7
11-10-75
28 up DWTLS

MASTER

UCID - 16901

This is an informal report intended primarily for internal or limited external distribution. The opinions and conclusions stated are those of the author and may or may not be those of the laboratory.

LAWRENCE LIVERMORE LABORATORY

University of California, Livermore, California

A NEW EOS FOR AIR

H. C. Graboske

September 16, 1975

NOTICE

This report was prepared as an account of work sponsored by the United States Government. Neither the United States nor the United States Energy Research and Development Administration, nor any of their employees, nor any of their contractors, subcontractors, or their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness or usefulness of any information, apparatus, product or process disclosed, or represents that its use would not infringe privately owned rights.

Prepared for U. S. Energy Research and Development Administration
Under Contract No. W-7405-ENG-48

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency Thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

A New EOS For Air

H.C. Graboske

A new air EOS has been developed for LLL hydrocode use. It accurately reproduces the detailed NBS ideal gas dissociation-ionization physics currently used as the tabular air EOS, over those ρ , T regions where this approximation is valid. For higher densities and both lower and higher temperatures, it includes dense molecular and atomic interactions, the dense partially ionized coulomb plasma, and the very dense metallic coulomb fluid. The new EOS covers the range $10^{-7} \leq \rho \text{ (g/cm}^3\text{)} \leq 15$ and $0.015 \leq T\text{(eV)} \leq 3 \times 10^4$.

1. INTRODUCTION

A complete new EOS for air has been generated for use in LLL hydrocodes. It extends from very low density (10^{-7} g/cm^3 , a 10^4 -fold expansion from normal density, $\rho_0 = 0.00129 \text{ g/cm}^3$) to high density (15 g/cm^3 , a 10^4 -fold compression from ρ_0). The current tabular air EOS is believed to be a composite of two detailed statistical mechanical calculations made in 1957-1959 by NBS theoreticians, one covering the dissociation region,¹ the other the ionization region.² These calculations are valid for the ideal gas regime, which for air covers a much wider span of ρ , T space than for most materials of interest at LLL. This is because the material is a low density gas in its normal state, so that very strong compressions are required to reach non-ideal conditions, while expansions and high temperature heating are even more "ideal" than the normal state. The NBS treatment involves using Saha dissociation and ionization equilibrium methods, with great care paid to the construction of the atomic and molecular partition functions. The effects of coulomb interactions, pressure ionization, metallic fluid behavior, and low temperature or high density (molecular) interactions are excluded. This leads to errors in the EOS for strong

shock compressions where $\rho/\rho_0 \geq 10$, and for adiabatic compressions. The improved EOS has to fulfill two main objectives, the accurate reproduction of the present ideal gas air equilibrium EOS over regions where ideal gas physics is appropriate, plus the inclusion of interaction effects in the dense molecular fluid, the partially ionized coulomb plasma and the pressure ionized dense metallic fluid.

2. PHYSICS OF THE LOW AND INTERMEDIATE DENSITY REGION

The complete air EOS is a composite, that is, different theoretical models were used to treat the high and low density regions, with a blending process used to join the two at intermediate density. The low to intermediate density calculations used a free energy model,³ using perturbation theory for the coulomb interactions⁴ and a specific fluid model for the neutral atom-molecule interactions.⁵

To accurately reproduce the NBS theoretical results, a very careful enumeration of the electronic, vibrational and rotational partition functions had to be made for all relevant species. The complete equilibrium mixture used for the LLL EOS included 25 species: N_2 , N_2^+ , O_2 , O_2^+ , NO , N , N^{+1} to N^{+7} , O , O^{+1} to O^{+8} , Ar , Ar^+ , e^- . Species neglected here which were included in the NBS study, such as NO^+ , are never more than 0.1% of the equilibrium mixture, and will not affect the EOS.

The major problem in reproducing the NBS results was a complete and accurate molecular partition function. The internal molecular free energy was computed for molecular species i from

$$F_{int}^i = -N_i kT \ln \left\{ \sum_j^{jmax} g_j e^{-\beta E_j} \sum_k^{kmax} e^{-\beta E_{vib}} \sum_{\ell}^{\ellmax} (2\ell + 1) e^{-\beta(E_{rot} + E_{v-r})} \right\}$$

where g_j , E_j , E_{vib} , $(2\ell + 1)$, E_{rot} , E_{v-r} are the electronic statistical weight and eigenvalue, the vibrational eigenvalue, the rotational statistical weight and eigen value and the vibration-rotation coupling eigenvalue.

$$E_{vib} = k(V_j - (k + 1) W_j)$$

$$E_{rot} = \ell(\ell + 1)[B_j - \ell(\ell + 1)(\alpha_j/2 - [d_j + \beta_j/2])]$$

$$E_{v-r} = -k\ell(\ell + 1)[\alpha_j - \ell(\ell + 1)]$$

$$D_j = \text{dissociation energy}$$

$$V_j = \text{harmonic oscillator energy}$$

$$W_j = \text{anharmonic correction}$$

$$B_j = \text{rigid rotor energy}$$

$$\alpha_j = \text{stretched rotor corrector}$$

Taken from tabulated experimental data when available.

If α_j , d_j , β_j are not known, they can be calculated from the other parameters,

$$\alpha_j = 6B_j^2[(W_j/B_j)^{1/2} - 1]/V_j$$

$$d_j \equiv 4B_j(B_j/V_j)^2$$

$$\beta_j \equiv d_j[8W_j/V_j - 5\alpha_j/B_j - \alpha_j^2 V_j/(24B_j^3)]$$

This form then describes an anharmonic oscillator, a stretched rotor, plus vibration-rotation coupling terms to order $k\ell^4$. Each molecule is tested, and homonuclear species are treated as either equilibrium or non-equilibrium ortho-para mixtures, as desired. The weighting factors for nuclei with nuclear spin s_j are

$$g_u = \frac{s_j + 1}{2s_j + 1}$$

$$g_g = \frac{s_j}{2s_j + 1}$$

for $2S_j$ odd, while for $2S_j$ even, these values are reversed.

For the equilibrium mixture case

$$Z_{\text{rot}} = g_u \sum_{\ell=1,3,\dots} (2\ell + 1) e^{-\beta E_{\text{rot}}} + g_g \sum_{\ell=0,2,\dots} (2\ell + 1) e^{-\beta E_{\text{rot}}}$$

while for the nonequilibrium case

$$Z_{\text{rot}} = \left[\sum_{\ell=1,3,\dots} (2\ell + 1) e^{-\beta E_{\text{rot}}} \right]^{g_u} \cdot \left[\sum_{\ell=0,2,\dots} (2\ell + 1) e^{-\beta E_{\text{rot}}} \right]^{g_g}$$

For the case of air there are 3 different molecular forms, heteronuclear (NO), homonuclear with even nuclear spin (O_2) and homonuclear with odd nuclear spin (N_2).

The upper limits on the electronic, vibrational and rotational sums, j_{max} , k_{max} , and ℓ_{max} , represent the sum-over-states terminations which prevent divergences. For the vibration and rotation cases, these limits are unambiguous. The value k_{max} is determined as the maximum value of k for which the inequality

$$k(V_j - (k + 1) W_j) \leq D_j$$

is satisfied. That is, the last vibrational eigenstate to be counted is the one whose energy is equal to or just below the molecular dissociation energy for the specific electronic eigenstate. The value of ℓ_{max} is the maximum value of ℓ for which the inequality

$$E_{\text{vib}} + E_{\text{rot}} + E_{\text{v-r}} \leq D_j$$

is satisfied. The termination of the electronic partition function is a very complex subject which is discussed below. It is important only in high temperature regions and will not affect the dissociation regime.

With a complete description of the molecular and atomic systems, taken from Herzberg⁶, Gaydon⁷ and JANAF⁸, a complete set of thermodynamic calculations were carried out for a mixture of 0.7809 N_2 , 0.2195 O_2 and 0.0096 Ar. Initial calculations of pure O_2 , N_2 and NO showed excellent

agreement with the JANAF ideal gas log K tabulations. A comparison of the mixture results with the two NBS studies was also made. A selected portion of these comparisons is shown in Figures 1 and 2. In Figure 1, the mole fractions of the various species dominating the mixture are plotted versus temperature, at normal density. At lowest T's, the mixture is that of normal air at room temperature, $N_2 + O_2$, but as it is heated the O_2 dissociates first, and a new molecule, NO, increases sharply, reaching 6-8% of the total particle number. Then as T increases beyond 4000K, NO and N_2 dissociate into N, O atoms, and at about 12000 K, the first ionization of N and O begins to occur. The circles show the NBS values, which compare very well with the LLL equilibrium for the major species. The only discrepancy is NO for $T \leq 5000$ K, whose source is not discernable, causing unimportant errors in the total EOS of the order of 0.1% in this range. The specific heat C_v is plotted in Figure 2 as a function of density for the ionization region, $\log T(K) = 4.1, 4.5, 5.0, 5.5, 6.0, 6.6$ (1.08 to 343. eV). This material property represents the stiffest test for EOS comparisons: pressures are much less sensitive to theoretical model differences than are energies, and the T-dependence of the energy exhibits the greatest variations of all the usual first and second order properties. As can be seen from the figure, the LLL and NBS EOS's are in very good agreement for the ideal gas regime.

One additional check was performed for the ideal ionization and dissociation region. A new molecular dissociation code using Saha equilibrium methods plus dissociation constants from the JANAF tables, (DISMOL), was used to calculate partial pressures (equivalent to mole numbers) for an air mixture. The DISMOL results agreed well with the FMIN values. In Figure 3, a comparison of the compressibility Z^* is given for an ideal (no interactions) LLL EOS with the NBS values, for the dissociation + first ionization region. The comparison covers a range of 10^8 in density and no significant discrepancies occur.

The treatment of the electronic (atomic) functions introduces the serious problems of treatment of the interacting coulomb plasma. Energy level shifts, continuum lowering, and bound state sum cutoffs are all related to this part of the free energy. A fairly rigorous theoretical approach has been developed by Rogers⁹ which is a generalization of the Beth-Uhlenbeck fluid partition function to the coulomb plasma, with a transformation to the grand canonical form. This activity expansion method is quite complex and requires extensive computational efforts; it already does provide a most accurate reference system against which less complete theoretical models can be tested. One such model, discussed by Ebeling and his co-workers¹⁰, proposes a Planck-Larkin (P-L) electronic partition of the form

$$F_i = -N_i kT \ln Z_i = -N_i kT \ln \left[\sum_{j=1}^{\infty} g_j \left\{ e^{-\beta E_j(\lambda)} - 1 + \beta E_j(\lambda) \right\} \right]$$

The electronic eigenstates are denoted here as $E_j(\lambda)$ to include the important effect of energy level perturbation, where the energy is density and temperature dependent, via the generalized screening length λ . In this calculation, as for Ebeling's approach, the unscreened (free atom) eigenstates, $E_j(\infty)$ are used in place of the screened eigenstates. Although this effect must be important, an accurate method of computing screened multi-electron eigenstates has not yet appeared. The reason for investigating the P-L form is that it resembles, to first order, the rigorous Beth-Uhlenbeck partition function, and has the useful feature of effectively truncating the electronic sum-over-states, thus removing the troublesome divergence.

A brief analysis of the effectiveness of the P-L p.f. was made to assess its usefulness. Its operation is best shown by examining the occupation number n_j of electronic eigenstate j

$$n_j \equiv Z_j / \sum_{j=1}^{\infty} Z_j \quad \text{where } Z_j \text{ is the partition function,}$$

representing the fraction of atoms or ions of the given species occupying the j th eigenstate. The results are shown for the O^{+6} ion in Fig. 4. The solid lines represent the normal Sahe p.f. ($g_j e^{-\beta E_j}$), and one sees that all O^{+6} ions are in the ground state at 100 eV ($T < T_{ion}$), with all levels $j \geq 3$ containing less than 1% of the number in $j=1$. At 10^3 eV ($T > T_{ion}$), the situation is reversed, with the upper levels occupied; n_j is a maximum for the 5th state, while n_1 is 0.036. This shift continues as T increases, leading to divergent sums if all eigenstates are included. Using the P-L form, the results shown as dashed lines demonstrate its effectiveness in truncating the sum. At 10^2 eV, the ground state is only slightly enhanced since so few ions were in excited states. But at 10^3 eV, the ground state population has increased 15-fold, to 0.53, while the original "maximum" eigenstate, $j=5$, has decreased from 0.27 to 0.063, and $n_{j=10}$ has decreased by 100.

A similar effect is shown in Figure 5 for atomic oxygen. An interesting effect is discernable here -- the demonstration that low and high T limiting behavior closely bracket the ionization temperature of each stage. For 0, with $T_{ion} = 13.614$, the n_j dependence for $T = 0.1$ and 1 eV are very similar, as are the curves for 10 and 100 eV. Thus, a temperature of the order of $T_{ion}/10$ is already a low T value, where the P-L form is fairly unimportant. Conversely a temperature of the order T_{ion} is already a high T limiting form; but since $T \approx T_{ion}$ means that ionization stage is already fully ionized, none will exist. Therefore, the effect of the P-L form will be limited to a very narrow range -- $T_{ion}/10$ to roughly $T_{ion}/3$, where T_{ion} refers to the dominant ionization stage. A direct assessment of the influence of the P-L

p.f. on an ideal partially ionized gas is given in Figure 6. The differences are negligible over much of the ρ , T region covered. Only at the high ρ ends of the higher T isotherms do differences in x_t approach 10%. And at this point, the other non-ideal contributions, especially the coulomb interactions became very important, generally well in excess of the 10% effects observed here. A tentative conclusion then is that although the P-L form is a theoretically useful concept, in that it removes high T divergences, its actual effect will be submerged in the more important coulomb interaction effects.

The three non-ideal (interaction) regions require additional theoretical treatment. The low T region must include molecular interactions, such as N_2-N_2 , O_2-O_2 , N_2-O_2 . At higher T and ρ , where dense partially dissociated fluid is present, we must include $NO-NO$, N_2-NO , N_2-N , $NO-N$, $N-N$, O_2-NO , O_2-O , $O-NO$, $O-O$, N_2-O , O_2-N , $N-O$ interactions. There are in principle $8^2 = 64$ neutral fluid interactions to be modeled, and only N_2-N_2 , O_2-O_2 , $NO-NO$ and $Ar-Ar$ potentials have been studied in any detail. The free energy model of Lebowitz' scaled particle theory⁵ for hard-sphere mixtures is adopted to treat the repulsive interactions. The best available intra-species intermolecular potentials are used, and interspecies potentials are developed by a standard (and partially successful) method from the intraspecies potentials. An attractive free energy of the Van der Waals form is used, and the low T EOS of 3 single species materials, O_2 , N_2 and NO , are calculated. By adjusting the Van der Waals constants, exact agreement with experimental critical point data is obtained. Then a mixture (air) low T EOS is calculated, and the resultant critical point pressure is only 7% off the experimental value. This is a maximum EOS error in the low T region, and errors generally will decrease below this rapidly as T increases above T_{crit} .

The partially ionized coulomb plasma is treated by a free energy form of the density perturbation expansion.⁴ The high density (pressure-ionized) metallic fluid regime is treated with a combination of Thomas-Fermi statistical theory for the electron gas plus Monte Carlo theory for the ion fluid.^{11,12} These theories are combined in the TFCMIX code, where the TFK form of TF theory is used together with the BST Monte Carlo ion fluid results. This high density theory is valid for densities approaching 1 g/cm^3 , while the low density models approach this limit from below. They do both fail in the vicinity of 1 g/cm^3 for $T \leq 100 \text{ eV}$, so that the EOS must be constructed by interpolation. The pressure is usually chosen as it is the "best-behaved" first order property, and then thermodynamically consistent TD potentials (E,S,H etc.) are calculated from the pressure by requiring the appropriate Maxwell relation to be satisfied. As the theoretical models are improved and extended, this interpolation region decreases in extent; for a fully fluid, low normal density material like air, the present set of theoretical codes is fairly complete. The interpolation region is thus small, covering two connected ranges: $[.015 \leq T \text{ (eV)} \leq 5, 1 \leq \rho \text{ (g/cm}^3\text{)} \leq 5]$ and $[5 \leq T \text{ (eV)} \leq 150, 0.3 \leq \rho \text{ (g/cm}^3\text{)} \leq 1.5]$.

The final air EOS is complete when these procedures have been carried out. It recovers, very accurately, the NBS ideal gas EOS presently in use, and determines the upper limit of validity of this form. The current (older) EOS is useful over the range $[0.025 \leq T \text{ (eV)} \leq 3 \times 10^4; 10^{-7} \leq \rho \text{ (g/cm}^3\text{)} \leq 0.01]$. The new EOS corrects the current tabular form for $\rho \geq 0.01 \text{ g/cm}^3$ to 0.1 g/cm^3 , and extends to 15 g/cm^3 . Likewise, improved values are available for $T \leq .025 \text{ eV}$ down to the critical temperature. Therefore, the shock and adiabatic compressions with $\eta = \rho/\rho_0 \gtrsim 10$ fold, the new EOS should give different and better values. Also, low T results, (.015 to .025 eV) will be more accurately calculated with the new EOS, at all densities.

The pressure and internal energy equations of state are shown in Figures 7 and 8, as a function of density (ρ), with temperature as a parameter. A different representation, Figure 10, displays the EOS in a combined form $P_{\rho}(E)$ where dissociation and ionization regions are discernible (a and b), as well as the high ρ Thomas-Fermi region (c), and the high T ideal plasma (d). The approximate interpolation region (e) is also indicated.

The basis for this work was a study carried out with Mark Frei and Bill Hoover, whose helpful collaboration is acknowledged.

REFERENCES

1. Hilsenrath, J., M. Klein and H. Worley, Report No. AEDC-TR-59-20, Arnold Engineering Development Center, 1959.
2. Hilsenrath, J., M. S. Green and C. W. Beckett, Report No. AFSWC-TR-56-35, Air Force Special Weapons Center (ASTIA No. AD 96303), 1957.
3. Graboske, H. C., D. J. Harwood & F. J. Rogers, Phys. Rev. 186, 210, 1969.
4. Graboske, H. C., D. J. Harwood & H. E. De Witt, Phys. Rev. A 3, 1419, 1971.
5. Graboske, H. C., R. J. Olness and A. S. Grossman, 1975, Astrophys. J. 199, 255.
6. Herzberg, G., The Spectra of Diatomic Molecules, D. Van Nostrand Co., New York, 1950.
7. Gaydon, A. G., Dissociation Energies, Chapman and Hall Ltd, London, 1968.
8. JANAF Thermochemical Tables, Second Edition, NSRDS-NBS 37, June, 1971.
9. Rogers, F. J., Phys. Rev. A, 10, 2441, 1974.
10. Ebeling, W. and R. Sandig, Ann. der Physik, 32, 1, 1972.
11. Mc Carthy, S. L., UCRL-14364, 1965.
12. Warren, D., Nuclear Correction for Genesis, UCID-15316, 1968.

FIGURE CAPTIONS

- Fig. 1 Mole fractions (N/N_{tot}) for various air component species as a function of T , at $\rho = \rho_0$. The LLL EOS (—) compares quite well with the NBS ($\odot$) equilibrium ideal gas values.
- Fig. 2 Specific heat, $C_v/10R$, versus density for $\log T(K) = 4.1, 4.5, 5.0, 5.5, 6.0, 6.6$ for the ideal ionization-dissociation regime. The LLL EOS (—) agrees well with the tabulated NBS specific heats ($\odot$).
- Fig. 3 Compressibility Z^* versus density for air, for 4 values of T spanning the dissociation and first ionization regions. The LLL ideal ionization-dissociation results (—) are in excellent agreement with the NBS ($\odot$) values.
- Fig. 4 Occupation number for the $j = 1$ to 12 levels of the O^{+6} ion, $I = 739.114$ eV. The Planck-Larkin electronic partition function (---) produces results differing significantly from the standard partition function (—). The truncation of the higher level contributions is evident at 1000 eV, as is the enhancement of the ground state.
- Fig. 5 Occupation number for the 12 lowest eigenstates of atomic oxygen, $I = 13.614$ eV. The limited range over which the Planck-Larkin effect operates is seen by the similarity of the 0.1 and 1 eV results and the 10 and 100 eV results.
- Fig. 6 Total mole number of an ideal equilibrium air mixture versus density for 5 T values. The standard partition function agrees well with the Planck-Larkin form at lower densities, only differing at high densities where coulomb interactions are important.
- Fig. 7 Pressure EOS for air.
- Fig. 8 Energy EOS for air.
- Fig. 9 Pressure isochores versus energy.

Fig. 2

Fig. 3

Fig. 4

Fig. 6

Fig. 7

Fig. 8

Fig. 9

DISTRIBUTION LIST

External

Prof. Allan S. Grossman
Physics Department
Iowa State University
Ames, Iowa

TIC, Oak Ridge (27)

Internal

L-504

H.C. Graboske (5)
H.E. DeWitt
M. Kamegai

L-24

D. Steinberg
R. Barlett

L-71

J. Hegarty

L-3

TID (15)

NOTICE

"This report was prepared as an account of work sponsored by the United States Government. Neither the United States nor the United States Energy Research & Development Administration, nor any of their employees, nor any of their contractors, subcontractors, or their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness or usefulness of any information, apparatus, product or process disclosed, or represents that its use would not infringe privately-owned rights."

Printed in the United States of America
Available from
National Technical Information Service
U. S. Department of Commerce
5285 Port Royal Road
Springfield, Virginia 22151
Price: Printed Copy \$ ____*; Microfiche \$2.25

<u>* Pages</u>	<u>NTIS Selling Price</u>
1-50	\$4.00
51-150	\$5.45
151-325	\$7.60
326-500	\$10.60
501-1000	\$13.60