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IONIZATION EQUILIBRIUM EQUATION OF STATE

PART I. SOLUTION OF EQUATIONS

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ABSTRACT

A simple solution to Saha's equation has been obtained. The method of solution involves iteration with respect to the electron pressure or concentration and can be applied to the simultaneous calculations of any number of ions. Sample results are given for lithium and aluminum.

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In the preliminary theoretical analysis of exploding wire phenomena reported by the author,¹ it was shown that a better theoretical equation of state of the wire material was needed. As an improvement over the assumption of a constant gamma-law gas in the temperature range of 1 ev to 1000 ev, Saha's² equation has been solved completely for a perfect monatomic element in ionization equilibrium. This report presents a simple method of solution which can be applied to the simultaneous calculations of any number of ions.

The form of Saha's equation used will be that presented by Landau and Lifshitz³ which was derived from the point of view of considering ionization equilibrium as a special case of chemical equilibrium. Their

¹Rouse, C. A., "Theoretical Analysis of the Hydrodynamic Flow in Exploding Wire Phenomena," UCRL 5519-T, March, 1959 and "Exploding Wires", Edited by William G. Chase, Plenum Press, Inc., New York.

²Rosseland, S.; "Theoretical Astrophysics" Oxford Press, 1936. see pp 153-159 and pp. 175-179.

³Landau, L. D. and Lifshitz, E. M. "Statistical Physics", Addison-Wesley Publishing Co., Inc. p 322.

resulting equations are

$$\frac{C_{n-1}}{C_n} = P K_P^{(n)}(T), \quad (1)$$

$$C = C_1 + 2C_2 + 3C_3 + \dots, \quad (2)$$

to which must be added

$$1 = C + C_0 + C_1 + C_2 + C_3 + \dots \quad (3)$$

The notation is as follows:

$$K_P^{(n)}(T) = \frac{E_{n-1}}{E_n} \frac{2\pi}{E_e}^{3/2} \frac{h^3}{(kT)^{5/2}} \exp \frac{I_n}{kT}$$

N_0 = number/cc of neutral atoms

N = number/cc of all particles, or $N_e + N_i$ if N_e = electrons/cc and

N_i = ions/cc (calling the neutral atom a neutral ion)

C_0 = concentration of neutral atoms = N_0/N

$C_1, C_2, \dots$ concentration of ions of different orders, $N_1/N, N_2/N$, etc.

C = concentration of electrons

m_e = electron mass

P = total pressure

P_e = electron pressure = CP

E_n = statistical weight of the ions' ground state

I_n = n th ionization potential of the atom

k = Boltzmann's constant

h = Plank's constant $/2\pi$

T = temperature

ρ = mass density

$\rho/\rho_0 = \eta$ = relative density of gas to that of the element at STP, ρ_0

A = atomic weight

ϵ = energy density

In the solution of Eqs. (1), (2) and (3), first substitute Eq. (2) into Eq. (3) for C yielding

$$1 = C_0 + 2C_1 + 3C_2 + 4C_3 + \dots \quad (4)$$

For convenience, write Eq. (1) as

$$\frac{C_{n-1}}{C_n} = P_e K_n$$

or

$$C_n = \frac{C_{n-1}}{P_e K_n} \quad (5)$$

One also has

$$C_{n-1} = \frac{C_{n-2}}{P_e K_{n-1}}, \quad (6)$$

$$C_{n-2} = \frac{C_{n-3}}{P_e K_{n-2}}, \text{ etc.}$$

Substituting Eq. (6) into Eq. (5),

$$C_n = \frac{C_{n-1}}{P_e K_n} = \frac{C_{n-2}}{P_e^2 K_n K_{n-1}} = \frac{C_{n-3}}{P_e^3 K_n K_{n-1} K_{n-2}} = \frac{C_{n-4}}{P_e^4 \prod_{j=n-3}^n K_j}, \text{ etc.} \quad (7)$$

Clearly, from Eq. (7) the concentration of any ion can be obtained as a function of any other ion. And by the proper choices of n, all of the concentrations can be obtained with respect to any single ion. For example,

$$\begin{aligned} C_1 &= \frac{C_0}{P_e K_1}, \quad (n = 1), \\ C_2 &= \frac{C_1}{P_e K_2} = \frac{C_0}{P_e^2 K_1 K_2}, \quad (n = 2) \\ C_3 &= \frac{C_2}{P_e K_3} = \frac{C_0}{P_e^3 K_1 K_2 K_3}, \quad (n = 3) \\ &\text{etc.} \end{aligned} \quad (8)$$

Such results substituted into Eq. (4) yields

$$n = C_0 + \frac{2C_0}{P_e K_1} + \frac{3C_0}{P_e^2 K_1 K_2} + \frac{4C_0}{P_e^3 K_1 K_2 K_3} + \dots + \frac{(n+1) C_0}{P_e^n \prod_{j=1}^n K_j}$$

or

$$C_0 = \frac{1}{1 + \frac{2}{P_e K_1} + \frac{3}{P_e^2 K_1 K_2} + \frac{4}{P_e^3 K_1 K_2 K_3} + \dots + \frac{n+1}{P_e^n \prod_{j=1}^n K_j} + \dots} \quad (9)$$

Once Eq. (9) is solved for C_0 , Eq. (6) can be used to obtain the other ion concentrations and then Eq. (2) or Eq. (3) used to calculate the electron concentration.

The method used to obtain solutions to Eqs. (2), (8) and (9) is simply by iterations on P_e or, equivalently, on C , the electron concentration. For a particular mass density the first guess of the electron concentration leads to a first guess of the electron pressure. Through Eqs. (9), (8) and (2), a new electron concentration is calculated. If different from the guess by a certain percentage, the calculated value is used to determine a better value for P_e . The process continues until the value of C converges to the desired accuracy.

Once the electron and ionic concentrations have been calculated for specific values of T and ρ , total pressures and internal energies are calculated from

$$P = \frac{P_e}{C} = \frac{N_e}{C} kT = NkT \quad (10)$$

$$\epsilon = \frac{3}{2} \frac{N_e}{C} kT + \sum_{i=1} N_i I_i, \quad (11)$$

from which

$$\gamma - 1 = \frac{P}{\epsilon}. \quad (12)$$

An IBM 650 code was written to solve the above equations for various elements. As inputs, the majority of the ionization potentials and ground state statistical weights were taken from C. E. Moore, "Atomic Energy Levels", Vols. I, II and III, National Bureau of Standards. Other ionization potentials were obtained from Mr. Richard White of this laboratory (unpublished) and other ground state statistical weights were obtained by extrapolation using the table given by C. W. Allen in his book "Astrophysical Quantities", p. 33. As more accurate data become available, the calculations can easily be corrected.

A variation in the code had to be made at the temperatures and densities where $C_0, C_1, C_2, \dots$ in turn become negligible. When C_0 becomes less than a certain amount, say 10^{-20} , the calculations can begin with C_1 by multiplying Eq. (9) by $\frac{1}{P_e K_1}$ resulting in

$$C_1 = \frac{1}{P_e K_1 + 2 + \frac{3}{P_e K_2} + \frac{4}{P_e^2 K_3} + \dots} \quad (13)$$

Similarly, as C_1 becomes negligible, C_2 is calculated by multiplying Eq. (13) by $\frac{1}{P_e K_2}$, etc.

Tables I and II give results for Li and Al, respectively, in the temperature range 1 ev to 40 ev. The concentrations are given to three decimal places. The exponents in the values of H_e represent the powers of ten. With the values given, the total pressure P , the total particle density N , the energy density ϵ , and the ratio P/ϵ , or $\gamma - 1$ in this solution, can be calculated by the use of Eqs. (10), (11), and (12). More complete data will be given in Part II of this report later.

The author wishes to thank Dr. Berni Alder for several interesting discussions of the phenomena of ionization equilibrium and the summer employees of Computation Division who coded the equations for the IBM 650. The summer employees whose interest and fine coding resulted in the rapid solution of the equations for several elements were Joe Yee, Norma Brennan, Frank Denny, Charles Elmonson, Alice Klus, Harold Oksen, William Scofield and Walter Willson.

TABLE I

IONIZATION EQUILIBRIUM EQUATION OF STATE FOR LITHIUM

Temp, eV Electron Density & Concen- trations	Density Ratio ρ/ρ_0						
	10^0	10^{-1}	10^{-2}	10^{-3}	10^{-4}	10^{-5}	10^{-6}
1 N _e	7.92^{+20}	2.46^{+20}	7.33^{+19}	1.93^{+19}	3.66^{+18}	4.49^{+17}	4.62^{+16}
C	0.0168	0.050	0.136	0.294	0.441	0.492	0.499
C ₀	0.966	0.899	0.727	0.412	0.117	0.016	0.002
C ₁	0.017	0.050	0.136	0.294	0.441	0.492	0.499
5 N _e	1.80^{+22}	3.54^{+21}	4.46^{+20}	4.62^{+19}	4.67^{+18}	4.95^{+17}	6.33^{+16}
C	0.280	0.433	0.490	0.499	0.502	0.516	0.577
C ₀	0.440	0.134	0.019	0.002	-	-	-
C ₁	0.280	0.433	0.490	0.498	0.494	0.450	0.268
C ₂	-	-	-	-	0.004	0.033	0.154
10 N _e	3.03^{+22}	4.48^{+21}	5.77^{+20}	7.96^{+19}	9.28^{+18}	1.06^{+18}	1.29^{+17}
C	0.395	0.492	0.555	0.632	0.667	0.697	0.735
C ₀	0.212	0.036	0.003	-	-	-	-
C ₁	0.390	0.452	0.329	0.105	0.014	0.001	-
C ₂	0.003	0.020	0.113	0.261	0.304	0.211	0.058
C ₃	-	-	-	0.002	0.015	0.091	0.207
20 N _e	5.24^{+22}	8.31^{+21}	1.07^{+21}	1.31^{+20}	1.38^{+19}	1.39^{+18}	1.39^{+17}
C	0.531	0.642	0.699	0.738	0.748	0.750	0.750
C ₀	0.069	0.003	-	-	-	-	-
C ₁	0.271	0.085	0.008	-	-	-	-
C ₂	0.127	0.252	0.189	0.047	0.006	0.001	-
C ₃	0.001	0.018	0.104	0.214	0.246	0.250	0.250

Continued

TABLE I (Cont'd)

Temp, ev Electron Density & Concen- trations	Density Ratio ρ/ρ_0						
	10^0	10^{-1}	10^{-2}	10^{-3}	10^{-4}	10^{-5}	10^{-6}
25 N_e	6.57^{+22}	9.74^{+21}	1.24^{+21}	1.37^{+20}	1.39^{+19}	1.39^{+18}	1.39^{+17}
C	0.586	0.678	0.729	0.747	0.750	0.750	0.750
C_0	0.038	0.001	-	-	-	-	-
C_1	0.174	0.030	0.001	-	-	-	-
C_2	0.194	0.226	0.083	0.012	0.001	-	-
C_3	0.008	0.065	0.187	0.241	0.249	0.250	0.250
30 N_e	7.73^{+22}	1.10^{+22}	1.32^{+21}	1.38^{+20}	1.39^{+19}	1.39^{+18}	1.39^{+17}
C	0.625	0.704	0.741	0.749	0.750	0.750	0.750
C_0	0.020	-	-	-	-	-	-
C_1	0.108	0.011	-	-	-	-	-
C_2	0.222	0.162	0.035	0.004	-	-	-
C_3	0.024	0.123	0.223	0.247	0.250	0.25	0.25
40 N_e	9.56^{+22}	1.26^{+22}	1.37^{+21}	1.39^{+20}	1.39^{+19}	1.39^{+18}	1.39^{+17}
C	0.674	0.731	0.748	0.750	0.750	0.750	0.750
C_0	0.006	-	-	-	-	-	-
C_1	0.042	0.002	-	-	-	-	-
C_2	0.202	0.070	0.009	0.001	-	-	-
C_3	0.076	0.197	0.243	0.249	0.250	0.250	0.250

TABLE II

IONIZATION EQUILIBRIUM EQUATION OF STATE FOR ALUMINUM

Temp, ev Electron Density & Concen- trations	Density Ratio ρ/ρ_0						
	10^0	10^{-1}	10^{-2}	10^{-3}	10^{-4}	10^{-5}	10^{-6}
1 N_e	3.89^{+20}	1.22^{+20}	3.76^{+19}	1.12^{+19}	2.84^{+18}	5.03^{+17}	5.90^{+16}
C	0.006	0.020	0.059	0.156	0.320	0.455	0.494
C_0	0.987	0.960	0.882	0.688	0.357	0.090	0.012
C_1	0.006	0.020	0.059	0.156	0.320	0.455	0.493
C_2	-	-	-	-	-	-	0.001
5 N_e	1.51^{+22}	4.69^{+21}	1.04^{+21}	1.45^{+20}	1.73^{+19}	1.60^{+18}	1.81^{+17}
C	0.200	0.437	0.633	0.706	0.741	0.749	0.750
C_0	0.629	0.254	0.024	-	-	-	-
C_1	0.141	0.184	0.079	0.007	-	-	-
C_2	0.029	0.122	0.238	0.160	0.034	0.004	-
C_3	-	0.003	0.026	0.126	0.224	0.247	0.250
22 N_e	1.20^{+23}	1.99^{+22}	2.49^{+21}	2.95^{+20}	3.59^{+19}	4.24^{+18}	-
C	0.666	0.767	0.805	0.830	0.856	0.875	-
C_0	0.049	-	-	-	-	-	-
C_1	0.032	0.001	-	-	-	-	-
C_2	0.140	0.026	0.001	-	-	-	-
C_3	0.100	0.112	0.020	0.001	-	-	-
C_4	0.013	0.090	0.129	0.038	0.002	-	-
C_5	-	0.004	0.044	0.111	0.044	0.001	-
C_6	-	-	0.001	0.018	0.059	0.016	-
C_7	-	-	-	0.001	0.038	0.085	-
C_8	-	-	-	-	0.001	0.022	-

Continued

END

TABLE II (Cont'd)

Temp, ev Electron Density & Concen- trations	Density Ratio n/p_0						
	10^0	10^{-1}	10^{-2}	10^{-3}	10^{-4}	10^{-5}	10^{-6}
30 n_e	1.63^{+23}	2.45^{+22}	3.02^{+21}	3.92^{+20}	4.55^{+19}	5.27^{+18}	-
C	0.730	0.802	0.834	0.866	0.883	0.896	-
C_0	0.015	-	-	-	-	-	-
C_1	0.012	-	-	-	-	-	-
C_2	0.081	0.004	-	-	-	-	-
C_3	0.095	0.027	0.001	-	-	-	-
C_4	0.063	0.121	0.034	0.001	-	-	-
C_5	0.003	0.044	0.100	0.019	-	-	-
C_6	-	0.001	0.025	0.037	0.003	-	-
C_7	-	-	0.006	0.067	0.049	0.005	-
C_8	-	-	-	0.009	0.060	0.052	-
C_9	-	-	-	-	0.004	0.028	-
C_{10}	-	-	-	-	-	0.018	-
C_{11}	-	-	-	-	-	0.001	-
40 n_e	2.13^{+23}	2.90^{+22}	3.93^{+21}	4.70^{+20}	5.73^{+19}	6.40^{+18}	-
C	0.779	0.828	0.867	0.886	0.905	0.914	-
C_0	0.003	-	-	-	-	-	-
C_1	0.003	-	-	-	-	-	-
C_2	0.029	-	-	-	-	-	-
C_3	0.051	0.003	-	-	-	-	-
C_4	0.109	0.054	0.002	-	-	-	-
C_5	0.025	0.091	0.021	-	-	-	-
C_6	0.001	0.018	0.031	0.002	-	-	-
C_7	-	0.005	0.064	0.034	0.001	-	-
C_8	-	-	0.015	0.066	0.017	-	-
C_9	-	-	-	0.009	0.019	0.001	-
C_{10}	-	-	-	0.003	0.048	0.029	-
C_{11}	-	-	-	-	0.010	0.055	-