations for C_p have been given by Spencer and Justice (93) and by Chipman and Fontana (8), both based on Davis and Johnston's calculations.

HD *and* D_2. Urey and Rittenberg (99) used theoretical spectroscopic relations to calculate the rotation-vibration levels of HD and of D_2 from those of H_2, and used these levels to calculate $-F/T$ from 50 to 700°K. and also the equilibrium constant for

$$H_2 + D_2 = 2HD$$

Johnston and Long (55) calculated C_p, H, S, and $-F/T$ for HD and D_2 up to 3000°K. They give C_p and H for D_2 for the pure para form, the pure ortho form, the 1:2 ratio, and the true equilibrium composition at temperatures up to 300°K.; at higher temperatures the values become essentially identical for all four cases. The calculated ortho–para equilibrium ratios have been confirmed by Farkas, Farkas, and Harteck (23). Farkas and Farkas (22) showed that the equilibrium constant for

$$H_2 + D_2 = 2HD$$

was about 4. More precise measurements by Rittenberg, Bleakney, and Urey (86) checked closely with the theoretical values over the range 298 to 741°K. Later experiments by Gould, Bleakney, and Taylor (44) using Cr_2O_3 and Ni catalysts to obtain equilibrium carried this confirmation down to 83°K., where $K = 2.2$.

OH. Villars (100, 101) calculated S_{298}, but made an error in electronic quantum weights. The lowest states of OH are an inverted $^2\Pi_{1/2,\,1\,1/2}$ doublet, each level of which has of course Λ-type doubling, which in this case is unusually large (due to the small moment of momentum). Johnston and Dawson (53) calculated C_p from 0.01 to 5000°K., the lower part of this range being of course only an amusing exercise. The Λ-doubling contribution to C_p reaches a maximum at 0.060°K., the $^2\Pi_{1/2}$ excitation contribution a maximum at 100°K., which is about the point where the rotation has become fully developed. Johnston and Dawson also calculated S from 250 to 5000°K. and H and $-F/T$ from 298.1° to 5000°K. The underlying spectroscopic data are precise, but exact equilibrium constants cannot be calculated since no heat of reaction involving OH is precisely known. Lewis and von Elbe (72), however, have determined an approximate value for ΔH_0 for

$$H_2O = OH + \frac{1}{2}O_2$$

This reaction is discussed in the following paragraph.

Water, H_2O. Gordon and Barnes (40) calculated rough values for C_p and S from 400° to 1200°K. Gordon (35) used somewhat more accurate data to calculate $-F/T$ to 3000°K. Finally, taking into account anharmonic terms and rotation-vibration interactions, Gordon (36) gave precise values for $-F/T$, S, and C_p to 1500°K. and less accurate values (37) up to 3000°K. Spencer and Justice (93) gave an empirical equation to represent these C_p values.

Lewis and von Elbe (73) used the data of Giauque (35) on H_2, of Johnston and Walker (57) on O_2 with an approximate correction for the $^1\Delta$ level, and Gordon's final values for H_2O, together with $\Delta H_0 = -57,111$ cal., based on Rossini's (90) precise heat of combustion of hydrogen, to calculate equilibrium constants for

$$H_2 + \frac{1}{2}O_2 = H_2O$$

from 300° to 3000°K. They used the same data for H_2 and H_2O, together with their (72) explosion value of $\Delta H_0 = -63,000$ cal. to calculate equilibrium constants for

$$OH + \frac{1}{2}H_2 = H_2O$$

from 300° to 3000°K.

Water, H_2O^{18}. Urey and Greiff (98) calculated the ratio of f values for H_2O^{18} and H_2O^{16} at 273, 298, and 600°K., and the equilibrium constant for

$$O_2^{16} + 2H_2O^{18}(g) = O_2^{18} + 2H_2O^{16}(g)$$

at the same temperatures, the values being 1.048, 1.041, and 1.006.

HDO *and* D_2O. Topley and Eyring (96), using theoretical frequencies for HDO and D_2O, estimated the equilibrium constant for

$$H_2O + D_2O = 2HDO$$

as 3.26 at 298°K. and 3.40 at 373°K. for the gaseous state; they predict that these values will apply also to the liquid. Crist and Dalin (11) calculated equilibrium constants for

$$HDO + H_2 = H_2O + D_2$$

from 300° to 900°K. and also determined an experimental value of 0.66 at 800°K. Upon correction of an error in the first calculation the theoretical values became (12) 0.35 at 300°K., 0.62 at 525°K., and 0.83 at 900°K. This calculation is based upon that of Urey and Rittenberg (99) for H_2 and HD and upon Topley and Eyring's (96) frequencies for H_2O and D_2O. Crist and Dalin (13) showed that the system H_2–HD–D_2–H_2O–HDO–D_2O depends upon three equilibrium constants which may be taken as

$$H_2 + D_2 = 2HD$$
$$D_2O + H_2 = H_2O + D_2$$
$$HDO + H_2 = H_2O + HD$$

The first and third of these had been calculated previously. Crist and Dalin calculated the second also, finding 0.2 at 373°K. and 0.606 at 800°K. They present curves giving the equilibrium concentrations of all six constituents as a function of the ratio D/(H + D) for the special case

$$(H_2) + (HD) + (D_2) = (H_2O) + (HDO) + (D_2O)$$

at 373° and 800°K. The calculated results at the higher temperature were shown to agree with experimental values.

Chlorine, Cl^{35} and Cl^{37}. Giauque and Overstreet (30) tabulate $-F/T$ for the normal isotopic mixture.

Chlorine, Cl_2^{35}, $Cl^{35}Cl^{37}$, and Cl_2^{37}. Giauque and Overstreet (30) calculated $-F/T$ for each of these molecules from 250° to 3000°K. They showed that at 298°K. the equilibrium constant for

$$Cl_2^{35} + Cl_2^{37} = 2Cl^{35}Cl^{37}$$

was 3.9997, against the value 4, which would correspond to no preference among the three types of molecules. They interpreted this close agreement to mean that no isotopic separations would occur to an appreciable extent at 298°K. or higher temperatures. They, therefore, combined the three $-F/T$ values to a weighted average "practical" $-F/T$ from which nuclear spin and mixing effects are excluded; they discuss in detail the use of such practical functions. It may be seen, however, that this averaging process is not allowable when the highest accuracy is desired. Thus one can calculate from the data given by Giauque and Overstreet[5] that $-\Delta F/T = 0.012$ and $K = 1.006$ for

$$Cl_2^{35} + 2HCl^{37} = Cl_2^{37} + 2HCl^{35}$$

---

[5] In making this calculation, it should be noted that the astonishing figures given by Giauque and Overstreet for the zero-point energies of the Cl_2^{35}, $Cl^{35}Cl^{37}$, and Cl_2^{37} molecules, 800.46, 789.60, and 778.56 cm.$^{-1}$ are numerically correct, but are calories instead of cm.$^{-1}$

These authors failed to make this calculation, and thus failed to note the possibility of slight isotopic separation. When this separation is not important, the weighted averages may be used.

Giauque and Overstreet (30) used their $-F/T$ values and a spectroscopic ΔE_0 of 56,900 cal. to calculate $\Delta F/T$ for

$$Cl_2 = 2Cl$$

from 250° to 3000°K. Spencer and Justice (93) calculated the specific heat from 300° to 1500°K. and gave an empirical equation to fit their values.

Urey and Greiff (98) calculated the ratio of f values for Cl_2^{37} and Cl_2^{35}.

Chlorine dioxide, ClO_2^{16} *and* ClO_2^{18}. The three fundamental frequencies of ClO_2^{16} are known from the work of Ku (67), but there is some uncertainty as to the shape of the molecule; the more probable value for the angle O—Cl—O is 65°, but 121° 20′ is not excluded. Using both sets of constants and theoretical isotope shifts, Urey and Greiff (98) calculated the f ratio, and found for the equilibrium constant of

$$ClO_2^{16} + 2H_2O^{18}(g) = ClO_2^{18} + 2H_2O^{16}(g)$$

the values 1.021, 1.015 at 298°K.

Hydrogen chloride, HCl^{35} *and* HCl^{37}. Giauque and Overstreet (30) gave $-F/T$ for HCl^{35}, HCl^{37}, and the equilibrium mixture, and $\Delta F/T$ for

$$\tfrac{1}{2}H_2 + \tfrac{1}{2}Cl_2 = HCl$$

from 250° to 3000°K. In calculating $\Delta F/T$ they used the value $\Delta F_{298.1} = -22{,}741$ cal. obtained by Randall and Young (84) from electromotive force measurements, corresponding to $\Delta E_0 = -21{,}984$ cal. Rossini (91) found the calorimetric value $\Delta H_{298.1} = -22{,}063 \pm 12$ cal., giving $\Delta E_0 = 22{,}019 \pm 12$ cal. He assigns an uncertainty of 33 cal. to the Randall and Young value, arising almost entirely from the step

$$HCl(aq) = HCl(g)$$

A slight revision of Giauque and Overstreet's $\Delta F/T$ values is thus perhaps desirable. Giauque and Overstreet also calculated $S_{298.1}$ more accurately than Giauque and Wiebe (31) had done, finding 44.658 (with entropy of mixing and of nuclear spin excluded) against the latter workers' experimental third law value of 44.5. Spencer and Justice (93) calculated C_p from 300° to 1500°K. and gave an empirical equation to fit their results. Urey and Greiff (98) calculated f ratios for HCl^{37} and HCl^{35} and K for

$$Cl_2^{35} + 2HCl^{37} = Cl_2^{37} + 2HCl^{35}$$

Deuterium chloride, DCl^{35}. Urey and Rittenberg (99) used theoretical spectroscopic relations to obtain energy levels of DCl^{35} from those of HCl^{35};

they calculated $-F/T$ for DCl^{35} from 200° to 700°K. Since they used a slightly different energy formula for HCl^{35} than that adopted by Giauque and Overstreet, and also a slightly different value of R, they calculated also the corresponding consistent values for HCl^{35}. They thus obtained the following values for K of

$$H_2 + 2DCl^{35} = D_2 + HCl^{35}$$

T	0°	200°	298.1°	400°	575°	700°K.
K	0.000	0.309	0.502	0.647	0.807	0.874

Atomic bromine, Br. $-F/T$ has not been tabulated explicitly, but dissociation constants are given below.

Bromine, Br_2. Gordon and Barnes (43) have calculated $-F/T$, S, and C_p from 200° to 1600° K., using the spectroscopic constants for $Br^{79}Br^{81}$. They show that this is equivalent within their limit of error to weighting the separate isotopic varieties as Giauque and Overstreet (30) did for chlorine. They calculated the equilibrium constant for

$$Br_2 = 2Br$$

using the accurate spectroscopic value $\Delta E_0 = 45{,}230$ cal. given by Brown (6). The experimental values of $R \log K$ given by Bodenstein (5) are about 0.5 cal. per degree less than the calculated values. It has been suggested to the writer (89) that this discrepancy may indicate the formation of Br_3. Spencer and Justice (93) have given an empirical equation to fit the C_p values of Gordon and Barnes. Urey and Greiff (98) calculated f ratios for Br_2^{81}, Br_2^{79}.

Hydrogen bromide, HBr^{79} and HBr^{81}. Giauque and Wiebe (32) calculated $S_{298.1}$, finding 47.53 as against their third law value of 47.6. This calculated value was revised subsequently (33) to 47.48. Gordon and Barnes (43) calculated $-F/T$, S, and C_p from 200 to 1600°K.; they give $S_{298.1} = 47.481$. They also calculated K for

$$\tfrac{1}{2}H_2 + \tfrac{1}{2}Br_2 = HBr$$

using a calorimetric heat of reaction. Spencer and Justice (93) have given an empirical equation to fit the above C_p values. Urey and Greiff (98) calculated f ratios for HBr^{81} and HBr^{79}, and found K for

$$Br_2^{79} + 2HBr^{81} = Br_2^{81} + 2HBr^{79}$$

The values of 1.001 at 273°K., 1.0008 at 298°K. and 0.99994 at 600°K. effectively discourage the use of isotopic exchange reactions to separate isotopes of elements with large atomic weights.

Iodine, I_2. Gibson and Heitler (34) used the spectroscopic values for I_0, ω_0, and D, with a slight anharmonic correction not clearly explained, to calculate K for

$$I_2 = 2I$$

from 1073° to 1473°K. Their results agree to within less than 1 per cent with experimental values of Starck and Bodenstein (94). Giauque (26) calculated $S_{298.1} = 62.29$ for I_2 gas at 1 atm. He combined spectroscopic data with accurate vapor pressure measurements to obtain $\Delta E_0 = 15{,}640 \pm 3$ cal. for

$$I_2(s) = I_2(g)$$

Hydrogen iodide, HI. Giauque and Wiebe (33) calculated $S_{298.1} = 49.4$, using the spectroscopic moment of inertia but assuming a rigid molecule, owing to lack of sufficient data; their third law value was 49.5.

Deuterium iodide, DI. Urey and Rittenberg (99), likewise handicapped by insufficient data, calculated the following K values for

$$H_2 + 2DI = D_2 + 2HI$$

T	0°	298.1°	400°	575°	700°K.
K	0	1.164	1.212	1.234	1.222

These values were confirmed experimentally by Rittenberg and Urey (87).

Iodine chloride, ICl. McMorris and Yost (77) calculated from spectroscopic data $S_{298.1} = 59.2$; by combination of this value with the values $S_{298.1} = 62.29$ for $I_2(g)$ and $S_{298.1} = 53.31$ for Cl_2 given by Giauque, and with a spectroscopic ΔE_0 they find

$$-\Delta F/T = 3461/T + 1.40$$

for

$$\tfrac{1}{2}I_2(g) + \tfrac{1}{2}Cl_2 = ICl$$

They quote a more recent calculation by Brown, according to which $S_{298.1}$ for ICl is 59.15 and $-\Delta F/T = 3280/T + 1.36$.

Sulfur, S. $-F/T$ values have been tabulated by Montgomery and Kassel (79) from 250° to 5000°K.

Sulfur, S_2. Montgomery and Kassel (79) calculated $-F/T$ from 250° to 5000°K. If the reinterpretation of the underlying spectroscopic data suggested by Badger (2) is accepted, these values must be increased by 0.55, as was shown by Cross (14). Montgomery and Kassel also gave $\log_{10} K$ for

$$S_2(g) = 2S$$

These values must be decreased by 0.120 to take care of the above correction. Cross calculated $S_{298.1} = 54.417$.

Sulfur monoxide, SO. Montgomery and Kassel (79) calculated $-F/T$ for SO and by the use of an accurate spectroscopic energy of dissociation and of Johnston and Walker's (57) values of $-F/T$ for O_2, uncorrected for the $^1\Delta$ state, calculated $\log_{10} K$ for

$$\tfrac{1}{2}S_2(g) + \tfrac{1}{2}O_2 = SO$$

These values must be decreased by 0.060 to take account of the changed values for S_2, and by 0.002 at 2000°, 0.015 at 3000°, 0.038 at 4000° and 0.065 at 5000°K. for the $^1\Delta$ level.

Sulfur dioxide, SO_2^{16} and SO_2^{18}. Gordon (39) calculated $-F/T$ for sulfur dioxide from 298° to 2800°K., using somewhat incomplete spectroscopic data. He obtained ΔE_0 for

$$\tfrac{1}{2}S_2(g) + O_2 = SO_2$$

from a combination of spectroscopic calculations with calorimetric data for

$$S_{rh} + O_2 = SO_2$$

and

$$S_{rh} + H_2 = H_2S$$

and thus calculated K for the first reaction above. He used the SO values of Montgomery and Kassel (79) as revised by Cross (14) and the O_2 values of Johnston and Walker (57) uncorrected for the $^1\Delta$ level, to calculate K for

$$SO + \tfrac{1}{2}O_2 = SO_2$$

Urey and Greiff (98) calculated the f ratio for SO_2^{18} and SO_2^{16}.

Hydrogen sulfide, H_2S. Cross (14) used incomplete spectroscopic data to calculate $-F/T$, S, C_p from 212.77° to 1800°K. Comparison of spectroscopic values with equilibrium measurements gives for

$$H_2S(g) = H_2 + \tfrac{1}{2}S_2(g)$$

the precise value $\Delta E_0 = 19620 \pm 30$ cal.

Nitrogen, N. $-F/T$ values have been tabulated up to 5000°K. by Giauque and Clayton (28).

Nitrogen, N_2^{14}. Giauque and Clayton (28) calculated $-F/T$ to 5000°K. and also $S_{298.1} = 45.788$ excluding the nuclear spin entropy $R \log 9$. The experimental value is 45.9. The agreement shows that ortho- and paranitrogen are present in the solid state at low temperatures in the high-temperature proportion of 6:3, but that the paranitrogen is present in the solid in a form carrying only the spin weight of 3. There are then nine forms present in the solid in equal quantities, giving a contribution R log 9 to the entropy which does not appear in the specific heat measurements; since this is just equal to the excluded spin entropy, the third law value agrees with the spectroscopic one. If the paranitrogen molecules were rotating in the crystal, they would have an extra weight factor of 3; the unmeasured entropy of the solid would then be $2/3\ R \log 9 + 1/3\ R \log 27 = R \log 9 + 1/3\ R \log 3$, and the third law value would be 0.7 cal. per degree less than the spectroscopic value.

Giauque and Clayton made a tentative calculation of K for

$$N_2 = 2N$$

based on $\Delta E_0 = 182{,}000$ cal. This value is still uncertain.

Johnston and Davis (52) gave a curve showing C_p for the ortho, para, equilibrium, and non-equilibrium mixtures up to 20°K. They have tabulated C_p and S from 50° to 5000°K., and H from 100° to 5000°K. Spencer and Justice (93) fitted an empirical equation to these C_p values.

Nitrogen, N_2^{15}. Urey and Greiff (98) calculated the ratio of f values for N_2^{15} and N_2^{14}.

Nitric oxide, NO. Johnston and Giauque (54) calculated $S_{121.36} = 43.75$, and interpolation of the later calculations of Johnston and Chapman gives $S_{121.36} = 43.753$. Johnston and Giauque found an experimental value of 43.0 from specific heat measurements. The discrepancy of $0.75 \sim R/2 \log 2$ was explained by them as due to the existence in the solid of two forms of N_2O_2 differing in coupling. Later Blue and Giauque (4) proposed that the extra entropy in the solid arises from two different orientations of a single kind of N_2O_2. Johnston and Chapman (50) calculated $-F/T$ from 50° to 5000°K., S from 1° to 5000°K., and C_p from 0.5° to 5000°K. A numerical error in the value of $-F/T$ at 1125°K. was corrected subsequently (51). Witmer (108) pointed out an error by Johnston and Chapman in interpretation of the spectroscopic data and gave revised tables for C_p, S, and $-F/T$ from 1° to 500°K.; at higher temperatures the error produces a negligible effect on the calculated thermodynamic functions. Johnston and Chapman used the estimate $\Delta E_0 = 142{,}000$ cal. to calculate approximate values of K for

$$NO = N + O$$

Giauque and Clayton (28) used their own $-F/T$ for N_2, those of Johnston and Chapman for NO, those of Johnston and Walker (57) uncorrected for the $^1\Delta$ level for O_2 and unusually concordant calorimetric data of Thomsen and Berthelot equivalent to $\Delta E_0 = 21{,}400$ cal. to calculate K for

$$\tfrac{1}{2}N_2 + \tfrac{1}{2}O_2 = NO$$

from 298° to 5000°K. These values must be considered provisional until a more certain value of ΔE_0 is available.

Nitric oxide, $N^{15}O$. Urey and Greiff (98) calculated K for

$$N_2^{14} + 2N^{15}O = N_2^{15} + 2N^{14}O$$

Nitrous oxide, N_2O. Kassel (64) used spectroscopic data which gave the anharmonic constants, but not the probably less important rotational stretching correction, to calculate $-F/T$, H, and C_p from 250° to 1500°K. Recent calorimetric data for the reaction

$$N_2 + \tfrac{1}{2}O_2 = N_2O$$

give $\Delta E_0 = 20{,}429$ cal. The equilibrium constant then was calculated as 6.87×10^{-19} at 300°K., 6.87×10^{-9} at 1000°K., and 1.98×10^{-7} at 1500°K., on the basis of Giauque and Clayton's (28) data for N_2 and Johnston and Walker's (57) data for O_2, uncorrected for the $^1\Delta$ level.

Kassel gave $S_{298.1} = 52.575$ with nuclear spin excluded. Blue and Giauque (4) calculated 52.581. Previous less accurate calculations had been made by Badger and Woo (3), who found 52.58, and by Rodebush (88), who used an incorrect moment of inertia. Blue and Giauque's experimental third law value is 51.44, 1.14 lower than the calculated value. If in the actual crystal at the lowest temperatures reached the orientations NNO and ONN occurred at random, the crystal would possess an entropy $R \log 2 = 1.377$ which would have to be added to $\int (C_p/T)\mathrm{d}T$. The discrepancy is slightly less than this, a fact which may be taken to indicate a partial orientational ordering.

Ammonia, NH_3. No extensive calculations have been made for ammonia. An old controversey involving Villars (102), Giauque, Blue and Overstreet (27), and MacDougall (75) with regard to the entropy need not be revived now. The absolute $S_{298.1}$ is 52.10; with all nuclear spin excluded the "virtual" entropy is 45.79. One or the other of these values should be used in all calculations.

Bryant (7) has given an empirical equation to fit his approximate spectroscopic C_p values from 300° to 2000°K.

Carbon, C. By integrating experimental heat-capacity data, Clayton and Giauque (9) have calculated $-F/T$ for β-graphite from 250° to 3000°K. These are not spectroscopic values, of course, but are included here for convenience.

Carbon monoxide, $C^{12}O^{16}$, $C^{13}O^{18}$, and $C^{12}O^{18}$. Clayton and Giauque (9) calculated $-F/T$ for CO to 5000°K.; they later (10) published a revised table, as the first had been based on an incorrect energy level equation. They gave $S_{298.1} = 47.316$; the experimental third law value was 46.2. The difference of 1.1, slightly less than $R \log 2 = 1.38$, was considered to indicate an almost random distribution as between CO and OC in the crystal, with a slight preference for regularity. They used heats of combustion of graphite and of carbon monoxide to calculate equilibrium constants for

$$\text{C } (\beta\text{-graphite}) + \tfrac{1}{2}O_2 = CO$$

up to 3000°K. These calculations, owing to the uncertainties in $-F/T$ and the heat of combustion for graphite, were not considered worth revising along with the $-F/T$ values for CO. Kassel (63) calculated the other thermodynamic functions for CO, using Giauque's original incorrect energy equation. Johnston and Davis (52) used correct data to calculate C_p and S from 50° to 5000°K. and H from 100° to 5000°K. Spencer and Justice (93) gave an equation to represent these C_p values. Urey and Greiff (98) calculated f ratios for $C^{13}O$, $C^{12}O$ and for CO^{18}, CO^{16}, and K for

$$\begin{aligned} C^{12}\ (\beta\text{-graphite}) + C^{13}O &= C^{13}\ (\beta\text{-graphite}) + C^{12}O \\ CO^{16} + H_2O^{18} &= CO^{18} + H_2O^{16} \\ 2CO^{16} + O_2^{18} &= 2CO^{18} + O_2^{16} \end{aligned}$$

Carbon dioxide, $C^{12}O_2^{16}$, $C^{12}O_2^{18}$, and $C^{13}O_2^{16}$. Approximate calculations for CO_2 were made by Gordon and Barnes (40) and Gordon (35). Kassel (64) later used more complete data to calculate accurate values for $-F/T$, H, and C_p up to 1500°K. and somewhat uncertain estimates up to 3500°K. He used the data of Clayton and Giauque (9) on C, their revised data (10) on CO, the data of Giauque (25) and of Davis and Johnston (15) on H_2, of Johnston and Walker (57) on O_2, and of Gordon (36, 37) on H_2O, together with precision heats of combustion, to calculate equilibrium constants for

$$\begin{aligned} 2CO_2 &= 2CO + O_2 \\ CO_2 + C &= 2CO \\ CO_2 + H_2 &= CO + H_2O \end{aligned}$$

The values for the water gas equilibrium agree well with the best experimental values. Those for the producer gas reaction suggest a "zero-point" entropy of 0.5 cal. per degree for graphite, as had been pointed out by Gordon (35).

Urey and Greiff (98) calculated f ratios for CO_2^{18}, CO_2^{16} and for $C^{13}O_2$,

$C^{12}O_2$, and K values for

$$\begin{aligned} CO_2^{16} + 2H_2O^{18}(g) &= CO_2^{18} + 2H_2O^{16}(g) \\ CO_2^{16} + CO_2^{18} &= 2CO^{16}O^{18} \\ C^{13}O + C^{12}O_2 &= C^{12}O + C^{13}O_2 \\ C^{12} + C^{13}O_2 &= C^{13} + C^{12}O_2 \end{aligned}$$

Methane, CH_4. Approximate values of $-F/T$ up to 5000°K. were calculated by Kassel (60a) and used to obtain K for

$$C\ (\beta\text{-graphite}) + 2H_2 = CH_4$$

Void (105) used essentially the same data to calculate C_p from 273° to 773°K.

Acetylene, C_2H_4. Kassel (60a) calculated $-F/T$ to 3000°K. and also K for

$$2C\ (\beta\text{-graphite}) + H_2 = C_2H_2$$

These later values are considerably in doubt, owing to the uncertain heat of combustion of acetylene.

Ethylene, C_2H_4. Kassel (60a) used very imperfect spectroscopic data to estimate $-F/T$ for ethylene and K for

$$2C\ (\beta\text{-graphite}) + 2H_2 = C_2H_4$$

up to 3000°K. He also calculated C_p at 300° and 350°K. Smith and Vaughan (92) calculated S and H from 298° to 973°K. and C_p from 143° to 464°K., using somewhat different frequencies than those given by Kassel; these frequencies were chosen in such a way as to give improved agreement with the experimental values of C_p.

Ethane, C_2H_6. Smith and Vaughan (92) used frequencies given by Eucken and Parts (21) as follows: 712 cm.$^{-1}$ (2), 826 (2), 990 (1), 1460 (2), 1465 (2), 1499 (2), 2975 (6), the multiplicity being indicated in parentheses. The 712 and 826 cm.$^{-1}$ frequencies have no appreciable support from spectroscopic work, but give low temperature C_p values in agreement with Eucken and Parts experiments. Smith and Vaughan calculated C_p from 143° to 373.5°K. and S and H from 298° to 973°K. They then calculated K for

$$C_2H_6 = C_2H_4 + H_2$$

The calculated values are larger than the experimental, the excess in R log K being about 1.2 cal. per degree. They made an error in calculating the largest moment of inertia of ethane from interatomic distances; when this error is corrected the discrepancy is increased by 0.27 cal. per degree. As was pointed out in an earlier section, ethane has an internal "free rotation." Smith and Vaughan are inclined to ascribe this disagreement to lack of freedom in that rotation.

Paraffins, C_nH_{2n+2}. Very rough, approximate values for $-F/T$, H, S, and C_p for the normal paraffins from ethane through hexane will be published by the author in the near future.

Chloromethanes, CH_3Cl, CH_2Cl_2, $CHCl_3$, and CCl_4. Vold (105) used incomplete data to calculate C_p from 273° to 773°K.

Hydrogen cyanide, HCN. Badger and Woo (3) calculated $S_{298.1} = 48.23$ exclusive of nuclear spin entropy. Bryant (7) calculated the specific heat and gave an approximate equation.

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