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TITLE: EQUATION OF STATE FOR THE DETONATION PRODUCTS OF SEVERAL SIMPLE EXPLOSIVES

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EQUATION OF STATE FOR THE DETONATION PRODUCTS OF SEVERAL SIMPLE EXPLOSIVES

M. S. Shaw, B. L. Holian, and J. D. Johnson

Effective spherical potentials for N_2 O_2, NO, CO, and CO_2 are obtained by fitting to various experimental and calculated quantities. An equation of state for mixtures of these molecules is determined by using ideal mixing and the hard-sphere perturbation theory of Ross.[1] Calculations are then compared with Hugoniot data for $N_2 + O_2$ mixtures and overdriven NO detonations with excellent agreement. Also, the detonation velocities of O_3/O_2 mixtures, NO, TNM, and HNB were calculated and were found to be in very good agreement with experiment.

In previous work,[2,3] we have shown that the configurational part of the Helmholtz free energy for an anisotropic molecular system can be obtained by using an equivalent spherical potential. We have also shown how to obtain that effective potential when the anisotropic potential is known or can be well approximated. We have chosen the Ross[1] procedure to evaluate the configurational free energy, A_c, for the spherical potential because it is both fast and accurate (2% or better in dense fluids). It is based on a variational principle (see, e.g., Mansoori and Canfield[4] and Rosaiah and Stell[5]),

$$A_c \leq A_0 + \frac{N\rho}{2} \int_0^\infty g_0(r)(\phi(r) - \phi_0(r))\, d^3r \quad . \tag{1}$$

That is, the true configurational free energy is bounded from above by the first two terms of the λ expansion perturbation theory of Zwanzig.[6] The reference system configurational free energy, radial distribution function, and pair potential are denoted A_0, g_0, and ϕ_0, respectively. The pair potential for the true system is ϕ. For a hard-sphere reference system, convenient and accurate representations of $g_0(r)$[7] and A_0[8] are known. Ross found that if one added a function $F_{12}(\eta)NkT = -(\eta^4/2 + \eta^2 + \eta/2)NkT$ to Eq. (1), then the free energy for an r^{-12} potential could be well reproduced by minimizing the right-hand side with respect to $\eta = \pi\rho d^3/6$, where d is the hard-sphere radius. He then approximated the radial distribution function for the r^{-12} system by that for the hard-sphere system. This gave

$$A_c \leq A_0 + \frac{\rho N}{2} \int_d^\infty g_0(r,\eta)\phi(r)d^3r + F_{12}(\eta)NkT \quad , \qquad (2)$$

which is then minimized with respect to η. In practice, the Laplace transform[4,7] is used when a simple functional form of $\phi(r)$ is chosen.

The other contributions to the Helmholtz free energy, A, for a single species are well approximated by several simple, separable contributions. (Note that the resulting procedure for obtaining A is essentially that of Ross[9] and Ree.[10] However, the spherical potentials are obtained in a totally different manner.) The translational and rotational degrees of freedom can be separated exactly to give ideal contributions provided the bond lengths are kept constant. (Hindered rotation effects and "collisions" are incorporated in the configurational free energy.) The vibrational degrees of freedom are treated as isolated quantum vibrators. We have shown that this is a very good approximation for nitrogen.[11] McQuarrie[12] is a convenient source for the form of these contributions. Electronic excitations are included using an isolated molecule Saha model.[13] Electronic levels up to about 60,000 cm^{-1} are included. This cutoff will not cause significant truncation errors below around 10,000°K.

We have used ideal mixing for our detonation products EOS. Ideal mixing takes into account the distinguishability of different molecules but assumes the total energy of a configuration of particles is independent of any interchange of particles. This is exact if all pair potentials are identical. For N_2, O_2, NO, and CO, this may be a very good approximation. For CO_2 mixed with any of the above, this may not be as good. However, more accurate mixing theories require cross potentials, i.e., not only ϕ_{aa} and ϕ_{bb} but also ϕ_{ab}. For zero pressure fluid mixtures, a few percent change in the cross potential may lead to a change in sign of excess properties.[28] Also, it is not certain that an accurate mixing theory for spherical potentials is still accurate for effective spherical potentials representing very anisotropic potentials. We intend to look at molecular mixtures with molecular dynamics, but we will continue with ideal mixing until it is clear what works better for molecular mixtures. Equilibrium composition of the detonation products is found by minimizing the Gibbs free energy of the mixture. A slightly modified form of the procedure of White et al.[14,15] was used.

The effective spherical potentials used are given in Table I. The parameters are for an exponential-six potential,

$$\phi(r) = \frac{\varepsilon}{\alpha - 6}\left(6e^{\alpha(1 - r/r^*)} - \alpha\left(\frac{r^*}{r}\right)^6\right) \quad . \tag{3}$$

The determination of the N_2 potential is well described in the previous paper.[3] The O_2 potential was fit directly to the Hugoniot data rather than finding the effective spherical potential that reproduces the nonspherical thermodynamics that fits the Hugoniot. The NO potential was from a fit by Pack[16] to viscosity and virial data. We chose the potential that not only had a good fit to this data but also was "parallel" to the N_2 and O_2 potentials in the repulsive region. Because there is considerable uncertainty in the NO potential, we decreased ε by 5% to get a slightly better fit to the liquid NO detonation velocity. However, the unadjusted potential gave results well within the experimental uncertainty. The CO potential was taken to be identical to that for N_2 since the two are isoelectronic. In addition, this potential gives a Hugoniot that agrees within experimental error with the data of Nellis, et al.[17] at 53.4 kbar and 99.6 kbar. Higher pressure data almost certainly includes some reaction to CO_2 + C and is, therefore, not useful for determining a CO potential. The CO_2 potential is a spherical potential fit to the thermodynamics of a very anisotropic potential. The anisotropic potential is an atom-atom potential with interaction sites only on the oxygens. The well depth, ε; well minimum position, r^*; and O-O separation, ℓ, were taken from a normal density simulation of solid CO_2 by Gibbons and Klein.[18] The steepness parameter α was fit to the cold curve of LeSar and Gordon,[19] whose theory agrees extremely well with the 296°K isotherm measured by Olinger[22] up to 100 kbar. This potential then agrees reasonably well with the CO_2 Hugoniot of Zubarev and Telegin.[21] However, an overall reduction by 10% gives the best fit to the data. The data is so sparse that there is a much greater uncertainty in the CO_2 potential than for N_2 and O_2. New CO_2 Hugoniot data would be very useful.

Results are given primarily in the form of figures comparing with data. First the fits to data are shown and then the comparison with data not used in fitting the potentials. Figure 1 shows our theory for N_2 compared with data. Above 40 GPa new physics such as dissociation, significant excitation of electronic levels, etc. enter in the problem and we have not tried to fit that region. Figure 2 shows our best least squares fit to the O_2 data with a spherical exponential-six potential. Figure 3 compares with reflected shock data and gives very good agreement. Figure 4 compares our theory with the CO_2

data. In Fig. 5 we show the repulsive part of the potentials given in Table I. Note that the parameters are not entirely independent. Therefore, a look at the table alone is not sufficient to order the potentials. Also, the attractive part of the potential makes a fairly small contribution to the thermodynamics in regions of interest to detonation products.

In Figs. 6 and 7, we compare in ρ,V and ρ,E space the Hugoniot for overdriven NO detonations and an equimolar mixture of N_2 and O_2. There is excellent agreement with Schott's[20] data. Where the two Hugoniots cross, the thermodynamic states are identical. The uncertainty in the crossing point is smallest in ρ,E and the calculated crossing is in excellent agreement with the data. Figures 8 and 9 compare with P,u_p data for the same systems. Figure 10 gives u_s,u_p comparisons for overdriven NO detonations. Note that the initial densities are lower than that for the Ramsay and Chiles[26] measurement of the detonation velocity of NO. In Fig. 11 we have the detonation velocity[25] for O_3/O_2 mixtures. Considering the scatter in the data, the agreement is very good. Finally, the detonation velocities and pressures for NO, TNM, and HNB are compared with experiment in Table II. Again the agreement is very good.

We have an equation of state for detonation products that is in very good agreement with experiment for explosives containing some or all of C,N,O and for which there is no solid carbon in the products. We will investigate the EOS for solid carbon, H_2O, and other products in order to extend the capability to the more common CHNO explosives. Also, mixing questions will be addressed using molecular dynamics.

TABLE I

EXPONENTIAL-SIX POTENTIAL PARAMETERS

	α	r^*(Å)	ε/k (°K)
N_2	13.474	4.251	75.0
NO	12.08	3.995	117.1
O_2	13.117	4.110	75.0
CO	13.474	4.251	75.0
CO_2	13.781	4.096	335.0

TABLE II

DETONATION VELOCITIES OF NO,[26] TNM,[15] HNB[27]

Explosive	Formula	ρ_0 (g/cm^3)	D_{expt} (m/s)	P_{expt} (kbar)	D_{calc} (m/s)	P_{calc} (kbar)
Nitric Oxide	NO	1.294	5620±70	100±15	5621	98
TNM	CN_4O_8	1.638	6360	159	6539	158
HNB	$C_6N_6O_{12}$	1.973	9335	400	9405	382

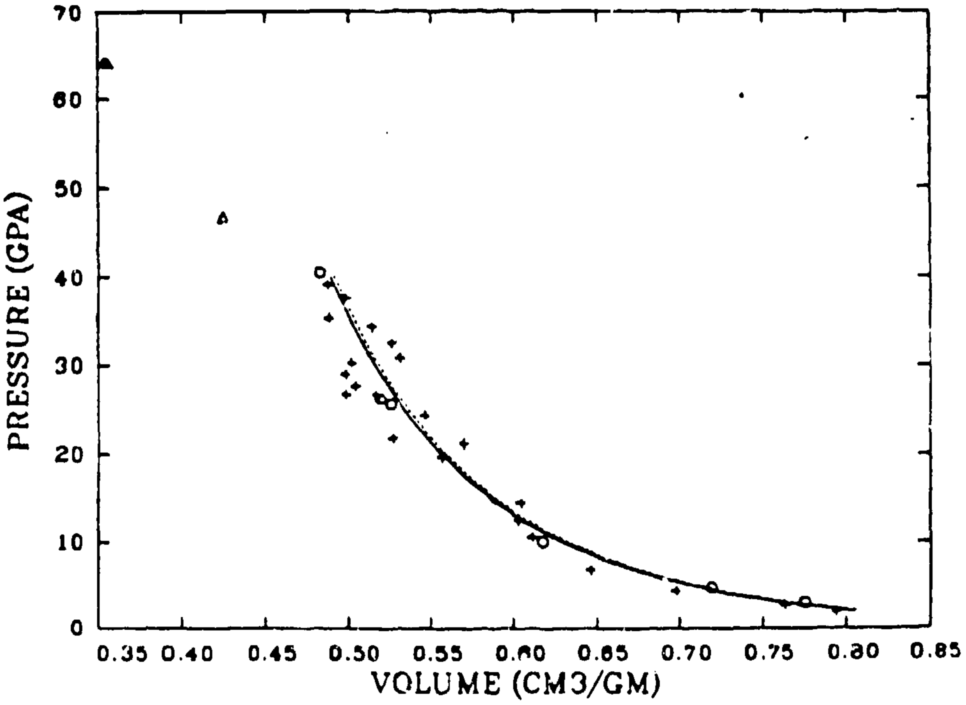

Fig. 1.
Hugoniot for nitrogen. Solid line is the theory with ρ_0 = 0.808 g/cm^3. Dashed line is the theory with ρ_0 = 0.820 g/cm^3. Data are +, LASL Shock Hugoniot Data;[23] o, Zubarev and Telegin;[21] Δ, Nellis and Mitchell.[24]

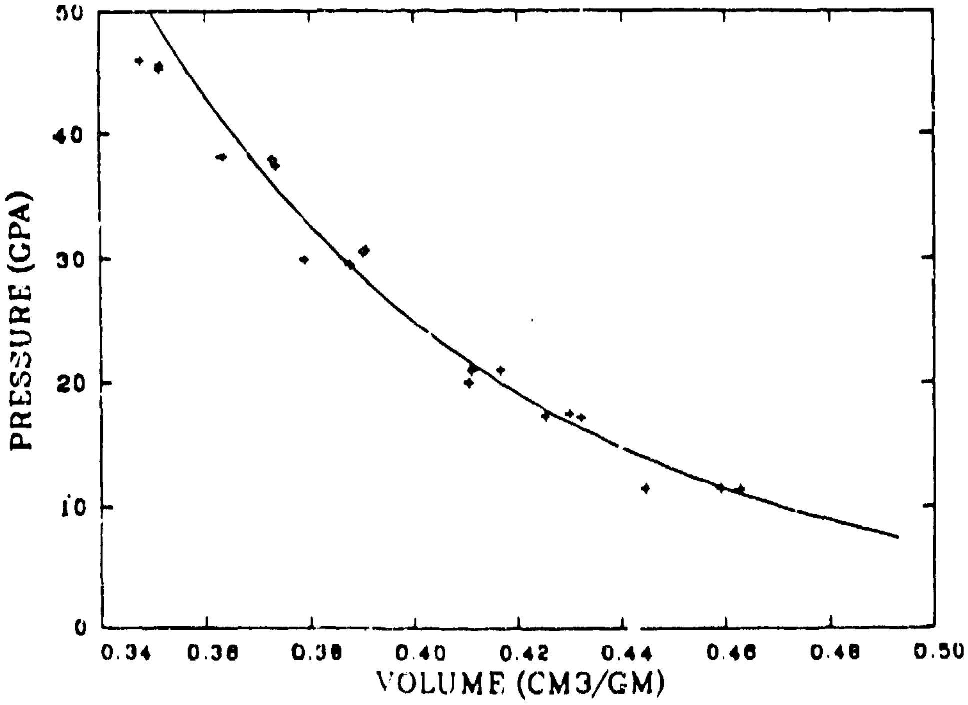

Fig. 2.
Hugoniot for oxygen. Solid line is the present theory. Data are +, LASL Shock Hugoniot Data.[23]

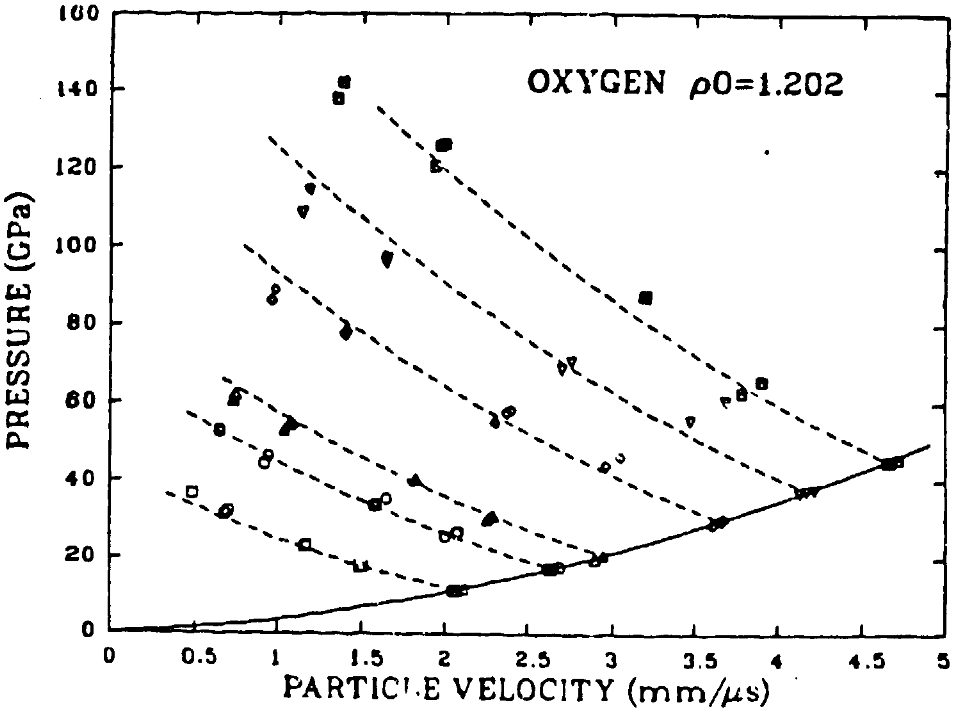

Fig. 3.
Reflected shock for oxygen. Solid line is the principal Hugoniot for the present theory. Dashed lines are the reflected Hugoniots for the present theory. Data are from LASL Shock Hugoniot data[23] with a different symbol for each first shock.

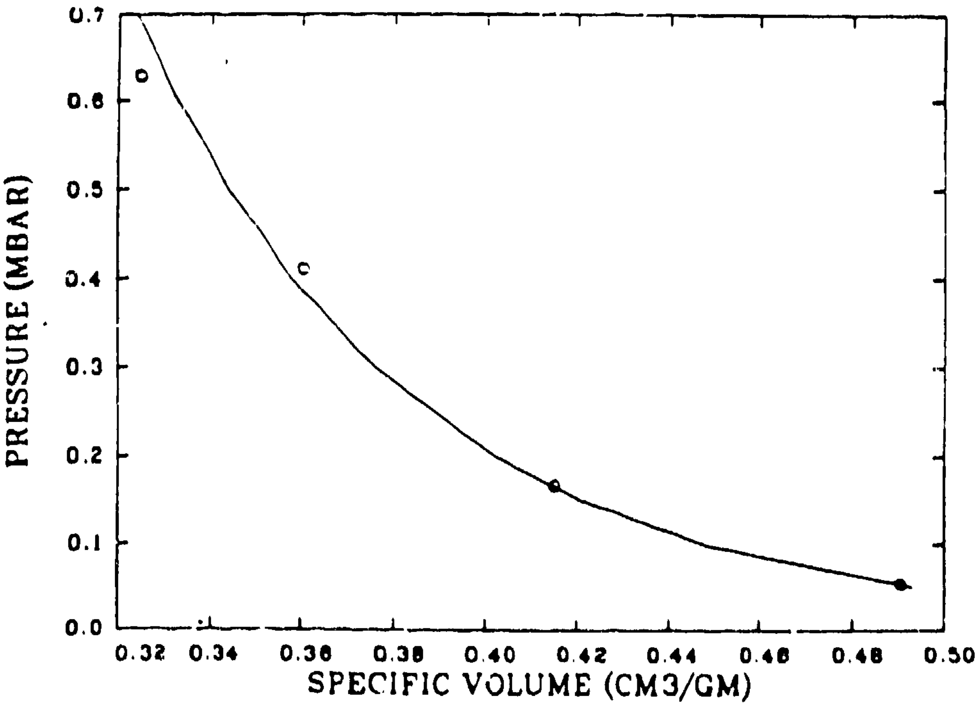

Fig. 4.
Hugoniot for carbon dioxide. Solid line is the present theory. Data are o, Zubarev and Telegin.[21] The initial density is 1.45 g/cm^3.

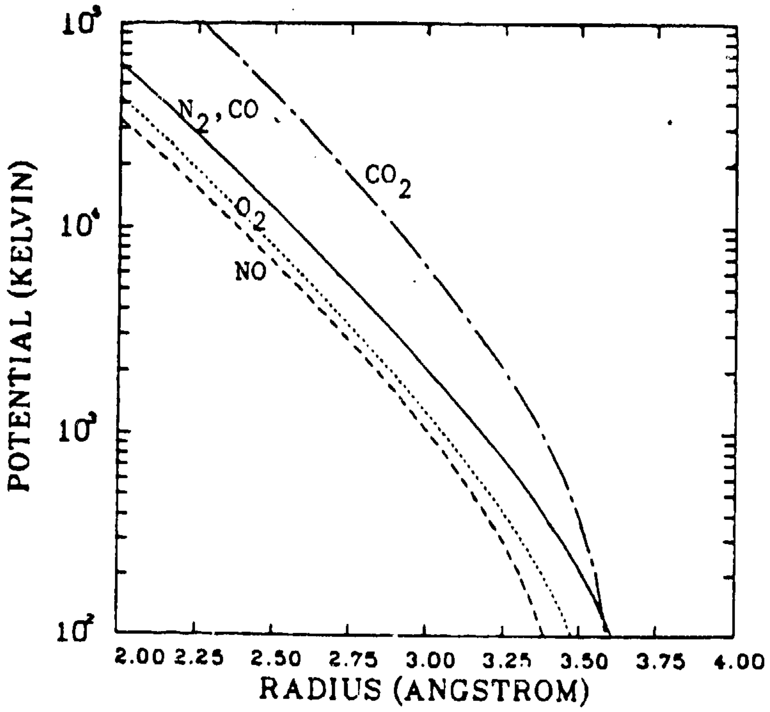

Fig. 5.
Effective spherical potentials. Parameters are given in Table I and the curves are labeled.

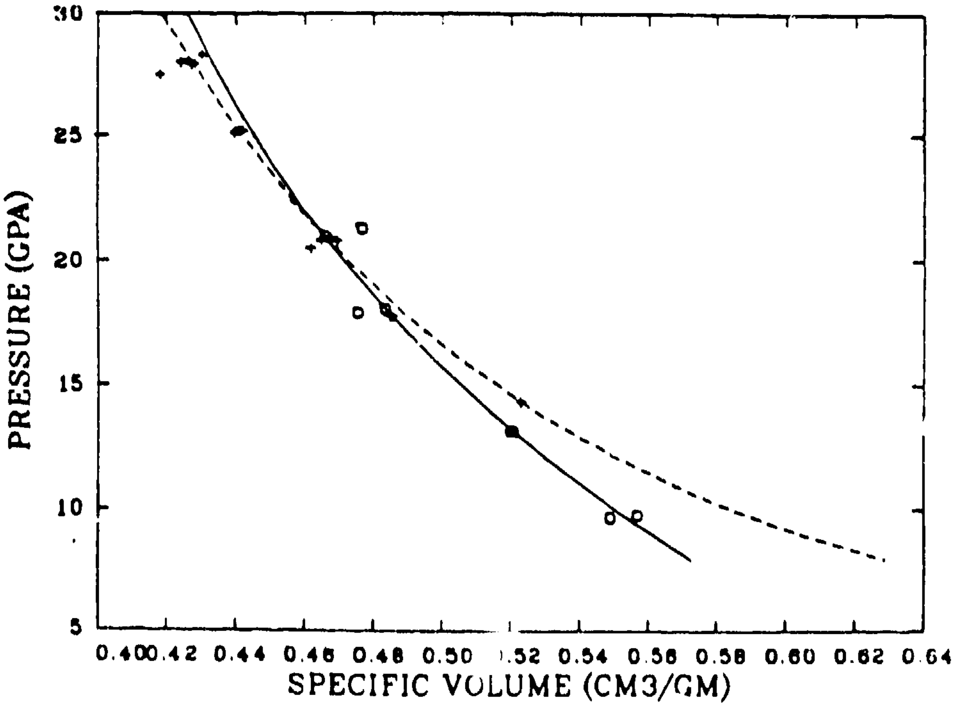

Fig. 6.
Hugoniots for NO and equimolar $N_2 + O_2$. Solid line is the present theory for $N_2 + O_2$ and o is the data from Schott.[20] Dashed line is the theory for overdriven NO and + is the data from Schott.[20]

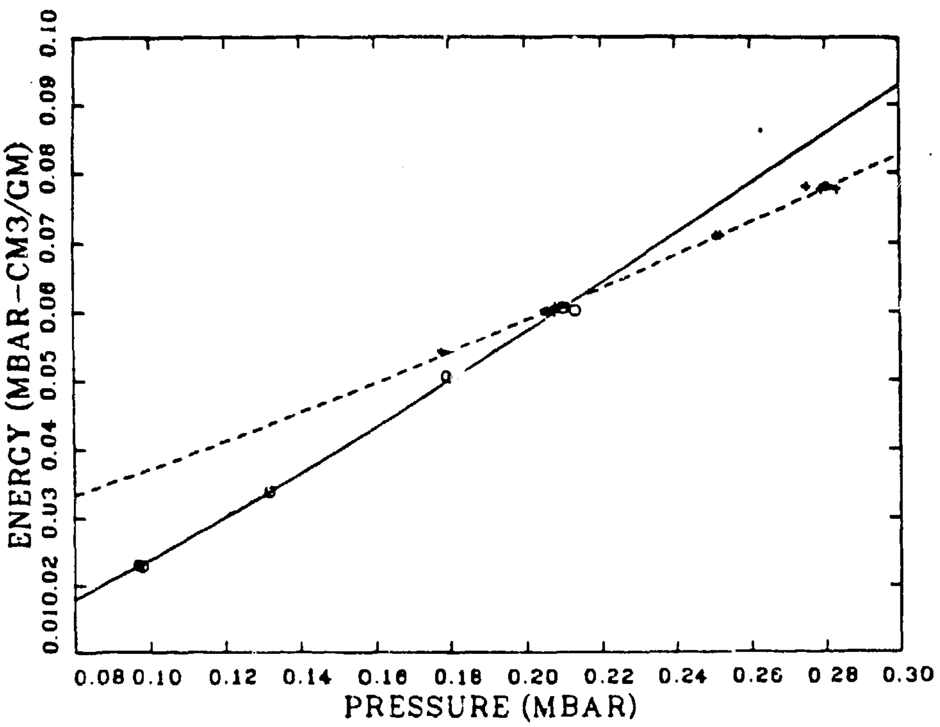

Fig. 7.
Hugoniots for NO and equimolar N_2 + O_2. Solid line is the present theory for N_2 + O_2 and o is the data from Schott.[20] Dashed line is the theory for overdriven NO and + is the data from Schott.[20]

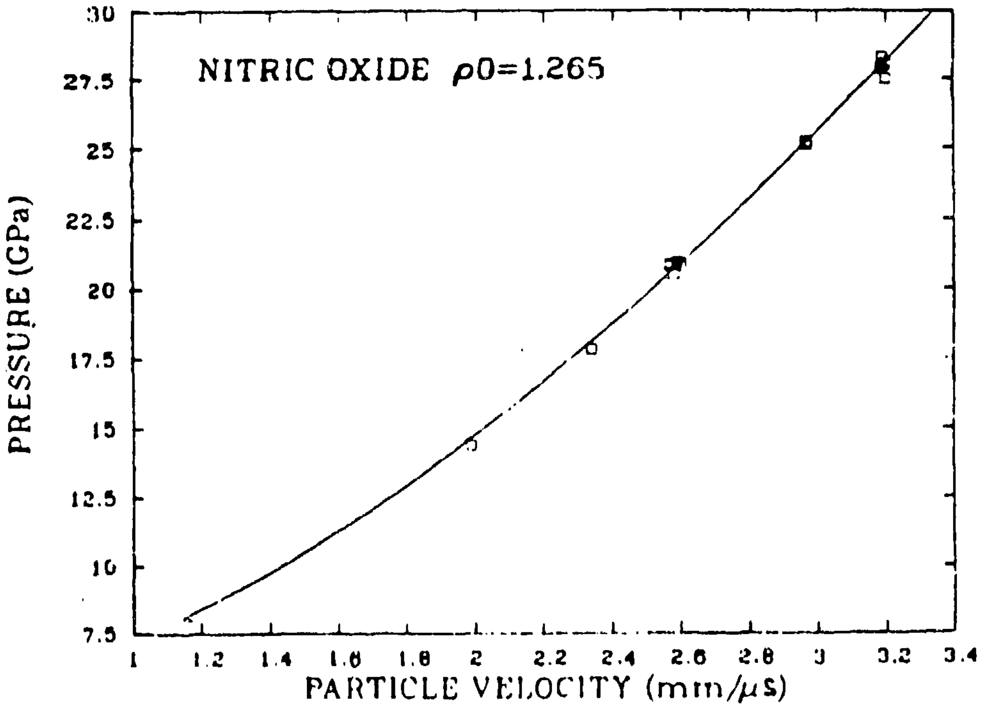

Fig. 8.
Pressure vs particle velocity for NO. Line is present theory. Data are □, Schott.[20]

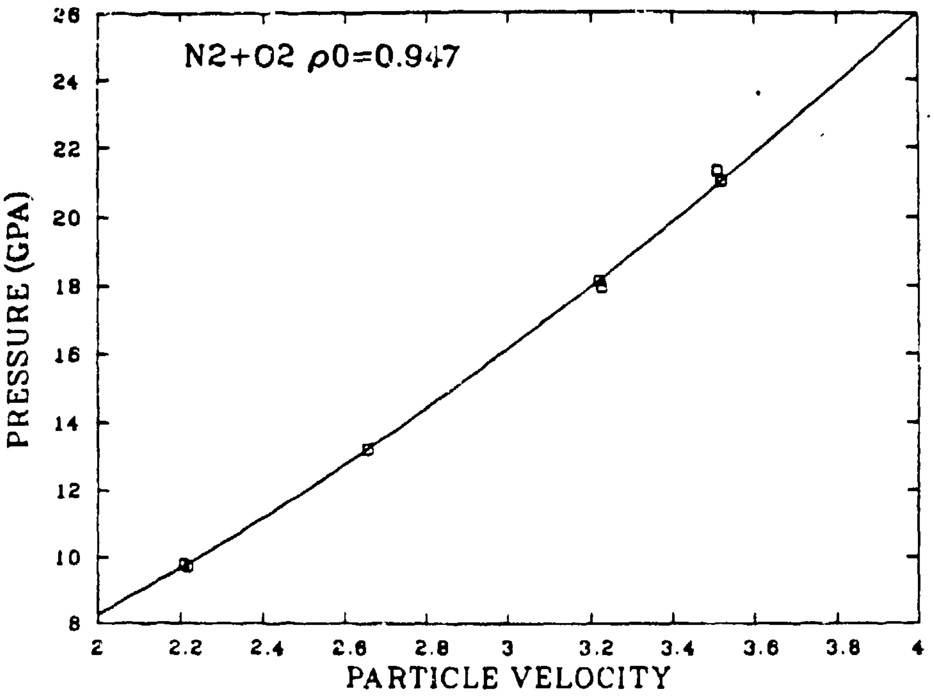

Fig. 9.
Pressure vs particle velocity for equimolar $N_2 + O_2$. Line is present theory. Data are □, Schott.[20]

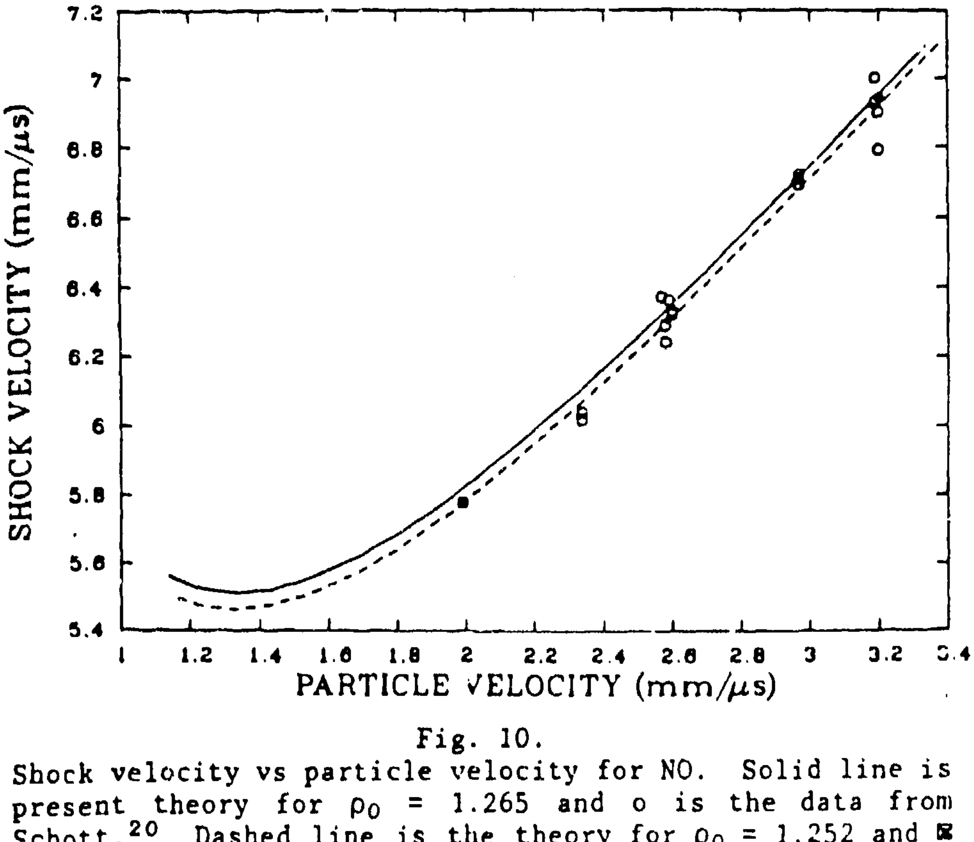

Fig. 10.
Shock velocity vs particle velocity for NO. Solid line is present theory for ρ_0 = 1.265 and o is the data from Schott.[20] Dashed line is the theory for ρ_0 = 1.252 and ☒ is the data from Schott.[20]

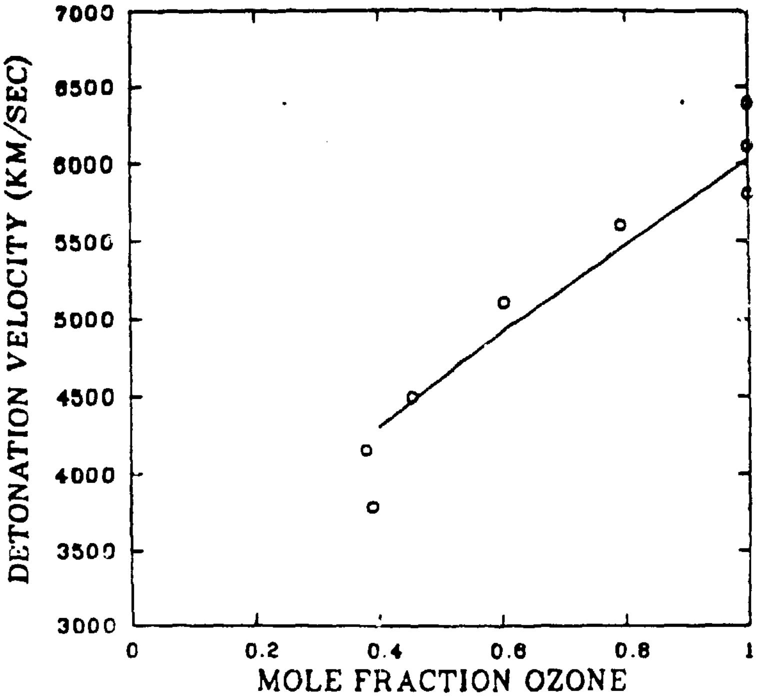

Fig. 11.

Detonation velocity of O_3/O_2 mixtures. Solid line is the present theory. Data are o, Miller.[25]

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