

Equilibrium Properties and Equation of State of a Hydrogen Plasma*

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(Received 7 June 1963; revised manuscript received 30 September 1963)

Equations are developed for the equilibrium composition and thermodynamic properties of a three-component hydrogen plasma. These are based on a formulation of the total Helmholtz free energy for the system, including corrections to ideal gas behavior due to electrostatic interactions and plasma perturbation of the bound electronic states of hydrogen atom. When a shielded Coulomb potential is used for the perturbation of the bound states and a Debye approximation for the collective electrostatic interactions, it turns out that for low-density, low-temperature plasmas, i.e., $\leq 10^{20}$ electrons/cc and a few electron volts, the bound-state correction, which has been largely ignored, is much more important than the electrostatic correction. The results of a specific calculation based on this model are analyzed and compared with indirect hydrogen plasma temperature-density measurements and with other theoretical calculations based on different approximate free-energy formulations.

I. INTRODUCTION

FOR the past several years, it has been the interest of the author^{1,2} to formulate a working model for a partially ionized multicomponent gas in order to calculate the thermodynamic properties of such a system over a wide temperature-density region. In the molecular model which has been used, the assumption is made that the total many-body system can be represented by a limited number of well-chosen atoms, molecules, and ions, with electrons either bound to these subsystems or free and counted as a component. Aside from this initial description of the plasma in terms of structured components rather than the more fundamental one in terms of bare nuclei and electrons, the remaining approximations of the model are in the formulation of the total free energy of the system. The free-energy expression itself then may be regarded as the model. From it, the equilibrium composition, equation of state, and other thermodynamic quantities of interest may be derived in a straightforward manner without any additional assumptions. Occupation numbers may also be calculated from these results provided the spectroscopic data are available.

In the specific calculation to be discussed here, as in the past, the total free energy is assumed to be the sum of four partial free energies: the contributions from the translational motion of classical nuclear species and from perfect Fermi electrons, the internal free energy of each composite species with electronic, vibrational, and rotational states, and finally a term due to the electrostatic interaction of the ions and free electrons. In the present work, this model is applied to the simplest of all multicomponent, partially ionized plasmas, i.e., a mixture of hydrogen atoms, protons, and electrons. This simple system was chosen in order to focus attention on the signifi-

cance of the different approximations that are made in the formulation of the free energy. In particular, the treatment of the bound states and the electrostatic interactions will be emphasized.

In previous calculations made by this author and others,¹⁻⁴ electrostatic interactions of the plasma were represented by a Debye-Huckel correction with various degrees of modification, for example a high-density or lattice-type extension or the use of a variable-density and temperature-dependent cutoff radius for the ion size. In the present calculation the Debye expression is again used, with both the point charge and finite-size expressions being considered. It is the treatment of the perturbation of the bound electronic energy levels by the plasma that is here different from previous thermodynamic calculations. It has seemed a very reasonable assumption for a long time that the energy eigenvalues of the isolated atoms and molecules are modified in the plasma sea and become density- and temperature-dependent. It is these modified energy levels, described in some appropriate manner, that one would like to use in the partition function for the internal degrees of freedom for each species. In previous thermodynamic calculations,² the perturbation used was a simple confinement effect of the plasma, i.e., the model of an atom or molecule in a box. However, inspired by some of the results of the rigorous perturbation-expansion treatment of the classical many-body problem, the author has reported quantum-mechanical calculations of 45 energy levels of the hydrogen atom in a shielded Coulomb (Yukawa) potential.⁵ Other people^{6,7} have previously done this calculation for "s" states, using different methods of calculation. While the results of these calculations have been used to determine a cutoff for the bound states, the shifted energy levels themselves have not, as far as can be determined,^{3,4} been used in a thermodynamic calculation. It seems very likely that this per-

* This work was supported in part by the U. S. Air Force Special Weapons Center, Air Force Systems Command under Contract AF 29(601)-5006 and in part by the Lockheed Missiles & Space Company Independent Research Program.

¹ G. M. Harris, *J. Chem. Phys.* **31**, 1211 (1959).

² G. M. Harris and J. Trulio, *J. Nucl. Energy, Part C, Plasma Physics* **2**, 224 (1961).

³ H. N. Olsen, *Phys. Rev.* **124**, 1703 (1961).

⁴ G. Ecker and W. Kroll, *Phys. Fluids* **6**, 62 (1963).

⁵ G. M. Harris *Phys. Rev.* **125**, 1131 (1962).

⁶ G. Ecker and W. Weizel, *Ann. Physik* **17**, 126 (1956).

⁷ H. Margenau and M. Lewis *Rev. Mod. Phys.* **31**, 569 (1959).

turbation is an improvement over the "atom in a box" model, especially at lower densities. In this calculation, then, the energy levels of an atom in a shielded Coulomb potential are used in the free-energy expression.

Another cogent reason for a study of this simple plasma at this time is that there now exists a few experimental data which, from a measurement of spectral line intensities and line shapes, allow the determination of the electron density and temperature of a hydrogen plasma.⁸ These measurements were done using the Balmer lines, i.e., emission from excited H-atom levels to the $n=2$ level, at atmospheric pressure, and temperatures around 1 eV. In this work, in order to obtain electron densities from the measured intensities, it was necessary to use the results of an equilibrium calculation of the composition of the H plasma as a function of temperature. One of the main aims of the present calculation is to compare the values of electron density obtained via different approximate thermodynamic calculations.

Because of the simplicity of the system and the relatively small experimental range of temperatures and densities, i.e., electron densities less than 10^{19} electrons/cc and temperatures around 1 eV, the free-energy equations have a much simpler form than those in past calculations. Numerical results to compare with the single piece of experimental data were obtained entirely by a hand calculation. These were checked by a simple machine calculation designed to calculate many results over a wider temperature—volume grid.

The next section presents the specific free-energy formulation relevant to this system. It is followed by the derivation of the equilibrium composition (Saha-type) equations and a discussion of the terms therein. Then the equation of state is derived and discussed and the occupation number equation presented. Finally, the specific method used to calculate numerical results is described, and the results are presented and compared with the experimental results and with those from other calculations.

II. FREE-ENERGY FORMULATION

A. Translational Free Energy

The general expression for the free energy of translation of classical particles is:

$$F_1 = T[Q_1 - (1.5 \ln T + 6.974 + \ln V)Q_2 - 1.5Q_3], \quad (1)$$

where

$$T = kT \text{ in electron volts,}$$

$$V = \text{volume/mole of original substance,}$$

$$Q_1 = \sum_i N_i \ln N_i,$$

$$Q_2 = \sum_i N_i,$$

$$Q_3 = \sum_i N_i \ln M_i,$$

N_i = number of moles of species i /mole of original species,

M_i = molecular weight of species i ,

and the sum is over all nuclear species.

For the case of the H-atom plasma:

$$\begin{aligned} N_{\text{H}} + N_{\text{H}^+} &= 1, \\ N_{\text{H}^+} &= N_e. \end{aligned}$$

Then

$$F_1 = T[N_e \ln(N_e/1 - N_e) + \ln(1 - N_e)] - T(1.5 \ln T + 6.974T + \ln V + 1.5T \ln M_{\text{H}}). \quad (2)$$

The exact expression for the free energy of a perfect Fermi gas of electrons F_3 involves an integral over the Fermi momentum distribution which can only be evaluated numerically. In previous calculations F_3 , a function of a parameter X , was evaluated in three ways. The choice of method was based on the numerical value of the argument X , which is a measure of the degeneracy of the gas.

$$X = 88.664N_e/V T^{3/2}. \quad (3)$$

For $0 \leq X \leq 0.016128$, the electron gas is classical and

$$F_3 = N_e T [\ln(1.1284X) - 1]. \quad (4)$$

For densities around 10^{18} and temperatures around 1 eV, X is of the order of magnitude of 10^{-4} and hence the system is well within the classical region. The above expression then is equivalent to including electrons in the sum in F_1 with the qualification that the electron spin, creating—as it does—twice as many states for the electron, adds a term— $\ln 2$ to the F_3 expression.

B. The Electrostatic Free-Energy (F_4)

From a solution of a linearized Poisson-Boltzmann equation comes the well-known and generously discussed Debye-Huckel expression for the electrostatic free energy:

$$F_4 = (-e^2 LK/3\mathcal{D})\tau(Ka), \quad (5)$$

where

$$K = \text{reciprocal Debye length} = 2(\pi)^{1/2}e(L/DkTV)^{1/2},$$

$$L = \text{ionic strength} = \sum_i N_i z_i^2,$$

$$a = \text{cutoff radius of the ion,}$$

$$\mathcal{D} = \text{dielectric constant (usually assumed to be unity),}$$

$$N_i = \text{concentration of ions with charge } z, \text{ sum is over all charged particles,}$$

$$\tau(Ka) = 3[\ln(1 + Ka) - Ka + \frac{1}{2}(Ka)^2]/(Ka)^3. \quad (6)$$

For high dilution, small (Ka) , $\tau(Ka) \rightarrow 1$ and the point-charge formula is obtained. For this specific system and

⁸ W. L. Wiese, D. R. Paquette, and J. E. Solariski, Phys. Rev. 129, 1225 (1963).

in the units used:

$$\begin{aligned} F_4 &= -\frac{2}{3}(27.216\delta)N_e\tau(Ka), \\ \delta &= Ka_0(a_0 = \text{Bohr radius}), \\ 27.216\delta &= e^2/D(D = \text{Debye length}). \end{aligned} \quad (7)$$

To estimate whether it is necessary to use a cutoff at values of (Ka) relevant to this particular problem, an estimate of the quantity $\tau(Ka)$ was made. The quantity a may be regarded as a radius of exclusion for an electron, preventing it from behaving completely like a classical particle. An expression for a related to a definition of a free electron was developed in previous work.²

$$a(A) = (14.367/E_3)\sum_i z_i N_i / \sum_i N_i, \quad (8)$$

where

$$E_3 = \text{average kinetic energy of the electron} \\ (\text{as a perfect Fermi particle}),$$

$\sum_i Z_i N_i / \sum_i N_i = \text{average positive charge.}$

E_3 for this system has the classical value of $\frac{3}{2}T$. For $T=1$ eV, then $a=9.578$. The expression for the reciprocal Debye length in the units of this problem is

$$K(A^{-1}) = 10.430(2N_e/VT)^{1/2}, \quad (9)$$

where $v = cc/\text{mole}$ of original species, $N_e = \text{number of electrons/mole of original species}$, and $T = \text{electron volts}$. For an electron density of 10^{18} , Ka then is 0.1826 and $\tau(Ka) = 0.833$. Thus, F_4 itself is lowered by 17% by including a finite ion size. Since experimental densities are considerably lower than this and the electrostatic correction itself is quite small compared to the translational energy at these densities and temperatures, the actual calculation was made using the point-charge formula, and an estimate of the size correction was obtained. The cutoff was originally designed to substitute for the correct quantum-mechanical effect on the collective interaction term. There is work in progress elsewhere⁹ evaluating the quantum-mechanical analog of the Debye correction which arises in the rigorous expansion of the partition function for the many-body system treating the electrons as plane waves. The quantum-mechanical term would also be lower than the classical point-charge one and the difference small for the dilute gas.

C. Internal Free-Energy (F_2)

1. General Expressions and Considerations

The total internal free energy of an atomic species comes from its electronic state

$$F_2 = -T \sum_i N_i \ln Q_i, \quad (10)$$

where the sum is over all atomic species with internal structure

$Q_i = \text{electronic partition function of the } i\text{th atomic species,}$

⁹ H. DeWitt and J. Klingert (private communication).

$$Q_i = \sum_k g_{ki} \exp(-E_{ki}/T),$$

$g_{ki} = \text{degeneracy of the } k\text{th electronic state of the } i\text{th species,}$

$E_{ki} = \text{electronic energy of the } k\text{th state of species } i.$

In the choice of values of E_{ki} and of a criterion for terminating the sum over states lie the most difficult and therefore the least satisfactorily resolved aspects of this model. This is really the few-electron subproblem of the many-electron problem treated in this component framework. The simplest idea is, of course, to use the isolated atom energy values. Even these are not too easily available for the many-electron atom. The more dilute the gas, of course, the more justifiable this approximation. As the density increases, these fixed bound-state energies become "energy holes" relative to the energy of the free electron. The latter is the sum of the kinetic energy of a perfect Fermi gas and the potential energy of interaction as approximated by the Debye term. Both of these are density and temperature-dependent. As the density increases, the kinetic energy rises faster than the potential energy. The result is that over a wide region of moderate to high density and moderate to low temperatures, a grossly wrong equilibrium composition is obtained if fixed bound-state energy levels are used. For example, the high-density limit of complete ionization is never attained. Also, there is no contribution to the pressure from these bound-state electrons. It is a big step then to include some kind of density-dependent perturbation of the bound states by the plasma. There are many types of interactions one can consider in this framework. Neutral or even neutral-charge interactions can be approximated by weak, short-range potentials of the Van Der Waals or Lenard-Jones form. This would be equivalent to adding virial coefficient corrections to the ideal classical gas. Another approximate perturbation is to consider the surrounding plasma to confine the electron density on any one atom to a given finite radius equal, for example, to some average interparticle separation. The change in boundary conditions on the atom affects the energy eigenvalues. Finally, as has been mentioned, a direct estimate of the effect of charge interaction on the bound states of any two particles in a plasma can be obtained by replacing the Coulomb potential by a shielded Coulomb potential.

2. Energy Eigenvalues and a Cutoff of States: The H-Atom Partition Function

In this calculation we are considering a low-temperature plasma, i.e., temperatures near 1 eV. At such temperatures, the contribution of the excited states to the partition function is negligible compared to the ground state due to the attenuation of the weighting factor $\exp(-E_n/kT)$ which multiplies each term. This factor has a value of the order of 10^{-5} for the excited states compared to a value of 1 for the ground state. Thus,

even the sum of a large, but finite number of excited states would make a relatively negligible contribution to the partition function. For a low-temperature plasma then, we can consider only the ground state and we do not need to specifically consider how to cut off our sum of states. The only assumption inherent in this approximation is that the number of bound states in a plasma is finite, which is a reasonable physical assumption for any model of plasma-perturbed states. It might be noted, however, that at temperatures when one excited state becomes important, they all do and a physical criterion for cutoff must then be invoked.¹⁰

In considering a plasma at 1 eV then, we need to consider only the ground state, and we are left with the problem of deciding how to calculate the energy of that state. For densities of 10^{19} and less, the effect of short-range interactions should be negligible compared to the effect of the Coulomb interactions of the two-particle bound states with the plasma sea. The question then remains as to whether the long-range interactions are also negligible. If this is so, then the best approximation to the ground-state energy would be to use the constant, unperturbed isolated atom value. There are several calculations in the literature^{3,4} which do this. In these calculations all of the deviations from an ideal gas are in one correction term, the Debye-electrostatic correction. There are really no definite experiments with which to compare theoretical results from these calculations and problem of the best model for the bound states is still quite unresolved. It thus seemed worthwhile at this time to see what the effect on the thermodynamic properties would be if some residual long-range perturbation of the bound states were included in a calculation.

In the model used here, this perturbation is approximated by replacing the Coulomb potential by a shielded Coulomb potential. The energy E_{ni} is then a function of the dimensionless screening length δ and hence is density- and temperature-dependent. The perturbed energy can be expanded as a power series in δ . The expanded energy expression is

$$E_{ni}(\delta) = E_{ni}(0) - Ze^2/D \left[1 - \frac{n^2 \langle r \rangle'}{2!Z} \delta + \frac{n^4 \langle r^2 \rangle'}{3!Z^2} \delta^2 + \dots \frac{n^{2p} \langle r^p \rangle'}{(p+1)!Z^p} \delta^p \right], \quad (11)$$

where n = principal quantum number, $\langle r^p \rangle'$ = average value of p th power of radius, and Z = nuclear charge. The first correction term in this expression has the same magnitude for all states. The value of all higher terms depends specifically on the state through the average value of powers of r appearing in these terms. For the $1s$ state the ratio value of the first to higher terms in this expansion is $1: \frac{3}{4}\delta: \frac{1}{2}\delta^2$. Values of δ in this density-tem-

perature region are of the order of 10^{-3} . Therefore, only the first term in this expansion need be used to correct the zero-order energy level.

With these considerations the partition function for the hydrogen atom becomes

$$Q(\text{H atom}) = 2 \exp(13.595 - 27.216\delta/T)$$

and the corresponding internal free energy is

$$F_2 = -T(1 - N_e) [\ln 2 + (13.595 - 27.216\delta/T)].$$

This expression for F_2 is the result of the model and approximations that have just been discussed. It is valid for a low-density, low-temperature plasma with a model allowing the ground state to be perturbed by the surrounding plasma sea via a screened Coulomb interaction. The calculations and results obtained in the following sections are based on this model. Different models for the perturbation of the bound states would give different expressions for F_2 . The effect of different expressions for F_2 on the calculated properties of the system can be traced. It is one of the aims of this investigation to do so, and Sec. VI C is devoted to this purpose.

III. THE CONDITIONS OF EQUILIBRIUM

A. Definitions and Equations

One of the definitions of a multicomponent system in thermodynamic equilibrium is that the change in Helmholtz free energy with respect to the relative concentrations of all independently varying species be zero for constant volume and temperature, i.e., $(\partial F / \partial N_i)_{V,T} = 0$. The set of coupled nonlinear equations obtained from this condition determine the equilibrium concentration of each species present at a given volume and temperature. The number of such equations is $(N - A - 1)$, where N is the total number of species and A is the number of different nuclei present. The reduction in the number of independent equations from N is due to the fact that the conditions of charge neutrality and stoichiometric balance are imposed upon the system.

The above condition for equilibrium is equivalent to the one for a chemical reaction from which ordinary "equilibrium constants" are obtained. A given reaction occurring in a system such as $A + B = C + D$ has reached equilibrium if

$$\Delta F = F(\text{products}) - F(\text{reactants}) = 0,$$

then

$$\sum_j F_j - \sum_i F_i = 0,$$

where j labels products and i labels reactants. Using the relationship

$$F = -kT (\ln Q_{j_1}^{N_{j_1}} + \ln Q_{j_2}^{N_{j_2}} + \dots - \ln Q_{i_1}^{N_{i_1}} - \ln Q_{i_2}^{N_{i_2}} - \dots) \quad (12)$$

¹⁰ The temperature criterion for ignoring excited states is analyzed in more detail in Appendix I.

and the definition of the equilibrium constant $K_{V,T}$

$$\Delta F = -kT \ln K = 0,$$

then

$$K_{V,T} = \prod_i Q_i^{N_i} / \prod_i Q_e^{N_e}. \quad (13)$$

Thus the equilibrium conditions may also be cast in the form of a series of equations for equilibrium constants, one for each reaction occurring in the system. This also leads to a set of coupled nonlinear equations, each equation being of the "Saha" type. Naturally, if formulated correctly from the same model for the free energy and solved correctly, both the equilibrium constant set of equations and the minimization equations should yield the same composition under the same conditions. Though it is largely a matter of choice, it seems to this author that the set of equations $(\partial F / \partial N_i)_{V,T} = 0$, coming as they do directly from the free-energy expression without any further knowledge needed about the system, are more general, straightforward and flexible for different models of the free energy of a complex multicomponent system. For a system with only one independent variable in which components are linked by one equation, the same single equation will be obtained from both formulations. This is the case for the H-atom plasma, considering only H atoms, protons, and electrons to be present.

Let us now look at the specific equilibrium expression obtained from the total free-energy equation formulated here for a low-temperature H-atom plasma. As will be recalled, F_1 and F_3 are ideal gas terms for nuclei and electrons, F_4 is the correction due to electrostatic interaction, and F_2 is the correction due to the internal structure of the H atom, including the effect of the plasma on the bound states. Choosing the electron concentration, N_e as the independent variable and differentiating each expression, we obtain

$$(\partial F_1 / \partial N_e)_{V,T} = T \ln [N_e / (1 - N_e)], \quad (14)$$

$$(\partial F_3 / \partial N_e)_{V,T} = T (\ln N_e - \ln VT^{3/2} + 4.6067), \quad (15)$$

$$(\partial F_4 / \partial N_e)_{V,T} = -27.216\delta, \quad (16)$$

$$(\partial F_2 / \partial N_e)_{V,T} = T \ln 2 + 13.595 + 27.216\delta(1 - 3N_e) / 2N_e. \quad (17)$$

By adding these four parts, setting them equal to zero and collecting terms, the equilibrium composition equation is obtained:

$$\ln(N_e^2 / (1 - N_e)) = C(V,T) + 27.216\delta(5N_e - 1) / 2N_e T, \quad (18)$$

where

$$C(V,T) = \ln VT^{3/2} - 4.6067 - \ln 2 - 13.595 / T. \quad (19)$$

The exponential form of this equation is the equilibrium constant expression, i.e., the "Saha" equation for this system.

B. Discussion of the Terms in the Equilibrium-Composition Equation

The constant $C(V,T)$ represents the equilibrium constant for an ideal gas with internal degrees of freedom. The remainder of the right-hand side of the equation is the correction to ideal-gas behavior due in part to the electrostatic interactions and in part to the perturbation of the bound states by the plasma. As far as could be determined from the literature, these correction terms *in toto* are what is generally called a "lowering of the ionization potential." The phrase then really means all terms in the equilibrium composition (Saha) equations that are present in addition to those due to the ideal gas with unperturbed internal degrees of freedom. This expression applied to such corrections is a very misleading one. Since we are discussing terms in an equilibrium-composition equation and not the free-energy equation itself, the correction terms should be labeled by their effect on the degree of ionization relative to the ideal-gas composition rather than by what they do to the ionization potential. These are not the same corrections. Ionization energies themselves i.e., bound-state electronic energies relative to a free-electron energy, appear in the free-energy equation. Ionization energies may be raised, lowered or unaltered relative to their values in isolated atoms, depending on the model used for plasma interactions. They also become density- and temperature-dependent. The composition equations are obtained from the density derivatives of the free-energy equation. Thus, the density dependence of the relative energy level shift, as well as the direction of the shift determines the effect it has on the equilibrium composition. A "lowering of the ionization potential" then, in the free-energy equation, need not always lead to an enhancement of ionization calculated from the composition equation.

The criterion for ionization enhancement, is that the total correction term in the composition equation be positive, i.e., of opposite sign from the unperturbed bound-state energy term. In previous calculations for a low-density plasma, i.e., $< 10^{20}$, the correction term came solely from a consideration of electrostatic interactions between ions and free electrons in some approximation, the most common being the Debye-Huckel expression used here or some modification of it. This leads to a correction term in the equilibrium-composition equation of 27.216δ , and is hence positive for all temperatures and densities. For this specific most widely used correction to ideal behavior, then the "lowering of the ionization potential" does lead to an enhanced ionization—hence, the interchangeability of these expressions in much of the literature. That these are, in general, separate effects not necessarily linked for all plasma corrections is one of the main results of the specific calculation made here.

Let us consider what happens when corrections due to density-dependent bound-state energy levels are added

to the Debye correction. For the particular model studied here, the correction term in the equilibrium-composition equation due to the shifting of the ground-state energy is $27.216\delta(3N_e-1)/(2N_e)$. This term alone then enhances ionization only above $\frac{1}{3}$ ionization, even though it comes from a perturbation of the ground state which "lowers the ionization potential" at all electron densities. Other models, giving density-dependent bound-state energies would have other specific behavior. However, the main point illustrated by this specific calculation has general validity. It is incorrect and misleading to examine terms in the free-energy equation alone and from this draw conclusions about the equilibrium-composition equation. We can now see, for example, that it is incorrect to assume an automatic enhancement of ionization from a perturbation that lowers ionization potentials. An additional point illustrated by this calculation is that it is also incorrect to draw conclusions about the magnitude of the composition effect from the magnitude of the effect on the "ionization potential lowering." This latter can be small for a certain density-temperature region, and hence, make a negligible change in the free energy of the system, while its density and temperature derivatives might be large, and hence, the correction to ideal composition, pressure, etc., appreciable. In practice, we are seldom interested in the total free energy itself, but in the various real properties of the system. Thus, it is not meaningful to neglect perturbations simply because they cause negligible energy shifts. As will be seen the specific calculations made here do indeed show that it is possible for a perturbation which causes a negligible energy shift to cause a significant change in composition.

Finally, since bound-state corrections have been ignored compared to the Debye electrostatic correction in reported equilibrium calculations for low-density plasmas, it might be of interest to consider the relative magnitude of these two corrections in this model. We see that for complete ionization, i.e., $N_e=1$, these two terms in the composition Eq. (18) are exactly equal and add to each other. At 20% ionization they are equal and opposite and hence, cancel. For all $N_e<0.2$, the bound-state correction exceeds the Debye correction and is opposite in sign, causing a net inhibition of ionization over the ideal gas value. Only at $\frac{1}{3}$ ionization then, when the bound-state term goes to zero, is it truly negligible compared to the Debye term.

IV. THE EQUATION OF STATE

The pressure is obtained from the volume derivative of the free energy: $(\partial F/\partial V)_{N_e,T}=-P$. The different contributions to the pressure are as follows: Ideal-gas term:

$$P_1 = -(\partial F_1/\partial V)_{N_e,T} = T/V, \quad (20)$$

$$P_3 = -(\partial F_3/\partial V)_{N_e,T} = N_e T/V. \quad (21)$$

The sum of these two terms gives the ideal-gas law

$$PV = \sum_i N_i T,$$

where $T=kT$ in electron volts, $V=\text{cc/mole of H}$, and $\sum_i N_i = (1+N_e)$. The Debye correction gives

$$P_4 = (\partial F_4/\partial V)_{N_e,T} = (-27.216\delta/2V)(2N_e/3). \quad (22)$$

The bound-state correction gives

$$P_2 = (\partial F_2/\partial V)_{N_e,T} = (27.216\delta/2V)(N_H), \text{ where } N_H = (1-N_e). \quad (23)$$

Then the total pressure is

$$P = T(1+N_e)/V + 27.216\delta(N_H - \frac{2}{3}N_e)/2V. \quad (24)$$

The first term in the pressure equation represents the ideal-gas contribution. However, since the total number of particles present at a given temperature and volume are determined from an equilibrium-composition equation which includes interactions, the P, V, T, N_i relationship will be different from an ideal gas even if the first term alone is used to determine the pressure. The equilibrium-condition equations and the equation of state are coupled and must be considered together to get a complete equilibrium picture of the system. The correction from the bound states is in the opposite direction from the electrostatic correction. The Debye correction lowers the pressure relative to the ideal gas. Hence, for a given pressure and temperature, a gas with only electrostatic interaction must be at a higher density than an ideal gas. The bound-state correction adds to the ideal-gas pressure. Then, the total number of particles present at a given pressure and temperature would be less than for the ideal gas. These two corrections are of equal magnitude for 60% ionization. They completely cancel at this point and the system behaves as an ideal gas except for the total number of particles present. For less ionization, the bound-state term exceeds the Debye correction. There would be no bound-state contribution to the pressure unless the explicit dependence of the bound-state energies on density were included in the partition function of the free-energy expression. Thus, if unperturbed energy levels, however accurate, had been used, this dependence would have been absent, and we would again have a situation where a correction to a thermodynamic property is omitted because the term in the free-energy equation from which it originates is small. As we see, there is a wide range of conditions under which the term so omitted is more significant than the one which has been included.

V. THE OCCUPATION NUMBER

Consider the calculation of the number of electrons in a given electronic state of hydrogen, i.e., the occupation number.

The occupation number of a given electronic level is

given by

$$N_{H_i} = \frac{N_H \times \sum_i g_{H_i} \exp(E_{H_i}(\delta)/kT)}{g_{H_i} \exp(E_{H_i}(\delta)/kT)}, \quad (25)$$

where N_H = total concentration of H atom, N_{H_i} = number of electrons in state i of the H atom, g_{H_i} = the degeneracy of state i , and E_{H_i} = the energy of state i . The sum is over all states included in the calculation.

For small values of screening the calculation will be insensitive to the use of corrected energy values in the exponents of this expression. However, as we have indicated, neglecting this correction in the free-energy expression can have a large effect on the equilibrium composition. The occupation number is proportional to the total H-atom concentration. Thus, through the value of N_H obtained from the equilibrium calculation, the use of perturbed energy levels can have a significant effect on the magnitude of the occupation numbers calculated.

VI. NUMERICAL CALCULATION AND RESULTS

A. General Method of Calculation

The single equilibrium-condition equation

$$\ln[N_e^2/(1-N_e)] = \ln VT^{3/2} - 4.6067 - \ln 2 - 13.595/T + 27.216\delta(5N_e - 1)/2TN_e, \quad (26)$$

where

$$\delta = 7.806(N_e/VT)^{1/2}$$

can be used for extensive calculations of the composition over a wide temperature—volume grid. A simple computer program was devised which uses Newton's method to search for the correct value of N_e , given a value of V and T and an initial guess of N_e as input. The sets of N_e , V , and T resulting from the solution of this equation are then used in the equation of state to determine the pressure:

$$P(\text{atm}) = 0.95155 \times 10^6 [T(1+N_e)/V + 27.216(1-5N_e/3)/2V]. \quad (27)$$

Occupation numbers and other thermodynamic quantities such as entropy and internal energy can also be calculated from these results.

B. Specific Calculation for Experimental Conditions

Recently,⁸ the temperature and electron density of a hydrogen plasma was determined by two different experimental methods, the measurement of line intensity and line shapes of several different Balmer emission lines. The most accurately measured line intensity, i.e., the Balmer H_β line, yielded a temperature of 1.052 eV and an electron density of 6.40×10^{16} electrons/cc at a pressure of 1 atm. To correlate measured line intensities with temperature and density, it is necessary to use the results of a thermodynamic equilibrium calculation. The intensity measurement alone cannot determine the den-

sity and temperature independently. Interdependent pairs of these are obtained from some thermodynamic calculation, and the intensity measurement selects the appropriate pair. It is of interest then to see the sensitivity of one member of this pair to different thermodynamic calculation.

We select as input the experimental conditions of 1-atm pressure and a temperature of 1.052 eV and use the two equations given above to calculate the electron density on the model described here. The following procedure was used with a desk calculator to obtain results for this one set of conditions.

Let the variables of the problem be P , V , T , and ρ_e , the electron density. From the equation of state, the volume is expressed as a function of P , T , and ρ_e

$$V = N_0(T + 13.608\delta)/[PN_0 - \rho_e(T - 22.68\delta)], \quad (28)$$

where $\delta = 1.006 \times 10^{-11}(P_e/T)^{1/2}$, N_0 = Avagadro's number, P = pressure (atm)/ 0.95155×10^{-6} , ρ_e = number of electrons/cc, V = volume in cc/mole H atom. The equilibrium condition equation gives N_e as a function of T , V , and ρ_e if we use the above expression for δ .

With these two equations the following method was used to obtain a consistent set of values for the quantities N_e , V , and ρ_e at a $T = 1.052$ eV and a $P = 1$ atm.

1. By means of the equation of state, the volume was calculated for a $P = 1$ atm, $T = 1.052$ eV, and an initial value of $\rho_e = 6.40 \times 10^{16}$. From the calculated volume a value of $N_e = (\rho_e V/N_0)$ was also obtained.

2. Using the value of ρ_e and V obtained from the first calculation and the same value of T , a value of N_e was calculated from the equilibrium equation by a direct search for a solution.

3. The value of N_e obtained from these two equations was compared. If they differed by $> 10^{-4}$, the value of N_e obtained from the equilibrium condition equation was used with the old value of V to calculate a new ρ_e .

4. The new ρ_e was used together with the same P and T to calculate a new V and steps 2 and 3 repeated until the N_e obtained from both equations was the same.

When this was done the following results were obtained: For a $P = 1$ atm and $T = 1.052$ eV, $N_e = 0.1081$; $V = 1.134 \times 10^6$ cc/mole, $\rho_e = 5.74 \times 10^{16}$ electrons/cc and the shielding parameter $\delta = 2.34 \times 10^{-3}$.

C. Analysis and Discussion of Results

The electron density obtained here is 10% lower than that reported from the line intensity measurements. In order to better understand the significance of these results, several comparative calculations were made. To examine the effect of the bound-state correction on the composition, a calculation was made with the same model, except that the energy shift was omitted and the isolated H-atom ground-state energy was used. The

equilibrium equation then becomes

$$\ln[N_e^2/(1-N_e)] = \ln VT^{3/2} - \ln 2 - 4.6067 - (13.595 - 27.216\delta)/T \quad (29)$$

and the pressure becomes

$$P = T(1+N_e)/V - 27.216N_e/3V. \quad (30)$$

When these two equations were solved iteratively in the manner described above, an electron concentration of 0.1175 corresponding to a density of 6.40×10^{16} was obtained. This, then must have been the model used to obtain the "experimental" density reported by Wiese *et al.*⁸ It is seen that omitting the bound-state correction causes an increase of 10% in the electron density calculated at the same pressure. Also, for this degree of ionization, the bound-state correction is three and one-half times as large as the electrostatic correction and is in the opposite direction.

To see what the bound-state correction does to the pressure, the various contributions to the pressure were calculated separately for the T , V , and N_e obtained here. When this was done, it was found that the pressure due to the ideal-gas term was 97.8% of the total pressure, the bound-state correction was 2.4%, while the correction from the Debye term lowered the pressure 0.2%. Thus we have the significant result that, for 10% ionization, the bound-state perturbation is 10 times that of the electrostatic condition.

The electrostatic correction used in this calculation is the Debye expression for classical point charges. For ions of finite size, a factor $T(ka)$ multiplies the free-energy term, where

$$T(ka) = 3[\ln(1+ka) - (ka)^2/2]/(ka)^3 \quad (31)$$

and k is the Debye length and a is the ion size. The magnitude of the ion-size correction was estimated at the conditions of the calculation. For a T of 1.052 eV and a δ of 2.34×10^{-3} , (ka) is 0.04266 and $T(ka)$ is 0.968. F_4 then would have been lowered by 3.2% and have an even small effect. The electrostatic correction to the composition equation would be reduced by 4.4% from the finite size of the ions.¹¹ Since the electrostatic correction is small compared to the kinetic-energy contribution, the finite ion size would have a negligible effect on the composition here but should be considered at higher densities.

Another perturbation of the bound states was also considered; that of the "atom in a box" which had been used previously for high-density calculations. With this model, the energy of the electronic orbitals takes the form

$$E_i = -13.595Z_i^2(1 - X^{-(a_i+B_iX)})/n_i^2, \quad (32)$$

where

$$X = Z_i R / R_{0i},$$

¹¹ See Appendix B for the numerical analysis leading to this result.

R_{0i} = radius at which the H-atom electron in state i has $E_i = 0$,

R = average interparticle distance = $(V/\sum_i N_i)^{1/3}$,

Z_i = effective nuclear charge,

a_i and b_i are parameters in the functional fitting of E versus R curves for the various electronic states in a box of size R .

For 1s state: $a_i = 10.11$ $b_i = 12.43$ $R_{0i} = 0.9701$ Å.

At a volume of about 10^6 cc/mole, corresponding to an electron density of about 10^{17} , the average interparticle distance is about 100 Å, and the effect of a spherical box of this size is about 100^{-1200} , or truly zero. The concentration derivative of the partition function with this perturbation explicitly included was also examined. It also contributes a term of negligible magnitude to the equilibrium condition equation. Thus, a confinement effect of the wave function may be ignored at these densities.

The situation, however, is quite different for the shielded Coulomb potential perturbation of the bound states. The value of the screening parameter, δ , of 2.34×10^{-3} obtained for this system gives a ground-state energy shift of only 0.4%. This is indeed a negligible effect. However, we have seen that including this effect in the calculation causes the electron density to change by 10%, and gives a contribution to the pressure that is 10 times greater than the electrostatic correction. The occupation number for all the H-atom states would also change by 10% since the total concentration of the H atoms is changed by that amount. We are considering a region where the screening is just beginning to be significant and yet the results are affected to an appreciable extent. The numerical results obtained are of course dependent on the model used for the bound-state perturbation. There is as yet no independent experimental verification of which model gives the best results. However, the results of this calculation certainly indicate quite strongly that careful consideration must be given to the bound-state perturbations as well as the electrostatic corrections over a wider region of temperature and density than has heretofore been thought.

ACKNOWLEDGMENTS

The author wishes to express many thanks to Dr. Baxter Armstrong for pointing out the experimental work which engendered this calculation and for many helpful discussions during its progress. She also wishes to thank Daniel Schlosky for writing the IBM-7090 program which mechanized the equilibrium calculation.

APPENDIX A

For a low-temperature plasma, the problem of a physically reasonable criterion for a cutoff may be circumvented because one may use the criterion of cutting off states when the value of the exponential weighting factor $\exp(-E_n/kT)$ becomes negligible. To obtain an esti-

mate of the number of excited states to include by this criterion, the partition function for hydrogen was examined, using isolated energy level values. The use of isolated energy level values is justifiable only for this purpose. This is so because temperatures around 1 eV, and electron densities of 10^{16} – 10^{19} span a δ range of 0.001 to 0.03, which is small enough to make the perturbation of the energies of the first few states quite small. Then

$$Q(\text{H atom}) = \sum_n g_n \exp(-E_n(0)/kT), \quad (\text{A1})$$

where

$$g_n = \text{weighting factor of all states with quantum number } n,$$

$$g_n = 2 \sum_{l=0}^{n-1} (2l+1),$$

$$E_n = -13.595/n^2.$$

Factoring out the ground-state energy the expression becomes

$$Q(\text{H atom}) = \exp(13.595/kT) \sum_n g_n \times [\exp(13.595(1-n^2)/n^2kT)]. \quad (\text{A2})$$

To obtain an estimate of the relative contribution of the ground and excited states numerical values of the H-atom energies were substituted into Q for the first five states. Then

$$Q(\text{H atom}) \times \exp(-13.595/kT)/2 = [1 + 4e^{-10.199/kT} + 9e^{-12.084/kT} + 16e^{-12.745/kT} + 36e^{-13.218/kT} + \dots g_{n_{\text{max}}} - 13.595/kT]. \quad (\text{A3})$$

At $T=1$ eV these terms in the partition function are

$$1 + 4.54 + 10^{-5}(3.275 + 1.124 + 1.0224 + \dots). \quad (\text{A4})$$

From the relative magnitude of the first and higher terms, it is apparent that only the ground state need be included in a calculation at 1 eV. Even if a large number of excited states are presumed present, as long as this number is finite, the sum of their contributions will be small compared to one. However, since the excited state

energies are quite close together and since the higher energy states are increasingly degenerate, the contribution becomes important, they all do, and some criterion other than temperature must be used to determine the cutoff of states. Table I gives an estimate of the relative contributions of the ground and 4 excited states to the partition function, as a function of temperature. It may be seen from this table that the highest temperature for

TABLE I. Ratio of excited-state/ground-state contribution to the partition function.

| Temp. (eV) | 1 | 2 | 3 | 5 | 10 |
|----------------|------|---|----|----|-----|
| % Contribution | 0.01 | 2 | 13 | 50 | 100 |

which only the ground state can be used is about 2 eV. Above this temperature then, a cutoff based on a physical model of the perturbation of the bound states must be used.

APPENDIX B

To examine the effect of the ion size on the composition, the value of $(\partial F_4/\partial N_e)_{V,T}$ was obtained including $T(X)$ in F_4 :

$$F_4 = -\frac{2}{3}(27.216\delta)N_e T(X) \quad (\text{B1})$$

$$\begin{aligned} (\partial F_4/\partial N_e)_{V,T} = & -\frac{2}{3}(27.216\delta) \\ & \times \{ [1 + (N_e/\delta)(\partial\delta/\partial N_e)] \\ & \cdot T(X) + N_e(\partial T(X)/\partial N_e) \}, \quad (\text{B2}) \end{aligned}$$

where

$$\begin{aligned} \partial T(X)/\partial N_e = & 3[1/(1+X) - 1+X]/2X^2N_e \\ & - 3t(X)/2N_e, \end{aligned}$$

$$X = Ka, \text{ and } \partial\delta/\partial N_e = \delta/2N_e.$$

Then

$$\begin{aligned} (\partial F_4/\partial N_e)_{V,T} = & -27.216\delta T(X) \\ & + 27.216\delta T(X) - 27.216\delta R, \\ (\partial F_4/\partial N_e)_{V,T} = & -27.216\delta R. \quad (\text{B3}) \end{aligned}$$

We see that this expression differs from the point charge one by the factor R which is $[1/(1+X) - 1 + X]/X^2$. For an $X=0.04266$, R is 0.956. Thus, the electrostatic correction to the composition equation would be reduced by 4.4% from the finite size of the ions.