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Calculation of Thermodynamic Functions for Polyatomic Molecules[1]

Harold W. Woolley

Formulas are given from which the thermodynamic functions may be obtained for polyatomic molecules not exhibiting special phenomena, such as internal rotation. The effects of first and second order anharmonicities and rotational-vibrational interaction are treated in detail, as also are the angular momentum effects of doubly degenerate vibrations in linear molecules. This paper presents formulas for the corrections carried to higher order than has hitherto been available.

1. Introduction

There is occasionally need for accurate thermodynamic functions for polyatomic molecules. A definite calculating procedure exists for approximate calculations via the rigid-rotator harmonic oscillator treatment, with small corrections for effects of anharmonicity, stretching, etc.

This paper presents formulas for the corrections carried to higher order than has hitherto been available. Calculations can thus be made via the approximation formulas with accuracy probably comparable with that of the direct summation method using extrapolated formulas for the energy levels, aside from effects related to vibrational and rotational cut-off, which have been omitted.

2. Nonlinear Polyatomic Molecules

The partition function for the internal molecular energy states may be written as

$$Q = Q_R Q_{Rc} Q_{H.O.} Q_c. \tag{1}$$

For nonlinear molecules,

$$Q_R = (1/\gamma)\sqrt{(\pi/A_0 B_0 C_0)(kT/hc)^3} \tag{2}$$

is the rigid rotator partition function for the lowest vibrational energy state, where A_0, B_0, and C_0 are the rotational constants for the ground vibrational state, and γ is the symmetry number. $Q_{H.O.}$ is the partition function for vibrational levels of harmonic oscillators. Q_{Rc} is a correction factor including (1) a factor $1+\rho T$. . . for rotational stretching, as shown by Wilson [1][2] and (2) a factor $1+\theta_1/T+\theta_2/T^2$ for a low temperature quantum correction for rotation as shown by Stripp and Kirkwood [2].[3] Q_c is a factor including rotational-vibrational interaction and the anharmonicity corrections, now to be treated in detail.

The rotational-vibrational interaction in its simple form arises from the vibrational dependence of the analogue of eq (2) for higher vibrational states. Before summation over vibrational quantum numbers, the dependence is introduced by including the factor

$$R_v = \exp[\Sigma a_i v_i + \Sigma a_{ii} v_i^2 + \Sigma a_{ij} v_i v_j + \Sigma a_{iii} v_i^3 + \Sigma a_{iij} v_i^2 v_j + \Sigma a_{ijk} v_i v_j v_k], \tag{3}$$

equivalent to a form introduced by Benedict [3].[4] With his formulation, the constants in the factor R_v come from sums of corresponding constants for A_v, B_v, and C_v. A summation procedure adequate to treat this with the anharmonicity effects follows, extending the latter beyond the linear terms of Stockmayer, Kavanagh, and Mickley [4].

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[1] Related to a thesis submitted to the Graduate School of the University of Michigan in partial fulfillment of the requirements for the Ph. D. degree in Physics.

[2] Figures in brackets indicate the literature references at the end of this paper.

[3] Expressions representing the T^2 rotational stretching effect and the T^{-3} low temperature correction as well as a low temperature correction for symmetry effects for different classes of rotational levels for the asymmetric rotator are included in the thesis.

[4] An equivalent representation in slightly different form is given in the thesis.

For a given vibrational level, specified by vibrational quantum numbers v_i, $1 \leq i \leq n$, the statistical weight is the product of the n quantities

$$p_i = (v_i + d_i - 1)!/[v_i!(d_i - 1)!], \tag{4}$$

where d_i is the degeneracy associated with the ith fundamental frequency.

The summation over the vibrational levels may be indicated as

$$Q = Q_R Q_{Rc} \sum_{v_i' \mathrm{s}} R_v \exp[-hcG_v/kT] \prod_i p_i \tag{5}$$

with the vibrational energy in wave numbers given by

$$G_v = \Sigma\omega_i v_i + \Sigma x_{ii} v_i (v_i - 1) + \Sigma x_{ij} v_i v_j + \Sigma y_{iii} v_i (v_i - 1)(v_i - 2) + \Sigma y_{iij} v_i (v_i - 1) v_j + \Sigma y_{ijk} v_i v_j v_k. \tag{6}$$

The relations between these constants and the more usual ones are indicated in appendix 1.

The Boltzmann factor is separated into two factors, one for harmonic oscillators fitting the lowest levels and a second giving the alteration due to anharmonicity

$$\exp[-hcG_v/kT] = \exp[-hc\Sigma\omega_i v_i/kT] \exp[-hc(G_v - \Sigma\omega_i v_i)/kT]. \tag{7}$$

Q_{vc}, the product of the second factor on the right hand side of (7) with R_v, is expanded into a power series whose terms are polynomials in the v's. Defining a function

$$f_i(Z) = v_i!/(v_i - Z)! \tag{8}$$

it can be shown that[5]

$$\sum_{v_i=0}^{\infty} p_i e^{-u_i v_i} = (1 - e^{-u_i})^{-d_i}, \tag{9}$$

where $u_i = hc\omega_i/kT$, and that

$$\sum_{v_i=0}^{\infty} f_i(Z) p_i e^{-u_i v_i} = [(d_i + Z - 1)!/(d_i - 1)!] \cdot [e^{-Zu_i}/(1 - \mathrm{e}^{-u_i})^{d_i + Z}]. \tag{10}$$

The factor Q_{vc} can be expressed as a sum of terms, each linear in whatever f_i's it contains.[6] The results of multiple summation over all v_i's follow by application of eq (10). If the right-hand side of eq (10) be designated by $f_i^*(Z)$, one has $\Sigma_v Q_v Q_{vc} = Q_{H.O.} Q_c$, where $Q_v = \exp[-\Sigma_i u_i v_i]$ $Q_{H.O.} = \Sigma_v Q_v$ and where Q_c is the same function of $f_i^*(Z)$ as Q_{vc} was of $f_i(Z)$. Thus eq (1) has been evaluated, $Q_{H.O.}$ being given by

$$Q_{H.O.} = \prod_i (1 - e^{-u_i})^{-d_i}. \tag{11}$$

There is some advantage in using the logarithm of the partition function from this point on because of analytic cancellations of some higher order terms. The terms removed are cross products without linkage in the subscripts, such as $x_{ij} x_{kl}$, $x_{ii} x_{jk}$, and $a_i x_{jj}{}^2$, for example.

The contribution to $\ln Q_c$ due to x_{ii} and x_{ij} terms, with $r_i = e^{-u_i}$ and $s_i = (1 - e^{-u_i})^{-1}$ is

$$\begin{aligned}-(hc/kT)\sum\{x_{ii} d_i (d_i + 1) r_i^2 s_i^2 + x_{ij} d_i d_j r_i r_j s_i s_j\} + \tfrac{1}{2}(hc/kT)^2 \sum\{2x_{ii}^2 d_i (d_i + 1) r_i^2 [1 + 2(d_i + 1) r_i] s_i^4 \\ + x_{ij}^2 d_i d_j r_i r_j [1 + d_i r_i + d_j r_j] s_i^2 s_j^2 + 2x_{ij} x_{ik} d_i d_j d_k r_i r_j r_k s_i^2 s_j s_k + 4x_{ii} x_{ij} d_i (d_i + 1) d_j r_i^2 r_j s_i^3 s_j],\end{aligned} \tag{12}$$

with terms of higher order for this and other contributions listed in appendix 4. At high temperature the first term varies as T and the second as T^2. The terms in the appendix are higher than T^2 in principal dependence at high temperature.

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[5] See appendix 2.

[6] Relations giving the simpler polynomials in terms of the f's will be found in appendix 3.

Similarly, the contribution of higher order anharmonic terms is

$$-(hc/kT)\sum\{y_{iii}d_i(d_i+1)(d_i+2)r_i^3s_i^3+y_{iij}d_i(d_i+1)d_jr_i^2r_js_i^2s_j+y_{ijk}d_id_jd_kr_ir_jr_ks_is_js_k\}. \tag{13}$$

The contribution due to rotational-vibrational interaction is

$$\sum\{a_id_ir_is_i+a_{ii}d_ir_i(1+d_ir_i)s_i^2+a_{ij}d_id_jr_ir_js_is_j+\tfrac{1}{2}a_i^2d_ir_is_i^2\} \tag{14}$$

as far as a's alone are concerned, while their mixing with anharmonicities gives

$$-(hc/kT)\sum\{2a_ix_{ii}d_i(d_i+1)r_i^2s_i^3+a_ix_{ij}d_id_jr_ir_js_i^2s_j\}. \tag{15}$$

In all of these (multiple) summations, if the terms are completely symmetric in the indices that are present, such as i, j, etc., the symmetric indices are to progress in size as with $i<j<k$, and so forth. For terms not completely symmetric in the indices, the indices not symmetric are simply not to be equal, thus $i\neq j\neq k$, and so forth.[7]

3. Linear Molecules

There is an additional kind of vibrational-rotational interaction, concerning vibrational angular momentum, which is important for linear molecules. When doubly degenerate vibrations occur, the vibrational energy, eq (6), contains an additional term $g=\sum_{i\leq j} g_{ij}l_il_j$. For linear molecules, in addition, there is dependence of the rotational energy upon l where $l=\Sigma l_i$, giving for the two together

$$F(J,\, l)=g+B_v[J(J+1)-l^2]-D_v[J(J+1)-l^2]^2, \tag{16}$$

where $J=l,\, l+1,\, l+2\;.\;.\;.$, with double degeneracy for $|l|>0$.

The sum over the rotational levels for $J\geq|l|$ follows from a half integer summation formula of the Euler-Maclaurin type [5]

$$\sum_{n=n_1}^{\infty} f(n)=\int_{n_1-\frac{1}{2}}^{\infty} f(n)dn+(1/24)f'(n_1-\tfrac{1}{2})-(7/5760)f'''(n_1-\tfrac{1}{2})+(31/967680)f^{(5)}(n_1-\tfrac{1}{2})\;.\;.\;., \tag{17}$$

giving

$$\sum_{J=|l|}^{\infty}(2J+1)\exp hcB[J(J+1)-l^2]/kT=kT/hcB+1/3+\;.\;.\;. \tag{18}$$

and

$$Q=\sum_{J=|l|}^{\infty}(2J+1)e^{-hcF/kT}=(1/\gamma)[kT/hcB+1/3+2(kT/hcB)^2D/B]\cdot e^{-hcg/kT}. \tag{19}$$

The exponential in g is expanded as a power series and the summations made with v_i increasing by steps of two from l_i to ∞, then summing l_i from $-\infty$ to $+\infty$. If g is extended to include possible contributions to ln Q_c varying as T^2 at high temperature, while retaining the g_{ij} term needed for nonlinear molecules, as in

$$g=\sum_i g_{ii}l_i^2+\sum_{i<j}g_{ij}l_il_j+\sum g_{iii}l_i^2v_i+\sum g_{iik}l_i^2v_k, \tag{20}$$

the contribution of g to ln Q_c becomes

$$-2(hc/kT)\Sigma\{g_{ii}r_is_i^2+g_{iii}r_i(1+3r_i)s_i^3+g_{iik}d_kr_ir_ks_i^2s_k-2g_{ii}a_ir_i^2s_i^3\}+(hc/kT)^2\Sigma\{g_{ii}^2(r_i+8r_i^2$$
$$+r_i^3)s_i^4+2g_{ij}^2r_ir_js_i^2s_j^2+4g_{ii}x_{ii}r_i^2(4+3r_i)s_i^4+2g_{ii}x_{ik}r_ir_k(1+r_i)s_i^3s_k\}. \tag{21}$$

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[7] For a case with 3 frequencies, for example, $x_{ii}x_{ij}$ which is not completely symmetric in the indices would include $x_{11}x_{13}$ and also $x_{33}x_{31}$. But $x_{ii}x_{jj}x_{ij}$ has complete symmetry in the indices, and $x_{33}x_{11}x_{13}$ is sufficient without $x_{33}x_{11}x_{31}$ also.

Constants of the latter two types in eq (20) are not experimentally available at present. For a linear molecule, when there is only one doubly degenerate frequency, with $l=l_2$, the $-B_vl^2$ term of eq (16) is commonly absorbed into the $g_{22}l_2^2$ term. In that case, g_{ii} of eq (21) represents $g_{22}+B_v$ of the spectroscopist.

The free energy function for a mole of a substance in the standard ideal gas state is given by

$$-(F^\circ-E_0^\circ)/RT=\ln Q+(5/2)\ln T+(3/2)\ln M+\ln (2\pi/N)^{3/2}k^{5/2}/h^3P_0,$$

P_0 being atmospheric pressure, M the molecular weight, and the others known physical constants. The other functions follow by differentiation as given in appendix 5.

A tabulation by Pennington and Kobe [6] may also be used for convenient evaluation of the more important of the contribution here treated.

4. References

[1] E. B. Wilson, Jr., J. Chem. Phys. **4,** 525 (1936).

[2] K. F. Stripp and J. G. Kirkwood, J. Chem. Phys. **19,** 1131 (1951).

[3] W. S. Benedict (with A. M. Bass), unpublished data.

[4] W. H. Stockmayer, G. M. Kavanagh, and H. S. Mickley, J. Chem. Phys. **12,** 408 (1944).

[5] L. M. Milne-Thompson, The calculus of finite differences (Macmillan and Co., Ltd., London, 1933).

[6] R. E. Pennington and K. A. Kobe, J. Chem. Phys. **22,** 1442 (1954).

5. Appendices

5.1. Appendix 1

The relation of the constants of eq (6) with those in

$$G_v=\sum\overline{\omega}_i(v_i+d_i/2)+\sum\overline{x}_{ii}(v_i+d_i/2)^2+\sum_{i<j}\overline{x}_{ij}(v_i+d_i/2)(v_j+d_j/2)+\sum\overline{y}_{iii}(v_i+\overline{d}_i/2)^3$$
$$+\sum_{i\neq j}\overline{y}_{iij}(v_i+d_i/2)^2(v_j+d_j/2)+\sum_{i<j<k}\overline{y}_{ijk}(v_i+d_i/2)(v_j+d_j/2)(v_k+d_k/2)$$

is

$$\omega_i=\overline{\omega}_i+(d_i+1)\overline{x}_{ii}+\sum_j \tfrac{1}{2}d_j\overline{x}_{ij}+(1/4)(3d_i^2+6d_i+4)\overline{y}_{iii}$$
$$+\sum_j(\tfrac{1}{2})(d_i+1)d_j\overline{y}_{iij}+\sum_j(d_j^2/4)\overline{y}_{ijj}+\sum_{j<k}\sum(d_jd_k/4)\overline{y}_{ijk}$$

$$x_{ii}=\overline{x}_{ii}+(\tfrac{1}{2})(3d_i+6)\overline{y}_{iii}+\sum_j(d_j/2)\overline{y}_{iij}$$

$$x_{ij}=\overline{x}_{ij}+(d_i+1)\overline{y}_{iij}+(d_j+1)\overline{y}_{ijj}+\sum_k(d_k/2)\overline{y}_{ijk}$$

$$y_{iii}=\overline{y}_{iii},\ y_{iij}=\overline{y}_{iij}\ \text{and}\ y_{ijk}=\overline{y}_{ijk}.$$

5.2. Appendix 2

To obtain eq (9) and (10), begin with the identity

$$\sum_{v=0}^{\infty}x^{-v}=(1-x^{-1})^{-1}.$$

Multiply by x^{Z-1} and differentiate n times with respect to x, getting

$$\sum_{v=0}(-1)^n\frac{(v+n-Z)!}{(v-Z)!}\,x^{-v-1+Z-n}=\frac{d^n}{dx^n}\,[x^Z(x-1)^{-1}].$$

For the second member of the identity, let $x-1=t$, giving

$$\frac{d^n}{dt^n}[(t+1)^Z t^{-1}] \qquad \text{or} \qquad \frac{d^n}{dt^n}\left[\sum_{r=0}^{r=Z}\frac{Z!}{(Z-r)!r!}t^{Z-r-1}\right].$$

For $n>Z-1$, the only contribution is from the one term with $r=Z$, giving $\frac{d^n}{dt^n}t^{-1}$ or $(-1)^n n!$ $(x-1)^{-1-n}$. Multiplying both members of the identity by $(-1)^n\frac{x^{1-Z+n}}{(n-Z)!}$, one has

$$\sum_{v=0}\frac{(v+n-Z)!\,x^{-v}}{(v-Z)!\,(n-Z)!}=\frac{n!}{(n-Z)!}x^{-Z}(1-x^{-1})^{-1-n}.$$

Inserting e^{-u_i} for x, one may obtain eq (10) by using $n=Z+d_i-1$, with eq (9) as the special case given by $Z=0$.

5.3. Appendix 3

Functions of v in terms of $(f(s)=v!/(v-s)!$:

$$v=f(1)$$

$$v^2=f(2)+f(1)$$

$$v^3=f(3)+3f(2)+f(1)$$

$$v^4=f(4)+6f(3)+7f(2)+f(1)$$

$$v^5=f(5)+10f(4)+25f(3)+15f(2)+f(1)$$

$$v^6=f(6)+15f(5)+65f(4)+90f(3)+31f(2)+f(1)$$

$$v^3-v^2=f(3)+2f(2)$$

$$v^4-v^3=f(4)+5f(3)+4f(2)$$

$$v^4-2v^3+v^2=f(4)+4f(3)+2f(2)$$

$$v^5-2v^4+v^3=f(5)+8f(4)+14f(3)+4f(2).$$

5.4. Appendix 4

Additional terms in the formulas given earlier are as follows:

Equation (12):

$$\begin{aligned}
&-(1/6)(hc/kT)^3\sum\{4x_{ii}^3d_i(d_i+1)r_i^2[1+(8d_i+12)r_i+(8d_i^2+22d_i+15)r_i^2+(2d_i^2+4d_i+2)r_i^3]s_i^6\\
&\quad+x_{ij}^3d_id_jr_ir_j[1+(3d_i+1)r_i+(3d_j+1)r_j+d_i^2r_i^2+d_j^2r_j^2+(6d_id_j+3d_i+3d_j+1)r_ir_j+d_i^2r_i^2r_j\\
&\quad+d_j^2r_ir_j^2]s_i^3s_j^3+12x_{ii}^2x_{ij}d_i(d_i+1)d_jr_i^2r_j[1+(3d_i+4)r_i+(d_i+1)r_i^2]s_i^5s_j+6x_{ii}x_{ij}^2d_i(d_i+1)d_jr_i^2r_j[2\\
&\quad+(2d_i+1)r_i+2d_jr_j+d_jr_ir_j]s_i^4s_j^2+3x_{ij}^2x_{ik}d_id_jd_kr_ir_jr_k[1+(2d_i+1)r_i+d_jr_j+d_jr_ir_j]s_i^3s_j^2s_k\\
&\quad+24x_{ii}x_{jj}x_{ij}d_i(d_i+1)d_j(d_j+1)r_i^2r_j^2s_i^3s_j^3+12x_{ii}x_{ij}x_{ik}d_i(d_i+1)d_jd_kr_i^2r_jr_k(2+r_i)s_i^4s_js_k\\
&\quad+12x_{ii}x_{ij}x_{jk}d_i(d_i+1)d_jd_kr_i^2r_jr_ks_i^3s_j^2s_k+6x_{ij}x_{ik}x_{il}d_id_jd_kd_lr_ir_jr_kr_l(1+r_i)s_i^3s_js_ks_l\\
&\quad+6x_{ij}x_{ik}x_{jl}d_id_jd_kd_lr_ir_jr_kr_ls_i^2s_j^2s_ks_l+6x_{ij}x_{ik}x_{jk}d_id_jd_kr_ir_jr_k(1+d_ir_i+d_jr_j+d_kr_k)s_i^2s_j^2s_k^2\}
\end{aligned}$$

Equation (13):

$$\begin{aligned}
&-(hc/kT)\sum\{z_{iiii}d_i(d_i+1)(d_i+2)(d_i+3)r_i^4s_i^4+z_{iiij}d_i(d_i+1)(d_i+2)d_jr_i^3r_js_i^3s_j\\
&+z_{iijk}d_i(d_i+1)d_jd_kr_i^2r_jr_ks_i^2s_js_k+z_{iijj}d_i(d_i+1)d_j(d_j+1)r_i^2r_j^2s_i^2s_j^2+z_{ijkl}d_id_jd_kd_lr_ir_jr_kr_ls_is_js_ks_l\}\\
&+(1/2)(hc/kT)^2\sum\{12x_{ii}y_{iii}d_i(d_i+1)(d_i+2)r_i^3[1+(d_i+1)r_i]s_i^5+4x_{ii}y_{iij}d_i(d_i+1)d_jr_i^2r_j[1\\
&+2(d_i+1)r_i]s_i^4s_j+4x_{ii}y_{jji}d_i(d_i+1)d_j(d_j+1)r_i^2r_j^2s_i^3s_j^2+4x_{ii}y_{ijk}d_i(d_i+1)d_jd_kr_i^2r_jr_ks_i^3s_js_k\\
&+6x_{ij}y_{iii}d_i(d_i+1)(d_i+2)d_jr_i^3r_js_i^4s_j+2x_{ij}y_{iij}d_i(d_i+1)d_jr_i^2r_j[2+d_ir_i+2d_jr_j]s_i^3s_j^2\\
&+4x_{ij}y_{iik}d_i(d_i+1)d_jd_kr_i^2r_jr_ks_i^3s_js_k+2x_{ij}y_{kki}d_id_jd_k(d_k+1)r_ir_jr_k^2s_i^2s_js_k^2+2x_{ij}y_{ikl}d_id_jd_kd_lr_ir_jr_kr_ls_i^2\\
&s_js_ks_l+2x_{ij}y_{ijk}d_id_jd_kr_ir_jr_k(1+d_jr_i+d_jr_j)s_i^2s_j^2s_k\}
\end{aligned}$$

Equation (14):

$$\begin{aligned}
&\Sigma\{a_ia_{ii}d_ir_i[1+(1+2d_i)r_i]s_i^3+a_ia_{ij}d_id_jr_ir_js_i^2s_j+(1/6)a_i^3d_ir_i(1+r_i)s_i^3+a_{iii}d_ir_i[1+(1+3d_i)r_i\\
&+d_i^2r_i^2]s_i^3+a_{iij}d_id_jr_ir_j(1+d_ir_i)s_i^2s_j+a_{ijk}d_id_jd_kr_ir_jr_ks_is_js_k\}
\end{aligned}$$

Equation (15):

$$\begin{aligned}
&-(hc/kT)\Sigma\{a_{ii}x_{ii}d_i(d_i+1)r_i^2[4+(4d_i+2)r_i]s_i^4+2a_{ij}x_{ii}d_i(d_i+1)r_i^2r_js_i^3s_j+a_{ii}x_{ij}d_id_jr_ir_j[1\\
&+(2d_i+1)r_i]s_i^3s_j+a_{ij}x_{ij}d_id_jr_ir_j[1+d_ir_i+d_jr_j]s_i^2s_j^2+a_{ij}x_{kj}d_id_jd_kr_ir_jr_ks_is_j^2s_k\}\\
&+\tfrac{1}{2}(hc/kT)^2\Sigma\{4a_ix_{ii}^2d_i(d_i+1)r_i^2[1+(3d_i+4)r_i+(d_i+1)r_i^2+(d_i^2+d_i)r_i^3]s_i^5+a_ix_{ij}^2d_id_jr_ir_j[1\\
&+(2d_i+1)r_i+d_jr_j+d_jr_ir_j]s_i^3s_j^2+4a_ix_{ii}x_{ij}d_i(d_i+1)d_jr_i^2r_j(2+r_i)s_i^4s_i+4a_jx_{ii}x_{ij}d_i(d_i\\
&+1)d_jr_i^2r_js_i^3s_j^2+2a_ix_{ij}x_{ik}d_id_jd_kr_ir_jr_k(1+r_i)s_i^3s_js_k+2a_jx_{ij}x_{ik}d_id_jd_kr_ir_jr_ks_i^2s_j^2s_k\}
\end{aligned}$$

Equation (21):

$$\begin{aligned}
&-(1/3)(hc/kT)^3\sum\{g_{ii}^3(r_i+50r_i^2+194r_i^3+50r_i^4+r_i^5)s_i^6+6x_{ii}g_{ii}^2r_i^2(16+99r_i+70r_i^2+3r_i^3)s_i^6\\
&+3x_{ij}g_{ii}^2d_jr_ir_j(1+19r_i+19r_i^2+r_i^3)s_i^5s_j+12x_{ij}g_{ii}g_{jj}r_ir_j(1+r_i)(1+r_j)s_i^3s_j^3\\
&+12x_{ii}^2g_{ii}r_i^2(4+55r_i+70r_i^2+9r_i^3)s_i^6+12x_{ii}x_{ij}g_{ii}d_jr_i^2r_j(8+17r_i+3r_i^2)s_i^5s_j\\
&+3x_{ij}^2g_{ii}d_jr_ir_j[1+8r_i+5r_i^2+d_j(r_j+4r_ir_j+r_i^2r_j)]s_i^4s_j^2+12x_{ij}x_{jj}g_{ii}d_j(d_j+1)r_ir_j^2(1+r_i)s_i^3s_j^3\\
&+6x_{ij}x_{ik}g_{ii}d_jd_kr_ir_jr_k(1+4r_i+r_i^2)s_i^4s_js_k+6x_{ij}x_{jk}g_{ii}d_jd_kr_ir_jr_k(1+r_i)s_i^3s_j^2s_k\}
\end{aligned}$$

5.5. Appendix 5

For a term of ln Q of the form

$$z=xu^pf_1\prod_i r_i^{m_i}s_i^{n_i}=Wf_1,$$

with $f_1=1+\sum_i t_ir_i^{q_i}$ and $u=hc/kT$ and with x, p, m_i, n_i, t_i, and q_i constants, the contributions to the various thermodynamic functions are: For $-(F^\circ-E_0^\circ)/RT$, $z=Wf_1$; for $(H^\circ-E_0^\circ)/RT$, $-udz/du=Wh_2$; for C_p°/R, $u^2d^2z/du^2=Wh_3$; with $h_2=f_1g_1+f_2$, $h_3=f_1g_2+2f_2g_1+f_3$, where

$$f_2=\sum_i t_iq_iu_ir_i^{q_i}$$

$$f_3=\sum_i t_iq_i^2u_i^2r_i^{q_i}$$

$$g_1=-p+\sum_i n_iu_ir_is_i+\sum m_iu_i$$

$$g_2=-p+\sum_i n_iu_i^2r_is_i^2+g_1^2.$$

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