THEORETICAL COMPUTATIONS OF PERFORMANCE PARAMETERS OF AMMONIUM NITRATE FUEL-OIL EXPLOSIVE

by

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ABSTRACT

The method used here in computing the detonation parameters of the ammonium nitrate fuel-oil mixture is the approximate method used by F. W. Brown (F. W. Brown, 1957, p. 123). This method appears to be satisfactory only when the explosive is oxygen balanced or slightly oxygen positive. When the explosive is oxygen negative, this method fails completely. The detonation parameters, calculated by the approximate method, continue to show an increase when the fuel-oil ratio is increased which of course is not the case.

To compute these parameters for oxygen balanced or oxygen positive mixtures, I have the following steps

1 - The Oxygen Balance Δ

For convenience I take 100 gm of explosive and calculate N_0, H_0, C_0, and O_0 which are the moles of nitrogen, hydrogen, carbon and oxygen in the original explosive. Also I assume that all the carbon goes to carbon dioxide and

that all the hydrogen goes to water, in case of oxygen-balanced explosives.

Then $\Delta = O_0 - 2C_0 - H_0/2$

2 - Gaseous Products

Computing N_0, C_0, and O_0 moles/wt of explosive, we can get the moles of $(CO_2) = C_0$ moles/wt of explosive

" " " $(H_2O) = H_0/2$ " " "

" " " $(N_2) = N_0/2$ " " "

Adding all these together, we get the total moles per the weight of the explosive, from which we can get the moles per one gram of the explosive.

3 - Heat of Explosion Q_E

$$Q_E = U_E - U_0$$

where U_E is the sum of the products of the moles of each gaseous product, multiplied by its heat of formation, and U_0 is the sum of the products of the moles of each original constituent, multiplied by its heat of formation.

$U = \Sigma\, n \cdot H$

n = Number of moles

H = Heat of formation

4 - Temperature of Explosion T_E

$$Q_E = \int_{T_0}^{T_E} C_V \, dT$$

Using Table (3) for the internal energies of gases at different temperatures, we can try a few temperatures and interpolate to obtain a temperature that would satisfy the above equation, i.e., to get a temperature at which Q is very close to Q_E. This temperature would be the right temperature of explosion.

5 - The Value (b_1/V_E)

b_1 is very close to b_E, so we shall use b_1 instead of b_E.

From Table (4) b_E can be calculated $b_E = \sum_1 n_i b_i$

V_E is supposed to be equal to V_0 or the density of the original explosive

6 - The Value λ_1

Using the differences in Table (3)

$$\frac{E_{T_2} - E_{T_1}}{T_2 - T_1} = C_V$$

$$C_V = \frac{C_V}{n}$$

and $$\lambda_E = \lambda_1 = 1 + \frac{R}{C_V}$$

Knowing (b_1/V_E) and λ we can interpolate in tables 5, 6, and 7 to find K, L, and M.

Getting all these values, we can calculate T_1, D, and P_1 using the following equations

$$T_1 = \frac{2\ \lambda_1}{\lambda_1 + 1}\ T_E \cdot L$$

$$D = 91.22\ \frac{\lambda_1 + 1}{\sqrt{\lambda_1}}\ \sqrt{N_1 T_1} \cdot K$$

$$P_1 = 0.009869\ D^2\ \rho_o\left[\frac{1}{\lambda_1 + 1}\right] \cdot M$$

In calculating these parameters in a 10 percent oil mixture, where the oxygen deficiency is about 1 mole per 100 gm of the mixture, a simple method to correct the gaseous products is used. The presence of carbon monoxide and hydrogen gases produced among the gaseous products is taken into consideration, other gases found in minute quantities, such as methane and nitrous gases are ignored. In this simple method, one equilibrium constant only is used. The results are close to those computed by the exact method used by Cook.

ACKNOWLEDGMENT

In preparing this thesis, I have drawn freely from numerous sources in literature on explosives published by many, to all of whom, but particularly to F. W. Brown and J. Taylor, my debt is great.

To all who helped me in preparing this thesis, I extend my most sincere thanks and appreciation.

CONTENTS

ILLUSTRATIONS

INTRODUCTION

Ammonium nitrate (AN) as an explosive has become one of the most interesting and profitable fields of study for the mining industry. Although AN is not considered as an explosive by itself, it is an important ingredient of many commercial explosives, often comprising 75 to 90 percent, because of its lower price; and moreover it produces a larger volume of gas upon detonation than any other explosive material commonly used.

AN has been used as an explosive by mixing it with carbon black, sulfur, sawdust, or other such combustibles to form more gas from excess oxygen available in the AN decomposition reaction. When this type of explosive is detonated, the speed of detonation is approximately that of AN by itself (2000 m/s).

When AN is mixed with fuel-oil (F.O.), approximately

6 percent by weight, the decomposition reaction is much stronger (4000 m/s), due to the fact that F.O. penetrates the grains of the AN, especially the prilled type through which the F.O. is distributed uniformly (Cook, 1958, p. 135).

AN-F.O. mixture has been adopted as a low-cost efficient blasting agent by a wide variety of mining and heavy-construction operations. Moreover, ready availability of the component supplies and ease of their formulation into effective blasting agents have made it possible for the blaster himself to prepare the mixes at the site of use. Although AN-F.O. mixture has partly displaced explosives such as dynamites in some applications, there are other blasting operations, where AN-F.O. mixture does not appear to be well-adapted.

When AN-F.O. mixture is initiated by an efficient booster, the mixture undergoes chemical decomposition at a rapid rate and produces gaseous products at very high pressure and temperature, capable of doing work by expansion. The energy and gaseous products are derived from exothermic rearrangements between oxygen, carbon, and nitrogen atoms.

The following reaction takes place with great rapidity and violence when AN detonates; in other words, under the

influence of extreme heating under confinement, or through initiation by a powerful priming explosive charge (Encyclopedia of Chemical Technology, 1947, p. 819).

$$2\ NH_4NO_3 = 2\ N_2 + 4\ H_2O + O_2$$

There is no well-known fixed chemical formula for the fuel-oil diesel No. 2. This fuel-oil is composed of three hydrocarbon compounds: aromatic 15 percent, naphthenic 32 percent, paraffinic 53 percent. The chemical formula of the paraffins, for example, is C_nH_{2n+2}, and (n) can be any number; therefore fixed formula is impossible. Dr. Clark (Bruzewski & Clark, 1959, p. 175) has used the simple formula (CH_2) for the fuel-oil in his calculations, apparently because any complicated formula is roughly a multiple of this simple one. I prefer to use the formula of Decane ($C_{10}H_{22}$), because Decane is a liquid and not a gas, and it is little denser than the kerosene. This choice will make little difference in the results, due to the differences in the heat of formations of the two compounds. Because the heat of formation of the Decane is 82 k cal/mole at 0° C, the heat of formation of (CH_2) is about 0 or $\pm$ 24 k cal/mole at the same temperature.

If there is enough oxygen to oxidize the carbon to carbon dioxide, and the hydrogen to water, the explosive is said to be oxygen balanced; otherwise it is oxygen negative or oxygen positive, depending on the amount of oxygen needed for that purpose.

DETONATION

Detonation is a process by which the explosive undergoes chemical reaction within a peculiar type of shock called the detonation wave. The detonation wave propagates through the explosive, supported and reinforced by the chemical reaction at a velocity ranging from 1 to 5 miles/sec (Clark, Some detonation properties of AN, Univ. of Miss., Sch. of Min. Bull., Tech., series No. 98), depending on the chemical reaction and the physical nature of the explosive. In general, detonation waves travel through a column of explosive at a constant speed, determined (through the thermodynamic laws) by the chemical energy released in detonation, the rate at which this energy is released, the density of the explosive, and the charge diameter.

The so-called ideal detonation corresponds to the theoretical maximum or hydrodynamic value D*; practically

it is the steady value attained at a sufficiently long distance from the initiator in a charge having a diameter sufficiently large that further increase in either length or diameter will not cause an increase in velocity.

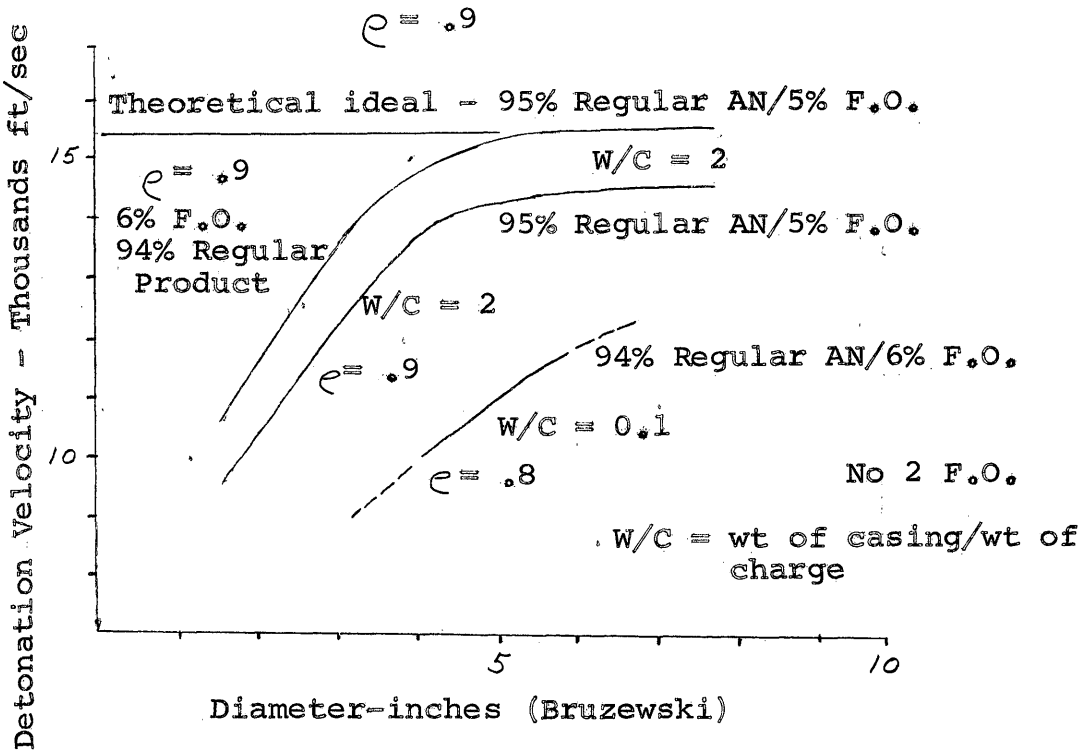
The velocity of ideal detonation is completely determined by the thermohydrodynamics of the explosive and its chemical composition; all quantities are calculable through the thermodynamic theory and an appropriate equation of state.

The non-ideal detonation is, however, steady and stable under the particular conditions (charge diameter and confinement) where it is observed.

In cylindrical charges between the critical diameter d_c, below which steady detonation will not propagate, and the minimum diameter d_m for ideal detonation, one observes in general velocity-diameter curves which increase steadily with diameter (Fig. 1 and 2).

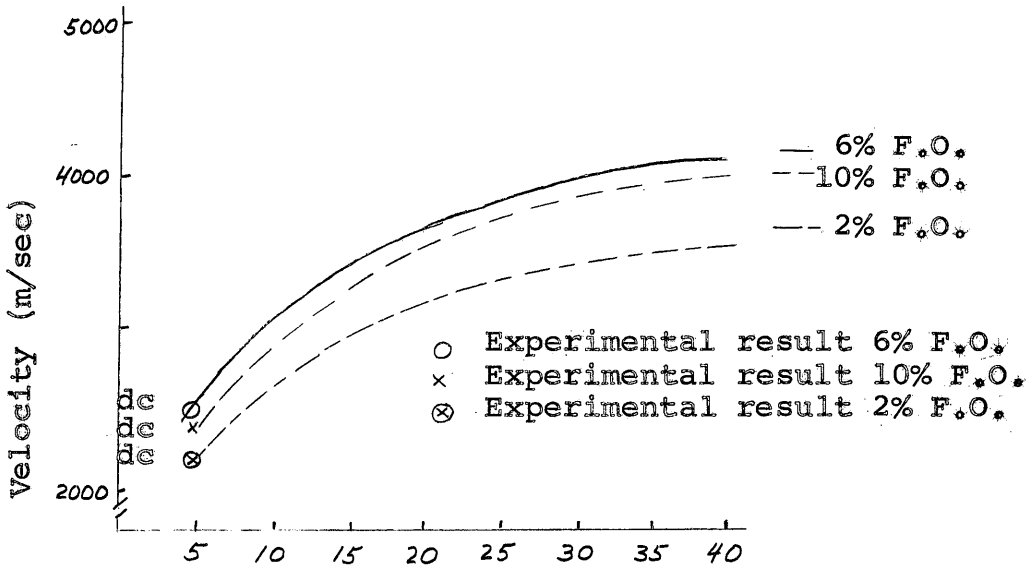
For many high explosives, particularly those which are fine-grained, the detonation velocity increases linearly with increase in loading density. For coarse-grained materials such as AN, the relationship does not appear to be linear, especially for charges smaller than the unconfined

Fig. 1



Influence of charge diameter on detonation velocity

Fig. 2



Diameter-inches (Cook)

Charge diameter-velocity curves for prilled AN-F.O. explosives

Calculated corresponding to the lower curve in Fig. 1

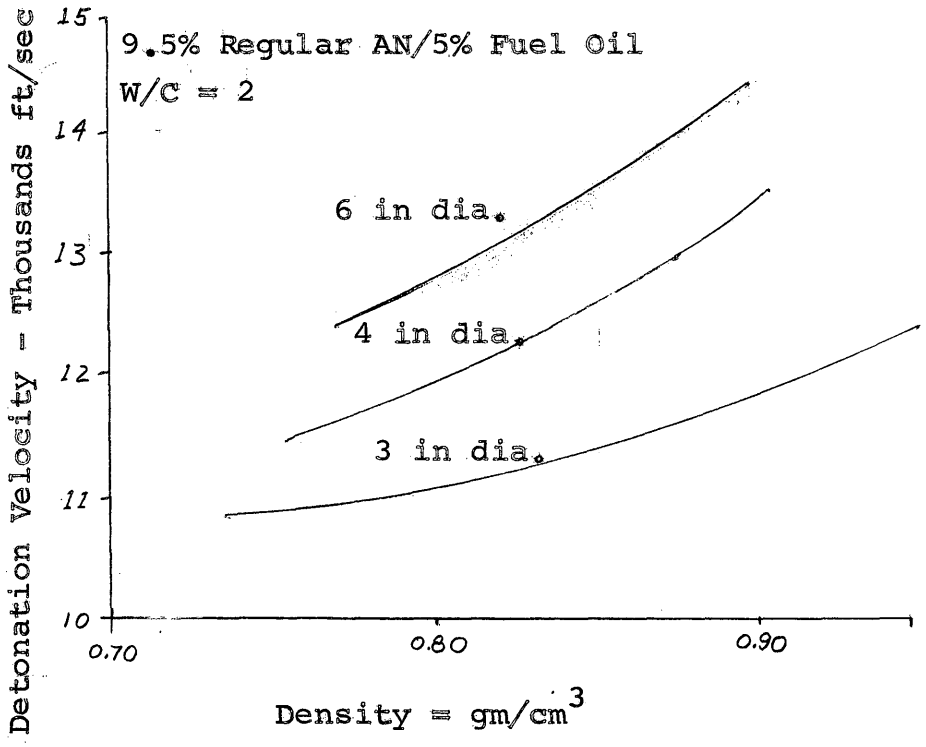
critical diameter (Fig. 3). Mixtures of AN and aluminum in small diameter charges, for example, show a nonlinear increase, and at a certain critical density the detonation velocity decreases and finally dies out with further increase in density (Fig. 4). For prilled AN it appears that it may follow a somewhat similar behavior for higher loading densities.

The influence of F.O. content on the detonation velocity is shown in figures 5 and 6. The general shape of the curves are very nearly parallel to the theoretical ideal velocity curves. An important fact shown by these curves is that the curves drop more quickly by decreasing the F.O. content, more than increasing the F.O. content.

Particle size and particle-size distribution play an important part in the sensitivity and rate of detonation of condensed explosives, particularly those which have an absolute reaction rate of the order of that of AN and in which the grain size is normally greater than 20 or 30 mesh. Figure 7 shows the relation between the particle size and the detonation velocity.

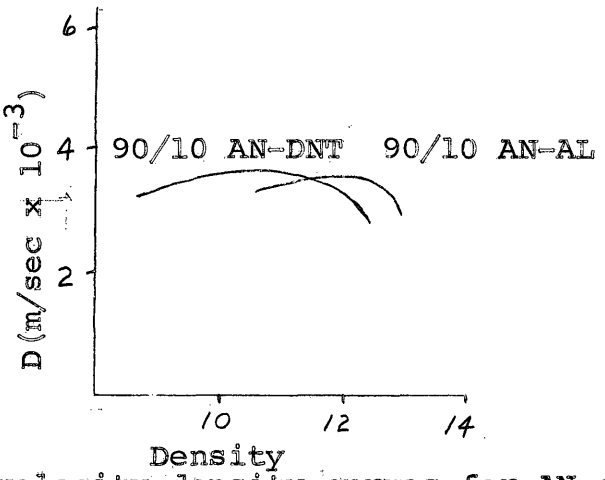
Maximum detonation velocity is achieved at 0.5 percent coating, whatever the type of coating may be. As more

Fig. 3
(Bruzewski)



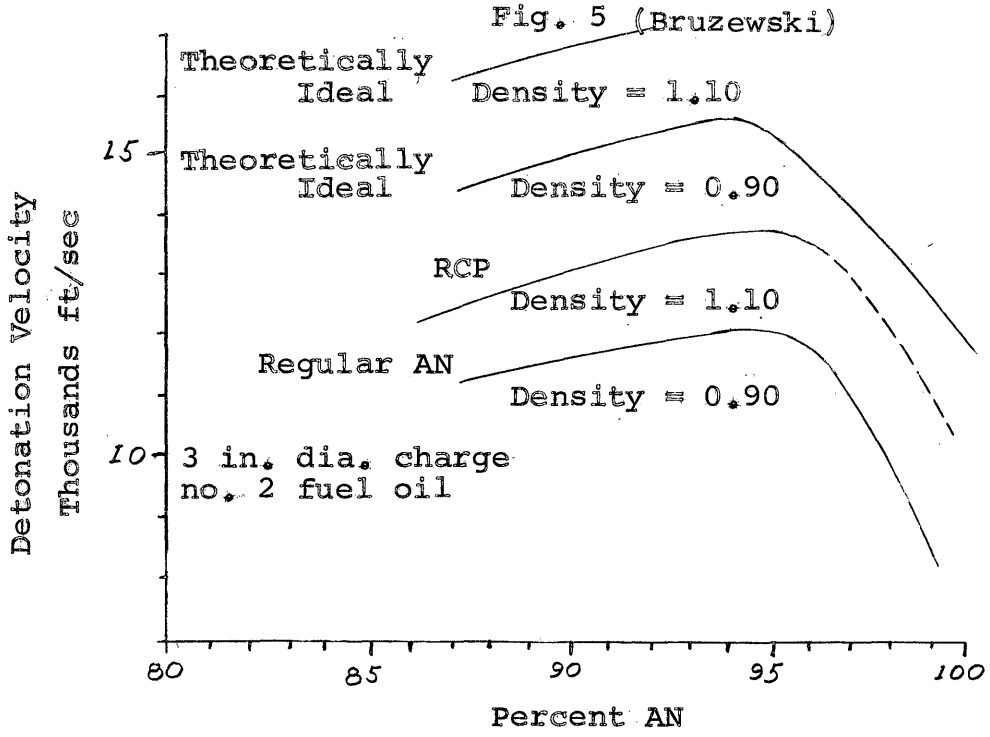
Influence of charge density upon detonation velocity

Fig. 4



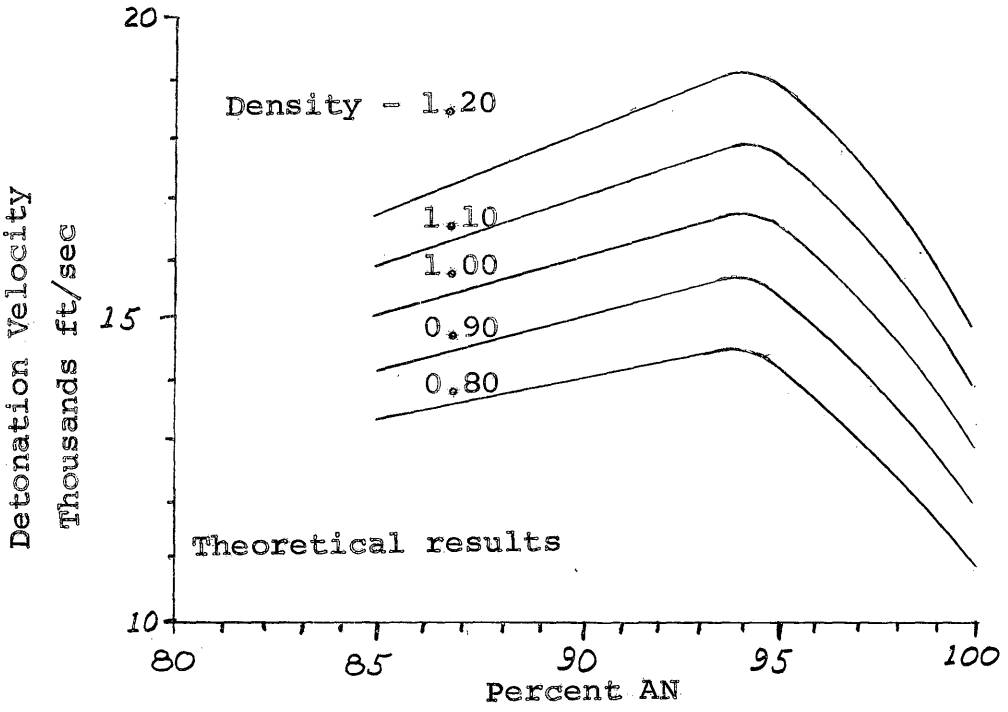
Typical velocity density curves for AN-combustible mixtures in small diameters (-65 + 100 mesh AN; D = 10 cm) (Cook)

Fig. 5 (Bruzewski)



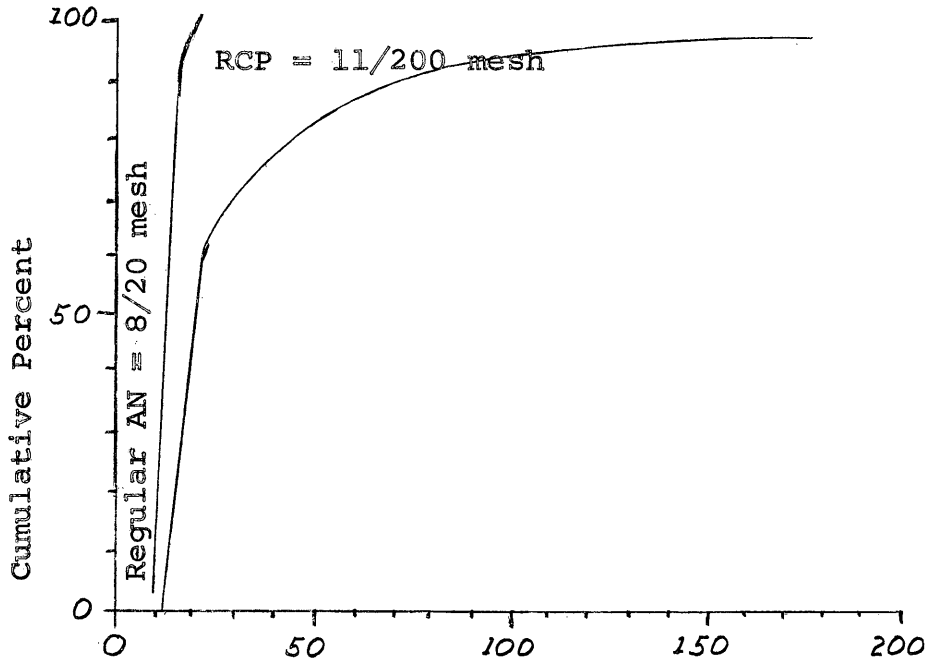
Influence of oil content upon detonation velocity (Bruzewski)

Fig. 6



Influence of oil content upon detonation velocity
(Bruzewski)

Fig. 7

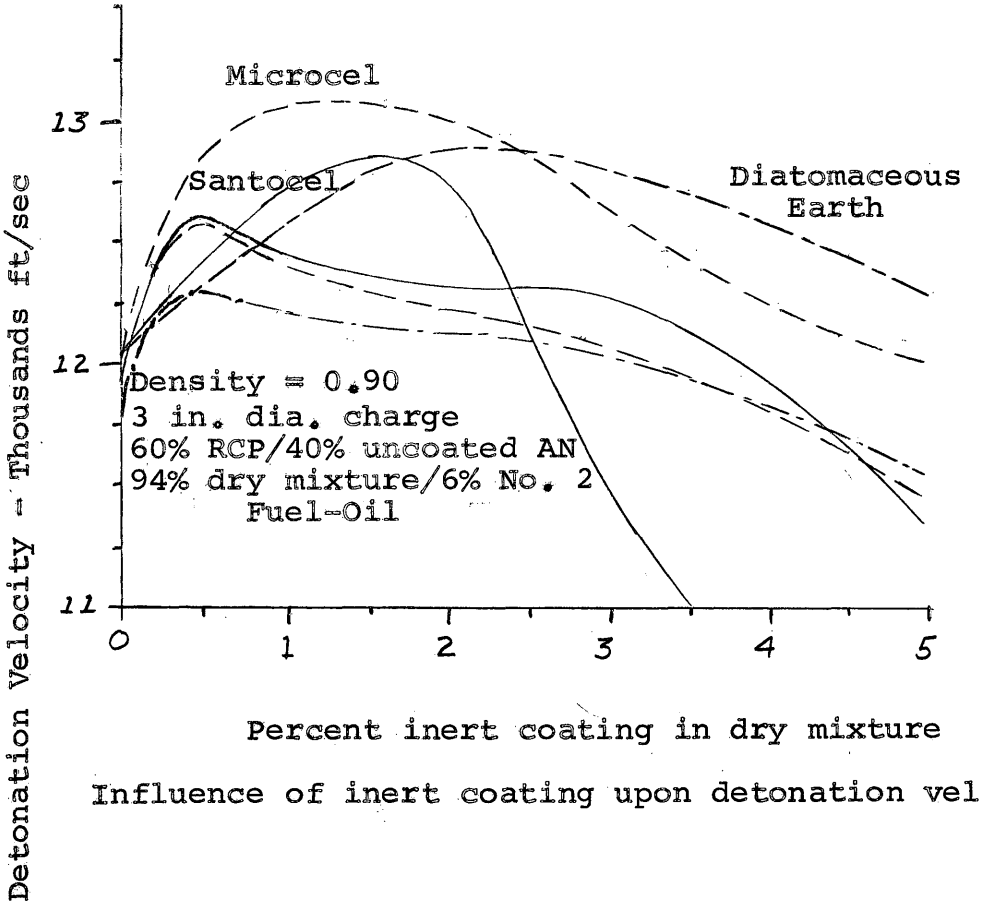

100
50
0
Cumulative Percent
RCP = 11/200 mesh
Regular AN = 8/20 mesh
0
50
100
150
200
Particle size distribution (Bruzewski)

coating agent is added, more oil is held at the surface, and consequently the reaction is damped slightly due to lack of penetration into the prill (Fig. 8).

Since AN is highly hygroscopic and very soluble in water, the amount of moisture contained in an AN explosive mixture has a marked effect on its performance (Fig. 9).

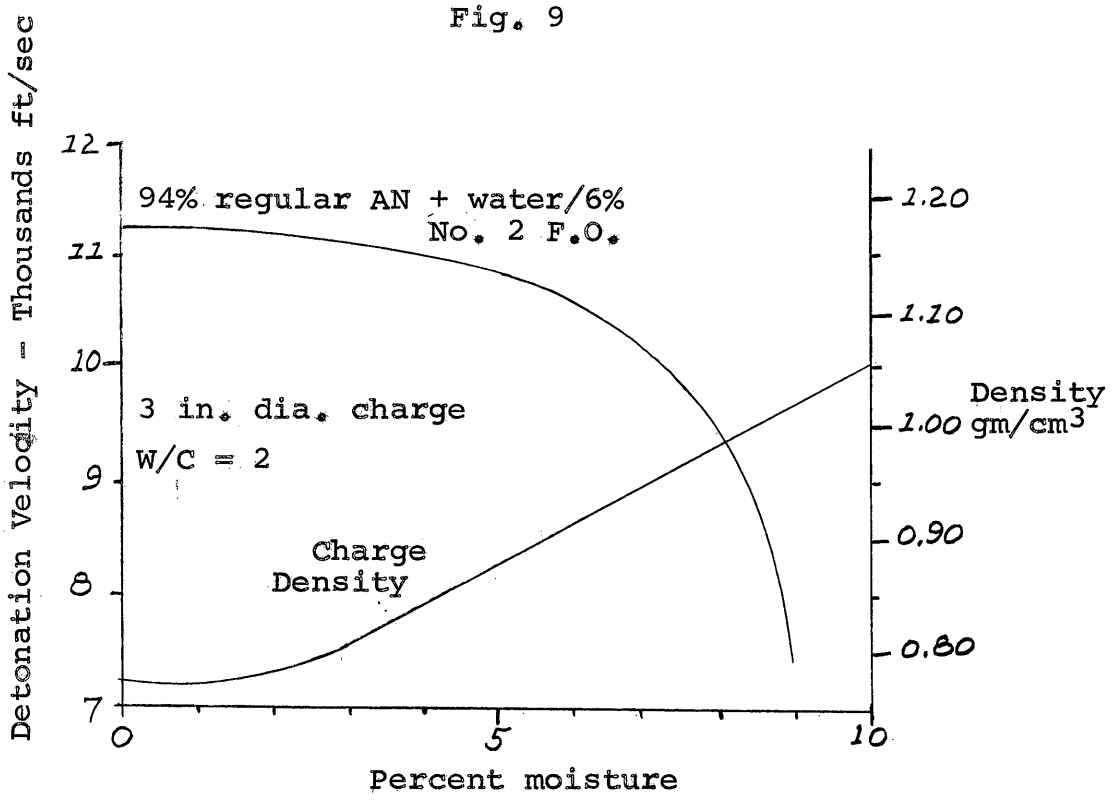
Figure 10 shows the relation between the detonation velocity and the distance from the booster. In an AN-FO mixture, the booster, if large enough, may push the detonation velocity of the AN more than usual; then the detonation velocity of the mixture establishes again to its own detonation velocity.

Fig. 8
(Bruzewski)



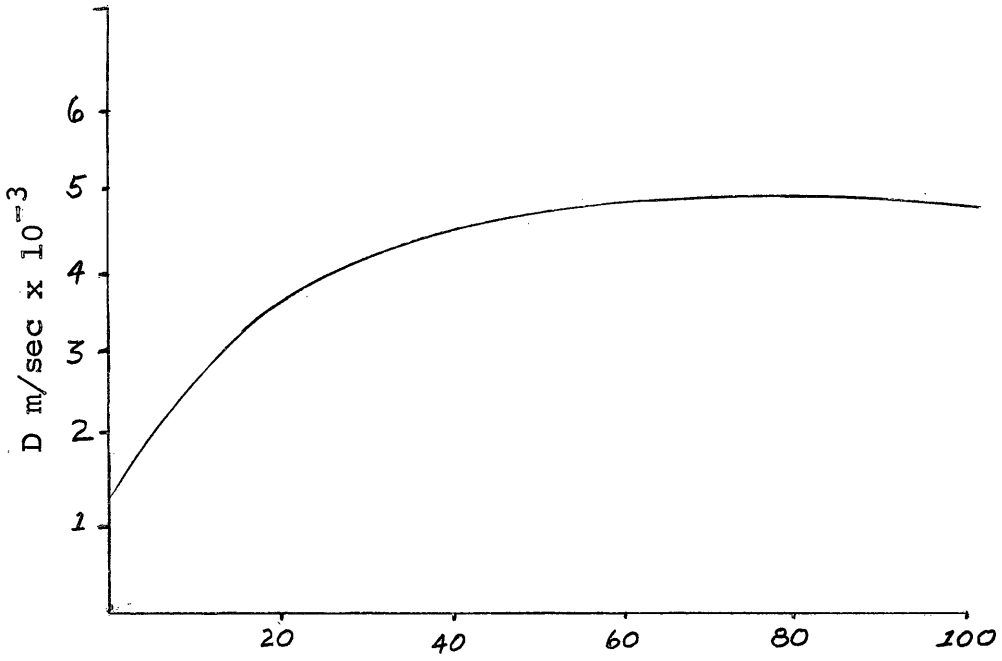
Influence of inert coating upon detonation velocity

Fig. 9



Influence of moisture content upon detonation velocity
(Bruzewski)

Fig. 10



(Cook)

Velocity-distance relations in 80/20 AN/TNT

DETONATION PHENOMENA

Eyring (1959, p. 69) said:

> At the high temperature inside a detonating explosive, the chemical reaction is much too fast to be studied directly. For a large class of phenomena, this does not matter; all that needs to be known is the composition of the detonation products. With only this knowledge and with the aid of thermodynamic and hydrodynamic theory, the detonation velocity and the pressure of the gaseous products can be calculated.

As previously mentioned, things affect the value of the detonation velocity, such as the density of the explosive, the type of booster, the confinement, the diameter of the charge, the grain size, and the type of coating. All these involve the reaction rate; but in my calculations, I use Brown's approximate method of computation which gives ideal values.

The development of the theory of detonation velocity breaks into two parts. The first part gives the relation between the pressure and the volume in a wave which propagates unchanged in type. This pressure-volume relation is

commonly known as the Rankine-Hugniot relation.

$$E_1 - E_0 = 1/2\ (P_1 - P_0)\ (V_0 - V_1) \qquad (1)\ \text{Appendix (3)}$$

This relation can be written in the form

$$E_1 - E_2 = \frac{N_1\ R\ T_1}{2\ K_1} \qquad (2)\ \text{Appendix (7)}$$

The second part of the theory of detonation velocity, relates the detonation velocity to the sonic velocity behind the detonation wave. This relation is called the Chapman-Jouguet condition.

$$\text{CJ-Condition } D = W_1 + C \qquad (3)$$

Where C is the velocity of sound in the gaseous products

$$C = \sqrt{\frac{dP}{d\rho}} \qquad \text{Appendix (8)}$$

The Molar Heat Capacity of a Gas

When a quantity of heat q_v is delivered to a gas under condition of constant volume, it may change the internal energy of the gas by the amount $E_1 - E_0$; therefore the molar heat capacity C_V is given by

$$C_V = \frac{q_v}{T_1 - T_0} = \frac{E_1 - E_0}{T_1 - T_0}$$

$$\text{or}\quad C_V\ (T_1 - T_0) = E_1 - E_0$$

Where the energy to maintain a stable shock wave is furnished by a chemical reaction, the quantity of heat Q_1

liberated by the reaction must be taken into consideration; therefore the energy equation becomes

$$E_1 - E_0 = C_V (T_1 - T_0) - Q_1 \qquad (4)$$

from (1) and (4)

$$C_V(T_1 - T_0) = 1/2 \ (P_1 - P_0)(V_0 - V_1) + Q_1 \qquad (5)$$

from (5) and (4)

$$V_1 = \frac{K_1 V_0 + \alpha}{K_1 + 1}$$

where $K_1 = 1 + \frac{N_1 R}{C_V} - \frac{d\alpha}{dV}$ Appendix (5)

THE EQUATION OF STATE OF THE PRODUCTS OF EXPLOSIONS

A gas law of the following form is used

$$PV = NRT\ f$$

where f depends on the volume and the gas composition. Its dependence on temperatures is ignored because it is sufficiently accurate law at high pressure and temperature.

$$f = 1 + b/v + 0.625(b/v)^2 + 0.2869(b/v)^3 + 0.193(b/v)^4$$

where b is the second virial coefficient and applies to single compounds.

The second virial coefficient of the gaseous mixture can be defined as

$$b = \Sigma_i\ n_i b_i$$

without excessive errors, where n_i is the number of moles of the i-th molecular species and b_i is the molar coefficient of that species.

The simple Abel equation of state with the covolume α is also used

$$P\ (V - \alpha) = NRT$$

$$\text{or}\quad 1 - \frac{\alpha}{v} = \frac{NRT}{PV}$$

$$\text{also}\quad \frac{1}{f} = \frac{NRT}{PV}$$

$$\text{then}\quad 1 - \frac{\alpha}{V} = \frac{1}{f}$$

$$\text{or}\quad \frac{\alpha}{V} = 1 - \frac{1}{f}$$

$$\text{and}\quad \frac{d\alpha}{dV} = 1 - \frac{1}{f} - \frac{b}{V}\ \frac{1}{f^2}\ \frac{df}{d(b/v)}$$

$$= \frac{\alpha}{V} - \frac{b}{V}\ \frac{1}{f^2}\ \frac{df}{d(b/v)}$$

VELOCITY OF DETONATION

$$D = V_0 \sqrt{\frac{P_1 - P_0}{V_0 - V_1}} \qquad \text{Appendix (2) - 4A} \tag{9}$$

$$= \frac{V_0}{V_0 - V_1} \sqrt{(P_1 - P_0)(V_0 - V_1)}$$

$$= \frac{V_0}{V_0 - V_1} \sqrt{\frac{N_1 R T_1}{K_1}} \qquad \text{Appendix (7) - 21A} \tag{10}$$

$$V = \frac{K_1 V_0 - \alpha}{K_1 + 1} \qquad \text{Appendix (6) - 20A}$$

$$\therefore D = \frac{K_1 + 1}{1 - \frac{\alpha}{V_0}} \sqrt{\frac{N_1 R T_1}{K_1}}$$

$$\sim \frac{1}{1 - \frac{\alpha}{V_E}} \cdot \frac{1 + K_1}{\sqrt{K_1}} \sqrt{N_1 R T_1}$$

$$= \sqrt{R} \; \frac{\lambda 1 + 1}{\sqrt{\lambda 1}} \; \sqrt{N_1 R} \cdot K$$

$$\lambda 1 = 1 + \frac{N_1 R}{C_V}$$

$$K_1 = \lambda 1 - \frac{d\alpha}{dV_1} \qquad \text{Appendix (5) - 19A} \qquad (11)$$

$$D = 91.22 \frac{\lambda 1 + 1}{\sqrt{\lambda 1}} \sqrt{N_1 T_1 K} \qquad (12)$$

R = 8.314 Joules/degree/mole

= 8.314 x 1000 dynes/nt/degree/mole

$\sqrt{8,314} = 91.22$

K is a constant to substitute for the differences between $\lambda 1$ and K and the other values.

DETONATION PRESSURE

Detonation pressure is a property of great importance in detonation technology. Its direct measurement cannot be made owing to its transient nature and its exceedingly high magnitude at least in condensed explosives. The detonation pressure is, however, accurately definited by the hydrodynamic equation.

$$P_1 - P_0 = \frac{D^2}{V_0^2} (V_0 - V_1) \qquad (13)$$

P_0 is negligible compared with detonation pressure P_1

$$\therefore P_1 \cong \frac{D^2}{V_0} \left[1 - \frac{V_1}{V_E} \right]$$

$$V_1 = \frac{K_1 V_0 + \alpha}{K_1 + 1}$$

$$P_1 = D^2 \rho_o \left[1 - \frac{K_1 + \frac{1}{V_E}}{K_1 + 1} \right]$$

$$= D^2 \quad \rho_o \left[\frac{1}{K_1 + 1} \right] \left[1 + \frac{\alpha 1}{V_E} \right]$$

$$= D^2 \quad \rho_o \left[\frac{1}{1 + 1} \right] \quad M$$

$$P_1 \ (13.6 \times 76 \times 980) = D^2 \quad \rho_o \left[\frac{1}{\lambda 1 + 1} \right] M$$

$$\therefore P_1 \text{ atmosphere} = .009869 \ D^2 \quad \rho_o \left[\frac{1}{\lambda 1 + 1} \right] M \qquad (14)$$

DETONATION TEMPERATURE

Equation (5)

$$C_V (T_1 - T_0) = Q_1 + \frac{N_1 R T_1}{2K_1}$$

$$T_1 = \frac{Q_1}{C_V} + \frac{N_1 R T_1}{2K_1 C_V}$$

$$T_1 \left[1 - \frac{N_1 R}{2K_1 C_V} \right] = \frac{Q_1}{C_V}$$

$$T_1 = \frac{Q_1}{C_V} \times \frac{2K_1 C_V}{2K_1 C_V - N_1 R}$$

$$= \frac{Q_1 \times 2K_1}{2K_1 C_V - N_1 R}$$

$$= \frac{Q_1 \; 2K_1}{C_V (2K_1 - K_1 + 1 - \frac{d\alpha}{dV_1})} \qquad K_1 = 1 + \frac{N_1 R}{C_V} - \frac{d\alpha}{dV_1}$$

$$= \frac{Q_1}{C_V} \cdot \frac{2K_1}{K_1 + 1 - \frac{d\alpha}{dV_1}}$$

$$\frac{T_1}{T_E} = \frac{Q_1}{C_V T_E} \cdot \frac{2K_1}{K_1 + 1 - \frac{d\alpha}{dV_1}} \qquad C_V T_E = Q_E + \frac{N_1 R T_E}{2K_1}$$

$$\frac{T_1}{T_E} \cong \frac{2K_1}{K_1 + 1 - \frac{d\alpha}{dV_1}}$$

$$= L \times \frac{2}{\lambda_1 + 1} \lambda_1$$

$$1 = \frac{Q_E}{C_V T_E} + \frac{N_1 R T_E}{2K_1 C_V T_E}$$

(15) $$\frac{Q_E}{C_V T_E} = 1 - \frac{N_1 R}{2K_1 C_V}$$

$$= 1 - \frac{CP - C_V}{2K_1 C_V}$$

EXPLOSION TEMPERATURE

F. W. Brown (1941, p. 632) said:

> If an explosive were detonated in a perfectly insulated, rigid, closed bomb having a volume equal to that of the explosive charge, the products would reach an equilibrium temperature and pressure that will be designated as the explosion temperature and pressure. Although the temperature and pressure vary widely during detonation, the explosion temperature and pressure represent an average result of the explosion and can be used as a basis for computing other quantities.
>
> In order to compute accurately the explosion temperature as defined, it would be necessary to know:
>
> a - The heat of formation of the original explosive
>
> b - The composition of the products
>
> c - The heat of formation of the products
>
> d - The specific heat of the products
>
> e - The gas law obeyed by the gaseous products

f - The heat losses

Actually only the upper limit of explosion temperature can be calculated.

The following assumptions are made:

1 - The explosion occurs at constant volume

2 - All the explosive reacts

3 - Heat losses are neglected

4 - Motion of the gases are neglected

5 - Spectroscopic thermodynamic data are used

6 - The gaseous products of detonation obey Abel's law

7 - The products of detonation are calculated by assuming thermodynamic equilibrium at the explosion temperature

Deviation from assumptions 1 to 5 would tend to give a lower temperature; hence the computed temperature must be considered as a probable upper limit.

Spectroscopic thermodynamic data are employed because no other data are available for all temperatures, and the agreement of the data with known experimental values is good.

The calculated products of explosion are used rather than those determined experimentally because:

1 - Secondary reactions are known to occur after the explosion.

2 - The detonator probably has an appreciable effect on the products determined experimentally.

Although it must be true that the computed products are not correct, as it is not likely that all the equilibria are reached during the explosion, and as some permissible explosives do not react completely, it seems more desirable to use the theoretical products for computing the explosion temperatures.

Most of the explosives consist of a combination of carbon, hydrogen, nitrogen, and oxygen with ingredients adjusted so that there is sufficient oxygen to oxidize almost completely the carbon and hydrogen to carbon dioxide and steam.

An approximate method is used for computing the important performance parameters of blasting explosives. This method is compared with more exact procedures and is shown to be adequate for the current state of explosive technology, for all except highly underoxidized explosives, which are rarely used in commercial blasting operations.

A calculation of the products of explosion of the ammonium nitrate fuel-oil mixture will be made in detail by the means of the approximate method.

Table 1 (After Taylor)

Atomic Weights

Element	Atomic Weight
Carbon	12
Hydrogen	1
Nitrogen	14
Oxygen	16

Table 2 (After Taylor)

Heats of Formations

Compound	Chemical Formula	Heat of Formation at 0°C at Const. Volume K cal/mole
AN	NH_4NO_3	84.70
F.O.	$C_{10}H_{22}$	82.00
Carbon dioxide	CO_2	94.03
Steam	H_2O	57.47
Nitrogen	N_2	00.00

Gram mole of AN NH_4NO_3 14 + 4 + 14 + 3 x 16 = 80 gm

Gram mole of Decane $C_{10}H_{22}$ 12 x 10 + 22 = 142 gm

Table 3 (After Taylor)

Internal Energies, Relative to 0°C of Gaseous Products in the Ideal Gas State (k.cal/mole) Taylor

Temp. °C	CO	CO_2	H_2	H_2O(g)	O_2	N_2
1600	9.46	17.11	8.61	12.78	10.00	9.33
1700	10.13	18.36	9.22	13.76	10.70	9.99
1800	10.80	19.62	9.84	14.77	11.41	10.65
1900	11.47	20.88	10.47	15.78	12.12	11.32
2000	12.14	22.14	11.11	16.81	12.84	11.99
2100	12.82	23.41	11.75	17.85	13.56	12.66
2200	13.50	24.70	12.40	18.89	14.28	13.33
2300	14.19	25.98	13.06	19.96	15.02	14.01
2400	14.87	27.27	13.72	21.03	15.76	14.69
2500	15.56	28.56	14.38	22.09	16.50	15.37
2600	16.25	29.86	15.06	23.19	17.25	16.06
2700	16.94	31.16	15.74	24.28	18.01	16.74
2800	17.63	32.47	16.42	25.38	18.77	17.43
2900	18.32	33.78	17.11	26.47	19.53	18.12
3000	19.01	35.09	17.79	27.57	20.28	18.81
3100	19.71	36.41	18.49	28.68	21.06	19.51
3200	20.41	37.74	19.19	29.79	21.84	20.20
3300	21.10	39.06	19.89	30.93	22.62	20.89
3400	21.80	40.39	20.60	32.06	23.39	21.59
3500	22.50	41.72	21.30	33.19	24.17	22.29
3600	23.20	43.05	22.01	34.33	24.97	22.99
3700	23.91	44.38	22.73	35.47	25.76	23.68
3800	24.61	45.72	23.45	36.61	26.56	24.38
3900	25.31	47.06	24.17	37.75	27.35	25.09
4000	26.01	48.40	24.88	38.90	28.15	25.79

Table 4 (After Taylor)

High Temperature Second Virial Coefficients of Gaseous Products of Explosion

Gas	Second virial coef. cm^3/mole	Gas	Second virial coef. cm^3/mole
Ammonia	15.2	Methane	37.0
Carbon dioxide (rotating)	63.0	Nitric ox	21.2
		Nitrogen	34.0
Carbon dioxide (non-rotating)	37.0	Nitrous ox	63.9
		Oxygen	30.5
Carbon monoxide	33.0	Water vapour	7.9
Hydrogen	14.0		

Table 5 (After F. W. Brown)

Values of K in the Relation $D = 91.22 \frac{\lambda_1^{+1}}{\sqrt{\lambda_1}} \sqrt{N_1 T_1 K}$

b_1/V_E	$\lambda_1 = 1.1$	$\lambda_1 = 1.2$	$\lambda_1 = 1.3$
.0	1.000	1.000	1.000
.2	1.213	1.213	1.215
.3	1.331	1.332	1.338
.4	1.461	1.463	1.464
.5	1.600	1.601	1.604
.6	1.756	1.759	1.764
.7	1.923	1.928	1.934
.8	2.103	2.112	2.121
.9	2.294	2.311	2.324
1.0	2.514	2.559	2.570
1.1	2.743	2.766	2.785
1.2	2.988	3.014	3.045
1.3	3.227	3.282	3.327
1.4	3.523	3.574	3.633
1.5	3.852	3.896	3.952
1.6	4.156	4.246	4.307
1.7	4.472	4.576	4.695

Table 6 (After F. W. Brown)

Values of L in the Relation $(T_1/T_E) = \frac{2\lambda_1}{\lambda_1 + 1} L$

(b_1/V_E)	$\lambda_1 = 1.1$	$\lambda_1 = 1.2$	$\lambda_1 = 1.3$
.0	1.000	1.000	1.000
.2	1.0017	1.0028	1.0035
.3	1.0034	1.0057	1.0071
.4	1.0059	1.0093	1.0116
.5	1.0083	1.0136	1.0170
.6	1.0115	1.0189	1.0236
.7	1.0153	1.0253	1.0312
.8	1.0197	1.0321	1.0449
.9	1.0250	1.0401	1.0497
1.0	1.0306	1.0489	1.0605
1.1	1.0372	1.0589	1.0723
1.2	1.0447	1.0689	1.0851
1.3	1.0527	1.0826	1.0993
1.4	1.0617	1.0951	1.1144
1.5	1.0712	1.1087	1.1297
1.6	1.0815	1.1229	1.1467
1.7	1.0931	1.1393	1.1638

Table 7 (After F. W. Brown)

Values of M in the Relation $P_1 = \frac{0.009869}{\lambda_1 + 1} D^2 \Delta M$

(b_1/V_E)	$\lambda_1 = 1.1$	$\lambda_1 = 1.2$	$\lambda_1 = 1.3$
.0	1.000	1.000	1.000
.2	.8387	.8369	.8351
.3	.7775	.7735	.7702
.4	.7258	.7174	.7128
.5	.6762	.6690	.6617
.6	.6346	.6241	.6150
.7	.5968	.5848	.5732
.8	.5638	.5482	.5361
.9	.5351	.5168	.5030
1.0	.5070	.4863	.4656
1.1	.4822	.4580	.4421
1.2	.4620	.4343	.4147
1.3	.4439	.4143	.3896
1.4	.4240	.3923	.3673
1.5	.4036	.3698	.3475
1.6	.3858	.3480	.3275
1.7	.3735	.3347	.3019

$$M = \frac{1}{1 + 0.88\,\lambda_1 (b_1/V_E)}$$

Let us take 100 gm AN - F_2O_3 mixture 6% F_2O_3

94 gm AN

6 gm F_2O_3

100 gm of the mixture

1. Moles in original explosive

$C_0 = \frac{120}{142} \times \frac{6}{12}$ = 0.422 moles/100 gm

$H_0 = \frac{4}{80} \times \frac{94}{1} + \frac{22}{142} \times \frac{6}{1}$ = 5.630 " "

$N_0 = \frac{28}{80} \times \frac{94}{14}$ = 2.350 " "

$O_0 = \frac{48}{80} \times \frac{94}{16}$ = 3.520 " "

$\Delta = O_0 - 2C_0 - H_0/2$

$= 3.52 - .844 - 2.815 = -0.139$

$\therefore$ 6% F_2O_3 gives oxygen - negative explosive

2. Moles of the Products

$(CO_2) = C_0$ = 0.422 moles/100 gm

$(H_2O) = H_0/2$ = 2.815 " "

$(N_2) = N_0/2$ = 1.175 " "

4.412 total moles/100 gm

or 0.04412 " " /1 "

3. Heat of Explosion Q_E

$Q_E = U_E - U_0$

U_E = Σ moles X ht of formation of the products

U_0 = Σ moles X ht of formation of the explosive ingredients

$U_E = 0.422 \times 94.03 + 2.815 \times 57.47 + 0 = 201.8$ K cal/100 gm

$U_0 = \frac{94}{80} \times 84.7 + \frac{6}{142} \times 82 = 103.6$ " " "

$Q_E = 98.2$ " " "

4. Temperature of Explosive T_E

$Q_E = \int C_V \, dT = C_V T_E$

Try $T_E = 2500^{\circ}C$ and find the internal energies from table (3).

Moles X internal energies of the products

(CO_2) .422 x 28.56 = 12.1

(H_2O) 2.815 x 22.90 = 64.5

(N_2) 1.75 x 15.37 = 18.0

$Q_{2500} = 94.6$ K cal/100 gm

$Q_{2600} = 96.9$ K cal/100 gm

$\therefore T_E = 2656.5^{\circ}C$ or $2929.5\ K^{\circ}$

5. b_1 the Second Virial Coef. of the Products

$b = \Sigma n_i b_i$

find b_i from table (4)

n x b (cc/mole)

(CO_2) .422 x 37 = 15.6

(H_2O) 2.815 x 7.9 = 22.2

(N_2) 1.175 x 34 = 40.0

77.8 cc/100 gm

or .778 cc/gm

$$\frac{b_1}{V_E} = b. \rho = .778 \times 0.8$$

$$= .6224$$

6. To Compute λ Use the Differences in Table 3

	(CO_2)	(H_2O)	(N_2)	
Q_{2700}	31.16	24.28	16.74	
Q_{2600}	29.86	23.19	16.06	
	1.3	1.09	.68	K cal/mole
	13	10.9	6.8	cal/mole/°C

(CO_2) = .422 x 13 = 5.48 cal/100 gm explosive

(H_2O) = 2.815 x 10.9 = 30.7 " " " "

(N_2) = 1.175 x 6.8 = 8.0 " " " "

44.18 cal/100 gm explosive

$$\therefore C_V = \frac{44.18}{4.412} = 10 \text{ cal/mole}$$

$$\lambda_1 = 1 + \frac{R}{C_V} = 1 + \frac{1.987}{10} = 1.1987$$

7. Interpreting in Tables 5, 6, 7 Find

K = 1.79

L. = 1.02

M = .6161

8. $\therefore T_1 = \frac{2\,\lambda_1}{\lambda_1 + 1}\ T_E \cdot L = \frac{2.3974}{2.1987} \times 2929.5 \times 1.02$

$= 3{,}260\ K^{o}$

$N_1T_1 = .04412 \times 3260 = 144$

9. $D = 9122\ \frac{\lambda_1 H}{\sqrt{\lambda_1}} \sqrt{N_1T_1} \cdot K = 91.22 \times \frac{2.1987}{\sqrt{1.1987}} \sqrt{144}$

$= 3940$ mt/sec

10. $P_1 = \frac{.009869}{\lambda_1 + 1}\ D^2\ \rho_M = \frac{.009869}{2.1987}\ (3940)^2 \times .8 \times .6161$

$= 34{,}400$ atmosphere

Taking 5.4% F.O. — 94.6 gm AN

5.4 gm F.O.
100 gm AN F.O. mixture

C_0 = .379

H_0 = 5.35

N_0 = 2.36

O_0 = 3.54

C_0 = .379

$H_0/2$ = 2.675

$N_0/2$ = 1.180

4.234 moles/100 gm

.4234 mole/gm

Δ = 3.54 - .758 - 2.675 = +0.007

Slightly oxygen - positive or balanced

U_E = .379 x 94.03 + +.675 x 57.47 = 219.4

$U_0 = \frac{94.6}{80}$ x 84.7 + $\frac{5.4}{142}$ x 82 = 100

Q_E = 119.4

For 2700°C Q_{2700} = 96.6

For 3000°C Q_{3000} =108.9

$\therefore$ T_E 3246°C or 3519 K°

	b	X	moles	
(CO_2)	37	x	.379	= 13.75
(H_2O)	7.9	x	2.675	= 21.10
(N_2)	34	x	1.18	= 40.00
				74.85

.7485 cc/gm

$\frac{b}{V_E} = \frac{.6}{}$

	CO_2	H_2O	N_2	
Q_{3200}	39.06	42.29	20.89	
Q_{3200}	37.74	41.16	20.20	
	1.32	1.13	.69	K cal/100 gm /100 degree
	13.2	11.3	6.9	cal/100 gm/ degree

$(CO_2) = 5.2$

$(H_2O) = 30.2$

$(N_2) = \frac{8.05}{43.45}$

$C_V = \frac{43.45}{4234} = 10.3$

$\lambda_1 = \frac{1.987}{10.3} + 1 = 1.192$

$K = 1.7578$

$L = 1.0183$

$M = .6267$

$T_1 = 3880\ K^o$

$D = 4100$ mt/sec $\qquad N_1T_1 = 164$

$P_1 = 37{,}800$ atmos.

Taking 5% F.O.

95 gm AN

5 gm F.O.

100 gm AN F.O. mixture

C_0 = 0.346 moles/100 gm

H_0 = 5.525 " "

N_0 = 2.375 " "

O_0 = 3.560 " "

(CO_2) = .3460

(H_2O) = 2.7625

(N_2) = 1.1875

4.2960 moles/100 gm

.04296 moles/one gm

Δ = 3.56 - .692 - 2.7625 = + 0.1055

U_E = 191.70

U_u = 102.97

Q_E = 88.73

Q_{2500} = 88.05

Q_{2600} = 91.4

T_E = 2520 °C or 2793 °K

(CO_2) = 37 x .3460 = 12.8

(H_2O) = 7.9 x 2.7625 = 21.8

(N_2) = 34 x 1.1875 = 41.5

76.1 or .761

$\frac{b}{V_E}$ = .607

$(CO_2) = .346 \times 13 = 4.50$

$(H_2O) = 2.7625 \times 11 = 30.40$

$(N_2) = 1.1875 \times 6.9 = 9.35$

44.25

$$C_V = \frac{44.25}{4.295} = 10.25$$

$\lambda = 1.194$

$K = 1.759$

$L = 1.0189$

$M = .6241$

$$T_1 = \frac{2.388}{2.194} \times 2793 \times 1.0189 = 3060\ ^{o}K$$

$$N_1T_1 = 131$$

$$D = 91.22 \frac{2.194}{\sqrt{1.194}} \sqrt{131} \times 1.759$$

$= 3680$ m/sec.

$$P_1 = \frac{.009869}{2.194} (3680)^2 \times .8 \times .6241$$

$= 30.600$ atmos.

Taking 2% F.O.

98 gm AN

2 gm F.O.

100 gm explosive

C_0 = .141 CO_2 = 0.141

H_0 = 5.210 H_2O = 2.605

N_0 = 2.450 N_2 = 1.225

O_0 = 3.68 3.971 moles/100 gm

or 0.03971 moles/one gm

Δ = 3.68 - 0.282 - 2.605 = + 0.795

U_E = 13.3 + 150 = 163.30

U_0 = 103.8 + 1.15 = 104.95

Q_E = 58.35

Q_{2000} = 3.12 + 43.90 + 14.65 = 61.67

Q_{1500} = 2.26 + 30.7 + 10.6 = 43.56

T_E = 1908.5 °C or 1598 K°

b x n

(CO_2) = 37 x .14 = 5.2

(H_2O) = 7.9 x 2.605 = 20.5

(N_2) = 34 x 1.225 = 41.6

67.3

or .673

$\therefore \frac{b_1}{V_E}$ = .538

	(CO_2)	(H_2O)	(N_2)
Q_{2200}	24.70	18.89	13.33
Q_{2100}	23.41	17.85	12.66
	1.29	1.04	.67
	12.9	10.4	6.7

(CO_2) = .14 x 12.9 = 1.82

(H_2O) = 2.605 x 10.4 = 25.71

(N_2) = 1.225 x 6.7 = 8.20

35.73

$$\therefore C_V = \frac{35.73}{3.97} = 8.95$$

$$\lambda_1 = 1.222$$

$\therefore$ K = 1.631

L = 1.0170

M = .6450

T_1 = 2440 K^o

D = 3240 m/sec

P_1 = 24,000 atmospheres

Let us take 10% F.O. mixture

90 gm AN

10 gm F.O.

100 gm mixture

Using Brown's approximate method, we get

C_0	= .705	(CO_2)	= .705
H_0	= 6.100	(H_2O)	= 3.050
N_0	= 2.250	(N_2)	= 1.125
O_0	= 3.380	Products	4.88 moles/100 gm

Δ = 3.38 - 1.41 - 3.05 = - 1.08

One mole of oxygen per 100 gm is too much, so CO and H_2 are to be expected in the products; also H_0, H, CH_4, N_0 and others, but these can be neglected because they are found in very small quantities.

If the computations are made without considering the carbon monoxide and the hydrogen gases, we would arrive at wrong results as

T_E = 4000 K^o

D = 5000 mt/sec

P_1 = 50,000 atmos.

which are much higher than should be. And if we increase the fuel ratio more than 10 percent, we would get higher values. This increase in the parameter values comes from

supposing that more oxygen is in the reaction than is really present; so we have to adjust for CO and H_2 only and neglect all the other gases.

In order to estimate the amounts of CO and H_2 approximately, we have the following steps:

I. Assume an explosion temperature T_E

II. 1 - Assume a value for X where $X = \frac{CO}{CO_2}$ for this assumed temperature T_E

2 - Calculate the explosion products from the assumed value of X -- supposing no free carbon occurs in the reaction

$$\therefore CO + CO_2 = C_0$$

$$CO_2 (x + 1) = C_0$$

$$\therefore CO_2 = \frac{C_0}{X + 1}$$

$$CO = C_0 - CO_2$$

If the hydrogen is considered to come from the following reaction

$$CO + H_2O \rightleftharpoons CO_2 + H_2$$

According to the mass law, the speed with which CO and H_2O react is proportional to the concentrations of CO and H_2O. Then

Rate for forward reaction $(R_f) \propto C_{(CO)} \cdot C_{(H_2O)}$

$$\text{or } R_f = K_1 \, C_{(CO)} \cdot C_{(H_2O)}$$

$$\text{and } R_r = K_2 \, C_{(CO_2)} \cdot C_{(H_2)}$$

Where R_f is the rate of forward reaction

and R_r is the rate of reverse reaction

$C_{(H_2)}$ is the concentration of the hydrogen

At equilibrium R_f and R_r

$$\therefore K_1 \, C_{(CO)} \cdot C_{(H_2O)} = K_2 \, C_{(CO_2)} \cdot C_{(H_2)}$$

$$\text{or simply } \frac{K_1}{K_2} = K_C = \frac{(CO)(H_2O)}{(CO_2)(H_2)}$$

$$\therefore K_C = \frac{(H_2O)}{(H_2)}$$

K_C = called the equilibrium constant

$$H_2 + H_2O = H_0/2$$

$$\therefore H_2O \left[\frac{X}{K_C} + 1 \right] = H_0/2$$

$$\text{or } H_2O = \frac{(H_0/2)K_C}{X + K_C}$$

3 - Calculate the oxygen balance Δ

$$\Delta = 0_0 - CO - 2CO_2 - H_2O$$

if $\Delta \neq 0$ choose another value of X

4 - Interpolate to determine the correct value of X

5 - Calculate the explosion products for the correct value of X

III. Calculate $Q_E = (U_E - U_0)$ by the usual method then calculate $C_V T_E$ for the assumed T_E.

If $U_E - U_0 \neq C_V T_E$, assume another value for T_E and repeat I and II.

Interpolate to find the correct T_E.

IV. Proceed with the computations as in the approximate method. In applying this method to 10 percent F.O., we have

$C_0 = .705$

$H_0 = 6.100$

$N_0 = 2.250$

$O_0 = 3.380$

I. Let $T_E = 2500^{\circ}K$

II. Assume $X = 1.5$

$\therefore CO_2 = \frac{.705}{2.5} = .282$ moles

$CO = .423$ "

$H_2O = \frac{(H_0/2)K_C}{X + K_C} = 2.490$ "

K_C for $2500\ K^{\circ} = 6.65$

$H_2 = 0.56$

$\Delta = 3.380 - 3.477 = - .097$

Let $X = 1.7$

$CO_2 = 0.261$

$CO = 0.444$

$H_2O = 0.430$

$H_2 = 0.620$

$N_2 = 1.125$

$\Delta = 3.380 - 3.396 = - 0.016$ which is o.k.

III. $U_E = .261 \times 94.03 + .444 \times 26.7 + 2.43 \times 57.47 + 0 + 0 = 176$

$U_0 = \frac{90}{80} \times 84.7 + \frac{10}{142} \times 82 = 100.77$

$U_E = U_0 = 75.23$

$T_E = 2500\ K^{\circ} = 2227^{\circ}C$

$$C_V T_E = .261 \times 24.78 + .444 \times 13.67 + 2.43 \times 16.04 + .62 \times 10.63 + 1.125 \times 11.49 = 130$$

$$U_E - U_0 \neq C_V T_E$$

I. Let $T_E = 2273\ K^{\circ}$

II. Take $X = 1.5$

CO_2	= .282	(CO_2)	= .282
CO	= .423	(CO)	= .423
K_C	= 5.678	(H_2O)	= 2.410
H_2O	= 2.41	(H_2)	= .640
H_2	= .64	(N_2)	= 1.125
N_2	= 1.125	Products	4.880 moles/100 gm

$\Delta = 3.38 - .564 - .423 - 2.410 = 0.017$

$U_E = .282 \times 94.03 + .423 \times 26.7 + 2.41 \times 57.47 = 176.8$

$U_0 = 100.77$

$U_E - U_0 = 76$

$T_E = 2000^{\circ}C$

$\therefore C_V T_{2000} = .282 \times 22.14 \times .423 \times 12.14 + .64 \times 11.11$
$+ 2.41 \times 16.81 + 1.125 \times 11.99 = 72.16$

Correct T_E is about $2290\ K^{\circ}$ which is close to that chosen.

III. Second virial coefficient b

	n x b	
(CO_2)	= .282 x 37	= 10.40
(CO)	= .423 x 33	= 14.00
(H_2O)	= 2.410 x 7.9	= 19.00
(H_2)	= .640 x 14	= 8.95
(N_2)	= 1.125 x 34	= 38.75
		90.75 or 0.9075 cc/gm

$$\frac{b_1}{V_E} = .725$$

Using the differences in Table 3

$(CO_2) = .282 \times 12.7 = 3.58$

$(CO) = .423 \times 6.8 = 2.88$

$(H_2O) = 2.410 \times 10.4 = 25.10$

$(H_2) = .640 \times 6.4 = 4.10$

$(N_2) = 1.125 \times 6.7 = 7.50$

43.16

$$\therefore C_V = \frac{43.16}{4.88} = 8.9$$

$\lambda = 1.224$

$K = 1.9760$

$L = 1.0285$

$M = 0.5727$

$$T_1 = \frac{2\ \lambda_1}{\lambda_1 + 1}\ T_E \cdot L$$

$$= \frac{2.448}{2.224} \times 2290 \times 1.085 = 2590\ K^\circ$$

$$D = 9122\ \frac{\lambda_1 + 1}{\sqrt{\lambda_1}}\ \sqrt{N_1 T_1} \cdot K$$

$$= 9122\ \frac{2.224}{\sqrt{1.224}}\ \sqrt{126} \cdot 1.976$$

$= 4080$ mt/sec

$$P_1 = \frac{.009869}{\lambda_1 + 1}\ D^2\ \rho_M$$

$$= \frac{.009869}{2.224} \quad (4080)^2 \times .8 \times .5727$$

$$= 33,800 \text{ atmos.}$$

For comparison, the exact method of Cook gives

$T_1 = 2750\ K^{\circ}$

$D = 4100$ mt/sec

$P_1 = 40$ kilobars $\approx 39,000$ atmos.

RESULTS

	2% F.O.	5% F.O.	(5.4% F.O.)	6% F.O.	10% F.O.
Δ	+ 0.795	+ 0.106	+ 0.007	- 0.139	- 1.08
CO_2 moles/100 gm	0.141	0.346	0.379	0.422	0.282
(CO)					0.423
H_2O moles/100 gm	2.605	2.7625	2.675	2.815	2.410
(H_2)					0.640
N_2 moles/100 gm	1.225	1.1875	1.18	1.175	1.125
N_1 total moles	3.971	4.2960	4.234	4.412	4.88
Q_E K cal/100 gm	58.35	88.73	119.4	98.2	76.0
T_E K^o	1598	2793	3519	2929	2290
b_1/V_E	0.538	0.607	0.600	0.622	0.725
$\bar{C}_V$ cal/mole	8.95	10.25	10.3	10	8.9
λ_1	1.222	1.194	1.192	1.1987	1.224
K	1.631	1.759	1.758	1.790	1.976
L	1.0170	1.0189	1.0183	1.020	1.028
M	0.6450	0.6241	0.6267	0.6161	.5727
T_1 K^o	2440	3060	3880	3260	2590
D mt/sec	3240	3680	4100	3940	4080
P_1 atm	24400	30600	37800	34400	33800

CONCLUSIONS

The most striking fact about AN-F.O. mixture is that near the critical diameter there is a great difference between its measured and calculated detonation velocity. This difference is so great that it may be thought to deflagrate and does not detonate. Deflagration differs from detonation in that the particle velocity is in the opposite direction to that of the detonation velocity in case of deflagration, whereas both are in the same direction in detonation.

Because the particle velocity is roughly one fourth of the detonation velocity, the maximum speed of deflagration under ideal conditions should not exceed one half of the ideal detonation velocity. All the measured detonation velocities in 5-inch diameter pipes (run by Cook) are greater than one half of the ideal detonation velocity (Brown, 1941, p. 632; 1942, p. 643).

The reason for such difference may be due to the incomplete reaction of the AN within the detonation zone.

According to the same experiments by Coo, the ratio D/D* in an oxygen-balanced mixture is about 0.6; that is to say, the fraction of reaction (N) that takes place within the detonation zone which can produce heat of reaction in supporting the detonation wave is very small and equals $(D/D^*)^2$ or only about 35 percent of the AN. The reaction may be completed under the explosion state conditions within the reaction zone which in this case is longer than the detonation zone.

If the ideal detonation is to be achieved, the total heat of reaction must be liberated within the detonation zone; in other words, both the detonation and the reaction zones must coincide, a point that can be verified by shortening the reaction zone which means decreasing the reaction time, if possible.

Eyring has shown the relationship between the reaction zone length and the detonation velocity by:

$$(a/a^*) = (D^*/D) \; e^{(\Delta H^*/RT)(D^*/D^2-1)}$$

where a* is the reaction zone length for ideal vel. D*

and a " actual vel. D

T is the temperature of ideal detonation

ΔH^* is the heat of activation

Then, in order to get a as small as possible, ΔH^* should be as small as possible. ΔH^* depends to some extent upon the heat of formation of the fuel.

Let us look to the reaction time relation, given by Cook

$$t = \frac{\bar{r}}{\lambda k_r}$$

$$k_r = (kT/h) \cdot e^{(-\Delta H^*/RT)} \cdot e^{(\Delta S^*/R)}$$

where

t is the total reaction time at temperature T

$\bar{r}$ is the average grain size of AN

λ is the AN molecule radius 7.10^{-8} cm

k is the Boltzmann's constant

h is the Plank's constant

R_* is the gas constant

ΔH_* is the enthalpy

ΔS is the entropy

It is clear that in order to decrease t, $\bar{r}$ must be decreased. So if we can find the fuel that can give minimum ΔH^* and can dissolve the AN, in such an amount to give oxygen balanced explosive and which could be used as a liquid explosive, we could arrive at the ideal detonation velocity, or at least very close to it.

AN is soluble in ethyl and methyl alcohols.

NOMENCLATURE

Δ	Oxygen balance
C_0	Moles of carbon per 100 gm of explosive
H_0	Moles of hydrogen per 100 gm of explosive
N_0	Moles of nitrogen per 100 gm of explosive
O_0	Moles of oxygen per 100 gm of explosive
D	Detonation velocity (meters/sec)
D*	Ideal detonation velocity (meters/sec)
W	Average particle velocity (meters/sec)
α	Covolume of gas (cc/gm)
T_0	Initial temperature of explosive. Taken as $0^{\circ}C$ in all calculations
T_E	Explosion temperature ($^{\circ}K$)
T_1	Detonation temperature ($^{\circ}K$)
P_E	Explosion pressure (atm)
P_1	Detonation pressure (atm)

V_0 Heat of formation at $0^{\circ}C$ of 100 gm explosive (K cal)

V_E Heat of formation at $0^{\circ}C$ of 100 gm of products as determined by conditions in detonation region (K cal)

$Q = V_E - V_0$ = Energy released in explosion (K cal/100 gm)

$Q_1 = V_1 - V_0$ = Energy released in detonation (K cal/100 gm)

C_V Specific heat at constant volume of products of detonation (cal/mole)

λ_1 $1 + \frac{R}{C_V}$

R Gas constant = 1.9871 (cal/mole $^{\circ}K$)

N_1 Moles of gaseous detonation products (moles/gm)

b_E Second virial coefficient for explosion products (cc/gm)

b_1 Second virial coefficient for detonation products (cc/gm)

$V_0 = \frac{1}{\rho}$ = Specific volume of explosion products (cc/gm)

V_1 Specific volume of detonation products (cc/gm)

APPENDIX

The Hydrodynamic Theory of Detonation

As an idealization, let us suppose a plane-detonation wave to have been established in any explosive medium of infinite extend (so perfectly confined that no lateral motion can occur).

In front of the wave is the intact explosive (subscript 0); behind the wave are the products of the explosion (subscript 1), separating these two regions is a reaction zone. The explosive at the end of the reaction zone is described by these properties: pressure P, specific volume V, temperature T, particle velocity W, and the detonation velocity D.

To solve for all these, I used the following conditions:

1. Conservation of Mass

Considering discontinuity at the shock front, we can say that, at the infinitismal time dt, the mass flowing into the front must be equal to that flowing away from it.

$$\frac{D - W_0}{V_0} = \frac{D - W_1}{V_1}$$

$$W_0 = 0$$

$$\therefore \frac{D}{V_0} = \frac{D - W_1}{V_1} \qquad (1A)$$

$$\frac{D}{W_1} = \frac{V_0}{V_0 - V_1} \qquad (2A)$$

2. Conservation of Momentum

Here the effects of viscosity and thermal conductivity are neglected. The mass leaving the front in time dT has momentum $\frac{D}{V_0}$ WdT. The difference or the change in momentum must equal to the impulse of the net force per unit area if the limit dT approaches 0.

$$\frac{D}{V_0} (W_1 - W_0) = P_1 - P_0$$

$$DW_1 = V_0 (P_1 - P_0) \qquad (3A)$$

From equations (2A) and (3A)

$$D^2 = \frac{V_0^2}{V_0 - V_1} (P_1 - P_0)$$

$$\text{or} \quad D = V_0 \sqrt{\frac{P_1 - P_0}{V_0 - V_1}} \qquad (4A)$$

also $W_1^2 = (V_0 - V_1)(P_1 - P_0)$

$$\text{or } W_1 = \sqrt{(V_0 - V_1)(P_1 - P_0)} \qquad (5A)$$

$$= (V_0 - V_1)\sqrt{\frac{P_1 - P_0}{V_0 - V_1}} \qquad (6A)$$

3. Conservation of Energy

The net work done by the pressures P_1 and P_0 must be equal to the increase in the kinetic energy KE and the increase in potential energy PE when the time dT becomes infinitesimal. The work done by P_1 is P_1W_1 dT for unit area of the front, and by P_0 it is 0 since W_0 is 0.

$$P_1W_1 - 0 = \frac{D}{V_0}\left[(E_1 - E_0) + 1/2\ (W_1^2 - W_0^2)\right]$$

$$P_1W_1 - 1/2\ \frac{D}{V_0}\ W_1^2 = \frac{D}{V_0}\ (E_1 - E_0)$$

From eq. n (3A) $DW_1 = V_0\ (P_1 - P_0)$

$$\therefore P_1W_1 - 1/2\ W_1\ (P_1 - P_0) = \frac{D}{V_0}\ (E_1 - E_0)$$

$$1/2(P_1 + P_0) = \frac{D}{W_1} \cdot \frac{1}{V_0}\ (E_1 - E_0)$$

From eq. (1A) $\frac{D}{W_1} = \frac{V_0}{V_0 - V_1}$

$$\therefore E_1 - E_0 = 1/2\ (V_0 - V_1)(P_1 + P_0) \qquad (7A)$$

4. Specific Volume of Gaseous Products

To find the specific volume of the gaseous products (V_1), let us consider, for simplicity the case of ideal gas, then transfer it to the case of real gas. From equation n (5)

$$C_V (T_1 - T_0) = Q_1 + 1/2 (P_1 + P_0)V_1 - V_1)$$

and the gas law $P_1V_1 = N_1RT_1$

$$C_P - C_V = N_1R$$

$$C_V = (\lambda_1 - 1) = N_1R$$

$$\therefore \lambda = \frac{N_1R}{C_V} + 1$$

$$\therefore C_V (T_1 - T_0) = \frac{N_1R}{\lambda_1 - 1} \left[\frac{P_1V_1}{N_1R} - \frac{P_0V_0}{N_0R} \right]$$

$$= \frac{P_1V_1 - PV'_0}{\lambda_1 - 1}$$

$$\frac{P_1V_1 - P_0V'_0}{\lambda_1 - 1} = Q_1 + 1/2 (P_1V_0 + P_0V_0 - P_1V_1 - P_0V_1)$$

putting $\pi = P_1/P_0$, $\phi = \frac{V_1}{V_0}$, $B = \frac{Q_1 (\lambda_1 - 1)}{P_0V_0} + V - 1$

and $\mu = \frac{\lambda_1 - 1}{\lambda_1 + 1}$

dividing by P_0V_0

$$\frac{\pi\phi - \nu}{\lambda_1 - 1} = \frac{Q_1}{P_0V_0} + 1/2\ (\pi + 1 - \pi\phi - \phi) \tag{8A}$$

$$\pi\phi = \frac{Q_1\ (\lambda_1 - 1)}{P_0V_0} + \nu - 1 + 1 + \frac{\lambda_1 - 1}{2}\ (\pi + 1 - \pi\phi - \phi)$$

$$\pi\phi = B + 1 + \frac{\mu}{1-\mu}\ (\pi + 1 - \pi\phi - \phi)$$

$$\pi\phi - \mu\pi + \mu\phi - \mu^2 = (B + 1 + \mu)(1 - \mu)$$

$$\therefore (\pi + \mu)\ (\phi - \mu) = (1 - \mu)(B + 1 + \mu) \tag{9A}$$

$$(\pi + \mu) + (\phi - \mu)\ \frac{d\pi}{d\phi} = 0$$

$$\therefore \frac{d\pi}{d\phi} = - \frac{\pi + \mu}{\phi - \mu}$$

The slope of the RH curve

$$\left[\frac{dP_1}{dV_1}\right]_{RH} = \frac{P_0}{V_0}\ \frac{d\pi}{d\phi} = - \frac{P_1 + P_0\mu}{V_1 - V_0\mu}$$

$$\frac{dP_1}{dV_1} = 1\ \frac{\lambda_1 P_1}{V_1} = - \frac{P_1 P0\ \mu}{V_1 - V_0\mu}$$

$$\frac{-2\lambda_1 P_1}{-2\ V_1} = \frac{P_1\lambda_1 + P_1 + P_0\lambda_1 - P_o}{V_1\lambda_1 + V_1 - V_0\lambda_1 - V_0}$$

$$= \frac{-P_1\lambda_1 + P_1 + P_0\lambda_1 - P_0}{V_1\lambda_1 - V_1 - V_0\lambda_1 - V_0}$$

$$\therefore \frac{\lambda_1 P_1}{V_1} = \frac{P_1 - P_0}{V_0 - V_1} \quad \text{or} \quad \frac{\lambda_1 \pi}{\phi} = \frac{\pi - 1}{1 - \phi}$$

$$\pi = \frac{\phi}{\phi - \lambda + \lambda\phi} \qquad (10A)$$

Substituting in equation (8A)

$$\pi\phi = 2B + 1 + \lambda - \lambda\phi + \phi + \lambda\pi - \lambda\pi\phi - \pi$$

$$\therefore \frac{\phi}{\phi - \lambda + \lambda\phi}\,(\phi - \lambda + \lambda\phi + 1) = 2B + 1 + (\phi + \lambda - \lambda\phi)$$

$$\lambda(1 + \lambda)\phi^2 - 2\phi(\lambda B + B + \lambda + \lambda^2) + \lambda(\lambda + 1) + 2B\lambda = 0$$

$$\phi^2 - \frac{2\phi}{\lambda}(B + \lambda) + 1 + \frac{2B}{1 + \lambda} = 0 \qquad (11A)$$

$$\therefore \phi = \frac{B + \lambda}{\lambda} \pm \sqrt{\frac{(B + \lambda)^2}{\lambda^2} - \frac{\lambda + 1 + 2B}{\lambda + 1}}$$

$$= \frac{B + \lambda}{\lambda} \pm \frac{B^2\lambda + B^2 + 2\lambda B}{\lambda^2(\lambda + 1)}$$

B is about 1 or little greater than 1

$$\therefore \phi = \frac{1 + \lambda}{\lambda} \pm \sqrt{\frac{3\lambda + 1}{\lambda^2(\lambda + 1)} \times \frac{\lambda + 1}{(\lambda + 1)}}$$

$$= \frac{1 + \lambda}{\lambda} \pm \frac{1}{\lambda(\lambda + 1)}\sqrt{3\lambda^2 + 4\lambda + 1}$$

The value of the $\sqrt{3\lambda^2 + 4\lambda + 1}$ is approximately $(2\lambda + 1)$

$$\therefore \phi = \frac{1+\lambda}{\lambda} - \frac{2\lambda + 1}{\lambda(\lambda + 1)} \cong \frac{\lambda}{\lambda + 1} \qquad (12A)$$

$$\therefore \phi = \frac{V_1}{V_0} = \frac{\lambda_1}{\lambda_1 + 1}$$

$$V_1 = \frac{\lambda_1 V_0}{\lambda_1 + 1} \qquad (13A)$$

5. For Real Gas

$$P\,(V - \alpha) = NRT$$

where α is a function of T and V

$$\therefore PV = NRT + \frac{\alpha}{TV}\,P \qquad (14A)$$

$$P + V\,\frac{dP}{dV} = \alpha\,\frac{dP}{dV} + P\left[\frac{\partial \alpha}{\partial T}\,\frac{dT}{dV} + \frac{\partial \alpha}{\partial V}\cdot\frac{dV}{dV}\right]$$

$$\frac{\partial \alpha}{\partial T} = \frac{NR}{P} \qquad (15A)$$

Find $\frac{dT}{dV}$ from the thermodynamic law

$$-C_V\,dT_s = \left[\frac{dE}{dV} + P\right] dV \qquad (16A)$$

$$\therefore \frac{dT}{dV} = -\frac{1}{C_V}\left[\frac{dE}{dV} + P\right] \qquad (17A)$$

$$-\frac{dP}{dV}\,(V - \alpha) = P\left[1 - \left\{-\frac{NR}{PC_V}\left(\frac{dE}{dV} + P\right) + \frac{\partial \alpha}{\partial V}\right\}\right]$$

$$-\frac{dP}{dV} = \frac{P}{V - \alpha}\left[1 + \frac{NR}{PC_V}\,\frac{dE}{dV} + \frac{NR}{C_V} - \frac{\partial \alpha}{\partial V}\right]$$

$$= \frac{P}{V - \alpha} K_1 \tag{18A}$$

$$\therefore K_1 \cong \frac{NR}{C_V} + 1 - \frac{\partial \alpha}{V} \tag{19A}$$

In real gases

$$\phi = \frac{V_1 - \alpha}{V_0 - \alpha} = \frac{K_1}{K_1 + 1}$$

$$\therefore V_1 = \frac{K_1 V_0 + \alpha}{K_1 + 1} \tag{20A}$$

6. RH - Equation

$$\bar{C}_V (T_1 - T_0) Q_1 + 1/2 (P_1 + P_0)(V_0 - V_1)$$

P_0 can be neglected comparable to P_1

$$\therefore P_1 (V_0 - V_1) = \frac{N_1 R T_1}{V_1 - \alpha} (V_0 - V_1)$$

$$\frac{V_0 - V_1}{V_1 -} = \frac{V_0 - \frac{K_1 V_0 + \alpha}{K_1 + 1}}{\frac{K_1 V_0 + \alpha}{K_1 + 1} - \alpha} = \frac{1}{K_1}$$

$$\therefore 1/2 P_1 (V_0 - V_1) = \frac{N_1 R T_1}{2K_1} \tag{21A}$$

$$\therefore \bar{C}_V (T_1 - T_0) = Q_1 + 1/2 (P_1 + P_0)(V_0 - V_1)$$

$$= Q_1 + \frac{N_1 RT}{2K} \tag{22A}$$

7. CJ - Condition

The RH and adiabatic curves must have the same slopes

R.H. equation: $E - E_0 = 1/2\ (P_1 + P_0)(V_0 - V_1)$

$$\left[\frac{dE}{dV_1}\right]_{RH} = -1/2\ (P_1 + P_0) + 1/2\ (V_0 - V_1)\ \frac{dP}{dV_1}$$

Adiabatic condition: $dE + P_1 dV = 0$

$$\therefore \left[\frac{dE}{dV}\right]_S = -P_1$$

$$\therefore -P_1 + 1/2\ (P_1 + P_0) = 1/2\ (V_0 - V_1)\ \frac{dP_1}{dV_1}$$

$$\frac{P_1 - P_0}{V_0 - V_1} = -\frac{dP_1}{dV_1}$$

$$D = V_0\sqrt{\frac{P_1 - P_0}{V_0 - V_1}} = V_0\sqrt{\frac{-dP_1}{dV_1}} = V_0\ \frac{C}{V_1}$$

$$= \frac{V_0}{V_0 - V_1}\ W_1$$

$$\frac{W_1}{V_0 - V_1} = \frac{C}{V_1}$$ eq. 284

$$V_1(W_1 + C) = CV_0$$

$$W_1 + C = C\ \frac{V_0}{V_1}$$

$$W_1 + C = D$$

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