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Statistical Thermodynamics of
Dissociating Gases and Plasmas

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ABSTRACT

When a dissociation equilibrium is present, the complete phase space should be allocated consistently to either the associated or dissociated species without duplication or omission of any important region. While this problem is trivial in many systems at low pressure, it becomes important and complex for an ionizing system at high pressure. A feasible division is proposed and equations are presented for both the dissociated (ionized) and associated species. It is suggested that any extensive tabulation of properties of ionizable species be made in a manner consistent with the principles outlined.

The general methods of statistical thermodynamics for dissociating gases are well established.^{1,2} The partition function is the sum over all quantum states (or classically over all phase space) of the Boltzmann factor. If separate species are assumed (i.e., separate thermodynamic states) then the partition functions of these various species must include, without duplication, all of the quantum states of the complete system. The problem arises in defining the partition functions of individual species in a manner to include all quantum states yet to avoid counting any states in more than one species.

At low densities and at low temperatures with respect to the dissociation energy, these details are often unimportant. There is negligible total thermal occupancy of any quantum states which are of ambiguous classification. But at higher densities and temperatures greater care is necessary.

When the dissociation is to ions, additional problems arise. A simple summation over the excited states of the hydrogen atom, for example, fails to converge because there are an infinite number of terms at finite energy. Also the dissociated ionic gas or plasma will depart strongly from the ideal gas equation because of the long-range electrostatic forces. The general pattern for the resolution of these problems is also well-known.³ The plasma must be treated by the Debye-Hückel equation, or its equivalent. And since the net effect of the electrical forces for the dissociated ions

is to lower their energy, one may "cut off" the sum for the partition function of the atom below the normal ionization potential.

While these general ideas are fully established, there is still uncertainty and controversy⁴ about the exact "cut off" which should be applied to the partition function for the atom and the exact form of the Debye-Hückel or equivalent equation for the ionized gas. It is my purpose to analyze this situation more carefully and propose a solution which is both self-consistent and practical.

One of the difficulties arises from the fact that the internal motion of the associated species is ordinarily treated in quantum terms and the partition function calculated by a sum over quantum states. On dissociation these motions become translations which are treated by classical mechanics. In classical statistical mechanics the kinetic and potential energies are treated separately; the integral for the former is simple, while that for the latter must consider the interparticle potential energy. But in quantum mechanics, the kinetic and potential energies are both combined in the equation for each quantum state. Thus the boundary in phase space between a region treated classically and one treated in quantum terms is not simple. Our solution will involve a boundary in ordinary space with respect to potential energy; in other words an assumed model potential. The dissociated species are treated classically with this model potential which approaches the true interparticle potential with

increase in distance. The internal partition function for the associated species is calculated by summing over the real quantum states and then subtracting terms for the calculated quantum states for the model potential. This subtraction removes the states already included in the classical calculation with the model potential. By appropriate choice of model potential, all of these calculations are feasible in reasonably high accuracy.

Ionized Gases

If we take as an example the case of ionized hydrogen gas, the coulombic potential applies between all particles down to nuclear distances of the order 10^{-15} m. There are two divergence problems. The first arises from the long-range nature of the coulombic potential; it may be handled by the method of Debye and Hückel⁵ or by similar methods developed subsequently.⁶⁻¹⁰ The second divergence arises at very small interparticle distances where the attractive potential becomes very large. Debye and Hückel were considering ions in aqueous solution where the potential becomes repulsive at a distance of several Å. Thus, their assumption that the largest negative potential is of the order of kT , or less, is valid, at least for singly charged ions in water.

But for protons and electrons the repulsive force, if any, does not arise until very small distances where the negative potential corresponds to thermal energy of at least 10^{10} K. In fact this short-distance divergence is ameliorated by quantum effects with the lowest quantum state corresponding

to thermal energy at 1.6×10^5 K. At temperatures less than 10^5 K these strong negative potentials violate the basic Debye-Hückel assumption which is required for the linearization of the Poisson-Boltzmann equation - a point which is ignored in many papers on ionized gases. In 1926, Bjerrum¹¹ noted that these strong negative potentials, as found for 2-2 electrolytes in water, would yield an association, and he showed how an association constant could be calculated. In the cases of gases, association is also observed but the relationship to departures from the Debye-Hückel treatment (or equivalent) has not been as clearly explained.

In the Bjerrum treatment the associated species is also treated by classical statistical mechanics; hence, the division of phase space can be a simple interionic distance. All pairs of ions (with unlike sign of charge) at shorter distances are associated; those at longer distances are dissociated. But the electronic motion in atoms must be treated by quantum methods, and no such simple division of phase space is possible. The best resolution of this problem appears to be the use of a model potential in which the coulombic curve is truncated at short distances in a manner to retain the validity of the Debye-Hückel treatment but avoiding the hard core which is unrealistic for hydrogen and most other atoms.

We assume a potential which is coulombic outside a radius a and has a flat bottom for r less than a . Thus for a positive charge $z_i e$ and an electronic charge $-e$ (i.e., $z_j = -1$ for the electron)

$$V_{ij} = -z_i e^2 / r \text{ for } r > a \quad (1a)$$

$$V_{ij} = -z_i e^2 / a \text{ for } r < a \quad (1b)$$

With SI units e^2 must be divided by $4\pi\epsilon_0$ in these and subsequent expressions.

For like charges one may assume the corresponding expressions with a positive sign. But the chance of finding like-charged ions at a distance less than a is very small in any case; hence it is unimportant whether the repulsive potential is truncated or not.

Figure 1 shows both the present potential and the conventional Debye-Hückel hard core potential.

The initial steps of the solution are the same for either potential. The distribution of ions at distances greater than a can be expressed by radial distribution functions (binary correlation functions)

$$g_{ij} = \exp(-q_{ij}) \quad (1)$$

$$q_{ij} = [z_i z_j e^2 / kT(1 + \kappa a + \kappa^2 a^2 / 3)] r^{-1} \exp[-\kappa(r-a)] \quad (2)$$

$$\kappa^2 = (4\pi e^2 / kT) \sum c_i z_i^2 \quad (3)$$

where c_i is the concentration of the i^{th} species and the sum covers all charged species. For $r < a$ one has g_{ij} constant at the value for $r = a$. In the linearization approximation g_{ij} becomes

$$g_{ij} = 1 - q_{ij} \quad (4)$$

The difference between the hard-core and flat-bottom potentials appears in q_{ij} only in the expression $(1 + \kappa a + \kappa^2 a^2 / 3)$ where the

last term $\kappa^2 a^2/3$ does not appear for the hard core. We omit the dielectric constant since we are concerned with a dilute gas.

The reduction in the energy of the gas from electrostatic effects may now be calculated by integration

$$E_e = \frac{1}{2} V \sum_i \sum_j c_i c_j \int_0^\infty g_{ij} V_{ij} 4\pi r^2 dr \quad (5)$$

where V is the volume and c_i is the concentration of the i^{th} species. With the linear approximation for g_{ij} , equation (4), one obtains

$$E_e = -\left(\frac{kTV\kappa^3}{8\pi}\right) \frac{1+\kappa a/3}{1+\kappa a+\kappa^2 a^2/3} \quad (6)$$

Here the $\kappa a/3$ in the numerator arose from the region with $r < a$.

It is important, also, to obtain at least the first-order correction to the linearization approximation. This may be obtained by expanding the exponential in equation (1), since more elaborate calculations^{9,12} have shown that this exponential form is a rather good approximation even though not fully consistent with the linearized Poisson-Boltzmann equation. Thus

$$g_{ij} = 1 - q_{ij} + \frac{1}{2} q_{ij}^2 - \frac{1}{6} q_{ij}^3 \dots \quad (7)$$

Because of electrical charge neutrality, there is no contribution from the first term nor from the third for a symmetrical electrolyte. The second term yields the result of equation (6). The correction can be approximated from the fourth term of equation (7) which yields a complex expression from which we take only the leading term

$$\delta E_e = -V(\kappa')^4 / 36\pi kTa \quad (8)$$

$$(\kappa')^2 = (4\pi e^4 / kT) \sum c_i z_i^4 \quad (9)$$

For further calculations we add equation (8) to equation (6) and expand the three-term expression into the numerator.

$$E_e = -\left[\frac{kTV\kappa^3}{8\pi}\right] \left[1 - \frac{2\kappa a}{3} + \frac{\kappa^2 a^2}{3} - \frac{\kappa^3 a^3}{9} + \frac{\kappa^5 a^5}{27} + \dots + \frac{2(\kappa')^4}{9\kappa^3 k^2 T^2 a}\right] \quad (10)$$

Although there are some approximations related to all terms beyond the Debye-Hückel limiting law, i.e., the first brackets in equation (10), these approximations are less severe for the additional terms arising from equation (6) than for equation (8); hence we retain the higher order terms through $\kappa^5 a^5$ from the former but only the leading term from the latter.

It is apparent that the radius a must be assigned a value such that no term in the second brackets is too large. Especially the last and relatively uncertain term should be small.

The thermodynamic relationships, $\partial(A/T)/\partial(1/T) = E$, $(\partial A/\partial V)_T = -P$, etc., may be used to obtain contributions to other functions from electrostatic forces as follows:

Helmholz energy

$$A_e = -\left[\frac{kTV\kappa^3}{12\pi}\right] \left[1 - \frac{\kappa a}{2} + \frac{\kappa^2 a^2}{5} - \frac{\kappa^3 a^3}{18} + \frac{\kappa^5 a^5}{72} + \dots + \frac{(\kappa')^4}{12\kappa^3 k^2 T^2 a}\right] \quad (11)$$

Pressure

$$P_e = -\left[\frac{kT\kappa^3}{24\pi}\right] \left[1 - \kappa a + \frac{3\kappa^2 a^2}{5} - \frac{2\kappa^3 a^3}{9} + \frac{\kappa^5 a^5}{12} + \dots + \frac{(\kappa')^4}{6\kappa^3 k^2 T^2 a}\right] \quad (12)$$

Enthalpy

$$H_e = - \left[\frac{kTV\kappa^3}{6\pi} \right] \left[1 - \frac{3\kappa a}{4} + \frac{2\kappa^2 a^2}{5} - \frac{5\kappa^3 a^3}{36} + \frac{7\kappa^5 a^5}{144} + \dots + \frac{5(\kappa')^4}{24\kappa^3 k^2 T^2 a} \right] \quad (13)$$

Gibbs Energy

$$G_e = - \left[\frac{kTV\kappa^3}{8\pi} \right] \left[1 - \frac{2\kappa a}{3} + \frac{\kappa^2 a^2}{3} - \frac{\kappa^3 a^3}{9} + \frac{\kappa^5 a^5}{27} + \dots + \frac{(\kappa')^4}{9\kappa^3 k^2 T^2 a} \right] \quad (14)$$

The activity coefficient of a particle with charge $z_j e$ is

$$\ln \gamma_j = - \left[\frac{z_j^2 e^2 \kappa}{2kT} \right] \left[1 - \frac{2\kappa a}{3} + \frac{\kappa^2 a^2}{3} - \frac{\kappa^3 a^3}{9} + \frac{\kappa^5 a^5}{27} + \dots + \frac{z_j^2 e^2 (\kappa')^2}{9\kappa k^2 T^2 a} \right] \quad (15)$$

At this point it is convenient to make the additional assumption that the ionized gas comprises positive ions of charge ze and concentration c with electrons of charge $-e$ and concentration zc . Then

$$\kappa^2 = (4\pi e^2 / kT) (z+1)zc \quad (16a)$$

$$(\kappa')^2 = (4\pi e^4 / kT) (z^3+1)zc \quad (16b)$$

and the last term in equation (14) becomes

$$\frac{(\kappa')^4}{9\kappa^3 k^2 T^2 a} = \frac{(z^3+1)^2 e^4 \kappa}{9(z+1)^2 k^2 T^2 a} \quad (17)$$

It seems best to choose the value of a such that this expression (17) is somewhat smaller than $2\kappa a/3$ which is the other and more accurately known term of the same order in κ . If we set the expression (17) at one-sixth of $2\kappa a/3$ we obtain

$$a = \frac{(z^3+1)e^2}{(z+1)kT} \quad (18)$$

and the truncation of the coulombic potential is at the level

$$V = - \frac{ze^2}{a} = - \frac{z(z+1)kT}{(z^3+1)} \quad (19)$$

As expected, this potential is of the order $-kT$ for any small value of z .

In view of this last discussion it might seem desirable to apply equation (18) at each temperature, making the radius temperature dependent. But this complicates the calculation of the partition function of the atom and causes even more difficulty in calculating the related sums needed for the enthalpy or the heat capacity. Hence it seems best to choose a constant value for the radius a which corresponds roughly to equation (18) at the temperature where there will be partial dissociation.

While the basic Debye-Hückel approach which has been followed is not the most exact, it is simple and yields all essential features. Also it is reassuring that a calculation of the activity coefficient by the coupling parameter (or charging process) method yields the identical result. The use of the virial or pressure equation, instead of the derivative of the Helmholtz energy for the pressure yields the same answer for the first two terms in the second brackets but slightly different coefficients for the remaining terms. Such small differences are expected when the basic equation for the radial distribution function is not exact.

Another option would be a choice of truncation radius such that the Debye-Hückel limiting law would apply for the ionized species. Even in the present approximation this would require a concentration dependence of $\underline{a}$; and with a more exact solution of the plasma equation, the implied equation for the radius would be modified and probably further complicated. Thus we see that this option (to use the limiting law) is not convenient or practical.

We turn now to the calculations for the associated species and first to the determination of the quantum states for the model potential.

Quantum States for the Truncated Coulomb Potential

The quantum mechanics of the truncated coulomb potential (with a flat bottom) is not particularly difficult although not in the literature to my knowledge. In the coulombic region the radial eigenfunction, acceptable as $r \rightarrow \infty$, is

$$R = e^{-zr/\alpha} \sum_{j=0} b_j r^{\alpha-1-j} \quad (20)$$

$$\epsilon = -z^2/2\alpha^2 \quad (21)$$

where ϵ is the energy eigenvalue and z is the number of positive charges on the nucleus. Thus $V = -z/r$ in atomic units which we use throughout this section. The series in equation (20) is defined by the relationship

$$b_{j+1} = b_j \frac{\alpha[\ell(\ell+1) - (\alpha-j)(\alpha-1-j)]}{2(j+1)} \quad (22)$$

where ℓ is the angular quantum number. If α is an integer, the series terminates and yields the usual hydrogen-like atom solutions. For non-integral α this is only an asymptotic series, but it usually suffices to yield reasonably accurate eigenvalues if terminated at the smallest term.

Alternatively one may integrate the radial equation numerically starting with the asymptotic solution at large r .

For the joining at $r = a$ to the solution in the inner region, one needs the value of the ratio of the slope to the amplitude defined as

$$Y = R^{-1} r(dR/dr) \text{ at } r = a. \quad (23)$$

This is readily obtained by differentiation

$$Y = \frac{\sum b_j (\alpha - 1 - j - az/\alpha) a^{-j}}{\sum b_j a^{-j}} \quad (24)$$

where each series is terminated at the same value of j chosen as yielding a negligible term or a very small term. The value of Y can also be obtained by numerical integration.

In the central region the potential is constant $V = -z/a$ and the solutions are spherical Bessel functions. The functions for $\ell = 0$ through 3 are listed in Table 1 where $x = \beta r$ and the energy is related to β by the equation

$$E = \frac{\beta^2}{2} - \frac{z}{a} \quad (25)$$

Two conditions are applied to match the inner and outer regions: the ratio of the slope to the value of the radial wavefunction

Table 1. Radial wave functions for the flat potential region and functions for the eigenvalue equation.

ℓ	Radial function $x = \beta r$	Eigenvalue Eq. function $y = \beta a$
0	$B \sin x / x$	$Y = y \operatorname{ctn} y - 1$
1	$B \left[\frac{\sin x}{x^2} - \frac{\cos x}{x} \right]$	$Y = \frac{2y \cos y + (y^2 - 2) \sin y}{\sin y - y \cos y}$
2	$B \left[\left(\frac{3}{x^3} - \frac{1}{x} \right) \sin x - \frac{3 \cos x}{x^2} \right]$	$Y = \frac{(4y^2 - 9) \sin y + (9y - y^3) \cos y}{(3 - y^2) \sin y - 3y \cos y}$
3	$B \left[\left(\frac{15}{x^4} - \frac{6}{x^2} \right) \sin x + \left(\frac{1}{x} - \frac{15}{x^3} \right) \cos x \right]$	$Y = \frac{(-60 + 27y^2 - y^4) \sin y + (60y - 7y^3) \cos y}{(15 - 6y^2) \sin y + (y^3 - 15y) \cos y}$

as defined by $Y(y)$ with $y = \beta a$, and the energy eigenvalue.

The latter relates α and β via equations (21) and (25).

Then the value of Y for a particular ℓ from Table 1 is equated to that from equation (24).

The results are shown in figure 2 in terms of α which is related to the energy by equation (21). It is apparent that, at small a , the energy levels depart only very slightly from the values for $a = 0$ and that this is especially true for larger ℓ values even at larger a values. At very large values of a , the energies are just slightly above the potential floor which is shown by the equivalent $\alpha_f = (az/2)^{1/2}$.

Internal Partition Function

The internal partition function is normally defined as

$$Q = \sum g_i \exp(-\epsilon_i/kT) \quad (26)$$

where g_i is now the degeneracy of the quantum state of energy ϵ_i and the sum covers all of the quantum states included in that chemical species (or thermodynamic state). The convergence problem for an entity which dissociates into ions has been noted. Since we have adopted a model potential, a truncated coulombic potential, of attractive interaction for dissociated ions, we have included in the partition function for the dissociated species the classical equivalent of the quantum states arising from this model potential. The possible quantum correction for the partition function for the dissociated species is expected to be very small at the temperatures of practical interest in view of the flat region of the potential well.

But the phase space corresponding to the quantum states for the model potential must not be duplicated in the internal partition function, hence terms for these states must be subtracted and we obtain as a corrected partition function

$$Q = \sum g_i \exp(-\epsilon_i/kT) - \sum g_j \exp(-\epsilon'_j/kT) \quad (27)$$

where the sum over i includes the real states of the atom (or ion) and the sum over j includes the calculated energies ϵ' of the states for the model potential. Each sum starts with the lowest-energy states of that category. For large quantum numbers the real and model states can be arranged into pairs of the same degeneracy and of almost identical energy. Thus a point will be reached after which the terms in the two sums will cancel one another and the sums are terminated. By this means the divergence at high quantum numbers is avoided.

As a practical matter it is preferable to break up the sums according to the angular quantum number ℓ of the electron being excited to a high-energy state. Then, if the core, the remaining ion, has a closed electron shell or is a bare nucleus (i.e., H, Li, Na, etc.) the internal partition function becomes

$$Q = 2g_n \sum_{\ell} (2\ell+1) \left\{ \sum_n \exp(-\epsilon_{\ell n}/kT) - \sum_{n'} \exp(-\epsilon'_{\ell n'}/kT) \right\} \quad (28)$$

where the first 2 is the electron spin degeneracy and g_n is the nuclear spin degeneracy, which is often omitted by convention. Also n and n' are the principal or radial quantum numbers for the real and model-potential states, respectively.

The pattern of real and model energy-levels for the hydrogen atom is illustrated in figure 3 which shows for each value of z the real energy-levels for H in the middle along with the model levels $a = 9.1$ a.u. on the left and $a = 6.4$ a.u. on the right. These model levels correspond to V/k values of approximately 35 000 K and 60 000 K, respectively. But the important point is that, regardless of the value of a within a reasonable range, the real and model levels can be paired as accurately as desired by approaching closely to dissociation. At larger values of a and z , it is best to pair a model level with an n -value one (or more) lower than the n -value of the real energy-level.

In case the core has an incomplete electron shell (or a closed-shell core has excited open-shell states within thermal range), the subdivision of the sums in equation (27) is more complex than that in equation (28) and is best worked out on an individual basis for each case. The same array of states included for the internal partition function of the core is also included for the terms calculated from the model potential. In other words, the interaction is that of the truncated coulomb potential without consideration of specific interaction of the dissociating electron with the incomplete shell of the core. But the real states are affected by such interactions with such an incomplete shell and the energies and degeneracies of these real states must be used in the first sum of equation (27). These details, and other features of possible interest in practical calculations, are discussed further in the Appendix.

The resulting internal partition functions for the hydrogen, lithium, and nitrogen atoms on the basis $a = 10$ a.u. are shown in figure 4 for the range 10 000 to 100 000 K. The situation in hydrogen is simple with excitation from the 1s state beginning at about 20 000 K. For lithium the excitation from 2s to 2p states begins at much lower temperature and is the dominant effect; the contribution of higher levels is largely cancelled by the model potential levels.

For nitrogen the spectral data¹³ are relatively extensive, but there are unavailable levels which could have a significant effect above 20 000 K and a very substantial effect by 100 000 K. Hence that portion of the curve is dashed in figure 4. Details of the assumptions made are given in the Appendix. Initially the three lowest terms 4S , 2D , and 2P dominate the sum. At higher temperature the subtractive terms become large - even those based on excited states of the N^+ core.

Detailed calculations for other atoms with complex electronic structure will be similar to or more complicated than that for nitrogen. While suggestions could be made concerning procedures, it seems best at this point to emphasize the general principles illustrated with these few examples.

Discussion

If other features of our theory were exact, the choice of the model potential which divides between associated and dissociated species would have no effect on measureable quantities.

Although this choice would affect the fraction stated to be associated, it would not affect the calculated percentage in a given quantum state which can be obtained from the ratio of the Boltzmann factor for that state to the total partition function for both associated and dissociated species. Our equations contain many approximations, yet exploratory calculations show this independence from the choice of division, i.e., the choice of a , to be reasonably good. For example, in hydrogen at 35 000 K and 215.15 g m^{-3} density, calculations were made with $a = 10$ and 6.383 a.u. The fraction of atoms is 0.2882 or 0.2675, respectively, but the pressure is calculated to be 1000.0 or 998.5 atm. The difference of 12.7 atm calculated from the difference in association is approximately cancelled by a difference of -14.2 atm in the Debye-Hückel correction.

Thus for approximate calculations one may choose any reasonable value of the radius a for the model potential. For highly accurate work, it will be desirable to develop more exact theories, especially for the electrostatic effects in the dissociated species. This is clearly feasible, since more exact theories exist for models appropriate to electrolyte solutions in water. If extensive tables of thermodynamic functions for potentially ionizing species are to be prepared, it would seem best to use the present method with a standard truncation radius a chosen at some reasonable value, possibly 10 a.u. The results could be used with the present equations for the ionized species to yield reasonably accurate results

and later with more exact equations when they become available.

Since earlier work assumed just the Debye-Hückel limiting law and made a division of phase space inconsistent with this assumption, the results are subject to uncertainty. For the calculations by Capitelli, et al.¹⁴ on hydrogen, the partition function for the atom (and the percentage of atoms at equilibrium) is too large to be consistent with the D-H limiting law. Over the range of temperature and pressure covered, however, the error is not large. For example at 35 000 K and 1 000 atm they obtain a density of 220.6 g m^{-3} as compared to our value 215.2. For the same conditions and with essentially the same assumptions Patch¹⁵ gives a density of 220.7 g m^{-3} . At lower pressure the difference decreases, of course.

Conclusions

It is shown that the partition function or equation of state for an ionized gas is affected significantly at high densities and temperatures by the assumption made about the division of phase space with the associated species (ion pairs, atoms, etc.). It is not easy to state the division implied by the use of the simple Debye-Hückel limiting law for the ionized species. But it is feasible to adopt a simple model potential as a division and to calculate properties for both associated and dissociated species on this basis. The division is implemented for the undissociated species by subtracting from the partition function sum over real states the sum over states calculated from the model potential. It is found that a convenient model potential is a coulomb potential truncated

with a level floor. Contrary to some proposals, this division is not concentration dependent, a major practical advantage.

Since no previous analysis has considered the full implication of this problem of phases space allocation, the present method, or comparably well-founded alternates, should be used in accurate calculations.

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APPENDIX

The sum for the partition function for an atom or ion with even a moderately complex spectrum such as N is best broken into two parts. First one sums over the valence levels, i.e., the states with all electrons in valence-shell orbitals. For nitrogen this means that all electrons are in 2s or 2p orbitals (in addition to the 1s shell). The partition function sum is taken over these valence levels without subtraction for the model potential states. The first several rows in Table A-1 illustrate this portion of the calculation. Actually the very-high-energy valence configuration $2p^5$ for N is omitted and probably would be negligible even at 100 000 K. Also there are no data for the 2P and 2S terms of the $2s2p^4$ configuration, and their energy values were estimated from the spectra of iso-electronic ions.

The remaining states with one electron excited above the valence shell are called Rydberg states, and it is well-known that their energies can be represented by a Rydberg expression

$$\epsilon_n = -z^2/2(n+\Delta_n)^2 + \epsilon_I \quad (A-1)$$

where n is the principal or radial quantum number and the quantity Δ_n is nearly independent of n . This is true for both the real states and the model-potential states. The quantity ϵ_I is the series limit, i.e., the energy when the outer electron is removed to infinity.

For each angular momentum and for each core state one has a contribution to the partition function which may be expressed

$$Q_{l,c} = 2(2l+1)g_c \sum_n [\exp(-\epsilon_n/kT) - \exp(-\epsilon'_n/kT)] \quad (A-2)$$

where g_c is the degeneracy of the core state while ϵ_n and ϵ'_n are the energies of the real and model states respectively.

As the quantum number n increases the pairs of Boltzmann factors cancel more and more exactly and the sum can be terminated. It is convenient, however, to replace the sum above a given n by an approximate total for all remaining terms. An approximate expression for this sum of terms from $n+1$ to ∞ is

$$\sum_{n+1}^{\infty} = \frac{(\Delta' - \Delta)}{(n+1/2)^2} \left(\frac{1}{2kT}\right) \exp(-\epsilon_I/kT) \quad (A-3)$$

where Δ' and Δ are the Rydberg parameters for model and real states which are assumed to be independent of n . Also k must be in atomic units in the factor $1/2kT$.

The contributions of various series of Rydberg states are shown in Table A-1. A few cases are shown where there are no experimental values but the contribution might be significant. In some other series there are only a few observed levels and it was estimated that Δ remained unchanged throughout the series.

From the general behavior of observed and calculated values and the fact that the f -series contribute very little, one can conclude that the omission of g and higher- l series will not be significant for the nitrogen atom.

It is important in all of the calculations for relatively high-energy terms to pair real and model states. Where real states may not have been observed and are omitted, the subtraction of a series of model states could cause a large error, whereas

Table A-1. Calculation of Q_{int} and $-(G^\circ - H^\circ)/RT$ for the Nitrogen Atom

State or Sequence	T = 10 000	20 000	35 000	50 000	100 000
$2s^2 2p^3, ^4S$	4.000	4.000	4.000	4.000	4.000
$2s^2 2p^3, ^2D$	.628	2.507	4.536	5.750	7.583
$2s^2 2p^3, ^2P$	.095	.753	1.833	2.616	3.962
$2s2p^4, ^4P$	.000	.021	.320	.949	3.375
$2s2p^4, ^2D$	.000	.002	.068	.305	1.748
$2s2p^4, ^2S$	(.000)	(.000)	(.006)	(.034)	(.259) ^a
$2s2p^4, ^2P$	(.000)	(.000)	(.009)	(.065)	(.626) ^a
$2s^2 2p^2(^3P)ns$	.000	.032	.325	.736	1.467
$2s^2 2p^2(^3P)np$	.000	.030	.408	1.024	2.289
$2s^2 2p^2(^3P)nd$	.000	.013	.211	.572	1.395
$2s^2 2p^2(^3P)nf$	.000	.001	.014	.039	.100
$2s^2 2p^2(^1D)ns$	.000	.006	.093	.251	.618
$2s^2 2p^2(^1D)np$	.000	.006	.125	.379	1.060
$2s^2 2p^2(^1D)nd$	.000	.002	.065	.215	.652
$2s^2 2p^2(^1D)nf$	.000	.003	.008	.028	.089
$2s^2 2p^2(^1S)ns$	.000	.000	.010	.033	.105
$2s^2 2p^2(^1S)np$	?	?	?	?	?
$2s2p^3(^5S)ns$	.000	.001	.026	.103	.403
$2s2p^3(^5S)np$	.000	.001	.031	.141	.623
$2s2p^3(^5S)nd$	?	?	?	?	?
Q_{int}	4.723	7.378	12.088	17.240	30.354
$-(G^\circ - H^\circ)/RT$	24.873	27.052	28.944	30.19	32.4 ₉

^a Energies of these states estimated from experimental values for O^+ , F^{++} , Ne^{+3} , and Na^{+4} .

the complete omission of nearly cancelling pairs of terms will lead to much smaller inaccuracies.

Also included in Table A-1 are values for the function $-(G^\circ - H_0^\circ)/RT$ for atomic nitrogen. It is a straightforward extension of the methods already presented to calculate related functions such as $(H^\circ - H_0^\circ)/R$, C_p/R , S/R , etc. While all of these functions have some dependence on the truncation radius for the model potential, this radius may be fixed independent of either temperature or pressure. Thus these functions are based on a definite pattern of energy levels and yield essentially normal values of these thermodynamic functions in contrast to the situation where a "cut-off" varies with temperature and possibly also with pressure.

Figure Captions

Figure 1. The truncated coulomb potential on the left and the hard-core coulomb potential on the right.

Figure 2. The energies of the model-potential quantum states, expressed as α -values, as a function of the truncation radius a and the core charge z .

Figure 3. Energy levels for the hydrogen atom (middle column for each ℓ -value) and model-potential levels for $a = 9$ (left) and $a = 6.4$ a.u. (right).

Figure 4. Internal partition functions with $a = 10$ for hydrogen, lithium, and nitrogen atoms.

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