Accurate Determination of Pair Potentials for a $C_w H_x N_y O_z$ System of Molecules: a Semiempirical Method

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March 1995

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Accurate determination of pair potentials for a $C_wH_xN_yO_z$ system of molecules: a semiempirical method

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ABSTRACT

Statistical mechanical chemical equilibrium calculations of the properties of high-pressure high-temperature reactive C, H, N, O mixtures are made to derive an accurate self-consistent set of inter molecular potentials for the product molecules. Our previous theoretical efforts to predict such properties relied in part on Corresponding States theory and shock wave data of argon. More recent high-pressure Hugoniot measurements on a number of elements and molecules allow more accurate determination of the potentials of these materials, and explicit inclusion of additional dissociation products. The present discussion briefly reviews the previous analysis and the method used to produce a self-consistent set of potentials from shock data on N_2 , O_2 , H_2 , NO , an $N_2 + O_2$ mixture, carbon, CO_2 , and CO , as well as some simple explosive product mixtures from detonation of hexanitrobenzene, PETN, and a mixture of hydrazine nitrate, hydrazine and water. The results are tested using the data from an HMX explosive formulations. The effect of the non-equilibrium nature of carbon clusters is estimated using data for TNT as a standard to determine a non equilibrium equation of state for carbon. The resulting parameter set is used in a survey of 27 explosives. For the subset that contains no fluorine or two-phase carbon effects the rms deviation from experimental detonation velocity is 1.2%.

I. INTRODUCTION

High speed laser drilling and cutting of polymers, catastrophic propellant ignition, and detonation of explosives produce high-pressure (P) and high temperature (T) mixtures of C,H,N,O compounds. These materials are also important in the study of planetary atmospheres. Theoretical prediction of the P,V,T (V =volume) properties of such reactive mixtures requires a large number

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P,V,T (V=volume) properties of such reactive mixtures requires a large number of accurate interaction potentials. The determination of such potentials in turn requires a study of like- and unlike-pair interactions among a number of reactive molecules. There are more unlike molecular pair interactions than like-pair interactions in such product mixtures. Nevertheless, information on unlike-pair interactions is mostly unavailable at present. Earlier analysis used an approximation known as the Lorentz-Berthelot rule,¹ which is still being used, to circumvent this lack of information. On the other hand, additional shock wave data of N₂, O₂, NO, N₂+O₂ mixtures, liquid air, CO, and CO₂ have recently become available. These data indicate that the molecular species will dissociate behind strong shock waves and that the use of the Lorentz-Berthelot rule cannot satisfactorily describe the shock wave data.

Earlier analyses used shock wave data on pure components only, assumed no dissociation, and used the Lorentz-Berthelot rule. The present approach includes shock data of all relevant detonation products and carries out the analyses in a cyclical self-consistent manner to obtain a set of potential parameters that is useful for all related product mixtures. Here we give an overview of all pertinent gas-phase products of the above mentioned molecules. In addition we include a study of interactions between CO₂ and N₂, H₂O and N₂, and CO₂ and H₂O using, respectively, the detonation properties of hexanitrobenzene (HNB), a mixture of hydrazine, hydrazinenitrate and water (RX23-AB), and pentaerythritol tetranitrate (PETN).

The present work explicitly includes melting and electronic degrees of freedom in a three-phase equation of state for carbon, while our previous analyses used only Murnahan forms for graphite and diamond.¹ Liquid carbon is here predicted when CO and CO₂ molecules are strongly shock-compressed and heated. The importance of including liquid carbon is illustrated by the fact that it explains a previous theoretical discrepancy in matching experimental Hugoniot data of liquid CO and CO₂.

II. THEORY

A One-Component Systems

The original equilibrium thermodynamics of one-component systems is due to van der Waals who more than one hundred years ago realized that the stiff repulsive portion, rather than the long-range attractive portion, of an intermolecular potential controls thermodynamics and structural properties of condensed phases. The development of this concept into the variational theory (VAR) used in the CHEQ code¹ and the perturbation theory (PT) has been discussed by one of us². A schematic representation of how the potential is split into the two parts, one important for high pressures and condensed phase changes, and the other a long range weak perturbation section, is indicated in Fig. 1. The process of formulating this idea into a mathematically rigorous framework in the P,T plane can be considered to include five principal parts.

Fig. 1. Schematic illustration of the van der Waals potential model

They are:

- (a) an optimum way to break an intermolecular potential, $\phi(r)$, into a hard-sphere-like interaction, $\phi_0(r)$, and a perturbation term, $W(r)$,

$$\phi(r) = \phi_0(r) + W(r) \quad (1)$$

- (b) a specific expression for $\phi_0(r)$ and

$$W(r),$$

- (c) an expression for the Helmholtz free energy A ,

$$A = A_0 + A_1, \quad (2)$$

in terms of the Helmholtz free energy (A_0) for the reference system and another (A_1) for the perturbation potential,

- (d) an expression for the hard-sphere (HS) diameter to represent the reference potential,
- (e) convenient expressions for the HS equation of state (EOS) and radial distribution function $g^{HS}(r)$.

The intermolecular potentials used for the gas-phase components are of the exponential repulsive and inverse sixth power attractive form,

$$\phi = \frac{\epsilon}{\alpha-6} \{ 6 \exp[\alpha(1 - r/r^*)] - \alpha(r^*/r)^6 \} \quad (3)$$

This so called (exp-6) potential which has been the preferred form for high pressure work for some time.³ For most systems we use a constant ϵ . A more general form of ϵ is

$$\epsilon_{ii} = \epsilon'_{ii} (1 + \lambda/T), \quad (4)$$

with $\lambda_{ii} \neq 0$ for polar molecules. The reason is the decreased accuracy of the spherically symmetric potential at low temperatures, where dipole-dipole alignment becomes a factor. The definition of the three potential parameters is indicated in Fig. 1.

Specific expressions needed for items (a) - (e) are available for classical fluids.^{2,4} One approach is to use our perturbation theory² (PT) which extends earlier theories of Weeks, Chandler, and, Anderson (WCA) theory to high pressure. The CHEQ code, used here, employs the variational theory (VAR) of Mansoori and Canfield, and of Rasaiah and Stell, as modified by Ross,⁴ (MCRSR theory) for high pressure work.

TABLE I: Comparison of the model and Monte Carlo calculations for the exp-6 potential with $\alpha = 13.5$ (ref. 2)

kT/ϵ	$\rho r^{*3}/\sqrt{2}$	PV/NkT MC	PV/NkT PT
20	0.9	3.27	3.27
"	1.0	3.81	3.80
"	1.5	8.08	8.04
"	2.05	16.58	16.65

Both give about equally reliable results. As an example, Table 1 compares PV/NkT (where P = pressure, V = volume, T = temperature; $\rho = N/V$) for PT and Monte Carlo (MC) simulations with an exponential-6 (exp-6) potential.

Parameters, α , ϵ , and r^* are specific to each chemical species and can be obtained from experimental data. It is noteworthy that the PT is about equally reliable as the MC results (within MC's statistical errors). Yet, its computational time is several orders of magnitude less than that required for MC calculations.

B. Mixtures

Compared to like-pair potentials described above, the exp-6 parameters for unlike-pairs are experimentally less well known. But they can be expressed as

$$\begin{aligned}\epsilon_{ij} &= k_{ij} \sqrt{\epsilon_{ii} \epsilon_{jj}} \quad , \\ r_{ij}^* &= \ell_{ij} (r_{ii}^* + r_{jj}^*)/2 \quad , \\ \alpha_{ij} &= m_{ij} \sqrt{\alpha_{ii} \alpha_{jj}} \quad ,\end{aligned}\tag{5}$$

in terms of like-pair parameters (r_{ii}^* , ϵ_{ii} , α_{ii}) and small multiplicative constants (k_{ij} , ℓ_{ij} , m_{ij}) which can be fixed if appropriate theoretical or experimental data are available. Otherwise, we set $k_{ij} = \ell_{ij} = m_{ij} = 1$, commonly referred to as the Lorentz-Berthelot rule.

We assume that mixtures of chemical species interacting with exp-6 potentials [Eqs. (3) and (5)] can be represented by a *hypothetical one-component* system with exp-6 parameters that are composition (x_i) weighted averages of the parameters of the component pair potentials, as follows:

$$\begin{aligned}(r^*)^3 &= \sum x_i x_j (r_{ij}^*)^3, \\ \epsilon &= \sum x_i x_j \epsilon_{ij} (r_{ij}^* / r^*)^3, \\ \alpha &= \sum x_i x_j \alpha_{ij} \frac{\epsilon_{ij} (r_{ij}^*)^3}{\epsilon (r^*)^3}.\end{aligned}\tag{6}$$

The connection between the statistical mechanical theories discussed above (including interaction potentials $\phi_{ij}(r)$) and $G(P, T, \{n_i\})$ occurs strictly through the chemical potentials μ_i . When chemical equilibrium is established between the molecules in the mixture, their concentrations $\{n_i\}$ will only change with T and P ,

and can, therefore, be determined by minimizing the Gibbs free energy $G(P, T, \{n_i\})$,

$$G(P, T, \{n_i\}) = \sum_i n_i \mu_i, \quad (7)$$

with respect to $\{n_i\}$. The minimization is done within the chemical equilibrium code CHEQ^{1,4} which also evaluates μ_i using the variational theory and the effective one-component mixture model.

The fact that one-component calculations are much simpler than mixture calculations provides a reasonable justification for using this so-called improved van der Waals one-fluid (1fvdW) model. In fact, comparisons with two-component MC for He-H₂ mixtures⁵ in Table II shows that the effective one-component model (using VAR) produces excellent results at high pressure and temperature.

TABLE II. Effective one-component (1fvdW) theory parameters and comparisons of the resulting pressure of an equimolar mixture of H₂ and He with the exact Monte Carlo results. (Ref. 5)

T (K)	V (cm ³ /mol)	P(MC) (GPa)	P(1fvdW) (GPa)
50	20	0.047 ± 0.01	0.05
100	14	0.338 ± 0.03	0.35
300	10	1.856 ± 0.02	1.91
4000	8	12.43 ± 0.02	12.6
7000	4.5	54 ± 1	55.3

C. Condensed Systems

Solids or liquids have been modeled by Murnaghan forms.¹ These are adequate as long as the amount of the material is small and has a simple single phase EOS. The reactive product mixtures of organic material are rich in carbon and sensitive to its EOS. In addition, carbon exists in at least three phases - graphitic, diamond-like and liquid- all of which occur in strong shock waves. A three phase EOS was therefore developed⁶ to describe these phases. The chemical potential

$$\mu_i(P,T) = \mu_i^0 + \int_{1\text{atm}}^P V_i(P,T) dP, \quad (8)$$

for the three phases are then used with those of the gas-phase species in Eq. (7) to determine the stable phase.

III. COMPARISONS WITH EXPERIMENT

The effective spherical exp-6 potential is determined by the available experimental data of simple systems. For high-pressure work these are primarily shock wave (Hugoniot) data of elements and di- or tri-atomic compounds. Conservation of mass momentum and energy across a steady shock front,⁷ that changes the material from state i to $i+1$, gives the internal energy, E_H , as

$$E_{H,i+1} = E_{H,i} + \frac{1}{2} (P_{H,i+1} + P_{H,i}) (V_{i+1} - V_i), \quad (9)$$

while conservation of mass and momentum allow us to write the conventional variables of shock pressure (P_H) and volume (V) in terms of the wave velocity (U_S) and the particle velocity (U_p) behind the wave relative to the particle velocity in front of the wave.

$$P_{H,i+1} = P_{H,i} + \rho_1 (U_{S,i+1} - U_{p,i}) (U_{p,i+1} - U_{p,i}) \quad (10)$$

$$V_{i+1} = V_i \left(1 - \frac{U_{p,i+1} - U_{p,i}}{U_{S,i+1} - U_{p,i}} \right). \quad (11)$$

The velocities are in the laboratory based system of coordinates and subscripts i and $i+1$ indicate that the equations apply to any of the shocks in a multiple shock event. In the case of single shock events subscript 0 is normally used for the initial state and $U_{p,0} = 0$.

Corresponding states theory has been a useful first-order means of estimating the potentials for a number of molecules, as long as the experimental data base was limited. That work showed that the products of CHNO compounds - the molecular products of polymers and explosives are H_2 , N_2 , H_2O , CO_2 , CO , NH_3 , CH_4 , and condensed carbon with generally smaller amounts of O_2 , O_3 , and NO_x , depending on composition and temperature.

While some detonation velocities were well predicted by the original theory, a recent survey of 17 explosives⁸ showed that, deviations from experiment were as high as 6%, when the original set of potentials is used. Furthermore, high pressure work on nitrogen⁹ showed the need for including atomic nitrogen.

The current effort is an outcome of that work and the effect it had on the accuracy of the EOS of other mixtures. For example, the detonation velocity of an LX-14 explosive, a mixture of HMX (with composition $C_4H_8N_8O_8$) and 4.5% Estane binder, increased by 3.3% as a consequence of improvements in the EOS of carbon and the potentials used to compute N_2 and CO_2 Hugoniot.¹⁰ That quantity should be predictable to within 0.5% by the mixture theory.

In principle, a large number of intermolecular potentials are needed for high pressure and temperature mixture analyses. Fortunately, a significant amount of new data is available to guide the effort. The unlike pair-interactions involving dissociation products of N and N_2 , for example, can be derived by means of the aforementioned statistical mechanical theory of mixtures and recent shock wave data of N_2 . Similarly O and O_2 interactions are defined by the shock data on O_2 . Somewhat more complex is the study of CO and CO_2 , which requires 10 $[(n^2+n)/2]$ interaction potentials among its ($n=$) 4 reactant and product molecules. These interactions involve single elements (O-O, O_2 - O_2 , O_2 -O), unlike-element molecule-molecule interactions (CO-CO, CO_2 - CO_2 , CO_2 -O, O_2 -CO, CO_2 -CO), and - molecule-atom interactions (CO-O, CO_2 -O). In addition, there will be condensed carbon in a graphite, diamond, or liquid phase. One of these three phases of carbon is selected in the minimization process involving Eqs. (7) and (8).

NO and its 7 reaction products, N, O, N_2 , O_2 , O_3 , NO_2 , and N_2O , have a larger number of interactions (28) between them. The problem is somewhat simplified by the fact that a number of components are generally present in minor amounts and need not have their potentials refined to the same degree as the major components. We deal with the simplest systems and proceed to more complex ones. What follows is the detailed discussion relating to each data set used.

A. N₂ and O₂

Both these molecules dissociate under shock compression, a factor that increases the compressibility along the Hugoniot, but the compressibility profile for O₂ appears to be different from that shown by N₂. The amount of ionization in this pressure regime is uncertain. Oxygen has an optical band gap¹¹ above 1 eV up to 37 GPa. Its conductivity¹² reaches 100 $\Omega^{-1} \text{ cm}^{-1}$ at 45 GPa. Extrapolation of this data could place the system in the metallic regime at 90 GPa. The Hugoniot data, however, show no additional increase in compressibility that could be assigned to a significant free electron concentration.

The experimental Hugoniots of oxygen appear to be smooth within the accuracy of the data.¹²⁻¹⁴ Figure 2a shows the single shock Hugoniot of liquid oxygen. Two theoretical curves are shown: one computed with the best potential assuming no dissociation and another which includes dissociation. Dissociation increases smoothly from 1% at 27 GPa to 40% at 90 GPa along the single shock Hugoniot, while the temperature rises from 3900° to 11,700° K. This dissociation causes a simple reduction in curvature of the Hugoniot without inflections. The reflected shock data and theory (see Fig 2b) are also in good agreement. In this case the highest temperature is only 8386 K (at P= 141 GPa), resulting in 25 % dissociation. Any deviations from the computed curves can be ascribed to random experimental error.

Nitrogen has been studied extensively by several investigators.^{11,14-16} The single shock Hugoniot data are shown in Fig. 2c. Zubarev's data¹¹ are the average of 4 to 12 experimental points and have been weighted heavily in this study. The two-stage-gun data near 26 GPa of Nellis et al^{14,15} have a similar accuracy. But at higher pressures the accuracy decreases. Some representative data points of Dick¹⁶ are also plotted in Fig 2c. His reported uncertainties are derived from the uncertainty in the timing of the probes that are used to determine the shock speeds in the sample and reference material for each experiment. This does not include the effect of pressure nonuniformity and shock flatness in these essentially one dimensional experiments. It is here assumed that those effects double the uncertainty reported. This assumption makes the individual pressure and volume uncertainties more consistent with the deviations of Dick's data points from the smoothed fit to the data. The initial sample density of Dick is

FIG. 2. Oxygen and nitrogen Hugoniots (see text for details): a. O_2 - single shock; ● ■ experiments; solid and dashed curves, theory (initial conditions: $E_0 = -13.85$ kJ/mole, $\rho_0 = 1.203$ g/cm³, $P_0 = 0.2$ MPa). b. O_2 refl - single and double shocks, solid and dashed curves from theory, experimental, points as shown in frame; c. N_2 single shock experiment and theory as labeled ($E_0 = -12.45$ kJ/mole, $\rho_0 = 0.8075$ g/cm³, $P_0 = 0.2$ MPa); d. N_2 refl - single and double shock curves from initial points shown as ■.

slightly higher than the initial density of Zubarev's and Nellis' samples (0.820 vs. 0.808 g/cm³). Here we have made the simplifying assumption that the relative compression is insensitive to initial density [i.e. $(\rho/\rho_0)_P \approx \text{const.}$] over this range and used the same $\rho_0 = 0.808 \text{ g/cm}^3$ for the graphical comparison in Fig. 2c. This approximation is well within the uncertainty of the data.

Several comparable fits, shown in Fig. 2c, illustrate the sensitivity to the potential parameters. Curves a and b are obtained with potential parameters that are close to those originally derived with a corresponding states argument from data on shock compressed liquid argon.¹⁷ At high pressure curve a offers a slight advantage. Both curves tend to be low at low pressure, and comparison with Zubarev's lowest points favors curve c. Note that in c we have changed the curvature (or $\partial \ln P_H / \partial V$) of the Hugoniot by using a small α and r^* , compensated by a larger ϵ . The data of Dick suggest the possibility of a weak first- or second-order phase change at 15 GPa, as indicated by an abrupt change of slope and curvature at that point (not shown here). If this change in slope is real, than even at these high temperatures none of the spherical potentials in Fig. 2c may be the best approximation of the N₂-N₂ potential. The choice of a larger ϵ than expected from corresponding states also affects the theoretical sublimation energy and increases the temperature of the Hugoniot. The temperature plot discussed below shows this effect.

At 45 GPa the experimental data in Fig. 2c indicate a more abrupt change to the dissociated high pressure phase than predicted by the current model. This sudden change in modulus suggests non random (liquid) structure and, therefore, an atomic packing that is more complex than a simple randomized (liquid) version of the proposed simple cubic¹⁸ atomic solid, even at this high a temperature (10,000 K at ~50 GPa). Polymeric structures have been proposed and could cause this effect. These are predicted for pure N₂¹⁹ and may not be significant in mixtures where these potentials will be useful.

In addition the apparent abruptness of the change in compressibility shown by experiment could be a kinetic effect. Transfer of energy from the translational and rotational degrees of freedom to the reaction coordinate may be sufficiently slow below 45 GPa to affect the shock front in these experiments.

Associated shock-temperature effects in Fig. 3 are peculiar to this molecule. Sufficient energy is absorbed in the transformation to decrease the temperature of a second shock below that of the first. This unusual shock cooling is also represented by this model. If one considers data between 26 and 45 GPa to be in a metastable diatomic state, the computed second shock temperatures are as shown. These temperatures are also consistent with those discussed before by one of us.⁹ The data are from Nellis¹⁵ and Voskobolnikov.²⁰ It may be noted that the low-pressure temperature is closer to that of a nonreactive molecule, while at higher pressure the reflected shock induces dissociation leading to a decrease in temperature.

Fig. 3. First and second shock temperatures of N_2 . Curves as labeled refer to Fig. 2 potentials. Long arrows cover the T and P difference between the first shock state and the experimental second shock state. Theoretical second shock states from the same first shock ($\blacksquare$) states are indicated by ($\blacktriangle$ — $\blacktriangle$) and ($\blacklozenge$ — $\blacklozenge$) for the strong and weak shocks resp.

B. CO and CO₂

This pair of molecules has the same products : CO, CO₂, O₂, O, and condensed carbon for a total of 10 gas-phase interaction potentials. CO₂ as the most stable molecule offers the simplest composition sequence along its Hugoniot. In Fig. 4a we show three different curves. The non-reactive theoretical curve uses only the CO₂-CO₂ interaction, and is the one used originally to fit the solid CO₂ Hugoniot of Zubarev.¹¹ The more recent liquid CO₂ data^{21,22} offer a better picture of the high temperature behavior of this system.

Two possible potentials are given, with ϕ_a offering a somewhat better fit at low pressures. At even lower pressure²³ ($T, \rho, P_{\text{exp}} = 1270 \text{ K}, 0.4305 \text{ g/cm}^3, 0.14 \text{ GPa}$), fits a and b are below the experimental pressure by 2.5 and 3.5% respectively, with the deviation decreasing as the pressure drops and the gas becomes more ideal. Both fits are shown as an indication of the sensitivity to the reaction products. The composition change in Fig. 4b shows that both oxygen atoms and liquid carbon become important at high pressure, as both CO₂ and CO dissociate. The results therefore depend both on CO₂ as well as that of O and the EOS of liquid carbon. The latter has some uncertainty associated with the fact that carbon precipitation is slow. Its non equilibrium EOS is under study. With the present form of the carbon EOS the value $\epsilon_{ij} = 0.905$ for the O-CO₂ interaction is preferred, as indicated in Fig 4a.

In contrast to CO₂, the equilibrium CO Hugoniot contains carbon at even very low pressures (Fig. 4c). This theory shows it to be a weak explosive. In reality, it is stable as a consequence of its activation energy for reaction. Two low pressure data points of Nellis et al,²¹ in Fig. 4d, fit calculation if no products are allowed. This indicates that, below 10 GPa and on this time scale, CO does not react to form CO₂ and carbon. The higher pressure data are more consistent with reactive mixture calculations.

Three different carbon equations of state are presented. Using the most recent carbon EOS⁶ and the above value of ϵ_{ij} for $\phi_{\text{CO}_2\text{-O}}$ the calculation agrees with the two highest data points. The curvatures of the theory and experiment do not allow a complete match with the data using the current carbon EOS, suggesting the need for a model of non-equilibrium carbon clusters.

Fig. 4. a. Single shock Hugoniots of CO_2 - experimental data (points) and theoretical curves (with $E_0 = -408.9$ kJ/mole, $\rho_0 = 1.173$ g/cm³ and, $P_0 = 0.1$ MPa), see text for details. b. compositions of CO_2 products behind the shocks. c. Single shock Hugoniots of CO ($E_0 = -123.4$ kJ/mole, $\rho_0 = 0.8068$ g/cm³, and $P_0 = 2$ MPa), and d. composition vs. pressure along the Hugoniot.

The results indicate the sensitivity to the location of the graphite-diamond and melting phase lines. In the calculation of the 'Equil-a' curve the transformations occurred at approximately the same pressure. In calculations with the present carbon model, curve 'Equil-b', the separation between the two transformations on the Hugoniot locus is larger. The liquid phase was not present in the calculation that produced the dashed curve, therefore, only the graphite-diamond transition shows up. The difference in temperature computed with and without the liquid phase also indicates the importance of the effect of the additional entropy of melting. We may expect that portion of the oxygen in the gas-phase is in fact trapped chemically on the carbon phase, a feature not included in the present calculations, perhaps accounting for the deviation from the three intermediate pressure points between 25 and 50 GPa.

C. Water

With a heat of formation [$\Delta H^f(298\text{ K})$] = -242 kJ/mole at 1 atm.] and with its small size, water is perhaps the most stable material under shock compression. At 90 GPa and 7000 K only 0.2% of the material is dissociated. It is also an important product of energetic materials. The description in terms of a spherical exp-6 potential presumes a neutral rapidly rotating molecule. Yet, the tendency of this molecule to form strong polar hydrogen bonds and its apparently high ion concentration at high pressure makes the detailed fluid structure mysterious.

To explain the fast charge transport between electrodes, Eigen²⁴ has argued for extended hydrogen bonded structures with rapid exchange of protons up to about 300 °C, after which there is a sharp drop in conductivity. These extended clusters do not break up sufficiently fast to increase the resistivity with increasing pressure, instead, behind shock waves the conductivity increases²⁵ from the ambient condition of 4.2×10^{-8} mho-cm to saturation at about 20 mho-cm, at 35 GPa shock pressure²⁶ and a temperature of 4000 K. At this temperature kT is the binding energy of the hydrogen bond. The molecule is essentially rotating freely at that temperature.

At the same point the O-H stretching mode of the water behind the shock²⁷ becomes very weak in the Raman spectrum, suggesting a loss of the hydrogen bonding that enhances the polarizability of the molecule and its absorption cross

Fig. 5. a. Single shock data and two theoretical Hugoniot of H₂O (with $E_0 = -282.1$ kJ/mole, $\rho_0 = 0.9982$ g/cm³, and $P_0 = 0.101325$ MPa), obtained with potentials a and b as shown. b. First (S_i) and second shock (R_i) data of H₂O with corresponding theoretical Hugoniot using potential b

section.²⁸ Also, the exchange of protons is thermally enhanced and sustains the conductivity at higher shock pressures, unlike the behavior at ambient conditions where the mobility is reduced by temperature.²⁴

Three sources of water Hugoniot data are presented in Fig. 5. The relatively accurate data of Rice and Walsh²⁹ has been extended by the more recent data of Mitchell and Nellis.²⁶ In addition some data points of Skidmore³⁰ are shown in a region where data from the former are lacking. The theoretical Hugoniot obtained with potential 'a' is refined by potential 'b' that fits the low pressure points better and attempts to improve the fit of a cluster of data points near 40 GPa. Agreement with reflected shock data is also good except for the highest pressure, where the compressibility of the Hugoniot suddenly seems to increase.

The relatively large curvature indicated by the data between 15 and 35 GPa causes the theoretical fit to miss some data points. This has been interpreted as possibly due to a first or second order transition.^{25,30} In Fig. 6 we show the

Fig. 6. Water, single shock pressure vs particle velocity data and fits. See text

variables in which the experimental data were measured (see Eq. (10)). Data in this plane are commonly fitted with straight lines. By contrast, the original data fit of Rice used a more strongly curving fit to match all the data available then. Later data, however, proved this to be a wrong assessment of the true pattern. The reader can convince himself that two straight lines can do a

somewhat better job of fitting the data, even though the data are insufficient to force that conclusion.

We may note here, however, that the region up to 35 GPa corresponds to a molecular fluid that is freeing itself from the constraints of hydrogen bonding as discussed above. Additional accurate data are needed between 15 and 35 GPa to

TABLE III: Exponential-6 coefficients

Material	ϵ_{ii}/k K	r_{ii}^* Å	α_{ii}	λ_{ii} K
H ₂ O _a	356	3.06	13.0	996.0
H ₂ O _b *	300.	3.06	13.1	1290.0
N _{2,a}	101.9	4.09	13.2	0.0
N _{2,b}	101.9	4.15	13.2	0.0
N _{2,c} *	293.0	3.91	11.5	0.0
N _a	600.	2.39	10.0	0.0
N _b *	600.	2.47	10.0	0.0
CO _{2,a} *	245.6	4.28	13.0	0.0
CO _{2,b}	245.6	4.20	13.5	0.0
CO _{2,c}	245.6	4.17	13.5	0.0
CO ₂	245.6	4.17	13.0	0.0
CO	108.3	4.12	13.0	0.0
O ₂	125.0	3.86	13.2	0.0
O	700.0	2.40	11.0	0.0
O ₃	211.0	4.82	13.0	0.0
NO	112.9	3.97	12.2	0.0
NO ₂	348.4	4.27	13.0	0.0
N ₂ O	250.0	4.257	13.0	0.0
H ₂	36.4	3.43	11.1	0.0
NH ₃	474.0	3.44	13.0	441.0
CH ₄	154.1	4.22	13.0	0.0

* These are the constants selected in this work.

g/cm³ by a factor of 1.305. The Chapman-Jouguet temperature is computed to be 2850 K in this work.

Figure 7 gives the equilibrium composition behind shock waves in NO and in a mixture of N₂ and O₂ with a mole ratio of 1. We may note that, at higher shock temperatures and pressures, NO becomes a significant component in these mixtures. It is therefore a significant part of any system containing nitrogen and oxygen, the major components of our atmosphere. In addition to N₂, O₂, N, O, and NO we need to include NO₂ and N₂O in the calculations. In total, this reactive system of 7 molecules requires the specification of 28 interaction potentials. The like-pair interaction potentials used are summarized in Table III and the 'extended Lorensz-Berthelot' constants for the unlike species interaction

determine the proper curvature in this region. Potential 'b' offers the most reasonable representation of the data under the circumstances.

D. NO and N₂+O₂

Under normal conditions NO, like CO, is a metastable molecule that disproportionates readily into N₂ and O₂ under weak shock loading. Liquid NO will detonate³¹ with a detonation pressure of 4.3 GPa, which increases the atmospheric liquid density of $1.28 \pm .005$

TABLE IV: Extended Lorenz-Berthelot coefficients

System	k_{ij}	ϵ_{ij}	m_{ij}
$N_{2,c} - N_b$	1.0	1.0	0.90
$NO - N_b$	1.0	1.0	0.93
$O_2 - O$	1.0	1.0	0.98
$N_{2,c} - NO^*$	1.0	1.0	1.0
$N_{2,c} - O_2$	1.0	1.0	1.04
$O_2 - NO$	1.0	1.0	0.93
$CO_{2,a} - O$	1.0	0.905	1.0
$N_2 - H_2O$	1.0	1.045	1.0
$N_2 - CO_2$	1.0	1.035	1.0
$CO_2 - H_2O^\dagger$	1.0	0.9765	0.90
$CO_2 - H_2O^\ddagger$	1.0	0.983	0.90
$NH_3 - H_2O^{**}$	1.0	0.972?	0.95?

* Used here; for $N_{2,b}$ $\epsilon(N_{2,b}-NO) = 1.03$.

† Assuming ideal equilibrium carbon.

‡ Used with nonideal C to fit TNT data.

** Very uncertain, unused trial numbers.

potentials in Table IV, together with those for the C-O-H-system molecules discussed below.

Figure 7 shows that N_2 and O_2 remain significant components over the whole range shown, but that NO becomes negligible at low pressures and temperatures. The principal cause for the differences observed behind low pressure shocks through NO and N_2+O_2 samples is the temperature, which is higher for NO at moderate shock pressures. This effect and the decrease of the

ratio, $T_{H,NO}/T_{H,N_2+O_2}$, with pressure is illustrated in Table V. The crossovers in temperature and component concentrations for the two systems, near 26 GPa,

Fig. 7. Equilibrium composition of reactive NO (—) and an equimolar mixture of N_2 and O_2 (points) along the Hugoniot

temperature and pressure.

are due to the relatively high compressibility of the $N_2 + O_2$ mixture ($\rho_0 = 0.945 \text{ g/cm}^3$) compared to that of NO (1.28 g/cm^3). The other components (NO_2 , N_2O , O, and N) are a small fraction of the total in this pressure range. Atomic nitrogen will become important at higher pressures, while N_2O and O are also increasing with increasing shock

Fig. 8. a. Single shock data points and theoretical curves for NO showing the effect of changing ℓ (Eqn 5), as indicated in the frame ($E_0 = 79.52$ kJ/mole, $\rho_0 = 1.2645$ g/cm³, $P_0 = 0.3$ MPa). b. Reflected shock data and theory ($\ell = 1.0$) with first shock as listed in frame. c. Single shock data points and theoretical curves for the equimolar N₂ + O₂ mixture, potentials as above ($E_0 = 11.89$ kJ/mole NO, $\rho_0 = 0.946$ g/cm³ and, $P_0 = 0.3$ MPa). d. Reflected shocks for the N₂ + O₂ mixture ($\ell = 1.0$).

TABLE V.: Temperature ratio of NO and N_2+O_2 Hugoniot

P_H	40.0	29.60	20.31	10.32	8.23	6.09	3.09
$T_{NO}(P_H)$	5751	4631	3821	3153	3040	2939	2842
$T_{H,NO}/T_{H,N_2+O_2}$	3.74	2.29	1.82	1.55	1.06	0.885	0.794

Figure 8 shows the single and reflected shock data³² and theoretical calculations for NO and the N_2+O_2 mixture. The NO data are sufficiently precise to indicate that the fit is improved with a value of $\ell_{N_2-NO} = 1.00$, with the $N_{2,c}$ potential selected above. The reflected shock data also show good agreement if $\ell_{N_2-NO} = 1.00$.

E. The H_2O-N_2 interaction (RX-23-AB)

There are a few explosives that produce simple product mixtures. One of these (RX-23-AB) has the nominal weight percent composition:^{33,34} hydrazine/hydrazinenitrate/water = 5.9/70/24.1. This explosive is a good candidate for the study of the nitrogen-water interaction since the explosion products are primarily water (H_2O) and nitrogen (N_2). Table VI shows that N_2 and H_2O remain the principal components over a wide range of overdriven shock pressures. The concentration of N atoms is negligible for normal detonation pressures as are the number of H and O atoms, H_2 and NH_3 molecules. These species are, however, included in the calculations since they have a noticeable effect on the entropy of the system at higher shock pressures.

TABLE VI: Product composition in moles/100g of RX-23-AB; P in GPa

P	H_2O	N_2	O_2	NO	N_2O	NO_2	NH_3	N
10	3.57	1.24	0.018	0.003	0.001	0.003	0.00	0.0
17	3.57	1.24	0.013	0.004	0.004	0.004	0.00	0.0
90	3.51	1.00	0.001	0.012	0.061	0.001	0.04	0.34

Since this work is more than a first order refinement of the EOS, we take a close look at the effect that the uncertainty in the explosive composition has on the EOS of the reaction products. The uncertainty in the exact composition of the undetonated liquid explosive may be inferred from the reported mixture analysis.³³ Computations with the nominal composition and the one derived

from chemical analysis proved to be indistinguishable, showing that composition uncertainty is negligible. However, subsequent to the mixture analysis it was noticed that the hydrazine-nitrate component may have contained as much as 3.88% by weight methanol solvent. The effect of this possible impurity is also addressed below and in Table VII.

TABLE VII: Effect of r_{ij}^* H₂O-N₂ on the theoretical CJ state of RX-23-AB

Source	$\epsilon_{ij}^{(1)}$	$T^{(2)}$ Kelvin	$P_{CJ}^{(2)}$ (GPa)	$D_{CJ}^{(2)}$ (km/s)	[N ₂]/[H ₂ O] in water phase	Methanol [†]
Theory	1.05	2645	17.3	7.464	2.3%	No
"	1.045	2640	17.45	7.492	3.4%	No
"	1.04	2634	17.66	7.531	5.2%	No
"	1.03	2633	18.75	7.635	11.2%	No
"	1.05	2650	17.46	7.498	2.9%	Yes
"	1.04	2648	17.9	7.567	5.8%	Yes
Experiment	—	4000 ⁽³⁾	18.6 ± 0.4	7.48 ± 0.5	—	?

(1) See Eq. (5).

(2) Obtained with the initial, undetonated sample, conditions: $E_0 =$ kJ/Mole, $\rho_0 =$ g/cm³ and, $P_0 = 0.1$ MPa.

(3) The theoretical average T of two other mixtures of hydrazine and hydrazine nitrate without water is 2540 K.

[†] Possible 3.8% impurity in the hydrazine nitrate component.

The experimental detonation characteristics of RX-23-AB, shown in the table, have been reported by Finger et al.³⁴ The relatively accurate detonation velocity³⁵ listed here is a guide for the computed equilibrium conditions. The calculated compositions in Fig. 9a show that nitrogen and water tend to form separate phases, and that the extent of phase separation at the Chapman Jouguet (CJ) point (as shown by the [N₂]/[H₂O] ratio in the table for the water-rich phase) depends on the magnitude of r_{ij}^* for the H₂O-N₂ interaction. The phase separation (Fig. 9a) occurs at lower pressures as the concentration of nitrogen in the water-rich phase at P_{CJ} is decreased with an increase in ϵ_{ij} (or r_{ij}^*). This phase separation increases the compression and decrease the detonation velocity. The equilibrium (or more generally the steady state) detonation velocity may be computed from the relation

Fig. 9. a. Composition of RX-23-AB products for isentropic expansion below - and shock compression above the CJ state showing phase separation above 7 GPa or 14 GPa depending on the value of the H_2O - N_2 interaction parameter, $\mathcal{L}$, as shown. b. Isentrope through the CJ point of RX-23-AB for the same two potentials compared to the experimentally determined JWL equation.

$$\text{Min}\{V_0 [P_H/(V_0 - V)]^{1/2}\} = V_0 [P_{CJ}/(V_0 - V_{CJ})]^{1/2} = D_{CJ}. \quad (12)$$

D_{CJ} is the minimum of the left hand side on the Hugoniot of the reaction products - the definition of the CJ state. It may be derived from Eqs. (10) and (11) by setting $i = 0$ ($U_{p,i} = 0$) and $U_{s,i+1} = U_{s,1} \equiv D_{CJ}$. The table shows good agreement for $\mathcal{L}_{ij} = 1.04$ to 1.05 if the sample is assumed to be pure, but $\mathcal{L}_{ij} = 1.05$ or greater if the suspected methanol solvent impurity is present. The methanol produces less than 0.1 mole of a relatively large CO_2 molecule and reduces the oxygen balance to produce ~ 0.1 mole NH_3 per 100 g of sample. The level of agreement with experiment does neither proof nor deny the presence of methanol. We therefore simplify the problem by excluding methanol and select 1.045 as the correct value of $\mathcal{L}_{ij}$.

The resulting isentrope through the CJ point is shown in Fig. 9b, where it is compared to the experimental JWL isentrope,

$$P_s = A \exp(-R_1 V_r) + B \exp(-R_2 V_r) + C V_r^{\omega+1}, \quad (13)$$

with coefficients $A = 465.7$ GPa, $B = 3.661$ GPa, $C = 0.433$, $R_1 = 4.40$, $R_2 = 1.20$, $\omega = 0.40$, and $V_r = V/V_0$. The theoretical curve has slightly higher pressures than the fit of the JWL function to experimental cylinder expansion measurements,³⁴ especially where the two phases dissolve in each other in the equilibrium mixture model. Whether this solution process also takes place on the time scale of the experiment would require additional study.

The formation rate of small N_2 and H_2O clusters appears to be relatively fast, and of the order of 30 to 100 ps. Koshi and Mtsui observed a relatively sudden nucleation effect (in the pair correlation functions) at 30 ps in molecular dynamics calculations using 256 particles in a periodic boundary system. Another jump occurred just beyond 50 ps.³⁶ These calculations were performed at 2000 K and at densities between $\rho_0 = 0.918$ and 1.99 g/cc. The calculation becomes expensive quite rapidly beyond this point. It is not clear at this time if the theoretical system is size sensitive. But it appears that 1000 ps could be a safe upper estimate for the appearance of reasonable size clusters. Turbulence in the detonation front may enhance growth somewhat, but the point at which the size is sufficient to yield an equilibrium cluster free energy is not clear. The

disappearance on the release isentrope is neither turbulent nor a nucleation process and may therefore take significantly longer.

Non-equilibrium effects can not be ruled out. The rate at which the second phase dissolves on expansion could affect the pressure along the dynamic release curve. Furthermore, if the experimental mixture is not in equilibrium near the shock front, the internal energy of the products will be somewhat above the minimum value, density will be higher, and $D_{\text{exp}} < D_{\text{CJ}}$. Under those conditions the deviation from equilibrium will be temperature dependent. The temperature drops from the CJ value of 2640 K to about 2300 K at 10 GPa. Over this pressure range the total number of moles calculated remains constant to 0.1%, suggesting that maintaining equilibrium on expansion is not a significant problem, as long as equilibrium is indeed established rapidly at 2650 K. With sufficiently accurate volume measurements, static high pressure experiments could throw some light on this subject. The present analysis assumes equilibrium conditions behind the detonation wave of this liquid explosive mixture.

F. The $\text{N}_2\text{-CO}_2$ interaction (HNB)

Hexanitrobenzene (HNB) is a light sensitive explosive that produces mostly CO_2 and N_2 on detonation. In Fig. 10a we show that the minor hexanitrobenzene products are more numerous at high pressures than below CJ. At the CJ state, CO plays a small (7%) role in the $\text{CO}_2\text{-N}_2$ mixture. Some atomic oxygen (3%) and NO (3%) are also present. At higher pressures a number of other species including liquid carbon play a (cumulative 43% at 100 GPa) role in the EOS.

A single experimental cylinder expansion experiment, yielding a detonation velocity and cylinder expansion velocities, has been done using hexanitrobenzene,³⁷ which has recently been reanalyzed.³⁸ The JWL EOS,

$$P = A\left(1 - \frac{\omega}{R_1 V}\right)e^{-R_1 V} + B\left(1 - \frac{\omega}{R_2 V}\right)e^{-R_2 V} + \frac{\omega E}{V}, \quad (14)$$

is traditionally determined by these velocities in a hydrodynamic simulation. Equations (13) and (14) form a self-consistent set because Eq. (14) reduces to Eq. (13) by substituting the integral function of volume

Fig. 10. a. Composition of HNB products for isentropic expansion below - and shock compression above the CJ state, showing the production of unstable species behind strong shocks. b. Pressure difference at constant density between two empirical JWL equations and theory.

$$E = E_S = \int_{\infty}^V P_S \cdot dV \quad (15)$$

The original analysis yielded coefficients (JWL₁) of: $A = 1131.79$ GPa, $B = 16.53$ GPa, $C = 1.976$ GPa, $\omega = 0.47$, $R_1 = 4.713$, $R_2 = 1.209$, and $E_0 = 12$ GPa. The JWL EOS from that test has been used to compute the CJ shock state using the energy conservation condition ($E = E_0 + [P + P_0][1 - V_r]/2$) with $V_r = \rho_0/\rho$ and $\rho_0 = 1.960$ g/cm³). The detonation velocity comparison in Table VIII shows the sensitivity and best value of $\ell_{N_2-CO_2}$. Use of $(k/\ell/m)_{N_2-CO_2} = 1/1.035/1$ allows an exact match of the experimental HNB detonation velocity (9.34 km/s), using the above mentioned potentials. No overdriven Hugoniot exists to test higher pressure calculations.

TABLE VIII. Shock states from theoretical calculations and jwl experimental fit for HNB with $\rho_0 = 1.965$ g/cm³ and $E_0 = 0.252$ kJ/g

Source	ℓ_{N-CO_2}	T_{CJ} (Kelvin)	P_{CJ} (GPa)	D (km/s)
Theory	1.00	5102	37.07	9.0506
Theory	1.035	4802	40.45	9.3397
Experiment	—	—	43.0	9.34

Analysis of the preliminary cylinder-expansion test yielded a JWL isentrope (with the above constants and $C = 1.976$ GPa) that may be compared to our calculations in Fig. 10b. The two maxima are a characteristic of the JWL form. The two exponential terms in Eqs. (13) and (14) impose two maxima on the $-d\ln P/d\ln V$ vs. P curve that also show up when a pressure difference is taken with a model that does not have that characteristic JWL derivative structure. This derivative structure is unique to the JWL form and makes an exact match of this practical form to theory impossible. The JWL coefficients obtained with the more recent analysis of the data³⁸ (which gave a JWL₂ with $A = 1047.883$ GPa, $B = 7.9824$ GPa, $C = 1.39612$ GPa, $\omega = 0.28$, $R_1 = 4.472$, $R_2 = 0.85$, $\rho_0 = 1.965$ g/cm³, and $E_0 = 13.2$ GPa) offers a better average deviation from theory. The difference curves between the two JWL equations and theory offer a sense of the uncertainty in the hydrodynamic simulations of the experimental data. Furthermore, the comparison with the two theoretical isentropes using $\ell_{N_2-CO_2} = 1$ and 1.035 indicate the sensitivity to the potential, which is also indicated in Table VIII.

G. The CO₂-H₂O interaction (PETN)

The two most prominent dissociation products of PETN (C₅H₈N₄O₁₂) are water and carbon dioxide (H₂O-CO₂) as shown below. The large dipole moment of H₂O and the quadrupole moment implies a strong non-ideal interaction between these two. There is also some tendency for the formation of the complex, carbonic acid (H₂CO₃), in the presence of sufficient water at normal pressures. Two questions need to be considered before discussing the potential constants for this interaction. a. The rate of H₂CO₃ formation and b. its stability under shock conditions.

a. Formation rate of H₂CO₃

The theoretical energy barrier ($E^\ddagger$) for the reaction is high enough to make the reaction slow. Some complication is introduced by the dependence of $E^\ddagger$ on the number of water molecules considered in the interaction (210 kJ for one and 170 kJ for two).³⁹ But the computed C to O van der Waals distance is too small⁴⁰ to inspire great confidence in the calculations. A better criterion for the value of $E^\ddagger$ is the reaction path kinetics for the formation of carbonic acid from CO₂ and H₂O in a water solution. This yields $E^\ddagger = 74$ kJ/mole (= 8300 K) at ambient pressure.⁴¹

At a CJ temperature of about 4500 K this implies a reaction time of

$$\tau = (\mathcal{P} \nu x_1 x_2 \exp -E^\ddagger/kT)^{-1} = 3 \cdot 10^{-12} / \mathcal{P} \text{ sec.}, \quad (16)$$

if we assume that the activation energy is pressure independent. Here we have used the Debye frequency (ν) of ice ($D_0 = 192$ K) and $\partial \ln D(V) / \partial \ln V = \gamma/V =$ constant as an estimate of the effect on $D(V)$ of the compression, of the 1 atm solid mixture ($\rho_0 \cong 1.2$ g/cm³), to the CJ density. The atom fractions of the two reacting components CO₂ and H₂O are $x_1 = 0.35$ and $x_2 = 0.36$. The probability ($\mathcal{P}$) that the two colliding molecules will have the proper orientation for reaction is not well known but may be estimated to be about 0.01. This offers a reaction time similar to that of the formation of CO₂ and water from the decomposition of PETN at the CJ point. This CO₂ formation rate is evidenced by the Von Neuman reaction spike that precedes the relatively cool (3700 K)⁴² TNT CJ point.⁴³ In addition, the relative compressibility of the activated complex⁴⁰ would imply that $E^\ddagger$ decreases with pressure, which would cause the reaction rate to increase.

The rate is therefore sufficiently high for the formation of carbonic acid. The reverse reaction can be expected to be high too, so that the probability that carbonic acid is present at the CJ point depends strictly on its Gibbs free energies (G) of the reactants and product.

b. *Stability of H_2CO_3*

In the gas-phase carbonic acid does not form under ambient conditions so that, unlike formic acid (H_2CO_2), pure carbonic acid is unstable. No direct information on $G_{H_2CO_3}$ at high pressure is available, but its stability may be estimated by comparison to that of formic acid (H_2CO_2). Its potential was estimated from an evaluation of its critical constants and the Corresponding States principle. Using this potential, our study of this molecule shows that it is not stable under shock conditions. But formic acid is stable under ambient conditions. Table IX shows a comparison of the enthalpies and Gibbs free energies of CO, CO_2 , and the water solution of their reaction products by reaction with water. This shows that carbonic acid is even more unstable than formic acid and therefore even less likely to occur under shock conditions. We have here assumed that it is not formed in the determination of the CO_2 - H_2O interaction constants. However, we may expect that the existence of soft collision configurations would make the interaction quite non-ideal.

TABLE IX: Enthalpy and Gibbs free energy of formation, for the components and the reactions: H_2O with CO and CO_2 .

Material-->	$H_2O(g)^a$	+ $CO(g) \rightarrow$	$H_2CO_2(aq)$	$X_{prod} - \sum X_{reac}$
$X = H_{298}^f$	-57.796	-26.416	-101.68	-17.468
$X = G_{298}^f$	-54.634	-32.780	- 89.0	-1.58
Material-->	$H_2O(g)$	+ $CO_2(g) \rightarrow$	$H_2CO_3(aq)$	$X_{prod} - \sum X_{reac}$
$X = H_{298}^f$	-57.796	-94.051	-167.22	-15.373
$X = G_{298}^f$	-54.634	-94.254	-148.94	-0.052

a. (g) indicates the gas-phase and (aq) is the water solution.

Fig. 11. a. Potential energy curves for the pair interactions among CO_2 and H_2O molecules: $\Phi_0(\text{CO}_2\text{-H}_2\text{O})$ is the Lorenz-Berthelot approximation. b. Major reaction products of PETN for strong shocks above - and along the expansion isentrope below the CJ pressure. Lines: phase 1, the water-rich state; points: phase 2, above $P = 17$ GPa.

c. Interaction constants between CO₂ and H₂O

The result of matching the detonation velocity of PETN is shown by the constants for the CO₂-H₂O interaction in Table IV. The effect that the constants have on the potential is shown in Fig 11a, where the ideal pair interaction potential is shown together with the actual H₂O-CO₂ potential. The potential energy curve is additional evidence for the instability of H₂CO₃ since the effective collision diameter is considerably larger than that calculated for the combined molecule.⁴⁰ Shock and detonation data of PETN (C₅H₈N₄O₁₂) offer the best experimental data to quantitatively study this interaction at high pressure. Figure 11b shows the major high-pressure high-temperature decomposition products of this molecule.

The mixture, consisting primarily of CO₂, H₂O and N₂, becomes heterogeneous just above the detonation pressure where a nitrogen-rich phase (with major components labeled N₂(ph2) and N(ph2)) separates out behind the overdriven shock front as the nitrogen content of the water-rich phase, N₂(ph1), decreases with increasing pressure. Another significant component is CO, which is roughly 3% of the total amount of gas just behind the detonation front, and rapidly increases as the pressure drops during the expansion of the product gasses and the small amount of condensed (diamond-like) carbon decreases. At the detonation pressure the major components are therefore N₂ and CO₂, with N₂ coming in at 20% of the gaseous mixture. The $\Phi(\text{N}_2\text{-CO}_2)$ and $\Phi(\text{N}_2\text{-H}_2\text{O})$ were determined above, so that the CO₂-H₂O interaction may be refined with these data(see Table IV).

d. Some effects of nonequilibrium C

The carbon component is not totally negligible at the detonation pressure. Carbon is produced in cluster form behind the detonation wave as evidenced by the detonation velocities of porous TNT⁴² samples and from recovered carbon.⁴⁴ The equilibrium EOS used here is therefore only approximately correct. One measure of the uncertainty due to this approximation can be tested by simply increasing the heat of formation of diamond by $\Delta H^f(298) = 0.1$ eV, as done before in the analysis of TNT,⁴² and consistent with the surface energy⁴⁵ of the recovered clusters. The change in the composition of the gas-phase species is not noticeable. The principal change is a transition from liquid carbon to graphite

Fig 12. PETN data and theory. a. deviation of the theoretical isentropes from the JWL Isentrope. b. Comparison of theoretical Hugoniot with shock data.

at a pressure ($P=21$ GPa) lower than the liquid to equilibrium diamond transition. graphite phase disappears at the same pressure on the expansion isentrope as the equilibrium diamond [$\Delta H^f(298) = 0$ eV] in Fig. 11.

Figure 12a shows the states reached by expansion from the CJ state as pressure differences from the experimental JWL isentrope of Green et al.⁴⁶ (with $A = 1032.16$ GPa, $B = 90.57014$, $C = 3.72735$ GPa, $R1 = 6.0$, $R2 = 2.6$, $\omega = 0.56$, $E_0 = 0.108$ GPa, and $\rho_0 = 1.763$ g/cm³). The best theoretical calculation includes the constants for the two major species ($[k/\ell/m]_{\text{CO}_2\text{-H}_2\text{O}}$) shown in Table IV. The small values of both ℓ_{ij} and m_{ij} are consistent with a relatively smaller collision distance between H₂O and CO₂ than predicted by the Lorentz-Berthelot rule. The original EOS used a much softer CO₂-CO₂ potential (Φ_n in Fig. 4a) as well as the softer N₂-N₂ potential with the standard Lorentz-Berthelot rule. The agreement between the JWL form and the current results, for $P < P_{\text{CJ}}$, using both equilibrium and non-equilibrium diamond are similar but distinguishable. As shown below, other changes in the carbon EOS have a small effect on the CO₂-H₂O constants in Table IV.

The overdriven Hugoniot data in Fig. 12b also show the effect of including the high-temperature species. The old potential set produces a much higher curvature than the newer equations of state. The data appear to show a slightly higher compression between 50 and 90 GPa than is predicted by the present theoretical EOS. This pattern is similar to that observed with pure CO₂ and could be related to high pressure cluster formation. Taking that factor into account, the high pressure compressibility is consistent with that of the simple systems discussed above.

IV. HMX MIXTURES

We will now compare the results of calculations of two HMX formulations with experiment. HMX with atomic composition⁴⁷ C₄H₈N₈O₈ has a lower oxygen balance than PETN. The higher carbon content of the detonation products tends to make the carbon coagulation rate a more important part of the description of the detonation process, than it is in PETN. We work here with two formulations:⁴⁷ PBX-9404 and LX-14 containing 94 weight % and 95.5 weight % HMX, respectively.

The number of major components in the equilibrium composition diagram of LX-14 (Fig. 13a) is larger than it is for PETN. The amounts of nitrogen and carbon are comparable to the water content, while the CO_2 content plays the secondary but still significant role. In the phase separated region the nitrogen content (both N and N_2) is primarily in the N_2 -rich phase, with only 10% or less atomic N in the water-rich phase. Other molecules and atoms used in the calculation remain below 0.05 moles/100 g. The theoretical CJ point marks the boundary between the expansion region and the shock compression region. At that point carbon is in the diamond form, which does not liquefy until the shock pressure reaches 80 GPa. The non-equilibrium character of carbon has a noticeable effect, on the location of the phase changes, since these are quite sensitive to any changes in the EOS of the mixture. The calculated effect is again roughly simulated with the above mentioned change in the heat of formation of diamond.

The JWL release isentropes used in Fig. 13b were obtained from the best hydrodynamic simulations of a number of experiments on various metal-explosive configurations: flat plates, cylindrical tubes, and other 2-D structures. Such a comprehensive process further constrains the set of parameters that are possible fits and has shown that more massive metal plates are less sensitive to the non-equilibrium flow characteristics near the Von Neuman spike. We therefore emphasize here two fits of the JWL form [Eq. (13) and (14)] that offer the best overall agreement with two-dimensional metal-explosive configurations. Figure 13b presents plots of the deviations of two empirical JWL isentropes, in Table X, from our theory. These $P_{\text{JWL}} - P_{\text{THEORY}}$ difference curves between empirical, JWL EOS forms and CHEQ theory reflect the differences between equilibrium and non-equilibrium [$\Delta H^f(298) = 0.1 \text{ eV}$] diamond calculations.

Two features stand out in this plot. They are the sharp fluctuations near 8.5 and 11.8 GPa which are due to the diamond to graphite transition and fluid phase separation observed in the equilibrium theory (18.7 GPa and 14.5 resp. for non-eq. diamond calculation). These are not described by the JWL form and therefore, do not cancel out in the differencing. The figure indicates the transformation from graphite to equilibrium diamond and to non-equilibrium diamond by the arrows near the top and bottom of the figure. The horizontal bars indicate the regions of uniformly mixed fluid and of phase separated

Fig. 13. LX-14 results. a. Major equilibrium reaction products of LX-14 for strong shocks above CJ and the release isentrope below the CJ pressure. Dashed curves represent the water-rich phase. Solid curves are the three carbon phases and the components of the nitrogen-rich phase; b. difference curves between theoretical isentropic release curves of LX-14 and JWL equations. The bars and arrows indicate regions of phase stability. See text for details

TABLE X. JWL equations use in Fig 13b

Symbol	JWLH	JWLQ
A (GPa)	3104.0	1161.8
B (GPa)	174.4	53.96
C (GPa)	1.304	2.1098
R ₁	7.66	5.40
R ₂	2.65	2.00
ω	0.50	0.50
ρ_0 (g/cc)	1.836	1.835
P _{CJ} (GPa)	35.8	36.0

N₂-rich and H₂O-rich fluids. These show that the phase separation point is also sensitive to the carbon EOS. The deviation of the theoretical CJ pressures from those of the table X JWL equations are also significant. The most likely interpretation is that the experimental shock pressure is affected by the reactive wave-front profile discussed above. Reactive flow is beyond the scope of this work.

The velocity of overdriven shocks is plotted as a function of pressure in Fig. 14. The experimental data of Kineke⁴⁸ have been re-analyzed using an appropriate strength function or the standard reference metal (Mo).⁴⁹ Additional data obtained with a two stage gun by Green and coworkers⁵⁰ is also presented. The

Fig. 14. Overdriven Hugoniot curves of PBX-9404, and LX-14 - experiment vs theory

original calculations have a stronger pressure dependence than experiment, as reported earlier.⁵¹ The present set of potential constants greatly improved the high pressure slope. The minimum in the theoretical curve (the detonation velocity) is somewhat higher than experiment, again suggesting a significant non-equilibrium character of the detonation wave. However, the

match of detonation velocity to experiment is important for accurate hydrodynamic simulations. It is therefore important for a complete theory to yield the experimental detonation velocity. Since carbon is a significant component in these systems, the effect of different carbon cluster structures on the EOS need to be evaluated to determine the cause for the deviation in Fig. 14.

V. HIGH CARBON SYSTEMS

If the deviation between the computed and the experimental EOS of LX-14 is due to carbon, its effect should be greater for high carbon materials like TNT or TATB. TNT has the higher CJ temperature of the two and was, therefore, selected for a test of the carbon EOS. In Figure 15a we see a deviation of about 8 % between the computed shock speeds and the experimental results of Kineke (K).^{48,52} This deviation is clearly larger than that of LX-14 which was of the order of 1%. This deviation is also larger than one may expect from simple carbon content scaling. This may be due to the fact that in the above comparison with PETN it was assumed that carbon reaction with gas-phase molecules is negligible.

However, since the deviation is associated with carbon, we make an initial simplifying assumption that the effect can be represented by a scaling of the carbon EOS. This is done with the realization that we are here concerned with a coupled set of equations, the diamond EOS, the graphitic EOS and the $\text{H}_2\text{O}-\text{CO}_2$ interaction constants. The data that are the standards for this part of the study are the overdriven TNT data of K, the lower pressure porous TNT data of Urizar and James⁵³ (UJ) and of Dremine and Pokhil⁵⁴ (DP), and the above mentioned PETN data.

A reduction of the diamond modulus from $B_{0K} = 439.7$ to 374 GPa has a negligible effect on the calculated overdriven TNT Hugoniot. Best agreement with K is obtained with an increase in initial (effective ambient) density. The diamond Hugoniot data in Fig 15a is matched if $\rho_0 = 4.475 \text{ g/cm}^3$ (27 % greater than the normal diamond density, $\rho_0 = 3.517 \text{ g/cm}^3$, at $T = 0 \text{ K}$) and $B_{0K} = 439.7$ to 374 GPa.

The computed TNT EOS has the same insensitivity to B_{0K} at low pressure where the graphitic phase is stable. The data of DP, and especially of UJ in Fig. 15b, show clearly the region of graphitic carbon stability and the point of conversion to diamond-like material discussed previously.⁵⁵ The latter is more unstable relative to the graphitic phase when formed in a detonation, requiring an elevated heat of formation for diamond-like material to match the experimental pattern. If we assume that the small size of the graphitic clusters does not affect

Fig. 15. Shock data for TNT. a. Overdriven Hugoniot data (points) and calculations with normal density diamond (---) and with raised density simulating 'non-equilibrium' carbon (—). b. Detonation velocity as a function of sample density: experiment (points), theoretical with normal graphite (---) and with 'non equilibrium' graphite with raised density (—).

their heat of formation, the diamond-like material has an apparent ΔH^f of at least 4050 cal/mole or 0.176 eV per atom, as opposed to the 0.1 eV needed without a density adjustment. This may still be an underestimate since the effective initial density of the graphitic clusters has to be increased to match the data.

This somewhat more realistic diamond 'cluster' EOS requires somewhat different $\text{CO}_2\text{-H}_2\text{O}$ interaction constants. With an adjusted $\ell_{\text{H}_2\text{O-CO}_2}$ the best EOS for graphitic carbon in Fig. 15b is obtained with $\rho_0^{\text{gr}} = 2.57 \text{ g/cm}^3$, 11% larger than its normal density of 2.27 g/cm^3 at $T = 0 \text{ K}$. The UJ data have been weighted more heavily in the determination of the graphitic EOS, since their internal consistency is higher and since they represent the detonation velocities for large diameter charges extrapolated to infinite diameter.

Fig. 16. Isotherms of carbon in its graphitic and diamond-like phases at $T=0.3 \text{ eV}$ and the liquid phase at $T=0.6 \text{ eV}$, showing the difference between equilibrium and simulated non-equilibrium C

These changes in apparent carbon density are significant, as can be seen from Fig. 16 where isotherms at 3500 and 7000 K are plotted. The high temperature isotherms are in the liquid and the low T isotherms completely in the solid. The diamond phase shows a much larger change than the graphite phase. This is qualitatively consistent with the larger chemically active surface of diamond and therefore its greater effect on the gas-phase through surface chemi-sorption.

These adjustments in the carbon EOS have a minor but noticeable effect on the computed CJ state of PETN. With the interaction constants in Table IV, we compute $D_{\text{CJ}}^{\text{PETN}} = 8.21 \text{ km/s}$, instead of the experimental value of 8.27 km/s , suggesting that the non-equilibrium character of PETN implies that $\ell_{\text{H}_2\text{O-CO}_2}$ should be raised from 0.9765 to 0.983. This change produces a $D_{\text{CJ}}^{\text{PETN}} = 8.27 \text{ km/s}$ consistent with its experimental value. With this value of $\ell_{\text{H}_2\text{O-CO}_2}$ this effective non-equilibrium carbon EOS also improves the agreement between the computed PBX-9404 CJ detonation velocity and experiment, as shown in Fig. 14.

VI. OTHER EXPLOSIVES

The way in which the above systematic, pair-potential and EOS, specifications affect the overall agreement with measured explosive detonation velocities can now be addressed to test the adequacy or sufficiency of the above considerations. We concentrate on the detonation velocities. Computed equilibrium CJ pressures are generally lower than measured detonation pressures, since the latter are affected more by a transient partially reacted zone near the pressure front that has a higher dynamic impedance ($\rho_0 D$) and, consequently, a higher pressure. These are, therefore, not compared in this study.

The properties of the materials studied are summarized in Table XI. A number of these are used as binder materials in multicomponent explosive formulations (mixtures). Some of these contain fluorene (F), which forms hydrofluoric acid (HF) in the reacting mixture. The interactions of these materials with themselves and their molecular environment had to be estimated and are not well defined. In addition, chlorine (Cl) is present in the binders CEF and Kel-F, while a small amount of phosphorus (P) is introduced through the use of CEF. Many of these heat of formation measurements have been discussed by Ornellas.³³

The results of the calculations are summarized in Table XII. A number of porous explosives are included in the comparison. For those post-detonation mixtures that contain free carbon, systems with equilibrium carbon (Ceq) (but with a $\Delta H^f(298) = 0.1$ eV, for diamond, to yield the experimental graphite to diamond transition pressure) and the adjusted-density 'non-equilibrium' carbon (Cne) EOS have been calculated for comparison. The use of Cne lowers the calculated detonation velocity. This is shown in the schematic representation in Figs. 17a and b. Figure 17a shows that using 'non-equilibrium' carbon makes a change in the detonation velocity comparable to the over all variability of the results. We will consider a number of features that are related to basic physics questions.

a. First of all, *the question of equilibrium* must be addressed. The temperature of the computed Chapman Jouguet state varies from a high of 5340 K for BTF to 2470 K for TNM. This temperature range implies a significant range in the reaction rate,

Table XI: Properties of Energetic Materials
A - Pure Compounds

Acronym	Chemical name	Number of atoms of CH/N/O/ Cl/F/P	$\rho_{\max}$ g/cm ³	T _{Melt.} °C	H_{298}^f kJ/g	formula Wt gm	ref
BTF	benzotrifuroxane	6/0/6/6/ 0/0/0	1.901 ²⁰	200.	2.386	252.1	47,56
BDNPF	bis (2,2-dinitropropyl)formal	7/12/4/10 0/0/0	1.39	<20	-1.913	312.19	56
CEF	tris-β-chloroethylphosphate	6/12/0/4/ 3/0/1	1.425 ²⁰	203.	-4.396	285.5	47,56
DNB	m-dinitrobenzene	6/4/2/4/ 0/0/0	1.575 ¹⁸	90.	-0.543	168.11	61,56
1,2DP	1,2-bis(difluoroamino)propane	3/6/2/0/ 0/2/0	1.26	<20	-1.374	146.09	56
ED	ethylenediamine	2/6/0/2/ 0/0/0	0.900	8.5	-1.048	60.11	61
estane	polyurethane polymer	47/70/1/17/ 0/0/0	~1.18	----	-3.970	921.08	61,56
FEFO	bis(2-fluoro-2,2-dinitroethyl)formal	5/6/4/10/ 0/2/0	1.607	14.5	-2.320	320.1	47
HNO ₃	nitric acid(100%)	0/1/1/3/ 0/0/0	1.503 ²⁵	-42.	-2.763	63.01	47
HN	hydrazine nitrate	0/5/3/2/ 0/0/0	1.665	62.-71.	-2.832	95.058	61,56
HYD	hydrazine	0/4/2/0/ 0/0/0	1.004 ²⁵	2.	1.580	32.045	61
HMX	octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazine	4/8/8/8/ 0/0/0	1.905	285.	0.253	296.2	47
HNB	hexanitrobenzene	6/0/6/12/ 0/0/0	2.02	240. ^d	0.19	348.11	56
HNS	2,2',4,4',6,6'-hexanitrostilbene	14/6/6/12/ 0/0/0	1.74	315.	0.174	450.3	61
Kel-F	chlorofluoroethylene/vinylidene fluoride copolymer	(8/2/0/0/ 3/11/0) _n	>2.02	----	-1.63	413.5	47
MF-1	2-fluoro-2,2-dinitroethyl-2,2-dinitropropyl)formal	6/9/4/10/ 0/1/0	>1.534	<20	-2.119	316.16	56
NM	nitromethane	1/3/1/2/ 0/0/0	1.137 ²⁰	-17.	-1.853	61.04	61
NP	2-nitropropane	3/7/1/2 0/0/0	0.9876 ²⁰	-23.	-2.023	89.09	61,56
PF	picril fluoride	6/2/3/6/ 0/1/0	1.833	<20	-1.122	231.1	56
PETN	pentaerythritol tetranitrate	5/8/4/12/ 0/0/0	1.78	140	-1.61	316.15	47
RDX	hexahydro-1,3,5-trinitro-1,3,5-triazine	3/6/6/6/ 0/0/0	1.82 ²⁰	205.	0.2771	222.12	61
TATB	1,3,5-triamino-2,4,6-trinitrobenzene	6/6/6/6/ 0/0/0	1.939	325. ^d	-5.972	258.15	61
TNGU	tetranitroglycoluril	4/2/8/10 0/0/0	2.04	----	0.1559	322.1	56
TNM	tetranitromethane	1/0/4/8 0/0/0	1.638 ²⁰	14.2	0.2775	196.03	61,56
TNT	2,4,6-trinitrotoluene	7/5/3/6 0/0/0	1.654 ²¹	82.	-0.3280	227.13	61,56

Table XI cont.: Properties of Energetic Materials
B - Mixtures

Acronym	Components	C / H / N / O / Cl / F / P	ρ_{max}^T g/cm ³	T _M °C	H ₂₉₈ ^f kJ/g	Weight gm	ref
CompB3	63% RDX, 36% TNT, 1% wax	2031/2641/2177/2653 0/0/0	1.742	<82	0.0538	100.00	47,58
Cyclotol	77% RDX, 23% TNT	175 /259/238/269 0/0/0	1.780	<82	0.145	100.00	57,58
FM-1	23% FEFO; 52% MF-1, 25% BDNPF	1906/2872/1265/3164/ 0/0.308/0	1.509	<20	-2.1128	100.00	56
HNO ₃ #1	60% nitric acid; 40% DNB	1427/1904/1428/3808/ 0/0/0	1.542	<20	-1.711	99.994	56
HNO ₃ #2	60% nitric acid; 30% DNB; 10% RDX	1205/1936/1579/3840/ 0/0/0	1.56	<20	-1.676	100.00	56
LX-14	95.5% HMX; 4.5 estane	1521/2917/2588/2659/ 0/0/0	1.849	270.d	0.0628	100.00	47
LX-17	92.5% TATB; 7.5% Kel-F	2295/2186/2150/2150/0.054/0.200/0	1.944	325.d	-1.088	100.00	47
NC	nitrocellulose	6/75/249/9.75/10/ 0/0/0 _n	>1.656	165	-2.871	268.38	61,47
NNE	39% NM; 56% NP; 5% ED	2691/6982/1434/2535 0/0/0	1.034	<20	-1.908	100.00	56
PBX-9011	90% HMX; 10% estane	1726/3191/2442/2616 0/0/0	1.795	250.d	-1.170	100.00	47
PBX-9404	94% HMX; 3% NC; 3% CEF	14/275/257/269/ 0.03/0/0.01	1.865	250.d	0.00331	100.00	47
RX-23-AA	79. % HN; 21% HYD	0/6.78/3.80/2.49 0/0/0	1.715	<2.	-1.715	99.90	35
RX-23-AB	69.02% HN; 5.08% HYD; 25.9% Water	0/7.140/2.495/3.616 0/0/0	1.384	<0.	-5.69	100.00	34,35
RX-23-AC	30. % HN; 70% HYD	0/10.31/5.32/0.95 0/0/0	1.135	<2.	0.1648	100.11	35
RX-26-AF	49.0% HMX; 46.7% TATB; 4.3% estane	1967/2736/2414/2488 0/0/0	1.870	~280	-0.3325	100.00	56,47

Table XII: COMPARISON OF EXPERIMENTAL AND COMPUTED EXPLOSIVE PROPERTIES

MATRL	ρ_0 g/cm ³	D_e km/s	D_{ne} km/s	D_{exp} km/s	P_e GPa	P_{ne} GPa	P_{exp} GPa	T_e Kelvin	T_{ne} Kelvin	Carbn phase	ref
BTF	1.852	8.621	8.569	8.49	33.5	35.0	34.0	4885.	5343.	liq,di	38,56
Comp-B3	1.720	8.052	7.818	7.89 (.95)	27.29	26.2	29.5	4218	4140.	di	47, 60
Cyclotol	1.743	8.314	8.168	8.25	30.2	28.95	31.3	4131	4263	di	57,59
1,2-DP	1.26	7.449	7.424	5.97	16.2	16.0	13.5	4763	4436	gr	56
FEFO	1.607	8.219	8.190	7.45	26.8	25.5	24.5	4412	4459	liq,di	38,56
FM-1	1.509	~7.58	7.477	6.57	~20	20.2	19.0	4000	4100	gr ?	38,56
FM-1	„	~7.3	7.262	6.57	23.5	19.7	„	4050	4000	di ?	38,56
HMX	1.894	9.291	9.128	9.118	38.2	37.11	39.0	4164	4181	di	38,56
HMX	1.613	8.173	8.151	8.015	27.85	28.1	~27*	4303	4488	di	59
HMX	1.200	7.078	7.080	6.59	14.6	14.66	15.0	4340	4375	gr	58, 47
HMX	1.188	7.02		6.68	14.3		15.5	4353		None	38,56
HMX	1.10	6.60		6.21	11.95			4423		None	59
HMX	1.00	6.133		5.80	9.60			4488		None	59
HMX	0.750	5.008		4.88	5.18			4618		None	59
HMX	0.561	4.234		3.98	3.03			4665		None	59
HNO3#1	1.542	7.375		7.23	19.8		21.0	4636		None	38, 56
HNO3#2	1.560	7.31-7.29		7.26	21.		20.4	4200		None	38, 56
HNB	1.965	9.340		9.34	40.45		43.0	4810		None.	38, 56
HNS	1.681	7.166	6.858	7.08	22.1	21.0	23.0	4126	4120	di ?	56
HNS	„	7.594	7.390	„	23.85	23.5	„	4205	4307	gr ?	56
HNS	1.655	7.104	6.805	7.03	21.45	20.8	21.5	4137	4120	di ?	38, 56

MATRL	ρ_0 g/cm ³	D_e km/s	D_{ne} km/s	D_{exp} km/s	P_e GPa	P_{ne} GPa	P_{exp} GPa	T_e Kelvin	T_{ne} Kelvin	Carbn phase	ref
HNS	"		7.35	"		21.0	"		4190	gr ?	38, 56
HNS	1.610	7.004	6.720	6.96	19.85	19.6	21.0	4050	4140	di ?	56
HNS	"	7.42	7.24	"	21.3	19.7	"	4145	4140	gr ?	56
HNS	1.597	7.380	7.195	6.96	21.0	19.75	21.5	4140	4195	gr ?	56
HNS	"	6.808		"	21.6		"	4015		liq ?	56
HNS	"	6.98	6.700	"	20.4	20.05	"	4050	4150	di ?	56
HNS	1.504	7.052	6.879	6.70	17.99	17.2	18.5	4108	4176	gr	56
HNS	1.402	6.690	6.546	6.34	15.2	14.9	16.0	4087	4150	gr	56
HNS	1.200	6.008	5.918	5.74	10.6	10.75	11.5	4000	4030	gr	56
HNS	1.001	5.346	5.295	5.10	7.04	7.35	7.3	3825	3860	gr	38, 56
LX-14	1.835	8.943	8.725	8.80	34.0	33.02	37.0	4100	4075	di	47, 38
LX-17	1.905	8.231	7.830	7.63 ^b	27.6	25.85	26.0	3130	3120	di	56
NM	1.130	6.427	6.363	6.299	12.19	12.12	13.4(±.4)	3748	3786	gr	60
NNE	1.034	5.433	5.297	5.31	7.585	7.67	8.9	2947	2973	gr	56
PBX-9011	1.770	8.514	8.263	8.50	29.65	28.4	29.8	3904	3903	di	58
PBX-9404	1.840	8.943 ₅	8.765	8.776	34.6 ₂	33.65	35.65	4146	4120	di	60
PEIN	1.763	8.333	8.271	8.275	31.2	31.13	31.5	4522	4529	di	38, 56
PETN	1.503	7.676	7.675	7.48	25.5	25.4	24.0	4707	4716	di	38, 56
PETN	1.263	6.59		6.59	13.7		16.0	4673		none	38, 56
PF	1.833	8.216	7.933	7.29 ^a	29.1	28.0	27.0	4015	4032	di	56
RDX	1.767	8.728	8.643	8.639	33.1	32.4	33.79	4174	4353	di	59
RDX	1.72	8.542	8.483	8.46-507	30.8	31.3	30.85	4191	4415	di	59

MATRL	ρ_0 g/cm ³	D _e km/s	D _{ne} km/s	D _{exp} km/s	P _e GPa	P _{ne} GPa	P _{exp} GPa	T _e Kelvin	T _{ne} Kelvin	Carbn phase	ref
RDX	1.048	6.362		6.188	10.66		10.44	4470		none	59
RDX	0.899	5.675		5.603	7.56		8.49	4560		none	59
RDX	0.61	4.433		4.390-.43	3.54		3.71	4672		none	59
RX23-AA	1.421	8.58		8.58	24.2		20.9*	3233		none	34
RX23-AB	1.384	7.494		7.48	17.55		18.6	2643		none	34
RX23-AC	1.135	8.137		7.88	15.5		16.9*	2535		none	34
RX-26-AF	1.844	8.448	8.136	8.24	29.3	27.58	33.7	3684	3697	di	56
TATB	1.83	7.891	7.521	7.58	24.5	23.3	26	3277	3298	di	56
TNGU	1.885	8.694	8.69	8.71 ^a	35.1	35.0	37.0	4421	4420	none	56
TNM	1.65	6.632		6.45	16.3		15.5	2469			56
TNT	1.447	6.690	6.491	6.48	15.1	14.65		3754	3806	gr	54
TNT	1.3005	6.155	6.018	6.018	12.06	11.60		3721	3760	gr	54
TNT	1.2008	5.817	5.700	5.700	10.17	9.98		3661	3710	gr	54
TNT	1.0511	5.331	5.2545	5.2229	7.65	7.575		3.534	3560	gr	54
TNT	0.9009	4.847	4.7985	4.7443	5.58	5.57		3388	3420	gr	54

Fig. 17. Difference between computed and experimental detonation velocities. a. normal density explosives, showing the C:O ratio to the left. b. porous explosives, with the porosity, V/V_{max} to the left.

$$\frac{1}{n} \frac{dn}{dt} = \frac{1}{2} v \exp(-\Delta G^\ddagger/kT) \quad \text{and} \quad n/n_0 \approx \exp(-t/\tau). \quad (17)$$

Here n is number density and $\Delta G^\ddagger$ is the difference between the activated or transition state of the reaction and the expectation value of the reactants. In general $G = E + PV - TS$. The PV term is often neglected and the exponent is written for the Helmholtz free energy of reaction ($E-TS$). As long as pressure dependence of $\Delta E^\ddagger$ and $\Delta S^\ddagger$ are small compared to effect of changing T , we may assume a generic $\Delta G^\ddagger$ and write the exponent of Eq. (17) as $T^\ddagger/T$. With $v = 10^{13} \text{ s}^{-1}$, $T=4000 \text{ K}$ and $T^\ddagger = 3.78 \times 10^4$, we have 98% reaction in 10^{-8} s . Then, when $T=2500 \text{ K}$ we get $t = 3 \times 10^{-6} \text{ s}$ for 98% reaction, i.e. a factor of 300 in the rate of reaction. The relatively large difference between calculated and measured detonation velocities of RX-23-AC and TNM may, therefore, be due to a non-equilibrium effect of the gas-phase. The shock state then becomes an apparent CJ state, strongly affected by sample size.

b. The exact *melting point curve of carbon* is in question. Melting affects both the density and internal energy of carbon and therefore the detonation velocity. In the case of BTF and FEFO the liquid diamond state clearly exists and shows that the liquid diamond state of the equilibrium calculation is close to that for the non-equilibrium diamond. In addition, HNS, FM-1 and TNT (not shown) samples that are near full density have their CJ points in a transition region where both graphitic and diamond clusters coexist. The present model is too simple to offer insight into the proportions of each state.

c. *Explosive porosity* too is a factor in the sensitivity of the detonation velocity to carbon EOS. Lower initial density increases the amount of CO formed and reduces the fraction of free carbon. This shows up in the comparatively small difference between the C_{eq} and C_{ne} calculations for RDX with its 3% porosity and TNGU with its 8% porosity. Free carbon is absent for sufficiently low density HMX and RDX as is shown in Fig. 17b.

d. The *interactions of HF* with other products, i.e., NH_3 , H_2O , and CO_2 , are likely to be quite non-ideal if ideal is defined by Eq. (5), with $k_{ij}, l_{ij}, m_{ij} \equiv 1$. The data in Fig 17a. indicate that such repulsive interactions are too high. Information that

could refine these interactions is currently not available, and extensive use of these systems is not advisable because of the corrosive nature of HF.

e. The *accuracy of the experimental detonation velocity* is in principle quite good. And for some explosives an uncertainty of 0.1% is a reasonable figure. In general, uncertainties in sample preparation, confinement, small voids etc. are additional factors limiting the accuracy of the measurement. Seven experiments⁵⁶ with LX-14 showed a $\Delta D_{\max} = \pm 1.4\%$ and a $\sigma_{\text{rms}} = \pm 0.3\%$. For LX-17 these values for nine experiments are⁵⁶ are $\pm 1.4\%$ and $\pm 0.43\%$. The deviation between theory and experiment for PBX-9011, which is similar in composition to LX-14, is too large to be explained by the above. One possibility is that the uncertainties were larger for experiments done in and before the early 1960's which are the source of the PBX-9011 data,⁶² and those of the mid 1970's and later, the source of the LX-14 data (ref. 56 and references therein).

f. Figure 17b displays the results of *porous explosives* only. Here the deviation between theory and experiment tends to be larger. Sufficiently porous materials appear to form a separate class of explosives. It has been shown by Ramsey and Popolato⁶³ that explosives require a certain minimum pressure to come to full detonation rapidly. They find that this minimum pressure is less for porous materials, an effect that is related to the initiation process of the detonation rather than the burn rate. The detailed mechanism of microscopic burn is different for porous materials. Each grain should behave like a full density explosive, and when the average pressure drops below about 150 kbars (i.e., for TNT and HMX or RDX formulations) the burn rate of the grain slows down and for sufficiently porous materials the initiation is facilitated mainly by relatively low pressure hot gasses from burning grains. These hot gasses move through the space between the grains ahead of the main pressure front. The result is a wider pressure wave which should result in a stronger sample size sensitivity.

Urizar, James, and Smith⁵⁴ show a 3.6% increase in detonation velocity between TNT sample diameters of 2 cm and infinity with $\rho_{\max}/\rho = 1.836$ and only a 0.16 % difference with $\rho_{\max}/\rho = 1.011$. The diameter effects for RDX⁵⁹ appear to be less than those for TNT and for HMX⁵⁹ little information is available on the effect of charge diameter. The HNS results⁵⁶ are for 2.54 cm diameter copper sheathed cylinders. Correcting these to infinite diameter using the data of Urizar and

James reduces the deviation, as shown in Appendix I, but does not remove it. It appears, therefore, that the relatively large deviations for porous explosives are only in part related to the diameter effect. For the higher HNS densities the diamond or liquid phase also may be important. Where the carbon phase is likely mixed the computed phase is listed with a '?'.

The observed deviations are therefore reasonably consistent with experimental uncertainties. If we exclude the mixed carbon phase systems and those containing fluorine, the rms deviation in Fig. 17a is 1.44% and 1.81% for the C_{ne} and C_{eq} calculations respectively, and larger for the porous systems in Fig. 17b.

VII. SUMMARY

We have obtained new information on like- and unlike-pair interactions for the chemical species N_2 , O_2 , NO , CO , CO_2 , and H_2O , that are important in combustion and explosions, by examining their shock wave data. Our self-consistent approach results in a set of potentials that reproduce all available Hugoniot data within experimental accuracy. This approach is essential for determining unlike-pair interactions, since such information is scarce. The present investigations also showed the importance of a reliable liquid carbon EOS in the simulation of the shock wave properties of reactive liquid- CO and $-CO_2$. In addition, close comparison of theory and data for N_2 and CO_2 at high pressure suggest higher order (structural or kinetic) effects that are not handled by this theory. No decomposition of CO is observed behind shocks below 10 GPa and 3800 K. Carbon dioxide starts decomposing on the Hugoniot above 40 GPa and 4500 K.

The improved accuracy of intermolecular potentials for the above molecules and their dissociation products required the investigation of simple mixtures to explain the deviation between computed and experimental detonation velocities. The 'non-ideal' interactions among N_2 , CO_2 , and H_2O are all important for explosives, especially in the region below 40 GPa. The unlike interactions between these molecules were obtained from shock and detonation data of HNB, RX-23-AB, and PETN explosives. Analysis of PETN data showed that the CO_2 - H_2O potential is considerably softer than predicted by the Lorenz-Berthelot rule. The resulting set of potentials gave a good match to the overdriven Hugoniot of

PBX-9404 and empirical release isentropes of LX-14. The detonation velocity, however, is 0.8 % larger than experiment. Since hydrodynamic simulations require a better match between experiment and theory, the effect of non-equilibrium carbon clusters needs to be evaluated. The possible liquid structure changes in hot dense N_2 and H_2O suggested by the shock data should only have a secondary effect.

A preliminary estimate of the effect of the carbon EOS uncertainty on the interaction constants in Eq. (5) was obtained by adjusting the carbon EOS to match the porous detonation and overdriven shock data for TNT. The resulting non equilibrium diamond EOS has a significantly higher density than the normal EOS. The change for non-equilibrium graphite is smaller and in the same direction. The interaction coefficient between H_2O and CO_2 is slightly affected by this adjustment as shown in Table IV.

A survey of a number of explosives indicates some significant features of the data:

- a. Some low energy materials (RX-23-AC and tetranitromethane) appear to show effects of gas-phase kinetics.
- b. The CJ pressures of TNT, hexanitrostilbene, and a formulation designated as FM-1 coincide with the graphite to diamond phase change of carbon, which occurs over a finite pressure range. The possibility of melting also needs to be considered in further cluster-EOS development.
- c. The results show that the sensitivity of the detonation velocity to carbon EOS decreases with decreasing density.
- d. For a number of explosives containing F_2 , the computed detonation velocities are high due to the uncertainty in the interaction constants of HF.
- e. The older experimental detonation velocity for PBX-9011 is low in comparison with the more-recent and extensive data on LX-14, a similar formulation,
- f. Experiments with porous explosives indicate a noticeable effect of the diameter of the explosive sample on the detonation velocity.

In spite of these constraints, the simple approach of adjusting the carbon EOS yielded improved results, and indicates that the effect of using an appropriate cluster EOS for carbon tends to increase the overall density and lowers the detonation velocity of the post-detonation-mixture.

ACKNOWLEDGEMENTS

The technical and financial support of a number of people is gratefully acknowledged: Dick Grover for his advice on implementing the liquid carbon 'Scaling EOS' in the CHECK code; the very effective reprogramming, streamlining and enhancement of the CHECK code by Al Nichols, as well as our useful discussions with him; Ellen Corey's support in implementation of the new code; the general advice on material properties of David Young and Philip Pagoria; the personal interest and financial support of B-Div and HET, in particular P. Clark Souers.

This work was performed under the auspices of the U. S. Department of Energy By LLNL under contract number W-7405-ENG-48

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APPENDIX I

The HNS data were for 2.54 cm copper sheathed cylinders. The detonation velocities of Urizar, James and Smith may be used to compute the infinite diameter detonation velocity (D_∞) of HNS, since the D, ρ_0 dependence- and therefore the EOS, is quite similar. From ref. 53 and Table XII the detonation velocity at $\rho = \rho_{\max}(\text{TNT}) = 1.654 \text{ g/cm}^3$ are 7.03 km/s and 7.14 km/s for HNS and TNT, respectively. Their data of $D(\rho_0)$ vs inverse diameter ($1/d$) offers a linear dependence for all densities listed. The data with their derived slopes ($D'[\rho, d^{-1}] = (-d^2 \partial D / \partial d)$) are listed in Table AI. Fitting the slopes to a linear form with d in cm, D in m/s, and ρ in g/cm^3 , we get,

$$D' = a + b \cdot \rho, \text{ with } a = -735 \text{ cm} \cdot \text{m/s}, \text{ and } b = 414 \text{ cm}^4 \cdot \text{m/g.s.} \quad (\text{A1})$$

TABLE AI: Urizar's TNT detonation velocities vs. charge diameter at the listed densities.

$1/d$ cm^{-1}	$D-D_\infty$ m/s	$1/d$ cm^{-1}	$D-D_\infty$ m/s	$1/d$ cm^{-1}	$D-D_\infty$ m/s	$1/d$ cm^{-1}	$D-D_\infty$ m/s
$\rho_0 = 0.9009 \text{ g/cm}^3$		$\rho_0 = 1.0511 \text{ g/cm}^3$		$\rho_0 = 1.2008 \text{ g/cm}^3$		$\rho_0 = 1.3005 \text{ g/cm}^3$	
0.51256	-157.10	0.51256	-170.50	0.51177	-131.20	0.52493	-117.80
0.38417	-112.00	0.38417	-119.90	0.38388	-101.70	0.38388	-91.800
0.25602	-80.700	0.25602	-89.200	0.25589	-76.400	0.38388	-92.100
0.12801	-30.900	0.12801	-42.100	0.12796	-37.900	0.25589	-65.900
0.	0.	0.	0.	0.	0.	0.25589	-62.400
						0.12796	-27.800
						0.12794	-35.600
						0.	0.
$1/d$ cm^{-1}	$D-D_\infty$ m/s	$1/d$ cm^{-1}	$D-D_\infty$ m/s	$1/d$ cm^{-1}	$D-D_\infty$ m/s	$1/d$ cm^{-1}	$D-D_\infty$ m/s
$\rho_0 = 1.4470 \text{ g/cm}^3$		$\rho_0 = 1.5342 \text{ g/cm}^3$		$\rho_0 = 1.5695 \text{ g/cm}^3$		$\rho_0 = 1.6359 \text{ g/cm}^3$	
0.51256	-83.500	0.51256	-29.700	0.51256	-32.400	0.51256	-15.200
0.51256	-85.800	0.38417	-40.600	0.38417	-24.000	0.38417	-13.600
0.38417	-67.000	0.25602	-20.400	0.25602	-15.100	0.25582	-9.7000
0.38417	-58.800	0.12799	-19.000	0.12794	-17.300	0.12783	-6.8001
0.25589	-42.600	0.	0.	0.	0.	0.	0.
0.25602	-40.800						
0.12794	-17.800						
0.12783	-14.900						
0.	0.						

Table AII lists the density dependence of the slopes, the detonation velocities of the 2.54 diameter cylinders as well as D_{∞} and the % deviation from theory before and after correcting to D_{∞} .

TABLE AII: Detonation velocities of TNT and HNS & deviations from theory before (ΔD) and after (ΔD_{∞}) correcting to D_{∞}

ρ_{TNT} g/cm ³	$D'_{\text{TNT}}(d^{-1})$ cm·m/s	ρ_{HNS} g/cm ³	D_{HNS} km/s	$D_{\infty\text{HNS}}$ km/s	$\Delta D/D$ HNS %	$\Delta D_{\infty}/D$ HNS %
0.90090	-301.01	1.001	5.10	5.23	3.6	2.0
1.0511	-328.46	1.200	5.74	5.83	2.9	2.2
1.2008	-265.89	1.402	6.34	6.41	3.2	1.3
1.3005	-236.21	1.504	6.70	6.74	2.6	1.1
1.4470	-163.19					
1.5342	-78.165					
1.5695	-64.822					
1.6359	-33.259					

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