NRL Report 6594

# Screened Coulomb Formulation of the Ionization Equilibrium Equation of State

CARL A. ROUSE

*E. O. Hulburt Center for Space Research*

and

*University of California*
*Space Sciences Laboratory*
*Berkeley, California*

September 18, 1967

APPROVED FOR PUBLIC RELEASE - DISTRIBUTION UNLIMITED

**NAVAL RESEARCH LABORATORY**
**Washington, D.C.**

**This page intentionally left blank.**

CONTENTS


| | |
|---|---|
| Abstract | iv |
| Problem Status | iv |
| Authorization | iv |
| INTRODUCTION | 1 |
| FORMULATION | 1 |
| Review of the Modified Saha Equation | 1 |
| Review of CSCP Solutions to the Schrödinger Equation | 2 |
| CSCP Partition Function | 4 |
| CSCP Hydrogenic Ionization Potentials | 5 |
| RESULTS AND DISCUSSION | 5 |
| SUMMARY AND CONCLUSIONS | 8 |
| ACKNOWLEDGMENTS | 9 |
| REFERENCES | 9 |
| APPENDIX — Analytic Expressions for the CSCP Electronic Partition Function | 11 |

## ABSTRACT

The ionization equilibrium equation of state (IEEOS) is formulated relative to the numerical solutions of the Schrödinger equation with the complete screened Coulomb potential (CSCP). A finite electronic partition function and the change in ionization potential with screening radius — the radius of the mean atomic volume — which have been derived elsewhere, are used in the author's modification of the Saha equation. The resulting IEEOS is used for hydrogen and iron, where pressures at high densities and temperature are compared with presures from the equation of state based upon the Thomas-Fermi-Dirac (TFD) statistical model of the atom. The present formulation is completely independent of TFD results; yet it gives very good agreement, for monatomic elements of all $Z$, with TFD pressures at high densities and temperatures, where the TFD results are believed to be reasonable; at low temperatures and densities, where the TFD pressures are either much too high or negative, the IEEOS yields the correct monatomic limit. Furthermore, in the region with $T \approx 1$ eV and $\rho \approx \rho_0$, the normal solid-liquid density, the IEEOS pressures are in good agreement with experimental extrapolations. Consequently, since mixtures of monatomic elements can also be handled with equal ease, the present IEEOS represents a significant improvement over the TFD equation of state.


## PROBLEM STATUS

This is a report of the work accomplished to date on the problem; work on various phases of the problem continues.

## AUTHORIZATION


NRL Problem A01-02
Project RR 004-02-42-5300
Sponsored jointly by the Office of Naval Research
and the National Science Foundation

Manuscript submitted May 18, 1967.

# SCREENED COULOMB FORMULATION OF THE IONIZATION EQUILIBRIUM EQUATION OF STATE

## INTRODUCTION

The ionization equilibrium equation of state (IEEOS) (1-7) will be formulated in terms of screened Coulomb solutions to the Schrödinger equation (8-12). Specific attention will be given to the equation of state (EOS) of hydrogen and iron at high densities and temperatures, where pressures calculated with the IEEOS will be compared to pressures calculated with the equation of state based upon the Thomas-Fermi (TF) and/or Thomas-Fermi-Dirac (TFD) statistical models of the atom.

No review of the well-known TFEOS or TFDEOS will be given. The reader is referred to the reviews by Gombás (13), March (14), and Brush (15,16) with their extensive bibliographies. However, the results given by Cowan and Ashkin (17), Cowan and Kirkwood (18), and in the review by Brush (15) will be used for comparison purposes.

The new contributions of this report are the inclusions of self-consistent electronic partition functions (pf) and ionization potentials (IP) based upon the author's numerical solutions (8) of the Schrödinger equation (SE) with the complete screened Coulomb potential (CSCP) (9-12). The quantities derived are used in the author's modification of the Saha equation (6).

In this report we will formulate the CSCP-IEEOS with a review of the modified Saha equation (MSE) (or modified ionization equation); then we will review the CSCP solutions to the SE with the derivation of expressions for the hydrogenic electronic partition function and ionization potentials as a function of effective screening radius. We will next present IEEOS results and a discussion of hydrogen and iron at high densities and temperatures.

Clearly, the temperature-density regions of astrophysical interest for the application of the present equation of state are the photospheres, the envelopes, and in the cores of those stars below nuclear densities.

## FORMULATION

In the present formulation all applications to atoms (ions) with two or more bound electrons will be developed as first-order approximations, using the independent electron picture of the many-electron atom. Furthermore, in the high-density region the IEEOS itself will be considered a first-order formulation for a monatomic gas, relative to the TFDEOS as a zero-order formulation. In general, the word "ion" will be used, where a neutral atom will be an "ion" with zero charge.

### Review of the Modified Saha Equation

In Ref. 6 the MSE was given by

$$\frac{C_j}{C_{j+1}} = P_e \, K_{j+1}(T) \, \Phi_j(\rho) \ , \tag{1}$$

where the $C_j$'s are the concentrations of the various ionic species (1,2); $P_e$ represents the electron pressure derived from Maxwell-Boltzmann statistics (MBS), $K_{j+1}(T)$ defines the standard Saha equilibrium constant, and $\Phi_j(\rho)$ expresses the postulated probability that a $j$th ion can exist at a density $\rho$ in a mean atomic volume of radius $r_0$. In expanded form Eq. (1) becomes

$$\frac{C_j}{C_{j+1}} = P_e \frac{h^3}{2(2\pi m_e)^{3/2}\ (kT)^{5/2}} \frac{u_j}{u_{j+1}} \left[\exp\left(I_j/kT\right)\right] \Phi_j(\rho), \tag{2}$$

where $j = 0, 1, 2, \ldots, Z$; the $u_j$'s are the electronic partition functions of ion $j$; and $I_j$ is the difference in the ground-state energies of ions $j$ and $j+1$, i.e., the ionization potential of ion $j$. The other symbols have their standard meanings.

Given a density and temperature, the method for the complete solution of the MSE is that derived by the author (1,2). Starting with Eq. (2) the present physical problem for a mixture of monatomic elements is the derivation of expressions for $u_j(\rho, T)$, $I_j(\rho, T)$, and $\Phi_j(\rho)$ which represent a first-order many-body interaction of the bound electron with the nucleus.

In the next part of this section the CSCP will be considered as a representative first-order, many-body potential (19-23).

## Review of CSCP Solutions to the Schrödinger Equation

We consider the SE with the CSCP, where the dielectric constant of the medium is equal to 1.0. As in Refs. 9 and 11 we make the standard transformations

$$x = 2Zr/a_0\lambda, \tag{3}$$

and

$$E_\lambda = -\frac{Z^2\ \mu e^4}{2\hbar^2}\ \frac{1}{\lambda^2} \tag{4}$$

and obtain the usual hydrogenic radial SE with $\lambda$ in place of $n$, or,

$$\frac{d^2R}{dx^2} + \frac{2}{x}\frac{dR}{dx} - \left[\lambda v(x) + b^2 + \frac{\ell(\ell+1)}{x^2}\right] R = 0\ , \tag{5}$$

with

$$v(x) = \begin{cases} v_i(x) = -\left(\dfrac{1}{x} - \dfrac{1}{d+a}\right), & 0 \leqq x \leqq a \\[2ex] v_0(x) = -\dfrac{d}{d+a}\ \dfrac{\exp\left[(a-x)/d\right]}{x}\ , & x \geqq a\ , \end{cases} \tag{6}$$

where $\lambda$ is the CSCP quantum number (qn); $d$ and $a$ are the values of $D$ and $A$ in $x$-space, and $b^2$ is a constant to be designated. In the analytic Coulomb solutions $b^2 = 1/4$. In $r$-space $D$ is the screening radius and $A$ is the mean minimum radius of the ion atmosphere, where

$$\frac{ZD}{a_0} = \frac{\lambda d}{2} \tag{7a}$$

and

$$\frac{ZA}{a_0} = \frac{\lambda a}{2} . \tag{7b}$$

The numerical method of the solution to Eq. (5) is that developed by the author. The wave function $R(x)$ and the slope of the wave function $m(x) = dR/dx$ are simultaneously expanded in a Taylor series between space steps, to the cubic terms, with the first and higher derivatives of the slope defined by the SE. Exact initial values are obtained from a series solution of the SE without $\exp(-x/2)$ factored out. We write the series solution in the form

$$R(x) = x^{\ell} \phi(x), \tag{8}$$

with

$$\phi(x) = \Sigma a_k x^k, \quad a_0 \neq 0. \tag{9}$$

Letting $(i)$ indicate the $i$th derivative, the initial values are given by

$$R_{n,\ell}^{(i)}(0) \equiv i!\, a_{i-\ell}, \tag{10}$$

where $a_{i-\ell} = 0$ for $i < \ell$. From the series solution the $a$'s are equal to

$$a_1 = -\frac{\lambda}{2(\ell+1)} a_0$$

and (11)

$$a_{t+1} = \frac{b^2 a_{t-1} - \lambda a_t}{(t+1)(2\ell+2+t)}, \quad t \geqq 1,$$

with

$$b^2 = \frac{1}{4} + \frac{\lambda}{d+a} .$$

All numerical solutions were obtained with $a_0 = 1.0$. The final values of this second constant in $r$-space were obtained from other physical considerations, as discussed in Ref. 9 and reviewed below.

Since the CSCP yields wave functions with the same shapes as Coulomb wave functions, the standard Coulomb designations are used.

A simple analytic fit to the CSCP q.n.'s for $s$-states is given by

$$\frac{\lambda_{n,s}}{n} \approx 1 + Cw - \left[\left(1 - \frac{2a}{d}\right)(0.525\, w^2 + 0.14\, w^3)\, e^{-w}\right], \tag{12}$$

with $w = n/d \lesssim 1.0$ and $0 \leqq a \leqq d$; $C = C_1 = 2/[1 + (a/d)]$ for $w \lesssim 1/12$, and $C = C_2 = 2[1 - (a/2d)]$ for $w \gtrsim 1/12$. For states with $\ell > 0$ Eq. (12) also gives $\lambda_{n,\ell}$ accurately for $D \gtrsim 3a_0 n^2/2Z$, which is about the same range above for $\lambda_{n,s}$. A more general analytic fit is discussed in Refs. 7 and 11.

The mean position of the electron in Coulomb $s$-states is given by

$$\bar{r}_n = 3a_0 n^2/2Z . \tag{13}$$

This happens to be near the critical screening radius for all CSCP solutions of interest. Note that this was deduced intuitively in the supplement of Ref. 7.

In Refs. 9 and 11 it is concluded that the CSCP yields an infinite number of bound states; hence, there is no explicit maximum bound principal quantum number (19,20,24-27). To replace this idea the concept of the relative probability of a screened Coulomb state is introduced in Ref. 9. Using the basic assumption that the relative charge probability density in $r$-space be proportional to the relative charge probability density calculated in $x$-space for $s$-states (9,28), the relative total probability of the screened to the Coulomb (unscreened) state is derived as

$$\Phi_{n,\ell}(\lambda, D, A) = \frac{\lambda^{2\ell+1} N(\lambda, \ell, d, a)}{n^{2\ell+1} N(n, \ell)} , \tag{14}$$

where the $N$'s are the corresponding normalization integrals calculated in $x$-space.

The analytical fit to the mean $\Phi$-function is given by

$$\Phi_{n,\ell}(\lambda, D, A) \approx \Phi_n(D) = \exp\left[-\left(\frac{\delta a_0 n^2}{ZD}\right)^m\right], \tag{15}$$

with $m = 1$ for $D \geqq \bar{r}_n$, $1 < m \lesssim 3$ for $D < \bar{r}_n$, and $\delta = 1.5$. If we define an effective maximum bound state as that state for which $\Phi = 1/e$, call it $n^*$, and if we define a maximum detectable level as that state for which $\Phi = 0.1$, call it $n_m$, then there is an excellent correlation between the present CSCP solutions with $A = D/2$ and the drop in intensity of hydrogen lines in the solar atmosphere — provided an effective screening radius is identified with the radius of the mean atomic volume $r_0$ (10). In addition, there is good agreement with the disappearance of the Balmer lines from laboratory hydrogen at 21°K (29). At the densities and temperatures of the solar photosphere and chromosphere the Debye radius leads to an error of one order of magnitude for the disappearance of $H$-lines.

Consequently, in what follows we will focus attention on CSCP solutions with $A = D/2$ and $D = r_0$. To obtain better agreement near $\Phi = 1/e$ we will use $\delta = 1.7$ (instead of 1.5) in the $\Phi$-function.

Now with $D = r_0$ and $\delta = \gamma$ the CSCP relative probability of a state — applied to the ground state — is in excellent agreement with the probability that an ion can exist at a density $\rho$. This was postulated in Ref. 6! Moreover, solutions with $A = D$, and the change in $\Phi_j$, deduced in the supplement of Ref. 7 for $r_0 = \bar{r}_n$ agree almost exactly! (See Ref. 9.)

## CSCP Partition Function

In Ref. 9 a finite electronic partition function is defined by

$$u^{\mathrm{CSCP}} = 2 \sum_{n,\ell} \Phi_{n,\ell}(\lambda, D, A) \exp(-E_\lambda/kT), \tag{16}$$

where the density-dependent $\Phi$-function is used to modify the Boltzmann factor. Two approaches to deriving a useful analytic expression are: (a) if $n^*$ is equal to or less than, say 10, then sum from $n = 1$ to $n = n^*$ and approximate the remainder by integration from $n^*$ to infinity, or (b) if $n^* > 10$, then approximate the sum by an integration throughout.

Furthermore, since the eigenvalues for states with $\ell > 0$ are about equal to those with $\ell = 0$ (and fixed $n$) until $D \lesssim \bar{r}_n$, we can use the Coulomb degeneracies (Refs. 9 and

11). From this point of view the integral and sum, plus integral forms of the p.f., have been derived (Ref. 12 and Appendix) for the useful hydrogenic approximation to the many-electron atom — analogous to the form obtained by Fowler (30) — by using the analysis of the gamma function given by Copson (31). There obtains

$$u_j = w_j + 5.53 \times 10^{11} \; w_{j+1} (Z'D)^{3/2} \exp(-I_j/kT), \tag{17}$$

where $w_j$ is the degeneracy of the ground state, $Z'$ is the core charge $(Z' = j+1)$, and $I_j$ is the ionization potential of ion $j$. This analytic CSCP p.f. is a little less in magnitude than the hydrogenic p.f.'s derived by Fowler (30) based upon the Urey-Fermi excluded volume and Planck's choice of an ionic volume.

However, since a better approximation for the energy levels between the ground state and $n^*$ is given by $E_\lambda \approx 0.9\, I_j$, the actual CSCP integral partition function used is given by

$$u_j = w_j + w_{j+1} (Z'D)^{3/2} [4.441^{11} \exp(-0.9 I_j/kT) + 1.089^{11} \exp(-I_j/kT)]. \tag{18}$$

In the approach (a), a sum plus integral, the second term of Eq. (18), in parentheses, is used for the integral remainder.

In the present IEEOS calculations the integral form of the p.f., Eq. (18), is used in mixture calculations; and the sum plus integral form, Eq. (A6) in the Appendix, as well as the integral p.f., are used for single elements.

## CSCP Hydrogenic Ionization Potentials

The many-electron hydrogenic ionization potentials are generalized from the CSCP ground state eigenvalue as a function of screening distance $D$. From solutions with $A = D/2$ a fit to the $1s$ eigenvalues is expressed by

$$|E_{1,s}(D)| \approx \frac{Z^2 \mu e^4}{2\hbar^2} \left[ \left(1 + \frac{C_2 a_0}{ZD}\right)^2 + C_3 \left(\frac{a_0}{ZD}\right)^3 \right]^{-1} = I_Z \left[ \left(1 + \frac{C_2 a_0}{ZD}\right)^2 + C_3 \left(\frac{a_0}{ZD}\right)^3 \right]^{-1}, \tag{19}$$

with $C_2 = 0.71248$, $C_3 = 6.4364$, and $I_Z$ equal to the theoretical ionization potential of the actual hydrogenic ion with nuclear charge $Z$. For the present first-order generalization we use Eq. (19) with $Z$ replaced by $Z'$ and with $I_Z$ replaced by $I_j$, the theoretical ionization potential for the isolated ion or the observed ionization potential obtained from a plasma at very low density (32). In the next section we will apply the above concepts to IEEOS calculations for hydrogen and iron.

## RESULTS AND DISCUSSION

If we considered only the equilibrium between the actual hydrogenic ion and the stripped nucleus, we would be ready to compute the equation of state using Eq. (16) without the $\Phi_j(\rho)$ in Eq. (2). However, in a first-order generalization to the many-electron ion we cannot use Eq. (16), since we do not have screened Coulomb solutions for many-electron ions. In the present approximate formulation we use the CSCP p.f., as given in Eq. (18), in the standard Saha equilibrium "constant," and we let the $\Phi_j(\rho)$ represent the probability, given a $(j+1)$ ion, of finding a $j$ ion in the ground-state configuration of the isolated ion. As indicated above and in Ref. 6 we use, for each ion, the $\Phi_n(D)$ of the outermost orbital for $\Phi_j(\rho)$. In general, we normalize the ground-state critical screening distances to 1.7 times the radius of the maximum charge probability density of each shell, as determined by self-consistent field calculations (33).

For configurations of two or more bound electrons we key on the closed-shell configurations of *He*, *Ne*, *Ar*, and *Kr* from Slater (33), with extrapolations for *Xe* and *Rn*. The respective values for $\delta$ used in Eq. (15) are, beginning with the value for the hydrogenic ion, 1.70, 1.93, 3.07, 4.63, 6.46, 6.80, 8.80, and 8.0. Consequently, our probability of an ion existing in a mean atomic volume of radius $r_0$ is, from Eq. (15),

$$\Phi_j(\rho) \equiv \Phi_j(r_0) = \exp\left[-\left(\frac{\delta_p a_0 n^2}{Z' r_0}\right)^m\right], \tag{20}$$

with $Z'$ equal to the net core charge; the $\delta_p$ for $p$-bound electrons arranged in shells with $n = 1$ to 7 are given by $\delta_1 = 1.70$, $\delta_2 = 1.93$, $\delta_{3-10} = 3.07$, etc.

Now, using the CSCP p.f., Eq. (18) (or the sum plus integral), the generalized one-electron screened ionization potential, Eq. (19), and the $\Phi_j$-probability, Eq. (20), the IEEOS was calculated for hydrogen and iron at high densities and temperatures. The results are graphically compared to the TF and the TFDEOS from Cowan and Ashkin (CA) (17), Cowan and Kirkwood (CK) (18), and Livermore-RAND (L-R) results reported by Brush (15).

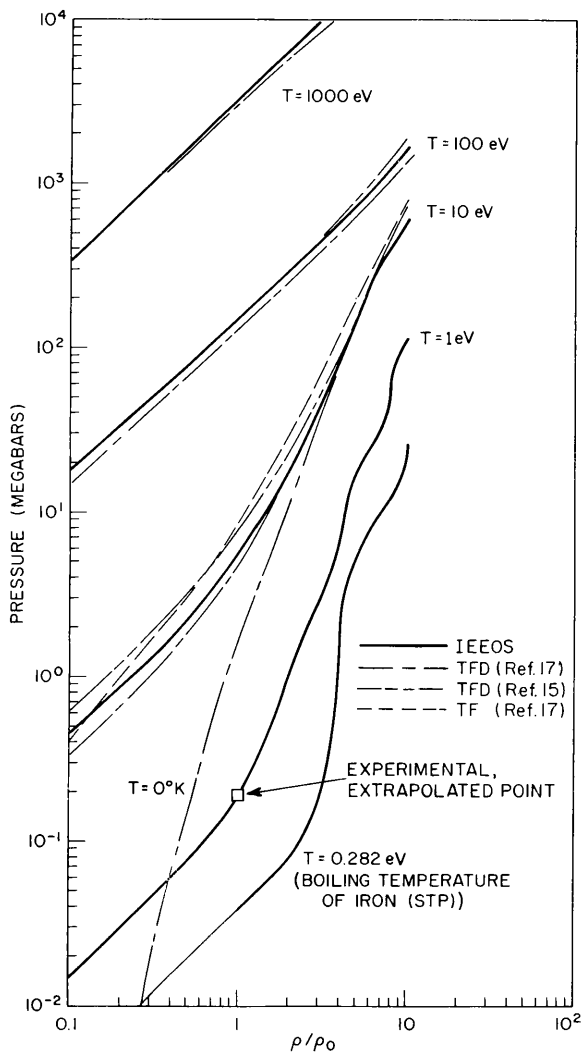


Fig. 1 - Pressure versus relative density for iron, from IEEOS, TF and TFDEOS ($\rho_0$ = 7.85 g/cc)

For comparison with the standard total TFDEOS the ions are treated as satisfying MBS, and the free or mobile electrons are considered as satisfying Fermi-Dirac statistics (FDS). For the free electrons the formulas of Tolman (34) are used.

Previous IEEOS calculations at low densities are not significantly changed in the present formulation; hence, they will not be reported here.

Figures 1 through 4 present the IEEOS results and other TF and TFD results. Figure 1 shows plots of IEEOS pressure versus density for iron, at five temperatures. The value of $\rho_0$ for iron is 7.85 g/cc. Also shown are the results from CA and L-R. Note the very good agreement with L-R results for $T \gtrsim 10$ eV.

Note particularly for $T = 1$ eV and $\rho/\rho_0 = 1$, where the TFD pressure is above the 0°-K curve, that the present theoretical IEEOS pressure is in very good agreement with the L-R experimental extrapolation — indicated by the square in Fig. 1.

The curve for $T = 0.282$ eV — the boiling point of iron — is included to provide comparison with that which is

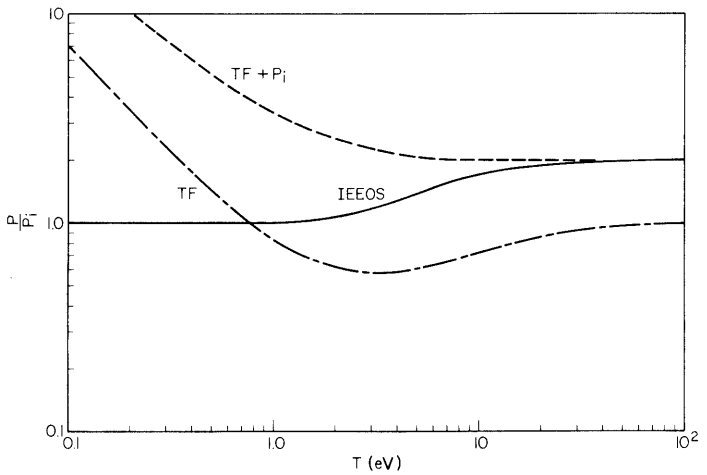


Fig. 2 - Total pressure/ion pressure versus temperature for hydrogen at $\rho$ = 0.085 g/cc (or deuterium at 0.17 g/cc) from the IEEOS and TFEOS

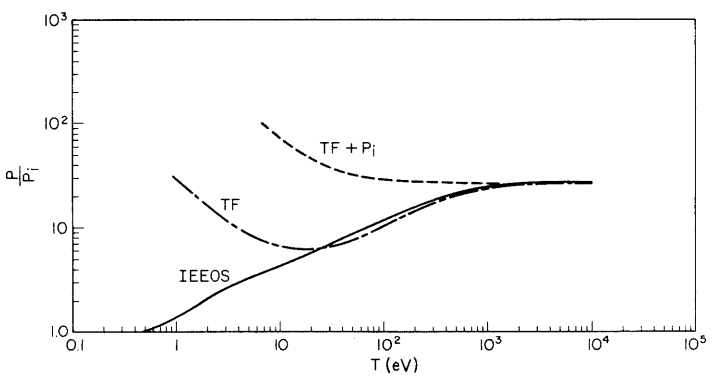


Fig. 3 - Total pressure/ion pressure versus temperature for iron at $\rho = \rho_0$ = 7.85 g/cc from the IEEOS and TFEOS

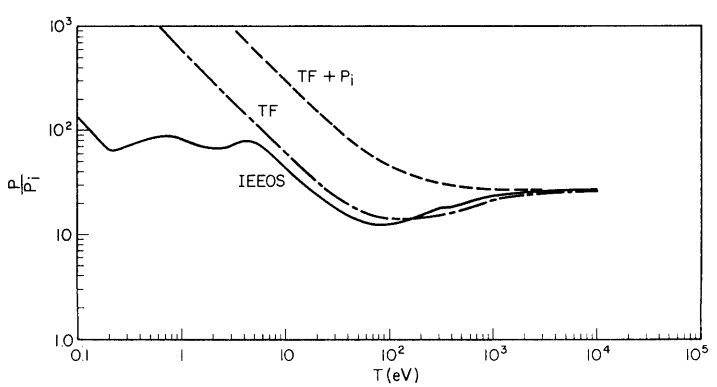


Fig. 4 - Total pressure/ion pressure versus temperature for iron at $\rho = \rho_0$ = 78.5 g/cc from IEEOS and TFEOS

well known. At $T \leq 0.282$ and $\rho = \rho_0$ the theoretical pressure should be 1 atmosphere ($10^{-12}$ megabars). In this region a monatomic gas approximation cannot be correct — one formulation can only be less in error than another formulation. In the present cases the IEEOS results are about two orders of magnitude less in error than the TFDEOS. Furthermore, since the IEEOS yields the correct monatomic results at low $T$ and $\rho$, the present results will be compatible with a theoretical solution of the condensation problem.

The wiggles in the two low-$T$ IEEOS curves of Fig. 1 result from the dominant density ionization in this $T$-$\rho$ region. See Fig. 2 of Ref. 6 for the correlations with the calculated number of "free" or mobile electrons.

Finally, for Fig. 1, the region where $\rho < \rho_0$ and $T < 0.282$ eV is an unstable region where the iron atoms cannot exist in equilibrium as a gas.

Figure 2 presents $P/P_i$ versus $T$ for hydrogen at $\rho = \rho_0$ (= 0.085 g/cc) or for deuterium at $\rho = 0.17$ g/cc. $P_i$ is the ion pressure, with $P_i = N_i kT$. $P$ is the total ion pressure plus FDS electron pressure; or, $P/P_i = 1 + (P_e^{\mathrm{FDS}}/P_i)$ is the value plotted for the TF curve. The other results of CK and the results of Harris, et al. (35), can be added to Fig. 2. Note that in both cases negative pressures (3) obtain at low temperatures due to the use of the first-order negative Debye-Hückel (DH) pressure correction, which becomes larger than the MBS gas pressure. Also, an unrealistic correction to the ionization potential (35) is used based upon the confinement of an atom in a spherical box (36).

In the present hydrogen results the classical DH pressure correction will not lead to negative pressures at the normal density $\rho_0$. However, the recent results obtained from more accurate solutions of the screened Coulomb problem show that the radius of the mean atomic volume is the more fundamental screening quantity — not the DH radius. Consequently, analysis and results based upon DH theory are open to question.

Figures 3 and 4 present $P/P_i$ for iron at $\rho = \rho_0$ (= 7.85 g/cc) and $\rho = 10\ \rho_0$, respectively. In Fig. 4 the wiggles in the IEEOS curve at low $T$ reflect nonlinear changes in $P$ with $T$ at constant $\rho$. (See also Fig. 1.)

Finally, relative to minimizing the "free energy," the basic quantity is the partition function itself. Consequently, for a system where the complete p.f. is not known, nothing is gained physically by operating on uncertain input. Once approximations are needed, minimizing the free energy appears to be using a sledge hammer to crack a peanut.

## SUMMARY AND CONCLUSIONS

The IEEOS has been formulated relative to recent screened Coulomb solutions to the Schrödinger equation which yield a self-consistent, hydrogenic, finite electronic partition function and density-dependent ionization potentials. The results have been used in the complete solution to the modified Saha equation to obtain EOS data for hydrogen and iron.

Pressures calculated with the IEEOS are in good agreement with the TFDEOS pressures in the high-temperature, high-density regions where the TFDEOS results are believed to be reasonable; the IEEOS yields the correct monatomic limit at the low-temperature, low-density regions where TFDEOS pressures are either much too high or become negative. Furthermore, IEEOS pressures for $T \approx 1$ eV and $\rho \approx \rho_0$ are in good agreement with experimental extrapolations. These agreements apply to elements of all $Z$.

In the present formulation no attempt was made to normalize results to published data: the present formulation is completely independent of the TF or TFD models of the atom.

Having developed a formulation that gives values comparable with accepted values at high and low densities, the next steps will involve the use of FDS in the MSE, real-atom ion contributions, higher-order corrections to the pressures, and self-consistent internal energies.

In conclusion, because of the present results at low and high temperatures and densities and because the IEEOS for a mixture of any number of monatomic elements can be calculated with equal ease, the IEEOS based upon the screened Coulomb interaction of electrons bound to real atoms represents a significant improvement over the equation of state based upon the Thomas-Fermi-Dirac statistical model of the atom.

## ACKNOWLEDGMENTS

With great pleasure, I acknowledge the cooperation and assistance of the E. O. Hulburt Center Staff and the Technical Information Division of the Naval Research Laboratory in the preparation of this manuscript.

This research was conducted while the author was an E.O. Hulburt Research Appointee supported by the Office of Naval Research and the National Science Foundation.

## REFERENCES

1. Rouse, C.A., Ap. J. 134:435 (1961)

2. Rouse, C.A., Ap. J. 135:599 (1962)

3. Rouse, C.A., Ap. J. 136:636 (1962)

4. Rouse, C.A., Ap. J. 136:665 (1962)

5. Rouse, C.A., Ap. J. 137:1286 (1963)

6. Rouse, C.A., Ap. J. 139:339 (1964)

7. Rouse, C.A., "Calculation of Stellar Structure Using an Ionization Equilibrium Equation of State," Report UCRL 7820-T, April 1964; Report UCRL 7820, rev. 1, July 20, 1964; Report UCRL 7820, rev. 1 supplement, Jan. 7, 1965

8. Rouse, C.A., "Accurate and Stable Numerical Solutions to the Schrödinger Equation," Feb. 7, 1966; APS Bull. 11:356 (1966); NRL Report 6558, published in the March 1967 issue of J. of Math and Phys. 46:63 (1967)

9. Rouse, C.A., "A Finite Electronic Partition Function from Screened Coulomb Interactions," June 21, 1966; revised Jan. 4, 1967 as NRL Report 6556; Physical Review (to be published)

10. Rouse, C.A., Nature 212:803 (1966); APS Bull. 12:32 (1967)

11. Rouse, C.A., "Screened Coulomb Solutions of the Schrödinger Equation," June 21, 1966; revised Feb. 14, 1967; Phys. Rev. 159:41 (1967)

12. Rouse, C.A., "The Screened Coulomb Electronic Partition Function," Mar. 8, 1967, for the 8th Int. Conf. on Phenomena in Ionized Gases, Vienna, Austria

13. Gombás, P., "Die Statistische Theorie des Atoms und Ihre Anwendungen," Wien: Springer-Verlag, 1949

14. March, N.H., "The Thomas-Fermi Approximation in Quantum Mechanics," in "Advances in Physics," Phil. Mag. Suppl. 6:1-101 (1957)

15. Brush, S.G., "Equation of State. A Survey of the Thermodynamic Properties of Matter at High Pressures and Temperatures," University of California, Lawrence Radiation Laboratory (Livermore) Report UCRL-7437, June 12, 1964

16. Brush, S.G., "Theories of the Equation of State of Matter at High Pressures and Temperatures," in "Progress in High Temperature Physics and Chemistry," Vol. 1, Carl A. Rouse, editor, London, New York: Pergamon, 1967

17. Cowan, R.D., and Ashkin, J., Phys. Rev. 105(No. 1):144-157 (Jan. 1, 1957)

18. Cowan, R.D., and Kirkwood, J.G., J. Chem. Phys. 29(No. 2):264-271 (Aug. 1958)

19. Ecker, G., and Weizel, W., Ann Physik 17:126 (1956)

20. Margenau, H., and Lewis, M., Rev. Mod. Phys. 31:569 (1959)

21. Hill, T.L., "An Introduction to Statistical Thermodynamics," Reading, Mass: Addison-Wesley, 1960

22. Brayles, A.A., et al., Phys. Rev. Letters 10:319 (1963)

23. Ecker, G., and Kröll, W., Phys. Fluids, 6:62 (1963)

24. Harris, G.M., Phys. Rev. 125:1131 (1962)

25. Rouse, C.A., 6th Int. Conf. on Ionization Phenomena in Gases, Paris, Vol. 1, p. 225, 1963

26. Smith, C.R., Phys. Rev. 134:A1235 (1964)

27. Schey, H.M., and Schwartz, J.L., Phys. Rev. 139:B1428 (1965)

28. Rouse, C.A., "Numerical Solutions of the Schrödinger Equation with the Complete Screened Coulomb Potential," Report UCRL 12101, Apr. 5, 1965

29. Shrum, G.M., Proc. Roy. Soc. A. 105:259 (1924)

30. Fowler, R.H., "Statistical Mechanics," Cambridge: Cambridge Univ. Press, 1936

31. Copson, E.T., "An Introduction to the Theory of Functions of a Complex Variable," Cambridge: Cambridge Univ. Press, 1935

32. Allen, C.W., "Astrophysical Quantities," 2nd ed., The Althone Press, 1963

33. Slater, J.C., "Quantum Theory of Atomic Structure," Vol. 1, Table 8-3, New York: McGraw-Hill, 1960

34. Tolman, R.C., "The Principles of Statistical Mechanics," Oxford: Oxford Univ. Press, 1938

35. Harris, G.M., Roberts, J.E., and Trulio, J.G., Phys. Rev. 119:1832 (1960)

36. de Groot, S.R., and ten Seldam, C.A., Physica 12:669 (1946)

## APPENDIX

## ANALYTIC EXPRESSIONS FOR THE CSCP ELECTRONIC PARTITION FUNCTION

The analysis in this appendix is taken from Rouse (12). Analytic expressions for the CSCP electronic p.f., Eq. (16), can be derived in a manner similar to that used by Fowler (30). The approximate p.f. is defined by

$$u = 2 \sum_{n=1}^{\infty} n^2 \Phi_n \exp(-E_\lambda/kT) , \tag{A1}$$

where $\Phi_n$ is the analytic approximation to $\Phi_{n,\ell}(\lambda, D, A)$, Eq. (15), and the differences in the energies of $\ell$ states are neglected. We first consider the two complete integral approximations to the sum in Eq. (A1). In this approximation the sum is replaced by an integration from zero to infinity; or, for no electrons or one excited electron,

$$\begin{aligned} u &\approx w + 2 \int_0^{\infty} n^2 \Phi_n \exp(-E_\lambda/kT)\, dn \\ &= w + 2 \int_0^{n^*} n^2 \Phi_n(m=1) \exp(-E_\lambda/kT) + 2 \int_{n^*}^{\infty} n^2 \Phi_n(m=3) \exp(-E_\lambda/kT) , \end{aligned} \tag{A2}$$

where $w$ is the degeneracy of the ground state. If we now assume that for the highly excited states $E_\lambda \approx I_j$, the ionization potential of the $j$th ion (atom), then we can take $\exp(-I_j/kT)$ outside the integral sign. Next, setting $t = (\delta a_0/ZD)^m n^{2m}$ and $s = 3/2m$, Eq. (A2) becomes

$$u_j = w_j + 2 \left(\frac{ZD}{\delta a_0}\right)^{3/2} e^{-I_j/kT} \left[ \frac{1}{m} \int_0^1 e^{-t} t^{(s-1)}\, dt + \frac{1}{m} \int_1^{\infty} e^{-t} t^{(s-1)}\, dt \right] . \tag{A3}$$

From Copson's discussions (31) of the gamma function,

$$\Gamma(s) = \int_0^{\infty} e^{-t} t^{(s-1)}\, dt ,$$

we can evaluate the integrals at once. Copson shows that

$$\Gamma(s) = \Psi(s) + \sum_{r=0}^{\infty} \frac{(-1)^r}{r!(s+r)} ,$$

where

$$\Psi(s) = \int_1^{\infty} e^{-t} t^{(s-1)}\, dt$$

and

$$\sum_{r=0}^{\infty} \frac{(-1)^r}{r!(s+r)} = \int_0^1 e^{-t}\, t^{(s-1)}\, dt \ .$$

Using the appropriate values of the gamma function for $m = 1$ and $3$, then in evaluating the p.f. for $\delta = 1.7$ Eq. (A3) becomes, in the one-electron, hydrogenic approximation to the many-electron ion (atom),

$$u_j^{(1)} = w_j + 5.53 \times 10^{11}\ w_{j+1}(Z'D)^{3/2} \exp(-I_j/kT)\,, \tag{A4}$$

where $Z'$ is the net core charge and $w_j$ is the ground-state degeneracy for ion $j$.

A better approximation for the eigenvalues for $n \lesssim n^*$ is $E_\lambda \approx 0.9\ I_j$. With this approximation we have different exponential functions with each integral in Eq. (A3). Proceeding as above we obtain

$$u_j^{(2)} = w_j + w_{j+1}(Z'D)^{3/2}\ [4.441^{11} \exp(-0.9\ I_j/kT) + 1.089^{11} \exp(-I_j/kT) \ . \tag{A5}$$

For the sum-plus-integral form for the p.f.,

$$u_j^{(3)} = w_j + 2w_{j+1} \sum_{n=2}^{n^*} n^2\, \Phi_n \exp(-E_n/kT) + w_{j+1}(Z'D)^{3/2}\ 1.089^{11} \exp(-I_j/kT)\,, \tag{A6}$$

where $E_n \approx I_j\ [1 - (1/n^2)]$. In practice, if $n^* \leqq 10$, Eq. (A6) is used; otherwise Eq. (A5) is used.

Security Classification

**DOCUMENT CONTROL DATA - R & D**

*(Security classification of title, body of abstract and indexing annotation must be entered when the overall report is classified)*

| | |
|---|---|
| 1. ORIGINATING ACTIVITY *(Corporate author)*<br>Naval Research Laboratory<br>Washington, D.C. 20390 | 2a. REPORT SECURITY CLASSIFICATION<br>Unclassified<br>2b. GROUP |

3. REPORT TITLE

SCREENED COULOMB FORMULATION OF THE IONIZATION EQUILIBRIUM EQUATION OF STATE

4. DESCRIPTIVE NOTES *(Type of report and inclusive dates)* A report of the work accomplished to date on the problem; work on other phases continues.

5. AUTHOR(S) *(First name, middle initial, last name)*

Carl A. Rouse

| | | |
|---|---|---|
| 6. REPORT DATE<br>September 18, 1967 | 7a. TOTAL NO. OF PAGES<br>16 | 7b. NO. OF REFS<br>36 |
| 8a. CONTRACT OR GRANT NO.<br>NRL Problem A01-02<br>b. PROJECT NO.<br>Project RR 004-02-42-5300<br>c.<br>d. | 9a. ORIGINATOR'S REPORT NUMBER(S)<br>NRL Report 6594<br>9b. OTHER REPORT NO(S) *(Any other numbers that may be assigned this report)* | |

10. DISTRIBUTION STATEMENT

Distribution of this document is unlimited.

| | |
|---|---|
| 11. SUPPLEMENTARY NOTES | 12. SPONSORING MILITARY ACTIVITY<br>Department of the Navy (Office of Naval Research), Washington, D.C. 20360 |

13. ABSTRACT

The ionization equilibrium equation of state (IEEOS) is formulated relative to the numerical solutions of the Schrödinger equation with the complete screened Coulomb potential (CSCP). A finite electronic partition function and the change in ionization potential with screening radius — the radius of the mean atomic volume — which have been derived elsewhere, are used in the author's modification of the Saha equation. The resulting IEEOS is used for hydrogen and iron, where pressures at high densities and temperature are compared with pressures from the equation of state based upon the Thomas-Fermi-Dirac (TFD) statistical model of the atom. The present formulation is completely independent of TFD results; yet it gives very good agreement, for monatomic elements of all $Z$, with TFD pressures at high densities and temperatures, where the TFD results are believed to be reasonable; at low temperatures and densities, where the TFD pressures are either much too high or negative, the IEEOS yields the correct monatomic limit. Furthermore, in the region with $T \approx 1$ eV and $\rho \approx \rho_0$, the normal solid-liquid density, the IEEOS pressures are in good agreement with experimental extrapolations. Consequently, since mixtures of monatomic elements can also be handled with equal ease, the present IEEOS represents a significant improvement over the TFD equation of state.

DD FORM 1 NOV 65 1473 (PAGE 1)



S/N 0101-807-6801

Security Classification

Security Classification

| 14. KEY WORDS | LINK A ROLE | LINK A WT | LINK B ROLE | LINK B WT | LINK C ROLE | LINK C WT |
|---|---|---|---|---|---|---|
| Ionization equilibrium equation of state | | | | | | |
| Ionization potential | | | | | | |
| Schrodinger equation | | | | | | |
| Bound states | | | | | | |
| Complete screened Coulomb potential | | | | | | |
| Electronic partition functions | | | | | | |
| Effective screening radius | | | | | | |
| Hydrogenic ion | | | | | | |
| Thomas-Fermi-Dirac atom | | | | | | |