THE PRESENT STATUS OF THE STATISTICAL METHOD OF CALCULATING THERMODYNAMIC FUNCTIONS[1]

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The formulas necessary for making approximate calculations of the entropy, free energy, heat content, and heat capacity of gases from a knowledge of their masses, moments of inertia, vibration frequencies, and internal hindrance potentials (if any) are given in a form ready for numerical calculation. Tables of vibrational contributions and energy levels for the internal libration problem are included. Higher-order effects are briefly discussed, as well as the question of securing the necessary data. Finally, an extensive bibliography of published calculations of the statistical type is appended, with a table by means of which the calculations dealing with any given molecule can readily be located.

The calculation of the thermodynamic properties of simple gases from a knowledge of the structure and vibration frequencies of their molecules is now a well-established and important method of obtaining data useful in engineering as well as scientific problems. Several descriptions (101, 42, 42a, 132a) of the principles and methods are available and a few reviews of applications have been published (101, 175, 176, 177, 178, 179). In this paper an effort will be made to describe advances in the theory made since the publication of the excellent review article by Kassel (101) and to tabulate the molecules which have been treated. In addition, a brief summary of the practical formulas will be given and some discussion of the methods of obtaining the required data. The appendices contain some useful tables.

I. SUMMARY OF PRACTICAL FORMULAS

As a practical proposition it is possible to consider the contributions of the electronic, vibrational, rotational, and translational energies separately, since they are very nearly additive. Refinements are considered later.

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A. Translational and rotational contributions

The translational plus rotational contributions for non-linear rigid molecules are given by:

$$S^0 = 2.2875(3 \log M + 8 \log T - 2 \log \sigma + \log ABC) - 7.659 \quad (1)$$

$$(F^0 - E^0_0)/T = -S + 7.948 \quad (2)$$

$$H^0 - E^0_0 = 7.948\,T \quad (3)$$

$$C^0_p = 7.948 \quad (4)$$

Here F^0, S^0, H^0, and C^0_p are the translational and rotational contributions to the free energy, the entropy, the heat content (enthalpy), and the heat capacity at constant pressure for 1 mole of a perfect gas at 1 atm. pressure. The unit of energy is the calorie. E^0_0 is the energy per gram-mole of the perfect gas at the absolute zero. T is the absolute temperature, M the molecular weight, σ the symmetry number (see below), and A, B, C are the principal moments of inertia in units such that mass is given in atomic weight units and distance in Ångström units. The values of R etc. are those in the *International Critical Tables.*[2]

For linear (including diatomic molecules) the formulas are:

$$S^0 = 2.2875(3 \log M + 7 \log T - 2 \log \sigma + 2 \log I) - 6.632 \quad (5)$$

$$(F^0 - E^0_0)/T = -S + 6.954 \quad (6)$$

$$(H^0 - E^0_0) = 6.954T \quad (7)$$

$$C^0_p = 6.954 \quad (8)$$

Here I is the moment of inertia in atomic weight-Ångström units.

The symmetry number σ is the number of indistinguishable positions into which the molecule can be turned by simple rigid rotations. For example, for hydrogen chloride, nitrogen, acetylene, ethylene, ammonia, and methane, σ is 1, 2, 2, 4, 3, and 12, respectively.

All the above are for the perfect gas at 1 atm. pressure. To correct for gas imperfection, see appendix I.

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[2] In the above equations, $2.2875 = 1/2\, R_1 \ln 10$, $7.948 = 4R_1$, $6.954 = (7/2)R_1$, $-7.659 = R_1 \ln (64\pi^5 k^3 R_2/h^6 N^4 10^{24}) + 4R_1$, in which R_1 is the gas constant in calories, R_2 the gas constant in cc-atm., $\ln = \log_e$, and $\log = \log_{10}$.

It is important to note that the I. C. T. values of the physical quantities are not in accord with the best values more or less accepted to-day. Certain discrepancies have so far prevented general agreement, however, on a "best" set, so that the I. C. T. values are still used.

B. Electronic contributions

Let

$$Q = \sum_n g_n e^{-\frac{W_n}{kT}} \tag{9}$$

where W_n is an electronic energy level of degeneracy g_n, k is Boltzmann's constant, and the sum is over all electronic levels or in practice over all levels whose Boltzmann factors are not negligible. Then the electronic contributions are:

$$S = R \ln Q + RT \frac{\mathrm{d} \ln Q}{\mathrm{d}T} \tag{10}$$

$$(F/T) = -R \ln Q \tag{11}$$

$$(H/T) = RT \frac{\mathrm{d} \ln Q}{\mathrm{d}T} \tag{12}$$

$$C = RT^2 \frac{\mathrm{d}^2 \ln Q}{\mathrm{d}T^2} + 2RT \frac{\mathrm{d} \ln Q}{\mathrm{d}T} \tag{13}$$

Here ln is the natural logarithm, and R is the gas constant. Ordinarily only the lowest electronic level is of any importance and for that g_n is usually unity, so that in such cases all the above become zero.

C. Vibrational contributions

The formulas under "Electronic contributions" apply equally well to the vibrational contributions if the W_n are taken to be the vibrational levels. Usually it is necessary to assume that the vibrations are harmonic, in which case *each* fundamental frequency of vibration contributes the amounts below. It should be remembered that a non-linear molecule has $3N - 6$ frequencies, and a linear molecule $3N - 5$, where N is the number of atoms.

$$S = -R \ln (1 - e^{-w}) + R \frac{we^{-w}}{1 - e^{-w}} \tag{14}$$

$$(F/T) = R \ln (1 - e^{-w}) \tag{15}$$

$$H = RT \frac{we^{-w}}{1 - e^{-w}} \tag{16}$$

$$C = \frac{w^2 R}{2(\cosh w - 1)} \tag{17}$$

where

$$w = \frac{h\nu}{kT} = \frac{hc\omega}{kT} \tag{18}$$

in which ν is the frequency, ω the wave number, c the velocity of light, and h Planck's constant. Numerically:

$$w = 1.4324\,\frac{\omega}{T}; \quad w_{298.1} = 0.0048052\,\omega \tag{19}$$

Appendix II contains a complete table of the vibrational contributions to C, F/T, etc., as a function of ω/T. This table was obtained by interpolation from a smaller one computed by Dr. H. L. Johnston. I am deeply indebted to Dr. Johnston for permission to make use of this.

D. Nuclear spin and other effects

Except for hydrogen and at impractically low temperatures for other molecules, the question of nuclear spin, ortho and para species, spin weights, and quantum effects in the rotational contributions (101) can be completely ignored in practical calculations. The entropy thus obtained is called the virtual entropy. The "absolute" entropy is greater by $R \ln g_s$, where g_s is the nuclear spin weight, but the virtual entropy is the quantity used in practice. The existence of isotopes can also be ignored except when dealing with artificially enriched systems, particularly of deuterium, or for calculations of very high accuracy.

The centrifugal distortion (168) of the molecule, due to rotation, and the coupling of rotational and vibrational angular momenta (170) are ordinarily quite small corrections which can be applied if necessary. The change of moment of inertia with vibrational state is another correction which usually cannot be made because the data are insufficient.

Probably the most serious error in the above simplified formulas is due to the assumption of harmonic vibrational levels. The actual levels are not equally spaced but converge as the dissociation limit is approached. For diatomic molecules sufficient information is usually available to enable this effect to be taken into account, and the same is true for a very small number of polyatomic molecules. The mathematical methods (101) are well developed, but the data required are seldom available for polyatomic molecules. The accuracy which can be attained in these cases therefore becomes less at high temperatures.

Another vibrational effect is the occurrence of resonance. Sometimes a pair of vibrational levels near to one another will interact in such a way as to be displaced from the positions predicted by the simple theory used above. This will cause a small change in the vibrational contribution, which can be computed if the actual positions of the levels are known experimentally. An example is carbon dioxide. The phenomenon is well understood but requires empirical information at present in order to be corrected for.

For precise calculations all these effects should be, and are, considered, but for most polyatomic molecules it is necessary to be content with the approximate results.

E. Non-rigid molecules

If the molecule contains groups which can rotate or oscillate with large amplitudes about bonds in the molecule, as is the case in ethane, the problem becomes more complicated. If the force resisting the torsional motion is very large (as in a double bond) it is sufficient to treat this motion as a vibration, and if the motion is unrestricted ("free internal" rotation) it may be treated as a classical rotation by methods developed by Eidinoff and Aston (40) and by Kassel (106, 107, 108). In general, however, the forces are intermediate. Pitzer (140) has published easily applicable tables for use in these cases, but they are based on a theory which neglects some important effects and they are therefore not always very close approximations although unquestionably useful. Crawford (25) has recently given a reasonably rigorous treatment for a wide class of molecules: namely, those in which any number of symmetrical groups (such as methyl groups) are attached to a rigid framework. Examples are dimethyl ether, propylene, tetramethylmethane, methyl alcohol, etc. His equations may be summarized as follows:

The contributions of the oscillating groups are additive and replace a corresponding number of vibrational contributions. For each group the contributions are given by:

$$S = R[\ln G + (K/G)] \tag{20}$$

$$(F/T) = -R(\ln G + Y_0) \tag{21}$$

$$(H/T) = R[(K/G) - Y_0] \tag{22}$$

$$C = R[(J/G) - (K/G)^2] \tag{23}$$

in which

$$G = (\Omega^{1/2} G_R + G_V), \quad K = (\Omega^{1/2} K_R + K_V), \quad J = (\Omega^{1/2} J_R + J_V) \tag{24}$$

and

$$G_V = \sum_V \exp(-Y_r); \quad G_R = \sum_R \exp(-\Omega Y_r) \tag{25}$$

$$K_V = \sum_V Y_r \exp(-Y_r); \quad K_R = \sum_R \Omega Y_r \exp(-\Omega Y_r) \tag{26}$$

$$J_V = \sum_V Y_r^2 \exp(-Y_r); \quad J_R = \sum_R \Omega^2 Y_r^2 \exp(-\Omega Y_r) \tag{27}$$

In addition:

$$Y_r = (m^2h^2/32\pi^2 D\Omega RT)a_r \tag{28}$$

$$\Omega = 1 - D[(\lambda_A^2/A) + (\lambda_B^2/B) + (\lambda_C^2/C)] \tag{29}$$

Here A, B, C are the principal moments of inertia of the whole molecule (including the attached groups), D is the moment of inertia about its axis of the symmetrical group under consideration, λ_A, λ_B, λ_C are the cosines of the angles between the group axis and the principal axes, m is the number of minima of depth V (calories) in the restricting potential of the group, while the a_r are the eigen-values of the equation below. R, D, A, B, C in equation 28 are in C.G.S. units.

$$\frac{d^2\psi}{dx^2} + (a_r + 2\theta \cos 2x)\psi = 0 \tag{30}$$

with

$$\theta = (8\pi^2 D\Omega/h^2m^2)V \tag{31}$$

A table of a_r as a function of θ is given in appendix III. The sums over R and V have the following significance: The energy levels of the torsional motion are vibrational in character for low levels, rotational in character for higher levels. In carrying out the summations the levels are divided into these two classes, the lower or vibrational levels being denoted by V, the upper or rotational by R. The selection of the dividing line is of course somewhat arbitrary but is indicated by a line in the tables of a_r.

The symmetry number to be used in calculating the over-all rotational contributions is the symmetry number for the rigid molecule, e.g., $\sigma = 1$ for CH_3OH (COH bent). The symmetry of the rotating group is most easily taken into account by summing over only part of the levels a_r: namely, over a_n and b_n with n even of Ince's tables (85), provided that m is the symmetry number of the group. The table in appendix III contains only these levels.

If $\Omega \rightarrow 1$, these equations go over into those used by Pitzer, and his tables may then be used. If Ω is small it may be necessary to use the still higher approximations described by Crawford, which are more difficult to apply than the approximations of equations 20 to 23.

In all of these treatments it has been assumed that the restricting potential has the form

$$\tfrac{1}{2} V (1 - \cos m\alpha) \tag{32}$$

where α is the angle of the rotating group, m is the number of minima in the restricting potential, and V is the depth of these minima.

II. DISCUSSION OF DATA REQUIRED

The most difficult part of the calculation of thermodynamic properties is the collection and interpretation of the necessary data. The translational part of the partition function offers no difficulty, because all that is required is the molecular weight. The rotational part requires a knowledge of the principal moments of inertia. These have not been obtained directly from spectroscopic investigations except for diatomic molecules and a very few simple hydrides, such as water, hydrogen sulfide, ammonia, and methane. However, the structures of a fairly large number of molecules have now been investigated by the electron diffraction method (13), so that their moments of inertia can be computed with sufficient accuracy for this purpose. In other cases the only information available is the structural information given by organic chemistry and the interatómic distances in tables of covalent radii (139). This is usually sufficiently reliable.

Since it is only necessary to have the product ABC of the principal moments, it is useful to note that

$$ABC = \begin{vmatrix} I_{xx} & -I_{xy} & -I_{xz} \\ -I_{xy} & I_{yy} & -I_{yz} \\ -I_{xz} & -I_{yz} & I_{zz} \end{vmatrix} \qquad (33)$$

in which

$$I_{xx} = \sum_i m_i(y_i^2 + z_i^2), \qquad I_{xy} = \sum_i m_i x_i y_i, \text{ etc.}$$

Here m_i is the mass of the i^{th} atom and x_i, y_i, z_i are its coördinates in any convenient system of Cartesian coördinates whose origin coincides with the center of gravity of the molecule.

If the molecule has an internal rotational or torsional degree of freedom, it is necessary to know something about the potential barrier restricting this rotation. At the present time there is no theoretical method of calculating this barrier and very little reliable empirical information upon which to base estimates. However, much work is being done in this field at the Pennsylvania State College, the University of California, Princeton University, Harvard University, and elsewhere. Up till now it has always been necessary to assume that the barrier has a simple cosine form with a suitable number of minima. Such a function has only one parameter, the height of the barrier, provided the number of minima is obvious from the symmetry of the molecule. This parameter must be obtained from a comparison with experimental data at some one temperature, for example, the entropy from third-law measurements or the heat capacity of the gas.

When it has been obtained, the properties at other temperatures can then be calculated. There is hope that spectroscopic studies may give the barrier height in some cases, such as that of methyl alcohol. Table 1 gives some values of barrier heights, although not all these figures are certain.

The vibrational frequencies

The problem of determining the vibration frequencies is ordinarily the most difficult step and therefore merits a separate discussion. The fundamental frequencies appear in the infrared spectrum and in the Raman spectrum of the substance. Neither spectrum ordinarily gives all the frequencies and frequently both together do not. Furthermore, these spectra usually include other lines that are not fundamentals. In addition, the lines observed carry no tags to tell whether they are fundamentals and if so whether they are singly, doubly or triply degenerate. (For example, the bending vibration of carbon dioxide is doubly degenerate, since it can occur in either of two planes at right angles, both motions having the same frequency.)

TABLE 1

Heights of potential barriers

SUBSTANCE	HEIGHT OF BARRIER	SUBSTANCE	HEIGHT OF BARRIER
	calories		*calories*
Ethane	2750	Methyl alcohol	~3000 (?)
Propane	~3300	Methylamine	~3000
Propylene	≈2100	Dimethylacetylene	<500
Neopentane	~4200	Acetone	~1000

In order to disentangle the observations a number of methods may be employed. In the Raman, the polarization should be measured. This sets apart the symmetrical vibrations. In the infrared, the contour of the rotational envelope is useful in sorting out the lines, but to observe it requires powerful equipment. If deuterium derivatives of the substance can be prepared and studied, the shifts caused by the heavier mass of deuterium often enable an interpretation to be made. The intensities of the lines are a property which ought to be of great service, but the theory is not very well developed. The temperature coefficient of intensity serves to eliminate difference bands. Comparisons with related molecules are very useful. Finally, the mathematical analysis of the vibrations of the molecule by means of the theory of small vibrations is almost essential for a complete and certain analysis, especially when there are frequencies which are not found in either spectrum and must therefore be calculated.

The mathematical calculation of vibration frequencies divides into two parts. It is first necessary to have a set of force constants for the bonds of the molecule, and then the actual calculation must be carried through. The second step may be laborious, but it is at least straightforward and will therefore be discussed first. The elementary mathematical methods (37) for the study of small vibration are very old, since quantum mechanics is not required. These methods are good enough for very simple molecules, but become almost impossibly laborious for molecules with even five or six atoms. In recent years many elaborations have been developed to simplify the calculations. Among the most important is the use of the symmetry of the molecule (146) to break the problem up into independent parts. In addition, a technique has recently been developed which replaces much of the algebra by the use of tabulated quantities (171). Furthermore, work done for simpler molecules can be carried over intact for larger molecules of which the simpler form parts. The operations which remain difficult are the evaluation of large determinants and the solution of high-order algebraic equations.

The choice of force constants cannot be treated so formally. It is often possible to use a smaller number of force constants than frequencies, treat them as adjustable parameters, and get a fairly good fit with the experimental data, a process which serves to check the assignment of the frequencies observed and perhaps to provide frequencies not observed. Often there are too many force constants for this and it is necessary to bring in the frequencies of the deuterium derivatives in order to get sufficient data to evaluate all the constants. The most promising attack, however, seems to be the possibility of carrying over force constants from one similar molecule to another. For example, the force constants for stretching and bending a C—H bond in a methyl group seem to remain fairly constant from one molecule to another. This systematic study of force constants is proceeding steadily at the present time and should produce some quite useful generalizations in the near future. It is at least possible that frequencies may eventually be calculated with sufficient accuracy for rough thermodynamic properties with no appeal to experiment. That stage is not yet here, however.

III. CONCLUSION

It is clear that the statistical method has progressed to a stage where simple rigid polyatomic molecules such as methane, ethylene, benzene, etc. can be treated with a practical degree of accuracy, provided that a careful study of the vibration frequencies has been made. Furthermore, simple molecules with one or two internal torsional degrees of freedom, such as ethane, propylene, dimethyl ether, etc., can also be dealt with, again assuming that a study of the vibrations has been carried out, and in addition if at least one experimental measurement of heat capacity, entropy, or free energy is available for use in determining the barrier height of the torsion.

The chief difficulties in handling molecules of the types which can now be computed are the determination of the vibration frequencies and the barrier heights, if any, the latter difficulty being insoluble until the former is settled. Experience has shown that we do not yet know enough about vibrations to guess at vibration frequencies by analogy with other molecules. Such guesses are likely to be too inaccurate to give a good barrier height, although, if only a very rough value of the thermodynamic quantities is helpful, estimated frequencies may suffice.

More complicated molecules, such as chain hydrocarbons, have not yet been solved by these methods, except very roughly, but there is hope that the classes of molecules which can be treated will continue to expand in the future as it has in the past.

APPENDIX I

Corrections for gas imperfection

If H, C_p, S, and F represent the heat content (enthalpy), heat capacity at constant pressure, entropy, and free energy for the real gas, and H^0, C^0, etc. the corresponding quantities for the ideal gas at the same temperature, then the following relations hold:

$$H = H^0 + \int_0^p \left[V - T\left(\frac{\partial V}{\partial T}\right)_p\right] dp$$

$$C_p = C_p^0 - T\int_0^p \left(\frac{\partial^2 V}{\partial T^2}\right)_p dp$$

$$S = S^0 - \int_0^p \left[\left(\frac{\partial V}{\partial T}\right)_p - \frac{R}{p}\right] dp - R\ln p$$

$$F = F^0 + \int_0^p [V - (RT/p)]\, dp + RT\ln p$$

in which V is the molar volume, R the gas constant per mole, T the absolute temperature, and p the pressure in atmospheres. The quantities $H^0 = E^0 + RT$, $C_p^0 = C_V^0 + \mathrm{R}$, S^0, and F^0 are given in the first part of the paper.

Evidently equation of state data, i.e., V, $\left(\frac{\partial V}{\partial T}\right)_p$, and $\left(\frac{\partial^2 V}{\partial T^2}\right)_p$ as functions of p, are required. In default of better information, Berthelot's equation with constants obtained from critical data has often been used.

TABLE 2

Harmonic oscillator contributions

(ω/T)	C	(H^0/T)	$-(F^0 - E_0^0)/T$	(ω/T)	C	(H^0/T)	$-(F^0 - E_0^0)/T$
0.10	1.9835	1.8480	4.0016	0.50	1.9041	1.3596	1.3324
0.11	1.9828	1.8345	3.8261	0.51	1.9009	1.3487	1.3056
0.12	1.9820	1.8210	3.6671	0.52	1.8975	1.3379	1.2796
0.13	1.9811	1.8076	3.5219	0.53	1.8942	1.3272	1.2542
0.14	1.9802	1.7943	3.3884	0.54	1.8907	1.3165	1.2295
0.15	1.9792	1.7810	3.2650	0.55	1.8872	1.3059	1.2054
0.16	1.9782	1.7679	3.1505	0.56	1.8836	1.2954	1.1820
0.17	1.9770	1.7547	3.0437	0.57	1.8801	1.2849	1.1592
0.18	1.9758	1.7417	2.9438	0.58	1.8764	1.2745	1.1369
0.19	1.9746	1.7287	2.8499	0.59	1.8728	1.2642	1.1151
0.20	1.9733	1.7158	2.7616	0.60	1.8690	1.2539	1.0940
0.21	1.9719	1.7030	2.6783	0.61	1.8652	1.2437	1.0734
0.22	1.9705	1.6902	2.5993	0.62	1.8613	1.2335	1.0533
0.23	1.9690	1.6775	2.5244	0.63	1.8573	1.2234	1.0336
0.24	1.9674	1.6649	2.4533	0.64	1.8534	1.2134	1.0144
0.25	1.9658	1.6523	2.3856	0.65	1.8493	1.2034	0.9956
0.26	1.9641	1.6398	2.3210	0.66	1.8453	1.1935	0.9773
0.27	1.9623	1.6274	2.2594	0.67	1.8411	1.1837	0.9595
0.28	1.9604	1.6150	2.2004	0.68	1.8370	1.1739	0.9420
0.29	1.9586	1.6027	2.1439	0.69	1.8328	1.1642	0.9249
0.30	1.9566	1.5905	2.0898	0.70	1.8285	1.1545	0.9082
0.31	1.9546	1.5783	2.0378	0.71	1.8241	1.1449	0.8919
.32	1.9525	1.5662	1.9879	0.72	1.8197	1.1354	0.8760
0.33	1.9504	1.5542	1.9399	0.73	1.8153	1.1259	0.8604
0.34	1.9482	1.5422	1.8937	0.74	1.8108	1.1165	0.8451
0.35	1.9458	1.5303	1.8492	0.75	1.8063	1.1071	0.8302
0.36	1.9435	1.5185	1.8062	0.76	1.8017	1.0978	0.8156
0.37	1.9411	1.5067	1.7648	0.77	1.7971	1.0886	0.8013
0.38	1.9386	1.4950	1.7248	0.78	1.7924	1.0794	0.7873
0.39	1.9361	1.4834	1.6861	0.79	1.7877	1.0704	0.7736
0.40	1.9335	1.4718	1.6487	0.80	1.7830	1.0613	0.7602
0.41	1.9309	1.4603	1.6125	0.81	1.7782	1.0523	0.7471
0.42	1.9281	1.4488	1.5774	0.82	1.7733	1.0434	0.7343
0.43	1.9253	1.4375	1.5435	0.83	1.7685	1.0345	0.7217
0.44	1.9224	1.4261	1.5105	0.84	1.7636	1.0257	0.7094
0.45	1.9195	1.4149	1.4786	0.85	1.7586	1.0169	0.6973
0.46	1.9166	1.4037	1.4476	0.86	1.7536	1.0082	0.6854
0.47	1.9135	1.3926	1.4176	0.87	1.7485	0.9996	0.6738
0.48	1.9105	1.3815	1.3884	0.88	1.7435	0.9910	0.6624
0.49	1.9074	1.3705	1.3600	0.89	1.7384	0.9825	0.6513

TABLE 2—*Continued*

(ω/T)	C	(H^0/T)	$-(F^0 - E_0^0)/T$	(ω/T)	C	(H^0/T)	$-(F^0 - E_0^0)/T$
0.90	1.7332	0.9740	0.6403	1.30	1.5001	0.6804	0.3354
0.91	1.7279	0.9656	0.6296	1.31	1.4937	0.6741	0.3302
0.92	1.7227	0.9573	0.6191	1.32	1.4874	0.6679	0.3252
0.93	1.7174	0.9490	0.6088	1.33	1.4810	0.6618	0.3202
0.94	1.7121	0.9407	0.5987	1.34	1.4747	0.6556	0.3152
0.95	1.7067	0.9326	0.5887	1.35	1.4683	0.6495	0.3104
0.96	1.7013	0.9244	0.5790	1.36	1.4619	0.6435	0.3056
0.97	1.6958	0.9164	0.5695	1.37	1.4555	0.6375	0.3009
0.98	1.6905	0.9084	0.5601	1.38	1.4491	0.6316	0.2963
0.99	1.6849	0.9004	0.5509	1.39	1.4426	0.6257	0.2918
1.00	1.6794	0.8925	0.5419	1.40	1.4362	0.6198	0.2873
1.01	1.6738	0.8847	0.5331	1.41	1.4297	0.6140	0.2829
1.02	1.6682	0.8769	0.5244	1.42	1.4233	0.6082	0.2786
1.03	1.6626	0.8692	0.5159	1.43	1.4168	0.6025	0.2743
1.04	1.6569	0.8615	0.5076	1.44	1.4104	0.5968	0.2701
1.05	1.6512	0.8539	0.4994	1.45	1.4038	0.5912	0.2660
1.06	1.6454	0.8463	0.4913	1.46	1.3973	0.5856	0.2619
1.07	1.6397	0.8388	0.4834	1.47	1.3908	0.5801	0.2580
1.08	1.6339	0.8314	0.4756	1.48	1.3843	0.5746	0.2541
1.09	1.6281	0.8240	0.4680	1.49	1.3777	0.5691	0.2502
1.10	1.6223	0.8166	0.4605	1.50	1.3712	0.5637	0.2464
1.11	1.6164	0.8093	0.4532	1.51	1.3646	0.5583	0.2427
1.12	1.6105	0.8021	0.4459	1.52	1.3580	0.5530	0.2390
1.13	1.6045	0.7949	0.4389	1.53	1.3515	0.5478	0.2354
1.14	1.5986	0.7878	0.4319	1.54	1.3449	0.5425	0.2319
1.15	1.5926	0.7807	0.4250	1.55	1.3383	0.5373	0.2284
1.16	1.5866	0.7736	0.4183	1.56	1.3317	0.5321	0.2249
1.17	1.5805	0.7667	0.4117	1.57	1.3251	0.5271	0.2215
1.18	1.5745	0.7597	0.4052	1.58	1.3186	0.5220	0.2182
1.19	1.5684	0.7528	0.3988	1.59	1.3120	0.5170	0.2150
1.20	1.5623	0.7460	0.3925	1.60	1.3054	0.5120	0.2117
1.21	1.5562	0.7392	0.3863	1.61	1.2988	0.5071	0.2086
1.22	1.5500	0.7325	0.3803	1.62	1.2922	0.5021	0.2054
1.23	1.5438	0.7258	0.3743	1.63	1.2857	0.4974	0.2024
1.24	1.5376	0.7192	0.3685	1.64	1.2791	0.4925	0.1993
1.25	1.5314	0.7126	0.3627	1.65	1.2725	0.4878	0.1964
1.26	1.5251	0.7060	0.3571	1.66	1.2659	0.4830	0.1934
1.27	1.5189	0.6996	0.3515	1.67	1.2593	0.4784	0.1905
1.28	1.5126	0.6931	0.3460	1.68	1.2528	0.4737	0.1877
1.29	1.5064	0.6867	0.3407	1.69	1.2462	0.4691	0.1849

TABLE 2—*Continued*

(ω/T)	C	(H^0/T)	$-(F - E_0^0)/T$	(ω/T)	C	(H^0/T)	$-(F^0 - E_0^0)/T$
1.70	1.2396	0.4645	0.1821	2.20	0.9217	0.2799	0.08690
1.71	1.2330	0.4600	0.1794	2.22	0.9097	0.2741	0.08441
1.72	1.2265	0.4555	0.1768	2.24	0.8977	0.2684	0.08197
1.73	1.2298	0.4510	0.1741	2.26	0.8859	0.2629	0.07961
1.74	1.2133	0.4466	0.1716	2.28	0.8742	0.2575	0.07731
1.75	1.2067	0.4422	0.1690	2.30	0.8625	0.2521	0.07508
1.76	1.2001	0.4379	0.1665	2.32	0.8509	0.2469	0.07293
1.77	1.1936	0.4335	0.1640	2.34	0.8394	0.2417	0.07084
1.78	1.1872	0.4293	0.1616	2.36	0.8280	0.2367	0.06880
1.79	1.1806	0.4250	0.1592	2.38	0.8167	0.2317	0.06683
1.80	1.1740	0.4208	0.1568	2.40	0.8055	0.2268	0.06490
1.81	1.1675	0.4166	0.1545	2.42	0.7944	0.2220	0.06304
1.82	1.1609	0.4125	0.1522	2.44	0.7834	0.2173	0.06123
1.83	1.1544	0.4084	0.1500	2.46	0.7724	0.2127	0.05948
1.84	1.1479	0.4044	0.1477	2.48	0.7615	0.2082	0.05777
1.85	1.1414	0.4003	0.1456	2.50	0.7508	0.2038	0.05611
1.86	1.1349	0.3963	0.1434	2.52	0.7401	0.1995	0.05451
1.87	1.1284	0.3924	0.1413	2.54	0.7295	0.1953	0.05296
1.88	1.1219	0.3885	0.1392	2.56	0.7190	0.1911	0.05144
1.89	1.1155	0.3846	0.1371	2.58	0.7086	0.1870	0.04997
1.90	1.1090	0.3807	0.1351	2.60	0.6983	0.1830	0.04853
1.91	1.1025	0.3769	0.1331	2.62	0.6881	0.1791	0.04715
1.92	1.0961	0.3731	0.1312	2.64	0.6780	0.1752	0.04580
1.93	1.0897	0.3694	0.1293	2.66	0.6680	0.1714	0.04450
1.94	1.0833	0.3656	0.1274	2.68	0.6581	0.1677	0.04323
1.95	1.0768	0.3620	0.1255	2.70	0.6483	0.1641	0.04199
1.96	1.0705	0.3583	0.1237	2.72	0.6386	0.1606	0.04080
1.97	1.0642	0.3547	0.1219	2.74	0.6290	0.1571	0.03964
1.98	1.0578	0.3511	0.1201	2.76	0.6194	0.1537	0.03850
1.99	1.0514	0.3475	0.1183	2.78	0.6100	0.1504	0.03740
2.00	1.0451	0.3440	0.1166	2.80	0.6007	0.1471	0.03633
2.02	1.0325	0.3371	0.1132	2.82	0.5915	0.1439	0.03530
2.04	1.0199	0.3303	0.1099	2.84	0.5824	0.1408	0.03429
2.06	1.0074	0.3236	0.1067	2.86	0.5733	0.1377	0.03332
2.08	0.9950	0.3170	0.1036	2.88	0.5644	0.1347	0.03237
2.10	0.9826	0.3105	0.1006	2.90	0.5556	0.1317	0.03144
2.12	0.9703	0.3042	0.09771	2.92	0.5469	0.1288	0.03056
2.14	0.9580	0.2979	0.09489	2.94	0.5383	0.1260	0.02969
2.16	0.9459	0.2918	0.09215	2.96	0.5298	0.1232	0.02885
2.18	0.9338	0.2858	0.08949	2.98	0.5214	0.1205	0.02802

TABLE 2—*Concluded*

(ω/T)	C	(H^0/T)	$-(F^0 - E_0^0)/T$	(ω/T)	C	(H^0/T)	$-(F^0 - E_0^0/T$
3.00	0.5131	0.1178	0.02722	6.3	0.0195	0.00216	0.000239
3.05	0.4927	0.1114	0.02533	6.4	0.0174	0.00190	0.000207
3.10	0.4730	0.1053	0.02356				
3.15	0.4538	0.0995	0.02193	6.5	0.0156	0.00167	0.000180
3.20	0.4353	0.0940	0.02041	6.6	0.0139	0.00147	0.000156
3.25	0.4174	0.0888	0.01899	6.7	0.0124	0.00130	0.000135
3.30	0.4001	0.0839	0.01767	6.8	0.0111	0.00114	0.000117
3.35	0.3833	0.0792	0.01644	6.9	0.00990	0.001002	0.0001013
3.40	0.3672	0.0748	0.01530				
3.45	0.3515	0.0707	0.01423	7.0	0.00883	0.000880	0.0000877
3.50	0.3365	0.0667	0.01325	7.1	0.00787	0.000774	0.0000760
3.55	0.3219	0.0630	0.01233	7.2	0.00701	0.000680	0.0000659
3.60	0.3079	0.0594	0.01148	7.3	0.00625	0.000597	0.0000571
3.65	0.2944	0.0560	0.01068	7.4	0.00556	0.000525	0.0000495
3.70	0.2814	0.0528	0.00994				
3.75	0.2689	0.0498	0.00925	7.5	0.00495	0.000461	0.0000429
3.80	0.2569	0.0470	0.00861	7.6	0.00441	0.0004048	0.0000371
3.85	0.2453	0.0443	0.00801	7.7	0.00392	0.0003553	0.0000322
3.90	0.2342	0.0418	0.00746	7.8	0.00346	0.0003119	0.0000279
3.95	0.2235	0.0394	0.00694	7.9	0.00310	0.0002738	0.0000242
4.00	0.2133	0.0371	0.00646	8.0	0.00275	0.0002402	0.0000210
4.1	0.1940	0.0330	0.00560	8.1	0.00245	0.0002108	0.0000182
4.2	0.1763	0.0292	0.00485	8.2	0.00217	0.0001849	0.0000157
4.3	0.1600	0.0259	0.00420	8.3	0.00193	0.0001622	0.0000136
4.4	0.1451	0.0230	0.00364	8.4	0.00171	0.0001422	0.0000118
4.5	0.1314	0.0204	0.00315				
4.6	0.1190	0.0180	0.00273	8.5	0.00152	0.0001247	0.0000102
4.7	0.1076	0.0160	0.00237	8.6	0.00135	0.0001093	0.0000089
4.8	0.0972	0.0141	0.00205	8.7	0.00119	0.0000958	0.0000077
4.9	0.0877	0.0125	0.00178	8.8	0.00106	0.0000840	0.0000067
				8.9	0.000939	0.0000736	0.0000058
5.0	0.0792	0.01104	0.00154				
5.1	0.0713	0.00976	0.001335	9.0	0.000832	0.0000645	0.0000050
5.2	0.0643	0.00862	0.001157	9.1	0.000737	0.0000565	0.0000043
5.3	0.0578	0.00762	0.001002	9.2	0.000653	0.0000495	0.0000037
5.4	0.0520	0.00672	0.000869	9.3	0.000578	0.0000434	0.0000032
				9.4	0.000512	0.0000380	0.0000028
5.5	0.0468	0.00593	0.000753				
5.6	0.0420	0.00524	0.000652	9.5	0.000454	0.0000332	0.0000024
5.7	0.0377	0.00462	0.000565	9.6	0.000401	0.0000291	0.0000021
5.8	0.0339	0.00407	0.000490	9.7	0.000354	0.0000255	0.0000018
5.9	0.0303	0.00359	0.000425	9.8	0.000314	0.0000223	0.0000016
				9.9	0.000277	0.0000196	0.0000014
6.0	0.0272	0.00316	0.000367				
6.1	0.0243	0.00279	0.000318	10.0	0.000245	0.0000171	0.0000012
6.2	0.0218	0.00245	0.000276				

APPENDIX II

Harmonic oscillator contributions

The contribution (in calories) of a fundamental vibration frequency ω (wave numbers) to the heat capacity, heat content, and free energy are given in table 2 as a function of (ω/T). The contribution to the entropy is given by $S = (H/T) - (F/T)$. All constants are from the *International Critical Tables*. This table was obtained by interpolation from unpublished calculations of Dr. H. L. Johnston, to whom I should like to express my gratitude. The last decimal place may be in error by several units, owing to the interpolation.

TABLE 3

Values of a_r for various values of θ and r

$\theta = 0$	1	2	3	4	5	6
0.0000	−0.4551	−1.5140	−2.8344	−4.2805	−5.8000	−7.3688
4.0000	3.9170	3.6722	3.2769	2.7469	2.0995	1.3518
4.0000	4.3713	5.1727	6.0452	6.8291	7.4491	7.8701
16.000	16.033	16.128	16.273	16.452	16.648	16.845
16.000	16.034	16.141	16.339	16.650	17.097	17.689
36.000	36.014	36.057	36.129	36.229	36.359	36.517
36.000	36.014	36.057	36.129	36.230	36.361	36.523
$\theta = 7$	8	9	10	12	14	16
−8.9737	−10.607	−12.262	−13.937	−17.332	−20.776	−24.259
0.5175	−0.3894	−1.3588	−2.3822	−4.5635	−6.8907	−9.3341
8.0866	8.1152	7.9828	7.7174	6.8787	5.7363	4.3712
17.027	17.183	17.303	17.381	17.395	17.207	16.819
18.417	19.253	20.161	21.105	22.972	24.651	26.009
36.704	36.917	37.157	37.420	38.006	38.648	39.315
36.715	36.94	37.21	37.51	38.24	39.16	40.22
$\theta = 18$	20	24	28	32	36	40
−27.773	−31.313	−38.459	−45.673	−52.942	−60.256	−67.606
−11.873	−14.491	−19.923	−25.562	−31.365	−37.303	−43.352
2.8331	1.1543	−2.5398	−6.5881	−10.914	−15.467	−20.208
16.242	15.494	13.553	11.121	8.2947	5.1467	1.7300
26.988	27.595	27.885	27.283	26.062	24.379	22.325
39.972	40.590	41.606	42.225	42.394	42.118	41.433
40.93	42.1					

TABLE 4

References for published calculations of thermodynamic quantities

SUBSTANCES	REFERENCES	SUBSTANCES	REFERENCES
Diatomic molecules			
Air	(99, 100)	HF	(136)
Br_2	(135, 150, 14, 78, 154, 166)	HI	(135, 134, 62)
C_2	(74)	I_2	(135, 134, 150, 63, 47)
D_2	(20, 100, 135, 166, 92)	ICl	(130)
DBr	(135)	Li_2	(71)
DCl	(135, 166a)	K_2	(71)
DI	(135, 166a)	Na_2	(71, 52, 89, 154, 166)
Cl_2	(135, 56, 150, 100, 165, 55, 166)	N_2	(149, 135, 100, 165)
CO	(149, 135, 100, 18, 19, 105, 89, 154, 166)	NO	(179, 149, 100, 91, 87, 172, 52)
F_2	(45, 136)	O_2	(149, 135, 100, 165, 94, 95, 154, 120, 122, 97, 166)
H_2	(100, 149, 135, 10, 36, 46, 76, 35, 154)	OH	(100, 90)
HBr	(135)	P_2	(66)
HCl	(135, 100, 55, 60, 154, 166)	S_2	(7, 65, 133, 34)
HD	(100, 135, 166, 92)	SO	(133)
Other inorganic substances			
$AsCl_3$	(173)	COS	(114, 7, 33, 100)
AsF_3	(173)	CS_2	(15, 7, 33, 100)
$B_3N_3H_6$	(28)	$Cl^{\cdot}$	(55)
CBr_4	(160)	ClO_2	(166)
CCl_4	(127, 160, 173, 100)	Cu vapor	(112)
CF_4	(173, 100)	D	(92, 93)
CF_2Cl_2	(100)	D_2O	(98, 149, 125)
C_2N_2	(100, 17, 161, 147, 159)	HDO	(163, 30, 31, 32)
CNBr	(159)	D_2S	(98)
CNCl	(159)	Fe vapor	(112)
CNI	(159)	H	(46)
CO_2	(76, 67, 103, 166, 53, 149, 135, 100)	HCN	(8, 16, 73, 100, 57)
$COCl_2$	(160)	H_2S	(34, 23, 135, 7, 21, 100, 98)
		HDS	(98)

TABLE 4—*Concluded*

SUBSTANCES	REFERENCES	SUBSTANCES	REFERENCES
Other inorganic substances—*Continued*			
H_2O	(50, 164, 76, 67, 68, 69, 154, 121, 166, 100, 98, 149, 135, 59, 49, 110, 48, 156)	P	(2)
		P_4	(11, 2)
		PBr_3	(173)
		PCl_3	(2, 173)
		PCl_5	(2)
		PF_3	(173)
I	(134)	PH_3	(22, 155, 100)
NH_3	(157, 51, 128, 16, 138, 149, 100, 80)	S	(133)
		SF_6	(100)
		$SiCl_4$	(81, 173)
N_2H_4	(41)	SiF_4	(173)
N_2O	(103, 12, 8, 145, 12, 100)	SO_2	(70, 166, 135, 7, 33)
NO_2	(179, 54)	$SnCl_4$	(81)
NOCl	(86, 9)	TeF_6	(100)
$Ni(CO)_4$	(27)	$TiCl_4$	(81)
O	(95, 96)	Xe	(24)
OsO_4	(1)	Electron gas	(72)
O_3	(104, 121)		
Organic compounds			
CH_4	(43, 100, 149, 131, 106, 102, 167, 158)	Allene	(124)
		Propylene	(141, 143, 100, 26, 107, 116)
CH_3D, etc.	(131)	Cyclopropane	(123)
CH_3Br	(160, 39)	Propane	(141, 107, 106, 113, 100, 116)
CH_3Cl	(160, 100, 167)		
CH_3NH_2	(6)	Isopropyl alcohol	(152)
CH_3OH	(108, 79)	Butane	(141, 106, 100)
CH_2Br_2	(160)	Isobutane	(141, 100, 106)
CH_2Cl_2	(160, 100, 167)	1-Butene	(141, 107, 100)
$CHBr_3$	(160)	2-Butene	(141, 107, 100)
$CHCl_3$	(160, 100, 167)	"Isobutene"	(141, 107, 100)
CH_2O	(160)	Butadiene	(107)
CHOOH	(160)	Dimethylacetylene	(29, 137)
		Neopentane	(4, 141, 106, 100)
C_2H_2	(100, 75, 102)		
C_2HD, C_2D_2	(75, 64)	$(CH_3)_2C{=}CHCH_3$	(107)
C_2H_4	(141, 38, 107, 162, 100, 102, 153)		
		C_6H_6	(100, 126, 106)
		C_6D_6	(126, 106)
C_2H_6	(115, 141, 162, 106, 117, 148, 100, 169, 153)	$(CH_3)_2C{=}C(CH_3)_2$	(107)
		Phenol	(3)
		Cresol	(3)
C_2H_5OH	(151)	Methyl derivatives of benzene	(106)
$(CH_3)_2CO$	(152)		
$(CH_3)_2NH$	(5)	Chain hydrocarbons	(83)

APPENDIX III

Energy levels for the torsional oscillator

Values of a_r for various values of θ and r are given in table 3. Only levels of symmetry A are included. The first six levels are taken from Ince (85). Levels higher than those given may be computed approximately by the asymptotic formula:

$$a_r = r^2 + \frac{1}{2}\,\theta/(r^2 - 1)$$

A line indicates the proper place to change from V to R levels.

APPENDIX IV

Tabulation of references of published calculations of thermodynamic quantities

Table 4 contains reference numbers for essentially all calculations which have been published up to 1940. References up to 1936 were taken from Kassel's review (101) or from that of Zeise (175 to 179). No attempt at a critical selection has been made, so that naturally many obsolete and incorrect results are included. The excellent critical discussion of Kassel should be consulted for the older results. Many references contain only the entropy at one or two temperatures.

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