

Appendix B

Essential Statistical Thermodynamics

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Some computational methods, particularly *ab initio* techniques, produce detailed molecular information but no thermodynamic information directly. Further calculations are needed to generate familiar, ideal-gas quantities such as the standard molar entropy (S°), heat capacity (C_p°), and enthalpy change [$H^\circ(T) - H^\circ(0)$]. This Appendix details the necessary procedures, including worked examples. Thermochemical calculations can be extended to transition states of chemical reactions. Procedures are provided for converting such information into rate constants. Tables are also provided for unit conversions and physical constants.

Statistical thermodynamics calculations are necessary to compute properties as functions of temperature. In some computations, such as *ab initio* electronic calculations of molecular energy, the raw results do not even correspond to properties at absolute zero temperature and must always be corrected. All the corrections are based upon molecular spectroscopy, with temperature-dependence implicit in the molecular partition function, Q . The partition function is used not only for theoretical predictions, but also to generate most published thermochemical tables. Many data compilations include descriptions of calculational procedures (1-3).

Corrections Unique to *Ab Initio* Predictions

By convention, energies from *ab initio* calculations are reported in hartrees, the atomic unit of energy (1 hartree = 2625.5 kJ/mol = 627.51 kcal/mol = 219474.6 cm^{-1}) (4). These energies are negative, with the defined zero of energy being the fully-dissociated limit (free electrons and bare nuclei). *Ab initio* models also invoke the approximation that the atomic nuclei are stationary, with the electrons swarming about them. This is a good approximation because nuclei are much heavier than electrons. Consequently, the

resulting energies are for a hypothetical, non-vibrating molecule. Although oscillators may be at rest in classical mechanics, real (quantum-mechanical) oscillators are always in motion. The small residual motion at absolute zero temperature is the *zero-point vibrational energy*, abbreviated ZPVE or ZPE. For a simple harmonic oscillator, the ZPE equals one-half the vibrational frequency. Although all real molecular vibrations are at least slightly anharmonic, they are usually approximated as harmonic. Thus, the molecule's ZPE may be taken as one-half the sum of the vibrational frequencies. In equation 1, N is the number of atoms in the molecule and the ν_i are the fundamental

$$\text{ZPE} = \frac{1}{2} \sum_{i=1}^{3N-6} \nu_i \quad (1)$$

vibrational frequencies. There are $3N-6$ vibrations in a non-linear molecule and $3N-5$ in a linear molecule; equation 1 is for the more common non-linear case. The ZPE must be added to the raw *ab initio* energy to obtain an energy corresponding to absolute zero temperature, $T = 0$ K.

In practice, the ZPE correction is slightly complicated by the observation that *ab initio* vibrational frequencies are often in error by +5% to +10%. To compensate for this error, the computed frequencies are usually multiplied by empirical scaling factors. The most recent recommendations are those of Scott and Radom (5). For example, they suggest scaling HF/6-31G* frequencies by 0.8953 to predict vibrational spectra (i.e., fundamental frequencies), by 0.9135 for the computation of ZPEs, by 0.8905 to predict enthalpy differences $H^\circ(298.15) - H^\circ(0)$, and by 0.8978 to predict $S^\circ(298.15)$. The methods for computing these quantities are described below. Common abbreviations and acronyms of the *ab initio* literature are defined in the glossary (Appendix D) of this book. In this Appendix, the degree sign ($^\circ$) that indicates ideality and standard pressure (1 bar) is omitted except where the thermal electron convention for ions is being emphasized (see below).

Enthalpies of formation depend upon the thermodynamic conventions for reference states of the elements. Since this information is not intrinsic to an isolated molecule, an *ab initio* reaction energy (i.e., energies for at least two molecules) must be combined with experimental data to compute an enthalpy of formation, $\Delta_f H^\circ$.

Example: $\Delta_f H^\circ_0$ of hydrogen fluoride. There are many levels of approximation in *ab initio* theory; several are described in the chapters of this book. For the present example, we choose the CCSD(T)/aug-cc-pVTZ//B3LYP/6-31G(d) level. The notation indicates that (1) molecular geometries are calculated at the density-functional B3LYP level using the 6-31G(d) basis set and (2) molecular electronic energies are calculated at the high CCSD(T) level of theory using the rather large aug-cc-pVTZ basis set. To compute an enthalpy of formation for HF, we must also choose a balanced chemical reaction for which to calculate an energy. We choose arbitrarily the reaction shown in equation 2. Note that the ideal-gas energy and enthalpy are equal at 0 K, since $H = E + PV = E + nRT = E$.



The optimized B3LYP/6-31G(d) bond lengths are 0.743, 1.404, and 0.934 Å for H₂, F₂, and HF respectively, in reasonably good agreement with the experimentally derived values $r_e = 0.741, 1.412, \text{ and } 0.917 \text{ \AA}$ respectively (6). The calculated (harmonic) B3LYP/6-31G(d) vibrational frequencies are 4451, 1064, and 3978 cm⁻¹ for H₂, F₂, and HF respectively, in modest agreement with the experimentally derived harmonic frequencies $\omega_e = 4401, 917, \text{ and } 4138 \text{ cm}^{-1}$ respectively (6). Since 1 cm⁻¹ equals only 0.01196 kJ/mol, small errors in ZPE will not cause significant errors in the final enthalpy of formation. Scaling the calculated frequencies by 0.9806 (5) and substituting them into equation 1 yields ZPE = 2182, 522, and 1950 cm⁻¹ = 0.009943, 0.002377, and 0.008887 hartree for H₂, F₂, and HF respectively. At these optimized geometries, the CCSD(T)/aug-cc-pVTZ energies are $E_e = -1.172636, -199.313519, \text{ and } -100.349402$ hartree for H₂, F₂, and HF respectively. Adding the ZPEs thus leads to enthalpies (or energies) at $T = 0 \text{ K}$ of $E_0 = -1.162693, -199.311142, \text{ and } -100.340515$ hartree for H₂, F₂, and HF respectively. The calculated enthalpy change is then $\Delta_r H^\circ_0(\text{reaction 2}) = -0.207194 \text{ hartree} = -544.0 \text{ kJ/mol}$. Using the experimental (defined, in these cases) enthalpies of formation for H₂ and F₂ of 0 and 0 kJ/mol (1), we obtain $\Delta_r H^\circ_0(\text{HF}) = -272.0 \text{ kJ/mol}$. This is in good agreement with the experimental value of $-272.5 \pm 0.8 \text{ kJ/mol}$ (1). All the *ab initio* calculations for this example were done on a personal computer.

General Relationships of Statistical Thermodynamics

In the present context, statistical thermodynamics is meant to include the methods used to convert molecular energy levels into macroscopic properties, especially enthalpies, entropies, and heat capacities. Molecular energy levels arise from molecular translation (i.e., motion through space), rotation, vibration, and electronic excitation. This information constitutes the spectroscopy of the molecule of interest and can be obtained experimentally or from calculations.

Partition Function. The molecular energy levels ε_i are used to compute the *molecular partition function*, usually denoted by the symbol Q , as shown in equation 3. The sum

$$Q(T) = \sum_i \exp(-\varepsilon_i/kT) \quad (3)$$

extends over all energy levels. (Sometimes this sum is written only over all unique energy levels, in which case a level degeneracy g_i must be included in the sum.) However, for very high temperatures at which the molecule becomes unstable, the extent of the sum may be ambiguous. Tabulated thermochemical data must be used with caution under such conditions; the values (1) may depend strongly upon the high-energy cutoff procedure adopted and (2) may deviate implicitly from the ideal-gas model.

One typically chooses the lowest energy level to be the zero of energy, so that no levels lie at negative energies. From equation 3 it follows that the largest contributions to Q are from the lowest energy levels. Conversely, levels that lie far above kT (207 cm⁻¹ at room temperature) have only a minor effect on Q and its derivative thermodynamic quantities.

Thermodynamic Functions. Given the partition function, the usual molar thermodynamic functions can be calculated based upon the following general equations. Equation 4 is for the entropy, equation 5 for the heat capacity at constant volume, equation 6 for the heat capacity at constant pressure, and equation 7 for the enthalpy

$$S = Nk \left[\frac{\partial}{\partial T} (T \ln Q) - \ln N + 1 \right] \quad (4)$$

$$C_v = NkT \frac{\partial^2}{\partial T^2} (T \ln Q) \quad (5)$$

$$C_p = C_v + R \quad (6)$$

$$H(T) - H(0) = \int_0^T C_p dT = \frac{RT^2}{Q} \frac{\partial Q}{\partial T} + RT \quad (7)$$

difference relative to absolute zero temperature. N is Avogadro's number (6.022137×10^{23}), k is the Boltzmann constant (1.38066×10^{23} J/K), and the ideal-gas constant $R \equiv Nk$ (4). The last two terms inside the brackets in equation 4 arise from the indistinguishability of identical molecules, which requires a factor of $(1/N!)$ in the partition function for the ensemble. Expressions 4-7 may more easily be evaluated using equations 8-11 for the various derivatives.

$$\frac{\partial}{\partial T} (T \ln Q) = \ln Q + \frac{T}{Q} \frac{\partial Q}{\partial T} \quad (8)$$

$$\frac{\partial^2}{\partial T^2} (T \ln Q) = \frac{2}{Q} \frac{\partial Q}{\partial T} + \frac{T}{Q} \frac{\partial^2 Q}{\partial T^2} - \frac{T}{Q^2} \left(\frac{\partial Q}{\partial T} \right)^2 \quad (9)$$

$$\frac{\partial Q}{\partial T} = \frac{1}{kT^2} \sum_i \varepsilon_i \exp(-\varepsilon_i/kT) \quad (10)$$

$$\frac{\partial^2 Q}{\partial T^2} = \frac{-2}{T} \frac{\partial Q}{\partial T} + \frac{1}{k^2 T^4} \sum_i \varepsilon_i^2 \exp(-\varepsilon_i/kT) \quad (11)$$

Practical Calculations

A complete set of molecular energy levels is almost never available. To simplify the problem, one usually adopts a model in which translation, rotation, vibration, and electronic excitation are uncoupled. In other words, one makes the approximation that the different types of motion are unaffected by each other and do not mix together. This leads to a separability of Q into four factors that correspond to separate partition functions for translation, rotation, vibration, and electronic excitation. This is shown in equation 12, where the explicit dependence upon temperature has been dropped for

$$Q = Q_{trans} Q_{rot} Q_{vib} Q_{elec} \quad (12)$$

simplicity. When electronically excited states are considered, one often assumes that the translational, rotational, and vibrational spectra of the excited state are the same as those of the ground electronic state. This is crude, but is convenient when no other information is available. Moreover, if the excited state lies far above kT , the final results will not be sensitive to such details.

Different energy units are used conventionally in the fields of molecular spectroscopy, quantum chemistry, and thermochemistry. To provide some feeling for magnitudes, the values of the thermal energy kT , at “room temperature” (298.15 K) and at 1000 K, are listed in Table I in several units. In this Appendix, all units are of the SI (*Système International*: kg, m, s, Pa, K) unless otherwise indicated.

Table I. Thermal energy (kT) at two temperatures, expressed in various units

<i>Unit</i>	<i>“Room temperature”</i>	<i>1000 K</i>
kelvin (K)	298.15	1000
wavenumber (cm ⁻¹)	207.2	695.0
Hertz (s ⁻¹)	6.212×10^{12}	2.084×10^{13}
kJ/mol	2.479	8.314
kcal/mol	0.592	1.987
electron volt (eV)	0.0257	0.0862
hartree (atomic unit)	0.000944	0.003167

Translational Partition Function. Rigorously, Q_{trans} must be calculated from a sum over all the translational energy levels that are available to a molecule confined to a cubic box of volume $V = RT/p$ (molar volume of an ideal gas at temperature T and pressure p). This is seldom done. Instead, the sum is approximated as an integral to obtain equations 13-16. This approximation is good as long as $m^{3/2}T^{5/2}p^{-1} \gg h^3(2\pi)^{-3/2}k^{-5/2}$ (3). At the standard pressure $p = 1 \text{ bar} = 10^5 \text{ Pa} = 0.986923 \text{ atm}$, this condition is met for sufficiently heavy molecules, m (in amu) $\gg 11.4 T^{-5/3}$, and for sufficiently high temperatures, $T \gg 4.31 m^{-3/5}$ (m expressed in amu). Fortunately, this covers the conditions of common chemical interest. For an atomic ideal gas, there is no vibrational or rotational motion.

$$Q_{trans} = (2\pi mkT)^{3/2} h^{-3} V \quad (13)$$

$$S_{trans} = R[(3/2) \ln(2\pi m/h^2) + (5/2) \ln(kT) - \ln(p) + 5/2] \quad (14)$$

$$C_{p,trans} = (5/2) R \quad (15)$$

$$[H(T)-H(0)]_{trans} = (5/2) RT \quad (16)$$

As an example, we can calculate the standard entropy for neon ideal gas at $T = 298.15$ K. The atomic mass is converted to SI units using the equivalence N_A amu = 0.001 kg, where $N_A = 6.022 \times 10^{23} \text{ mol}^{-1}$ is the Avogadro constant. Thus for ^{20}Ne ($m = 19.992$ amu), $m = 3.320 \times 10^{-26}$ kg. The values of the physical constants are $h = 6.626 \times 10^{-34}$ J s, $k = 1.381 \times 10^{-23}$ J K $^{-1}$, and $R = kN_A = 8.3145$ J mol $^{-1}$ K $^{-1}$ (7,4). The standard pressure is $p = 10^5$ Pa. Substituting these values into equation 14 yields $S_{298.15}(^{20}\text{Ne}) = 146.21$ J mol $^{-1}$ K $^{-1}$. For ^{21}Ne ($m = 20.994$ amu), $S_{298.15}(^{21}\text{Ne}) = 146.82$ J mol $^{-1}$ K $^{-1}$, and for ^{22}Ne ($m = 21.991$ amu), $S_{298.15}(^{22}\text{Ne}) = 147.40$ J mol $^{-1}$ K $^{-1}$. Averaging these values using the natural abundances of 90.48%, 0.27%, and 9.25%, respectively (7,8), we find $S_{298.15} = 146.32$ J mol $^{-1}$ K $^{-1}$ for the naturally occurring isotopic distribution. This agrees well with the accepted value of 146.33 J mol $^{-1}$ K $^{-1}$ (9).

Rotational Partition Function. The free rotation of a rigid molecule is also quantized (the angular momentum and its projection are integer multiples of $h/2\pi$), so the rotational energy is restricted to certain discrete levels. Rotational spectra are characterized by the constants A , B , and C , where $A \equiv h/(8\pi^2 I_A)$ and likewise for B and C . The quantities $I_{A,B,C}$ are the principal moments of inertia of the molecule, with the convention $I_A \leq I_B \leq I_C$ (or $A \geq B \geq C$). Many computer programs, including *ab initio* packages, report the rotational constants when provided with a molecular geometry. The moments can also be calculated manually as the eigenvalues of the inertial tensor, which has elements like $I_{xy} = -\sum m_i x_i y_i$ and $I_{xx} = +\sum m_i (y_i^2 + z_i^2)$, where the index i runs over all atoms in the molecule and the coordinate origin is at the center of mass. Linear molecules ($I_A = 0$) are described by a single rotational constant, B , and a single moment of inertia, I . Details may be found in textbooks of molecular spectroscopy.

Fortunately, at high enough temperatures ($kT \gg hA$), the sum can be replaced by an integral as it is for translation. In the general case, the rotational partition function is given by equation 17. For linear molecules, equation 18 should be used instead. In these

$$Q_{rot} = \frac{8\pi^2}{\sigma h^3} (2\pi kT)^{3/2} (I_A I_B I_C)^{1/2} = (kT/h)^{3/2} (ABC)^{-1/2} \pi^{1/2} \sigma^{-1} \quad (17)$$

$$Q_{rot}^{linear} = \frac{8\pi^2 I kT}{\sigma h^2} = kT/(\sigma h B) \quad (18)$$

and subsequent equations, the symbol σ denotes the “rotational symmetry number” or “external symmetry number” for the molecule. This is the number of unique orientations of the rigid molecule that only interchange identical atoms. It preserves parity restrictions on the interchange of identical nuclei when summation is replaced by integration. Identifying the correct symmetry number is a common point of difficulty; it is discussed further below.

For the typical case (equation 17), the thermodynamic functions are given by equations 19-21. For linear molecules (equation 18), equations 22-24 are used instead.

$$S_{rot} = R[\ln(8\pi^2/\sigma) + (3/2) \ln(2\pi kT/h^2) + (1/2) \ln(I_A I_B I_C) + 3/2] \quad (19)$$

$$= R[(3/2) \ln(kT/h) - (1/2) \ln(ABC/\pi) - \ln(\sigma) + 3/2]$$

$$C_{p,rot} = (3/2) R \quad (20)$$

$$[H(T)-H(0)]_{rot} = (3/2) RT \quad (21)$$

$$S_{rot}^{linear} = R[\ln(8\pi^2 I kT/\sigma h^2) + 1] = R[\ln(kT/\sigma h B) + 1] \quad (22)$$

$$C_{p,rot}^{linear} = R \quad (23)$$

$$[H(T)-H(0)]_{rot}^{linear} = RT \quad (24)$$

External Symmetry Number. Some computer programs, such as many *ab initio* packages, determine the molecular symmetry and external symmetry number (σ) automatically. If such a program is unavailable, σ may be determined by hand. With practice, this becomes very fast.

If you are familiar enough with group theory to identify the molecule's point group (I), then σ can be determined from Table II (I). Without identifying the point group, one can count manually the number of orientations of the rigid molecule that interchange only identical atoms.

Table II. Symmetry numbers corresponding to symmetry point groups

<i>Group</i>	σ	<i>Group</i>	σ	<i>Group</i>	σ	<i>Group</i>	σ
$C_1, C_i, C_s, C_{\infty v}$	1	$D_{\infty h}$	2	T, T_d	12	O_h	24
I_h	60	S_n	$n/2$	C_n, C_{nv}, C_{nh}	n	D_n, D_{nh}, D_{nd}	$2n$

For example, the benzene molecule (C_6H_6) belongs to the D_{6h} point group. From Table II, $\sigma = 12$. Alternatively, one can draw the molecule as a hexagon with numbered vertices. Rotating the drawing by $n \times 60^\circ$, where n runs from 0 to 5, generates six different orientations that are distinguished only by the artificial numbering of the vertices. Each of these six orientations can be flipped over to generate another orientation, for a total of 12 unique orientations, $\sigma = 12$.

Another example is methyl chloride, CH_3Cl . This belongs to the C_{3v} point group, so $\sigma = 3$. Alternatively, one can artificially number the hydrogen atoms and see that there are three unique orientations, related by rotations of $n \times 120^\circ$ ($n = 0-2$) around the C-Cl bond axis.

Chlorobenzene, C_6H_5Cl , belongs to the C_{2v} point group, so $\sigma = 2$. Alternatively, one can again number the hydrogen atoms and see that there are two unique orientations, related by rotations of $n \times 180^\circ$ ($n = 0-1$) around the C-Cl bond axis. In contrast, toluene ($C_6H_5CH_3$) belongs to the C_s point group, so $\sigma = 1$. There are no ways to rotate or flip the molecule *rigidly* that will leave it unchanged. Allowing the methyl group to rotate leads to an *internal* symmetry number which is discussed below, following the section on internal rotation.

Vibrational Partition Function. To complete the simple rigid-rotator/harmonic oscillator (RRHO) model, one must consider the molecular vibrations. As indicated in the discussion of ZPE (equation 1), a molecule that contains N atoms has $3N-6$ vibrational frequencies ($3N-5$ for linear molecules). The partition function is given in equation 25, where the product runs over all vibrational frequencies ν_i . The corresponding thermodynamic functions are given by equations 26-28.

$$Q_{vib} = \prod_i \left(1 - e^{-h\nu_i/kT}\right)^{-1} \quad (25)$$

$$S_{vib} = -R \sum_i \ln\left(1 - e^{-h\nu_i/kT}\right) + R \sum_i \frac{h\nu_i}{kT} \frac{e^{-h\nu_i/kT}}{\left(1 - e^{-h\nu_i/kT}\right)} \quad (26)$$

$$C_{p,vib} = R \sum_i \left(\frac{h\nu_i}{kT}\right)^2 \frac{e^{-h\nu_i/kT}}{\left(1 - e^{-h\nu_i/kT}\right)^2} \quad (27)$$

$$[H(T) - H(0)]_{vib} = RT \sum_i \left(\frac{h\nu_i}{kT}\right) \frac{e^{-h\nu_i/kT}}{\left(1 - e^{-h\nu_i/kT}\right)} \quad (28)$$

Example: Hydrogen Fluoride. Earlier we used the results of *ab initio* calculations to obtain a value for $\Delta_f H^\circ_0(\text{HF})$. The other equations above permit us to compute *ab initio* thermodynamic functions, which will provide an enthalpy of formation at the more useful temperature of 298.15 K. Results are summarized in Table III. For simplicity, we will neglect the naturally occurring heavy isotopes of hydrogen. The molecular weight of $^1\text{H}^{19}\text{F}$ is 20.006 amu. Using equation 14, as done above for neon, leads to $S_{trans} = 146.22 \text{ J mol}^{-1} \text{ K}^{-1}$. HF is a linear molecule, so we use equation 22 to calculate S_{rot} . The *ab initio* calculation reports a rotational constant $B = 605.64 \text{ GHz} = 6.0564 \times 10^{11} \text{ s}^{-1}$ based upon the calculated B3LYP/6-31G(d) equilibrium geometry and the most common isotopes. This molecule belongs to the $C_{\infty v}$ point group ($\sigma = 1$); there are no identical nuclei that can be interchanged by any rotation. Hence $S_{rot} = 27.67 \text{ J mol}^{-1} \text{ K}^{-1}$. For the vibrational contribution, we scale the B3LYP/6-31G(d) frequency of 3987 cm^{-1} by 1.0015 as suggested for entropies (5) to obtain $\nu = 3993 \text{ cm}^{-1}$. This is multiplied by the speed of light, $c = 2.998 \times 10^{10} \text{ cm s}^{-1}$ (7,4), to convert wavenumbers to SI frequency units, $\nu = 1.197 \times 10^{14} \text{ s}^{-1}$. Thus $h\nu/kT = 19.27$ and equation 26 yields $S_{vib} = 7.22 \times 10^{-7} \text{ J mol}^{-1} \text{ K}^{-1}$. The total entropy is $S_{298.15} = S_{trans} + S_{rot} + S_{vib} = 173.89 \text{ J mol}^{-1} \text{ K}^{-1}$, in good agreement with the accepted value of $173.78 \text{ J mol}^{-1} \text{ K}^{-1}$ (9).

For enthalpy and heat capacity, the B3LYP/6-31G(d) frequency is scaled by 0.9989 (5) to obtain $\nu = 3983 \text{ cm}^{-1}$. The heat capacity $C_p(\text{HF})$ is calculated using equations 15, 23, and 27, leading to $C_p = C_{p,trans} + C_{p,rot} + C_{p,vib} = (5/2)R + R + 1.38 \times 10^{-5} \text{ J mol}^{-1} \text{ K}^{-1} = 29.10 \text{ J mol}^{-1} \text{ K}^{-1}$. This compares well with the accepted value of $29.14 \text{ J mol}^{-1} \text{ K}^{-1}$ (1). Finally, the enthalpy difference can be computed using equations 16, 24, and 28 to be $[H(298.15)-H(0)] = (5/2)RT + RT + 2.14 \times 10^{-4} \text{ J mol}^{-1} = 8.68 \text{ kJ mol}^{-1}$. This can be used to compute $\Delta_f H^\circ_{298.15}(\text{HF}) = \Delta_f H^\circ_0(\text{HF}) + [H(298.15)-H(0)]_{\text{HF}} - [H(298.15)-H(0)]_{\text{elements}}$. Taking the *ab initio* value $\Delta_f H^\circ_0(\text{HF}) = -272.0 \text{ kJ/mol}$ from above, the calculated enthalpy difference of 8.68 kJ/mol for HF, and the accepted enthalpy differences of $(8.47)/2$ and $(8.83)/2 \text{ kJ/mol}$ for $1/2\text{H}_2$ and $1/2\text{F}_2$ (9), we obtain $\Delta_f H^\circ_{298.15}(\text{HF}) = -272.0 \text{ kJ/mol}$, in agreement with the accepted value of $-273.3 \pm 0.7 \text{ kJ mol}^{-1}$ (9) [$-272.5 \pm 0.8 \text{ kJ/mol}$ is listed in older ref (1)].

Table III. Results for Hydrogen Fluoride Example

<i>Contribution</i>	<i>S, J/(mol·K)</i>	<i>C_p, J/(mol·K)</i>	<i>[H(298.15)-H(0)], kJ/mol</i>
Translation	146.22	20.79	6.20
Rotation	27.67	8.31	2.48
Vibration	7×10^{-7}	1×10^{-5}	2×10^{-4}
<i>Total</i>	<i>173.89</i>	<i>29.10</i>	<i>8.68</i>

Electronic Partition Function. Although they may not have low-lying electronic excited states, some molecules have degenerate electronic ground states. Free radicals are a common example. They may have unpaired electrons in their electronic ground states and a net electron spin of $S = n_{\text{unpaired}}/2$, where n_{unpaired} is the number of unpaired electrons. (Beware not to confuse the spin quantum number S with the entropy.) The multiplicity, or degeneracy g , of such a state is $g = (2S+1)$. Using degeneracy numbers is equivalent to an explicit count of all states, including degenerate ones. Thus, $Q_{elec} = g$ is a constant and only affects the entropy: $S_{elec} = R \ln(g)$ and $C_{p,elec} = [H(T)-H(0)]_{elec} = 0$. Since most free radicals have only a single unpaired electron, the usual effect is to increase the entropy by $R \ln(2)$. In addition to spin degeneracies, some states have spatial degeneracies. This situation is most common for diatomic molecules. Linear molecules with a spatial symmetry other than Σ (e.g., Π or Δ) have a spatial degeneracy of 2. For example, the OH radical has a $^2\Pi$ ground state, so its degeneracy is $g = 2$ (spin) \times 2 (spatial) = 4. If there are both spin and spatial degeneracies, spin-orbit coupling lifts the degeneracy, often significantly. In the example of OH, the 4-fold degenerate ground state is split into two doubly-degenerate levels separated by 139.2 cm^{-1} (6). In such a case the low-lying excited states should be included in the calculation of thermodynamic quantities. The partition function is given by equation 29, where ϵ_i and g_i are the excitation energies

(spectroscopic T_0) and degeneracies of the excited states, g_0 and $\varepsilon_0 \equiv 0$ are for the ground state, and the sum runs over all the electronic states being considered, including the ground state. The contributions to the thermal functions are given by equations 30-32. This treatment assumes, rather crudely, that the rotations and vibrations are unaffected by electronic excitation.

$$Q_{elec} = \sum g_i \exp(-\varepsilon_i/kT) \quad (29)$$

$$S_{elec} = R \ln \left(\sum g_i e^{-\varepsilon_i/kT} \right) + R \frac{\sum g_i (\varepsilon_i/kT) e^{-\varepsilon_i/kT}}{\sum g_i e^{-\varepsilon_i/kT}} \quad (30)$$

$$C_{p, elec} = R \left(\frac{\sum g_i (\varepsilon_i/kT)^2 e^{-\varepsilon_i/kT}}{\sum g_i e^{-\varepsilon_i/kT}} \right) - R \left(\frac{\sum g_i (\varepsilon_i/kT) e^{-\varepsilon_i/kT}}{\sum g_i e^{-\varepsilon_i/kT}} \right)^2 \quad (31)$$

$$[H(T) - H(0)]_{elec} = RT \frac{\sum g_i (\varepsilon_i/kT) e^{-\varepsilon_i/kT}}{\sum g_i e^{-\varepsilon_i/kT}} \quad (32)$$

Example: Entropy of Methyl Radical. For simplicity, we again neglect minor isotopes. Results are summarized in Table IV. The molecular weight of CH_3 is then $m = 15.023$ amu, so $S_{trans} = 142.65 \text{ J mol}^{-1} \text{ K}^{-1}$. This is a flat, triangular molecule that belongs to the D_{3h} point group, $\sigma = 6$. The experimental bond length is $r_e = 1.0767 \text{ \AA} = 1.0767 \times 10^{-10} \text{ m}$ (12-14). The moments of inertia can be evaluated using the symmetry of this oblate top, or more generally by diagonalizing the inertial tensor. We place the molecule in the yz plane with one hydrogen atom on the z axis. The center of mass coincides with the carbon atom. The cartesian coordinates then lead to an inertial tensor with components $I_{xx} = 3m_{\text{H}}r_e^2$, $I_{xy} = I_{yx} = 0$, $I_{xz} = I_{zx} = 0$, $I_{yy} = (3/2)m_{\text{H}}r_e^2$, $I_{yz} = I_{zy} = 0$, and $I_{zz} = (3/2)m_{\text{H}}r_e^2 = 2.910 \times 10^{-47} \text{ kg m}^2$. This is already diagonal, with eigenvalues $I_A = I_B = 2.910 \times 10^{-47} \text{ kg m}^2$ and $I_C = 5.820 \text{ kg m}^2$ so that $S_{rot} = 43.50 \text{ J mol}^{-1} \text{ K}^{-1}$ (equation 19). The observed vibrational frequencies of CH_3 are 3004.4, 606.5, 3160.8, and 1396 cm^{-1} for ν_1 , ν_2 , ν_3 , and ν_4 respectively (15). Since ν_3 and ν_4 are both doubly degenerate (e' symmetry), they are counted twice and we have the correct number of vibrations, $3N - 6 = 6$. Converting to SI units leads to $S_{vib} = 6.51 \times 10^{-5} + 1.84 + 6.42 \times 10^{-5} + 0.15 = 1.99 \text{ J mol}^{-1} \text{ K}^{-1}$. In this case, this is a radical with one unpaired electron, $S = 1/2$ (electronic ground state is $^2\text{A}_2''$), so the degeneracy $g = 2$ and $S_{elec} = R \ln(2)$. Adding the four contributions to the entropy gives $S_{298.15} = 193.9 \text{ J mol}^{-1} \text{ K}^{-1}$, in agreement with the literature value of $194.2 \pm 1.3 \text{ J mol}^{-1} \text{ K}^{-1}$ (1).

Example: Entropy of Hydroxyl Radical. For simplicity, we again neglect minor isotopes. Results are summarized in Table IV. The molecular weight of OH is then $m = 17.003$ amu, so $S_{trans} = 144.19 \text{ J mol}^{-1} \text{ K}^{-1}$. Again using the simple RRHO model, the observed bond length is $r_e = 0.96966 \text{ \AA}$ (6) and the symmetry number $\sigma = 1$ ($C_{\infty v}$ point

group). Hence $I = 1.480 \times 10^{-47}$ kg m² and $S_{rot} = 28.22$ J mol⁻¹ K⁻¹. Using the observed vibrational fundamental for the vibrational frequency, $\nu = \omega_0 = 3568$ cm⁻¹ (6) leads to $S_{vib} = 5.04 \times 10^{-6}$ J mol⁻¹ K⁻¹. If spin-orbit splitting is ignored, $Q_{elec} = 4$ as explained above, so $S_{elec} = 11.53$ J mol⁻¹ K⁻¹. Combining these four contributions yields $S = 183.9$ J mol⁻¹ K⁻¹. If instead the spin-orbit splitting is included, so that $g_0 = g_1 = 2$ and $\epsilon_1 = 139.2$ cm⁻¹ = 2.765×10^{-21} J, then equation 30 yields $S_{elec} = 11.08$ J mol⁻¹ K⁻¹ and so the total $S = 183.5$ J mol⁻¹ K⁻¹. The literature value is 183.71 ± 0.04 J mol⁻¹ K⁻¹ (1).

Table IV. Methyl and Hydroxyl Examples, S°_{298} , J/(mol·K)

<i>Contribution</i>	<i>Methyl</i>	<i>Hydroxyl^a</i>	<i>Hydroxyl^b</i>
Translation	142.65	144.19	144.19
Rotation	43.50	28.22	28.22
Vibration	1.99	5×10^{-6}	5×10^{-6}
Electronic	5.76	11.53	11.08
<i>Total</i>	<i>193.9</i>	<i>183.9</i>	<i>183.5</i>

^aSpin-orbit splitting ignored. ^bSpin-orbit splitting included.

Internal Rotation. This refers to torsional motion, most commonly involving methyl groups. There are three ways to treat such a rotor, depending upon its barrier to rotation. The free and hindered rotor models require that an internal symmetry number, σ_{int} , be included. σ_{int} equals the number of minima (or maxima) in the torsional potential energy curve. The harmonic oscillator model does not require σ_{int} because it ignores all but one of the energy minima. For intermediate barrier heights (hindered rotor), the appropriateness of an internal symmetry number may be confusing. In such cases, avoid over- or under-counting states by ensuring that the limiting case of infinite barriers (harmonic oscillator model, no σ_{int}) moves smoothly into the limiting case of zero barrier (free rotor model, σ_{int} needed) as the barrier height decreases. Note that the vibrational frequency corresponding to the torsion must be deleted if the torsion is treated as a free or hindered rotation.

Free Rotor. If the barrier to rotation is much less than kT , then the rotor may be considered freely rotating. For a symmetric rotor such as a methyl group, the partition function is given by equation 33, where I_{int} is the reduced moment of inertia for the internal rotation and is given by equation 34 (3). Asymmetric rotors can be treated using

$$Q_{free\ rotor} = (\sigma_{int} h)^{-1} (8\pi^3 I_{int} kT)^{1/2} \quad (33)$$

$$I_{int} = I_{top} - I_{top}^2 \left(\frac{\alpha^2}{I_A} + \frac{\beta^2}{I_B} + \frac{\gamma^2}{I_C} \right) \quad (34)$$

an appropriate formula for the reduced moment (3). In equation 34, I_{top} is the moment of inertia of the rotating fragment about the axis of internal rotation. This is expressed as $I_{top} = \sum m_i r_i^2$, where the m_i are atomic masses, r_i is the distance of atom i from the axis of internal rotation, and the sum runs over all atoms in the rotating fragment. The quantities α , β , and γ are the cosines of the angles formed between the internal rotation axis and the principal axes of the overall molecule that correspond to I_A , I_B , and I_C , respectively. Contributions to the thermodynamic functions are given in equations 35-37.

$$S_{free\ rotor} = R[(1/2) \ln(8\pi^3 I_{int} kT) - \ln(\sigma_{int} h) + (1/2)] \quad (35)$$

$$C_{p, free\ rotor} = (1/2) R \quad (36)$$

$$[H(T) - H(0)]_{free\ rotor} = (1/2) RT \quad (37)$$

Harmonic Oscillator. If the barrier to internal rotation is much greater than kT , one can consider the torsion to be a non-rotating, harmonic oscillator. Treatment is the same as for other vibrations.

Hindered Rotor. This is the common, intermediate case, when the torsional barrier V is comparable to kT . If the torsional potential is assumed to have the simple form $U(\varphi) = V(1 - \cos \sigma_{int} \varphi)/2$, then the tables of Pitzer and Gwinn are usually used to compute the contribution of the hindered rotor to the thermodynamic functions (16,17). Their tables are in terms of the dimensionless variables x and y , where $x = V/(kT)$ and $y = \sigma_{int} h(8\pi^3 I_{int} kT)^{-1/2}$ and I_{int} is defined as for a free rotor (see above).

Example: Entropy of Ethane at $T = 184$ K [adapted from ref (17)]. Results are summarized in Table V. Ignoring minor isotopes as before, for C_2H_6 we have $m = 30.047$ amu, so $S_{trans} = 141.26$ J mol⁻¹ K⁻¹. The experimental geometry is staggered (D_{3d} point group, $\sigma = 6$) and defined by $r_{CC} = 1.535$ Å, $r_{CH} = 1.094$ Å, and $\theta_{CCH} = 111.2^\circ$ (12-14). If we choose coordinates so that the origin is at the center of mass, the carbon atoms lie on the z -axis, and the yz plane is a reflection plane of symmetry, then the elements of the inertial tensor are, in (amu Å²), $I_{xx} = I_{yy} = 25.46$, $I_{xy} = I_{yx} = I_{xz} = I_{zx} = I_{yz} = I_{zy} = 0$, and $I_{zz} = 6.291$ amu Å². This is already diagonal, with eigenvalues $I_A = 1.045 \times 10^{-46}$ kg m² and $I_B = I_C = 4.228 \times 10^{-46}$ kg m² so that $S_{rot} = 62.17$ J mol⁻¹ K⁻¹ (equation 19). The observed vibrational frequencies (18) are 2954, 1388, 995, 289 (torsion), 2896, and 1379 cm⁻¹ (non-degenerate), and 2969, 1468, 1190, 2985, 1469, and 822 cm⁻¹ (doubly degenerate), for a total of $3N-6 = 18$ vibrational modes and $S_{vib} = 3.36$ J mol⁻¹ K⁻¹ (0.25 J mol⁻¹ K⁻¹ excluding the torsional mode). The total entropy in the RRHO model is thus $S_{184}^\circ = 206.8$ J mol⁻¹ K⁻¹, which is below the experimental value $S = 207.7 \pm 0.6$ J mol⁻¹ K⁻¹ (17).

If we consider the torsion to be a free, unhindered rotor, then we require the corresponding reduced moment of inertia. In this case, in the rotor axis is aligned with the A axis of the molecule, so that $\alpha = 1$ and $\beta = \gamma = 0$ in equation 34. This gives $I_{int} = I_{top} - I_{top}^2/I_A$. The symmetry of this molecule requires that $I_A = 2I_{top}$, because the moment of

inertia of the whole molecule around the A axis (viz., the C-C bond axis) is twice that of a single methyl group. Thus $I_{int} = 2.613 \times 10^{-47} \text{ kg m}^2$. The internal symmetry number is $\sigma_{int} = 3$, since there are three equivalent values of the torsion angle (0° , 120° , and 240°). Equation 35 yields $S_{free\ rotor} = 10.09 \text{ J mol}^{-1} \text{ K}^{-1}$, for a total entropy of $S^\circ_{184} = 213.8 \text{ J mol}^{-1} \text{ K}^{-1}$ in the free-rotor model, which is higher than the experimental value.

To apply the hindered-rotor model we need a value for the torsional barrier height. This can be estimated from the observed torsional vibrational frequency ν (in s^{-1}) as $V \approx 8\pi^2 I_{int} \nu^2 / \sigma_{int}^2 = 1.720 \times 10^{-20} \text{ J}$ (or 10.4 kJ/mol). Thus the parameters are $x = 6.77$ and $y = 0.490$. Interpolating within the standard tables (16,17), $S_{hindered\ rotor} = 3.99 \text{ J mol}^{-1} \text{ K}^{-1}$, so that the total entropy is $S = 207.7 \text{ J mol}^{-1} \text{ K}^{-1}$, in agreement with the experimental value.

Table V. Ethane Example, S°_{184} ($\text{J mol}^{-1} \text{ K}^{-1}$)

<i>Contribution</i>	Harmonic Rotor	Free Rotor	Hindered Rotor
Translation	141.26	141.26	141.26
Rotation	62.17	62.17	62.17
Vibration	0.25	0.25	0.25
Torsion	3.11	10.09	3.99
<i>Total</i>	<i>206.8</i>	<i>213.8</i>	<i>207.7</i>

Charged Molecules: Two Conventions. The balanced chemical equation describing an ionization process involves at least one free electron. There are two major conventions for the thermodynamic properties of the electron. Most compilations of thermochemical data adopt the *thermal electron convention*. In this convention, the free electron is treated as a chemical element, so that its ideal-gas enthalpy of formation is zero at all temperatures. In contrast, most of the literature in mass spectrometry and ion chemistry adopts the *ion convention*, sometimes also called the *stationary electron convention*. In this convention, the enthalpy content of the electron is ignored. At absolute zero temperature there is no difference between the two conventions, but in general enthalpies of formation under the two conventions are related by equation 38, where q is the

$$\Delta_f H^\circ_{thermal\ electron\ convention} = \Delta_f H^\circ_{ion\ convention} + (5/2)qRT \quad (38)$$

(signed) charge on the ion in question (± 1 in most cases). A thorough discussion is provided in the introduction to the *GIANT* tables (19). When reporting the thermochemistry of ions, it is important always to indicate which convention is being used. Especially beware not to combine enthalpies of formation that were derived using different conventions.

Chemical Kinetics

The equilibrium constant for a reaction is $K_{eq} = \exp(-\Delta G/RT)$, where $\Delta G = \Delta H - T\Delta S$ and the differences are between the reactants and products, e.g., $\Delta S = S_{products} - S_{reactants}$. Simple transition-state theory for chemical kinetics assumes that the reaction rate is limited by formation of a transient *transition state*, which is the point of maximum energy along the path from reactants to products. The transition state is considered to be in quasi-equilibrium with the reactants. If differences between reactants and the transition state are denoted with a double dagger, e.g., $\Delta S^\ddagger = S_{TS} - S_{reactants}$, then the rate constant (denoted r here to avoid confusion with the Boltzmann constant) is given by equation 39.

$$r(T) = \frac{kT}{h} \exp\left(-\frac{\Delta G^\ddagger}{RT}\right) \quad (39)$$

As for stable species, $\Delta G^\ddagger = \Delta H^\ddagger - T\Delta S^\ddagger$. Thus rate constants can be calculated easily from the “thermochemistry” for transition states. In such calculations, the imaginary vibrational frequency is ignored, so that there are only $3N-7$ molecular vibrations in the transition structure ($3N-6$ if linear). If all internal and external symmetry numbers are included in the rotational partition functions, then any reaction path degeneracy will usually be included automatically. Occasionally, however, stereochemical factors are also needed (20).

Experimental, temperature-dependent rate constants are often presented as an *Arrhenius plot* of $r(T)$ vs. $1/T$. This is motivated by the observation that such plots are nearly linear, $r(T) = A \exp(-E_a/RT)$, where the pre-exponential factor A is usually called simply the *A-factor* and E_a is the phenomenological *activation energy*. It is often desirable to report A and E_a in computational studies, for comparison with the values derived from experimental data. They may be determined using equations 40 and 41,

$$E_a = RT^2 \frac{\partial}{\partial T}(\ln r) = \Delta H^\ddagger + MRT \quad (40)$$

$$A = r(T) \exp(+E_a/RT) \quad (41)$$

where M is the molecularity of the reaction (e.g., $M = 1$ for a unimolecular and $M = 2$ for a bimolecular reaction). The derived A and E_a are weakly temperature-dependent. This is consistent with experimental results, which are often fitted using the three-parameter modified Arrhenius expression $r(T) = A' T^n \exp(-E_a'/RT)$. This functional form leads to a better fit than the ordinary Arrhenius expression, but the parameters may have little physical interpretation. If the RRHO approximation is accepted, then the three parameters are given by equations 42-44, where the y_i in equation 42 are the reduced vibrational frequencies, $y_i = h\nu_i/kT$. However, in practice it is often best to determine the parameters A' , n , and E_a' by fitting calculated rate constants to the modified Arrhenius expression.

$$n = 1 + \sum_{\text{TS}} \frac{y_i^\ddagger e^{-y_i^\ddagger} (1 + e^{-y_i^\ddagger})}{(1 - e^{-y_i^\ddagger})^2} - \sum_{\text{reactants}} \frac{y_i e^{-y_i} (1 + e^{-y_i})}{(1 - e^{-y_i})^2} \quad (42)$$

$$E_a' = RT^2 \frac{\partial}{\partial T} (\ln r) - nRT = \Delta H^\ddagger + (M - n)RT \quad (43)$$

$$A' = r(T) T^{-n} \exp(+E_a'/RT) \quad (44)$$

Ab initio energies are now precise enough that it is becoming common to use kinetic theories more sophisticated than simple transition-state theory. When the reaction coordinate is dominated by motion of a hydrogen atom, corrections for quantum-mechanical tunneling are often made (21). The simplest is the Wigner correction, which requires only the imaginary vibrational frequency $\nu^\ddagger i$ associated with the reaction coordinate. To apply this correction, the calculated rate is multiplied by F_{tunnel} (equation 45). Better results may be obtained by fitting the energy profile of the reaction to an

$$F_{\text{tunnel}} = 1 + \frac{1}{24} (h\nu^\ddagger/kT)^2 \quad (45)$$

Eckart potential function (see the chapter by Petersson in this book). The location of the transition state can also be refined. Variational transition-state theory defines the transition state as the maximum in the free energy along the reaction path, instead of the maximum along the vibrationless potential energy curve. Such a definition is essential for reactions such as simple bond cleavage, which usually has no barrier in excess of the bond energy.

Units and Constants

In actual calculations, many practical difficulties involve incompatible units. In addition to the standard units of the SI, many others are in use, usually for historical reasons. Conversion factors among selected units are provided in Table VI. For convenience, the values of commonly-used constants are collected in Table VII. Detailed information is available on-line at <http://www.physics.nist.gov/PhysRefData/contents.html#SI>.

Table VI. Unit Conversions

<i>Quantity</i>	<i>Unit</i>	<i>Conversion^a</i>	<i>SI Unit</i>
energy	hartree (atomic unit)	2 625.500	kJ/mol
energy	cal	4.184	J
energy	cm ⁻¹ (wavenumber)	0.011 962 66	kJ/mol
energy	eV	96.485 31	kJ/mol
energy	K (temperature)	$8.314 511 \times 10^{-3}$	kJ/mol
distance	Å	10^{-10}	m
distance	bohr (atomic unit)	$5.291 772 \times 10^{-11}$	m
mass	amu <i>or</i> u	$1.660 540 \times 10^{-27}$	kg
pressure	bar	10^5	Pa
pressure	atm	101 325	Pa
pressure	Torr <i>or</i> mm-Hg	133.322 37	Pa
pressure (density)	cm ⁻³ (at 298.15 K; ideal gas)	$4.166 43 \times 10^{-15}$	Pa
pressure (density)	cm ⁻³ (arb. temp.; ideal gas)	$10^6 kT$	Pa
pressure (density)	M <i>or</i> mol/L (ideal gas)	$10^3 RT$	Pa
dipole moment	atomic unit	$8.478 358 \times 10^{-30}$	C·m
dipole moment	D (debye)	$3.335 641 \times 10^{-30}$	C·m

^aMultiply the quantity expressed in the units of column 2 by the conversion factor in column 3 to obtain the quantity expressed in units of column 4 (SI units).

Table VII. Physical Constants

<i>Quantity</i>	<i>Value</i>
k	$1.380 66 \times 10^{-23} \text{ J K}^{-1}$
N_A	$6.022 137 \times 10^{23} \text{ mol}^{-1}$
$R = kN_A$	$8.314 510 \text{ J mol}^{-1} \text{ K}^{-1}$
h	$6.626 076 \times 10^{-34} \text{ J s}$
c	$299 792 458 \text{ m s}^{-1}$

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