CHAPTER 8
BOLTZMANN'S AND SAHA'S EQUATIONS

8.1 *Introduction*

A measurement of the strength of a spectrum line can in principle enable us to determine the number of atoms *in the initial level of the transition* that produces it. For an emission line, that initial level is the upper level of the transition; for an absorption line it is the lower level. In order to determine the total number of atoms (in all energy levels) in the source, it is necessary to know, in addition to the number of atoms in a particular level, how the atoms are distributed, or partitioned, among their numerous energy levels. This is what Boltzmann's equation is concerned with. But even this will tell us only how many atoms there are in a particular ionization stage. If we are to determine the total abundance of a given element, we must also know how the atoms are distributed among their several ionization stages. This is what Saha's equation is concerned with.

8.2 *Stirling's Approximation. Lagrangian Multipliers.*

In the derivation of Boltzmann's equation, we shall have occasion to make use of a result in mathematics known as Stirling's approximation for the factorial of a very large number, and we shall also need to make use of a mathematical device known as Lagrangian multipliers. These two mathematical topics are described in this section.

8.2i *Stirling's Approximation.*

Stirling's approximation is

$$\ln N! \cong N \ln N - N. \qquad 8.2.1$$

Its derivation is not always given in discussions of Boltzmann's equation, and I therefore offer one here.

The gamma function is defined as

$$\Gamma(x+1) = \int_0^\infty t^x e^{-t} dt \qquad 8.2.2$$

or, what amounts to the same thing,

$$\Gamma(x) = \int_0^\infty t^{x-1} e^{-t} dt. \qquad 8.2.3$$

In either case it is easy to derive, by integration by parts, the recursion formula

$$\Gamma(x+1) = x\Gamma(x). \qquad 8.2.4$$

If x is a positive integer, N, this amounts to

$$\Gamma(N+1) = N!. \qquad 8.2.5$$

I shall start from equation 8.2.2. It is easy to show, by differentiation with respect to t, that the integrand $t^x e^{-t}$ has a maximum value of $(x/e)^x$ where $t = x$. I am therefore going to divide both sides of the equation by this maximum value, so that the new integrand is a function that has a maximum value of 1 where $t = x$:

$$\left(\tfrac{e}{x}\right)^x \Gamma(x+1) = \int_0^\infty \left(\tfrac{t}{x}\right)^x e^{-(t-x)} dt. \qquad 8.2.6$$

Now make a small change of variable. Let $s = t - x$, so that

$$\left(\tfrac{e}{x}\right)^x \Gamma(x+1) = \int_{-x}^\infty \left(1+\tfrac{s}{x}\right)^x e^{-s} ds = \int_{-x}^\infty f(s) ds. \qquad 8.2.7$$

Bearing in mind that we aim to obtain an approximation for large values of x, let us try to obtain an expansion of $f(s)$ as a series in s/x. A convenient way of obtaining this is to take the logarithm of the integrand:

$$\ln f(s) = x \ln\left(1+\tfrac{s}{x}\right) - s, \qquad 8.2.8$$

and. provided that $|s| < x$, the Maclaurin expansion is

$$\ln f(s) = x\left(\tfrac{s}{x} - \tfrac{1}{2}\cdot\left(\tfrac{s}{x}\right)^2 + \ldots\right) - s. \qquad 8.2.9$$

If x is sufficiently large, this becomes

$$\ln f(s) = -\frac{s^2}{2x}, \qquad 8.2.10$$

so that

$$\left(\tfrac{e}{x}\right)^x \Gamma(x+1) = \int_{-\infty}^\infty \exp\left(-\frac{s^2}{2x}\right) ds. \qquad 8.2.11$$

While this integral is not particularly easy, it is at least well known (it occurs in the theory of the gaussian distribution, for example), and its value is $\sqrt{2\pi x}$. Thus we have, for large x,

$$\Gamma(x+1) = \left(\tfrac{x}{e}\right)^x \sqrt{2\pi x}, \qquad 8.2.12$$

or, if x is an integer,

$$N! = \left(\tfrac{N}{e}\right)^N \sqrt{2\pi N}. \qquad 8.2.13$$

On taking logarithms of both sides, we obtain

$$\ln N! = \left(N + \tfrac{1}{2}\right)\ln N - N + \ln\sqrt{2\pi}, \qquad 8.2.14$$

or, since N is large:

$$\ln N! \cong N \ln N - N. \qquad 8.2.15$$

For very large N (i.e. if $\ln N >> 1$), we can make the further approximation

$$\ln N! = N \ln N \qquad 8.2.16$$

or

$$\log N! = N \log N. \qquad 8.2.17$$

Any of equations 8.2.12 - 17 may be referred to as Stirling's approximation.

The largest value of N for which my hand calculator will return $N!$ is 69. For this, it gives

$$\ln N! = 226.2, \qquad N \ln N - N = 223.2.$$

For very large numbers, the approximation will be much better. The extreme approximation represented by equations 8.2.16 or 8.2.17, however, becomes reasonable only for unreasonably large numbers, such as the number of protons in the Universe. We shall be making use of the much better approximation equation 8.2.15, which does not require such unimaginably huge numbers.

For smaller numbers that we commonly deal with in spectroscopy (where we are typically dealing with the number of atoms in a sample of gas) the following approximation is remarkably good:

$$\ln N! = \left(N + \tfrac{1}{2}\right)\ln N - N + \frac{1}{12N} + \ln\sqrt{2\pi}. \qquad 8.2.18$$

This almost the same as equation 8.2.14, except that, in deriving it, I have taken to expansion of equation 8.2.9 to one more term. Thus, to eight significant figures, 20! = 2.432 902 0 × 10^{18}, while equation 8.2.18 results in 2.432 902 9 × 10^{18}.

8.2ii *Lagrangian Multipliers.*

This topic concerns the problem of determining where a function of several variables is a maximum (or a minimum) where the variables are not independent but are connected by one or more functional relations.

Let $\psi = \psi(x, y, z)$ be some function of x, y and z. Then, if x, y and z are independent variables, one would ordinarily understand that, where ψ is a maximum, the derivatives are zero:

$$\frac{\partial\psi}{\partial x} = \frac{\partial\psi}{\partial y} = \frac{\partial\psi}{\partial z} = 0. \qquad 8.2.19$$

However, if x, y and z are not completely independent, but are related by some constraining equation such as $f(x, y, z) = 0$, the situation is slightly less simple. An example from thermodynamics comes to mind. Entropy, S, is a function of state: $S = S(P, V, T)$. However, for a particular substance, P, V and T are related by an *equation of state*. In effect, we cannot determine S for the system at any point in P, V, T space, but we are restricted to explore only on the two-dimensional surface represented by the equation of state.

We return now to our function ψ. If we move by infinitesimal displacements dx, dy, dz from a point where ψ is a maximum, the corresponding changes in both ψ and f will be zero, and therefore both of the following equations must be satisfied:

$$d\psi = \frac{\partial\psi}{\partial x}dx + \frac{\partial\psi}{\partial y}dy + \frac{\partial\psi}{\partial z}dz = 0, \qquad 8.2.20$$

$$df = \frac{\partial f}{\partial x}dx + \frac{\partial f}{\partial y}dy + \frac{\partial f}{\partial z}dz = 0. \qquad 8.2.21$$

Consequently any linear combination of ψ and f, such as $\phi = \psi + \lambda f$, where λ is an arbitrary constant, also satisfies a similar equation. The constant λ is sometimes called an "undetermined multiplier" or a "Lagrangian multiplier", although often some additional information in an actual problem enables the constant to be identified - and we shall see an example of this in the derivation of Boltzmann's equation.

In summary, the conditions that ψ is a maximum if x, y and z are related by a functional constraint $f(x, y, z) = 0$ are

$$\frac{\partial\phi}{\partial x} = 0, \quad \frac{\partial\phi}{\partial y} = 0, \quad \frac{\partial\phi}{\partial z} = 0, \qquad 8.2.22$$

where $\phi = \psi + \lambda f$.

Of course, if ψ is a function of many variables x_1, x_2…, not just three, and the variables are subject to several constraints, such as $f = 0$, $g = 0$, $h = 0$…, etc., where f, g, h, etc., are functions connecting all or some of the variables, the conditions for ψ to be a maximum (or minimum) are

$$\frac{\partial \psi}{\partial x_i} + \lambda \frac{\partial f}{\partial x_i} + \mu \frac{\partial g}{\partial x_i} + \nu \frac{\partial h}{\partial x_i} + \ldots = 0, \qquad i = 1, 2, 3, \ldots \tag{8.2.23}$$

8.3 *Some Thermodynamics and Statistical Mechanics*

Besides needing to know Stirling's approximation and the method of Lagrangian multipliers, before we can embark upon Boltzmann's equation we also need to remind ourselves of two small results from thermodynamics and statistical mechanics. I mention these only briefly here, with barely adequate explanations. Fuller treatments are given in courses or books on thermodynamics and statistical mechanics. If you are rusty on these topics, or perhaps have never studied them thoroughly, the only consequence is that you may not be able fully to understand the derivation of Boltzmann's equation. This will not matter a great deal and should not deter you from reading subsequent sections. It is more important to understand what Boltzmann's equation means and how to apply it, and this can be done even if you have missed some of the details of its derivation.

Most readers will either understand this section very well and will not need prolonged explanation, or will not understand it at all, and will be happy to skip over it. Therefore, for brevity's sake, I do little more than quote the results, and I do not even explain what many of the symbols mean.

Those who *are* familiar with thermodynamics will have no difficulty in recalling

$$dU = TdS - PdV. \tag{8.3.1}$$

The result that we shall be needing in section 8.4 is $(\partial U/\partial S)_V = T,$ or more likely its reciprocal:

$$\left(\frac{\partial S}{\partial U}\right)_V = \frac{1}{T} \quad . \tag{8.3.2}$$

The relation we need from statistical mechanics is Boltzmann's relation between entropy and thermodynamic probability. Suppose we have an assembly of N particles that can be distributed or "partitioned" among m distinct states. If X is the number of ways in which this partition can be achieved, Boltzmann's equation for the entropy (indeed, his conception of entropy) is

$$S = k \ln X. \tag{8.3.3}$$

Here, k is Boltzmann's constant, 1.38×10^{-23} J K^{-1}. Those who remember having seen this before might just like to be reminded of the gist of the argument leading to it. It presupposes some functional relation between S and X, and it notes that, if you have several assemblies, the total "X" for the ensemble as a whole is the product of the X's of the individual assemblies, whereas the total entropy is the sum of the individual entropies, and therefore the entropy must be proportional to the logarithm of the number of possible configurations.

That was very brief, but it will do for the purposes of section 8.4.

8.4 *Boltzmann's Equation*

If we have a large number of atoms in a hot, dense gas, the atoms will constantly be experiencing collisions with each other, leading to excitation to the various possible energy levels. Collisional excitation will be followed, typically on timescales of the order of nanoseconds, by radiative de-excitation. If the temperature and pressure remain constant, there will exist a sort of dynamic equilibrium between collisional excitations and radiative de-excitations, leading to a certain distribution of the atoms among their various energy levels. Most of the atoms will be in low-lying levels; the number of atoms in higher levels will decrease exponentially with energy level. The lower the temperature, the faster will be the population drop at the higher levels. Only at very high temperatures will high-lying energy levels be occupied by an appreciable number of atoms. Boltzmann's equation shows just what the distribution of the atoms will be among the various energy levels as a function of energy and temperature.

Let's imagine a box (constant volume) holding N atoms, each of which has m possible energy levels. Suppose that there are N_j atoms in energy level E_j. The total number N of atoms is given by

$$N = \sum_{i=1}^{m} N_i . \qquad 8.4.1$$

Here, i is a running integer going from 1 to m, including j as one of them.

The total internal energy U of the system is

$$U = \sum_{i=1}^{m} N_i E_i . \qquad 8.4.2$$

We now need to establish how many ways there are of arranging N atoms such that there are N_1 in the first energy level, N_2 in the second, and so on. We shall denote this number by X. To some, it will be intuitive that

$$X = \frac{N!}{N_1! N_2! \ldots\ldots N_j! \ldots\ldots N_m!} . \qquad 8.4.3$$

That is,

$$X = \frac{N!}{\prod_{i=1}^{m} N_i !} . \qquad 8.4.4$$

I don't find it immediately obvious myself, and I am happier with at least a minimal proof. Thus, the number of ways in which N_1 atoms can be chosen from N to occupy the first level is $\binom{N}{N_1}$, where the parentheses denote the usual binomial coefficient. For each of these ways, we need to know the number of ways in which N_2 atoms can be chosen from the remaining $N - N_1$. This is, of course, $\binom{N-N_1}{N_2}$. Thus the number of ways of populating the first two levels is $\binom{N}{N_1}\binom{N-N_1}{N_2}$

On continuing with this argument, we eventually arrive at

$$X = \binom{N}{N_1}\binom{N-N_1}{N_2}\binom{N-N_1-N_2}{N_3}\ldots\ \ldots\binom{N-\sum_1^{m-1}N_i}{N_m} \qquad 8.4.5$$

If the binomial coefficients are written out in full (do it - don't just take my word for it), there will be lots of cancellations and you almost immediately arrive at equation 8.4.3.

We now need to know the most probable partition - i.e. the most probable numbers N_1, N_2, etc. The most probable partition is the one that maximizes X with respect to *each* of the N_j - subject to the constraints represented by equations 8.4.1 and 8.4.2.

Mathematically it is easier to maximize ln X, which amounts to the same thing. Taking the logarithm of equation 8.4.3, we obtain

$$\ln X = \ln N! - \ln N_1! - \ln N_2! - \ldots \qquad 8.4.6$$

Apply Stirling's approximation to the factorials of all the variables. (You'll see in a moment that it won't matter whether or not you also apply it to the constant term ln N!) We obtain

$$\ln X \cong \ln N! - (N_1 \ln N_1 - N_1) - (N_2 \ln N_2 - N_2) - \ldots \qquad 8.4.7$$

Let us now maximize ln X with respect to one of the variables, for example N_j , in a manner that is consistent with the constraints of equations 8.4.1 and 8.4.2. Using the method of Lagrangian multipliers, we obtain, for the most probable occupation number of the jth level, the condition

$$\frac{\partial \ln X}{\partial N_j} + \lambda \frac{\partial N}{\partial N_j} + \mu \frac{\partial U}{\partial N_j} = 0. \qquad 8.4.8$$

Upon carrying out the differentiations, we obtain

$$-\ln N_j + \lambda + \mu E_j = 0. \qquad 8.4.9$$

That is to say: $$N_j = e^{\lambda + \mu E_j} = C e^{\mu E_j}. \qquad 8.4.10$$

What now remains is to identify the Lagrangian multipliers λ (or $C = e^{\lambda}$) and μ. Multiply both sides of equation 8.4.9 by N_j . Recall that i is a running subscript going from 1 to m, and that j is one particular value of i. Therefore now change the subscript from j to i, and sum from i = 1 to m, and equation 8.4.9 now becomes

$$-\sum_{i=1}^{m} N_i \ln N_i \; + \; \lambda N \; + \; \mu U = 0, \qquad 8.4.11$$

where we have made use of equations 8.4.1 and 8.4.2. From equation 8.4.7, we see that

$$-\sum_{i=1}^{m} N_i \ln N_i \; = \; \ln X - \ln N! \; - \; N, \qquad 8.4.12$$

so that
$$\ln X \; = \; \ln N! - (\lambda + 1)N \; - \; \mu U. \qquad 8.4.13$$

Now apply equation 8.3.3, followed by equation 8.3.2, and we immediately make the identification

$$\mu \; = \; -\frac{1}{kT}\cdot \qquad 8.4.14$$

Thus equation 8.4.10 becomes

$$N_j \; = \; Ce^{-E_j/(kT)}. \qquad 8.4.15$$

We still have to determine *C*. If we change the subscript in equation 8.4.15 from *j* to *i* and sum from 1 to *m*, we immediately find that

$$C \; = \; \frac{N}{\sum_{i=1}^{m} e^{-E_i/(kT)}}. \qquad 8.4.16$$

Thus
$$\frac{N_j}{N} \; = \; \frac{e^{-E_j/(kT)}}{\sum e^{-E_i/(kT)}}, \qquad 8.4.17$$

where I have omitted the summation limits (1 and *m*) as understood..

However, there is one factor we have not yet considered. Most energy levels in an atom are degenerate; that is to say there are several states with the same energy. Therefore, to find the population of a level, we have to add together the populations of the constituent states. Thus each term in equation 8.4.17 must be multiplied by the statistical weight ϖ of the level. (This is unfortunately often given the symbol *g*. See section 7.14 for the distinction between *d*, *g* and ϖ. The symbol ϖ is a form of the Greek letter pi.) Thus we arrive at *Boltzmann's Equation*:

$$\frac{N_j}{N} = \frac{\varpi_j e^{-E_j/(kT)}}{\sum \varpi_i e^{-E_i/(kT)}}. \qquad 8.4.18$$

The denominator of the expression is called the *partition function* (`die Zustandsumme`). It is often given the symbol u or Q or Z.

The statistical weight of a level of an atom with zero nuclear spin is $2J + 1$. If the nuclear spin is I, the statistical weight of a level is $(2I + 1)(2J + 1)$. However, the same factor $2I + 1$ occurs in the numerator and in every term of the denominator of equation 8.4.18, and it therefore cancels out from top and bottom. Consequently, in working with Boltzmann's equation, under most circumstances it is not necessary to be concerned about whether the atom has any nuclear spin, and the statistical weight of each level in equation 8.4.18 can usually be safely taken to be $(2J + 1)$.

In equation 8.4.18 we have compared the number of atoms in level j with the number of atoms in all level. We can also compare the number of atoms in level j with the number in the ground level 0:

$$\frac{N_j}{N_0} = \frac{\varpi_j e^{-E_j/(kT)}}{\varpi_0}. \qquad 8.4.19$$

Or we could compare the number in level 2 to the number in level 1, where “2” represent any “two” level, 2 lying higher than 1:

$$\frac{N_2}{N_1} = \frac{\varpi_2}{\varpi_1} e^{-(E_2 - E_1)/(kT)} = \frac{\varpi_2}{\varpi_1} e^{-h\nu/(kT)}. \qquad 8.4.20$$

8.5 *Some Comments on Partition Functions*

The topics we discuss in this section are

i. *Divergence of partition functions.*
ii. *Metals and nonmetals.*
iii. *Product of partition functions.*
iv. *Particles in a box.*

i. *Divergence of partition functions.*

We can perhaps start by computing the partition function of atomic hydrogen. We have seen that each "level" (technically each *shell*) of hydrogen is actually a group of several terms, and that the total number of states in the shell - i.e. its statistical weight - is $2n^2$. See section 7.16. If we include nuclear spin, the statistical weight of each shell is actually $4n^2$ for ordinary hydrogen and $6n^2$ for deuterium. However, as agreed in section 8.4, we need not be concerned with nuclear spin, and we can take the statistical weight of each shell to be $2n^2$. The energy levels are given by equation 7.4.8:

$$E = \text{const.} \times \left(1 - \tfrac{1}{n^2}\right), \qquad 8.5.1$$

but how many "levels" are there? That is, what is the upper limit *m* of the sum in the partition function? Our first response is that there are an infinite number of energy levels converging towards the ionization limit at 13.6 eV. The same is true of other atoms; they, too, have infinite series of Rydberg levels. Evidently to calculate the partition function, we have to sum an infinite series, in this case, the series being

$$\sum_{n=1}^{\infty} 2n^2 \exp\left[-\left(1-\tfrac{1}{n^2}\right)/(kT)\right]. \qquad 8.5.2$$

We can take anything that does not contain *n* outside the summation symbol and absorb it in the constant, and so we have to evaluate the sum

$$\sum_{1}^{\infty} n^2 \exp\left(\frac{1}{n^2 kT}\right). \qquad 8.5.3$$

Now we all remember that there are several tests to determine whether or not a series converges, and that, during an exam, all the tests that we remember fail, and the one test that we need is the one and only test that we cannot remember or never understood. Here is our chance now - Determine whether the above series converges or diverges!

I'll let you pause for a while you do that.

Darn it! The series diverges! The partition function is infinite! Although the uppermost "levels" have a high excitation potential and therefore cannot individually have high occupation numbers, there is an infinite number of them. The atoms are partitioned among an infinite number of levels, and the probability of any individual level being occupied approaches zero! Disaster!

This is a difficult subject, and not one in which I can claim much expertise, but a qualitative explanation goes something like this. The Coulomb potential of an isolated electric charge (in the present case we are thinking of the hydrogen nucleus; for heavier atoms we are thinking of the atom less the outermost, optical electron) is hyperbolic, approaching the ionization limit asymptotically, becoming horizontal as $r \to \infty$ if you draw a graph of the potential. In a partially ionized gas (which includes all stellar atmospheres) there are numerous charged particles - electrons and ions, and they all interact with one another. If two charged particles approach each other, the electric potential in the space between them becomes slightly lowered beneath the theoretical zero potential for an isolated charge. This is all one needs to resolve the difficulty. The ionization potential is lowered just a little (the exact amount will depend on the density of charged particles) and this eliminates the infinite number of Rydberg levels just beneath the ionization limit. There remains then a finite number of levels, and a finite number of terms in the partition function.

We do not, for our present purpose, necessarily need to know the exact amount of the lowering of the ionization potential, or how many "levels" remain, because we soon find that after the first few levels, the occupation numbers rapidly decrease and do not contribute much to the partition function. Where we choose to terminate the summation depends on the temperature and the precision we hope to achieve. Try calculating, for example, exp $(-E/(kT))$ for E = 10 eV and T = 20,000 K. This should give you some idea.

Here is another insightful semiclassical guide. Consider the electron orbits in a Bohr model of the hydrogen atom. The radii of the orbits increase as n^2. There comes a time when this radius becomes comparable to the average nearest-neighbour distance between atoms. If we assume an ideal gas equation of state, $P = NkT$, where N is the number of atoms per unit volume, we might take the nearest-neighbour distance to be $N^{-1/3}$, and we could equate this to the radius of the largest existing Bohr orbit. Presumably this will limit the number of Balmer lines we could see in a stellar atmosphere, and it will also tell us where to cut off the summation in calculating the partition function. Radio astronomers observe transitions involving very large quantum numbers - e.g. H 109α. Presumably these come from hydrogen atoms in a region of space where the nearest neighbour distance is large enough the permit the existence of Bohr orbits of high quantum number.

ii. *Metals and Nonmetals.*

There is a difference between calculating the partition functions of metals and of nonmetals - but first it is necessary to say what I mean by a "metal". It would be difficult to find two chemists or two physicists or two engineers who would agree on the exact definition of a metal. Among astronomers, however, there is near unanimity: the periodic table comprises hydrogen, helium, and all the remaining elements are "metals". This is a distressing misuse of the English language, and I strongly discourage it. I should make it plain that in this section - indeed in this chapter or book - this is not what I mean when I write the word "metal". Although, as I say, few scientists would agree on the precise definition, if I say "a metal is an element which, in the solid state, is hard, shiny, and conducts electricity", I should not be far off the mark. Almost everyone will find some immediate objection to that definition - but it is still not far off the mark, and certainly much better than the astronomers' "any element other than hydrogen and helium". In brief, elements that we think of in everyday life as being metals - such as iron, zinc, titanium, copper, lead, vanadium, tin, and so on - are metals. Neon, argon, chlorine, carbon, germanium, are not. From the spectroscopic point of view, a metal is characterized by having many, many energy levels, including many not far above the ground level. The calculation of the partition function is long and tedious, because so many levels, especially low-lying levels, must be taken into account. In the old days when these calculations were done by hand calculator, the levels were taken term by term, the statistical weight of each term being $(2S+1)(2L+1)$. The partition functions are fairly sensitive to temperature. Nonmetals, on the other hand, are characterized by typically having a large gap between the ground term and the first excited term. Consequently, the Boltzmann factors for terms other than the ground term are small, and, as a result, the partition function of a nonmetal is, to a good approximation, merely equal to the statistical weight of the ground term - and it hardly changes with temperature.

Now here is a question I used to enjoy asking students, both graduate and undergraduate. I would take particular pleasure in asking graduate students during a thesis defence. Think of a fairly hot star, such as Vega - say its temperature is something like 20,000 K. You will recall having seen the spectrum if Vega - it shows a beautiful development of the Balmer series of hydrogen. Obviously many of the higher "levels" are excited in the hot atmosphere; not all of neutral hydrogen atoms are still in the ground "level". The question is: At 20,000 K, what fraction of the neutral hydrogen atoms in the atmosphere remain in the ground "level"? And, just to make it clear that I was not expecting detailed precise calculations, I would give the question as a "multiple-choice" question, with just three alternatives:

(a) Nearly all of them?
(b) About half of them?
(c) Hardly any of them?

Usually answers would be pretty evenly divided among the three. Have a go at it yourself. All the information you need is to be found in this chapter and chapter 7. It is important that you should have some feeling for the answer.

You will probably also be asking yourself how many of the hydrogen atoms are neutral, and how many are ionized. We shall come back to that when we have discussed Saha's equation. The answer will depend not only on the temperature but also on the pressure.

iii. *Product of partition functions.*

In some systems, the total energy may be made up of several different sources of energy. Consider, for example, a simple diatomic molecule. Its energy may be the sum of the electronic excitation energy, energy of vibration, and kinetic energy of rotation. If these several sources of energy are independent of each other, the total energy will be merely the sum of the separate contributions:

$$E_{\text{tot.}} = E_{\text{el.}} + E_{\text{vib.}} + E_{\text{rot.}}. \qquad 8.5.4$$

In practice, for real molecules, this is just a first approximation - in reality, there is some interaction between the several contributions to the energy, but the intention here is not to get bogged down in the finer details of molecular structure but merely to make a small point concerning partition functions, as follows. Provided that the several energy contributions are independent and do not interact significantly and the energies are consequently additive, the total wavefunction is the product of the three wavefunctions:

$$\psi = \psi_{\text{el.}}\psi_{\text{vib.}}\psi_{\text{rot.}} \qquad 8.5.5$$

Here $\psi_{\text{vib.}}$ and $E_{\text{vib.}}$ are the wavefunctions and energy levels for a simple harmonic oscillator and $\psi_{\text{rot.}}$ and $E_{\text{rot.}}$ are the wavefunctions and energy levels of a rigid rotator. It will be easily understood that a molecule cannot simultaneously be a rigid rotator and a harmonic oscillator, which is why equations 8.5.4 and 8.5.5 are just first approximations. However, the vibrations of a molecule are generally far faster than the relatively slow and ponderous rotations, and electron motions are faster still, so the first approximation is not too bad. More to the point for our present purpose is that every term of the partition function is of the form $e^{-E/(kT)}$, and consequently, *if the total energy is the sum of the individual contributions*, as in equation 8.5.4, *the total partition function is the product of the partition functions of the individual contributions*:

$$u = u_{\text{el.}}u_{\text{vib.}}u_{\text{rot.}} \qquad 8.5.6$$

The extent to which this approximation is valid in real molecules is not the main subject of discussion here. I merely wished to establish that, provided equation 8.5.4 holds, then equation 8.5.6 follows.

iii. *Particles in a box.*

The reader may vaguely remember studying, in an introductory quantum mechanics course, perhaps without quite knowing why, something called "particle in a box". This was actually useful, and we shall need it before proceeding to the next section. Perhaps the topic would better have been called "waves in a box", because it was the wavefunctions that describe the wave aspect of a particle that were under discussion. If the particle (and its associated wave) is confined in a box, the wavefunctions are restricted to functions that have an integral number of antinodes between opposite walls, and consequently the energy levels can have only discrete values - another example of the inevitability of discrete energy levels resulting from boundary constraints. If the box is a cube of side *a*, the energy levels are given by

$$E_{n_xn_yn_z} = \frac{h^2}{8ma^2}\left(n_x^2+n_y^2+n_z^2\right). \qquad 8.5.7$$

Problem: Verify that the above expression has the dimensions of energy.

If we have many particles in a box, we may be interested to know how the numerous particles are distributed or *partitioned* among the energy levels. In other words, we need to know the partition function, which is just

$$\sum_{n_x=0}^{\infty}\sum_{n_y=0}^{\infty}\sum_{n_z=0}^{\infty}\exp\left[-\frac{h^2\left(n_x^2+n_y^2+n_z^2\right)}{8ma^2kT}\right]. \qquad 8.5.8$$

If the box is very large, the energy levels are very close together and almost continuous. (If the box is infinitely large, there are no boundary constraints and hence there is a continuum of possible energies). If the levels are almost continuous, we can replace the summations with integrals:

$$\text{Partition function} = \int_0^\infty \int_0^\infty \int_0^\infty \exp\left[-\frac{h^2\left(n_x^2+n_y^2+n_z^2\right)}{8ma^2kT}\right] dn_x dn_y dn_z$$

$$= \left[\int_0^\infty \exp\left(-\frac{h^2n^2}{8ma^2kT}\right) dn\right]^3$$

$$= \left(\frac{2\pi mkT}{h^2}\right)^{\frac{3}{2}} V, \qquad 8.5.9$$

where $V = a^3$ is the volume of the box. We shall need this result in section 8.6.

Problem: What are the dimensions of the expression 8.5.9?

8.6 *Saha's Equation.*

Consider the reversible reaction

$$\text{A} \leftrightarrow \text{A}^+ + e^-, \qquad 8.6.1$$

where A is a neutral atom and A^+ its first ion. Let N_0 , N_i , N_e be the numbers of neutral atoms, ions and electrons respectively, held in a box of volume V. Then

$$\frac{N_eN_i}{N_0} = S(T,P) \qquad 8.6.2$$

is the *Saha function.* It is a function of temperature and pressure, high temperature favouring ionization and high pressure favouring recombination. (Students of chemistry will recognize this as an application of Le Chatelier's principle.) The equation tells us the relative numbers of the three types of particle (i.e. the degree of ionization) in an equilibrium situation when the number of ionizations per second is equal to the number of recombinations per second.

Now the number of particles in a given energy level is proportional to the Boltzmann factor for that level, and the total number of particles is proportional to the sum of the Boltzmann factors for all the levels - i.e. to the partition function. Thus, using the symbol Q to denote partition functions, we have, for Saha's equation:

$$\frac{N_eN_i}{N_0} = \frac{Q_eQ_i}{Q_0}. \qquad 8.6.3$$

The partition function is the sum of the Boltzmann factors over all the states, translational and internal (electronic). The total energy of a particle is the sum of its translational and internal energies, so that total partition function is the product of its translational and internal partition functions, for which we shall use the symbol u. Therefore

$$\frac{N_e N_i}{N_0} = \left(\frac{2\pi mkT}{h^2}\right)^{\frac{3}{2}} V \frac{u_e u_i}{u_0}. \qquad 8.6.4$$

Here $m = \frac{m_e m_i}{m_0}$, which is very little different from m_e.

The internal partition function of the electron is merely its statistical weight $2s + 1 = 2$. In calculating the internal partition functions of the atom and ion, it is, of course, essential to measure all energies from the same level - the ground level of the neutral atom, for example. You would not be so foolish, of course, as to calculate the partition function of the atom by using, in the Boltzmann sum, the energies of each level above the ground level of the atom, and then calculate the partition function of the ion by using the energies above some quite different level, such as the energy of the ground stage of the ion, would you? Most of us probably *would* be so foolish; we should, of course, add χ_i (the ionization energy) to each level of the ion. If we do calculate the partition function of the ion using energies above the ground level of the ion, we must then multiply the result, u_i , by $e^{-\chi_i/kT}$. Being even more careful, we should remember, from section 8.5, that the ionization energy is in practice lowered by a small amount $\Delta\chi_i$. Finally, let us now use the symbol n to denote number of particles per unit volume (so that $n = N/V$, and on no account to be confused with the quantum numbers n used in section 8.5) and we arrive at the usual form for Saha's equation:

$$\frac{n_e n_i}{n_0} = \left(\frac{2\pi mkT}{h^2}\right)^{\frac{3}{2}} \frac{2u_i}{u_0} \exp\left(-\frac{(\chi_i - \Delta\chi_i)}{kT}\right). \qquad 8.6.5$$

It might be noted that $\Delta\chi_i$ is a function of n_e, which leads to a slight complication in the computation of Saha's equation, which we shall encounter in one of the problems that follow.

It should be remarked that Saha's equation played an extremely important role in the understanding of the stellar spectral sequence. As is well known, the sequence of spectral types OBAFG… is a result of the degree of ionization and excitation of the elements as a function of temperature, and the difference in the degree of ionization between main sequence stars and giants of a given temperature is the result of the higher degree of ionization in the relatively low pressure atmospheres of the giant stars. This could not be understood at a quantitative level until the development of Saha's equation and its application to stellar atmospheres by Saha, Fowler, Milne and Payne (later Payne-Gaposhkin) in the 1920s.

Problems.

Problem 1. Verify that equation 8.6.5 balances dimensionally.

Problem 2. In the bad old days, we did calculations using logarithm tables! You probably will never have to do that, but this exercise will nevertheless turn out to be useful. Show that Saha's equation can be written as

$$\log\frac{n_e n_i}{n_0} = A + \tfrac{3}{2}\log T + \log\frac{u_i}{u_0} - B\left(\frac{V_i - \Delta V_i}{T}\right) \qquad 8.6.6$$

and determine the numerical value of the constants A and B if n is expressed in m^{-3}, T is in K, V_i is the ionization potential in volts, and logarithms are common logarithms (i.e. to the base 10). I make them $A = 21.68$ and $B = 5039.7$. It is common also to write equation 8.6.6 in the form

$$\log\frac{n_e n_i}{n_0} = 27.24 - \tfrac{3}{2}\log\theta + \log\frac{u_i}{u_0} - \theta(V_i - \Delta V_i), \qquad 8.6.7$$

in which $\theta = 5039.7/T$.

Problem 3. You are going to calculate the Saha function for hydrogen, and so you need the partition functions for the electron, the neutral hydrogen atom and the hydrogen ion. The electron is easy. Its spin is 1/2, so its partition function is 2, as already discussed and indeed already incorporated into Saha's equation. The partition function for neutral hydrogen can be taken to be the statistical weight of its $n = 1$ shell, which is $2n^2 = 2$. Now what about the statistical weight of the hydrogen ion? The hydrogen ion is a proton, which has spin = 1/2. Therefore, as for the electron, should the partition function be 2? The answer is no! When calculating the Saha equation for hydrogen, you should take the partition function of the proton to be 1. This probably seems entirely illogical and you are probably quite sure that I am wrong. But before coming to this conclusion, read again the last paragraph of section 8.4 and the first paragraph of section 8.5i. You can include the effect of the proton spin provided that you take it into account for both H and H^+. If you insist that the statistical weight of the proton is 2, you must also insist that the statistical weight of the $n = 1$ shell of H is $4n^2 = 4$. As with the Boltzmann equation, you usually need not be concerned with nuclear spin - it cancels out in u_i / u_0. There is nothing, however, to cancel out the factor 2 for the electron partition function.

Problem 4. A kilogram of water is contained is a box of volume one cubic metre. The box is made of material that won't melt or vaporize. (!) Draw a graph showing, as a function of temperature, from 10,000 K to 20,000 K, the logarithm of the numbers per unit volume of each of the species *e*, H, H^+, O, O^+. (Assume there are no higher ionization stages, and no molecules.)

This is going to be difficult, and will involve some computation. The first thing you are going to need to do is to calculate the Saha functions of the species involved as a function of temperature., and for this, you will need the partition functions . For the electron, the partition function is 2 and is already incorporated in the Saha equation. As discussed in Problem 3, the partition function of H^+ should be taken to be 1, and, as for the electron, it is mercifully independent of temperature. For neutral H, the statistical weight of the ground shell is 2, and, as you will already have discovered if you carried out the little calculation in section 8.5ii, you can probably take this to be the partition function at all temperatures between 10,000 and 20,000 K. The ground term of neutral oxygen is ^{3}P, and the first excited term is ^{1}D at a term value of 15868 cm^{-1}. Probably only the ground term contributes appreciably to the partition function, but you might want to check that. The ground term of O II is $^4\mathrm{S}^\mathrm{o}$ and the first excited term is a long way up. Thus, for all species, you can probably take the partition function to be the statistical weight of the ground term and independent of temperature. You are very lucky that I did not throw a metal into the mix!

The ionization limits of H and O are at 101678 and 109837 cm^{-1} respectively. We don't yet know by how much, $\Delta\chi_i$ the ionization energy is lowered, so we'll ignore $\Delta\chi_i$ to begin with. You now have enough information to calculate the Saha functions for hydrogen and for oxygen as a function of temperature.

We have been asked to calculate the numbers of five species and we are therefore going to need four equations. We started with one kilogram of water. We know that 18 grams of water contain *A* molecules, where *A* is Avogadro's number. (You may want to look up the exact molar mass of H_2O.) Thus, we started with $1000A/18$ molecules. Let's call that number *N*.

Now see if you agree with the following five equations.

$$N_{\mathrm{H}} + N_{\mathrm{H^+}} = 2N \qquad 8.6.8$$

$$N_{\mathrm{O}} + N_{\mathrm{O^+}} = N \qquad 8.6.9$$

$$N_{\mathrm{H^+}} + N_{\mathrm{O^+}} = N_e \qquad 8.6.10$$

$$N_e N_{\mathrm{H^+}} = VS_{\mathrm{H}} N_{\mathrm{H}} \qquad 8.6.11$$

$$N_e N_{\mathrm{O^+}} = VS_{\mathrm{O}} N_{\mathrm{O}} \qquad 8.6.12$$

We do indeed have five equations in the five unknowns, and all other quantities in the equations are known. The first two express the stoichiometry of the water molecule. The third expresses electrical neutrality. The last two are Saha's equations for hydrogen and oxygen. They five equations are not very difficult equations, although the last two are nonlinear, which makes them slightly awkward. We can make them a little easier. I am going to re-write them:

$$\begin{array}{lr}
N_{\mathrm{H}} + N_{\mathrm{H^+}} \qquad\qquad -2N = 0 & 8.6.13 \\
N_{\mathrm{O}} + N_{\mathrm{O^+}} - N = 0 & 8.6.14 \\
N_{\mathrm{H^+}} + N_{\mathrm{O^+}} - N_e = 0 & 8.6.15 \\
VS_{\mathrm{H}} N_{\mathrm{H}} - N_e N_{\mathrm{H^+}} = 0 & 8.6.16 \\
VS_{\mathrm{O}} N_{\mathrm{O}} - N_e N_{\mathrm{O^+}} = 0 & 8.6.17
\end{array}$$

If we now, just for the moment, suppose that N_e is a quantity whose value is known. In that case, equations 8.6.13 to 8.6.17 would comprise five *linear* equations in just *four* unknowns. The condition for these equations to be consistent is that the determinant of the coefficients and the constant terms be zero:

$$\begin{vmatrix} 1 & 1 & 0 & 0 & -2N \\ 0 & 0 & 1 & 1 & -N \\ 0 & 1 & 0 & 1 & -N_e \\ VS_{\rm H} & -N_e & 0 & 0 & 0 \\ 0 & 0 & VS_{\rm O} & -N_e & 0 \end{vmatrix} = 0 \qquad 8.6.18$$

If I have done my algebra right (you might like to check this), this is a cubic equation in N_e:

$$N_e^3 + V(S_{\rm O} + S_{\rm H})N_e^2 + V[VS_{\rm H}S_{\rm O} - (2S_{\rm H} + S_{\rm O})N]N_e - 3V^2 S_{\rm H}S_{\rm O}N = 0. \qquad 8.6.19$$

You can now solve this for N_e. Remember, however, that, in calculating the Saha functions, you ignored the lowering of the ionization potential ΔV_i, so what you have found is but a first approximation for N_e. This is a function of the electron density. One rather old formula, due to Unsöld, is

$$\Delta V_i = 7 \times 10^{-5} n_e^{1/3}, \qquad 8.6.20$$

where V_i is in volts and n_e ($= N_e/V$) is in m^{-3} (indicating that the lowering of the potential is proportional to the distance between the charged particles.). If you can find a more recent and perhaps better formula, by all means use it. You can use your first approximation for n_e to calculate the Saha functions, and then repeat the entire calculation and continue to iterate until you obtain an acceptably small change in n_e. It is probable that only one iteration will be necessary. Having found n_e (and N_e) it is then straightforward to find the remaining unknowns from equation 8.6.13 to 8.6.17. Just make sure that you make use of all five equations as a check for arithmetic mistakes.

Problem 5. A bottle of methyl cyanate CH_3CNO is held in a cylinder with a movable piston such that the pressure remains constant at one pascal. Heat it up to some temperature at which you can assume that the only species present are electrons and the neutral atoms and singly ionized stages of C, H, O and N - i.e. no higher ionization stages and no molecules. The cylinder and piston are not allowed to melt - they are required only to provide constant pressure conditions, in contrast to the previous problem in which you had a constant volume. You have nine unknowns, and you will need nine equations. In this problem you are asked merely to write down the nine required equations, not necessarily to solve them unless you particularly want to. There will be Saha equations for each element, an equation expressing electrical neutrality, and four equations reflecting the stoichiometry. You may assume the ideal gas equation $P = nkT$.

8.7 *The Negative Hydrogen Ion.*

The word "ion" in the gas phase is often thought of as the positively charged remnant of an atom that has lost one or more electrons. However, any electrically charged atom (or molecule or radical), whether positively charged (as a result of loss of an electron) or negatively charged (having an additional electron) can correctly be called an "ion". In this section, we are interested in the negative hydrogen ion, H^-, a bound system consisting of a proton and two electrons.

The formation of such an ion can be qualitatively described, in classical terms, as follows. A hydrogen atom, consisting of a proton and an electron, is approached by a second electron. The electric field of the second electron (which falls off with distance as r^{-2}) induces a dipole moment in the neutral hydrogen atom, with the two electrons then being at opposite sides of the proton. The induced dipole moment is proportional to the electric field of the polarizing electron, and hence to r^{-2}. The second electron now finds itself immersed in the electric field of the dipole that it has itself induced in the neutral H atom, and can be captured by it. The field of the dipole falls is proportional to p/r^3, where p, the induced dipole moment, is already proportional to r^{-2}. Thus the force between the neutral (but dipolar) hydrogen atom and the intruding second electron falls off as r^{-5}, and the second electron moves in a potential varying as r^{-4}. Because of this, the energy level structure of H^- is very different from that of H. In H, the potential falls off as r^{-1}, which results in the familiar infinite Rydberg series of levels. For a potential of the form r^{-n}, if $n > 1$ the Schrödinger equation predicts a *finite* number of bound levels below the ionization limit, and, in the case of H^-, there is just *one* bound level, and it is a mere 0.7 eV below the ionization limit. The 0.7 eV can be called the *ionization potential* of the H^- ion or the *electron affinity* of the H atom. Perhaps the latter term is preferable, because it is a little odd to refer to removing an electron from the H^- ion (so that it is then no longer an ion) as "ionization"! As Professor Joad might have said: "It all depends what you mean by 'ionization'". In any case, an electron can easily be removed from H^- either by a mild collision or by any photon of (vacuum) wavelength shorter than about 1771 nm.

In the solar atmosphere, most hydrogen atoms are neutral and have the electron in the $n = 1$ shell (K shell). Only a few are in the form of H^+ or H^- . (I am not sure offhand which is more numerous, H^+ or H^- – that would make a good lunchtime discussion.) But because H^- is so readily stripped of an electron by almost any old photon, H^- makes an appreciable contribution to the continuous opacity of the solar atmosphere. The continuous absorption can be either by "bf" (bound-free) transitions or so-called "ff" (free-free) transitions. In the latter case the second electron is unbound, but it swerves in the field of the dipole that it has itself induced in the neutral H atom.

8.8 *Autoionization and Dielectronic Recombination.*

The ionization energy as discussed until this point has meant the energy required to remove an electron from an atom, initially in its ground level, leaving the removed electron with no kinetic energy. The neutral atom has a number of discrete energy levels below the ionization limit; above that limit, there is a continuum of energy states - which merely means that the electron is unbound and there are no restrictions on its kinetic energy.

However, it is possible for more than one electron in an atom to be excited, and in that case it is quite possible for an atom to exist in a discrete bound level whose energy is above the ionization limit as described in the previous paragraph. Although this is quite possible, an atom generally does not stay long in one of these highly excited levels. One of the electrons can easily slip away from the atom without the absorption of any additional energy, thereby leaving behind an ion in an excited state. Such a process is called *autoionization*, and the levels or states concerned are autoionization levels or states.

The converse process is quite possible. An ion in an excited state can capture a hitherto free electron, thus forming the neutral atom with two excited electrons. The process is *dielectronic recombination.* Downward transitions from these autoionization levels to lower discrete level can occur.

As mentioned above, the mean lifetime of the atom in one of these autoionization levels is rather short. As a consequence of Heisenberg's uncertainty principle, there is a corresponding uncertainty in the energy level that is inversely proportional to the lifetime. Stated otherwise, the autoionization energy levels are relatively broad. Consequently lines resulting from downward transitions originating from these autoionization levels are relatively broad, and indeed such lines are often recognized or at least suspected from their relatively diffuse appearance. Such lines are readily observed, for example, in the spectra of copper, zinc and cadmium among others.

8.9 *Molecular Equilibrium*

The dissociation of diatomic molecules can be treated in a way that is very similar to Saha's equation for ionization. Consider, for example, the following reversible reaction

$$\mathrm{AB} \leftrightarrow \mathrm{A} + \mathrm{B} \qquad 8.9.1$$

The equilibrium is governed by an equation that is essentially identical to the Saha equation:

$$\frac{n_{\mathrm{A}} n_{\mathrm{B}}}{n_{\mathrm{AB}}} = K_{\mathrm{AB}} = \left(\frac{2\pi mkT}{h^2} \right)^{\frac{3}{2}} \frac{u_{\mathrm{A}} u_{\mathrm{B}}}{u_{\mathrm{AB}}} e^{-D_0^0/(kT)} . \qquad 8.9.2$$

Here K_{AB} is the equilibrium constant, m is $m_{\mathrm{A}}m_{\mathrm{B}}/(m_{\mathrm{A}}m_{\mathrm{B}})$, and D_0^0 is the dissociation energy. To a first approximation the partition function u_{AB} of the molecule is the product of the electronic, vibrational and rotational partition functions, although usually today more precise calculations are made. The equation is often written in terms of partial pressures:

$$\frac{p_{\mathrm{A}} p_{\mathrm{B}}}{p_{\mathrm{AB}}} = K'_{\mathrm{AB}} , \qquad 8.9.3$$

in which $K'_{AB} = kTK_{AB}$ where the gases may be considered to be ideal.

Let us consider again Problem 5 of section 8.6, in which we have methyl cyanate CH_3CNO held at some pressure *P*, but this time we'll work at some temperature where we shall suppose that the only species to be expected would be neutral atoms and neutral diatomic molecules. The species concerned are C, H, O, N, C_2, CN, CO, CN, H_2, OH, NH, O_2, NO, N_2. We shall evidently need 14 equations. They are:

$$n_{\mathrm{C}} + n_{\mathrm{H}} + n_{\mathrm{O}} + n_{\mathrm{N}} + n_{\mathrm{C_2}} + n_{\mathrm{CH}} + n_{\mathrm{CO}} + n_{\mathrm{CN}} + n_{\mathrm{H_2}} + n_{\mathrm{OH}} + n_{\mathrm{NH}} + n_{\mathrm{O_2}} + n_{\mathrm{NO}} + n_{\mathrm{N_2}} = P/(kT) \ , \qquad 8.9.4$$

$$n_{\mathrm{C}} + 2n_{\mathrm{C_2}} + n_{\mathrm{CH}} + n_{\mathrm{CO}} + n_{\mathrm{CN}} = 2\left(n_{\mathrm{N}} + n_{\mathrm{CN}} + n_{\mathrm{NH}} + n_{\mathrm{NO}} + 2n_{\mathrm{N_2}}\right), \qquad 8.9.5$$

$$n_{\mathrm{H}} + n_{\mathrm{CH}} + 2n_{\mathrm{H_2}} + n_{\mathrm{OH}} + n_{\mathrm{NH}} = 3\left(n_{\mathrm{N}} + n_{\mathrm{CN}} + n_{\mathrm{NH}} + n_{\mathrm{NO}} + 2n_{\mathrm{N_2}}\right), \qquad 8.9.6$$

$$n_{\mathrm{O}} + n_{\mathrm{CO}} + n_{\mathrm{OH}} + 2n_{\mathrm{O_2}} + n_{\mathrm{NO}} = n_{\mathrm{N}} + n_{\mathrm{CN}} + n_{\mathrm{NH}} + n_{\mathrm{NO}} + 2n_{\mathrm{N_2}}, \qquad 8.9.7$$

$$n_{\mathrm{C}}^2 = K_{\mathrm{C_2}} n_{\mathrm{C_2}}, \quad n_{\mathrm{C}} n_{\mathrm{H}} = K_{\mathrm{CH}} n_{\mathrm{CH}}, \quad n_{\mathrm{C}} n_{\mathrm{O}} = K_{\mathrm{CO}} n_{\mathrm{CO}}, \quad n_{\mathrm{C}} n_{\mathrm{N}} = K_{\mathrm{CN}} n_{\mathrm{CN}}, \quad n_{\mathrm{H}}^2 = K_{\mathrm{H_2}} n_{\mathrm{H_2}}, \qquad 8.9.7\text{-}11$$

$$n_{\mathrm{O}} n_{\mathrm{H}} = K_{\mathrm{OH}} n_{\mathrm{OH}}, \quad n_{\mathrm{N}} n_{\mathrm{H}} = K_{\mathrm{NH}} n_{\mathrm{NH}}, \quad n_{\mathrm{O}}^2 = K_{\mathrm{O_2}} n_{\mathrm{O_2}}, \quad n_{\mathrm{N}} n_{\mathrm{O}} = K_{\mathrm{NO}} n_{\mathrm{NO}}, \quad n_{\mathrm{N}}^2 = K_{\mathrm{N_2}} n_{\mathrm{N_2}}. \qquad 8.9.12\text{-}16$$

The first of these equations is the ideal gas equation. The next three express the stoichiometry of methyl cyanate. The remaining ten, which are nonlinear, are the equilibrium equations. Some skill and experience in the solution of multiple nonlinear simultaneous equations is necessary actually to solve these equations.

8.10 *Thermodynamic Equilibrium*

Those who have studied thermodynamics will be familiar with such elementary and easy concepts as entropy, enthalpy, Gibbs free energy, chemical potential, activity and fugacity, and will have no difficulty in grasping their meaning. Much more difficult to grasp, however, is the very difficult concept of *temperature.* I have vague memories of something called the Zeroth Law of Thermodynamics which, I seem to recall, went something like this: "If two bodies are in thermodynamic equilibrium with each other, and each is in thermodynamic equilibrium with a third, then all three bodies are at the same temperature." I understood that this was a law of great profundity, though I was never quite sure whether any part of the Universe could ever truly be in thermodynamic equilibrium and that the Universe would be a pretty dull place if it were. This section may or may not (more likely the latter) make the concept of temperature any easier.

Let us try to imagine a system consisting of a hot gas with a solid body suspended in it.

Let us imagine that we are somehow able to measure the distribution of the translational speeds of the molecules in the case, and the distribution is found to conform to a Maxwell-Boltzmann distribution with a root-mean-square speed *V*. We could then calculate the quantity $mV^2/(3k)$ and call this quantity *T*. We could call this quantity the *kinetic temperature* of the gas. We might, for example, say that the kinetic temperature of the gas is 300 K. Some may think that it would be simpler merely to say how fast the molecules are moving. In any case, the *kinetic temperature* of the gas is merely a way of expressing what the root-mean-square speed of the molecules is.

Let us also imagine that we are able to determine how the molecules are partitioned among their numerous discrete energy levels. We may find that they are distributed according to the Boltzmann distribution with parameter T, and we could call that parameter the *excitation temperature*, which would then merely be a way of saying how fast or how slowly the occupation numbers of the levels fall off with energy.

We might also be able to determine the extent to which the atoms are ionized, and we could apply Saha's equation and hence define an *ionization temperature.*

Unless the molecules are single atoms, we might also be able to determine how the molecules are partitioned among their various vibrational levels or among their numerous rotational levels, and we could assign to these distributions a *vibrational temperature* and a *rotational temperature* respectfully.

If we look at the solid, it may be glowing with heat, and we may be able to determine how its exitance per unit wavelength interval varies with temperature, and we might observe that it conforms to Planck's radiation formula. We might be able to measure its total exitance, M. We could then pretend that it is a black body, and we could define $(M/\sigma)^{1/4}$, where σ is the Stefan-Boltzmann constant, as the *effective temperature*. Or we could note the wavelength at which the exitance per unit wavelength interval is greatest, and we could define W/λ_{max} as the *colour temperature* where W is Wien's constant..

Small wonder that "temperature" and "thermodynamic equilibrium" are such difficult concepts to grasp! However, I think it is fair to make the following statements: If the system is in thermodynamic equilibrium, then all of these various possible measures of "temperature" (kinetic, excitation, ionization, vibrational, rotational, effective, colour) are equal. If they are not equal, the system is not in thermodynamic equilibrium.