Appendix A
Statistical Weights and Statistical Sums

Assuming that the internal and translational motions of particles are independent, the expression for the total statistical sum referred to a volume of $1\,\text{cm}^3$, is written down as the product

$$Q = Q_{tr}Q_{in}, \tag{A.1}$$

where Q_{tr} is responsible for the motion of the mass centers of the particles. It is well known from statistical mechanics that

$$Q_{tr} = \left(\frac{2\pi Mk_BT}{h^2}\right), \tag{A.2}$$

where h and k_B are the Planck and Boltzmann constants, M is the particle mass and T is the kinetic temperature. The main problem is usually to find the internal statistical sum Q_{in}, defined by expression (1.7). Generally speaking, this requires direct summation, which is extremely difficult to do in a multilevel energy structure. A helpful simplification can be attained by using expressions (1.6) and (1.8), but in this case it is also necessary to know the statistical weights and the positions of the levels involved.

A.1
Statistical Weight of Energy Levels in Atoms and Ions

For atoms and atomic ions, the statistical weight g_l determining the level degeneration depends on the quantum numbers L, S and J, the total orbital momentum, total spin and total electron momentum:

$$g_l = (2L+1)(2S+1) \quad \text{for the } L-S \text{ term,}$$
$$g_l = 2J+1 \quad \text{for the } J \text{ level.}$$

A.2
Statistical Weight of Electronic States in Molecules

The statistical weights of various electronic states in molecules are also determined by the type of the states (for the nomenclature of the states with the symbol $^{2S+1}\Lambda$, see [1–3] and Appendix D). For diatomic and linear polyatomic molecules, the quantity g_l allows for the spin splitting into $2S + 1$ components and additional splitting into two components in the states whose quantum number of the electronic momentum projection on the internuclear axis is $\Lambda > 1$ (Λ-doubling [1–3]), see Table A.1.

Table A.1 Statistical weights of diatomic and linear polyatomic molecules [1–3].

e	$^1\Sigma$	$^2\Sigma$	$^3\Sigma$	$^1\Pi$	$^2\Pi$	$^3\Pi$	$^1\Delta$	$^2\Delta$
g_e	1	2	3	2	4	6	2	4

For nonlinear polyatomic molecules, see Table A.2.

Table A.2 Statistical weights of nonlinear polyatomic molecules [1–3].

e	$^1A_1$	$^2A_1$	$^3A_1$	$^1A_2$	$^2A_2$	$^3A_2$	$^1B_1$	$^2B_1$	$^3B_1$
g_e	1	2	3	1	2	3	1	2	3

A.3
Statistical Weight of Vibrational Levels of Molecules

In all diatomic and some polyatomic molecules, the vibrational levels v of their electronic states are not degenerate, and so $g_v = 1$.

In some polyatomic molecules, depending on their symmetry, some vibrations can be degenerate. If a molecule has l degenerate vibrations, the number of normal vibrations differing in frequency will then be, for linear molecules with N_a atoms,

$$n_v = 3N_a - 5 - l , \tag{A.3}$$

and for nonlinear molecules,

$$n_v = 3N_a - 6 - \sum_{n=1}^{n=l} (d_n - 1) , \tag{A.4}$$

where d_n is the degeneracy multiplicity of the normal vibration. When $d_n = 1$, the vibration and its associated levels are not degenerate. The

statistical weight of any vibrational level v of a diatomic harmonic oscillator is $g_v = 1$. The statistical weight of the vibrational levels of the nth doubly degenerate vibration of a polyatomic molecule (which is also attributed the sense of an individual oscillator) is $g_{v_n} = v_n + 1$, and for a triply degenerate vibration, $g_{v_n} = (v_n + 1)(v_n + 2)/2$. The total statistical weight of the vibrational state $\{v_1 v_2 v_3 \dots\}$ of a polyatomic molecule is

$$g_{\{v_1 v_2 v_3 \dots\}} = \prod_{n=1}^{n=n_v} \frac{(v_n + d_n - 1)!}{v_n!(d_n - 1)!}. \tag{A.5}$$

The quantity d_n is determined by the affiliation of the molecule to a certain point symmetry group and its electronic state. These data for concrete molecules can be found in [2–4, 7]. Table A.3 lists selected data on the normal vibration frequencies of simple 3- to 5-atom molecules. The d_n values other than 1 are indicated in parentheses next to the vibration frequency values (in cm^{-1}).

Table A.3 Frequencies and multiplicity of normal molecular vibrations.

	CO_2	CS_2	OCS	C_2O	CH_2	CH_3	CF_3	CF_4	C_2N_2	SiO_2	SiH_3
$v1$	1333	664	863	1978	3000	3000	1090	908	2330	960	1955
$v2$	667(2)	395(2)	520(2)	379(2)	1362	607	701	435(2)	845	380(2)	996
$v3$	2350	1535	2055	1074	3200	3162(2)	1259(2)	1282(3)	215	1350	1999(2)
$v4$						1398(2)	512(2)	632(3)	502(2)		925(2)

	SnO_2	BH_3	AlO_2	GaOH	InOH	Be_2O	MgF_2	CaOH	CrO_3	Na_2O	CsOH
$v1$	745	2623	1096	600	520	620	540	570	800	320	336
$v2$	230(2)	1125	496	310(2)	300(2)	320(2)	165(2)	305(2)	400	60(2)	306(2)
$v3$	864	2808(2)	550	3600	3600	1200	800	3700	980(2)	600	3705
$v4$		1605(2)							350(2)		

A.4
Statistical Weight of Rotational Levels of Molecules

Let us fix the electronic and the vibrational state of a molecule. Its energy structure in that case is determined by the rotational structure of its terms. To calculate the statistical weight g_J of a rotational level with the moment of momentum quantum number J, one should take into consideration the presence of the intrinsic spin in the nuclei of the atoms constituting the molecule:

$$g_J = g_n(2J + 1). \tag{A.6}$$

Here g_n is the statistical weight of the nuclei. For polyatomic and heteronuclear diatomic molecules,

$$g_n = \frac{1}{\sigma} \prod_{n=1}^{N_a} (2I_n + 1), \tag{A.7}$$

where I_n is the nuclear spin of the nth atom, N_a is the number of atoms in the molecule and σ is the so-called symmetry number. For heteronuclear diatomic molecules, the quantity σ depends on the affinity of the molecule in the fixed electronic state to a certain point symmetry group (see Table A.4).

Table A.4 Symmetry numbers and groups.

σ	Symmetry group	σ	Symmetry group
1	$C_1, C_i, C_s, C_{\infty v}$	6	$C_6, C_{6v}, C_{6h}, D_3(=S_{6v}), D_{3h}$
2	$C_2, C_{2v}, C_{2h}, D_{\infty h}$	8	$D_4, D_{4d}(=S_{8v}), D_{4h}$
3	C_3, C_{3v}, C_{3h}, S_6	12	$D_6, D_{6d}, D_{6h}, T, T_d$
4	$C_4, C_{4v}, C_{4h}, D_2(=V), D_{2d}, D_{2h}(=V_h)$	24	O_h
5	C_5, C_{5v}, C_{5h}		

Table A.5 gives examples of assigning some simple molecules in the electronic ground states to the numbers σ indicated in Table A.4.

Table A.5 Symmetry numbers for some molecules.

$\sigma = 1$	All diatomic heteronuclear molecules and also HDO, HCO, HNO, HO$_2$, FCO, ClCO, ClCN, HCN, FCN, NCO, COS, CHF, CHCl, CFCl, HBO, HFCO, FBO, HBO$_2$, HDO$_2$, N$_2$O, S$_2$O, HOCl, NOCl, N$_3$H NHFCO, FClCO, SOF$_2$, N$_2$H$_4$, C$_2$H$_3^*$, C$_2$HF, CH$_2$F, CHF$_2$, CHFClBr, ClBrHC$-$CHBrCl, HC$_2$Cl, SiC$_2$, CX$_2$YZ(X$_{YZ}$=H$_{FC}$l$_B$r · I), CXYZV(X$_{YZV}$=H$_{FC}$l$_B$r$_I$), C$_2$X(X=F$_C$l$_O$), C$_2$X$_3$Y(X$_Y$=H$_{FC}$l), GeX$_2$(X=O$_{FC}$l$_S$)
$\sigma = 2$	All homonuclear diatomic molecules and also Al$_2$O, AlO$_2$, AlF$_2$, AlCl$_2$, Li$_2$O, C$_3$O$_2$, H$_2$O, D$_2$O, F$_2$O, ClO$_2$, Cl$_2$O, SO$_2$, H$_2$S, SF$_2$, BeF$_2$, BeCl$_2$, NO$_2$, H$_2$CO, F$_2$CO, Cl$_2$CO, SF$_4$, CH$_2$Cl$_2$, SO$_2$F$_2$, C$_6$H$_2$Cl$_2$Br$_2$, SiX$_2$(X=O$_{FC}$l), Si$_2$C, BX$_2$(X=O$_C$l$_F$), B$_2$O$_2$, B$_2$O$_3$, MgF$_2$, MgCl$_2$, CX$_2$Y$_2$(X$_Y$=H$_{FC}$l$_B$r$_I$), C$_2$X$_2$(X=H$_{FN}$), LiOH, ZrO$_2$, PbF$_2$, N$_3$, NF$_2$, PF$_2$, H$_2$O$_2$, D$_2$O$_2$, N$_2$H$_4^*$, CX$_2$(X=H$_{FC}$l$_B$r$_{IOS}$), C$_3$C$_2$X$_2$Y$_2$(X$_Y$=H$_{FC}$l), SnX$_2$(X=F$_C$l$_{OS}$), PbX$_2$(X=F$_C$l$_{OS}$)
$\sigma = 3$	NH$_3$, NF$_3$, POF$_3$, POCl$_3$, CX$_3$(X=H$_{FC}$l$_I$), CX$_3$Y(X$_Y$=H$_{FC}$l$_B$r$_I$), CH$_3$CCl$_3^*$, SiX$_3$(X=H$_{FC}$l$_B$r), H$_3$BO$_3^*$,
$\sigma = 4$	Al$_2$O$_2$, BCl$_4$, Li$_2$F$_2$, Li$_2$Cl$_2$, Na$_2$Cl$_2$, PtCl$_4^-$, C$_2$H$_4$, O$_4$, N$_2$O$_4$, C$_3$H$_6$, C$_2$X$_4$(X=H$_{FC}$l)
$\sigma = 6$	AlX$_3$(X=H$_{FC}$l), C$_2$H$_6^*$, BF$_3$, BCl$_3$, GaF$_3$, InF$_3$, SO$_3$, PF$_5$, PCl$_5$, C$_6$H$_3$Cl$_3$, H$_3^+$
$\sigma = 8$	S$_8$, C$_4$H$_8$, Be$_4$O$_4$
$\sigma = 12$	C$_6$H$_6$, C$_6$Cl$_6$, P$_4$, CX$_4$(X=H$_{FC}$l$_B$r), P$_4$O$_6$, C(CH$_3$)$_4^*$, SiX$_4$(X=H$_F$ · Cl · Br · I), BF$_4^-$
$\sigma = 24$	SF$_6$, PtCl$_6^-$

The asterix * indicates molecules possessing internal rotation (see below). Identical atoms in molecules are understood to be isotopically equivalent.

Homonuclear diatomic molecules, each of whose atoms has a spin of I_n, have two sequences of statistical weights for rotational levels with J values differing in parity. They are defined, as before, by expression (A.6), but with different nuclear statistical weights g_n:

$$g_{n1} = I_n(2I_n + 1), \tag{A.8}$$
$$g_{n2} = (I_n + 1)(2I_n + 1). \tag{A.9}$$

The decision on which of the above formulas (A.8) or (A.9) should be substituted into formula (A.6) for different (in the parity of J) rotational levels is made with the aid of Table A.6.

Table A.6 To the calculation of the statistical weights of rotational levels in homonuclear molecules

Electronic state indices	+	−	−	+
	g	u	g	u
Nuclear spin	integral	half-integral	integral	half-integral
For even J	g_{n_1}	g_{n_2}	g_{n_2}	g_{n_1}
For odd J	g_{n_2}	g_{n_1}	g_{n_1}	g_{n_2}

Let us recall the meaning of the standard indices used in spectroscopy [1–4, 7] to reflect the properties of the wave function with respect to various symmetry operations. They indicate whether the wave function maintains or changes sign on reflection in the plane containing the molecular axis $(+, -)$ or on the change of sign of the coordinates of the electrons (g, u). It is appropriate to note here that one and the same symbol, g, is generally used to denote both the statistical weight and the result of a symmetry operation. However, no confusion usually occurs, for the attribute relating to symmetry is indicated as an index in the designation of the term. The symbols s and a, respectively, show whether or not the wave function changes sign on the permutation of nuclei. To denote the electronic states of molecules with zero projection of the orbital moment of the electrons on the internuclear axis, $\Lambda = 0$, the indices g, u, $+$ and $-$ (if any) are denoted directly on the symbol Σ. For example, $^1\Sigma_g^+, {}^2\Sigma_g^-, {}^3\Sigma_u^-$, and so on. If $\Lambda \neq 0$ ($\Pi, \Delta,\ldots$, states) and the Λ-doubling takes place, for each number J of a split rotational level there exist different sets of indices g, u, $+$ and $-$. By virtue of this fact, as J is successively changed, the upper and lower components of Λ-doublets change their statistical weight from g_{n_1} to g_{n_2} and vice versa as successively. This can be illustrated by Table A.7 which indicates comparative symmetry prop-

Table A.7 Symmetry of rotational levels of Σ-Π-states.

Dissimilar nuclei				Similar nuclei			
$J =$	0	1	2	3	$J =$	0	1	2	3
Σ^+	$+$	$-$	$+$	$-$	Σ_g^+	$(+,s)$	$(-,a)$	$(+,s)$	$(-,a)$
Σ^-	$-$	$+$	$-$	$+$	Σ_u^+	$(+,a)$	$(-,s)$	$(+,a)$	$(-,s)$
Π		$(+,-)$	$(-,+)$	$(+,-)$	Π_g		$(+,s)$	$(-,a)$	$(+,s)$
							$(-,a)$	$(+,s)$	$(-,a)$
					Π_u		$(+,a)$	$(-,s)$	$(+,a)$
							$(-,s)$	$(+,a)$	$(-,s)$

erties of the rotational levels of hetero- and homonuclear molecules in the Σ ($\Lambda = 0$) and Π ($\Lambda = 1$) states (for the Π state, $J \geq 1$).

Specifically, one can see from formulas (A.6), (A.8), and (A.9) and Table A.7 that in homonuclear molecules every second rotational level is missing.

A.4.1
Statistical Sum of Atoms and Ions

In that case, the sum over internal states is the sum over the electronic states of the particles, (1.7) or (1.8) at equilibrium. The values of the statistical weights are given by relations (A.1) and (A.2). The practical problem is to limit the number of the electronic states to be considered. The limiting factor in plasma is the interaction of the charged particles. As stated in Section 1.1, the Debye interaction energy of electrons is e^2/r_D, and atoms in the states of lower binding energy become spontaneously ionized. This effect is called the reduction of the ionization potential in plasma. To illustrate, for the hydrogen atom in plasma with an electron concentration of n_e ca. $10^{15}\,\mathrm{cm}^{-3}$ and a thermal particle energy of $k_B T = 1.600 \times 10^{-19}\,\mathrm{J}(1\,\mathrm{eV})$ ($T = 11605\,\mathrm{K}$), the ultimate value of the principal quantum number $n = 47$.

Use is also made of a much cruder approximation, provided that the temperature of plasma (only at equilibrium) is below the potential of the first excited state. This condition is generally satisfied in practice, especially for ions, and the statistical sum then can be replaced, in accordance with expression (1.6), by the statistical weight of the ground state.

A.4.2
Statistical Sum of Molecules

If the assumption, made in elucidating formula (A.1), that the different types of motion of particles are independent is extended to their internal degrees of freedom, the expression for the internal statistical sum of a

molecule will then assume its most frequently used form

$$Q_{in} = Q_e Q_v Q_r \, , \tag{A.10}$$

where Q_e, Q_v and Q_r are the electronic, vibrational and rotational statistical sums of the molecule.

The electronic statistical sum Q_e is found by analogy with atoms.

The vibrational statistical sum is calculated most often, and with an accuracy acceptable for the problems of low-temperature plasma spectroscopy, using the harmonic oscillator approximation.

For diatomic molecules, direct summation by formula (1.8), with due regard for the equidistance of vibrational energy levels, $\Delta E_{v_0} = vv$ (here, instead of k, use is made of the generally accepted symbol v to denote the serial number f the vibrational level and v is the oscillator frequency), and with infinite upper limit, yields

$$Q_v = \left[1 - \exp\left\{-hcv/k_B T\right\}\right]^{-1}, \tag{A.11}$$

the dimensions being as follows: $h[\mathrm{erg \cdot s}]$, $v[\mathrm{cm}^{-1}]$, $c[\mathrm{cms}^{-1}]$, $T[\mathrm{deg, K}]$, $k_B[\mathrm{erg/deg}]$, $hc/k_B = 1.44$.

The vibrations of a polyatomic molecule are described in the same harmonic oscillator approximation by a set of harmonic oscillators of normal vibration frequencies v_n. Summation by formula (1.8) extended over a finite number of types of normal vibration yields, with consideration for degeneracy and statistical weights (A.5), [2, 4]

$$Q_v = \prod_{n=1}^{n_v'} (1 - Z_n)^{-d_n} \, , \quad Z_n = \exp\left\{-hcv_n/k_B T\right\} . \tag{A.12}$$

When calculating the rotational statistical sum by formula (1.8) with the above-indicated statistical weights, use is most frequently made of the rigid rotator model. For diatomic molecules,

$$Q_r = \frac{1}{\sigma} \frac{k_B T}{hc B_v}, \tag{A.13}$$

where B_v is the rotational constant and $\sigma = 1$ for heteronuclear molecules and $\sigma = 2$ for homonuclear ones. For polyatomic molecules,

$$Q_r = \sqrt{\frac{\pi}{A_v B_v C_v} \left(\frac{k_B T}{hc}\right)^3}, \tag{A.14}$$

where A_v, B_v, and C_v are rotational constants, not equal to one another, in asymmetric top molecules. In symmetric top molecules, two of these constants coincide. To determine σ, one should use Table A.4.

Note in conclusion, that the use of the harmonic oscillator and rigid rotator approximations to calculate the appropriate statistical sums provides for small vibration amplitudes of molecules and their small stretching, compared to the internuclear separation, under the action of centrifugal forces. Experience shows that such approximations prove quite satisfactory for molecules with a small number (2–5) of atoms and relatively not very high excitation (heating) level. An important example of violation of these conditions is the class of molecules with internal rotations or torsional vibrations.

If the potential barrier preventing the free internal rotation of molecular fragments is high enough, in comparison with the excitation energy (temperature at equilibrium), this corresponds to the case of torsional vibrations, and these can be treated as an additional vibrational degree of freedom in the general scheme and so be properly included in the vibrational statistical sum. If the barrier can be overcome, so that free internal rotation can take place, this motion should then be considered a rotational rather than vibrational degree of freedom and allowed for in the rotational statistical sum. What is more, the symmetry numbers σ will in that case change in comparison with those listed in Table A.4. These questions are considered in [2, 4]. We will restrict ourselves here to some examples of individual molecules. Table A.8 lists the values (in kelvins) of the potential barriers V_{CH_3} and V_{OH} preventing the internal rotation of the CH_3 and OH groups.

Direct calculations show (e.g. [7]) that failure to allow for the internal rotation in C_2H_6 at 300 K results in the reduction of the internal statistical sum Q_{in} by ca. 40 %, and at 1000 K, by a factor of ca. 3.5.

Table A.8 Potential barriers for internal rotation.

Molecule	C_2H_2	CH_3CF_3	CH_3CH_2OH	$CH_3CHOHCH_3$	HNO_3
V_{CH_3}, K	1460	1740	1510	1710	
V_{OH}, K			5030	2520	3520

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