THE ADIABATIC EXPANSION OF DETONATION PRODUCTS AND THE SPHERICAL TAYLOR WAVE FOR TNT

by

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SUMMARY

A new equation of state for gases at high densities and temperatures is formulated. This is based on Monte-Carlo calculated compressibilities for rigid non-attracting spheres determined elsewhere. The equation of state for a gas mixture is taken to be that of a pure hard sphere gas with a temperature-dependent diameter. This diameter is expressed in terms of the gas composition and the Lennard-Jones(6-12) pair potential constants of the constituent gas species. This equation of state is applied to the calculation of detonation front behaviour and to the adiabatic expansion of, and Taylor wave in, the products following detonation in TNT at loading densities of 1.0 and 1.5 g/cc. At the higher loading density, agreement of the calculated with the observed detonation wave speed is to better than 1%. At the lower loading density, the departure of the calculated from the observed wave speed is about 4 times as great.

The computations are also carried out using a co-volume formula, originally due to Jones and Miller, but modified here so as better to match the observed detonation wave speed at cast densities.

The computations are presented in a form applicable to the products of any condensed explosive of the CHON type. The composition, however, is only treated in a manner suitable

for strongly oxygen-negative explosives. The detailed equation of state relations are given, not only for the two equations mentioned, but also for a real gas virial equation of state. In this case the composition is assumed to be fixed.

The validity of the approximations recommended for use at very high pressures by Jones and Miller are examined in detail for each successive stage of approximation proposed and the calculations are carried out for each stage so as to separate the numerical errors of Jones and Miller from their acknowledged approximations.

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SYMBOLS

$B(T)$ - second virial coefficient

b - $(2\pi/3)N\sigma^3$

$C(T)$ - third virial coefficient

C_p - specific heat at constant pressure

D_∞ - detonation wave speed

E, U - internal energy

f - fugacity

H - enthalpy

$K^\circ(T)$ - ideal gas condition equilibrium constant

M - mass

N, n - number of molecules, number of moles

p - pressure

Q - chemical energy released

R - universal gas constant

r - radius

S - entropy

T - temperature

t - time

u - centre-of-mass velocity

V, v - volume

X - co-volume

y - $p\overline{b}/RT$

Z - compressibility factor $(=p\overline{V}/RT)$

γ_{Ad} - adiabatic exponent

δ - a small quantity

Δ - loading density

ε - heat of reaction

θ - pair potential constant

σ - pair potential constant

ρ - density

Modifying Symbols

$(\ )_o$ - standard state

$(\ )^{\#}$, $(\ )^{\circ}$ ideal gas condition

$(\ )_r$ - attributable to non-ideal behaviour

$(\ )_g$ - gas

$(\ )_j$ - of species j

$(\ )_i$ - for reaction i

$(\ )_{th}$ - thermal component

$(\bar{\ })$ - per mole

$(\ )_1$ - per unit mass

$(\ )_e$ - in unreacted explosive

$(\ )^*$ - a dimensionless variable

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CHAPTER 1

GENERAL INTRODUCTION

1.1 Purpose

When a column of condensed explosive is struck a sharp blow, or a section of it is suddenly heated by some means such as a shock wave, a steady detonation wave may develop. This is characterized by a nearly plane front moving at constant speed, one very much higher than for similar behaviour in reactive gases. According to the accepted view, this is a wave of reaction consisting of a leading non-reactive shock, followed by a reaction zone in which conditions are invariant in a frame of reference moving at the velocity of the wave front, followed, in turn, by a non-steady wave where the reaction products expand into the space behind the advancing front. The pressure behind the detonation front in condensed explosives generally exceeds 10^5 atmospheres.

The speed of the steady detonation wave is observed to depend on the chemical and physical nature of the explosive, on its loading density (density in the unreacted state) and on the diameter of the column. When this diameter alone is varied, the steady wave speed is found to increase with it, the rate of increase ultimately becoming very slow. When the detonation front speed is specified without reference to the diameter, it generally refers to the limiting speed obtained from an extrapolation to zero inverse-diameter using a plot of observed values or an equivalent fitted curve. When a detonation wave is properly initiated in a sphere of high explosive, the speed of the spherical wave is observed to approach this upper limit as the wave expands.

Attempts to provide quantitative theories accounting for the behaviour observed have furnished a considerable body of literature. Most of this has dealt only with the detonation front in columns of explosive, assuming no lateral expansion in the reaction zone. There have been very few studies devoted to the more general problem of the thermodynamic behaviour of the products as they expand behind the front and of the instantaneous distribution in space of the thermodynamic and flow variables in this expanding wave. Such a distribution is here called a Taylor wave when it refers to a hypothetical wave of constant speed in which the motion is adiabatic, non-viscous and one-dimensional, though it may well be reactive. One-dimensional motions may, of course, be only plane, cylindrical or spherical.

As just stated, there have been relatively few studies dealing with this more general problem in high explosives. In these, certain formulae are used which are alleged to be equations of state suitable for the products of condensed explosives. However, only one study[1.1] is known to the author in which the general problem (or certain features of it) was treated using an equation having sufficient generality as to deserve the term equation of state, although such general equations have seen wider application to the calculation of detonation front properties[1.2,1.3,1.4].

The primary purpose of this dissertation is to discuss the calculation of the adiabatic behaviour of, and Taylor wave in, detonation products using a general gas equation of state not previously used. While the numerical computations given here are confined to TNT products, the gas equation of state, being very general, is in no way restricted to such products, nor to any gas mixture, provided only that it is composed primarily of non-polar molecules of not grossly different size. A secondary purpose of the discussion is to carry out the same computations using a gas formula applicable only to TNT products, due originally to Jones and Miller[1.5], but slightly modified here to ensure that calculated detonation wave speeds agree with those observed for the loading densities characteristic of cast TNT.

1.2 Preliminary Discussion

The remarks which follow immediately are intended to outline the main notions and restrictions involved in the subject matter which is later treated mathematically. These remarks are intentionally kept free of formulae so that the reader may better appreciate the arguments without reference to any particular habituation to symbols. The problem of habituation to adjectives remains and for this reason a rough guide is given to the author's terms expressing magnitude in the present discussion.

Adjective	Pressure (atmospheres)	Temperature (°K)
ultra-high	$>10^6$	-
very high	$>10^5$	$>10^4$
high	$>10^4$	$>10^3$
moderate	$>10^3$	>300
low	$<10^2$	-

The following table lists the best known solid explosives.

Table 1.1

Some Pure Solid Explosives of the CHON Type

Explosive Name	Abb.	Empirical Formula	Crystal Density g/cc	Molar Mass g
2,4,6,-Trinitrotoluene	TNT	$C_7H_5N_3O_6$	1.654	227
2,4,6,-Trinitrophenyl-methylnitramine	tetryl, CE	$C_7H_5N_5O_8$	1.73	351
Pentaerythritol tetranitrate	PETN	$C_5H_8N_4O_{12}$	1.77	316
Cyclomethylene trinitramine	RDX, cyclonite	$C_3H_6N_6O_6$	1.816	228

The gas equation of state employs the best available compressibility factor calculations for a gas of identical rigid non-attracting spheres[1.6]. The results of these calculations, which involved the use of Monte-Carlo methods, are here fitted by an equation relating the compressibility factor to a parameter which is proportional to the product of the volume of the hard sphere and the pressure-temperature ratio. In a gas of identical rigid non-attracting spheres of immutably fixed diameter, the imperfection component of the internal energy is zero. Furthermore, if the volume of the sphere is calculated from the low-velocity collision diameter (not the "diameter" of the older kinetic theory), it will be found that the minimum volume required to accommodate these spheres, namely the close-packing volume occupied by spheres all in contact, exceeds that which may confidently be stated to be available to the gas behind detonation fronts in condensed explosives.

Accordingly, the available rigid sphere data may be applied only if the sphere diameter can be defined in a plausible way. To this end, it is imagined that the sphere is rigid only at a particular temperature, adjusting instantaneously to smaller values as the temperature increases. To be more specific, the behaviour of the gas phase of the product mixture (at high pressures and temperatures) is assumed to be represented by that of a hypothetical gas of identical rigid sphere molecules of diameter taken to be equal to a value approximating the most probable closest-approach distance in a pure gas of non-polar spherical molecules having symmetrical force fields described by species-averaged intermolecular potential constants and colliding with a Boltzmann distribution of velocities.

It should be borne in mind that a theoretically rigorous equation of state for a mixture of real gases has yet to be developed, even for the simplest mixture imaginable, namely a 2-component one containing an equal number of different sized rigid non-attracting spheres. At high temperatures and pressures the choice lies between simulating the gas mixture by a hypothetical pure hard-sphere gas, the compressibility factor for which has been precisely calculated over a wide range of conditions, simulating it by a pure hypothetical non-polar gas of spherical molecules with fields of force, the compressibility factor for which is difficult to calculate and but poorly represents observed behaviour except at liquid densities,* or representing the compressibility factor for the gas mixture by virial terms involving virial coefficients which are species-averaged combinations of the virial coefficients for the pure species, a procedure without theoretical foundation and limited to low densities. The present seemingly artificial proposal might be viewed with more charity in this light.

The main detonation products of condensed pure CHON explosives of oxygen-negative balance are the gaseous species CO, CO_2, CH_4, H_2, N_2, H_2O: for strongly oxygen-negative explosives like TNT and tetryl, considerable quantities of solid carbon are also present. For other CHON explosives the composition is relatively invariant with pressure and temperature. However, even in the case of explosives which are strongly oxygen-negative, the dependence of the diameter of the mixture-equivalent hypothetical hard sphere gas on the composition is so slight that the approximation of a common fugacity for the gas species may be used without serious error.

Practically nothing is known about the size of the solid carbon particles in detonation product mixtures.

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*That is, when the Lennard-Jones and Devonshire equation of state or other cell theory equations are used.

It is assumed that they are in the form of graphite, that they are sufficiently small that their motion is identical with the centre-of-mass velocity of the mixture and that they have negligible coefficients of thermal expansion and baric compression.

Subject to the above assumptions, the adiabatic behaviour of the gas-solid mixture at, and following detonation, is described by equations quite generally applicable to the products of any condensed pure CHON explosive. As stated earlier, the numerical computations are here confined to TNT. For conciseness, only two loading density values are treated, namely, 1.0 and 1.5 g/cc. The former is typical of lightly pressed TNT, the latter of low-density cast TNT.

A moderately high degree of agreement between the calculated and the observed detonation wave speed is a necessary (but not sufficient) condition for establishing the validity of a detonation product equation of state. The agreement obtained for TNT or 1.5 g/cc (i.e., 1%) is comparable to the uncertainty in the observed detonation wave speed. At 1.0 g/cc the departure of the calculated from the observed wave speed is about 4%. In view of the assumptions made regarding the solid carbon, it is possible that a similar degree of agreement would not be obtained were application of the (gas) equation of state extended to the (gas) products of any condensed explosive.

Any hard sphere equation of state is less plausible than a real gas virial equation of state when the concentration of molecules becomes sufficiently low that use of the latter becomes valid. This is, of course, particularly true at temperatures below the Boyle temperature of the mixture. Accordingly, the adiabatic computations for a real gas virial equation of state are also described. However, a virial equation of state for a pure real gas cannot be reliably specified beyond the third virial coefficient: this coefficient itself is somewhat uncertain. As stated earlier, the virial coefficients for a gas mixture are much less certainly specified. It is found that when the calculated gas concentration on the adiabats (calculated with the hard sphere gas equation of state) falls to a level permitting the use of such a truncated real virial, the temperature is sufficiently low that the composition may be regarded as fixed. Accordingly, the adiabatic computations using the real virial are described only for the case of invariant composition.

All treatments here are based on a choice of temperature (T) and pressure (p) as the independent state variables. However, the virial coefficients for pure gases are most readily calculated for a (temperature, volume) system. In such a system the representation of p/T is an infinite power series in the molar density. For a (T,p) system the corresponding expression is a representation of the molar volume by a power series in p/T. The relation between the virial coefficients in the two forms is well known.

In the hard sphere computations, the intermolecular potential constants used are those suitable at high to moderate temperatures, and the assignment of a single set of constants to describe a species-averaged potential for the gas mixture requires that the potential for water, the only polar molecule concerned, be represented by an orientation-independent or orientation-averaged equivalent non-polar potential. In the present application, the Lennard-Jones (6-12) two-constant potential is used throughout for the non-polar molecules, and a suitable pair of (non-polar equivalent) constants is chosen for water. However, in the virial relations the polar character of water is formally accounted for.

For application of the virial equation all potential constants must be reassigned, at least for the calculation of the second coefficient. The scheme proposed here is to calculate the second coefficient for the gas mixture using the potential constants obtained from measurements of the second virial coefficients for the pure gas species, and to calculate the third coefficient for the gas mixture using the high-temperature species-averaged potential constant values as for the hard-sphere case. Simple mathematical expressions for the virial coefficients for a pure gas are known for an LJ (6-12) representation of the intermolecular potentials for non-polar molecules and for the corresponding Stockmayer (6-12) representation for polar molecules. An approximate expression fitting numerically calculated values for the third coefficient is also available for the LJ (6-12) form. Accordingly, these potentials are advocated on the grounds of mathematical simplicity. No similar expressions are available for more complicated potentials.

The third virial coefficient for water is not successfully represented by any potential suggested to date. Furthermore, the intermolecular potential for a pair of unlike molecules is also unknown, as are the true expressions for the second and third (and higher) virial coefficients for a mixture. For this reason, it appears justifiable to replace the usual, (but theoretically unsupported), expression for the second virial coefficient - - which involves the pair potential constants not only for like but also for unlike molecules - - by the simpler approximate expression involving potentials only for pairs of like molecules. The same uncertainties also underlie the advocated replacement of the complicated relations for the third virial coefficient for a gas mixture by the simpler expression for a representative pure species.

While the treatment for the virial form is completely described in terms of general relations, the numerical computations for this form are not given here, although some values are given for the mixture virial coefficients for TNT gas products in frozen equilibrium. In transferring from the hard sphere to the virial equation of state on the adiabats, a smoothing technique or similar procedure must be used because if, as appears most desirable, the transfer is made at that point at which the calculated compressibility factor is the same for both equations of state, then a (weak) discontinuity is generated. This must be so because, at the transfer point, the imperfection component of the internal energy changes from a (small) positive to a (small) negative value.

The transfer point defined above occurs at a temperature of about 1150°K for both the high and low loading density adiabats. Here the calculated compressibility factors are less than 1.15, so that one might be tempted to calculate the continued adiabats (continued down to a pressure of one atmosphere) by treating the gas phase as a mixture of ideal gases were it not for the contained water vapour which increasingly dominates the mixture second virial coefficient. The latter rapidly assumes a negative value, causing the compressibility factor to fall below unity near the Boyle point. The error involved here in using the hard molecule equation throughout is very small, but it is of course true that, in principle, below the Boyle point (about 450°K for TNT products of frozen composition), the hard molecule equation, or any hard molecule equation of state, is very poor, being worse even than that for a mixture of ideal gases.

The co-volume of the gas portion of the mixture may be defined quite generally as that volume which must be subtracted from the volume available to the gas phase so that the perfect gas law appears to apply in the volume remaining. Jones and Miller assumed that the co-volume per mole of gas mixture could be defined as a function of pressure only, and for TNT, they expressed this function as a second degree polynomial. The three (constant) coefficients given by Jones and Miller lead to calculated detonation velocities which are grossly in excess of those observed[1.7] at high loading densities. Accordingly, the power series is extended and two additional constant coefficients are determined by matching the calculated to the observed detonation wave speed at loading densities of 1.5 and 1.52 g cc^{-1} TNT. The improved co-volume so obtained now reproduces the observed detonation velocity to within the experimental uncertainty for all loading densities of TNT that may be realized in low pressure casting.

Chemical equilibrium is assumed to obtain in the adiabatic expansion until a certain point is reached. For the modified JM co-volume equation, the calculated mole number of carbon passes through a minimum at about 2100°K for a 1.0g/cc loading density. This agrees with the Jones and Miller value of the carbon minimum temperature. The same value of the carbon minimum temperature is found with the hard molecule equation of state. For this equation the minimum occurs at 1800°K at a loading density of 1.5 g/cc, whereas Jones and Miller calculated this minimum to be at 1600°K, and assumed frozen equilibrium below this temperature. In the present application, the composition is assumed to be frozen at the value attained at 1450°K in all cases.

Other physical and mathematical approximations of Jones and Miller are discussed and the errors consequent on their use are calculated. However, in the present computations no significant approximations are made other than the use of the JM equation itself. The JM assumptions regarding the solid carbon were identical to those given above. The same assumptions have been made by Brinkley and Wilson[1.8], J. Taylor[1.2], Paterson[1.3], and Cook[1.9]. However, Fickett[1.1] has used a compressible solid equation of state for carbon obtained from the analysis of shock data in solid graphite rods, but assumes carbon particle entrainment by, and thermodynamic and chemical equilibrium with, the surrounding gas mixture.

Some thought was given to the desirability of using Fickett's carbon compressibility data. However, in view of the fact that Jones and Miller obtained the coefficients in their expression for the co-volume on the assumption that the carbon was incompressible, it was felt essential to continue with the same assumption for this form. Furthermore, it was also felt better not to introduce this additional variable in a first examination of the effect of the hard sphere equation of state, especially since, in order to appreciate the effects of the different equations, it is important to ensure that no other factors, either physical or numerical, are significant. This is probably the first study in which such a comparison has been made. Here the entire computations for both equations were carried out within the same computation program, using the same physical constants and the same numerical procedure throughout.

Conditions at the equilibrium detonation front are established conditional on the usual assumptions that the mass motion is one-dimensional and adiabatic, that the Chapman-Jouguet postulate applies, and that the width of the reaction zone is negligible compared with the instantaneous radius of the detonation front. The available data on the width of the reaction zone for TNT[1.10], together with the approximate analysis of Eyring and coworkers[1.11], indicates that, were it possible, in fact, to initiate a stable detonation wave in a sphere of TNT by a central spherical detonator of negligible volume, errors arising from this assumption would be insignificant at detonation front radii exceeding 5 cm* A more realistic consideration would have to recognize that, in practice, TNT is usually initiated by a two-stage detonator-booster combination, consisting of a small detonator fired centrally in a booster sphere of tetryl/TNT mixture which is placed concentric with the main charge of TNT.

Another practical consideration is that in a cast explosive, the local loading density tends to be higher at the surface than at the centre. Reasons for this are well known[1.12]. One may conclude that computations of the kind given here cannot be expected to be in accord with actual behaviour unless the radius of the explosive charge be on the one hand sufficiently large that the radius of the (smallest available) central booster be small compared with it, and on the other hand be sufficiently small that the gradient in the local loading density may be safely ignored. The latter deficiency may be ameliorated by casting large charges in relatively small sections and joining them in the geometry desired. This has been done for some time at the Suffield Experimental Station[1.13]. In these large TNT charges, the (smooth-faced) subsections were merely placed together and it is interesting to note that the measured detonation wave speed[1.14] (measured to 0.5% uncertainty) agreed in all cases with the Bruceton data[1.7] to within 1%.

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*That is, for a 1.5 g/cc loading density.

For a Taylor wave, the partial differential equations of motion and continuity may be replaced by ordinary differential equations. This was first shown by G.I. Taylor[1.15] and Sedov[1.16]. Thermodynamic behaviour in adiabatic non-viscous motion is not affected by the motion at all since the thermodynamic properties of an element of the mixture depend only on the initial (i.e., CJ point) state variables and on the equation of state. Accordingly, the instantaneous centre-of-mass velocity of an element of mixture may readily be calculated from the state variables by numerical integration of the ordinary differential equations relating the mass motion to the thermodynamic properties. If this is attempted as a separate calculation after the properties on the adiabat have been tabulated, large errors are difficult to avoid. Such was the case for G.I. Taylor's[1.15] calculations for TNT using the tabulated adiabatic values of Jones and Miller. When, as in the present case, integration of the equations of motion is carried out simultaneously with the computation of the properties on the adiabat, this type of error does not arise.

The Taylor wave calculations are given here only for spherical detonations. Those for plane and cylindrical detonations could have been calculated with relatively little additional effort, but these cases are of less practical interest for condensed explosives.

In cylindrical and spherical Taylor waves, the assumption of a zero-width reaction zone (implicit in that of an invariant detonation front speed) leads to a singularity in the differential equations at the CJ point. This is due to the artificial contiguity of the non-reactive and reactive Hugoniots inherent in this assumption. Such artificial detonation fronts demand infinite reaction rates and are sometimes referred to as "reactive shocks". Mathematical methods of circumventing the difficulty occasioned by this singularity have been described by G.I. Taylor and by practically everybody who has discussed the Taylor wave problem. Too much has been made of this relatively trivial issue. In the present formulation, special measures at this point are not necessary. A Runge-Kutta representation of finite differences correct to 4th order is used: some difficulty would exist only in a first order representation.

In the equations about to be described, such extensive quantities as the energy, enthalpy, etc., are represented as the sum of a component which would arise were the gas state ideal, together with an additional component attributable to intermolecular forces. The ideal component is, in turn, represented as a sum over the species contributions. It is a necessary preliminary step to obtain a concise and precise representation of the ideal gas functions required for the pure species concerned. Such representations were obtained by least squares fits of suitably chosen functions to the constant pressure specific heats given in the (1961) JANAF[1.17] tables. Expressions representing the ideal gas equilibrium constants for the reactions concerned were also derived from these tables in the same way. The heats of formation for the product species were also taken from the JANAF tables.

Some discussion is devoted to other equations of state. However, only slight attention is paid to detonation front formulae. Such formulae have already received considerable publicity[1.18]. Cook[1.9] describes several of these. In the absence of proofs to the contrary, these formulae appear to be merely effective fits to reproduce the detonation front speed. The JM equation belongs to this class but it appears to have a more general basis than most.

The present lack of experimental high pressure data from sources other than detonation has, so far, prevented the establishment of reliable criteria by which the validity of equations of state may be judged. The degree of agreement obtained between calculated and observed detonation velocity - - the most frequently used criterion - - is not adequate, nor is the observed first shock velocity in the medium surrounding the explosive, because neither of these is very sensitive to the equation of state. For example, it is a consequence of a general argument due to Jones [1.19] that regardless of the equation of state used, the calculated detonation wave speed will not be in accord with that observed in condensed explosives at high loading density unless the calculated adiabatic exponent has a value close to 3 at the equilibrium front. Considerable use has been made of this well known empirical requirement, and if the viewpoint is taken that that value of the adiabatic exponent obtained by inserting the observed detonation wave speed in the simple Jones formula for it is more reliable than any other, then a gamma law gas equation of state might be said to have been constructed.

Arguments essentially of this inverse or hydrodynamic nature underlie all the so-called "inverse equations of state". Conversely, it follows that, for the limited purpose of describing conditions not far from those obtaining at such detonation fronts, the very simple assumption that the products will behave like a gamma law gas with the exponent equal to 3 is adequate to reproduce the observed detonation speed with reasonable precision when a value for the chemical energy is assumed. The latter may also be taken to be constant. However, it would be absurd to argue that it is such a gas and that the gamma law relation assumed is a general equation of state simply because the observed detonation wave speed is thereby reproduced.

Furthermore, when it is borne in mind that thermodynamic conditions in a Taylor wave lie within a fairly narrow range on the calculated adiabats, (volume changing only by about 60%), it may be appreciated that even fairly good agreement between an instantaneously observed spatial distribution of one of the properties and that of the Taylor wave would not be an adequate criterion of the validity of an equation of state. Alternatively expressed, the Taylor wave may be said to be insensitive to the equation of state. That this is so will be illustrated in chapter 7 by comparing the Taylor waves calculated here with those calculated by others using very different equations.

Observations of the kind referred to have not so far been obtained for condensed explosives but in gaseous detonations, where the pressure is fairly low, the instantaneous spatial distribution of pressure may be readily deduced from pressure gauge records. Such distributions agree with the corresponding Taylor wave. In gaseous detonations, the product mixture is almost invariably assumed to be a gamma law gas, but agreement of the Taylor wave so deduced with that observed is quite unremarkable (except in so far as the agreement obtained supports the hydrodynamic assumptions) and only indicates that the adiabatic exponent does not change greatly over the fairly limited range of temperatures obtaining in the Taylor wave, a feature known in advance.

It is now opportune to clarify the distinction drawn here between an equation of state and other formulae used for the same purpose. A protracted and dangerous discussion can only be avoided by admitting that any relation allowing the calculation of all thermodynamic properties in terms of two of them may be regarded as an equation of state. However, we are not concerned with detailed classifications, but rather with attempting to draw a clear distinction between equations applied to detonation products which are based on phenomena other than detonation and are free from the related general hydrodynamic assumptions, and those which are deduced from observed detonations with all the necessary assumptions that this entails. As indicated earlier, the former are here called equations of state and the latter are called detonation front formulae or simply formulae. It is generally agreed that an equation of state should be applicable to several kinds of phenomena and to a fairly wide range of conditions. To attempt to define just how wide is out of the question: all that one may do is to describe some as more general than others, the generality referring particularly to the range of conditions. Finally, since virtually all practical equations of state are empirical - - and, indeed, should be so if they are to describe reality - - the term theoretical equation of state will generally be avoided except where the intention is to emphasize the process of derivation rather than the final application.

Returning now to the topic of criteria of validity, Lutzky[1.20] has proposed that the second shock in the blast wave in the fluid surrounding a spherical charge of explosive be used to judge the order of merit of equations of state. A series of computations of the trajectory of the second shock would be made using the equation of state as the only variable. The degree to which these agreed with the observed second shock trajectory would decide their relative validity. However, as Lutzky pointed out, it would have to be taken into consideration that all calculations of product behaviour (including the present ones) neglect the reaction zone and other possibilities such as turbulence and incomplete combustion. Nevertheless, the second shock twice traverses the product mixture before passing into the surrounding fluid and the calculated path should be a sensitive function of the product equation of state. It is noteworthy that for spherical blast waves in air initiated by high explosives, the second shock calculated using hitherto proposed product equations of state differs[1.20] more strikingly from that observed than is the case for any other reliably observed phenomenon.

This paper is concerned with calculations that may be made only requiring specification of the explosive and of its loading density. Thus, observed phenomena are not required except in so far as they relate to already calculated values. For the JM formula, the observed detonation wave speed is used, as described earlier, to correct the formula. Those more interested in observed phenomena are referred particularly to Cook[1.9], which is also a good general reference on condensed explosives. Others are J.Taylor[1.2] and Kistiakowsky [1.21]. Data on detonation wave speeds have been released by the Bruceton[1.7] laboratories. Reaction zone phenomena are described in Combustion, Flame, etc.[1.18]. Of particular interest with regard to TNT are the data of Cybulski[1.22], Jacobs[1.23], and Urizar[1.10]. Details on the properties of unreacted explosives, on their manufacture, and on the history of their discovery and development, are given in Davis[1.24] and Urbanski[1.25] and by Pennie[1.26].

The gas equation of state is dealt with in chapter 2, and the general thermodynamic relations for the mixture are treated in chapter 3, the detailed relations for the composition being given in chapter 4. The calculation of the Taylor wave is described in chapter 5 and chapter 6 deals with high-pressure approximations. The numerical results for TNT are given in chapter 7, which also contains a brief concluding discussion. It may be noted that the references are to be found immediately following the text in each chapter.

The main feature of the notation used is that the nature of a function or thermodynamic property Y is consistently denoted by an appropriate modifying symbol. In addition to Y_r, denoting that component attributable to real or non-ideal conditions, and Y_{th} denoting the thermal or ideal condition component, the following are used:

Y^* - dimensionless ; $\overline{Y}_j$ - per mole of species j
$Y^\circ, Y^\#$ - in the ideal gas state ; Y_c, Y_1 - solid carbon
$\overline{Y}$ - per mole ; Y_g - gas phase
Y_o - at 0° Absolute ; Y_e - unreacted explosive state

In the computations, and generally in the text, energy is expressed in kilocalories (kcal), temperatures in large degrees (1 DEG = 1000°K) in computations and in °K at various parts of the text, and pressure is expressed in both kilobars (kbar) and in kcal/cc units. The last named is the natural pressure unit in the computations with the energy unit chosen, but the kbar unit is more familiar and is used in the text and especially in the tables. Mass is expressed in grams (g), length in centimetres (cm) and time in microseconds (μsec). If the detonation wave speed and loading density are expressed in these units the corresponding pressure is obtained in megabar units if no conversion constants are applied.

Considerable computation is involved. Several short preliminary computation programs were written so as to calculate the required functions used in the later main program. This was designed to handle all the calculations described in the present paper. All features relating to programming and computation were carried out by the author: this involved a very considerable time. The program however, is quite fast. The entire computations for a prescribed loading density including the iteration to the Chapman-Jouguet conditions, the Taylor wave, and the continued computations along the adiabats at temperature intervals of 0.25 DEG down to 0.3 DEG takes about 1.5 minutes using the (McGill University) IBM 7044 computer. The method of regula falsi was used exclusively for iterative calculations because, unlike other methods, slopes are not needed, divergence cannot occur, and convergence is fast. For quadrature, a Runge-Kutta relation correct to 4th order is used. Functions were represented as power series wherever their nature permitted such a representation.

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CHAPTER 2

GAS EQUATION OF STATE

2.1 Introduction

Particular attention will be paid to high pressure equations of state which are in no way dependent on observed detonation front behaviour. The effective experimental data for such equations are the constants entering into the various formulae that have been proposed to describe the species-dependent instantaneous potential energy existing between a pair of like molecules, also called the intermolecular or pair potential.

In the detailed relations for the composition, only the six gaseous species CO, CO_2, CH_4, H_2, $N_2$and $H_2O(g)$ are assumed to be present in non-negligible quantities. In order to be able to concentrate more strongly on the main gaseous products of CHON explosives, attention will be confined to only these gases, together with O_2, which is present in the products of oxygen-positive explosives, such as nitroglycerine.

2.2 The Intermolecular Potential

Comprehensive references on such information are the textbooks by Hirschfelder, Curtiss and Bird (HCB)[2.1] and by Taylor and Glasstone[2.2]. More recent information on the molecules with which we are particularly concerned is given by Fickett[2.3,2.4]. Among the recent reviews of high pressure physics and chemistry containing information relating to intermolecular potentials are those of Bradley and co-authors [2.5] and Hamann [2.6].

Our immediate concern is to present a necessarily brief appraisal of existing information on intermolecular potentials, restricting attention to the species mentioned and to the simplest realistic representations which have been proposed, that is, to those for spherical molecules. The constants in these relations have been derived from observed phenomena. We are most particularly concerned with potential constants determined from phenomena observed at high temperatures.

It is now well established that intermolecular forces arise from Coulomb interaction between the nuclei and electron clouds representing the separate molecules, so that if it were possible to state the position of all nuclei and electrons at every instant, the time-averaged, or macroscopically observable potential energy arising from the configuration of space change could be derived from Coulomb's law. The potential energy between the nuclei and electrons within a given molecule could also, in principle, be calculated in the same way.

In practice, an inverse procedure must be used. Invariably, a very simple model is assumed for the molecule. Unless it is known to be grossly non-spherical, the molecule is generally taken to be a sphere. The electronic charge distribution of a rare gas atom in its ground state is spherically symmetrical and therefore, although the atom has an instantaneous dipole moment $\sum_i e_i \vec{r}_i$ due to charges e_i at positions $\vec{r}_i$, the permanent dipole moment is zero. The same is so nearly true for many diatomic and polyatomic molecules that they may be classed as non-polar. Except for the H_2O molecule, which is strongly polar,[2.7] the molecules of present interest belong to this class.

The inverse procedure referred to is as follows. For a given pure gas of spherical non-polar molecules, the pair-potential is symmetric and therefore depends only on the pair spacing. A formula approximating the potential is assumed which consists of a sum of functions of the spacing. These functions contain certain unknown constants, which are obtained from a set of experimental data by a perturbation fitting procedure. A guess is made as to the value of all the potential constants, the potential so obtained is employed in a calculation of the observed phenomenon which is then compared to all the observations. The comparison is repeated until a set of constants is found which best reproduces or fits the available set of data. The same procedure is used for polar molecules, or for potentials describing non-spherical molecules, except that the potential formula now requires that orientation-dependent terms be included.

For some of the molecules with which we are concerned, certain potential representations recognizing their non-spherical[2.1] shape have been compared to data so as to determine the corresponding potential constants. Since the labour involved using such potentials is much greater, it is not surprising to find that little information is available regarding potential constants for such representations. The (polar) H_2O molecule is less non-spherical than CO_2. The potential, however, is non-spherical. For spherical, but polar molecules, a simple pair potential formula consists of that for a pair of non-polar spherical molecules modified by a term which is dependent on the relative orientation of the pair of permanent dipoles imagined to be imbedded in the spheres. Potential constants for a model more sophisticated than this are not available for water.

For these, and other, practical reasons the adoption of a symmetric potential for our non-polar molecules, and of a non-symmetric potential for a spherical molecule of water of the type just described, appears to be justified, provided that it is kept in mind that the corresponding potential constants pertain, not to the molecule itself, but to the equivalently behaving spherical model.

When it is imagined that a spherical molecule has a definite diameter (at a prescribed temperature), this can only refer to a hard sphere or to the collision-averaged mean diameter of a soft sphere, collisions being perfectly elastic in both cases. It is evident that this diameter can be defined in terms of intermolecular potential constants.

At very high pressures, rotation of non-spherical molecules is expected to be inhibited[2.8] to a degree dependent on the departure from sphericity, and at infinite pressure, rotation of such molecules may be presumed to be zero. Accordingly, if it is possible to construct a three-dimensional model of the nearly incompressible hard core of a molecule, then the low-velocity collision diameter of the molecule may be placed within rough bounds on the expectation that it is somewhere between the diameter of that sphere which has the same volume as the core, and of that sphere swept out in space by a freely rotating core. An approximate model of the core may be constructed using the bond-distances and angles of the atoms in the molecule, and their "van der Waals radii": this has been done by Fickett[2.3] using the values given in Pauling[2.9]. His estimates of their volume-equivalent diameters are given below. The ratio of these diameters is an indication of the degree to which the shape is non-spherical. Also shown for comparison are room temperature handbook[2.10] values and the low velocity collision diameters $\underline{c}$ which were used in the calculation of the TNT product equation of state.

Table 2.1

Molecular Diameters (in Angstroms)

Molecule	Diameter[2.3] (a) non-rotating	(b) rotating	σ	Handbook Diameter** v	VDW	K
CO*	3.5	4.1	3.706	3.19	3.12	-
CO_2	3.7	5.1	3.897	3.34	3.23	3.40
CH_4	3.5	4.6	3.796	-	-	-
H_2	2.7	3.5	2.915	2.40	2.34	2.32
N_2	3.5	4.1	3.749	3.15	3.15	3.53
H_2O	3.2	4.3	2.970	-	-	-
O_2	3.3	4.0	-	2.98	2.92	-

* Presumed to be equal to Fickett's values for N_2

** v-viscosity; VDW-van der Waals eqn.; K-heat conductivity.

The best known realistic symmetric pair potentials (for spherical non-polar molecules) are the Lennard-Jones (LJ(6-12)) and the modified Buckingham(MB) representations. In these, the force potential $\underline{\phi}(r)$ between a pair of molecules at a spacing $\underline{r}$ is represented as

$$\text{LJ(6-12):}\quad \phi(r) = 4k\theta[(\sigma/r)^{12}-(\sigma/r)^{6}] \qquad \ldots\ldots\ldots\ldots \quad (2.1)$$

$$\text{MB:}\quad \begin{cases} \phi(r) = k\theta(\alpha-6)^{-1}[6e^{\alpha(1-r/r_0)}-\alpha(r_0/r)^{6}], & r\geq r_m \\ \phi(r) = \infty & , r<r_m \end{cases} \ldots\ldots \quad (2.2)$$

where $\underline{\sigma}$ is the low-velocity collision-diameter defined by the value of r for which $\phi=0$, $\underline{k}$ is Boltzmann's constant,

$\underline{\theta}$ is a parameter with the dimensions of temperature, $\underline{k\theta}$ being the well-depth or minimum in the pair potential occuring at the (force-free) spacing $\underline{r_o}$, $\underline{\alpha}$ is a number lying between 14 and 17 for our molecules, and $\underline{r_m}$ is that value of r at which a maximum occurs in the MB potential, which, were it not for the modification $\phi=\infty$ for $r<r_m$, would fall to a value $-\infty$ as $r\to 0$. The MB potential is also referred to as the "exp-six", the Mason-Rice[2.11], or the Mayer-Careri potential.

Values of the potential constants for a pair of unlike molecules are not known from experiment and are not provided by theory. Guggenheim[2.12] lays considerable emphasis on this point. Certain empirical combining rules are generally used: these are empirically not contradicted only at low densities, i.e., at large average spacings. These rules are:

$$\left.\begin{aligned}\sigma_{ij} &= (\sigma_{ii}+\sigma_{jj})/2 \quad ; \quad \theta_{ij} = (\theta_{ii}\cdot\theta_{jj})^{1/2} \\ r_{oij} &= (r_{oii}+r_{ojj})/2 \quad \text{provided that } \alpha_{ii} = \alpha_{jj}\end{aligned}\right) \ldots. \quad (2.3)$$

where the double subscript refers to the potential constants for a pair of like molecules.

For O_2, and for a sphericalized (i.e., non-polar equivalent) high-temperature representation of H_2O, Fickett suggests potential constants only for a modified Morse (MM) potential

$$\text{MM:}\ \phi = k\theta(\alpha-6)^{-1}[6e^{\alpha(1-r/r_o)}-\alpha e^{6(1-r/r_o)}] \quad . \quad \ldots\ldots \quad (2.4)$$

While the LJ and MB potentials are infinite at $r=0$, the MM potential is positive and finite.

The inverse 6th power term accounting for the long range, weakly attractive, so-called "van der Waals forces" has long been known to be fairly realistic at $r \gg r_o$. These forces are known to include the London[2.13] or dispersion forces, accounting for the dispersion of light, and the induction and orientation forces, which, for non-polar molecules are much less important[2.2,p301]. Representation of the strongly repulsive forces that obtain for $r < r_o$ is much less certain. These forces are also referred to as "overlap forces" because at such close spacings the previously separate electron clouds overlap or become distorted, or "exchange forces", because in the Heitler-London[2.14] treatment of intra-molecular forces in a hydrogen molecule, the principal contribution to the repulsive potential was shown to be accompanied by the exchange between the atoms of a pair of spin-parallel electrons.

The available information indicates that the choice of 12 for the inverse power of the spacing to represent the repulsive term in the LJ potential must be regarded merely as the best overall choice for the representation of low temperature data when (for mathematical convenience only) choice is restricted to multiples of 3 in a more general LJ(6-n) potential

$$LJ(6-n) = \phi(r) = Ar^{-n}-Br^{-6} \quad .\qquad \ldots\ldots\ldots \quad (2.5)$$

It cannot be said that there is any correct value of n because the power law functional form is known to be not correct. The MB form is essentially Slater's[2.15] repulsive term

$$\phi = Ae^{-r/r_s} \qquad \ldots\ldots\ldots \quad (2.6)$$

added to the inverse 6th power attractive term. The success of his well known application of (2.6) to helium indicates that this repulsive term is functionally more correct. This is supported by molecular beam scattering data. Repulsive potentials thus obtained from various sources are reported by Fickett[1.3] for N_2, CH_4 and O_2: such high-velocity collison data are equivalent to high-temperature values. However, that the MB functional form is not fully correct at close spacing may be deduced from the fact that, as in the case of LJ constants, the potential constants obtained differ significantly not only according to the kind of behaviour from which they are determined but also with the temperature range over which the phenomena are observed.

The MB form must be regarded as the superior form not only for this reason, but also because the additional constant provides greater flexibility in fitting data than the (2-const) LJ form. However, with the exception of the recently reported molecular beam data, which are qualitatively most important, but so far fragmentary, most of the data from which readily available[2.1] constants have been obtained appear to have been derived at temperatures we call low, so that the relative physical advantage of the MB form is diminished. The mathematical simplicity of the LJ form is, of course, the major reason for its formulation and continued widespread use. Not only have far more data been fitted by the latter, but its use results in simple power series expressions for the second virial coefficient and its derivatives. It is also much simpler to use in our approximate, temperature adjusted, hard molecule equation of state: indeed, use of a more sophisticated potential relation in this equation of state would be difficult to justify. However, in selecting LJ potential constants from those available, we must keep in mind that the inverse 12th power term gives too steep a repulsion for most of our non-polar gases and that, in order to compensate for this, extra weight must be given to constants derived from high-temperature data.

For polar gases, the best known potential of the kind discussed earlier is that of Stockmayer[2.16]. The original potential suggested for a spherical, but polar, molecule was that of Keesom[2.17], who visualized a polar molecule as a hard sphere containing an embedded point dipole: for this model the pair potential is entirely due to the strength of the dipoles, their spacing and their orientation with respect to the intermolecular axis or line joining their centres. The original Stockmayer potential consisted of Keesom's term added to the general LJ (6-n) potential (2.5), and using this, he found potential constants for water by fitting to virial coefficients at temperatures between 400° and 700°K. He also found potential constants for ammonia (NH_3), only traces of which have been calculated to be present in the products of TNT.

Here, the less general, but more widely applied, Stockmayer form, the Stock(6-12) relation, for which more recently determined constants are available[2.1], is used. This consists of the LJ (6-12) component (2.1) added to the Keesom orientation dependent polar term, but we may note that how far the n=12 assumption is in doubt is indicated by Stockmayer's choice of n=24 for water, a value he defends as most likely among multiples of 6. The Stock(6-12) potential for a pair of like polar molecules, each imagined to contain an imbedded point dipole of strength or moment $\underline{\mu}$, is

$$\left.\begin{array}{l}\text{Stock(6-12):}\quad \phi(r,\phi_1,\phi_2,\psi_1-\psi_2)=4k\vartheta[(\sigma/r)^{12}-(\sigma/r)^{6}]-\mu^2 r^{-3}g\ , \\ \qquad \text{where}\quad g = 2\cos\phi_1\cos\phi_2-\sin\phi_1\sin\phi_2\cos(\psi_1-\psi_2)\end{array}\right\} \qquad \ldots\ldots\ldots\ldots (2.7)$$

where ϕ, ψ are respectively the polar coordinates of latitude and longitude specifying the instaneous orientations of the two dipole moments with respect to the intermolecular axis $\vec{r}_{12}$ between the molecules 1, and 2 in the pair.

A high-temperature angle-independent (i.e., non-polar equivalent, or spherical) approximation for polar molecules is ascribed to Krieger[2.18]. Such high-temperature spherical approximations are needed for our temperature-adjusted hard molecule equation of state. Krieger's approximation refers to a model in which the angle-dependent term $\underline{\mu^2 g}$ is replaced by one due to the interaction of two dipoles which are perfectly aligned on the axis $\vec{r}_{12}$. It follows from (2.7) that the potential may now be expressed

$$\left.\begin{array}{l} \text{Krieg(6-12)}: \ \phi(r) = 4k\theta[(\sigma/r)^{12} - (\sigma/r)^{6} - \delta^*(\sigma/r)^{3}] \\ \qquad\qquad\qquad \text{where} \quad \delta^* = 2\mu^2/4k\theta\sigma^3 \end{array}\right) \ldots (2.8)$$

For water (μ=1.83 debyes), Krieger's values are

$$\sigma = 2.834 \text{Å} \quad , \quad \theta = 231°\text{K} \quad , \quad \delta^* = 2.333 \qquad \ldots\ldots (2.8a)$$

It is evident that the Krieger potential may, in turn, be approximated over a chosen range by any of the non-polar potentials described: this merely requires that suitable constants be assigned. For a range of ϕ/k from 1000° to 4000°K, one readily finds adequate constants for the LJ(6-12) form for water, viz.,

$$\sigma_{LJ} \simeq 2.97 \text{Å} \quad , \quad \theta_{LJ} \simeq 52°\text{K} \qquad \ldots\ldots\ldots (2.8b)$$

It is not suggested that these values are unique, nor is it suggested that either (2.8b) or (2.8) be used for a calculation of the second virial coefficient for water, even at high temperatures. However, it is proposed that an approximation of the kind given in (2.8b) is adequate for use in an approximate equation of state at high temperatures, when water is the only polar gas present in a mixture containing a preponderance of non-polar molecules.

Fickett[2.3], using a Lennard-Jones and Devonshire equation of state, and an MM (spherical) potential for water, has attempted to find corresponding potential constants for water by successively calculating shock Hugoniots and comparing these to those obtained by Rice and Walsh[2.19] from an approximate equation of state devised to fit very high pressure shock data for water. The potential constants thus obtained, assuming $\alpha=14$ are

$$r_o = 3.35\text{Å} \qquad \theta = 138°\text{K} \qquad \ldots\ldots\ldots \quad (2.9)$$

It cannot be said that these values successfully fit the Rice and Walsh temperature-pressure Hugoniot, nor does Fickett claim this, but the pressure-volume Hugoniot in the range 200 to 350 kbar is not more than about 10% in error at a given volume: here the temperatures according to Rice and Walsh are from about 1600°K to 2700°K. The constants (2.9) are subject to errors arising from the thermodynamic assumptions made by Rice and Walsh.

The principal data for the determination of potential constants are measurements of second virial coefficients, Joule-Thomson coefficients and viscosity in pure gases, the density and energy of sublimation of crystals, and, more recently, (reactionless) shocks and the scattering of molecular beams. Measurements of transport phenomena other than viscosity, such as diffusion and thermal conductivity are generally less precise and fewer constants appear to have been derived from them. Viscosity data have generally extended to higher temperatures than for other observations and are therefore of particular interest here. Shocks in dense gases appear to be the most promising source of high-temperature high-pressure equation of state data but little is so far available for the species concerned here.

The purpose of this appraisal has been not only to review, but to engender a realistic attitude to the present state of pair potential information, particularly in regard to the strongly repulsive portion of potentials, which is most important for high-velocity collisions, and, therefore, at high temperatures. It is not realistic to regard the potential relations which have so far been proposed, particularly those mentioned here, as more than functionally approximate representations, strictly applicable only to pure gases, the constants in which are subject to continuous, and sometimes drastic, review as fresh data become available. The last remark is particularly supported by the recent Stockmayer potential constants for water[2.20]. A summary of recently obtained potential constants is given in the new (1964) edition[2.21] of HCB.

Table 2.2 contains the LJ(6-12) potential constants which were used in the determination of the hard molecule equation of state for the gaseous detonation products of TNT. When Fickett is claimed as a source, this means that his constants for the MB (or the MM) potential were assumed to apply to the LJ(6-12) potential in the following way:

$$\theta_{LJ} = \theta_{MB} \quad , \quad \sigma_{LJ} = \sigma_{MB} \qquad \ldots\ldots\ldots\ldots (2.10)$$

Whereas for the LJ(6-12) relation σ/r_o=const=$2^{-1/6}$, for the MB relation σ/r_o depends on $\underline{\alpha}$. The following values are taken from HCB[2.21,p34]

α	σ/r_o (MB)
13	0.88320
14	0.88910
15	0.89417

It is not claimed that the choice of constants made is the best, especially in the light of recent** information. However, the best choice of constants for a particular

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** The author did not become aware of the summaries of pair potential constants reported in the new edition of HCB until the computations were completed.

calculation is a matter here regarded as of less importance than the general notions of the equation of state. Some of the LJ(6-12) constants obtained at the highest temperatures reported[2.21,p1212] are given in Table 2.3 for comparison.

Table 2.2

LJ(6-12) High-Temperature Pair Potential Constants

Species		Run(a)	Constants σ(Å)	Constants θ(°K)	Data(b)
CO	(A)	2	3.706	88	V
	(B)	1	3.621	120	V,B
CO_2	(A)	2	3.897	213	V
	(B)	1	3.755	200	V,B
CH_4	(A)	1,2	3.796	144	V
H_2	(A)	1,2	2.915	38	V
N_2	(A)	2	3.749	79.8	V
	(B)	1	3.621	120	V,B
H_2O**	(C)	2	2.97	52	
	(B)	1	2.978	138	Shock

(a) In TNT product computations: 1-initial; 2-final calculations.
** Sphericalized potential.
(b) V-viscosity; B-second virial coeff.
A-HCB(ref 2.1); B-Fickett(ref 2.3); C-this paper.

Table 2.3

Lennard-Jones and Stockmayer (6-12) Pair Potential Constants

Species	Constants Found from Second Virial Coefficient			Constants Found from Other Data		
	σ(Å)	θ(°K)	Data Range(°K)	σ(Å)	θ(°K)	Data
(a)	(b)	(c)	(d)	(e)	(f)	(g)
CO	3.763	100.2		3.92(N)	32.8	D
				3.706	88	V(H)
				3.59	110	V
CO_2	4.07	205		4.00(N)	190	V
	3.91(N)	203.3	600-900	4.07(N)	150	D
	4.47(N)	187.5	300-500	4.11(N)	221	C
				3.897	213	V(H)
CH_4	3.817	148.2		3.697(N)	156.7	K
	3.809(N)	148.1	300-450	3.822	137	V
				3.796	144	V(H)
				3.808(N)	140	V
H_2	2.928	37		2.915	38	V(H)
	2.959(N)	36.7	100-430	2.968	33.3	V
N_2	3.71	95.9		3.85(N)	47.6	D
	3.698	95.05		3.749	79.8	V(H)
				3.681	91.5	V
H_2O	2.65	380(1.2)	300-700	2.52(N)	775(0.707)	V
	**2.99(S)		300-700	2.76(S)		X
				2.53(S)		V(Suth.)
O_2	3.58	117.5		3.541	88	V(H)
	3.46	118		3.433	113	V

Note (1) Except where the σ column shows (N) or (S), values are from the 1954 edition of HCB(ref2.1); (S)-values from Stockmayer (ref2.16); (N)-values from (1964) addendum to HCB(ref2.21)

(2) Symbols under column (g) refer to: D-diffusion; V-viscosity; C-third virial coefficient; K-heat conductivity; X-X-Ray scattering; V(Suth.)-viscosity using Sutherland potential. (H) here refers to a higher temperature range 300-1000°K generally, extending still higher for CO, N_2

(3) **Using Keesom potential for a hard polar molecule. $(\delta^*/\sqrt{2})$

(4) Underlined values are those used in the computation of the second virial coefficient for TNT gas product mixture

2.3 The Detonation Front Relations of H. Jones[2.22]

The following well-known relations due to Jones are the basis of most inverse equations of state. For the immediate present, we are interested only in the values derivable directly from these relations as a reference magnitude which equations of state must explain, rather than in inverse equations of state.

Jones showed that fairly precise estimates of the pressure, mass density and adiabatic exponent at the equilibrium detonation front in a column of explosive could be made without invoking any equation of state provided that precise values of the observed detonation front speed D_∞ and its derivative with respect to loading density are available. His relations are

$$\left.\begin{aligned} p &= D_\infty^2\Delta/(2+\beta)z_\infty && (1)\\ \Delta/\rho &\equiv (v_1\Delta) \equiv V/V_e = a/D_\infty = 1-1/(2+\beta)k_\infty && (2)\\ \gamma_{Ad} &\equiv (\partial \log p/\partial \log \rho)_s = a^2/pv_1 = (2+\beta)z_\infty - 1 && (3)\end{aligned}\right)(2.11)$$

where $z_\infty \equiv 1 + d\log D_\infty / d\log\Delta$

and where $\underline{\Delta}$ is the explosive loading density, $(\ )_e$ refers to the unreacted explosive, v_1 is the specific volume of the product mixture and $\underline{\rho}$ its density, and $\underline{\beta}$ is a parameter defined by

$$\beta \equiv p/[\partial(E-Q)/\partial V]_p = [\gamma_{Ad}C_v/v_1(\partial p/\partial T)_v - 1]^{-1} \quad \ldots \quad (2.11a)$$

where C_v is the product specific heat at constant volume, E is the internal energy of the products and Q is the chemical energy released in the detonation reaction.

As Jones has pointed out, no results may be obtained from these relations without formulating some equation of state, but even a very approximate form is adequate to give reasonably precise estimates of p, v_1 and γ, because it may confidently be estimated that

$$\beta << 2 \qquad \text{........ (2.11b)}$$

Jones estimated that $\beta \simeq 0.2$ for PETN. It is here found that for the modified Jones and Miller formula for TNT, $\beta \simeq 0.12$. Cook[2.23,p67] gives estimates for β in PETN ranging from 0.05 to 0.65 according to the loading density and the equation of state assumption made. For present purposes, it is adequate to estimate

$$\left.\begin{aligned} \beta &\simeq 0.2 \pm 0.15 \\ \text{so that } (2+\beta) &\simeq 2.2 \pm 7\% \end{aligned}\right) \qquad \text{........ (2.11c)}$$

which is a fair estimate of the reliability of values estimated from (2.11)

Observed detonation wave speeds D_∞ are generally fitted by a polynomial

$$D_\infty = \sum_{n=1}^{m} k_n \Delta^{n-1} \quad , \qquad \text{........ (2.12)}$$

and for high loading densities, $\Delta > 0.8$g/cc, the Bruceton laboratory observations[2.24] are given as linear in the density

$$\left.\begin{aligned} D_\infty &= k_1+k_2\Delta \\ \text{so that} \quad z_\infty &= (k_1+2k_2\Delta)/D_\infty = (2D_\infty-k_1)/D_\infty \end{aligned}\right\} \quad \ldots\ldots\ldots \quad (2.12a)$$

Estimates of properties derived from (2.11) using (2.11c) and (2.12a) are given in the following table. These serve as an adequate guide to the magnitude involved.

Table 2.4

Estimates For an Explosive Loading Density Δ of 1.6g/cc

Explosive	Observed Quantities				Derived Values		
	k_1 m/sec	k_2 m cc/g sec	D_∞ m/sec	z_∞ -	p kbar	$V/V_e=\Delta/\rho$ -	γ -
TNT	1785	3225	6945	1.74	202	0.739	2.82
tetryl	2375	3225	7535	1.69	245	0.732	2.70
PETN	1600	3950	7920	1.80	253	0.748	2.95
RDX	2490	3590	8234	1.70	290	0.733	2.72

2.4 Virial Equations of State

That expression which represents the pressure as a power series in the inverse volume is known as a virial. The coefficients of V^{-n} are functions of temperature only because they are defined by conditions in the limit p→0. The virial expression for p/RT for a pure gas is

$$p/RT = \sum_{n=1}^{\infty} \bar{B}_n(T)\bar{\rho}^{n} \quad ; \quad \bar{\rho} \doteq 1/\bar{V} \quad , \qquad \ldots\ldots\ldots \quad (2.13.1)$$

where $(\bar{\ })$ refers to one mole of gas, and $\bar{B}_n$ is the n^{th} virial coefficient, so that $B_1=1$. The corresponding expression for the compressibility factor Z is therefore

$$Z \equiv p\bar{V}/RT = 1+\sum_{n=2}^{\infty} \bar{B}_n(T)\bar{\rho}^{n-1} \quad , \qquad \ldots\ldots\ldots \ (2.13.2)$$

where the coefficients have the meaning

$$\bar{B}_{n+1} = (1/n!) \lim_{\bar{\rho}\to 0}(\partial^n Z/\partial\bar{\rho}^n)_T \quad , \qquad \ldots\ldots\ldots \ (2.13.3)$$

which establishes their significance as coefficients in a Taylor series

$$f(\bar{\rho},T) = f(0,T)+\sum_{n=1}^{\infty}(\partial^n f_o/\partial\bar{\rho}^n)_T\bar{\rho}^n/n! \qquad \ldots\ldots\ldots \ (2.13.4)$$

While expressions of the form (2.13.2) have been in use for the representation of pV at near-ideal conditions since at least the time of Onnes(1901), recognition that they have a sound theoretical basis has been more recent. In principle, the coefficients $\bar{B}_n$ are calculable by the methods of statistical mechanics from the pair potential formulae. In practice, difficulties in computations, together with the previously outlined uncertainties in these potential formulae have so far prevented reliable computations beyond $\bar{B}_3$, the third coefficient. It follows that, in practice, only such relatively low densities $\bar{\rho}$ as permit the use of the truncated form

$$Z = 1+\bar{B}_2(T)/\bar{V}+\bar{B}_3(T)/\bar{V}^2 \qquad \ldots\ldots\ldots \ (2.14.1)$$

may be treated by a virial equation of state with realistic coefficients $\bar{B}_n(T)$.

When the (non-polar) gas pair-potential is represented by the LJ(6-12) formula, the second coefficient is given by

$$\left.\begin{aligned} \bar{B}_2(T) &= \bar{b}_o B^* \\ \text{where}\quad \bar{b}_o &\equiv 2\pi\bar{N}\sigma^3/3 \quad , \\ B^*(T^*) &= \sum_{k=1}^{\infty} g_k^* T^{*(1-2k)/4} \quad , \\ \text{where}\quad g_k^* &= -[2^{k-3/2}/(4k-4)!]\,\Gamma[(2k-3)/4] \quad , \\ T^* &= T/\theta \end{aligned}\right\} \quad \text{.. (2.14.2)}$$

and Γ is the gamma function. Values of g_k^* are available up to k=41[2.1]. It may be noted that the term $\bar{b}_o$ is equal to 4 times the volume of $\bar{N}$ molecules.** It is therefore a van der Waals type co-volume, though it is not equal to the van der Waals co-volume $\bar{b}$, nor to the general co-volume defined earlier. When σ is in Å units, the value of $\bar{b}_o$ is given by

$$\bar{b}_o = 1.2615\sigma^3 \text{ cc mole}^{-1} \qquad \text{........ (2.14.2a)}$$

For polar molecules, the second virial coefficient may be represented by

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[**] of collision diameter σ

$$\left.\begin{aligned} \bar{B}(T) &= \bar{b}_o[B^*(T^*)-P^*(T^*,t^*)] \\ \text{where}\quad t^* &= \mu^2/8^{1/2}k\theta\sigma^3 = \delta^*/2^{1/2} \end{aligned}\right\} \quad \ldots\ldots\ldots\ (2.14.3)$$

Here, B* is the dimensionless non-polar component and -P* is the polar component. When the Stockmayer(6-12) pair potential is used, B* is defined by (2.14.2). We are only concerned with the term P* for water, where t*=1.2. The theoretical expression for P* is an infinite series. At high temperatures the correction is small, and since Rowlinson's calculations of B*-P* are available[2.1] for a number of values of t*, including t*=1.2, it seemed more practical to fit the correction term by a simpler expression. Examination of the tabulated values of

$$B^*(T^*,t^*) \equiv B^*(T^*)-P^*(T^*,t^*) \quad \ldots\ldots\ldots\ (2.14.4)$$

shows that P* is nearly linear in 1/T* for a particular polar gas, i.e., for a particular value of t*. Accordingly the expression

$$P^*_j = \sum_{k=1}^{4} w^*_{jk}\, T^{*^{-k}} \quad \ldots\ldots\ldots\ (2.14.5)$$

may be fitted to the values of

$$B^*(T^*)-B^*(T^*,t^*_j)$$

where each of these functions is available. It is found here that

$$\left.\begin{array}{ll} w_1^* = 0.0565796 & w_3^* = 1.02539 \\ w_2^* = 5.08838 & w_4^* = 7.89453 \end{array}\right) \begin{array}{l}\text{for } H_2O \\ (t^*=1.2)\end{array} \quad (2.14.6)$$

when fitted over the range 0.8 to 20 of T*, or 304 to 7600°K for water. The relative error in $\overline{B}$ for water using (2.14.5) with the values (2.14.6) is less than 10^{-4}, a trivial departure compared with uncertainties in observed values of $\overline{B}(T)$.

For the third virial coefficient for a non-polar gas, usually represented, not as $\overline{B}_3(T)$ but as $\overline{C}(T)$, no expression comparable to the infinite series for B* arises out of the integral in a statistical mechanical formulation, even for an LJ(6-12) pair potential representation. The only values available are those found by quadrature. Taylor and Glasstone[2.2,p.350] give the expression

$$\left.\begin{array}{l} C^*(T^*) \equiv \overline{C}(T)/(\overline{b}_o)^2 = \sum_{k=1}^{3} h_k^* T^{*(1-k)} \\ \text{where} \quad h_1^* = 0.268 \quad , \quad h_2^* = 0.086 \quad , \quad h_3^* = 0.488 \end{array}\right) \quad (2.15)$$

obtained by fitting to the values calculated by deBoer and Michels[2.25]. The more recent and more accurate calculations of C*[2.26] given in HCB[2.1] could readily be fitted by a comparable or higher power expression, but (2.15) appears sufficiently accurate for T*=1.5 to 10*, as illustrated below.

Table 2.5

T*	C*(T*)		Error %
	Eqn.2.15	Ref.2.1,Table I-C	
1.5	0.542	0.54339	0.26
2	0.433	0.43710	0.92
4	0.320	0.32662	2.0
6	0.296	0.30771	3.8
8	0.286	0.29618	3.5
10	0.282	0.28610	1.4
20	0.274	0.24643	10

The temperature range of adequacy of (2.15) is thus about 150° to 1000°K for the TNT product gas mixture, for which $\bar{\theta}_{gas} \simeq 100°K$ using the high temperature constants given in Table 2.2. These temperatures cover the range of application of the virial on the detonation product adiabatics.

The compressibility factor Z may also be expressed as a power series in (p/RT) , that is, by

$$Z = 1 + \sum_{n=2}^{\infty} \bar{D}_n(T)\,(p/RT)^{n-1} \qquad \ldots\ldots\ldots\ (2.16.1)$$

The coefficients $\bar{D}_n(T)$ may be determined from $\bar{B}_n(T)$ by demanding that

$$\lim_{\bar{\rho}\to 0} [\partial^n Z(T,p/RT)/\partial\bar{\rho}^n]_T = \lim_{\bar{\rho}\to 0} [\partial^n Z(T,\bar{\rho})/\partial\bar{\rho}^n]_T \qquad \ldots\ (2.16.2)$$

One readily obtains the following relations

$$\left.\begin{aligned} \bar{D}_2 &= \bar{B}_2 \\ \bar{D}_3 &= \bar{B}_3 - \bar{B}_2^2 \\ \bar{D}_4 &= \bar{B}_4 - 3\bar{B}_2\bar{B}_3 - 2\bar{B}_2^3 \\ \bar{D}_5 &= \bar{B}_5 - 4\bar{B}_2\bar{B}_4 - 2\bar{B}_3^2 + 10\bar{B}_2^2\bar{B}_3 - 5\bar{B}_2^4 \end{aligned}\right) \qquad \ldots\ldots\ldots\ (2.16.3)$$

However, since $\bar{B}_n > 3$ are not known, the only practical virial of the form (2.16) with realistic coefficients is the truncated form

$$Z = 1+\bar{B}(p/RT)+(\bar{C}-\bar{B}^2)(p/RT)^2 \qquad \ldots\ldots\ldots \ (2.16.4)$$

which may be expressed more simply by

$$Z = 1+(\bar{b}_o p/RT)B^*(T^*)+(\bar{b}_o p/RT)^2[C^*-B^{*2}] \qquad \ldots\ldots\ldots \ (2.16.4a]$$

when the same pair potentials are used for both $\bar{B}$ and $\bar{C}$. This cannot be the case except for a pure gas, and is not necessarily the case even then, because of the uncertainty in the pair potentials. The conventional notation

$\bar{B}$ for $\bar{B}_2$

$\bar{C}$ for $\bar{B}_3$

has now been adopted.

The empirically adequate expression for the second virial coefficient of a mixture of m non-polar gases is

$$\left.\begin{array}{l} \bar{B}_g = n_g^{-2} \sum\limits_{i=1}^{m} \sum\limits_{j=1}^{m} n_i n_j \bar{b}_{oij} B^*_{ij}(T^*_{ij}) \\ \text{where } \bar{b}_{oij} = [(\bar{b}_{oii})^{1/3}+(\bar{b}_{ojj})^{1/3}]^3 8^{-1} \\ T^*_{ij} = (T^*_{ii} \cdot T^*_{jj})^{1/2} = T/\theta_{ij} \quad , \quad \text{where } \theta_{ij} = (\theta_{ii} \cdot \theta_{jj})^{1/2} \\ \qquad\qquad n_g = \sum\limits_{j=1}^{m} n_j \end{array}\right) \qquad \ldots\ldots\ldots \ (2.17.1)$$

where n_j is the number of moles of species j in the mixture.

For an invariant composition, the only one of present concern, we may write $\overline{B}_g=\overline{B}_g(T)$. It is known that the mixed terms B^*_{ij} involving a non-polar and a polar gas are non-polar so that for a gas mixture containing a single polar gas, the expression for $\overline{B}_g$ remains unaltered, except that

$$\overline{b}_{oik} = \overline{b}_{oin}/\beta^2 \quad ; \quad \theta_{ik} = \theta_{in}\beta^2 \qquad \ldots\ldots\ldots \ (2.17.2)$$

where k denotes the polar gas and i, n denote non-polar** gases and

$$\beta = 1+0.892(\alpha_i t^*_k/\overline{b}_{oii})(\theta_k/\theta_i)^{1/2} \qquad \ldots\ldots\ldots \ (2.17.2a)$$

where α_i is the polarizability of the non-polar molecule in cubic Ångströms and $\overline{b}_{oii}$ is in cc/mole. Thus the only polar term in $\overline{B}_g$ is $(n_k/n_g)^2\overline{b}_{okk}B^*_{kk}(T^*_{kk},t^*_k)$.

The expression (2.17) for $\overline{B}_g$ is unsatisfactory both theoretically and numerically. When the number of gaseous species m is large, calculations are not only time-consuming but inaccurate because of accumulation of round-off errors. The number of different terms in (2.17) is

$$(m)(m+1)/2 \qquad \ldots\ldots\ldots \ (2.18.1)$$

so that even the 6 gas species detonation product mixture with which we are concerned (say, j=2 to 7 where j=7 is water, j=1 being solid carbon) contains 21 unlike terms, i.e.,

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**n denotes a hypothetical non-polar gas with pair potential constants identically equal to those of k, polar one.

$$\left.\begin{aligned} n_g^2\overline{B}_g = {} & n_2^2\overline{b}_{o22}B^*(T^*_{22})+\cdots+n_7^2\overline{b}_{o77}B^*(T^*_{77},t^*_7) \\ & + 2(n_2n_3\overline{b}_{o23}B^*(T^*_{23})+\cdots+n_2n_7\overline{b}_{o27}B^*(T^*_{27})) \\ & + 2(4\ \text{terms})+2(3\ \text{terms})+2(2\ \text{terms}) \\ & + 2n_6n_7\overline{b}_{o67}B^*(T^*_{67}) \end{aligned}\right) \quad \ldots \quad (2.18.2)$$

The representation of B* by the series (2.14.2) requires an increasing number of terms as T* decreases. In the present application the first 21 terms were used in order to avoid a relative mathematical error exceeding 10^{-6} at $T^*=1$ ($T \approx 150$°K for most pairs). At T* exceeding 20, the first 5 terms in (2.14.2) would give about the same accuracy. With choice of $k_{max}=21$ we may therefore discount mathematical errors. However, the accuracy with which (2.14.2) represents the observed physical quantity cannot exceed experimental uncertainties. The latter may confidently be assumed to be in excess of 1%. For the 6-species mixture virial coefficient representation (2.18.2) the physical error may well be 20%. More important is the fact that the pair potentials for unlike molecules are unknown. It is known[2.2,p.351] that the additive rule for diameters, true for hard spheres, is supported by crystal data, but the combination rule for potential well depths (θ) is an upper limit, i.e., we are justified only in the statement

$$\theta_{ij} \leq (\theta_{ii}\theta_{jj})^{1/2} \qquad \ldots\ldots\ldots \quad (2.19)$$

Guggenheim[2.27] contains a notably insistent denial of the theoretical validity of the combination rules.

The combination rules are better regarded as physically adequate than as physically supported because other combination rules give equally good agreement with observations. For example, representation of $\bar{B}_g$ for a mixture of the non-polar gases concerned here by the coefficient for a mixture-representative pure species is not significantly different from that given by the conventional expression. The mixture representative species was defined to have pair potentials

$$\left.\begin{aligned} \sigma_g &= n_g^{-2} \sum_i \sum_j n_i n_j \sigma_{ij} \quad ; \quad \sigma_{ij} = (\sigma_{ii}+\sigma_{jj})/2 \\ \theta_g &= n_g^{-2} \sum_i \sum_j n_i n_j \theta_{ij} \quad ; \quad \theta_{ij} = (\theta_{ii}\cdot\theta_{jj})^{1/2} \end{aligned}\right\} \quad (2.20)$$

as in Fickett's study of detonation using the Lennard-Jones and Devonshire equation of state[2.4]. These definitions were suggested by Nosanow[2.28]. The labour in applying (2.20) is very much less than for (2.17): it has additional advantages for our application. These will be described presently.

When one of the gases in the mixture is polar, the relations (2.17) are even more doubtful because experimental data on second virial coefficients are lacking for such cases. Bearing all these factors in mind, and noting that (2.20) is relatively poor when one of the gases present is polar, except at high temperatures where the necessary sphericalization of the polar pair potential is acceptable, it appears preferable to calculate $\overline{B}_g$ from the relation involving only like molecular pair potentials, viz.,

$$\left.\begin{array}{l} \overline{B}_g \simeq n_g^{-1} {}_{j}\, n_{jj}\overline{b}_{ojj}B^*(T^*_{jj},t^*_j) \\ \\ \text{where} \quad B^*(T^*_{jj},t^*_j) = B^*(T^*_{jj})-P^*(T^*_{jj},t^*) \\ j(\text{non-polar})P^* = 0 \quad ; \quad j(\text{polar})P^* = \sum_{k=1}^{4} w^*_k/T^{*k} \end{array}\right) (2.21)$$

Furthermore, when one bears in mind that the truncated virial (2.14.1) is not applicable unless

$$\overline{C}/\overline{V} << \overline{B} \quad ,$$

we may replace the extremely complicated (and theoretically unjustified) expression for $\overline{C}_g$ given in Hirschfelder's text (reference 2.1, Tables I-C, I-D) by the simpler one for a pure species with pair potentials defined by (2.20) using the fitted expression (2.15) and the sphericalized pair potential constant for water given in table 2.2. To summarize, the expression here recommended for representation of the compressibility factor for the detonation product gas phase on the adiabatics after the composition has become fixed (T < 1000°K) becomes

$$Z = 1+(p/RT)\overline{B}_g(T)+(p/RT)^2[\overline{C}(\sigma_g,T^*_g)-\overline{B}_g(T)^2] \quad \ldots\ldots\ldots \ (2.22)$$

where $\overline{B}_g$ is found using (2.21) and the pair potential constants given in table 2.3 and $\overline{C}$ is found using (2.15), (2.20) and the constants given in table 2.2.

2.5 The Co-Volume and Internal Energy

As stated earlier, the co-volume, here denoted by $\overline{X}$, is essentially the imperfect component of the gas volume, that is, for a pure gas

$$\left.\begin{aligned}\overline{X}(p,T) &\equiv \overline{V}-\overline{V}^\circ = \overline{V}-RT/p \\ &= (RT/p)(p\overline{V}/RT-1) \equiv RT/p(Z-1)\end{aligned}\right\} \quad \ldots\ldots\ldots \; (2.23.1)$$

where Z is the compressibility factor $p\overline{V}/RT$. Also for a gas mixture

$$\overline{X}_g(p,T,n_1,- - - n_m) \equiv RT/p(Z_g-1) \quad \ldots\ldots\ldots \; (2.23.2)$$

by definition, where $(\ )_g$ refers to the gas mixture. Thus the co-volume $\overline{X}$, as here defined, and the compressibility factor Z, are mutually definitive. In the hard molecule equation of state, $\overline{X}$ is defined by numerically calculated values $Z(\sigma_o,p,T)$, where, for practical application, σ_o, the hard molecule diameter, must be related to intermolecular potentials, and in the Jones and Miller formula an assumption $\overline{X}_g=\overline{X}_g(p)$ is made, the coefficients in a power series expression for it are calculated from relations of the type (2.11) and Z is defined by $\overline{X}(p)$. For a virial equation of state with realistic (i.e., temperature-dependent) coefficients, $\overline{X}(p,T)$ or $\overline{X}(T,\overline{V})$ is defined by Z, and when, as here, a p,T system is used, Virial: $\overline{X}_g(p,T) = \overline{B}_g(T)+(p/RT)[\overline{C}(\sigma_g,T^*_g)-\overline{B}_g(T)^2]$ ... (2.24)

from 2.22.

In the statistical treatment of an ideal gas the separability of the internal energy into a sum of translational, rotational, vibrational and electronic terms (the sum total of which is here referred to as $E_{thermal}$) is based on the provable assertion that spacings of permissible energy levels in each mode are so widely different that they may be regarded as uncoupled. For a real gas of molecules with force fields, the separability of the energy into a sum of thermal and real components, neither of which affects the other, is an assumption that cannot be avoided if a quantitative solution is to be obtained. This assumption is justified only if the interaction of the force fields does not distort the shape of the potentials and is therefore poorest at high densities. Presently available information[2.2,2.4] indicates that the assumption is not seriously unsound even at the highest pressures encountered in detonation and that complete breakdown does not occur until a pressure of about 1 megabar** is reached. Accordingly, we assume, for a pure gas

$$\overline{E} = \overline{E}^{\circ}+\overline{E}_r \qquad \text{........ (2.25.1)}$$

and for a mixture of gases

$$E_g = E_{th}+E_r \quad , \qquad \text{........ (2.25.2)}$$

where $(\;)_r$ refers to the real component and $(\;)_{th}$ to the thermal component. The thermal component is

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**For hydrogen, it is argued that this (metallic state) occurs at not less than 250 kbar (ref.2.1,p.271).

$$\left.\begin{array}{l} E_{th} = \sum_{j=1}^{m} n_j \bar{E}_j^{\circ} \\ \\ \text{where} \quad \bar{E}_j^{\circ} = \bar{E}_{trans}^{\circ} + \bar{E}_{rot}^{\circ} + \bar{E}_{vib}^{\circ} + \bar{E}_{el}^{\circ} \end{array}\right) \quad \ldots\ldots\ldots \; (2.26)$$

and E_r is defined by invoking the general thermodynamic relation

$$(\partial E/\partial p)_T = -[p(\partial V/\partial p)_T + T(\partial V/\partial T)_p] \qquad \ldots\ldots\ldots \; (2.27)$$

which, from the definition of $\bar{X}$ becomes

$$(\partial \bar{E}/\partial p)_T = -[p(\partial \bar{X}/\partial p) + T(\partial \bar{X}/\partial T)] \qquad \ldots\ldots\ldots \; (2.27a)$$

so that

$$\bar{E}_r = -\int_0^p [p(\partial \bar{X}/\partial p)_T + T(\partial \bar{X}/\partial T)_p]\,dp\,\Big|_T \quad . \qquad \ldots\ldots\ldots \; (2.28)$$

In particular, the imperfection component of the internal energy for a nearly ideal pure gas $(\bar{X}=\bar{B}(T))$

$$\bar{E}_r = -\int_0^p [Td\bar{B}/dT)\,dp = -pTd\bar{B}/dT \qquad \ldots\ldots\ldots \; (2.28a)$$

and if the gas is non-polar with an LJ(6-12) pair potential,

$$\bar{E}_r = -p\theta\bar{b}_o T^* dB^*/dT^* = (p\theta\bar{b}_o/4) \sum_{k=1}^{\infty} (1-2k) g_k^* T^* \quad , \ldots (2.28b)$$

and since $dB^*/dT^* \gtrless 0$ for $T^* \lessgtr 25$, $\bar{E}_r$ is positive zero, or negative depending on T^*. Typically $T^* \approx 150$°K for the molecules concerned here (see Table 2.3) so that were B(T) the only force field component in $\bar{X}$, the imperfection component $n_g\bar{E}_r$ of the gas mixture would be near zero at about 3700°K and negative at temperatures below this value, which is typical of detonation front temperatures in condensed explosives.

Near $T^* \simeq 25$, the slope dB/dT is very slow so that more generally one may say that for such a co-volume the imperfection component of the internal energy is virtually zero at the detonation front, even though here the compressibility factor Z is typically about 10. Such a co-volume is hardly credible for high loading density detonation products. Hirschfelder[2.29] has used such a form for gun powder gas at densities less than about 0.85 g/cc, where the approximation appears to be justified. Paterson[2.30] and J. Taylor[2.31] have applied a virial form $Z=Z(\overline{B},\overline{V})$ to the high explosives listed in table 2.4 up to near-crystal loading densities. In such cases, the imperfection component of the internal energy appears to be much too small. We shall return to this point shortly. Finally, for a pure gas of hard spheres of immutably fixed diameter without force fields, the imperfection component of the internal energy is, of course, exactly zero because intermolecular forces are absent.

2.6 The Lennard-Jones and Devonshire Cell Theory Equation of State

A virial equation of state is increasingly valid as $r_o/\overline{r} \rightarrow 0$, where $\overline{r}$ is the average spacing of molecules, and r_o is the equilibrium pair spacing described earlier. At the opposite extreme, the equation of state for a crystal becomes increasingly valid as $r_o/\overline{r}$ exceeds unity. Here a molecule spends most of its time in a repulsive force field and the imperfection component of internal energy must be positive. However, even at high densities, a gas lacks the perfect order of a crystal and is expected to resemble a liquid more closely.

The best known equations of state for liquids are essentially those for imperfect crystals. In a (pure) crystal, each atom may only vibrate about a fixed position. As the average spacing r in a gas decreases below an equivalent hard sphere diameter $\underline{\sigma_o}$ (as yet undefined) each molecule tends to become locked in the cell formed by its nearest neighbours. In the cell theories of Lennard-Jones and Devonshire (LJD)[2.32] and of Eyring, each fixed lattice-site in a crystal is replaced by a cell centred at it. Each molecule has more freedom than the atom in a perfect crystal in that it may move freely in the cell of its neighbours regarded as fixed, but like a perfect crystal, every site, or cell, is supposed occupied by a molecule. In hole theories attempts are made (without notable success) to extend the notion of imperfect crystals to lower densities by allowing some cells to be unoccupied.

The LJD equation of state is fully described in standard texts and Fickett[2.4] has demonstrated its application to the calculation of detonation front behaviour so that a description of it here is not required. Fickett's successful reproduction of observed detonation front speeds for a number of explosives leaves little doubt as to its applicability to detonation front conditions. Thus, we are here concerned merely with estimating the density range of its application, with emphasis on the low density limit, so as to appreciate how its application might describe adiabatic expansion following detonation.

It is evident that description would begin to be poor when the average spacing $\bar{r}$ of molecules is such that a molecule of diameter σ_o may just squeeze its way past its neighbours out of its cell into the next, giving double or triple occupancy of some cells and leaving holes in others. This problem has been described by Buehler et al[2.33] for rigid sphere molecules, where the essential argument is most simply demonstrated.

If, for simplicity, we take the high-density ordered disposition of (hard sphere) molecules to be a simple cubic lattice, each molecule has 26 nearest neighbours. If these 26 are regarded as fixed and the central one, the "wanderer", is allowed to move freely in the cell formed by its nearest neighbours, the space that the centre of the wanderer may occupy before the surface collides with that of one or more cell spheres is the free volume v_f per molecule. This has a very complicated shape (see Hirschfelder's text[2.1], Fig. 4.6-2). If a $(\equiv \bar{r})$ is the lattice spacing and σ_o the hard sphere diameter, it is apparent that the smallest spacing at which the wanderer may just escape through a cell wall is

$$a_{escape} = 2^{1/2}\sigma_o \qquad \ldots\ldots\ldots (2.29.1)$$

Since $a^3 = v$, the specific volume (per molecule), then the gas molar volume at escape is

$$\overline{V}_{escape} = 2^{3/2}\overline{N}\sigma_o^3 = 2^{3/2}\cdot 6.023\cdot 10^{23}\sigma_o^3 \qquad \ldots\ldots\ldots (2.29.2)$$

The main difficulty in hard sphere arguments is to relate the hard sphere diameter σ_o to the potential constants σ,θ so that relations may be made quantitatively relevant to a particular gas or mixture. This topic has received little attention in the literature. For the immediate present we shall assume that $\sigma_o \approx 3.15\text{Å}$, the van der Waals hard diameter for nitrogen given in table 2.1: this is approximately representative of a TNT detonation product gas. Accordingly,

$$\overline{V}_{escape} \approx 38\text{cc/mole} \quad ; \quad \rho_{escape} \approx 0.52\text{g/cc} \qquad \ldots\ldots\ldots (2.29.3)$$

The rare gases crystallize in a face-centred cubic lattice, as do nitrogen and methane. Here, molecules are to be found, not only at the corners of a cube, but also at the centre of each of the 6 faces. The same disposition is obtained by imagining the neighbours to be at the centre of each of the 12 edges of a cube. The escape condition $a/\sigma_o = \sqrt{2}$ is of course the same, but here the cell is formed by 12 nearest neighbours and

$$v = a^3/\sqrt{2} \quad , \quad \text{so that} \quad v_{escape} = 2\sigma_o^3 \quad , \; (2.29.4)$$

and making the same choice of σ_O and of the molecular weight of the gas,

$$\overline{V}_{escape} \simeq 32 \text{ cc/mole} \quad , \quad \rho_{escape} \simeq 0.74 \text{ g/cc} \qquad \text{........ (2.29.5)}$$

J. Taylor[2.31] recommends 0.5 g/cc as the lower limit of application of relations derived from cell theories: this is in fair agreement with the present values. A table comparing LJD calculated properties to those observed, is available for nitrogen at densities not greater than 0.25 g/cc (see ref.2.1, Table 4.7-6). This shows that for this density, and for a temperature of 50°C, the LJD equation gives errors of 30% in the compressibility factor, 12% in the imperfection component of the internal energy and 22% in the imperfection component of the entropy.

It may be noted that for a hard sphere gas, the compressibility factor given by cell methods is

$$Z = pv/kT = (v/v_f)(dv_f/dv) \qquad \text{........ (2.30)}$$

and that this must be infinite at the tightest possible packing $a = \sigma_O$, which, for a face-centred cubic lattice is $v = \sigma_O^3/\sqrt{2}$ or $\overline{V}$(cc/mole) $\simeq 0.43\sigma_O^3$ when σ_O is expressed in Ångstrom units. For N_2, taking $\sigma_O = 3.15$Å as before, $\rho \simeq 2.1$ g/cc, a value about equal to that of detonation products at the equilibrium front at high loading density (see table 2.4).

2.7 Gas Mixture Equation of State by Rigid Sphere Simulation

It has been seen that a satisfactory equation of state is available for a pure gas at very high and very low densities but not at intermediate values. A suitably chosen hard sphere equation of state may represent both the compressibility factor and the imperfection component of the internal energy of a pure gas over a very wide range of densities with reasonable precision if the diameter of the hypothetical hard sphere gas can be properly defined in terms of some observed property of the real gas. If the definition of the pure hard sphere gas diameter can be plausibly extended to a mixture of gases, an equation of state suitable for the description of gaseous behaviour in detonation and subsequent expansion will have been found. There are therefore three stages in devising the equation of state, viz., choosing the immutably rigid sphere relation, allowing the diameter to vary both with the temperature and with the gas, and finally extending this definition of the diameter to a gas mixture.

Choosing an equation of state for rigid spheres merely requires judgement. Compressibility factors calculated for a rigid sphere gas by Monte-Carlo methods are the yardstick by which lesser methods are judged. This must be so, because this method of quadrature allows integrals to be determined which are normally discarded, not because they are not important, but rather because they cannot be solved by other methods. The Monte-Carlo method merely requires expensive computer time. The Monte-Carlo calculations of Rosenbluth and Rosenbluth[2.34] covered a range of 29 dimensionless densities ($\bar{b}_o/\bar{V}$), not all of which were tabulated in their paper. Their compressibility factor computations dealt with the random motion of 256 spheres after each had been moved 100 times to ensure statistical equilibrium. An earlier paper by them[2.35] dealt with a two-dimensional molecular model. Their calculated compressibility factors are compared to other calculations in the following table.

Table 2.6

Compressibility Factors for Non-Attracting Hard Spheres

Dimensionless Density $w=\bar{b}_o/\bar{V}$	$Z = pv/kT = p\bar{V}/RT$			
	Monte Carlo[2.34]	A	B	C
0.1	-	1.1065	-	1.5
0.2	-	1.2275	-	1.65
0.4	-	1.5213	-	2.0
0.6	-	1.9019	-	2.4
0.740	(2.21)	2.2	-	2.7
1.185	(3.82)	3.8	3.3	3.8
1.481	(5.25)	5.35	4.25	4.9
1.692	(6.50)	6.80	4.95	5.9
1.975	(8.85)	9.40	6.1	7.9
2.370	(14.80)	14.60	7.85	14.2
2.690	32.0	-	-	31.4
2.820	59	-	-	57
2.962	∞	-	-	∞

A - Virial
B - Superposition approximation, Kirkwood[2.36]
C - Eyring cell theory, face-centred lattice
( ) - Monte Carlo values selected for representation by fitted equation.

The column B values were interpolated from a table given in Hamann[2.37]. It is evident that the Kirkwood results are very poor. The Eyring cell theory expression for the compressibility factor for non-attracting hard spheres is

$$Z = 1/[1-(cw)^{1/3}] \qquad \ldots\ldots\ldots \quad (2.31)$$

where $c^{1/3} = 0.6962$ for a face-centred cubic lattice assumption and 0.7816 for a simple cubic lattice. It may be seen that these values are very poor below $\bar{b}_o/\bar{V} \approx 1.2$, and it may be noted that with the previous assumptions regarding the hard sphere diameter for nitrogen,

$$\bar{b}_o = 1.2615[\sigma_o(\text{Å})]^3 \approx 40 \text{ cc/mole} \quad , \quad \ldots \quad (2.31a)$$

so that here $\bar{V} \approx 33$ cc/mole, in agreement with (2.29.5).

The Eyring compressibilities are increasingly reliable as $w \to 2.962$, the limiting value for a face-centred cubic lattice. The series expression for (2.31) is

$$Z = 1+\sum_{k=1}^{\infty} (cw)^{k/3} \qquad \ldots\ldots\ldots \quad (2.31b)$$

This together with the virial expression for Z for hard spheres

$$Z = 1+w+0.625w^2+0.2869w^3+(-)0.115w^4+\sum_{k=5}^{x} b_n w^n \qquad \ldots\ldots\ldots \quad (2.32)$$

suggests that the Monte-Carlo compressibility factors might be fitted over a wide range by relations of the form

$$Z = 1+y\exp\left(\sum_{k=1}^{m} a_k y^{(k-1)/3}\right) \qquad \ldots\ldots\ldots \quad (2.33)$$

or by $Z = 1+yF(y) \quad ; \quad F(y) = 1+\sum_{k=1}^{m} A_k y^{1/3}$ .... (2.34) where $y \equiv (\bar{b}_o p/RT)$ .... (2.34a)

This is obviously possible because if $Z = Z(\bar{b}_o,\bar{V})$, then

$$\left.\begin{aligned} \bar{V} &= f(pb_o/RT) = f(y) \\ \text{so that}\quad Z &= g(y) \end{aligned}\right)$$

This kind of representation is required in a (p,T) system.

Now since,

$$\bar{b}_o/\bar{V} = (\bar{b}_o p/RT)/Z = y/Z \quad , \qquad \text{........ (2.34b)}$$

(2.33) would be a suitable choice if a plot of

$$\log_e[(Z-1)/Z\bar{b}_o/\bar{V}] \qquad \text{........ (2.34c)}$$

relative to $(Z\bar{b}_o/\bar{V})^{1/3}$ were linear. This is very nearly the case. The data given in brackets in table 2.6 were therefore fitted by (2.33) with m=3. The fit was excellent; however it was no better than (2.34) also with m=3. This form is far more convenient than the first, particularly in regard to the relation

$$\int_o^p \bar{X}(p,T)\,dp \qquad \text{........ (2.34d)}$$

which enters into the expression for the fugacity. The second relation (2.34) was adopted for this reason and it was found that

$$A_1 = -0.174417 \quad , \quad A_2 = -0.062245 \quad , \quad A_3 = 0.0180363$$

.... (2.34e)

The standard deviation for this 6-point fit is 0.35% in the quantity

$$y^{-1}(Z-1)-1 \quad , \qquad \ldots\ldots\ldots \; (2.34f)$$

and the deviation of the fitted relation $\sum_{k=1}^{3} A_k y^{k/3}$ from this data function does not exceed 1%. A suitable equation of state for rigid non-attracting spheres of diameter σ_0 and molar volume $\bar{b}_r$ has now been obtained.*** The form of F(y) was chosen so as to ensure application all the way to the ideal gas state Z=1.

It may be noted that J. Taylor and Paterson in their application of the hard sphere virial to detonations, follow Hirschfelder et al[2.38] in replacing the hard sphere 4th virial coefficient $0.115\bar{b}_r^4$ by that derived from Eyring's expression (2.31), viz., $0.1928\bar{b}_r^4$. The Rosenbluths deduce

$$b_4/b_r^4 = (8.6)(2.962)^{-4} = 0.119 \quad \ldots\ldots \; (2.35)$$

from their Monte Carlo results. These were presented in the form of a table of (Z-1) relative to $(v/v_0)-1$. The argument v/v_0 may be transformed to the more familiar one $\bar{b}_r/\bar{V}$ using

$$b_r/V_0 \equiv \bar{b}_r/\bar{V}_0 \doteq (2\pi/3)\sigma_0^3/v_0 = 2.962 \quad , \qquad \ldots\ldots\ldots \; (2.35a)$$

where v is the specific volume (per molecule) and v_0 is that at the closest possible packing.

*** It is now necessary to emphasize the distinction to be drawn between $\bar{b}_0 \equiv (2\pi/3)\bar{N}\sigma^3$ $(\sigma \doteq \sigma_{LJ(6-12)\,\text{say}})$, and $\bar{b}_r \equiv (2\pi/3)\bar{N}\sigma_0^3$ where σ_0 is the hard sphere diameter, as yet undefined.

At close packing, most collisions are nearly head on. For consistency, it must be assumed that the distribution of molecular velocities is of the Maxwell-Boltzmann type. This has already been implied by acceptance of the JANAF ideal state properties. The most probable spacing of molecules at point of closest approach should then be close to that value obtained by inserting 3/2 kT, the most probable translational energy, into the pair potential relation. The same result is obtained formally from the Boltzmann-weighted expression for the rebound spacing when the relation for the spacing (with xT* substituted for 1.5T*) is expanded, and high order terms are discarded: here x is a dimensionless kinetic energy varying from 0 to ∞. The approximate closest approach spacing thus obtained is taken to be the hard sphere diameter $\sigma_r (\equiv \sigma_o)$. Replacing ϕ in the LJ(6-12) pair potential by 3/2kT one readily obtains

$$\sigma_r(T^*)/\sigma_{LJ} = (2/[1+F^*])^{1/6}$$

$$\text{where } F^* = (1+1.5T^*)^{1/2} \quad ; \quad T^* \equiv T/\theta \; .$$

so that

$$b_r^* \equiv \bar{b}_r(T)/\bar{b}_o = [2/(1+F^*)]^{1/2}$$

$$\text{where } \bar{b}_r/\sigma_r^3 \equiv \bar{b}_o/\sigma^3 = 1.2615 \text{ cc mole}^{-1} \text{ Ångstroms}^{-3} \qquad \text{........ (2.36)}$$

At the closest packing, the dimensionless temperature derivative db_r^*/dT^*, which, as may be noted, is always negative, is probably too small$^\phi$ because here, molecules spend most of

---

$^\phi$ in absolute value

their time in a repulsive field. However, the slope is much greater than that of the second virial coefficient dB^*/dT^*. Furthermore, the relation (2.36) gives the correct value $\sigma_r/\sigma \to 1$ as $T^* \to 0$. It will have been noted that the notation σ_0 to represent a hard sphere has been discarded in favour of σ_r in order to obviate the possible misconception that it is fixed at all temperatures.

The justification that has been presented for (2.36) is by no means theoretically rigorous: it is better justified by its performance relative to other definitions. At least two other definitions of an equivalent hard sphere diameter are known. The oldest, that due to van der Waals was devised long before the notion of intermolecular potentials was put forward in its modern form, and in his equation of state

$$Z = 1 - a/RTV + \sum_{n=1}^{\infty} (b/V)^n \qquad \text{........ (2.37)}$$

the terms b, representing the hard sphere diameter, and -a, associated with the average attractive force (at near-ideal dilution) were purely empirical constants. At high temperatures, the term $\bar{a}/RT\bar{V}$ is negligible and his equation degenerates to the Abel-Nobel relation

$$Z = 1 + \sum_{n=1}^{\infty} (\bar{b}/\bar{V})^n \quad , \quad \text{i.e.,} \quad p(\bar{V} - \bar{b}) = RT \quad , \quad \bar{b} = \text{const.} \qquad \text{........ (2.38)}$$

used in early studies of detonation at low loading densities.

When the first term in a real gas virial is compared to that in (2.37) it is seen that

$$\bar{b}-\bar{a}/RT \equiv \bar{b}_o[b^*_{VDW}-(\bar{a}/R\bar{b}_o)T^{*-1}]$$

is an inverse linear approximation to $\bar{b}_oB^*(T^*)$, which, when plotted against T^{*-1}, is nearly a straight line at temperatures not too far removed from the Boyle temperature, where, by definition $B^* = 0$. This occurs at $T^* = 3.42$ for non-polar molecules in the LJ(6-12) representation and at $T^* = 4.9$ for water with $t^* = 1.2$. Thus, if a straight line $A^*+D^*x^*$ (with $x^*\equiv 1/T^*$) is fitted to B^* in any selected interval Δx^* the appropriate dimensionless van der Waals diameter $b^*_{VDW}=A^*$ may be found. It is thus evident that van der Waals constants, being dependent on the temperature interval ΔT^* selected for fitting, are not uniquely defined. Nothing can be obtained from them that cannot be better obtained directly from B^*.

Hirschfelder[2.29] applied a hybrid virial form

$$Z=1+\bar{B}_g(T,n_j)/\bar{V}_g+0.625(\bar{b}_g/\bar{V}_g)^2+0.2869(\bar{b}_g/\bar{V}_g)^3+0.1928(\bar{b}_g/\bar{V}_g)^4 \quad \ldots\ldots\ldots \quad (2.40.1)$$

to the gas mixture resulting from the combustion of gun powder. Here,

$$\left.\begin{array}{l} \bar{B}_g(T) \simeq n_g^{-1}\sum_{j=1}^{m} n_j\bar{b}_{oj}B^*(T^*_j); \quad n_g = \sum_{j=1}^{m} n_j \\ \bar{b}_{oj} \equiv (2\pi\bar{N}/3)\sigma^3 \quad ; \quad T^*_j = T/\theta_j \end{array}\right) \ldots\ldots \quad (2.40.2)$$

where σ, θ are LJ(6-12) pair potential constants, and

$$\bar{b}_g = n_g^{-1} \sum_{j=1}^{m} n_j \bar{b}_{oj} \quad . \qquad .... (2.40.3)$$

He argued that the approximation

$$b^*_r = B^*(T^*) \quad , \qquad .... (2.40.4)$$

at least in the first term, appeared to be reasonable at high temperatures ($T \simeq 1500$-5000°K) because, at such temperatures the second virial coefficient is fairly constant ($B^* \simeq 0.5$ for $20 < T^* < 50$) and appears to play the role of a van der Waals b^*_{VDW}. Paterson and J. Taylor extended the association, $b^*_r = B^*$, to all coefficients using the same equation of state, that is, using

$$\left.\begin{aligned} Z &= 1+x+0.625x^2+0.2869x^3+0.1928x^4 \\ \text{where } x &= \bar{B}_g/\bar{V}_g \end{aligned}\right) \qquad ....(2.41)$$

and $\bar{B}_g$ is the mixture virial coefficient defined as in (2.40.2).

We may justify the choice (i) $b^*_r = b^*_r$(Eqn.2.26) relative to the choice (ii) $b^*_r = B^*$ (at least at high densities) by noting that

(a) $\bar{E}_r$ is wrongly < 0 for (ii), regardless of the density, if $T^* < 25$. $\bar{E}_r$ for (i) is always > 0.

(b) (ii) gives worse transport coefficients than rigid spheres of immutably fixed diameter: the choice (i) gives better ones. That is, if $\underline{\eta}$ is the viscosity coefficient, then

$Y \equiv (\eta/\eta_o)/(T/T_o)^{1/2}$ = const for perfectly rigid spheres

$dY/dT > 0$, observed

$dY/dT < 0$ for choice (ii) for $T^* < 25$

$dY/dT > 0$ for choice (i) for all T^*

(c) The identification $0.625\ b_r^{*2} \leftrightarrow C^*(T^*)$ is very poor indeed by (ii). For (i) it is quite good, as shown in the following table.

Table 2.7

Simulation of Third Virial Coefficient by $0.625\ (b^*_{hard})^2$

T^*	$C^*_{LJ(6-12)}(T^*)$	$0.625\ b_r^{*2}$ Choice (i)	$0.625\ b_r^{*2}$ Choice (ii)
1	0.42966	0.485	4.02
2	0.43710	0.415	0.245
4	0.32662	0.342	0.0083
6	0.30771	0.300	0.065
8	0.29618	0.271	0.107
10	0.28610	0.250	0.133
20	0.24643	0.191	0.172
30	0.21954	0.161	0.173

An equation of state for a pure gas particularly suited to high densities and temperatures has now been devised. We must now extend the equation to include gas mixtures before it is of practical value for the problem concerned here. It should be borne in mind that the Monte-Carlo data refer to a gas of identical hard spheres. We cannot use the data at all for mixtures of non-identical rigid spheres, that is for mixtures of spheres of different diameters. Thus a single diameter σ_g must be defined for the complete gas mixture. Sufficient has been said to justify its definition by

$$\left.\begin{aligned}
&\sigma_g \equiv \sigma_{og}\sigma_g^* \\
\text{where}\quad &\sigma_{og} \equiv n_g^{-2}\sum_{i=1}^{m}\sum_{j=1}^{m} n_i n_j \sigma_{ij} \quad ; \quad \sigma_{ij} = (\sigma_{ii}+\sigma_{jj})/2 \\
&\sigma_g^* \equiv [2/(1+F^*)]^{1/6}; \qquad F^* = \sqrt{1+1.5T^*} \\
&\text{where}\quad T^* = T/\theta_g \\
\text{and}\quad &\theta_g \equiv n_g^{-2}\sum_{i=1}^{m}\sum_{j=1}^{m} n_i n_j \theta_{ij} \quad ; \quad \theta_{ij} = \sqrt{\theta_{ii}\cdot\theta_{jj}}
\end{aligned}\right)\quad(2.42)$$

The equation of state for the gas mixture is now defined.

It may be noted from table 2.7 that the simulation of C^* by $0.625b_r^*$ with b_r^* defined by (2.42) is sufficiently good as to warrant its use rather than the expression (2.15) in a real gas virial equation of state. For $T^*>10$ it is increasingly better than (2.15) and is therefore to be preferred for those problems in which the truncated virial is applicable at these temperatures.

2.8 Inverse Equations

The best known of these are the relations due to Jones and Miller[2.39] and to Wilson and Kistiakowsky[2.40].

The Jones and Miller equation, which refers to TNT only, is

$$\left.\begin{aligned}
&\overline{X} = \overline{X}(p) = \sum_{k=1}^{3} d_k p^{k-1} \\
&d_1 = 25.4\text{cc mole}^{-1}\ ;\ d_2 = -4.43715\text{cc mole}^{-1}(\text{kcal/cc})^{-1} \\
&d_3 = 0.424129\text{cc mole}^{-1}(\text{kcal/cc})^{-2}
\end{aligned}\right)\quad(2.43)$$

These coefficients were obtained by fitting to the detonation speeds given by Friedrich at loading densities <1.5g/cc. For reasons stated earlier, this relation was here modified to

$$\left.\begin{aligned}
&\overline{X}(p) = \sum_{k=1}^{5} d_k p^{k-1} \\
&d_4 = -4.66272 \cdot 10^{-3}\text{cc mole}^{-1}(\text{kcal/cc})^{-3} \\
&d_5 = -5.01624 \cdot 10^{-5}\text{cc mole}^{-1}(\text{kcal/cc})^{-4} \\
&d_1,\ d_2,\ d_3 \text{ as in } (2.43)
\end{aligned}\right) \quad (2.43a)$$

The value of d_4 was found by matching to the observed detonation front speed at 1.5g/cc loading density, iterating at constant temperature from that final CJ temperature obtained using the 3 constant relation. The value of d_5 was then found by matching in the same way for a loading density of 1.52g/cc. For this purpose an approximate composition was used. The resulting 5 constant relation reproduces the observed detonation speed particularly for loading densities greater than 1.5. The error in wave speed at 1.0 g/cc loading density is about 4%, only slightly better than that using the original 3 constant relation.

It is immediately evident, purely from logic, that the relation $\overline{X} = \overline{X}(p)$, cannot be both true and at the same time be limited only to TNT products. Jones and Miller were not explicit about how they obtained the first constant d_1. It appears to have been obtained from some method other than detonation. The notion $\overline{X} = \overline{X}(p)$ is evidently a result of Jones' earlier calculations using a direct equation of state, i.e., one not based on observed detonation wave speeds. This equation was apparently** based on a solid state equation due to Bridgeman (see Cole[2.41], p.82). This in turn was fitted by a set of constants d'_k using the same virial form, i.e.,

$$\overline{X}(p) = \sum_{k=1}^{3} d'_k p^{k-1}$$

where d'_k are not reported. This gave detonation front speeds about 17% too high. Then the d'_k were adjusted to fit the Friedrich's data as described earlier, but it would appear that d'_1 was retained at the value given in (2.43). Detailed speculation as to precisely what might have been assumed is inappropriate. What is important is that the functional form $\overline{X}(p)$, while approximate, has some basis not related to observed detonations. It is interesting to compare the following quantities.

	cc/mole	
(A)	25.4	- d_1 of JM$^{\varnothing}$ equation (2.43a)
(B)	24.4	- constant term obtained if one expands the H. Jones equation given on p.82 of Cole.

**The wartime reports of H. Jones are listed in Cole but it was not possible to obtain them.

Ø For brevity the Jones and Miller equation with modified constants (2.43a) will be referred to as JM, while the hard sphere or hard molecule equation of state (2.34), (2.42) will be referred to as HM.

(c) $\frac{\text{cc/mole}}{25}$ - $(\overline{B}_{gNR}+\overline{B}_{gR})/2$ $2500<T<4000$ using high pressure composition of chapter 6. Here R refers to the normal rotating molecule pair potential constants and NR refers to σ_{LJ} adjusted to a non-rotating value using column 1, 2 of table 2.1.

The basis for the formula, or inverse equation of state, of Wilson and Kistiakowsky is not explained in the available literature. It appears to be a general purpose detonation front fit in that a set of specially defined species co-volumes have been devised by trial and error adjustment so as to reproduce the observed detonation front velocity for a number of condensed explosives. A description is given in Cole (p.84). A somewhat different account is given in Hirschfelder (Ref.2.1-Eqn.4.3-3). Its description of adiabatic expansion at low and moderate temperatures is bound to be poor because at constant composition the compressibility factor is

$$Z = 1+(\text{const}/T^{1/4})\exp(\text{const}/T^{1/4}) \quad \ldots\ldots\ldots \quad (2.44)$$

Fickett[2.4] has given a table relating the WK detonation front species co-volumes to equivalent pair potential constants. The WK equation is probably the most flexible of the detonation front formulae.

Chapter 2 References

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CHAPTER 3

THERMODYNAMIC RELATIONS FOR THE PRODUCT MIXTURE

3.1 General Relations

The equation of state for a two-phase gas/solid mixture consists of an equation of state for the solid, (here graphite), an equation of state for each gaseous species or one for the gas mixture as a whole, together with an assumption relating the chemical potential of a species in the mixture to its value when pure. Taylor and Glasstone[3,1] give a complete review of the three main methods that have been proposed to deal with the chemical potential. These are (i) the general limit method proposed by Gillespie[3.2] and Beattie[3.3], (ii) the Lewis and Randall rule and (iii) the Gibbs-Dalton rule (or "law"). The present computations conform to the general limit (GL) method.

In the GL method an equation of state for the mixture as a whole is required in order to solve the definite integrals appearing in the general relations. The resulting general relations may be considered 'exact', inaccuracies in numerical solutions being introduced only by errors in the equation of state for the mixture and by the numerical approximations necessary in any computation of physical behaviour. The general relations resulting from either the Lewis-Randall rule or the Gibbs-Dalton rule are approximate, the former generally holding to higher pressures than the latter. As pointed out earlier we do not, and cannot, assert a gas equation of state based on the Monte-Carlo data except in terms of a pure hypothetical gas representative of the gas phase of the mixture, so that the GL method is not only the best for our purpose, but is also the only permissable approach. The Jones and Miller equation also falls into this category.

Since chemical reactions are involved, a standard state must be defined. Standard conditions are generally taken to be $p_o=1$ atm, $T_o=298.1°K$, so that we may replace

$$\left.\int_{p_o}^{p°} (\ )dp\right|_T \qquad \text{.........} \quad (3.1.1)$$

by zero without significant error, for an integrand which is zero for an ideal gas. Here p° indicates an arbitrarily low pressure. For simplicity in notation, we shall represent the internal energy by two symbols U, and E, related by

$$E = U-U_o \quad , \qquad \text{.........} \quad (3.1.2)$$

and shall represent

$$U_o^\circ \text{ , by } E_o^\circ \quad , \qquad \text{.........} \quad (3.1.3)$$

when T=0° absolute, which is now taken to be the standard temperature to which the heats of formation shall refer.

The formal procedure for obtaining an expression for the internal energy is well known. For a pure gas, the expression for a molar enthalpy increment

$$d\overline{H} = \overline{C}_p dT+(\partial\overline{H}/\partial p)_T dp \quad , \qquad \ldots\ldots\ldots (3.2.1)$$

in which, from general thermodynamics

$$(\partial\overline{H}/\partial p)_T \equiv [\partial(\overline{E}+p\overline{V})/\partial p]_T = \overline{V}-T(\partial\overline{V}/\partial T)_p \quad , \qquad \ldots\ldots\ldots (3.2.2)$$

may be integrated, first at constant standard temperature $\underline{T_o}$ to some arbitrarily low (ideal) gas pressure $\underline{p^\circ}$, then at this pressure to the final temperature $\underline{T}$, and then at this temperature to the final pressure $\underline{p}$. As indicated earlier, $(\overline{\ })$ indicates one mole and $(\ )^\circ$ indicates ideal gas conditions. Using (3.1.1), and then setting $T_o=0°$absolute, one readily obtains

$$\left.\begin{aligned} &\overline{E} = \overline{E}_{th}+\overline{E}_r = \overline{H}^{\#}(T)-RT+\overline{E}_r \\ &\text{where,}\quad \overline{H}^{\#}(T) \equiv \overline{H}^\circ(T)-\overline{E}^\circ_o \equiv \int_o^T \overline{C}^\circ_p(T)\,dT\Big|_{p=p^\circ} \\ &\overline{E}_r = -\int_o^p [p\partial\overline{V}/\partial p+T\partial\overline{V}/\partial T]\,dp\Big|_T \end{aligned}\right) \qquad \ldots\ldots\ldots (3.2.3)$$

Here, $(\ )_r$ refers to the imperfect or real component arising from intermolecular forces, and $(\ )_{th}$ refers to the remainder or thermal component. As noted earlier, it follows from our definition of the gas co-volume $\overline{X}$ that

$$-\overline{E}_r = \int_o^p (p\partial\overline{X}/\partial p + T\partial\overline{X}/\partial T)\,dp \qquad \text{.........} \quad (3.2.4)$$

The internal energy U of a detonation product mixture at the equilibrium, or Chapman-Jouguet, front is related to the energy of the unreacted explosive by the well-known relation for the Hugoniot, viz.,

$$\left.\begin{aligned} U-U_e &= (p+p_e)(V_e-V)/2 \\ &= p(V_e-V)/2 \text{ - - closely - - } \end{aligned}\right) , \quad \text{..} \quad (3.3.1)$$

where the subscript e refers to the unreacted explosive. The second expression is amply justified by the relative triviality of p_e in the case of condensed explosives. This relation, of course, refers to a definite mass, which we shall hereafter take to be one mole of explosive, initially occupying the volume V_e at temperature T_e. The energy U of the product mixture includes the chemical energy released. The above relation may now be expressed

$$p(V_e-V)/2 = U-U_e \equiv (U-U_o)-(U_e-U_{eo})-(U_{eo}-U_o) \quad \text{.........} \quad (3.3.2)$$

where the additional subscript o refers to a standard state p_o, T_o. If we now define the heat of reaction Q, the energy of the products above that at the standard state E, and the initial (thermal) energy above the standard state of the unreacted explosive $\underline{E_e}$ by

$$\left.\begin{aligned} Q &= U_{eo}-U_o \\ E &= U-U_o \\ E_e(T_e) &= U_e-U_{eo} \end{aligned}\right) \quad , \qquad \ldots\ldots\ldots \ (3.3.3)$$

the expression for the Hugoniot becomes

$$E-Q-E_e = p(V_e-V)/2 \quad . \qquad \ldots\ldots\ldots \ (3.3.4)$$

The quantity $\underline{Q}$ represents the internal energy change in a hypothetical transformation of explosive into Chapman-Jouguet (CJ) composition products at the standard state p_o, T_o, and may be expressed

$$Q = \sum_{j=1}^{m} n_j(p,T)\varepsilon_j-\varepsilon_e \quad , \qquad \ldots\ldots\ldots \ (3.4.1)$$

where the mixture contains $\underline{m}$ products of species j=1, 2,..m, and ε_j are the heats of reaction

$$\varepsilon_j \equiv -\bar{E}^{\circ}_{oj} \quad , \qquad \ldots\ldots\ldots \ (3.4.2)$$

a convenient change in notation, because the product heats of formation $\bar{E}^{\circ}_{oj}$ must be negative if heat is to be evolved at the detonation front. The initial thermal energy of the explosive $E_e(T_e)$ is not regarded as a variable in the later calculations. The energy E of the products relative to the standard state may be expressed

$$E = E_{th}+E_r+E_{rc} \quad , \qquad \text{.........} \ (3.4.3)$$

where E_{th} is the ideal component of the internal energy of a two phase solid-gas mixture, and E_r, E_{rc} are the imperfection components of the internal energy of the gaseous and condensed phases respectively.

If the explosive is pure and of the CHON type, the only solid that can be present is carbon. If, as we now assume (for reasons stated earlier), the carbon, taken to be in the form of graphite, has zero coefficients of thermal expansion and baric compression, then

$$E_{rc} = 0 \quad , \qquad \text{.........} \ (3.5.1)$$

and if we assign the species label j=1 to carbon, the energy E may be expressed

$$\left.\begin{aligned} & E = E_{th}+n_g\overline{E}_r \quad , \\ \text{where} \quad & \overline{E}_r = -\int_0^p [p\partial\overline{X}/\partial p+T\partial\overline{X}/\partial T]\Big|_T \quad , \\ \text{and} \quad & E_{th} = \sum_{j=1}^{m} n_j(p,T)\overline{H}_j^{\#}(T)-n_gRT \quad , \end{aligned}\right) \qquad \text{.........} \ (3.5.2)$$

where n_j is the number of product moles of species j, and where the standard temperature is now taken to be the absolute zero so that $\overline{H}_j^{\#}(T)$ is defined by (3.2.3). Here n_g is the total number of moles of gas defined by

$$n_g \equiv \sum_{j=2}^{m} n_j \quad , \qquad \text{.........} \ (3.5.3)$$

and $\overline{X}$ is the co-volume of the gas phase.

The total volume of the products is

$$\left.\begin{aligned} V &= V_{solid}+V_{gas} \\ &= n_c\overline{k}_c+n_g\overline{V}_g \\ \text{where,} \quad \overline{V}_g &= RT/p+\overline{X}(p,T) \end{aligned}\right) \quad , \qquad \text{.........} \ (3.6.1)$$

and where $\overline{k}_c$ is the molar volume of crystal graphite of value

$$\overline{k}_c = 5.338 \text{ cc/mole} \quad , \qquad \text{.........} \ (3.6.2)$$

and $n_c(\equiv n_1)$ is the mole number of carbon per mole of unreacted explosive. When an explicit expression for the gas co-volume $\overline{X}(p,T)$ is available, the equation of state of the product mixture is completely defined by (3.5) and (3.6).

The Hugoniot relation (3.3), and that for the Chapman-Jouguet condition, together with the equations for chemical equilibrium, may be solved simultaneously to determine the independent variables p_{CJ}, T_{CJ}. When this has been achieved, the equilibrium properties at the front, the centre-of-mass velocity u and the detonation wave speed D are completely determined. Thermodynamic conditions in the following expansion may then be obtained using the adiabatic assumption $dQ_{ext}=0$, and the Taylor wave may be determined by integrating the hydrodynamic equations.

The CJ condition may be expressed

$$\left|\frac{dV}{dp}\right|_{Ad}^{CJ} = \left|\frac{dV}{dp}\right|_{RH}^{CJ} = -(V_e-V)/p \quad , \qquad \ldots\ldots\ldots \; (3.7.1)$$

where RH refers to the (Rankine)-Hugoniot and Ad to the adiabatic curve in the V,p plane. When the pressure and volume have been found, the equilibrium front velocity u and the speed of the wave front D may be determined from

$$\left.\begin{aligned} D^2 &= p(V_e^2/M_e)/(V_e-V) \\ u^* &\equiv u/D = 1-V/V_e \end{aligned}\right) \quad , \qquad \ldots\ldots\ldots \; (3.7.2)$$

which follow immediately from the well-known relations expressing the conservation of mass and momentum at the detonation front. Here M_e is the molar mass of the unreacted explosive, and

$$V_e = M_e/\Delta \qquad \ldots\ldots\ldots \; (3.7.3)$$

where Δ is the explosive loading density.

It may be shown[3.4] that, when the force field is the same for all molecules, an assumption which applies approximately if the co-volume $\overline{X}$ is only slightly dependent on the composition, the partial pressure derivative of the chemical potential μ_j of any species j in the mixture is

$$\left[\frac{\partial \mu_j}{\partial p}\right]_{T,n_j(\text{all } j)} = \bar{V}_g \quad . \qquad \text{.........} \; (3.8.0)$$

The fugacity is now common to the species, and the expression for it is readily obtained.

The fugacity <u>f</u>, an effective pressure, is a notion due to Lewis[3.5]. For an ideal gas it is known that

$$\mu_j^\circ - RT \log_e(p^\circ n_j/n_g) \qquad \text{.........} \; (3.8.1)$$

is a function of temperature only. The fugacity is essentially that idealized pressure[3.6] which leaves this function unaltered for a real gas. That is, the expression

$$\mu_j - RT \log_e(f n_j/n_g) \qquad \text{.........} \; (3.8.2)$$

is equal to the same function of temperature as (3.8.1), provided that we define the fugacity by

$$\log_e(f/p) = (\mu_j - \mu_j^\circ)/RT \quad , \qquad \text{.........} \; (3.8.3)$$

where μ_j° is the partial potential in the ideal gas condition, so that

$$\left[\frac{\partial \mu_j^\circ}{\mu p}\right]_{T,n_j(\text{all } j)} = RT/p \quad . \qquad \text{.........} \; (3.8.4)$$

Accordingly, the fugacity is given by the relation

$$\log_e(f/p) = (RT)^{-1}\int_0^p \bar{X}(p,T)\,dp \quad . \qquad \ldots\ldots (3.8.5)$$

The equilibrium condition for the reaction

$$\left.\begin{aligned}\textstyle\sum_j m_j A_j = 0 \quad ; \quad & m_j > 0, \text{ 'reactants'} \\ & m_j < 0, \text{ 'products'}\end{aligned}\right) \qquad \ldots\ldots (3.8.6)$$

in a mixture of ideal gases may be expressed

$$\textstyle\sum_j m_j \log_e n_j + (\sum_j m_j)\log_e(p°/n_g) = \log_e K_p^\circ(T) \quad , \qquad \ldots\ldots (3.8.7)$$

where $K_p^\circ(T)$ is the (constant pressure) equilibrium constant for the reaction, and m_j are the stoichiometric coefficients for the species taking part in it. Thus, for the detonation product mixture, the same equilibrium constant is equal to the above expression with <u>f</u> substituted for <u>p</u>°. That is,

$$\left.\begin{aligned}&\textstyle\sum_j m_j \log_e n_j + (\sum_j m_j)\log_e(f/n_g) = \log_e K_p^\circ(T) \\ &\qquad\qquad\qquad \text{or} \\ &(f/n_g)^{\Sigma m_j} \cdot \prod_j (n_j)^{m_j} = K_p^\circ(T)\end{aligned}\right)^{**} \qquad \ldots\ldots\ldots (3.8.8)$$

The detailed relations for the composition are treated in the next chapter. We now consider the adiabatic relations.

3.2 General Adiabatic Relations

When the CJ point on an adiabat has been found,

** Here f is relative to one atmosphere, i.e., f is dimensionless.

all thermodynamic properties at every other point may be determined by quadrature in finite steps of one of them. This is so regardless of whether the thermodynamic system is in motion or not, provided that the previously stated assumption of zero entropy production by viscosity applies. Here ΔT is assigned and the other finite steps are calculated. The adiabatic relations now given below are later integrated from the starting values p_{CJ}, T_{CJ} down to 0.3 DEGREES** for TNT products. They are also used in the determination of the CJ values.

When, as implied by the assumption of a Taylor wave, the reaction zone thickness is negligible, and conditions in the unreacted explosive are uniform, the velocity of the detonation wave, and the equilibrium or CJ properties at the wave front are invariant, so that specification of the loading density completely establishes a particular adiabat in the products of a given explosive provided that the initial pressure, which is here neglected, is not grossly in excess of atmospheric pressure. Deviations of the initial explosive temperature from 0.3 DEG may generally be discounted. The present relations deal only with the equation of state variables on the adiabats. The instantaneous spatial distribution of these variables, and of the centre-of-mass

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** Note: 1 DEGREE = 10^3°K.

velocity in one-dimensional adiabatic motion, here called a Taylor wave, is treated in chapter 5.

It is assumed that chemical and thermal equilibrium applies in the initial stages of expansion. This is consistent with the notion of infinite reaction rate at the equilibrium front demanded by a Taylor wave. When this assumption is applied, the calculated composition eventually changes so slowly that the assumption of chemical equilibrium becomes increasingly questionable. Jones and Miller[3.4] suggested that since the calculated mole number of solid carbon eventually passes through a minimum, this point appeared to be a reasonable lower limit for the equilibrium assumption because in this vicinity the reaction rates must be slow. In the present computations for TNT, the onset of frozen equilibrium was arbitrarily assumed at a temperature of 1450°K. This temperature was chosen as the end of reactions purely to be sufficiently below the temperature at the carbon minimum as to allow its study and yet to be not so low that the composition would be seriously different from that at the minimum.

The adiabatic condition

$$dQ_{\mathrm{external}} = 0 = d(E-Q_{\mathrm{internal}})+pd(V_g+V_c) \qquad \ldots\ldots\ldots (3.9.1)$$

allows us to express the total derivative dp/dT in terms of (p,T) along the adiabat.

For conciseness, we define the following

$$\left.\begin{array}{lll} h_1 \equiv \partial(E-Q)/\partial p & ; & f_1 \equiv p\partial V/\partial p \\ & & \\ h_2 \equiv \partial(E-Q)/\partial T & ; & f_2 \equiv p\partial V/\partial T \end{array}\right) \quad \ldots\ldots\ldots \quad (3.9.2)$$

$$\left.\begin{array}{ll} \text{where} & V = V_c+V_g = n_c\bar{k}_c+n_g[RT/p+\bar{X}(p,T)] \\ & \\ \text{and} & d(E-Q) = d(\sum_{j=1}^{m} n_j[\bar{H}_j^{\#}(T)-\varepsilon_j])+d(n_g[\bar{E}_r-RT]) \end{array}\right) \quad \ldots\ldots\ldots \quad (3.9.3)$$

The adiabatic relation (3.9.1) now becomes

$$(dp/dT)_{Ad} = -(h_2+f_2)/(h_1+f_1) \quad \ldots\ldots\ldots \quad (3.9.4)$$

where the expressions for these terms are evident from their definitions. They are

$$h_1 = \sum_{j=1}^{m} (\bar{H}_j^{\#}(T)-\varepsilon_j)\partial n_j/\partial p+(\bar{E}_r-RT)\partial n_g/\partial p+n_g\partial\bar{E}_r/\partial p \quad , \quad \ldots\ldots \quad (3.10.1)$$

$$f_1 = p\bar{k}_c\partial n_c/\partial p+(RT+p\bar{X})\partial n_g/\partial p+n_g(-RT/p+p\partial\bar{X}/\partial p) \quad , \quad \ldots\ldots\ldots \quad (3.10.2)$$

so that using (3.5.2),

$$\begin{aligned} h_1+f_1 = {} & p\bar{k}_c\partial n_c/\partial p+(p\bar{X}+\bar{E}_r)\partial n_g/\partial p-n_g(RT/p+T\partial\bar{X}/\partial T) \\ & +\sum_{j=1}^{m} (\bar{H}_j^{\#}(T)-\varepsilon_j)\partial n_j/\partial p \quad , \quad \ldots\ldots \quad (3.10.3) \end{aligned}$$

$$h_2 = \sum_{j=1}^{m} (\bar{H}_j^\#(T) - \varepsilon_j)\partial n_j/\partial T + \sum_{j=1}^{m} n_j \bar{C}^\circ_{pj}(T) + (\bar{E}_r - RT)\partial n_g/\partial T$$

$$+ n_g(\partial \bar{E}_r/\partial T - R) \quad \ldots\ldots \quad (3.10.4)$$

$$f_2 = p\bar{k}_c \partial n_c/\partial T + (RT + p\bar{X})\partial n_g/\partial T + n_g(R + p\partial \bar{X}/\partial T) \quad \ldots\ldots\ldots \quad (3.10.5)$$

so that

$$h_2 + f_2 = p\bar{k}_c \partial n_c/\partial T + (p\bar{X} + \bar{E}_r)\partial n_g/\partial T + n_g(\partial \bar{E}_r/\partial T + p\partial \bar{X}/\partial T)$$

$$+ \sum_{j=1}^{m} n_j \bar{C}^\circ_{pj}(T) + \sum_{j=1}^{m} (\bar{H}_j^\#(T) - \varepsilon_j)\partial n_j/\partial T \quad \ldots \quad (3.10.6)$$

The species mole numbers n_j and their partial derivatives are obtained from the relations expressing the equilibrium chemical composition described in the next chapter.

The expressions used here to describe the pure species ideal gas condition functions $\bar{H}_j^\#(T)$, $\bar{C}^\circ_{pj}(T)$ (and $\bar{S}^\circ_j(T)$) are:

$$\bar{C}^\circ_{pj}(T)/R = \sum_{k=1}^{6} a_{jk} T^{k-3} \quad \ldots\ldots\ldots \quad (3.11.1)$$

so that the thermodynamically consistent expressions for $\bar{H}^\#$ and $\bar{S}^\circ$ are,

$$\bar{H}_j^\#(T)/R \equiv H_j^\#(0.3)/R + \int_{0.3}^{T} (\bar{C}^\circ_{pj}/R)\,dT = b_{j1}\log_e T + \sum_{k=2}^{7} b_{jk} T^{k-3} \quad , \quad (3.11.2)$$

and

$$\bar{S}^\circ_j(T)/R \equiv S^\circ_j(0.3)/R + \int_{0.3}^{T} (\bar{C}^\circ_{pj}/RT)\,dT = q_{j1}\log_e T + \sum_{k=2}^{7} q_{jk} T^{k-4} \quad . \quad (3.11.3)$$

The primary coefficients a_{jk} were obtained by least squares fits to the (1961) JANAF[3.7] tabulated data for $\bar{C}_p^\circ$. The secondary coefficients b_{jk} and q_{jk} were found from the a_{jk} and from the tabulated values of $\bar{H}_j^\#$ and $\bar{S}_j^\circ$ at 0.3 DEG by suitably choosing the coefficients b_{j3} and q_{j4}. The coefficients a_{jk}, b_{jk}, and q_{jk} are given below for the main product species of oxygen-negative explosives. While the coefficients q_{jk} for the (ideal condition) entropies were derived as a matter of general interest, the entropy of the product mixture was not calculated in the detailed computations because it does not appear explicitly in the relations necessary to describe the Taylor wave.

It may be noted that terms in T^{-2} are required in order to fit $\bar{C}_p^\circ$ near 0.3 DEG, which is not far above the rotational temperatures. For temperatures above 0.8 DEG, a power series without inverse T terms is adequate. Fickett and Cowan[3.8] used such a form, but their fits are poor below 0.5 DEG. The expression (3.11.1), with the coefficients given below, describes the JANAF $\bar{C}_p^\circ$ values for the species concerned over the fitted range 0.3-3.9 DEG to an approximation generally small compared to the reliability ($\approx$1%) of the data fitted. The tabulated data are given at 0.1 DEG intervals: the maximum departure of fits from the JANAF values are also given in the table.

Table 3.1

Constants$^{(A)}$ for the Calculation of Pure Species Properties in the **Ideal** State

Part 1: Fitted Constants for $\bar{C}^{\circ}_{pj}$ in (3.11.1) — Max Rel Dev'n $\delta 10^4$

j^B	a_{jj}						$T \leq 1.2$		$T > 1.2$	
	k=1	k=2	k=3	k=4	k=5	k=6		(T_δ)		(T_δ)
1	+ (-6) 186349	- (-5) 163126	+ (-5) 459734	- (-6) 696707	+ (-6) 151776	- (-7) 111995	52	0.5	9	1.3
2	+ (-7) 910299	- (-6) 447289	+ (-5) 377445	+ (-6) 801214	- (-6) 260733	+ (-7) 289263	66	0.4	23	1.3
3	+ (-6) 189515	- (-5) 162840	+ (-5) 769303	+ (-6) 424442	- (-6) 170442	+ (-7) 211447	40	0.4	14	1.3
4	+ (-6) 496476	- (-5) 295807	+ (-5) 718931	+ (-5) 539754	- (-5) 166388	+ (-6) 174408	140	0.4	37	1.3
5	- (-6) 126479	+ (-6) 853108	+ (-5) 155395	+ (-5) 168409	- (-6) 361000	+ (-7) 309246	60	0.5	35	1.3
6	+ (-7) 607703	- (-6) 230364	+ (-5) 330173	+ (-5) 110492	- (-6) 343807	+ (-7) 370788	64	0.4	24	3.9
7	- (-7) 697706	+ (-6) 668493	+ (-5) 158224	+ (-5) 361476	- (-6) 915786	+ (-7) 850045	17	0.9	16	3.9

Part 2: Derived Constants for $\bar{H}^{\#}_j$ in (3.11.2)

j	Constants b_{jk}						
	k=1	k=2	k=3	k=4	k=5	k=6	k=7
1	- (-5) 163126	- (-6) 186349	- (-5) 256420	+ (-5) 459734	- (-6) 348354	+ (-7) 505919	- (-8) 279988
2	- (-6) 447289	- (-7) 910299	- (-6) 351457	+ (-5) 377445	+ (-6) 400607	- (-7) 869110	+ (-8) 723156
3	- (-5) 162840	- (-6) 189515	- (-5) 252008	+ (-5) 769303	+ (-6) 212221	- (-7) 568140	+ (-8) 528616
4	- (-5) 295807	- (-6) 496476	- (-5) 307779	+ (-5) 718931	+ (-5) 269877	- (-6) 554626	+ (-7) 436021
5	+ (-6) 853108	+ (-6) 126479	+ (-5) 109182	+ (-5) 155395	+ (-6) 842044	- (-6) 120333	+ (-8) 773116
6	- (-6) 230364	- (-7) 607703	- (-7) 627737	+ (-5) 330173	+ (-6) 552460	- (-6) 114602	+ (-8) 926970
7	+ (-6) 668493	+ (-7) 697706	+ (-5) 114170	+ (-5) 158224	+ (-5) 180738	- (-6) 305262	+ (-7) 212511

Note

(A) For temperature in DEGREES.
The number in the bracket is the power of 10 by which the relevant integer must be multiplied.

B	Species j	1	2	3	4	5	6	7
		C(s)	CO	CO_2	CH_4	H_2	N_2	H_2O

Table 3.1 (continued)

Part 3: Derived Constants for $\bar{S}_j^\circ$ in (3.11.3)

j	Constants q_{jk}						
	k=1	k=2	k=3	k=4	k=5	k=6	k=7
	+ (-5)	- (-7)	+ (-5)	+ (-5)	- (-6)	+ (-7)	- (-8)
1	459734	931746	163126	202552	696707	758879	373317
	+ (-5)	- (-7)	+ (-6)	+ (-4)	+ (-6)	- (-6)	+ (-8)
2	377445	455150	447289	271113	801214	130366	964208
	+ (-5)	- (-7)	+ (-5)	+ (-4)	+ (-6)	- (-7)	+ (-8)
3	769303	947575	162840	304958	424442	852210	704822
	+ (-5)	- (-6)	+ (-5)	+ (-4)	+ (-5)	- (-6)	+ (-7)
4	718931	248238	295807	223777	539754	831939	581361
	+ (-5)	+ (-7)	- (-6)	+ (-4)	+ (-5)	- (-6)	+ (-7)
5	155395	632394	853108	192491	168409	180500	103082
	+ (-5)	- (-7)	+ (-6)	+ (-4)	+ (-5)	- (-6)	+ (-7)
6	330173	303851	230364	262830	110492	171903	123596
	+ (-5)	+ (-7)	- (-6)	+ (-4)	+ (-5)	- (-6)	+ (-7)
7	158224	348853	668493	254249	361476	457893	283348

The relations (3.9), (3.10) and (3.11), together with the expressions for the mole numbers and their partial derivatives are all that is necessary to describe all adiabatic properties once the CJ values have been determined for each loading density (Δ) selected for examination. All other functions of interest may then readily be determined from relations in terms of p, T, f_1, f_2, h_1 and h_2. In particular, expressions for the adiabatic exponent $\underline{\gamma_{Ad}}$, the (chemical equilibrium) speed of sound $\underline{a}$, and the related derivative $(dV/dp)_{Ad}$ are immediately evident. They are:

$$\left.\begin{aligned}(dV/dp)_{Ad} &\equiv (dV/dT)/(dp/dT) = (f_2+p'f_1)/pp' \\ \gamma_{Ad} &\equiv -(d\log p/d\log V)_{Ad} = -Vp'/(f_2+p'f_1) \\ a^2 &\equiv (dp/d\rho)_{Ad} = (\gamma_{Ad}p/\rho) = -(V^2/M_e)pp'/(f_2+p'f_1)\end{aligned}\right\} \quad (3.12)$$

where p' is $(dp/dT)_{Ad}$, and ρ is the mass-density of the product mixture. The CJ condition (3.4.1) may now be expressed

$$(dV/dp)_{Ad}+(V_e-V)/p = 0 = (f_2+h_2)(V_e-V)+f_1h_2-f_2h_1 \quad , \quad \ldots\ldots(3.13)$$

and the CJ pressure and temperature are found by simultaneously solving this relation and (3.3), (3.5.2), (3.6), (3.9), (3.10), (3.11) and the composition equations and their derivatives subject to (3.8.5) and (3.8.8).

The method of regula falsi may be applied to an iterative solution of these equations to find the properties at the equilibrium front in the following way. A pair of values p_a, T_a are assumed and the pressure is adjusted at constant T until

$$z = (V_e)^{RH}_{calc}-V_e = 2(E-Q-E_e)/p+V(p,T)-V_e \quad \ldots\ldots\ldots\ldots\ldots(3.14.1)$$

changes sign. The values of p,V before and after the sign change are classed as A or B type depending on whether z is less than or greater than 0 and the sign of Δp until this stage is reached is set equal to that of the first z. When the sign change in z has occurred, the next value of p chosen is

$$p = p_A-(p_A-p_B)|z_A|/(|z_A|+|z_B|) \quad . \qquad \text{........} \quad (3.14.2)$$

This is very close to the correct value and is classified in turn as A, or B type depending on whether $z(p,T_a)$ is negative or positive. The iteration is continued until

$$|z/V_e| \leq \delta_{RH} \qquad \text{........} \quad (3.14.3)$$

where δ_{RH} is a defined relative error, here chosen as 10^{-4}.

The point thus found is on the Hugoniot but is not the CJ point unless y=0, where

$$y = (V_e)^{slope}_{calc}-V_e = (f_2h_1-f_1h_2)/(f_2+h_2)+V(p,T)-V_e \quad \text{....} \quad (3.14.4)$$

The temperature is now changed, and the Hugoniot pressure is again found as described above until y changes sign. Again, if A, B represent classes for which $y<0$, $y>0$ respectively, then the CJ point is close to that at which

$$\left.\begin{aligned} p &= p_A+(p_B-p_A)\cdot|y_A|/(|y_A|+|y_B|) \\ T &= T_A+(T_B-T_A)\cdot|y_A|/(|y_A|+|y_B|) \end{aligned}\right) \qquad \text{........} \quad (3.14.5)$$

These values are classed A or B depending on the sign of y subsequently calculated, and the iteration is continued until

$$|y/V_e| \leq \delta_{slope} \qquad \text{........} \quad (3.14.6)$$

where δ_{slope} is a defined relative error, here chosen as $2\cdot10^{-4}$.

The (computer) time required for such computations is reduced considerably by the use of approximate forms in the initial stages such as those described in chapter 6. Estimates of start values p_a, T_a may be found in a number of ways. When the explosive is one for which observations $D\infty$ and $dD\infty/dT$ are available, then start values p_a, $(v_1)_a$, γ_a are available using the H.Jones[3.9] relations given in chapter 2, and hence a start value T_a may readily be found using the equation of state. However, it is possible that the explosive considered is a new one. In this case the start values may be taken to be those of the most chemically similar explosive.

3.3 Special Relations

Here, the special relations for Z, $\overline{X}$, $\overline{E}_r$, f and their derivatives for the hard molecule gas equation of state, for the truncated virial equation of state with temperature-dependent coefficients, and for the Jones and Miller formula are summarized for ready reference. The relations follow from the definitions given in chapter 2.

For the hard molecule equation of state

$$\left.\begin{aligned} \overline{X} &\equiv (Z-1)RT/p = \overline{b}_g F(y) \simeq \overline{b}_g(T)\cdot F(y) \\ \partial\overline{X}/\partial p &\simeq (\overline{b}_g/p)\,y\,dF/dy = (\overline{b}_g/RT)(dF/dy) \end{aligned}\right) \quad \ldots\ldots\ldots (3.15.1)$$

$$\left.\begin{aligned}
&\partial\overline{X}/\partial T \simeq -(\overline{b}_g/T)[H^*\cdot F+(1+H^*)ydF/dy]\\
&\text{where}\\
&\qquad H^* = 0.375[F^*(1+F^*)]^{-1}\,T^*\\
&\qquad ydF/dy = \sum_{k=1}^{3}(k/3)A_k y^{k/3}
\end{aligned}\right)\quad \ldots\ldots\ldots\ (3.15.1a)$$

$$\left.\begin{aligned}
\overline{E}_r &= p\overline{X}H^*\\
\partial\overline{E}_r/\partial p &= (1+d\log F/d\log y)\overline{X}H^*\\
\partial\overline{E}_r/\partial T &= [1-(H^*/F^*)(2+5F^*)-(1+H^*)(d\log F/d\log y)](p/T)H^*\overline{X}
\end{aligned}\right)(3.15.2)$$

$$\left.\begin{aligned}
\log_e(f/p) &= \int_0^y F(y)dy = y\cdot(1+\sum_{k=1}^{3}3(3+k)^{-1}A_k y^{k/3})\\
\partial\log f/\partial p &= (1+p\overline{X}/RT)/p = Z/p = \overline{V}_g/RT\\
\partial\log f/\partial T &= -(1+H^*)yF/T = -(1+H^*)(Z-1)/T
\end{aligned}\right)\ \ldots\ (3.15.3)$$

For the truncated virial equation of state with temperature-dependent coefficients, the virial expression for the compressibility factor of the gas phase is

$$Z = 1+(p/RT)\overline{B}(T)+(p/RT)^2[\overline{C}(T)-\overline{B}^2] \qquad \ldots\ldots\ldots\ (3.16.1)$$

where $\overline{B}$, $\overline{C}$ are respectively the second and third virial coefficients when p/RT is represented as a power series

$$p/RT = (\overline{V})^{-1}+\overline{B}(T)(\overline{V})^{-2}+\overline{C}(T)(\overline{V})^{-3}+\sum_{n=4}^{\infty}D_n(T)(\overline{V})^{-n} \qquad (3.16.1a)$$

For reasons given earlier, this equation is only applied when the composition becomes fixed. When the intermolecular potentials are described by the Lennard-Jones (6-12) pair potential formula for the non-polar gas species, and by the Stockmayer (6-12) pair potential for polar molecules, approximate expressions for these coefficients are

$$\bar{B}(T) \simeq n_g^{-1} \sum_{j=2}^{m} n_j b_{oj} [B^*(T^*_j) - P^*_j(T^*_j, t^*_j)] \qquad \ldots\ldots\ldots \quad (3.16.2)$$

and $$\bar{C}(T) \simeq (\bar{b}_{og})^2 C^*(T^*_g) \qquad \ldots\ldots\ldots \quad (3.16.3)$$

where P^*_j is the correction term required when the species is a polar gas, and $\bar{C}$ is the third virial coefficient for a pure non-polar gas having species averaged LJ(6-12) pair potential constants. For reasons given earlier, the LJ(6-12) pair potential constants used in $\bar{C}(T)$ are not necessarily the same as those used for the calculation of $\bar{B}$, and in addition, in $\bar{C}$ the pair potential constants for polar molecules are those for sphericalized potentials.

Using the well known expression for B^*_j when the LJ potential is used, viz.,

$$B^*_j = \sum_{k=1}^{21} g^*_k T^{*(1-2k)/4}_j \quad , \qquad \ldots\ldots\ldots \quad (3.16.4)$$

and using the fitted expression to the third virial computations of de Boer and Michels,

$$C^* = \sum_{k=1}^{3} h^*_k T^{*(1-k)} \quad , \qquad \ldots\ldots\ldots \quad (3.16.5)$$

and the functions fitted to the Rowlinson calculations of the correction term P* for water (j=7), - - and for any other polar molecules that may be taken into consideration such as NH_3 - -,

$$P^*_j = \sum_{k=1}^{4} w^*_{jk} (T^*)^{-k} \quad ; \quad P^*_{j<7} = 0 \quad . \qquad \ldots\ldots \quad (3.16.6)$$

Accordingly, one may readily obtain the following expressions

$$\left.\begin{aligned} \bar{X} &= \bar{B}(T)+(p/RT)[\bar{C}(T)-\bar{B}^2] \\ p\partial\bar{X}/\partial p &= \bar{X}-\bar{B} \\ T\partial\bar{X}/\partial T &= T\bar{B}'+(p/RT)[(T\bar{C}'-2\bar{B}T\bar{B}')-(\bar{C}-\bar{B}^2)] \end{aligned}\right) \quad \ldots\ldots\ldots \; (3.16.7)$$

where ( )' means d( )/dT. From these expressions,

$$\left.\begin{aligned} -\frac{\partial\bar{E}_r}{\partial p} &= p\partial\bar{X}/\partial p+T\partial\bar{X}/\partial T = T\bar{B}'+(p/RT)(T\bar{C}'-2\bar{B}T\bar{B}') \\ \text{and} \quad \bar{E}_r &= -p[T\bar{B}'+(p/RT)(T\bar{C}'/2-\bar{B}T\bar{B}')] \\ \partial\bar{E}_r/\partial T &= -(p/T)\{(T^2\bar{B}'')+(T\bar{B}')+(p/RT)[T^2\bar{C}''/2-(T\bar{B}')^2-\bar{B}(T^2\bar{B}'')]\} \end{aligned}\right) \quad \ldots\ldots\ldots \; (3.16.8)$$

$$\left.\begin{aligned} \text{where} \quad T\bar{B}' &\simeq n_g^{-1}\sum_{j=2}^{m} n_j\bar{b}_{oj}\theta_j(B^*_{j1}-P^*_{j1}) \\ T^2\bar{B}'' &\simeq n_g^{-2}\sum_{j=2}^{m} n_j\bar{b}_{oj}\theta_j^2(B^*_{j2}-P^*_{j2}) \\ \text{where} \quad B^*_{j1} &\equiv T^*_j dB^*_j/dT^*_j = (1/4)\sum_{k=1}^{\infty}(1-2k)g^*_k T^{*(1-2k)/4} \\ B^*_{j2} &\equiv T^{*2}_j d^2B^*_j/dT^*_j = (1/16)\sum_{k=1}^{\infty}(1-2k)^2 g^*_k T^{*(1-2k)/4} \\ P^*_{j1} &\equiv T^*_j \, dP^*_j/dT^*_j = \sum_{k=1}^{4}(-k)w^*_{jk}(T^*_j)^{-k} \\ P^*_{j2} &\equiv T^{*2}_j d^2P^*_j/dT^{*2}_j = \sum_{k=1}^{4}k^2 w^*_{jk}(T^*_j)^{-k} \end{aligned}\right) \; (3.16.9)$$

All the relations required for the calculation of the adiabatic properties are now determined for this equation of state.

For the modified Jones and Miller form of $\overline{X}$, viz.,

$$\overline{X} = \overline{X}(p) = \sum_{k=1}^{5} d_k p^{k-1} \qquad \text{........ (3.17.0)}$$

$$\partial\overline{X}/\partial T = 0 \quad ; \quad p\partial\overline{X}/\partial p = -\partial\overline{E}_r/\partial p = \sum_{k=2}^{5} (k-1) d_k p^{k-1} \qquad \text{.... (3.17.1)}$$

and therefore

$$\overline{E}_r = -\sum_{k=2}^{5} (k-1) k^{-1} d_k p^k \quad ; \quad \partial\overline{E}_r/\partial T = 0 \qquad \text{........ (3.17.2)}$$

Since these forms are applied both when the composition is fixed and when it is variable, expressions are also required for the fugacity and its derivatives. It is evident that

$$\left.\begin{aligned} \log_e(f/p) &= (RT)^{-1} \sum_{k=1}^{5} k^{-1} d_k p^k \\ \partial \log f/\partial p &= [1+(p/RT)\overline{X}]/p = Z/p = \overline{V}_g/RT \\ \partial \log f/\partial T &= -R(RT)^{-2} \sum_{k=1}^{5} k^{-1} d_k p^k \end{aligned}\right) \qquad \text{..... (3.17.3)}$$

Chapter 3 References

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CHAPTER 4

EQUILIBRIUM COMPOSITION

The reaction expressing the chemical transformation of a pure CHON explosive into detonation products may be represented

$$C_{m(C)}\ H_{m(H)}\ O_{m(O)}\ N_{m(N)} \rightarrow \sum_j n_j A_j \qquad \text{........ (4.1)}$$

where A_j are the detonation products, n_j are the number of moles of species A_j per mole of unreacted explosive, and m( ) are small numbers descriptive of the explosive concerned. In order to examine the influence of the equation of state on the calculated thermodynamic properties of the product mixture, it is most desirable to eliminate all rare product species from consideration and to consider the same set of possible products for each equation of state. The product mixture resulting from the detonation reaction in strongly oxygen-negative CHON explosives is assumed to contain only the following 7 species:

j	1	2	3	4	5	6	7
A_j	C(s)	CO	CO_2	CH_4	H_2	N_2	H_2O(g)

........(4.2)

All other products are assumed to be present only in negligible proportions. For convenience in notation and in mathematical treatment, the species will hereafter be described by the subscripts assigned. All but the first of these products are gaseous. That is,

$$n_g = \sum_{j=2}^{7} n_j \qquad \text{........ (4.2a)}$$

is the total number of moles of gas present in the product mixture.

It is apparent from (4.2) that only seven relations are required to determine the composition. Four elementary relations, including the trivial one for n_6, are provided by atom balance requirements for C, H, O and N. That is,

$$\begin{array}{llllll}
\text{C):} & n_1+n_2+n_3+n_4 & = m(C) & & (= 7 \quad \text{for TNT}) & (4.3.1) \\
\text{H):} & 2n_4+n_5+n_7 & = m(H)/2 & \equiv \beta & (= 2.5 \quad \text{"} \quad \text{"}) & (4.3.2) \\
\text{O):} & n_2+2n_3+n_7 & = m(O) & \equiv \gamma & (= 6 \quad \text{"} \quad \text{"}) & (4.3.3) \\
\text{N):} & n_6 = \text{constant} & = m(N)/2 & & (= 1.5 \quad \text{"} \quad \text{"}) & (4.3.4)
\end{array}$$

Any three of the four following reactions are independent, and these three, together with the atom conservation relations (4.3), determine the equilibrium composition completely for a given pressure and temperature.

$$\begin{array}{llll}
\text{Reaction 1 :} & H_2+CO_2 \leftrightarrow & CO+H_2O(g) & \text{....... (4.4.1)} \\
\text{" \quad 2 :} & CH_4 \leftrightarrow & C(s)+2H_2 & \text{....... (4.4.2)} \\
\text{" \quad 3 :} & CO_2 \leftrightarrow & CO+1/2\ O_2 & \text{....... (4.4.3)} \\
\text{" \quad 4 :} & CO \leftrightarrow & C(s)+1/2\ O_2 & \text{....... (4.4.4)}
\end{array}$$

Thus, at equilibrium,

$$K^{\circ}_{1p}(T) = n_2 n_7 / n_5 n_3 \quad \ldots\ldots\ldots (4.5.1)$$

$$K^{\circ}_{2p}(T) = (n_5{}^2/n_4)(f/n_g) \quad \ldots\ldots\ldots (4.5.2)$$

$$K^{\circ}_{3p}(T)/K^{\circ}_{4p}(T) = (n_2{}^2/n_3)(f/n_g) \quad \ldots\ldots\ldots (4.5.3)$$

where $K^{\circ}_{ip}(T)$ is the (constant pressure) equilibrium constant for the i^{th} reaction in the ideal gas condition and f is the (common) fugacity. It is useful to define an additional equilibrium constant for another (dependent) reaction, viz.,

Reaction 5 : $2C(s)+2H_2O \leftrightarrow CO_2+CH_4$

$$K^{\circ}_{5p}(T) \equiv \frac{K^{\circ}_3/K^{\circ}_4}{(K^{\circ}_1)^2 K^{\circ}_2} = n_3 n_4 / n_7{}^2 \quad \ldots\ldots\ldots (4.5.4)$$

When the fugacity is common to all species its value is given by

$$\log_e(f/p) = (RT)^{-1} \int_0^p \overline{X}(p,T)\,dp \Big|_{T=\text{const.}} \quad \ldots\ldots\ldots (4.6)$$

For the two equations of state with which we are concerned

$$\text{JM:} \quad \overline{X} = \overline{X}(p) = \sum_{k=1}^{5} d_k p^{k-1} \quad \ldots\ldots\ldots (4.7)$$

$$\text{HM:} \left(\begin{array}{l} \overline{X} = \overline{X}(p,T) = b_g(T)F(y) \\ \\ \text{where} \quad y \approx pb_g(T)/RT \\ \\ \\ \text{and} \quad F(y) = 1+\sum_{k=1}^{3} A_k y^{k/3} \end{array} \right) \quad \ldots\ldots\ldots (4.8)$$

so that,

$$\text{JM}\;\left(\begin{array}{lll}
\log_e(f/p) = (RT)^{-1}\sum_{k=1}^{5} k^{-1}d_k p^k & \ldots\ldots & (4.7.1)\\
(\partial\log_e f/\partial p)_T = (1+\bar{X}p/RT)/p = Z/p & \ldots\ldots & (4.7.2)\\
(\partial\log_e f/\partial T)_p = -R(RT)^{-2}\bar{X} = -(Z-1)/pT & \ldots & (4.7.3)
\end{array}\right.$$

and,

$$\text{HM}\;\left(\begin{array}{lll}
\log_e(f/p) = \int_0^y F(y)\,dy = y[1+\sum_{k=1}^{3} 3(3+k)^{-1}A_k y^{k/3}] & \ldots & (4.8.1)\\
(\partial\log_e f/\partial p)_T = (1+\bar{X}p/RT)/p = Z/p & \ldots\ldots\ldots & (4.8.2)\\
(\partial\log_e f/\partial T)_p = -(y/T)F(y)(1+H^*) = -(Z-1)(1+H^*)/T & & (4.8.3)\\
\text{where}\quad H^* = \dfrac{1.5T^*/4}{F^*(1+F^*)} \quad\text{and}\quad F^* = [1+1.5T^*]^{1/2} & \ldots\ldots & (4.8.3a)
\end{array}\right.$$

where all symbols have been defined earlier. The relations for the partial derivatives are given here because they will be needed presently.

Since the relations between the mole numbers n_j are non-linear, a solution must be found by an iterative method. The general procedure in common practice is to express the n_j in terms of one of them ($n_k \equiv w$) and to determine w by successive adjustments until the correct values are found, at which point the other n_j are determined by the dependent relations $n_j = n_j(w)$.

An oxygen-balanced CHON explosive may be defined as one the detonation products of which are entirely carbon dioxide and water vapour. Accordingly, in a generally applicable treatment of the equilibrium composition of the products of all condensed CHON explosives it appears advisable to select the mole number of one of these as the primary unknown w. We choose water vapour.

$$\text{Let}\;\left(\begin{array}{lcl} w \equiv n_{H_2O(g)} \equiv n_7 & ; & a_1(T) \equiv 4K_5-1 \\ a_2(T) \equiv 1-2/K_1 & ; & a_3(T) \equiv 1-2K_1K_2 \end{array}\right) \quad ..... \quad (4.9)$$

Then, from (4.5),

$$n_2 \equiv n_{CO} = [a_1w^2+(\beta+\gamma)w-\beta\gamma]/(a_2w-\beta) \quad .... \quad (4.10.1)$$

$$n_5 \equiv n_{H_2} = [a_1w^2+(\beta+\gamma)w-\beta\gamma]/(a_3w-\gamma) \quad .... \quad (4.10.2)$$

$$n_3 \equiv n_{CO_2} = (\gamma-n_2-w)/2 \quad .... \quad (4.10.3)$$

$$n_4 \equiv n_{CH_4} = (\beta-n_5-w)/2 \quad .... \quad (4.10.4)$$

$$n_6 \equiv n_{H_2} = m(N)/2 = \text{const.} \quad .... \quad (4.10.5)$$

$$n_g \equiv \sum_{j=2}^{7} n_j = n_6+(\beta+\gamma)/2+(n_2+n_5)/2 \quad .... \quad (4.10.6)$$

$$n_1 \equiv n_{C(s)} = m(C)-(\beta+\gamma)/2+w+(n_5-n_2)/2 \quad .... \quad (4.10.7)$$

where w is the solution to

$$C(p,T) \equiv \log_e f+\log_e(K_4/K_3) = \log_e n_3+\log_e n_g-2\log_e n_2 \quad (4.10.8)$$

The well-known method of regula falsi may be applied to the solution of (4.10). It is apparent that the absolute upper limit to w is β. Thus, in order to find a first pair of start values, it is merely necessary to start with the value $\underline{\beta}$ for $\underline{w}$ and to decrease this by a definite amount until the function

$$g(w) \equiv C-\log_e(n_3 n_g/n_2^2) \qquad \ldots\ldots (4.10.9)$$

changes sign. If g_A, g_B are the values just before and after sign change, then

$$w = w_A-(w_A-w_B)|g_A|(|g_A|+|g_B|)^{-1} \qquad \ldots\ldots (4.10.10)$$

is very close to the value for which $g(w)=0$. The new $g(w)$ is defined to be g_A if $g(w)<0$, and to be g_B if $g(w)>0$ and the iteration is continued until $|g(w)|\leq\delta_w$ where δ_w is a relative accuracy which has been decided on. In the application to TNT δ_w was set at 10^{-4}. The same procedure is, of course, applicable in the computation of the composition in the adiabatic expansion except that here, in proceeding from the k^{th} to the $(k+1)^{th}$ pair of (p,T),

$$w_{max}(p_{k+1}, T_{k+1}) \simeq w_{final}(p_k,T_k) \qquad \ldots\ldots (4.10.11)$$

provides more economy in computation.

When the composition has been found, the partial derivatives $(\partial n_j/\partial T)_p$, $(\partial n_j/\partial p)_T$ may be readily determined. The partial derivatives of three of the species n_7, n_3, n_4 are first calculated. The derivatives of the remaining three variable species and of the gas mixture are then found from the eight secondary relations

$$\left.\begin{aligned}
(\partial n_2/\partial y)_Z &= -[(\partial n_7/\partial y)_Z+2(\partial n_3/\partial y)_Z] \\
(\partial n_5/\partial y)_Z &= -[(\partial n_7/\partial y)_Z+2(\partial n_4/\partial y)_Z] \\
(\partial n_1/\partial y)_Z &= -[(\partial n_2/\partial y)_Z+(\partial n_3/\partial y)_Z+(\partial n_4/\partial y)_Z] \\
(\partial n_g/\partial y)_Z &= -[(\partial n_7/\partial y)_Z+(\partial n_3/\partial y)_Z+(\partial n_4/\partial y)_Z]
\end{aligned}\right)\quad\ldots\ldots(4.11)$$

where Z=T or p when y=p or T. The primary derivatives (i.e., of n_7, n_3, n_4) are readily found using the six relations

$$\begin{bmatrix} (\partial n_7/\partial y)_Z \\ (\partial n_3/\partial y)_Z \\ (\partial n_4/\partial y)_Z \end{bmatrix} = \begin{bmatrix} \\ A^{-1} \\ \\ \end{bmatrix} \begin{bmatrix} (\partial B_1/\partial y)_Z \\ (\partial B_2/\partial y)_Z \\ (\partial B_3/\partial y)_Z \end{bmatrix} \quad\ldots\ldots\ldots\ldots(4.12)$$

where A^{-1} is the inverse matrix of

$$[A] = \begin{bmatrix} (n_2n_5/n_7)+n_2-n_1 \;, & -n_5[2+(n_2/n_3)] \;, & 2n_2 \\ n_4[(n_5/n_g)-2] \;, & n_4(n_5/n_g) \;, & (n_4n_5/n_g)-n_5-4n_4 \\ -2(n_4/n_7) \;, & n_4/n_3 \;, & 1 \end{bmatrix} \quad (4.12a)$$

and

$$\left.\begin{aligned}
(\partial B_1/\partial p)_T &= 0 \\
(\partial B_2/\partial p)_T &= -n_4n_5\cdot\partial\log_e f/\partial p \\
(\partial B_3/\partial p)_T &= 0 \\
(\partial B_1/\partial T)_p &= n_2n_5\cdot d\log_e K_5/dT \\
(\partial B_2/\partial T)_p &= n_4n_5[d\log_e K_2/dT-\partial\log_e f/\partial T] \\
(\partial B_3/\partial T)_p &= n_4\cdot d\log_e K_5/dT
\end{aligned}\right)\quad\ldots\ldots\ldots(4.12b)$$

It may be noted that the form of [A] has been chosen so as to be quite generally applicable with precision to oxygen-negative CHON explosives because the only inverse species terms n_3^{-1}, n_7^{-1} appearing in the matrix elements are for those which are always present in considerable quantities in the products of such explosives.

Expressions representing the ideal gas equilibrium constants $K^\circ_{ip}(T)$ were obtained in the following manner. The JANAF data for the species equilibrium constants $K^\circ_{pj}(T)$ were combined in accordance with the various reactions i=1, 2, ..., and the resulting combinations were fitted by functions thermodynamically consistent with those which were chosen to represent the ideal gas species specific heats at constant pressure.

Fits were made for each reaction rather than for each species so as to obtain the greatest possible accuracy. Bearing in mind the fact that reactions above 1.0 DEG* are of most importance, thermodynamically consistent representations of the equilibrium constants are:

$$\log_e K^\circ_{ip}(T) = \frac{-(\Delta\bar{E}^\circ_o)_i}{RT} + G_{i1}\log_e T + \sum_{k=2}^{5} G_{ik}T^{k-2} \quad \ldots\ldots(4.13.1)$$

where
$$(\Delta\bar{E}^\circ_o)_i = \sum_{j=1}^{8} m_{ij}\bar{E}^\circ_{oj} \quad , \quad \ldots\ldots(4.13.2)$$

---

* Note 1 DEG ≡ 1000°K

and where m_{ij} are the coefficients in the reaction equations when these are expressed in the form

$$\sum_{j=1}^{8} m_{ij} A_j = 0 \quad ; \quad \left.\begin{array}{ll} m_{ij}>0 & \text{'products'} \\ m_{ij}<0 & \text{'reactions'} \end{array}\right) \quad \ldots (4.13.3)$$

Here $\bar{E}^\circ_{oj}$ are the species molar energies of formation at absolute zero temperature, and j=8 refers to O_2. The constants are found by fitting

$$G_{i1} \log_e T + \sum_{k=2}^{5} G_{ik} T^{k-2} \quad \ldots\ldots\ldots \ (4.13.4)$$

to functions y_i derived from the JANAF tables. These are defined by

$$y_i(T) \quad = \quad (\Delta \bar{E}^\circ_o)_i / RT + \sum_{j=1}^{8} m_{ij} \log_e K_{pj}(T) \quad \ldots\ldots\ (4.13.4a)$$

The scheme which was used is set out in the following table.

Table 4.1

	j	1	2	3	4	5	6	7	8
	A_j	C(s)	CO	CO_2	CH_4	H_2	N_2	$H_2O(g)$	O_2
	$-\bar{E}^\circ_{oj}$(kcal)	0	27.2	93.965	15.991	0	0	57.103	0
	$\log_e K_{pj}$	0	JANAF	JANAF	JANAF	0	0	JANAF	0
Reaction	1 m_{1j}	0	1	-1	0	-1	0	1	0
	2 m_{2j}	1	0	0	-1	2	0	0	0
	3 m_{3j}	0	1	-1	0	0	0	0	1/2
	4 m_{4j}	1	-1	0	0	0	0	0	1/2
	5 m_{5j}	-2	0	1	1	0	0	-2	0

The values thus obtained for the coefficients G_{ik} are given in the following table. These constants refer to temperature expressed in the large DEGREE and to the natural logarithm. The reaction energies $(\Delta\bar{E}^\circ_o)_i$, referred to the absolute zero of temperature, are also given. The precision with which the expression (4.13.1) provides the equilibrium constants K_i, using the constants below, is comparable to that obtained for the representation of $\bar{C}^\circ_{pj}(T)$ given earlier.

Table 4.2

Fitted Constants for the Calculation of the Equilibrium Constants

i	$(\Delta E^\circ_0)_i$	G_{ik}				
	kcal/mole	k=1	k=2	k=3	k=4	k=5
1	9.662	-0.302177	+ 5.02601	-0.634430	+0.116390	-0.00898004
2	15.991	+4.95325	+12.8451	-2.77100	+0.318756	-0.0176849
3	66.765	+1.31287	+11.1607	-1.25739	+0.173080	-0.0113621
4	27.20	-1.12219	-11.4991	+1.26202	-0.174263	+0.0120058
5	4.25	-1.91254	- 0.236031	+1.51859	-0.203934	+0.0122437

Chapter 5

COMPUTATION OF THE TAYLOR WAVE

The equation of motion for one-dimensional, spherically symmetric, non-viscous flow and the equation of continuity are

$$\left.\begin{aligned} \partial u/\partial t+u\partial u/\partial r+(a^2/\rho)\partial\rho/\partial r &= 0 \\ \partial\rho/\partial t+u\partial\rho/\partial r+\rho(\partial u/\partial r+2u/r) &= 0 \end{aligned}\right)\ldots\ldots\ldots \quad (5.1)$$

where r is the radial position of a spherically symmetric element of fluid, u is its (entirely) radial velocity, ρ is its mass density, and t is time. In the equation of motion, δp has been replaced by $a^2\delta\rho$, where a is the speed of sound defined earlier.

Assuming initiation at r=0 t=0 to the constant detonation speed D which thereafter leaves the products at rest at this point, the motion is self-similar. In this case all the quantities behind the front are functions only of r/t. Accordingly, the partial differential equations (5.1) can be reduced to ordinary differential equations. This was first shown by G.I. Taylor[5.1] in his application to the tabulated adiabatic properties calculated by Jones and Miller[5.2]**. The reduced equations are

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**Although Taylor gave Jones and Miller as his reference, it appears that, in fact, he obtained his values from an earlier wartime report of H. Jones (see Cole[5.3], p.97).

$$\left.\begin{aligned} \frac{d\log u}{d\log x} &= \frac{2a^2}{(u-x)^2-a^2} \\ \frac{d\log a^2}{d\log x} &= \frac{2u(x-u)}{(u-x)^2-a^2}\, f^* \end{aligned}\right) \quad , \qquad \ldots\ldots\ldots \quad (5.2)$$

where $x \equiv r/t$

and $f^* \equiv d\log a^2/d\log\rho$

a form similar to that originally derived.

It follows from (5.2) that

$$\frac{da^2}{du} = (x-u)f^* \qquad \ldots\ldots\ldots \quad (5.2a)$$

These equations are not in a form suited to the present calculations where the quadrature is best effected with temperature chosen as the prime variable. Using the first of (5.2) and replacing f^* in (5.2a) by its defining terms

$$\left.\begin{aligned} \frac{d\log u}{d\log\rho} &= \frac{a^2}{(x-u)u} \\ \frac{d\log x}{d\log\rho} &= \frac{(u-x)^2-a^2}{2u(x-u)} \end{aligned}\right) \qquad \ldots\ldots\ldots \quad (5.3)$$

It is convenient to use the dimensionless quantities

$$u^* = u/D \quad , \quad a^* = a/D \quad , \quad r^*=x/D=r/r_{CJ} \qquad \ldots\ldots\ldots \quad (5.4)$$

where D is the constant speed of the wave front, and to eliminate $d\log\rho$ using

$$d\log\rho = -d\log V = V^{-1}(dV/dT)_{Ad}\cdot dT \qquad \ldots\ldots\ldots \quad (5.5)$$

The differential equations (5.3) may now be expressed

$$\left.\begin{aligned} u^{*\prime} &= -(V'/V)(a^*)^2/(r^*-u^*) \\ r^{*\prime} &= (V'/V)(r^*/2u^*)[(a^*)^2-(r^*-u^*)^2]/(r^*-u^*) \end{aligned}\right) \;\ldots\ldots\; (5.6)$$

where ( )' means $(d(\ )/dT)_{Ad}$. Now from (3.12),

$$\left.\begin{aligned} V'/V &= (f_2+p'f_1)/pV \\ (a^*)^2 &= -(V^2/K)pp'/(f_2+p'f_1) \\ \text{where } K &\equiv M_eD^2 \end{aligned}\right) \;\ldots\ldots\ldots\; (5.7)$$

so that

$$\left.\begin{aligned} u^{*\prime} &= (V/K)p'/(r^*-u^*) \\ r^{*\prime} &= -[r^*/2u^*(r^*-u^*)][(V/K)p'+(r^*-u^*)^2(f_2+p'f_1)/pV] \end{aligned}\right). \; (5.8)$$

The relations (5.8) may be integrated numerically down the adiabats starting at the equilibrium front where the conditions are

$$r^*_{CJ} = 1 \quad , \quad u^*_{CJ} = 1-a^*_{CJ} = 1-V_{CJ}/V_e \qquad \ldots\ldots\ldots\; (5.9)$$

At the CJ position $r^{*\prime}=0$, as may be noted most readily from (5.6). This will occasion no difficulty unless a first order relation is used to determine the finite steps Δu^*, Δr^*.

Let Y represent any of the variables p, u^*, or r^*. If ΔT is a small assigned temperature increment, the value of Y after N such steps have been made is

$$Y = Y_{CJ}+\sum_{n=1}^{N}\Delta Y_n \qquad \ldots\ldots\ldots\; (5.10)$$

where ΔY_n is the nth increment arising from the nth temperature step ΔT_n. The Runge-Kutta relation between ΔY_n and ΔT_n which is correct to the 4th order is

$$\Delta Y_n = (c/3)[Y_1'+2Y_2'+2Y_3'+Y_4'] \qquad \text{.........}(5.11.1)$$

where $c \equiv \Delta T_n/2$ .... (5.11.2)

and if $Y' = Y'(T,p,q,s)$ .... (5.11.3)

then

$$\left.\begin{aligned} Y_1' &\equiv Y'(T,p,q,s) \\ Y_2' &\equiv Y'(T+c,p+cp_1',q+cq_1',s+cs_1') \\ Y_3' &\equiv Y'(T+c,p+cp_2',q+cq_2',s+cs_2') \\ Y_4' &\equiv Y'(T+2c,p+2cp_3',q+2cq_3',s+2cs_3') \end{aligned}\right) \qquad \text{........}\ (5.11.4)$$

so that

$$\left.\begin{aligned} \Delta p &= (c/3)[p_1'+2p_2'+2p_3'+p_4'] \\ \Delta u^* &= (c/3)[u^{*\prime}_1+2u^{*\prime}_2+2u^{*\prime}_3+u^{*\prime}_4] \\ \Delta r^* &= (c/3)[r^{*\prime}_1+2r^{*\prime}_2+2r^{*\prime}_3+r^{*\prime}_4] \end{aligned}\right) \qquad \text{........}\ (5.12.1)$$

where

$$\left.\begin{aligned} p_1' &= p'(T,p) \\ u_1^* &= u^*(T,p,u^*,r^*) \\ r_1^* &= r^*(T,p,u^*,r^*) \\ &- - - - - - - - - \\ &- - - - - - - - - \\ p_4' &= p'(T+2c,p+2cp_3') \\ u^{*\prime}_4 &= u^*(T+2c,p+2cp_3',u^*+2cu^{*\prime}_3,r^*+2cr^{*\prime}_3) \\ r^{*\prime}_4 &= r^*(T+2c,p+2cp_3',u^*+2cu^{*\prime}_3,r^*+2cr^{*\prime}_3) \end{aligned}\right)\text{....}\ (5.12.2)$$

In the application to TNT, the complete calculations described in chapters 3 and 4 were carried out for each

Runge-Kutta substage, and ΔT was assigned the value -0.025 DEG until the value of u* became sufficiently small that it could be regarded as 0. Here, the Taylor wave calculations are complete because the conditions at smaller radii are the same as those at this point. The calculations continued to lower temperatures on the adiabats were made with ΔT=-0.050 DEG as the assigned step. Checks were made to ensure that smaller steps gave no significant change in the numerically integrated values.

Chapter 5 References

(5.1) TAYLOR, G.I., The Dynamics of the Combustion Products Behind Plane and Spherical Detonation Fronts in Explosives, Proc. Roy. Soc. A200, 1061, p.235-247 (1950)

(5.2) JONES, H. and MILLER, A.R., Proc. Roy. Soc. A194, p.480-507 (1948)

(5.3) COLE, R.H., Underwater Explosions, Princeton Univ. Press, Princeton, New Jersey, (1948)

CHAPTER 6

HIGH PRESSURE APPROXIMATIONS

6.1 High Pressure Composition

It was pointed out by Jones and Miller[6.1] that the chemical equilibrium relations show clearly that high fugacities (and hence high pressures) tend to suppress the formation of carbon monoxide and hydrogen. This conclusion is obviously not limited to TNT products nor to any particular equation of state. The very large values of the fugacity for pressures greater than about 150 kbar indicates that the approximation

$$n_{CO} = 0 \quad ; \quad n_{H_2} = 0 \qquad \ldots\ldots\ldots \ (6.1)$$

is fairly accurate at the head of the wave when the explosive loading density is high. Under these conditions it follows that

$$n_j = n_j(T) \quad ; \quad n_g = \text{constant} \qquad \ldots\ldots\ldots \ (6.1a)$$

It will be shown that, for TNT at $\Delta > 1.5$ g cc^{-1}, this approximation leads to errors of less than 1% in n_g and similarly small consistent errors in the thermodynamic properties on the Hugoniot.

The rapidity with which the fugacity rises with pressure is evident from the exponential nature of its pressure dependence (see 2.6). The following values for the JM equation of state emphasize this point.

Table 6.1. Fugacity for T = 3.0 DEG

pressure (p)		f/p
kbar	kcal cc^{-1}	-
10.1	0.24	2.75
50.5	1.2	$1.01\cdot10^{2}$
101	2.4	$4.45\cdot10^{3}$
155	3.7	$1.33\cdot10^{5}$
188	4.5	$8.9\cdot10^{5}$
210	5.0	$2.68\cdot10^{6}$

The calculated equilibrium temperature at the head of the wave changes slowly with increasing loading density for both the equations of state considered here. This changes the fugacity loading-density dependence only slightly, and it is evident that for equilibrium pressures corresponding to high loading densities (the last 3 rows in the table above), the Jones and Miller approximation (6.1) is very good.

In the limit $f = \infty$, where $n_5 = 0 = n_2$, the equilibrium relations of Chapter 4 show that

$$\left.\begin{aligned} n_g &= n_6+(\beta+\gamma)/2 = \text{constant} \\ n_7 &\equiv w = \gamma-2n_3 = \beta-2n_4 \\ a_1w^2&+(\beta+\gamma)w-\beta\gamma = 0 \end{aligned}\right) \quad \ldots\ldots\ldots \quad (6.3)$$

It is now more convenient to express the species in terms of n_4, which we now represent as $\underline{\phi}$ (as did Jones and Miller). Thus,

$$\left.\begin{aligned} n_1 &= m(C)-(\gamma-\beta)/2-2\phi \\ n_3 &= (\gamma-\beta)/2+\phi \\ n_4 &\equiv \phi \qquad ; \qquad n_7 = \beta-2\phi \\ n_g &= n_6+\beta+\gamma = \text{const.} \end{aligned}\right) \quad \ldots\ldots\ldots \quad (6.4)$$

and ϕ is the positive root of the quadratic obtained by replacing n_3, n_4, and n_7 by these expressions in (4.5.4). Thus,

$$\phi = \phi(T) \qquad ; \qquad n_j = n_j(T) \quad . \qquad \ldots\ldots\ldots \quad (6.4a)$$

The expression for ϕ is easily determined. It is

$$\phi(T) = \frac{[\gamma^2+2\gamma\beta(8K_5-1)+\beta^2]^{1/2} - [\gamma+\beta(8K_5-1)]}{4(1-4K_5)} \quad \ldots\ldots \quad (6.5)$$

and for TNT ($\gamma=6$, $\beta=2.5$, $m(C)=7$, $m(N)=3$) ,

$$\phi(T)_{\text{TNT}} = \frac{(49/4+240K_5)^{1/2} - (7/2+20K_5)}{4(1-K_5)} \quad , \qquad \ldots\ldots\ldots \quad (6.6)$$

$$\text{and}\quad \left.\begin{array}{lll} n_1 = 5.25-2\phi & ; & n_3 = 1.75+\phi \\ n_4 \equiv \phi & ; & n_6 = 1.5 \\ n_7 = 2.5-2\phi & ; & n_9 = 5.75 \end{array}\right) . \quad \ldots\ldots (6.6a)$$

The special relations (6.6) for TNT were given previously by Jones and Miller.

The parameter ϕ is very insensitive to temperature in the case of TNT. The general expression for its temperature derivative is

$$\frac{d\phi}{dT} = K_5(d\log_e K_5/dT).\frac{8\beta(1-\gamma/F)-(G-F)}{(1-4K_5)^2} \quad \ldots\ldots\ldots (6.7)$$

$$\text{where}\quad F=[(\gamma-\beta)^2+16\gamma\beta K_5]^{1/2} \quad ; \quad G=\gamma-\beta+8\beta K_5 \quad \ldots\ldots\ldots (6.7a)$$

Now $K_5 = 1$ at 3000°K, and here,

$$\phi_{TNT} = 0.6349 \quad , \quad (d\phi/dT)_{TNT} = 1.207\cdot 10^{-4}\,\text{degK}^{-1} \quad \ldots (6.7b)$$

Accordingly, the high pressure composition is not only virtually independent of the pressure, but is nearly invariant with temperature also. In addition, the chemical energy Q becomes constant to a remarkable degree. In this case

$$\left.\begin{array}{l} Q = \varepsilon_3(\gamma-\beta)/2+\varepsilon_7\beta+\phi[\varepsilon_3+\varepsilon_4-2\varepsilon_7]-\varepsilon_e \\ \\ \dfrac{dQ/dT}{d\phi/dT} = \varepsilon_3+\varepsilon_4-2\varepsilon_7 \end{array}\right) \quad \ldots\ldots\ldots (6.8)$$

The applicability of these high pressure approximations is, of course, confined to detonation front pressures obtained with explosives at high loading density and to pressures in this vicinity. The calculated detonation front temperatures for TNT under these conditions are found to differ by less than 300°K, and, in practice, one may put $\phi_{CJ} \simeq 0.64$ to obtain a very good first approximation to the product composition and chemical energy, viz.,

$$\left.\begin{array}{lll} n_1=3.97\ , & n_3=2.39\ , & n_4=0.64 \\ n_7=1.22\ , & n_2=n_5=0\ , & n_6=1.5 \\ n_g=5.75\ , & Q=Q_o=291.5\text{ kcal} & \end{array}\right)\text{per mole TNT} \quad \ldots\ldots \quad (6.9)$$

Such approximate composition estimates are of considerable value in saving computation in an iterative determination of the CJ conditions. The gross iteration may thus be carried out rapidly and the final delicate iteration without constraints then requires only one or two additional steps. In this context, one should note that a clear distinction must be drawn between the validity of the high pressure JM approximation (6.1) and the accuracy of their published calculations. The former appears to be sound. The latter are poor, but only a small part of their total errors are attributable to (6.1).

6.2 The Jones and Miller Computations for TNT

Jones and Miller only applied their equation of state

$$\bar{X}(p) = \sum_{k=1}^{3} d_k p^{k-1}$$

to TNT at two loading densities, 1.0 and 1.5 g cc^{-1}. For the former case, and along the adiabatic for the latter, they carried out a general computation using

$$n_j = n_j(p,T)$$

but introduced considerable numerical errors by using linear representations of non-linear functions. That is, they used

$$\bar{E}_j^\circ(T) \simeq a_{1j}+a_{2j}T \qquad \ldots\ldots\ldots (6.10)$$

$$E_{\text{thermal}} \simeq \sum_{j=1}^{7} n_j a_{1j} + T\sum_{j=1}^{7} n_j a_{2j} \qquad \ldots\ldots\ldots (6.10a)$$

$$\log_e K_{pi} + (\Delta\bar{E}_o^\circ)_i/RT \simeq b_{1i}+b_{2i}\log_e T \qquad \ldots\ldots\ldots (6.11)$$

where a_{kj}, b_{ki} are constants. In addition, they integrated along an approximate adiabatic

$$d(E-Q)+pdV_g \simeq 0 \quad ; \quad dV_c \simeq 0 \qquad \ldots\ldots\ldots (6.12)$$

rather than along the correct adiabatic

$$d(E-Q)+p(dV_g+dV_c) = 0 \quad ; \quad dV_c = \bar{k}_c dn_c \qquad \ldots\ldots\ldots (6.13)$$

It might be thought that the approximation (6.12) is reasonable because, as the earlier discussion has shown, at high pressures, $n_c \simeq n_c(T)$, and therefore, $(\partial V_c/\partial p)_T \simeq 0$, whereas at low pressures (i.e., large gas volumes) the volume of solid carbon becomes increasingly negligible compared to that of the gas phase. However, dV_c/dV_g is by no means negligible compared with unity. For example, at very high pressures, where $n_j \simeq n_j(T)$, $n_g = 5.75$, and at a temperature near 3.0 DEG

$$dV_c/dV_g \simeq (\partial V_c/\partial T)/(\partial V_g/\partial T) = p.2\bar{k}_c.(d\phi/dT)/n_g R \simeq 0.11p \qquad \ldots\ldots\ldots \text{(6.13a)}$$

where the pressure p is expressed in kcal cc^{-1} units. As shown earlier, the latter may have a value of about 4 to 5 such units near the detonation front in TNT at high loading densities.

In their computations of the CJ conditions for the higher loading density (1.5 g cc^{-1}) of TNT, Jones and Miller introduced two approximations in addition to the approximation $n_j=n_j(T)$. The first of these is really a consequence of (6.1) and of (6.10a). The thermal energy on the high pressure portion of the Hugoniot is expressed as a linear relation. That this follows from their other approximations is evident because

$$E_{th} \simeq \sum_{j=1}^{7} (b_{1j}+b_{2j}\phi)\ (a_{1j}+a_{2j}T)$$

i.e.,

$$\begin{aligned}(E_{th})^{RH}_{TNT} &= (5.25-2\phi)(a_{11}+a_{21}T)+(1.75+\phi)(a_{13}+a_{23}T) \\ &\quad +\phi(a_{14}+a_{24}T)+1.5(a_{16}+a_{26}T) \\ &\quad +(2.5-2\phi)(a_{17}+a_{27}T) \\ &= C_1+C_2T+C_3\phi+C_4T\phi \\ &\simeq (C_1+0.64C_3)+(C_2+0.64C_4)T \\ &= K_1+K_2T \qquad \text{........ (6.14)}\end{aligned}$$

The values of K_1 and K_2 they obtained are based on the (1938) thermodynamic data of Lewis and Von Elbe[6.2]. These are, per mole of TNT,

$$K_1 = -38.0 \text{ kcal} \quad ; \quad K_2 = 87.5\text{kcal DEG}^{-1} \qquad \text{........ (6.14a)}$$

A linear representation of the thermal component of the energy on the Hugoniot at high pressures is certainly useful in making slide-rule accuracy initial computations, but it is by no means acceptable for a final one. Furthermore, any such linear representation must be based on a definite temperature range: the authors do not state their choice of range. For TNT, all detonation temperatures calculated with the improved JM equation of state

$$\overline{X} = \sum_{k=1}^{5} d_k p^{k-1} \qquad \text{........ (6.15)}$$

lie between about 3.8 and 3.0 DEG for $\Delta > 1$ g cc^{-1}. Choosing a fairly broad range, $2.5 \leq T_{CJ} \leq 3.5$ DEG, and calling on the JANAF[6.3] data, one obtains the following Hugoniot thermal energy constants: these appear to be considerably better than the JM values.

$$K_1 = -50.67 \text{ kcal} \quad ; \quad K_2 = 93.08 \text{ kcal DEG}^{-1} \quad \ldots\ldots\ldots \quad (6.15a)$$

The second high loading density detonation front approximation of Jones and Miller arises in the following way. A set of approximate relations describing the CJ properties is sought and it is assumed that both

$$n_j = n_j(\phi(T)) \quad \text{and} \quad E_{th} = K_1 + K_2 T \quad \ldots\ldots\ldots \quad (6.16)$$

apply, and that the covolume is

$$\overline{X} = \sum_{k=1}^{3} d_k p^{k-1} \quad , \quad \text{so that,} \quad \overline{E}_r = -p^2(d_2/2 + 2d_3 p/3) \quad , \quad (6.17)$$

Accordingly, for TNT,

$$\left.\begin{array}{ll} Q \simeq Q_0 & \text{(an invariant)} \\ n_g = 5.75 \quad ; & n_c = 5.25 - 2\phi \end{array}\right) \quad \ldots\ldots\ldots \quad (6.18)$$

The two primary unknowns sought are the independent variables p, T at the equilibrium front. The two equations to be solved simultaneously to determine these are, of course, the Hugoniot and the equation for the CJ condition. That is,

$$\left.\begin{aligned} U-U_e &= E_{th}+E_r-Q = p(V_e-V)/2 && (1) \\ (dV/dp)^{CJ}_{RH} &= (dV/dp)^{CJ}_{Ad} = -(V_e-V)/p && (2) \end{aligned}\right) \quad \ldots\ldots\ldots \; (6.19)$$

where the subscript e refers to the state of the unreacted explosive. The linear form (6.14) for the thermal energy, together with the other approximations, allows one to eliminate the temperature from the Hugoniot. Equating the expressions for the temperature obtained from the Hugoniot and from the equation of state

$$n_gRT = p(V_g-n_g\overline{X}) = [p(V_e-V)/2+A_1-n_g\overline{E}_r]/A_2 \quad \ldots\ldots\ldots \; (6.20)$$

where $A_1 = Q_o-K_1$; $A_2 = K_2/Rn_g$ . ... (6.20a)

This gives immediately

$$\begin{aligned}(A_2+1/2)(V_e-V) = -A_1/p+A_2V_{eg}-n_g[A_2d_1+(A_2+1/2)d_2p \\ +(A_2+2/3)d_3p^2] \quad \ldots. \; (6.20b)\end{aligned}$$

where the intermediate parameter V_{eg} is defined by

$$V_{eg} \equiv V_e-V_c(T) \equiv (V_e-V)-(V_c-V) \equiv (V_e-V)+V_g \quad \ldots\ldots\ldots \; (6.20c)$$

The equation for the CJ condition is readily obtained by differentiating (6.20b) with respect to p, subject to (6.19(2)). That is,

$$\begin{aligned}(A_2+1/2)(V_e-V)/p = (A_1/p^2)[1+p^2(A_2/A_1)(dV_{eg}/dp)^{RH}] \\ -n_g[(A_2+1/2)d_2(A_2+2/3)d_3p] \quad \ldots.. \; (6.21)\end{aligned}$$

If, as appears to have been assumed,

$$p^2(A_2/A_1)(dV_{1g}/dp)^{RH} << 1 \quad , \qquad \ldots\ldots\ldots (6.22)$$

then, the expression (6.21) for the CJ condition becomes

$$V_e - V \equiv V_{eg} - V_g = 2A_1/(1+2A_2)p - n_g d_2 p$$
$$-(4n_g/3)[(2+3A_2)/(1+2A_2)]d_3 p^2 \quad \ldots\ldots (6.23)$$

When, using this expression, V and V_e-V are eliminated from the expressions for the equation of state and for the Hugoniot, one readily obtains the following simple approximate relations.

$$\left.\begin{array}{ll} d_3 p^3 = G_1 + G_2 T & (1) \\ V_{eg} = n_g d_1 + G_3/p + G_4 d_3 p^2 & (2) \\ V_g = V_{eg} + n_g d_2 p + G_5 d_3 p^2 + G_6/p & (3) \end{array}\right) \qquad \ldots\ldots\ldots (6.24)$$

where the G_k are constants defined by

$$\left.\begin{array}{ll} G_1 = 3A_1/n_g \; ; & G_2 = -(3/2)A_2 R(1+2A_2)/(1+A_2) \\ G_3 = 2A_1/A_2 \; ; & G_4 = -n_g(2+3A_2)/3A_2 \\ G_5 = (4n_g/3)(2+3A_2)/(1+2A_2) \; ; & G_6 = -2A_1/(1+2A_2) \end{array}\right) \quad (6.24a)$$

It may also be noted that when the thermal energy is approximated by the linear relation (6.14), the quantity β_{CJ} required when seeking to estimate the pressure and specific volume from the observed detonation velocities D_∞ using the Jones relations[6.4] given earlier is

$$\beta_{CJ} \equiv \left[\frac{p}{(\partial U/\partial V)_p} \right]^{CJ} = \frac{p(\partial V/\partial T)_p}{(\partial U/\partial T)_p} = \frac{1}{A_2} \qquad \ldots\ldots\ (6.25)$$

The various constants given by Jones and Miller, and the improved values found using (6.15) are summarized below.

Table 6.1

Constants For Approximate Detonation Front Relations

Constant	Jones and Miller[6.1]	Improved
K_1 kcal (mole TNT)$^{-1}$	-38.0	-50.67
*K_2 kcal (mole TNT)$^{-1}$DEG^{-1}	87.5	93.08
Q_o kcal (mole TNT)$^{-1}$	289.9	291.5
A_1 kcal (mole TNT)$^{-1}$	327.9	342.2
A_2 - - - - - - - - - - - - - - - -	7.658	8.146
$\beta(\equiv 1/A_2)$ - - - - - - - - - - - -	0.1306	0.1228
G_1 kcal (mole gas)$^{-1}$	171.1	178.5
G_2 kcal (mole gas)$^{-1}$DEG^{-1}	-43.48	-45.91
G_3 kcal (mole TNT)$^{-1}$	86.27	84.01
G_4 moles gas (mole TNT)$^{-1}$	-6.254	-6.221
G_5 moles gas (mole TNT)$^{-1}$	11.74	11.72
G_6 k cal (mole TNT)$^{-1}$	-40.47	-39.57

*Note: 1 DEG = 10^3 deg K

The approximation involved in neglecting the dimensionless function (6.22) may be seen from the following

$$\delta \equiv p^2(A_2/A_1)[dV_{eg}/dp]^{CJ}_{RH} = p^2(A_2/A_1[dV_{eg}/dp]^{CJ}_{Ad}$$

$$= -p^2(A_2/A_1)(dV_c/dT)(dT/dp)_{Ad}$$

$$= 2\bar{k}_c p^2(A_2/A_1)(d\phi/dT)(dT/dp)_{Ad} \qquad \ldots\ldots\ (6.26)$$

Now, when (6.1) applies,

$$(dT/dp)_{Ad} = \frac{RTn_g/p}{n_gR(1+A_2)+p\bar{k}_c(d\Phi/dT}$$

so that

$$\begin{aligned}\delta &= \frac{2(A_2/A_1)RT}{1+n_gR(1+A_2)/[p\bar{k}_c d\phi/dT]} \\ &\simeq [2\bar{k}_c/A_1(1+\beta_{CJ})]pT(d\phi/dT) \\ &= 0.028\ pT(d\phi/dT) \qquad \ldots\ldots\ (6.26)\end{aligned}$$

The quantity $T(d\phi/dT)$ increases with decreasing temperature, and using its values for 3.0 DEG as an upper limit,

$$Td\phi/dT \leq 0.36 \quad ; \quad \delta \leq 0.01p \qquad \ldots\ldots\ (6.26a)$$

where p is in kcal cc^{-1} units. If we estimate p_{max} from the observed detonation velocity using the maximum possible loading density 1.654 g cc we obtain

$$\left.\begin{aligned} p_{max} &\simeq 225\ \text{kbar} = 5.35\ \text{kcal cc}^{-1} \\ \text{so that} \quad \delta_{max} &\simeq 0.054 \end{aligned}\right) \ldots\ldots\ (6.26b)$$

The approximation $\delta = 0$ thus appears to be fairly sound. The overall effect of these high pressure approximations on the calculated detonation front properties and flow variables may be seen from the following table.

Table 6.2

Effect of Approximations on the Calculated CJ Conditions for TNT at 1.5 g/cc Loading Density

Computation**	p kbar	T DEG	v1 cc/g	γ_{Ad} -	D* cm/μsec	u/D -
(JM[6.1])	158.8	3.400	0.5136	3.36	0.6790	0.2296
(Aa)	159.0	3.387	0.5089	3.225	0.6692	0.2367
(Ab)	159.0	3.388	0.5088	3.224	0.6692	0.2367
(Ac)	163.7	3.357	0.5069	3.174	0.6750	0.2396
(Ba)	165.2	3.386	0.4953	2.890	0.6545	0.2570
(Bb)	165.2	3.387	0.4953	2.890	0.6545	0.2571
(Bc)	169.6	3.359	0.4930	2.838	0.6587	0.2605

* Observed[6.5] value is $D_\infty = 0.6622$ cm/μsec

** Code: A Original covolume of JM

$$\bar{X} = \sum_{k=1}^{3} d_k p^{k-1}$$

B Improved covolume

$$\bar{X} = \sum_{k=1}^{5} d_k p^{k-1}$$

(a) Approximating $n_j = n_j(T)$, and $E_{th} = K_1 + K_2 T$ but not using (6.24).

(b) Approximating $n_j = n_j(T)$. No other approximations.

(c) General case $n_j = n_j(T,p)$. No approximations.

On the adiabatics, the accumulated effect of the Jones and Miller approximations is that their published values but poorly represent the effect of their equation of state. The departure of their results for TNT at a loading density of 1.5 g cc^{-1} from the corresponding values calculated here (with the improved form of the same equation of state) is so great as to indicate that, in addition to the approximations which have already been described, large errors were incurred in quadrature also. This is to be expected because this involved the choice of large temperature steps ($\Delta T=200°K$) in conjunction with a first order relation to describe finite differences in the pressure in terms of its slope in the temperature.

In G.I. Taylor's[6.6] well-known application of the tabulated adiabatic properties of Jones and Miller (to the calculation of the instantaneous spatial distribution) additional, and much larger, numerical errors were introduced. Numerical errors, but not necessarily of this magnitude, are unavoidable unless the spatial distribution is calculated in parallel with the adiabatic properties in a manner such as described in the previous chapter.

It has been known for some time[6.7] that G.I. Taylor's computations were seriously in error. That most of the errors in his calculated spatial distributions are due to his numerical errors rather than to those of Jones and

Miller was demonstrated by the recalculation of the spatial distributions for a spherical detonation wave in TNT at a loading density of 1.5 g cc^{-1} by Dasgupta and Penney[6.8], also using the Jones and Miller adiabatic properties but using a more refined numerical procedure. The difference of these from those originally calculated by G.I. Taylor is a striking example of the importance of numerical precision. It will shortly be demonstrated that the calculated instantaneous pressure-radius distributions behind a spherical detonation wave in TNT - - according to (a) Dasgupta and Penney, (b) the author, using the improved JM equation, (c) the author, using the hypothetical hard sphere equation of state, and (d) Lutzky[6.9], using the Landau-Stanyukovich-Zeldovich-Kompaneets crystal-based equation - - are all in fair agreement. The numerical procedures in these cases were of similar precision. This indicates not only that the calculated distribution is relatively insensitive to the equation of state used, but that one must beware of ascribing calculated differences to the effect of the equations of state that may be used unless the numerical procedures are of such precision that this effect may safely be ignored. Brode's[6.10] calculations of the air blast wave arising from the explosion of a sphere of TNT are based on G.I. Taylor's calculations and are, therefore, unreliable to at least this extent.

However, Brode introduced more serious errors in calculating the blast wave proporties by misrepresenting the ideal component of the total internal energy on the adiabatic as a linear relation in the temperature, a general notion he incorrectly ascribes to Jones and Miller. Empirical corrections to Brode's computations that allow quantitative use of his charts are discussed elsewhere[6,11].

Chapter 6 References

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CHAPTER 7

APPLICATION TO TNT AND FINAL DISCUSSION

7.1 Introduction

We now describe the results obtained when the relations discussed earlier are applied to TNT ($C_7H_5N_3O_6$). For conciseness, only 1.0 and 1.5 g/cc loading densities are treated. For the former loading density, the detonation front, the adiabatic and the Taylor wave are calculated both for the hard molecule (HM) equation of state and for the (modified) formula of Jones and Miller (JM). The same calculations are applied to the higher loading density using only the HM equation of state but the detonation front properties and speed are also calculated using the modified JM formula. Sufficient has been stated as to now require specification only of the heat of formation of TNT and the initial thermal energy of the unreacted TNT. The following value is derived from Cook[7.1]

$$\varepsilon_e - E_e(T_e = 300°K) = 13 \text{ kcal/mole TNT} \qquad \ldots\ldots \quad (7.1)$$

7.2 Conditions at the Detonation Front (CJ Conditions)

Tables 7.1A, B show the values obtained here compared with those calculated by Jones and Miller[7.2] using the 3-constant formula described earlier, by Fickett[7.3] using the LJD equation of state, by Lutzky[7.4] using the

Landau-Stanyukovitch-Zeldovitch-Kompaneets crystal-based formula and by J. Taylor using the virial form (2.41). The observed detonation wave speeds due to Urizar[7.6] agree well with the Bruceton[7.7] values here called the "observed" values (symbol D_∞) and in the absence of adequate criteria we must regard agreement of the calculated detonation speed with these values as a strong index of merit of the equation of state used. This does not, of course, apply to the detonation front formulae. The departure of formulae-calculated wave speeds from those observed is merely an indication of imperfect fitting: this is pronounced in the case of the original unmodified (3-constant) formula of Jones and Miller as demonstrated in Chapter 6 for the 1.5 g/cc loading density. This deficiency persists at the lower density of loading as shown in Table 7.1A and the improvement designed to be effective at high loading density has little effect at low densities of loading. That this is the case may be seen from the following comparison for 1.0 g/cc

	D_{calc} m/sec	p kbar	v_1 cc/g	E_1 kcal/g	γ -	n_g -	n_c -
3-constant JM	5226	82.00	0.6998	1.468	2.331	6.390	3.244
5-constant JM	5218	82.39	0.6974	1.473	2.304	6.387	3.248
3-constant JM[7.2]	5266	82.24	0.7035	-	2.43	6.453	3.104

It may be noted from these values that the difference due to the change introduced into the formula for $\overline{X}$ (the covolume) has far less effect than that due to the different calculation procedures used by Jones and Miller and by the author. The JM formula, either in the 3 or the 5-constant form, appears to be of little merit as regards the calculated properties for low loading densities. However, the composition is in fairly close agreement with that by the HM equation of state and this agreement persists along the adiabats as will be illustrated presently.

The HM calculated wave speed agrees with that observed to better than 1% at the higher loading density. Here, it surpasses even the LJD equation of state, the wave speeds from which, as Fickett's calculations demonstrate, depart from that observed by over 3.5% at 1.4 and by 2.5 at 1.64 g/cc loading densities. Another factor, of course, is the different choice of pair potential constants and pair potential formulae in the two cases. It will have been noted that at high loading density the dominant gases at the CJ front are CO_2, N_2 and $H_2O(g)$: for the HM equation of state, choice of larger diameters $\underline{\sigma}$, particularly in the first two species would be expected to increase the calculated pressure while choice of smaller θ values would be expected to increase the imperfection component of internal energy and reduce the calculated temperature. However the calculated temperature - - which is very insensitive to loading density for this equation of state - - and the value of θ have less effect on the imperfection component of energy than does the pressure. Confirmation of these expectations is provided by the following comparison for 1.5 g/cc loading density using the HM equation of state and the initial and final pair potential constants given in Table 2.2.

	p kbar	v_1 cc/g	T °K	E_1 kcal/g	E_r kcal	D_{calc} m/sec
Initial choice	140.1	0.5160	3616	1.510	58.86	6429
Final choice	143.6	0.5182	3594	1.517	62.10	6557

At the lower loading density the LJD calculations appear to be far superior to those using the HM equation as may be noted from Table 7.1A. Here CO becomes a major component and variation of its pair potential constants would more profoundly affect the results. The (small) effect of the change of constants at 1.0 g/cc loading density is illustrated below.

	p kbar	v_1 cc/g	T °K	E_1 kcal/g	E_r kcal	D_{calc} m/sec
Initial constants	62.22	0.7238	3484	1.309	36.70	4746
Final constants	62.88	0.7242	3488	1.319	38.04	4775

It may be concluded that if, as appears to be the case, the relation $b_g^*(T^*)$ is at fault (by virtue of its dependence on the LJ(6-12) pair potential formula), then use of a more realistic pair potential in the calculation of b_g^* should improve agreement. This must await further investigation.

7.3. Properties and Composition in Adiabatic Expansion Following Detonation and the Spherical Taylor Wave

The calculations are summarized in Tables 7.1, 7.2 and 7.3 and in Figures 7.3 and 7.4, as regards properties and composition and in Table 7.4 and Figures 7.1 and 7.2 as regards the Taylor wave.

It may be noted that, considered as functions of temperature, the properties and composition are very similar for the HM and JM equation of state except at the lowest temperatures. For the lower loading density, the temperature at the first graphite minimum is the same in both cases, viz. 2100°K in agreement with Jones and Miller. At the higher density, the HM equation of state determination of the minimum occurs at 1800°K: this is in fair agreement with the Jones and Miller calculation of 1600°K for this case. These authors quote the experimentally determined n_{CO}/n_{CO_2} final equilibrium values as 1.66 for a loading density of 1.5 g/cc. This is in precise agreement with the value obtained here using the HM formula at 1800°K for this loading density. We have

$$\text{HM}; \quad n_{CO}/n_{CO_2} = 2.254/1.361 = 1.66$$

This is a significant improvement over the value calculated by Jones and Miller at their minimum (1600°K) viz. 1.33. The agreement is strong support for the assumptions made regarding the fugacity and more generally supports the

HM equation of state. In view of the fair agreement in composition according to the HM and JM equations, the JM estimates of the mole number of the gases NH_3 and HCN appear acceptable. These are

$$n_{HCN} \approx 0.021 \quad ; \quad n_{NH_3} \approx 0.01$$

at 2000°K, which supports our initial assumption regarding the unimportance of reactions involving nitrogen.

The Taylor wave calculations are only tabulated (Tables 7.4) for the HM equation of state, while the JM calculations are presented only graphically (Figure 7.2) because the CJ values are most unreliable for this case and these start values, more than the equation of state, determine the shape of the pressure and particle velocity curves. It may be noted that the pressure falls much more rapidly according to the JM than to the HM equation of state. This appears to be due to the rapidly decreasing imperfection energy for the former equation. For the 1.5 g/cc loading density, the fair agreement between the normalized pressure for the different equations illustrates the remarks made earlier in Chapter 6.

While computations of air blast propagation resulting from the explosion of a sphere of TNT using the HM equation of state have not yet been carried out, the less sharply peaked pressure, energy and particle velocity distributions of this equation offer promise that the initial air shock velocity, which is calculated to be too high when other equations are used, will be more faithfully calculated when the detonation products are assumed to obey it.

Chapter 7 References

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Table 7.1A

Calculated Properties and Composition at the (CJ) Detonation Front

(1.0 g/cc loading density; D_∞ = 5010 m/sec)

Item	(a) HM	(a) JM	[7.4] Lutzky	(b)	[7.3] Fickett
D_{calc}(m/sec)	4775	5218	5030	5266	5001
p(kbar)	62.88	82.39	72.2	82.24	70.93
T(°K)	3488	3782	2357	3800	3631
v_1(cc/g)	0.7242	0.6974	0.7142	0.7035	0.7164
γ_{Ad}	2.625	2.304	2.55	2.43	2.526
E_1(kcal/g)	1.319	1.473	1.27	-	-
Q_1(kcal/g)	1.112	1.175	(1.018)	1.111	1.108
E_r(kcal/mole TNT)	38.04	41.49	-	-	-
$u^*=1-a^*=1-V/V_e$	0.2758	0.3026	0.286	0.2965	0.2836
Product Composition (moles/mole TNT)					
j=1 Graphite	2.8665	3.2480	-	3.104	3.807
2 CO	1.8858	1.1924	-	1.286	1.9978
3 CO_2	1.5646	1.8768	-	1.889	1.0731
4 CH_4	0.6831	0.6828	-	0.721	0.0122
5 H_2	0.1488	0.0805	-	0.122	0.0400
6 N_2	(1.5000)	(1.5000)	-	(1.500)	1.4997
7 H_2O	0.9850	1.0539	-	0.937	1.8555
total gas	6.7673	6.3865	-	6.453	6.9492

( ) - assumed or invariant values

(a) - calculated here

(b) - original calculations of Jones and Miller[7.2].

Table 7.1B

Calculated Properties and Composition at the (CJ) Detonation Front

(1.5 g/cc loading density; $D_\infty = 6622$ m/sec)

Item	(a) HM	(a) JM	[7.5] J. Taylor
D_{calc}(m/sec)	6557	6587	6480
p(kbar)	143.6	169.6	111
T(°K)	3594	3359	3870
v_1(cc/g)	0.5182	0.4930	0.55
γ_{Ad}	3.491	2.838	-
E_1(kcal/g)	1.517	1.625	-
Q_1(kcal/g)	1.262	1.274	1.295
E_r(kcal/mole TNT)	62.10	108.0	-
$u^*=1-a^*=1-V/V_e$	0.2227	0.2605	0.3666
Product Composition (moles/mole TNT)			
j=1 Graphite	3.8048	3.8921	4.88
2 CO	0.2336	0.1065	0.68
3 CO_2	2.3010	2.3508	1.43
4 CH_4	0.6605	0.6506	(0.00)
5 H_2	0.0146	0.0069	0.023
6 N_2	(1.5000)	(1.5000)	(1.50)
7 H_2O	1.1644	1.1918	2.48
total gas	5.8741	5.8067	6.11

( ) - assumed or invariant values

(a) - calculated here

Table 7.2

Composition in Adiabatic Expansion (moles/mole TNT)

T °K/1000	Gas a	b	c	Carbon a	b	c	CO a	b	c
3.7	6.46	-	-	3.17	-	-	134	-	-
3.6	6.56	-	5.87	3.07	-	3.80	1.51	-	0.233
3.5	6.65	-	5.93	2.98	-	3.75	1.68	-	0.336
3.4	6.75	6.85	5.94	2.89	2.79	3.74	1.85	2.03	0.362
3.3	6.85	6.94	5.99	2.79	2.70	3.70	2.04	2.19	0.457
3.2	6.95	7.04	6.03	2.70	2.61	3.67	2.21	2.37	0.516
3.1	7.06	7.14	6.07	2.61	2.52	3.63	2.39	2.53	0.597
3.0	7.16	7.24	6.12	2.51	2.43	3.59	2.56	2.70	0.694
2.8	7.36	7.43	6.27	2.35	2.27	3.46	2.88	3.02	0.950
2.6	7.55	7.63	6.45	2.20	2.13	3.30	3.18	3.31	1.27
2.4	7.72	7.80	6.62	2.09	2.02	3.16	3.42	3.55	1.56
2.2	7.87	7.95	6.80	2.03	1.96	3.01	3.60	3.72	1.86
2.0	7.97	8.05	7.00	2.03	1.957	2.91	3.68	3.80	2.10
1.8	7.80	8.09	7.10	2.11	2.04	2.87	3.62	3.76	2.25
1.6	7.93	8.02	7.16	2.30	2.22	2.93	3.40	3.54	2.25

Table 7.2 (Continued)

T °K/1000	CO_2 a	b	c	H_2O a	b	c
3.7	1.81	-	-	1.04	-	-
3.6	1.73	-	2.301	1.03	-	1.16
3.5	1.65	-	2.25	1.01	-	1.16
3.4	1.58	1.50	2.24	0.993	0.970	1.16
3.3	1.49	1.42	2.19	0.974	0.953	1.16
3.2	1.42	1.35	2.16	0.956	0.933	1.16
3.1	1.34	1.27	2.12	0.936	0.913	1.16
3.0	1.26	1.20	2.08	0.915	0.893	1.16
2.8	1.12	1.07	1.95	0.873	0.850	1.14
2.6	0.995	0.943	1.80	0.830	0.807	1.12
2.4	0.893	0.843	1.67	0.790	0.765	1.10
2.2	0.822	0.772	1.54	0.757	0.730	1.07
2.0	0.792	0.743	1.43	0.738	0.709	1.04
1.8	0.818	0.763	1.36	0.740	0.709	1.02
1.6	0.917	0.863	1.36	0.770	0.736	1.02

a - 5-constant JM formula; 1.0 g/cc loading density
b - HM equation of state; 1.0 g/cc loading density
c - HM equation of state; 1.5 g/cc loading density

Table 7.3.1

Detonation Product Properties in Adiabatic Expansion

T	p(kbar)			v_1(cc/g)		
°K/1000	a	b	c	a	b	c
3.7	75.80	-	-	0.7228	-	-
3.6	68.73	-	-	0.7536	-	-
3.4	56.33	57.80	115.5	0.8169	0.7467	0.5508
3.2	45.76	46.89	90.90	0.8856	0.8063	0.5906
3.0	36.60	37.29	70.57	0.9619	0.8780	0.6376
2.8	28.62	28.87	53.94	1.049	0.9673	0.6954
2.6	21.68	21.56	39.71	1.154	1.083	0.7714
2.4	15.78	15.32	28.87	1.288	1.242	0.8616
2.2	10.73	10.13	19.86	1.479	1.479	0.9870
2.0	6.664	6.127	12.63	1.789	1.868	1.174
1.8	3.612	3.236	7.097	2.389	2.613	1.496
1.6	1.590	1.397	3.275	3.855	4.392	2.191
1.4	0.5728	0.5156	1.245	7.906	8.936	3.915
1.2	0.2358	0.2437	0.5498	15.46	15.38	6.737
1.0	0.0855	0.1038	0.2184	34.34	29.06	13.05
0.8	0.0260	0.0382	0.0746	88.74	61.82	29.13
0.6	0.0061	0.0112	0.0203	280.7	155.7	78.42
0.4	0.00093	0.0022	0.0037	1231	525.6	286.9
0.3	0.00026	0.00072	0.0011	3280	1212	691.9

a - 5-constant JM formula; 1.0 g/cc loading density
b - HM equation of state; 1.0 g/cc loading density
c - HM equation of state; 1.5 g/cc loading density

Table 7.3.2

Detonation Product Properties in Adiabatic Expansion

T	γ			E_1(kcal/g)		
°K/1000	a	b	c	a	b	c
3.7	2.341	-	-	1.412	-	-
3.6	2.390	-	-	1.343	-	-
3.4	2.506	2.608	3.276	1.216	1.272	1.396
3.2	2.635	2.578	3.111	1.099	1.164	1.273
3.0	2.766	2.550	2.985	0.9914	1.058	1.154
2.8	2.874	2.515	2.874	0.8920	0.9558	1.040
2.6	2.923	2.460	2.781	0.7999	0.8570	0.9236
2.4	2.869	2.369	2.704	0.7158	0.6720	0.8196
2.2	2.673	2.223	2.606	0.6367	0.6707	0.7183
2.0	2.338	2.016	2.451	0.5630	0.5858	0.6221
1.8	1.928	1.756	2.194	0.4940	0.5069	0.5318
1.6	1.550	1.490	1.830	0.4285	0.4342	0.4487
1.4	1.368	1.410	1.585	0.3646	-	-
1.2	1.293	1.359	1.445	0.3001	-	-
1.0	1.261	1.332	1.363	0.2382	-	-
0.8	1.255	1.325	1.325	0.1798	-	-
0.6	1.270	1.335	1.321	0.1258	-	-
0.4	1.306	1.360	1.344	0.0777	-	-
0.3	1.327	1.370	1.356	0.0561	-	-

a - 5-constant JM formula; 1.0 g/cc loading density
b - HM equation of state; 1.0 g/cc loading density
c - HM equation of state; 1.5 g/cc loading density

Table 7.4A

Spherical Taylor Wave for 1.0 g/cc TNT Loading Density Using the HM Equation of State

$10^4 r^*$	$10^4 u^*$	p	T	v_1	γ
-	-	kbar	°K	cc/g	-
10000	2758	62.88	3488	0.7242	2.626
9996	2665	60.75	3453	0.7333	2.617
9974	2535	57.80	3403	0.7461	2.608
9877	2285	52.17	3303	0.7751	2.592
9706	2045	46.89	3203	0.8063	2.578
9459	1812	41.94	3103	0.8405	2.564
9132	1582	37.29	3003	0.8780	2.550
8721	1352	32.94	2903	0.9201	2.534
7620	881	25.08	2703	1.021	2.491
6903	632	21.56	2603	1.083	2.460
5914	334	17.96	2491	1.164	2.415
5236	158	16.16	2432	1.215	2.385
4756	55	15.23	2399	1.245	2.367

Table 7.4B

(As above - but for 1.5 g/cc TNT Loading Density)

10000	2227	143.6	3594	0.5182	3.491
9993	2135	137.7	3559	0.5240	3.452
9958	2013	129.9	3509	0.5337	3.347
9896	1898	122.5	3459	0.5420	3.314
9810	1786	115.4	3409	0.5508	3.276
9564	1577	102.6	3309	0.5703	3.177
9225	1378	90.90	3209	0.5906	3.111
8798	1185	80.24	3109	0.6130	3.046
8290	996	70.57	3009	0.6376	2.985
7707	810	61.83	2909	0.6647	2.929
7053	623	53.94	2809	0.6954	2.874
6324	433	46.85	2709	0.7292	2.827
5378	208	39.71	2597	0.7714	2.781
4220	1	34.36	2505	0.8107	2.745

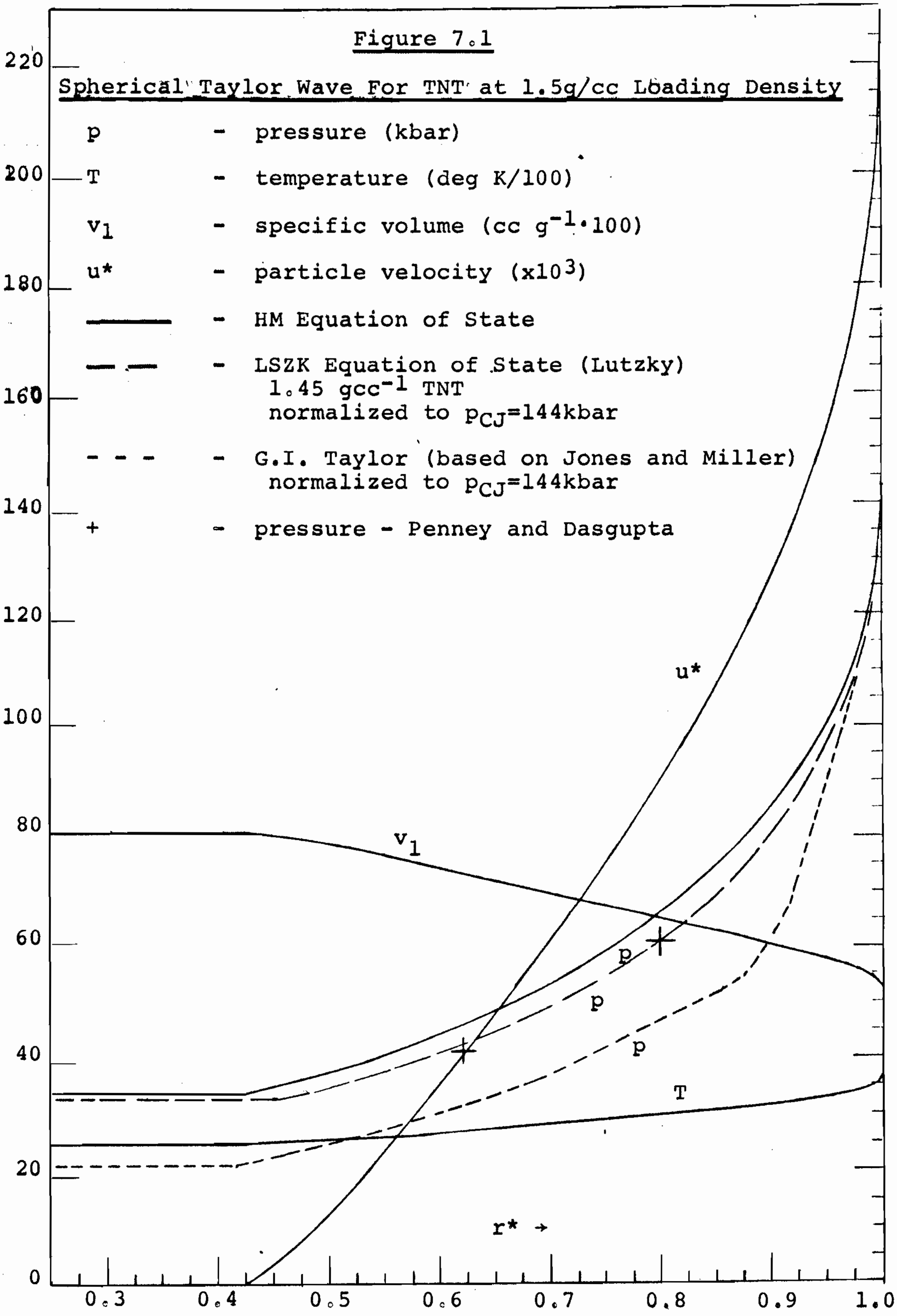

Figure 7.1

Spherical Taylor Wave For TNT at 1.5g/cc Loading Density

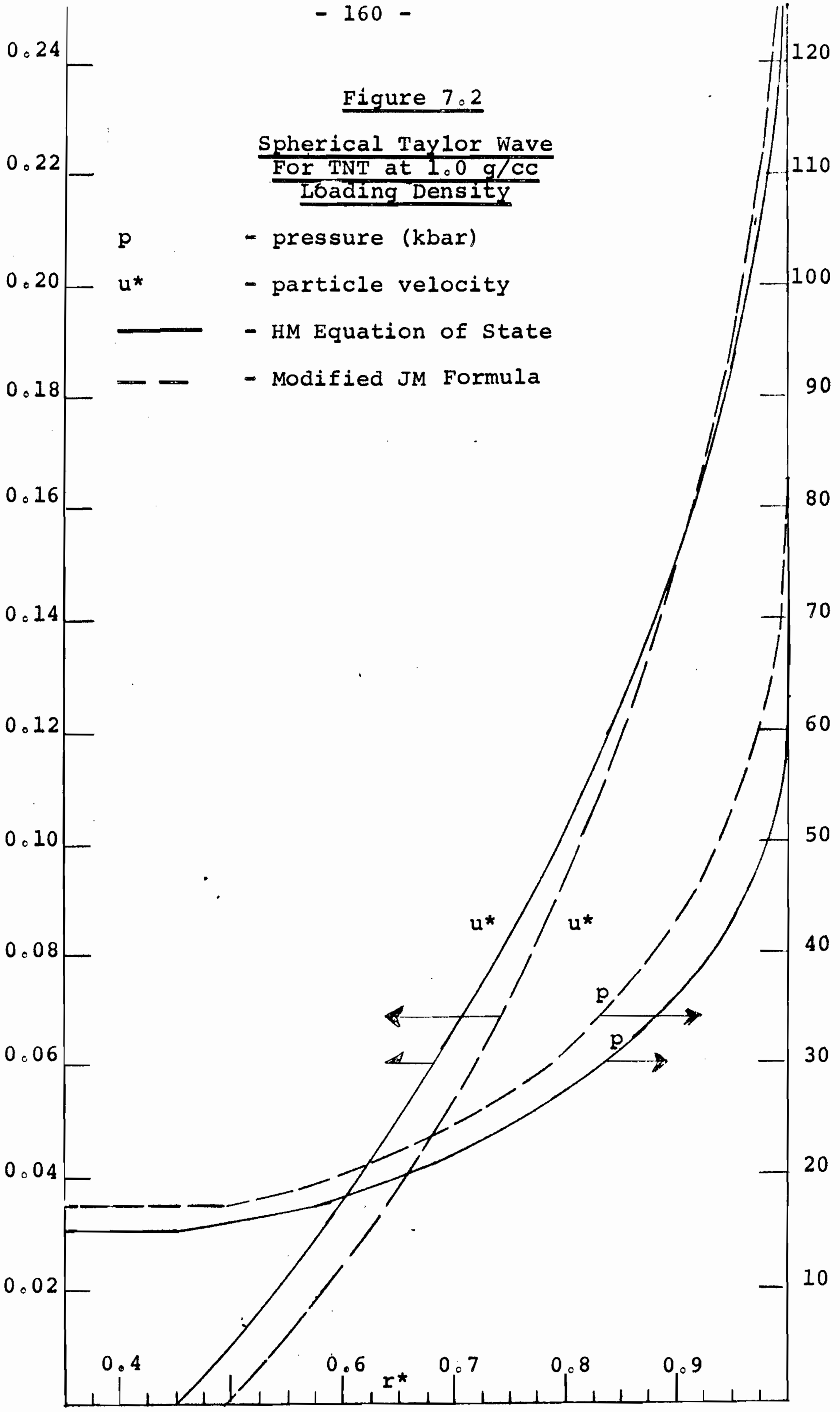

Figure 7.2

Spherical Taylor Wave
For TNT at 1.0 g/cc
Loading Density

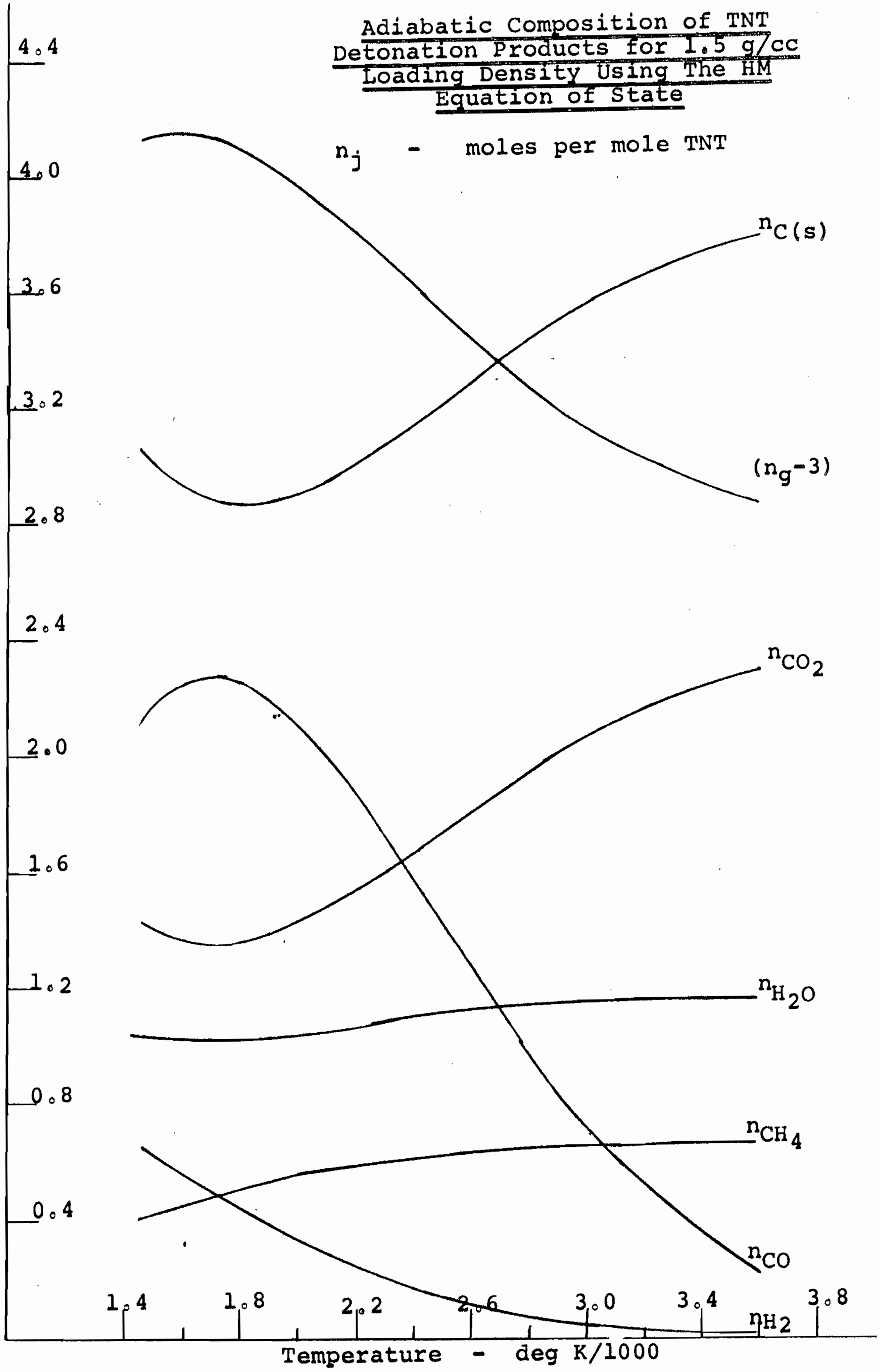

Figure 7.3

Adiabatic Composition of TNT Detonation Products for 1.5 g/cc Loading Density Using The HM Equation of State

n_j - moles per mole TNT

Figure 7.4

Adiabatic Composition of TNT Detonation Products For 1.0 g/cc Loading Density Using the Modified JM Formula