

as in the case of ship propellers, pumps, etc. The results described in the paper show the importance of considering the possibility of bubbles or dispersed surface, the frequency, and the amplitude, in any problem involving the transmission of negative pressure through a liquid.

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The detonation of solid explosives: the equilibrium conditions in the detonation wave-front and the adiabatic expansion of the products of detonation

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Assuming chemical and thermal equilibrium to be maintained in the detonation wave-front, and using the equation of state in the form of the virial expansion, the velocity of detonation has been determined as a function of the loading density. In the absence of data at sufficiently high pressures and temperatures for the products of detonation of T.N.T., it has been assumed that the virial coefficients are constant and their values have been determined to give agreement with the measured values of the detonation velocity for loading densities less than 1.5 g.cm.^{-3} . The pressure-volume-temperature relation in the detonation wave-front can then be determined. The pressure in the detonation wave-front is found to be of the order of $2 \times 10^{11} \text{ dyne cm.}^{-2}$ for a loading density of 1.5 g.cm.^{-3} , compared with the value of $9.4 \times 10^{10} \text{ dyne cm.}^{-2}$ given in the earlier work of other authors using the co-volume method. With the equation of state adopted in this paper it is found that at a high loading density only negligibly small amounts of hydrogen and carbon monoxide are present in the detonation wave-front, a fact which facilitates the calculation of the adiabatic relations in this case. It is shown (part B) that these gases do, however, develop rapidly during the initial stages of the adiabatic expansion.

The calculation of the equilibrium conditions in the detonation wave-front with the adopted equation of state (part A) determines the initial conditions for the calculation of the adiabatic relations for a high loading density. The chemical composition of the gases during the adiabatic expansion and the external work done during it have been calculated for a loading density of 1.5 g.cm.^{-3} (part B). It is shown that the large amount of chemical energy

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released in the early stages of the expansion is to be correlated with the high effective value of the exponent in the adiabatic in this region, and this is due to the dominant role of the repulsive forces between the molecules of the tightly compressed gases during the early stages of the expansion. The same effect is also observed in the case of a low loading density (part C).

The difference with regard to the amounts of hydrogen and carbon monoxide present in the detonation wave-front for a low loading density complicates the solution of the equations in this case. In part C it is shown how this can be done for a loading density of 1.0 g.cm.^{-3} , and the detonation velocity and the pressure, density and temperature in the wave-front have been determined using the same equation of state as in parts A and B. The adiabatic pressure-volume relation for the expansion of the products of detonation, and the chemical composition during, and up to the end of, the adiabatic expansion have also been determined. Compared with the results for a high loading density, there is considerably more carbon monoxide and less carbon dioxide and a substantial rise in the total number of moles of gas produced per mole of explosive. The ratio is found to be sensitive to the pressure in the detonation wave-front, from which, by comparison with the observed values of this ratio, independent evidence is obtained for the detonation pressure calculated in part A. The chemical energy released per gram of explosive is less for a loading density of 1.0 g.cm.^{-3} than for a loading density of 1.5 g.cm.^{-3} , and the external work done is also less in the former than in the latter case.

The amounts of ammonia and of hydrocyanic acid in chemical equilibrium with the other gases are determined and they are found to be negligibly small. It is concluded that these gases, observed in experiments, are probably formed by catalytic action with the bomb fragments during the cooling period after the adiabatic expansion has been completed. The calculations have been compared with the available experimental data and are in reasonable agreement with it. An explanation is suggested for the observed difference in the composition of the gaseous products of the detonation of T.N.T., initiated at a given loading density, with detonators of different power.

1. INTRODUCTION

1.1. For a solid explosive the pressure, temperature and molecular volume in the detonation wave-front have values which lie far outside the range which has been studied in other connexions, so that little guidance is available for the purpose of setting up the equation of state appropriate to the conditions in the detonation wave-front. Mainly for this reason, but also because the products of the detonation of a solid explosive are more complicated than those of the detonation of a gas, the study of the process of the detonation of solids presents greater difficulties than of that in gases.

1.2. Many investigations of the properties of explosives have made use of a form of van der Waals's equation (Cranz 1926; Crow & Grimshaw 1930), which is obtained from that for a perfect gas by diminishing the specific volume by a certain constant amount referred to as the co-volume. This has been used widely for the interpretation of experiments in which the pressure is measured after an explosion in a closed bomb. The value of the co-volume obtained in this way is much less than that determined under ordinary conditions, and the discrepancy is generally too great to be accounted for by the high temperature of the explosion. Although this equation of state fits the experimental results obtained in closed bomb experiments approximately (Cranz 1926, p. 40), it is entirely inadequate for the study of the detonation process. For, immediately behind the detonation wave-front the density is greater than that of the unexploded material, and the molecular volume is actually less than the excluded volume which it would be necessary to assume in applying this equation of state. Furthermore, it requires that the internal energy shall be a function of the temperature only, but under the high compression which exists in the detonation

wave it is clear that the repulsive forces between the tightly packed molecules will make a significant contribution to the energy. It is, therefore, clear that a theory of detonation with this equation of state as basis can only be built up by fixing the value of the co-volume arbitrarily so as to give the observed rate of detonation (cf. Langweiler 1938); co-volumes so determined can have little physical significance.

1.3. In this paper the detonation velocity is determined as a function of loading density by assuming chemical and thermal equilibrium to be maintained in the wave-front. By comparing this relation with the observed values of the detonation velocity the virial coefficients in the equation of state have been determined. The pressure, temperature and volume in the detonation wave-front have then been determined. The initial conditions calculated in this way can then be used as the starting-point from which to calculate the pressure-volume-temperature relations and the chemical composition during the adiabatic expansion of the material in the detonation wave-front of a solid explosive at different loading densities. Detailed application is made to T.N.T., and the effect of varying the loading density is determined.

1.4. In determining the adiabatic it is assumed that complete chemical and thermal equilibrium exists at each instant during the expansion. The validity of this assumption must be judged by the results to which it leads, but in any case it is a useful assumption to make since it provides a precisely defined limiting case. It should, however, be noted that while it is probable that complete chemical equilibrium exists in the initial stages of the expansion it is certain that in the later stages chemical equilibrium is not maintained. The experiments of Robertson & Garner (1923), for example, show that the relative amounts of the product gases when they have cooled to room temperature still correspond to an equilibrium temperature of about 1800° K. It would appear at first sight that the calculation of the adiabatic relations is faced with an almost insuperable arbitrariness in that, without a detailed knowledge of the reaction velocities of the various reactions taking place, it is not possible to determine with certainty the pressure and temperature under which the chemical equilibrium is to be considered to be frozen out. However, when the composition is determined during adiabatic expansion assuming chemical equilibrium it is found that the amount of free carbon present decreases rapidly at first as the volume increases, and then, passing through a minimum, it increases slowly and steadily. At about the same stage as there is a minimum of free carbon there is a maximum of carbon monoxide and of the total amount of gas present. Further, it is found that, in this region of the adiabatic expansion, the composition changes only very slowly in relation to the volume or the pressure. The reaction velocities are known to decrease rapidly with decreasing pressure and temperature; accordingly, in the present calculations, it is assumed that if chemical equilibrium is maintained up to the stationary values of the composition, the reaction velocities will then have fallen to values negligible compared with the speed of the expansion before the composition has changed appreciably from that at the stationary point. More precisely, it is assumed that chemical equilibrium exists up to the stage at which there is a minimum of free carbon and that thereafter the composition is fixed.

PART A. EQUATIONS DETERMINING THE CONDITIONS IN THE
DETONATION WAVE-FRONT FOR SOLID EXPLOSIVES

2. ENERGY EQUATION

The equations of continuity of mass and momentum across the wave-front can be written

$$U = (p\rho')^{\frac{1}{2}}/\rho_0, \quad (1)$$

$$u = (p/\rho')^{\frac{1}{2}}, \quad (2)$$

with

$$\frac{1}{\rho'} = \frac{1}{\rho_0} - \frac{1}{\rho}, \quad (3)$$

where U is the velocity of the detonation wave-front, u is that of the material in the wave-front; ρ_0 is the density of the unexploded material, ρ is that of the material in the wave-front; p is the pressure in the wave-front, and the pressure of the unexploded material is taken as zero since atmospheric pressure is completely negligible compared with p .

As the wave-front advances through the solid explosive, solid material passes into it and acquires a velocity u , and is subject to work done by the pressure difference p . At the same time chemical energy, H per mole of explosive, is released in the chemical reactions which take place in the wave-front. Thus if the molecular weight of the explosive be denoted by M , the total internal energy per gram of material in the detonation wave-front is given by

$$\frac{H}{M} + \frac{pu}{\rho_0 U} - \frac{1}{2}u^2,$$

and, using equations (1), (2) and (3), this reduces to

$$E - H = \frac{1}{2}p(v_0 - v), \quad (4)$$

where v_0 and v are the molecular volumes and E is the internal energy of the exploded material per mole. Equation (4) is generally referred to as the Hugoniot equation. The energy of the material in the wave-front is a function of the molecular volume and the temperature or, when the equation of state is known, it may be expressed as a function of the pressure and the volume. The energy of the chemical reaction can also be expressed as a function of the pressure and the volume. Thus, the Hugoniot equation expresses a relation between the pressure and the volume in the detonation wave-front. To determine them a second relation is required. This is provided by the Jouguet (1906) condition which is usually expressed by the equation

$$\left(\frac{dp}{dv}\right)_h = -\frac{p}{v_0 - v}, \quad (5)$$

in which $(dp/dv)_h$ denotes the gradient of the line which represents the Hugoniot equation in the p - v diagram.

3. EQUATION OF STATE

It was explained in the introduction that there is very little information available to indicate the correct form of the equation of state to be used in calculations dealing with the detonation wave. First, it is to be noted that there is no virtue in using any of the usual complicated empirical equations of state. For the complicated form of these equations is designed to cover the critical phenomena which are controlled by the weak molecular attractions, while in the range of pressure and temperature which exist in the detonation wave these weak molecular attractions are negligible compared with the mean molecular energies. The best that can be done therefore is to choose the simplest type of equation which is yet sufficiently general to include the effects of molecular repulsion on the internal energy. In this paper the virial equation in powers of the pressure, terminated at the term in p^3 , is used, so

$$p \frac{v'}{N'} = RT + bp + cp^2 + dp^3, \quad (6)$$

where v' is the volume and N' the number of moles at temperature T and pressure p of the gaseous products of the detonation of 1 mole of explosive. To assume a constant co-volume, as is done by Schmidt (1935, 1936) and by Langweiler (1938), corresponds to terminating the expansion at the first power. The virial coefficients b , c and d are, of course, functions of the temperature and of the mole fractions of the constituents of the gas. In the absence of any specific knowledge of the nature of these functions in the range of pressure and temperature in the wave-front, or for the products of detonation, the drastic assumption of regarding them as constants is made. On the basis of this assumption a relation can be determined between the detonation velocity and the loading density and is given by equations (1) and (2) with the values of p and v determined from equations (26), (27) and (28) below. The values of the virial coefficients are then determined by comparing the calculated relation between detonation velocity and loading density with the observed values, for loading densities less than 1.5 g.cm.^{-3} . It is probably best to state immediately the values which are obtained for the virial coefficients when this procedure is carried out. The result is'

$$b = 25.4, \quad c = -0.104, \quad d = 2.33 \times 10^{-4}, \quad (7)$$

when 1000 kg.cm.^{-2} is taken as the unit of pressure.

4. HEAT ENERGY OF THE PRODUCTS OF DETONATION

4.1. Let there be N_A moles of species A (all A) derived from 1 mole of explosive, and N moles in all, so that

$$N = \sum_A N_A, \quad (8.1)$$

and the total energy per mole of explosive is given by

$$E = \sum_A N_A E_A + N' E_1, \quad (8.2)$$

where N' is the total number of moles of gaseous products, that is, $N' = N - N_s$, where N_s is the number of moles in the solid state. The E_A are defined to be functions of the temperature only. If A denotes a molecular species which is in the gaseous

phase in the detonation products, then E_A denotes the energy of this gas at pressures low enough to ensure that the energy depends only on the temperature. If A denotes a species which is in the solid phase in the detonation products, then E_A is taken to be the internal energy at atmospheric pressure. The contribution to the total energy arising from the compression of any solid phase is neglected throughout these calculations. E_1 is the energy per mole of gas arising from the mutual interactions between the gas molecules.

From equations (6) and (7) and the well-known thermodynamical relation

$$\left[\frac{\partial}{\partial p} (E + pv) \right]_T = v - T \left(\frac{\partial v}{\partial T} \right)_p,$$

it follows immediately that $E_1 = -\frac{1}{2}cp^2 - \frac{2}{3}dp^3$, (9)

since by definition E_1 vanishes at zero pressure.

4.2. We now express the heat energy as a function of the pressure, volume and the number of moles of the different species, taking into account the field of force of the molecules but assuming that it is the same for all molecules. To do this we make use of the relations

$$\left(\frac{\partial G}{\partial N_A} \right)_{T, p, N_B, \dots} = \mu_A, \quad \left(\frac{\partial G}{\partial p} \right)_{T, N_A, N_B, \dots} = v,$$

where G is the Gibbs function for the detonation products and μ_A is the partial potential of the species A (all A). The assumption that all the molecules have the same field of force is expressed by the equation

$$\left(\frac{\partial v}{\partial N_A} \right)_{T, p, N_B, \dots} = \left(\frac{\partial v}{\partial N_B} \right)_{T, p, N_A, \dots} = \frac{v'}{N'}, \quad (10)$$

where A, B, \dots denote molecular species in the gaseous phase and N' is the total number of moles of gas in the volume v' . Thus

$$\left(\frac{\partial \mu_A}{\partial p} \right)_{T, N_A, \dots} = \frac{v'}{N'} \quad (\text{all } A). \quad (11)$$

A quantity p^* is now defined by the relation

$$\mu_A = \mu_{A,0} + RT \log (p^*/p), \quad (12)$$

where $\mu_{A,0}$ is the partial potential of the species A in the perfect gas condition, so

$$\left(\frac{\partial \mu_{A,0}}{\partial p} \right)_{T, N_A, \dots} = \frac{RT}{p}.$$

Thus

$$\left(\frac{\partial \log p^*}{\partial p} \right)_T = \frac{v'}{RTN'}.$$

Integrating this and using the equation of state we get

$$\log \frac{p^*}{p} = \frac{bp + \frac{1}{2}cp^2 + \frac{1}{3}dp^3}{RT}, \quad (13)$$

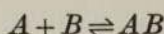
in which the constant of integration has been determined by the condition that p^* and p vanish together. For a perfect gas it is known that

$$\mu_{A,0} - RT \log (N_A/N') - RT \log p \quad (14.1)$$

is a function of the temperature only, and therefore for the material of the detonation wave

$$\mu_A - RT \log (N_A/N') - RT \log p^* \quad (14.2)$$

is the same function of the temperature. Now, the equilibrium condition for the reaction



between perfect gases is

$$\mu_{A,0} dN_A + \mu_{B,0} dN_B + \mu_{AB,0} dN_{AB} = 0.$$

Since the number of atoms is conserved this can be written as

$$\mu_{A,0} + \mu_{B,0} = \mu_{AB,0},$$

whence, for a perfect gas,

$$\log \frac{N_A N_B}{N_{AB}} + \log \frac{p}{N'} = \log K(T), \quad (15)$$

where $K(T)$ is the equilibrium constant for the reaction. Thus for the material of the detonation wave

$$\frac{N_A N_B}{N_{AB}} \frac{p^*}{N'} = K(T) \quad (16)$$

is the required equilibrium condition. Thus the effect of the intermolecular forces is expressed in the equation for chemical equilibrium by replacing the pressure p by the function p^* given by equation (13).

At 3000°K the values given in table 1 are obtained for p^* from equations (6) and (13), assuming the values (to be justified later) for the virial coefficients given by equation (7). It will be noticed that as p increases, and v'/N' decreases, p^* increases very rapidly so that even at high temperatures $N'T/p^*$ is negligibly small for pressures greater than 10^4 atm. This result is of importance in the calculation of the conditions in the detonation wave-front, from equations (19), (20) and (21) below.

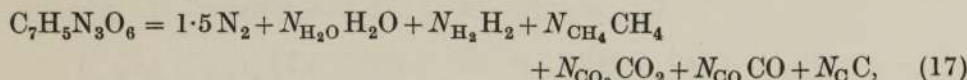
TABLE 1. VALUES OF p^* AT 3000°K

p (atm.)	p^*/p	v'/N'
1×10^4	2.88	51.1
5×10^4	98.1	27.5
1×10^5	2.28×10^3	21.6
2×10^5	2.31×10^5	16.5

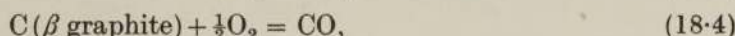
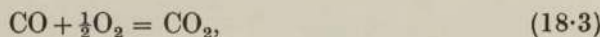
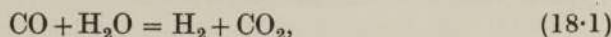
4.3. From an equation like (16) for each reaction which takes place in the detonation wave-front, the composition of the products of detonation can be calculated and thence the values of E and H can be determined. It is found below that the detonation pressure is of the order of that in the last two lines of table 1, so that in the detonation wave-front p^* is very great and $N'T/p^*$ differs insignificantly from zero. This justifies the procedure of § 5.2 below, and it is for this reason that table 1, which is based on the values eventually determined for the virial coefficients, is included at this stage. This simplifies the calculations which are necessary to determine the conditions in the wave-front greatly. Having determined E and H , the Hugoniot equation and the Jouguet condition can then be used with the equation of state to determine the pressure and temperature in the wave-front and the detonation velocity. This procedure will be illustrated by considering the detonation of solid T.N.T.

5. CHEMICAL EQUILIBRIUM FOR T.N.T.

5.1. It is assumed that no compounds of nitrogen are formed in the wave-front, and, in fact, it will be shown in part C that only negligible amounts of ammonia and hydrocyanic acid are formed even during the adiabatic expansion of the gaseous products of the detonation. With this assumption the decomposition of T.N.T. is represented by the equation



in which N_A is the number of moles of species A and the carbon is produced as graphite. Consider the reactions



and let $K_1(T)$, $K_2(T)$, $K_3(T)$ and $K_4(T)$ be the equilibrium constants applicable to the perfect gas condition for these four reactions. The values of these constants have been tabulated over a considerable range of temperatures by Lewis & von Elbe (1938, appendix A, table 2). If

$$\log_{10} K(T) + 0.4343\Delta E_0^\circ/RT,$$

where ΔE_0° is the energy of reaction at the absolute zero, be plotted against $\log_{10} T$ a straight line is obtained. In this way the tables given by Lewis & von Elbe were extrapolated to higher temperatures.

5.2. The equations which determine the composition are then

$$N_{\text{CH}_4} + N_{\text{CO}_2} + N_{\text{CO}} + N_{\text{C}} = 7, \quad (19.1)$$

$$2N_{\text{H}_2\text{O}} + 2N_{\text{H}_2} + 4N_{\text{CH}_4} = 5, \quad (19.2)$$

$$N_{\text{H}_2\text{O}} + 2N_{\text{CO}_2} + N_{\text{CO}} = 6, \quad (19.3)$$

$$N_{\text{CO}}N_{\text{H}_2\text{O}} = K_1(T)N_{\text{H}_2}N_{\text{CO}_2}, \quad (20.1)$$

$$N_{\text{H}_2}^2 = K_2(T)(N'/p^*)N_{\text{CH}_4}, \quad (20.2)$$

$$N_{\text{CO}}^2 = \frac{K_3(T)N'}{K_4(T)p^*}N_{\text{CO}_2}. \quad (20.3)$$

Eliminating all the molar fractions except that of hydrogen, we obtain the equation

$$(\lambda a_0 + \lambda a_1 f + a_2 f^2)(2.5 - f - a_3 f^2/\lambda) - 6f^2 = 0, \quad (21)$$

in which f has been written for N_{H_2} , λ for $N'T/p^*$ and the coefficients a_0 , a_1 , a_2 and a_3 , which are functions of T only, are given by the equations

$$a_0 = \frac{5K_3}{TK_1^2K_4}, \quad a_1 = \frac{K_3(K_1 - 2)}{TK_1^2K_4},$$

$$a_2 = 1 - \frac{4K_3}{K_1^2K_2K_4}, \quad a_3 = \frac{2T}{K_2}.$$

In the detonation wave-front p^* is very large and the parameter $\lambda = N'T/p^*$ is so small that the composition in the wave-front is given quite accurately by taking $(N'T/p^*)$ to be zero. In this case the total number of moles of gas is constant and equal to 5.75 and it can be verified by using equation (21) that f^2 is of the order of λ and that the composition is given by

$$\left. \begin{aligned} N_{\text{H}_2} = 0, \quad N_{\text{CO}} = 0, \quad N_{\text{N}_2} = 1.5, \quad N_{\text{H}_2\text{O}} = 2.5 - 2\phi(T), \\ N_{\text{CH}_4} = \phi(T), \quad N_{\text{CO}_2} = 1.75 + \phi(T), \end{aligned} \right\} \quad (22.1)$$

$$\text{with} \quad \phi(T) = \left[\left\{ \frac{49}{4} + \frac{240K_3}{K_1^2 K_2 K_4} \right\}^{\frac{1}{2}} - \left\{ \frac{7}{2} + \frac{20K_3}{K_1^2 K_2 K_4} \right\} \right] / 4 \left\{ 1 - \frac{4K_3}{K_1^2 K_2 K_4} \right\}. \quad (22.2)$$

Typical values of $\phi(T)$ are given in table 2.

TABLE 2. VALUES OF $\phi(T)$

T ($^{\circ}\text{K}$)	1000	2000	3000
$\phi(T)$	0.470	0.603	0.666

This determines the composition in the detonation wave-front at any temperature. We thus get the rather remarkable result that hydrogen and carbon monoxide are present in the detonation wave-front only in negligible amounts. It will be shown in parts B and C below, however, that, due to chemical reaction in the wave-front, both of these gases develop rapidly as the material of the detonation wave-front expands adiabatically. The energies of the gases are known (Lewis & von Elbe 1938, appendix A, table 1), so that the total energy per mole of explosive can be calculated using equations (8). It is found to be very nearly a linear function of the temperature and the energy E kcal./mole T.N.T. can be represented quite accurately by

$$E = 0.0875T - 38.0 + N'E_1, \quad (23)$$

where E_1 is given by equation (9).

5.3. If the heat of formation of a molecule AB be denoted by ϵ_{AB} and of T.N.T. by $\epsilon_{\text{T.N.T.}}$, all being taken as positive for energetically stable molecules, then the energy liberated by the chemical reaction in the detonation wave-front is given by

$$H = \sum_{AB} N_{AB} \epsilon_{AB} - \epsilon_{\text{T.N.T.}} \quad (24)$$

For the molecules involved we take the following values (Lewis & von Elbe 1938, appendix A, table 3; Garner & Abernethy 1921, 1930) which all refer to carbon in the form of β -graphite:

$$\epsilon_{\text{H}_2\text{O}} = 57.11, \quad \epsilon_{\text{CO}_2} = 94.16, \quad \epsilon_{\text{CO}} = 27.40, \quad \epsilon_{\text{CH}_4} = 16.17, \quad \epsilon_{\text{T.N.T.}} = 15.0 \text{ kcal./mole.}$$

Using the values of the N_{AB} given by equations (22) it is found that

$$H = 292.57 - 3.888\phi(T),$$

so that in the range 1000 to 3000 $^{\circ}\text{K}$, H varies by less than 0.25%. Accordingly, to calculate the conditions in the detonation wave-front for T.N.T., H has been taken as constant and equal to 290 kcal./mole T.N.T.

5.4. From equations (9), (23) and the equation of state (6), the Hugoniot equation can be written in the form

$$v' \left(\frac{\alpha}{RN'} + \frac{1}{2} \right) = \frac{1}{2} v'_0 + \frac{\alpha}{RN'} bN' + \left(\frac{\alpha}{RN'} + \frac{1}{2} \right) cpN' + \left(\frac{\alpha}{RN'} - \frac{2}{3} \right) dp^2N' + \frac{H-\beta}{p}, \quad (25)$$

where α is the coefficient of T in the expression for the internal energy. The Jouguet condition leads to the equation

$$v'_0 = N'b + 2(H-\beta) \left/ p \frac{\alpha}{RN'} - \left(\frac{\alpha}{RN'} + \frac{2}{3} \right) N'dp^2 \right/ \frac{\alpha}{RN'}. \quad (26)$$

Thus equations (25) and (26) have to be solved with the equation of state.

From equations (6), (25) and (26), v'_0 and v' can be eliminated to yield

$$p^3 \left(\frac{\alpha}{RN'} + 1 \right) = 3(H-\beta) \left(\frac{\alpha}{RN'} + 1 \right) \left/ N'd - 3RT \left(\frac{\alpha}{RN'} + \frac{1}{2} \right) \frac{\alpha}{RN'} \right/ \left(\frac{\alpha}{RN'} + 1 \right) d. \quad (27)$$

Also, from equations (25) and (26), we obtain

$$v' = v'_0 + N'cp - (H-\beta) \left/ p \left(\frac{\alpha}{RN'} + \frac{1}{2} \right) + 2 \left(\frac{\alpha}{RN'} + \frac{2}{3} \right) N'dp^2 \right/ \left(\frac{\alpha}{RN'} + \frac{1}{2} \right). \quad (28)$$

Thus, for a given value of T , equation (27) determines the pressure. Then equation (26) determines v'_0 and (28) determines v' . Then we have

$$v_0 = v'_0 + N_s v_s, \quad (29)$$

where v_s is the specific volume of the solid phase. Thus for a given loading density, that is, for a given value of v_0 , the corresponding values of pressure, volume and temperature in the detonation wave-front can be calculated. The velocity of the detonation wave-front can then be calculated from equations (1) and (2).

6. RESULTS FOR T.N.T.

With the appropriate values of the various constants, the conditions in the detonation wave-front for T.N.T. are determined by the equations

$$p^3 = (171.1 - 43.48T/1000)/d, \quad (27')$$

$$v'_0 = 5.75b + 86.27/p - 6.254dp^2, \quad (26')$$

$$v' = v'_0 + 5.75cp + 11.74dp^2 - 40.47/p. \quad (28')$$

Further, the molecular volume of carbon is 5.4 cm^3 and, since at the temperature of the detonation wave-front there are approximately 3.9 moles of carbon, then

$$v_0 - v'_0 = v - v' = 21. \quad (29')$$

These equations determine the pressure in the detonation wave-front and the detonation velocity as functions of the loading density, once values have been

assigned to the virial coefficients. As has been explained above, the values of the virial coefficients have been chosen to give agreement with the measured values of the detonation velocity for loading densities less than 1.5 g.cm.^{-3} , corresponding to the lower detonation pressures. With the simple virial expansion which has been assumed for the equation of state it is not possible to get exact correspondence between the experimental and calculated values throughout the whole range of pressure or of detonation velocity. To determine the adiabatic expansion, in which the pressure falls off greatly from its value in the detonation wave-front, it is preferable to have better agreement for lower pressures. This implies that in using the measured values of the detonation velocity to determine the virial coefficients, the

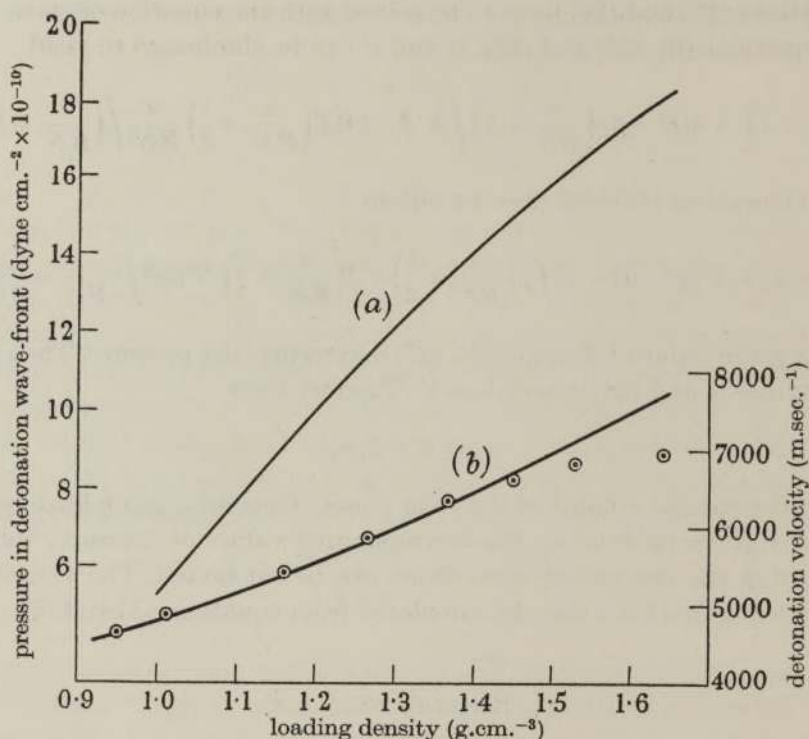


FIGURE 1. (a) Detonation pressure in the wave-front, and (b) detonation velocity as functions of loading density.

equations of state will provide a better approximation if they are chosen to give agreement for low loading densities. The values which are obtained in this way have already been given in equation (7). The detonation pressure and the detonation velocity are shown as functions of loading density in figure 1. The circles represent the experimental determination of the detonation velocity by Friederich (1933, 1936); the departure of the calculated detonation velocity from these values for high loading densities illustrates the remarks made earlier in this paragraph about the determination of the virial coefficients. The values of the pressure show, by reference to table 1 above, that p^*/p is very large in the wave-front and consequently that $N'T/p^*$ is negligibly small, thus justifying the assumptions made in § 5.2 above.

PART B. THE ADIABATIC EXPANSION OF THE PRODUCTS OF
DETONATION OF T.N.T. AT A HIGH LOADING DENSITY

7. INITIAL CONDITIONS

The initial conditions are determined by the calculations of part A. The equation of state is

$$pv'/N' = RT + 25.4p - 0.104p^2 + 2.33 \times 10^{-4}p^3, \quad (30)$$

where the pressure is expressed in 1000 kg.cm.⁻² as unit. For a loading density of 1.5 g.cm.⁻³ the pressure in the detonation wave-front is 15.9×10^{10} dyne cm.⁻², the volume per mole of T.N.T. is 117 cm.³ and the temperature is 3400° K. These are the initial conditions for the calculation of the adiabatic relation at this loading density.

8. THE EQUATION FOR ADIABATIC EXPANSION IN A FORM
SUITABLE FOR APPLICATION TO SOLID EXPLOSIVES

8.1. The high initial compression of the gases implies both an elaborate equation of state and that the internal energy will depend on the pressure as well as on the temperature. Further, the composition of the products of detonation changes during that part of the adiabatic expansion in which chemical equilibrium is maintained. These two factors make the calculation of the conditions during the adiabatic expansion somewhat complicated. The differential equation for the adiabatic expansion is

$$d(E - H) + p dv = 0, \quad (31)$$

where E , which is the internal energy, and H , which is the energy liberated by the chemical reactions, are both complicated functions of pressure and temperature. In order to share these complications between the two terms of equation (31), it has been found advantageous to use T as the independent variable and

$$y = \log_e p^* = \log_e p + (bp + \frac{1}{2}cp^2 + \frac{1}{3}dp^3)/RT \quad (32)$$

as the dependent variable, for $E - H$ can be expressed more easily in terms of y and T than it can be in terms of p and v .

Equations (8) and (24) can be combined to give

$$E - H = \sum_A N_A E_A + N' E_1 - \sum_{AB} N_{AB} \epsilon_{AB} + \epsilon_{\text{T.N.T.}}, \quad (33)$$

where the first summation is taken over each molecular species and the second summation over all compound molecules, and E_1 is given by equation (9).

8.2. It is convenient to define three functions of p and T by the equations

$$\Phi = RT/(RT + bp + cp^2 + dp^3), \quad (34.1)$$

$$\Psi = (RT + \frac{1}{2}cp^2 + \frac{2}{3}dp^3)/(RT + bp + cp^2 + dp^3), \quad (34.2)$$

$$X = 1 + y - \log_e p, \quad (34.3)$$

each of which reduces to unity for the perfect gas condition. From these definitions it follows that

$$\left(\frac{\partial p}{\partial y}\right)_T = p\Phi,$$

$$\frac{T}{p}\left(\frac{\partial p}{\partial T}\right)_y = 1 - \Psi,$$

$$\left[\frac{\partial(XT)}{\partial T}\right]_y = \Psi + pv'(1 - \Psi)/RTN'.$$

Using these relations it can be shown that

$$\left[\frac{\partial(N'E_1)}{\partial y}\right]_T + p\left(\frac{\partial v'}{\partial y}\right)_T = XRT\left(\frac{\partial N'}{\partial y}\right)_T - RN'T\Phi \quad (35)$$

and

$$\left[\frac{\partial N'E_1}{\partial T}\right]_y + p\left(\frac{\partial v'}{\partial T}\right)_y = XRT\left(\frac{\partial N'}{\partial T}\right)_y + RN'\Psi. \quad (36)$$

Equation (31) can be written

$$\left\{\left[\frac{\partial(E-H)}{\partial y}\right]_T + p\left(\frac{\partial v'}{\partial y}\right)_T\right\} dy + \left\{\left[\frac{\partial(E-H)}{\partial T}\right]_y + p\left(\frac{\partial v'}{\partial T}\right)_y\right\} dT = 0,$$

and therefore, using equations (33), (35) and (36), we get

$$-\left(\frac{dy}{dT}\right)_a = \frac{\sum\{(E_A - \epsilon_A)(\partial N_A/\partial T)_y + N_A(dE_A/dT)\} + RN'\Psi + XRT(\partial N'/\partial T)_y}{\sum(E_A - \epsilon_A)(\partial N_A/\partial y)_T + XRT(\partial N'/\partial T)_y - RTN'\Phi}, \quad (37)$$

in which the summations extend over all molecular types and ϵ_A is to be put equal to zero for any chemical elements.

When y has been obtained as a function of T it is easy to obtain p in terms of T from equation (32), $(dp/dT)_a$ from the equation

$$\frac{T}{p}\left(\frac{dp}{dT}\right)_a = T\Phi\left(\frac{dy}{dT}\right)_a + 1 - \Psi \quad (38)$$

and $(dv'/dp)_a$ from the equation

$$-\frac{p}{v'}\left(\frac{dv'}{dp}\right)_a = \Phi\left[1 + \frac{p}{RT}\left(\frac{\partial E_1}{\partial p}\right)_T - \frac{p}{T}\left(\frac{\partial T}{\partial p}\right)_a\right]. \quad (39)$$

Equation (37) can be used for any explosive; it will later be reduced to a form suitable for actual calculation in the special case of T.N.T. The effects of the imperfection of the gas and the changing composition can be seen separately in equation (37). If Φ , Ψ and X are each put equal to unity the effect of varying composition in the perfect gas condition is obtained. If $(\partial N_A/\partial T)_y$ and $(\partial N_A/\partial y)_T$ are each put equal to zero for all A , the adiabatic equation for an imperfect gas of fixed composition is obtained. As, in the later stages of expansion, the composition is fixed, the equation for fixed composition will be determined now.

9. EQUATION FOR ADIABATIC EXPANSION WITH FIXED COMPOSITION

When the composition is fixed, equations (37) and (38) reduce to

$$\frac{T}{p}\left(\frac{dp}{dT}\right)_a = 1 + \frac{1}{R}\frac{d}{dT}\left\{\frac{\sum_A N_A E_A}{N'}\right\}, \quad (40)$$

and, since the right-hand side of this equation is a function of temperature only, it can be integrated without difficulty. In this case, equation (39), making use of equation (40), reduces to

$$-\frac{v'}{p} \left(\frac{dp}{dv'} \right)_a = \Gamma / \Phi \left[1 + \frac{\Gamma p}{RT} \left(\frac{\partial E_1}{\partial p} \right)_T \right], \quad (41)$$

where

$$\Gamma = \left[R + \frac{d}{dT} \left\{ \frac{\sum N_A E_A}{N'} \right\} \right] / \frac{d}{dT} \left\{ \frac{\sum N_A E_A}{N'} \right\}.$$

In the limit of low pressures Γ reduces to the ratio of the specific heats at constant pressure and constant volume, and ultimately becomes the exponent of v in the ordinary adiabatic relation. Equation (41) shows that at higher pressures the $\log p$ - $\log v$ curve becomes steeper because, although $(\partial E_1 / \partial p)_T$ is positive, Φ diminishes rapidly with increasing pressure; this is a consequence of the repulsive forces between the molecules.

Equation (41) can be written in a slightly different form which is of special interest in the case of solid explosives. We have

$$-\left(\frac{dv'}{dp} \right)_a = \frac{N' RT}{p^2} \left[\frac{1}{\Gamma} + \frac{p}{RT} \left(\frac{\partial E_1}{\partial p} \right)_T \right]. \quad (42)$$

The initial velocity of the shock wave in a gas is given by the integral of $(-dv'/dp)^{\frac{1}{2}}$ with respect to p from the initial pressure in the detonation wave-front to the pressure in the layer of the shock wave next to the explosive. The effect of the repulsive forces, which is represented by the second member of the right-hand side of equation (42), is to increase the calculated shock wave velocity, and to make p decrease more rapidly with increasing v for low values of v .

10. CALCULATION FOR T.N.T.

10.1. Equations (19.2), (19.3) and (20.1) and the equation obtained by eliminating p^* from equations (20.2) and (20.3) give four equations connecting the relative amounts of water, hydrogen, carbon monoxide, carbon dioxide and methane. Thus, if one of these concentrations be taken as a parameter, say N_{H_2O} which will be written as x , the other concentrations can be expressed in terms of x and T . We then have

$$N_{H_2} = (\theta_1 x^2 + 8.5x - 15) / (\theta_3 x - 6) \equiv f(x, T), \quad (43.1)$$

$$N_{CO} = (\theta_1 x^2 + 8.5x - 15) / (\theta_2 x - 2.5) \equiv g(x, T), \quad (43.2)$$

where

$$\theta_1 = \frac{4K_3}{K_1^2 K_2 K_4} - 1, \quad (44.1)$$

$$\theta_2 = 1 - \frac{2}{K_1}, \quad (44.2)$$

$$\theta_3 = 1 - \frac{2K_3}{K_1 K_2 K_4} = \frac{\theta_1 + \theta_2}{\theta_2 - 1}, \quad (44.3)$$

and are functions of T only.

The other concentrations then follow from equations (19) and (20) and are given by

$$N_{\text{CO}_2} = 3 - 0.5x - 0.5g, \quad (45.1)$$

$$N_{\text{CH}_4} = 1.25 - 0.5x - 0.5f, \quad (45.2)$$

$$N_c = 2.75 + x + 0.5f - 0.5g, \quad (45.3)$$

$$N' = 5.75 + 0.5f + 0.5g. \quad (45.4)$$

Five of the six equations (19) and (20) have been used; the remaining one gives a relation

$$y = \log_e p^* = \log_e N_{\text{CO}_2} + \log N' - 2 \log_e N_{\text{CO}} + \log_e (K_3/K_4),$$

which can be written as

$$0.4343y = \log_{10} (3 - 0.5x - 0.5g) + \log_{10} (5.75 + 0.5f + 0.5g) - 2 \log_{10} g + \log_{10} (K_3/K_4). \quad (46)$$

10.2. At each stage of the integration, that is, for a given pair of values of y and T , it is necessary to determine x from equation (46) using equations (43). Having determined x , f and g , the partial derivatives of f , g and y with respect to x and T , can be calculated. From them, the partial derivatives required in the integration of equation (37) can then be obtained readily.

10.3. If equations (43), (44) and (45) are introduced into equation (37), and the energy terms are grouped together suitably (equations (49) below) the adiabatic equation can be expressed finally as

$$-\left(\frac{dy}{dT}\right)_a = \frac{F(y, T)}{G(y, T)}, \quad (47)$$

where

$$F(y, T) = 5.75R\Upsilon + \frac{d\mathcal{E}_1}{dT} + x \frac{d\mathcal{E}_2}{dT} + f \left(\frac{d\mathcal{E}_3}{dT} + \frac{1}{2}R\Upsilon \right) + g \left(\frac{d\mathcal{E}_4}{dT} + \frac{1}{2}R\Upsilon \right) + \mathcal{E}_2 \left(\frac{\partial x}{\partial T} \right)_y + (\mathcal{E}_3 + \frac{1}{2}XRT) \left(\frac{\partial f}{\partial T} \right)_y + (\mathcal{E}_4 + \frac{1}{2}XRT) \left(\frac{\partial g}{\partial T} \right)_y, \quad (48.1)$$

$$G(y, T) = -(5.75 + 0.5f + 0.5g) RT\Phi + \mathcal{E}_2 \left(\frac{\partial x}{\partial y} \right)_T + (\mathcal{E}_3 + \frac{1}{2}XRT) \left(\frac{\partial f}{\partial y} \right)_T + (\mathcal{E}_4 + \frac{1}{2}XRT) \left(\frac{\partial g}{\partial y} \right)_T, \quad (48.2)$$

$$\text{with } \mathcal{E}_1(T) = 1.25(E_{\text{CH}_4} - \epsilon_{\text{CH}_4}) + 3(E_{\text{CO}_2} - \epsilon_{\text{CO}_2}) + 2.75E_C + 1.5E_{\text{N}_2}, \quad (49.1)$$

$$\mathcal{E}_2(T) = (E_{\text{H}_2\text{O}} - \epsilon_{\text{H}_2\text{O}}) - 0.5(E_{\text{CH}_4} - \epsilon_{\text{CH}_4}) - 0.5(E_{\text{CO}_2} - \epsilon_{\text{CO}_2}) + 0.5E_C, \quad (49.2)$$

$$\mathcal{E}_3(T) = E_{\text{H}_2} - 0.5(E_{\text{CH}_4} - \epsilon_{\text{CH}_4}) + 0.5E_C, \quad (49.3)$$

$$\mathcal{E}_4(T) = (E_{\text{CO}} - \epsilon_{\text{CO}}) - 0.5(E_{\text{CO}_2} - \epsilon_{\text{CO}_2}) - 0.5E_C. \quad (49.4)$$

When the values of the functions $\mathcal{E}(T)$ are calculated from the known internal energies and the heats of reaction of the various gases involved and plotted as functions of T ,

it is found that the points are very nearly collinear. These quantities were therefore represented by linear functions of T as follows:

$$\mathcal{E}_1(T) = 89.3T - 343, \quad (50.1)$$

$$\mathcal{E}_2(T) = -0.623T - 0.513, \quad (50.2)$$

$$\mathcal{E}_3(T) = -1.23T + 11.5, \quad (50.3)$$

$$\mathcal{E}_4(T) = -2.51T + 21.9, \quad (50.4)$$

where the temperature is written in terms of 1000°K as unit and the $\mathcal{E}(T)$ are given in kcal. Thus starting from the initial conditions equation (47) can be integrated numerically, the values of the equilibrium constants (and functions of them) being obtained as explained in part A.

10.4. It should be noted that with the given initial conditions

$$p = 3.8 \text{ kcal.cm.}^{-3}, \quad T = 3.4,$$

equations (32) and (43) to (46) give

$$x = 1.102, \quad f = 0.0035, \quad g = 0.0626.$$

These figures verify in detail that, with the adopted equation of state, only negligible amounts of hydrogen and carbon monoxide are present in the detonation wave-front when the loading density is not less than 1.5 g.cm.^{-3} (cf. the statement following table 2). This is no longer the case for lower loading densities, and the calculation of the adiabat is then more complicated and has to be carried out as indicated in part C below.

10.5. The integration is continued to the neighbourhood in which there is a minimum amount of free carbon present, which occurs at about 1600°K . From this stage it has been assumed that the composition remains fixed. Using equations (43) to (46) and (49), equation (40) becomes

$$\frac{T}{p} \left(\frac{dp}{dT} \right)_a = 1 + \frac{1}{RN'} \left(\frac{d\mathcal{E}_1}{dT} + x \frac{d\mathcal{E}_2}{dT} + f \frac{d\mathcal{E}_3}{dT} + g \frac{d\mathcal{E}_4}{dT} \right), \quad (51)$$

where

$$x = 1.049, \quad f = 0.3660, \quad g = 1.975,$$

their values at 1600°K , calculated in the integration of equation (47). Equation (51) then determines the adiabat in the region in which the composition remains fixed.

10.6. The concentrations of the products of detonation throughout the expansion are shown in figure 2 and the pressure, volume and temperature relations are shown in table 3. The minimum amount of free carbon present and maximum in the total amount of gas present is evident between 310 cm.^3 (corresponding to 1800°K) and 410 cm.^3 (corresponding to 1600°K). In the fourth column of table 3 the values of $-d \log p / d \log v$ are shown. This gives the effective exponent of v in the adiabat relation during the adiabat expansion. The high value of this differential coefficient has important consequences which can be seen by considering the variation of $\int p dv$ from the initial volume (v_0) up to a given volume (v) with $(v_0/v)^{\frac{1}{2}}$ (which is shown by the broken curve in figure 3). This integral measures the external work done during the expansion, and is equal to the difference between the values of $E - H$ at the

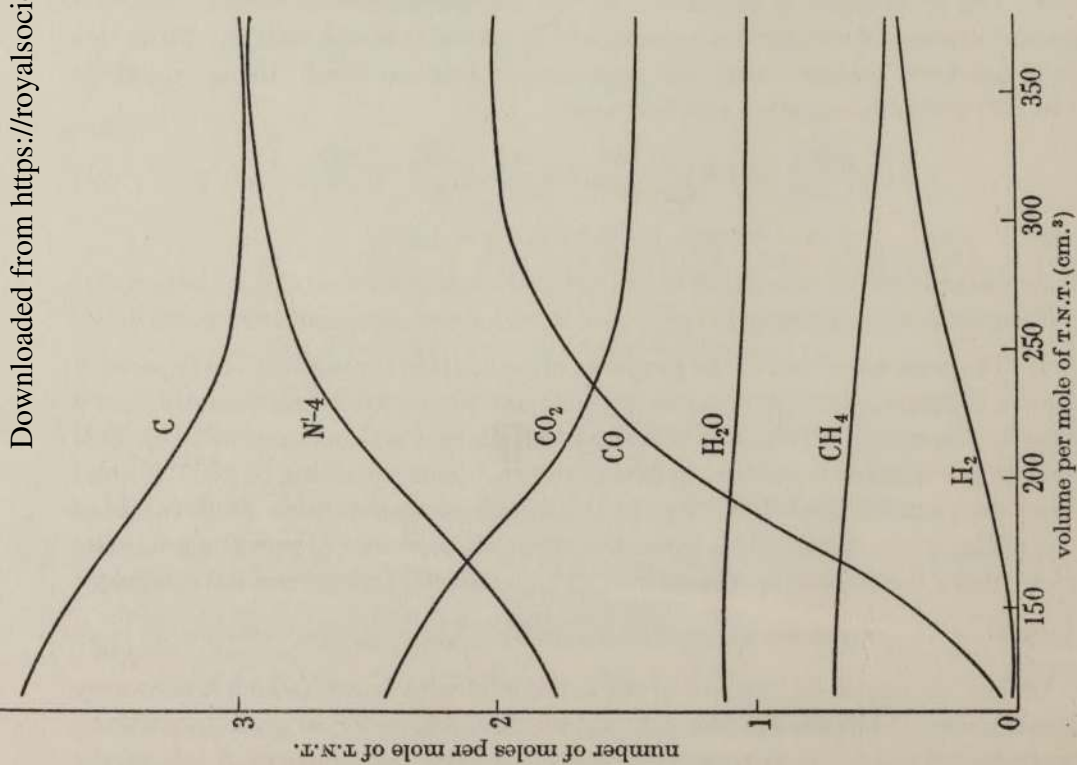


FIGURE 2. Chemical composition of the products of detonation for a loading density of 1.5 g.cm.⁻³.

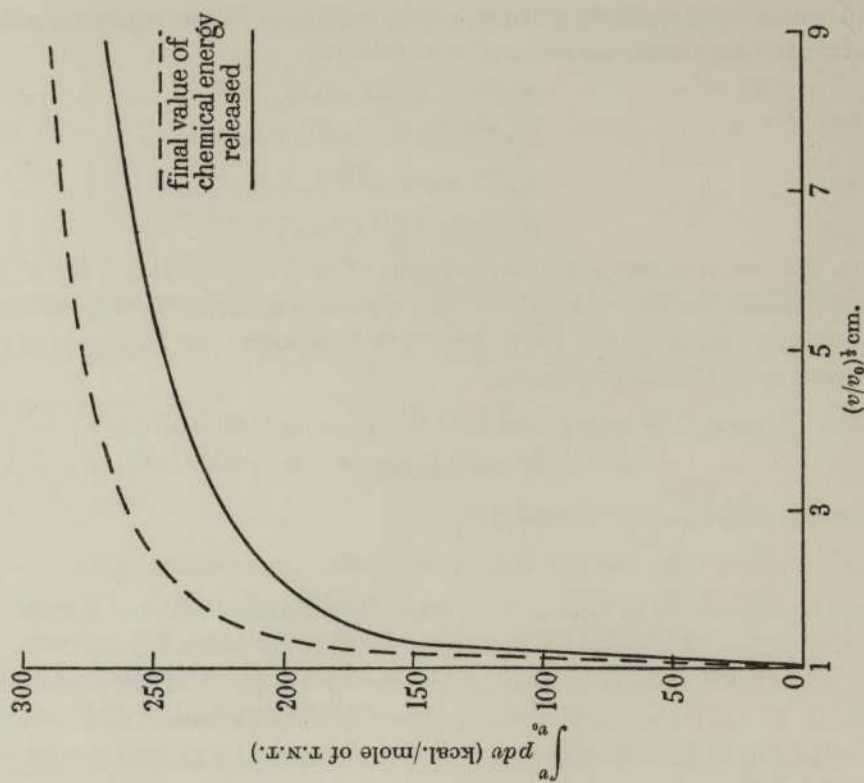


FIGURE 3. Work done during adiabatic expansion from the initial volume (v_0 cm.³) to a volume v cm.³. The full curve is for a loading density of 1.0 g.cm.⁻³; the broken curve is for a loading density of 1.5 g.cm.⁻³.

initial volume and the volume in question. From figure 3 it can be seen that a large amount of chemical energy is released as work in the very early stages of the expansion. The work done in an adiabatic expansion from a volume v_0 to a volume v , divided by the initial energy of the gas, is

$$1 - (v_0/v)^{\gamma-1},$$

where γ is written for $-(d \log p/d \log v)$, and this quantity increases as γ increases. Thus the property of yielding a large part of the chemical energy as work in the early stages of the expansion is associated with the high effective value of γ initially, which corresponds to a sharp fall in pressure for increasing volume for small values of v . As has been noted already this is due to the dominant effect of the repulsive forces between the molecules in the early stages of the expansion.

TABLE 3. TEMPERATURE, PRESSURE AND VOLUME DURING ADIABATIC EXPANSION OF THE DETONATION WAVE-FRONT IN T.N.T. AT A LOADING DENSITY OF 1.5 G./CM.³

temperature (T° K)	pressure (p dyne/cm. ²)	volume (v cm. ³ /g.)	γ
3400	15.88×10^{10}	0.5136	3.36
3200	10.77	0.5911	2.63
3000	7.809	0.6676	2.76
2800	5.833	0.7421	2.93
2600	4.371	0.8189	3.10
2400	3.238	0.9022	3.27
2200	2.299	1.002	3.30
2000	1.517	1.136	3.05
1800	8.898×10^9	1.355	2.76
1700	6.245	1.540	2.39
1600	4.318	1.797	2.09
1500	2.931	2.162	1.86
1400	1.947	2.693	1.68
1300	1.264	3.484	1.54
1200	7.980×10^8	4.697	1.44
1100	4.882	6.607	1.37
1000	2.880	9.718	1.32
900	1.626	14.97	1.29
800	8.707×10^7	24.29	1.27
700	4.360	41.79	1.27
600	1.999	77.35	1.27
500	8.159×10^6	157.0	1.27
400	2.818	362.8	1.27

10.7. For the initial conditions, the chemical energy is 288.6 kcal./mole T.N.T. This is the energy given up in the detonation wave-front, but part of this chemical energy is reabsorbed during the adiabatic expansion as the amount of carbon monoxide increases. When the composition becomes fixed the chemical energy is 247.9 kcal./mole T.N.T. It can be seen from figure 3 that the total work done during the expansion of an element of gas in the detonation wave-front is greater than the chemical energy released. This is because the internal energy of the wave-front is augmented by the work done on it by the detonation wave itself. The maximum kinetic energy in all forms, which can be obtained from the detonation of the explosive is naturally not greater than the final value of the chemical energy released.

11. COMPARISON WITH EXPERIMENT

11.1. Consider an idealized experiment in which the explosive is placed in a large evacuated space, but where the explosive itself is surrounded by a heavy casing. When the explosion takes place under these conditions nearly all the chemical energy is absorbed by the casing, in the early stages of the expansion before the gases have filled the bomb. During this process each element of the products of the explosion is expanding adiabatically except when it passes through the wave-front of a shock wave, and the resulting gases should have very nearly the composition which has been calculated for the adiabatic expansion.

11.2. These ideal conditions are very closely satisfied in the experiments of Robertson & Garner (1923) and in those carried out at the Chemisch-Technische Reichsanstalt (Haid & Schmidt 1929, 1931; Marshall 1932). In the latter experiments, a cartridge of T.N.T. weighing 10 g. at a loading density of 1.52 was fitted into a massive lead block, the end of the hole being filled with sand and the whole placed in an evacuated steel bomb. It was fired with a detonator containing some tetryl. The results of the analysis, compared with the calculations of this paper, are given in table 4 in which the figures give moles of gas per mole of T.N.T. The agreement is fairly good, particularly since in the calculations nitrogen compounds were excluded. In §15 of part C below, where this question is discussed, evidence will be adduced to show that the nitrogen compounds are probably formed by reactions between the products of detonation while they are cooling to room temperature *after* the expansion has occurred. Thus the occurrence of nitrogen compounds in the experimental analysis indicates that it does not give the products of the adiabatic expansion precisely, and that the values given by it show the effects of chemical reaction after the adiabatic expansion is completed. This probably accounts for differences between the observed and calculated values, particularly in the case of methane.

TABLE 4. DETONATION OF T.N.T. AT A LOADING DENSITY OF 1.5 G.CM.⁻³

	H ₂ O	CO	CO ₂	H ₂	CH ₄	N ₂	HCN	NH ₃	C	N'
exp.	1.60	1.99	1.20	0.384	0.007	1.23	0.325	0.211	3.41	6.95
calc.	1.05	1.98	1.49	0.366	0.543	1.50	—	—	2.99	6.92

11.3. The same authors give results of another experiment in which a lead azide detonator is used to fire the charge. The discussion of these results, as also those of Robertson & Garner who carried out experiments at a loading density of 1.3 g.cm.⁻³, can best be deferred until the adiabatic expansion at a low loading density has been considered in part C below.

PART C. THE ADIABATIC EXPANSION OF THE PRODUCTS OF
DETONATION OF T.N.T. AT A LOW LOADING DENSITY

12. In the previous part dealing with a high loading density it could be assumed that only negligible amounts of hydrogen and carbon monoxide are present in the detonation wave-front, and this simplified the solution of the equations relating

pressure, volume and temperature. This assumption is no longer valid for a low loading density and this requires that the equations be used differently, as is explained below.

13. THE HUGONIOT CURVE FOR A LOW LOADING DENSITY

13.1. It is assumed that the equation of state (6) holds throughout the expansion with the values of the virial coefficients which have been determined already (equation (30)). The amounts of various substances formed, in terms of the amounts of water, carbon monoxide and hydrogen, are given by equations (43), (44) and (45) and a further equilibrium condition is given by equation (46). For given values of pressure and temperature, equation (30) determines v'/N' and equation (32) determines y . Equations (43) determine f and g for an assumed value of x ; these values are then substituted in the right-hand side of equation (46), and the process is repeated until a value of x is chosen which satisfies equation (46). Equations (45) then determine the chemical composition and the total number of moles of gas. This latter value, with the value of v'/N' obtained from equation (30), determines v' . The total volume is then given by

$$v = v' + N_c v_c,$$

where N_c is the number of moles of carbon and v_c , which is equal to 5.4 cm.^3 , is the volume of 1 mole of carbon.

13.2. The difference between the internal energy, E , and the energy, H , liberated by the chemical reaction in the detonation wave-front is given by

$$E - H = \mathcal{E}_1(T) + x\mathcal{E}_2(T) + f\mathcal{E}_3(T) + g\mathcal{E}_4(T) + \epsilon_{\text{T.N.T.}} + N'E_1, \quad (52)$$

where the $\mathcal{E}(T)$ are given by equations (50) and E_1 is given by equation (9). For a given temperature, the values of $E - H$ and of v can be determined in the way indicated in the preceding paragraph. From the Hugoniot equation,

$$E - H = \frac{1}{2}p(v_0 - v), \quad (4)$$

the value of v_0 , the initial volume of the explosive, can be determined. For a given temperature, the value of p is varied until this calculation gives a value of v_0 corresponding to the loading density for which it is desired to determine the chemical composition of the products of detonation and the detonation velocity. This determines one point on the Hugoniot curve, and it can be determined completely by carrying through this calculation for a number of different temperatures. By the usual construction of drawing the tangent to this curve from the point on the line $p = 0$ at which $v = v_0$ the detonation velocity can be determined.

13.3. The points which are obtained in this way, assuming that chemical equilibrium is maintained in the wave-front, are plotted as the full curve in figure 4, in which the abscissa is the volume in cm.^3 and the ordinate is the pressure in $10^{10} \text{ dyne cm.}^{-2}$. If α is the inclination of the tangent from the point (227, 0) to this curve, the detonation velocity $U \text{ m. sec.}^{-1}$ is given by

$$U^2 = 2.27 \tan \alpha. \quad (53)$$

This gives a detonation velocity of 5266 m./sec. which is about 5 % greater than the measured detonation velocities at this loading density. The broken curve in figure 4 shows the curve which is obtained when it is assumed that the total number of moles of gas is fixed, and the tangent to this curve (also shown broken) determines the detonation velocity on that assumption. It gives a value about 12 % less than the observed detonation velocity.

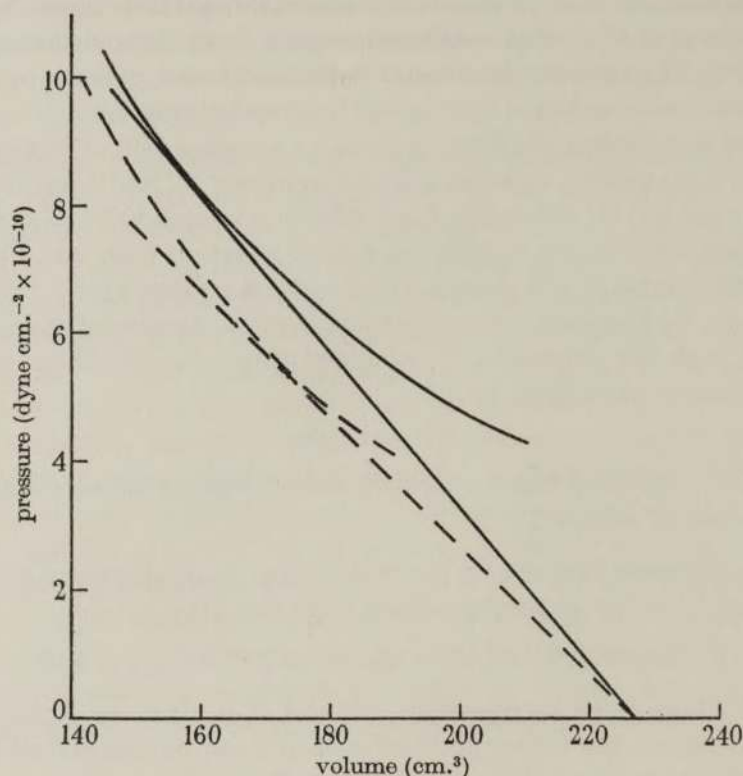


FIGURE 4. Hugoniot curve for a loading density of 1.0 g.cm.^{-3} . The full curve is obtained by assuming that chemical equilibrium is maintained in the wave-front, and the broken curve is obtained when the total number of moles of gas is assumed to be constant.

14. THE ADIABATIC EXPANSION OF T.N.T. AT A LOW LOADING DENSITY

14.1. The Hugoniot curve determines the initial conditions for the adiabatic expansion. The starting-point for the integration is given by the values

$$T = 3800^\circ \text{K}, \quad p = 8.22 \times 10^{10} \text{ dyne cm.}^{-2}, \quad v = 159.6 \text{ cm.}^3.$$

$$N_{\text{H}_2\text{O}} = 0.937, \quad N_{\text{H}_2} = 0.122, \quad N_{\text{CO}} = 1.286, \quad N_{\text{CO}_2} = 1.889,$$

$$N_{\text{CH}_4} = 0.721, \quad N_{\text{C}} = 3.104, \quad N' = 6.453.$$

From this point, equations (47) and (48) can be integrated numerically. The integration was carried out by determining $(dy/dT)_a$ at the mid-point of each integration interval and using this value of the gradient to determine the value of y at the end of the interval. The pressure and the chemical composition corresponding to these values of y and of the temperature were then determined in the way which has already been indicated (§ 13.1).

14.2. The variation of the chemical composition during the adiabatic expansion is shown in figure 5 and the pressure-volume-temperature relations are given in table 5. From these it can be seen that the amounts of free carbon and of carbon dioxide are a minimum at about 2000° K while the amount of carbon monoxide and the total number of moles of gas are a maximum at about 1950 and 1850° K respectively. Furthermore, for the adiabatic expansion, the composition changes very slowly in relation to volume or pressure in this neighbourhood. It has therefore been assumed (as in part B) that the equilibrium freezes out in this neighbourhood and that thereafter the chemical composition remains fixed. The composition of the gases at this stage (2000° K) is

$$\left. \begin{aligned} N_{\text{H}_2\text{O}} = 0.7372, \quad N_{\text{H}_2} = 0.6991, \quad N_{\text{CO}} = 3.5948, \quad N_{\text{CO}_2} = 0.8340, \\ N_{\text{CH}_4} = 0.5319, \quad N_{\text{C}} = 2.0393, \quad N' = 7.897. \end{aligned} \right\} \quad (54)$$

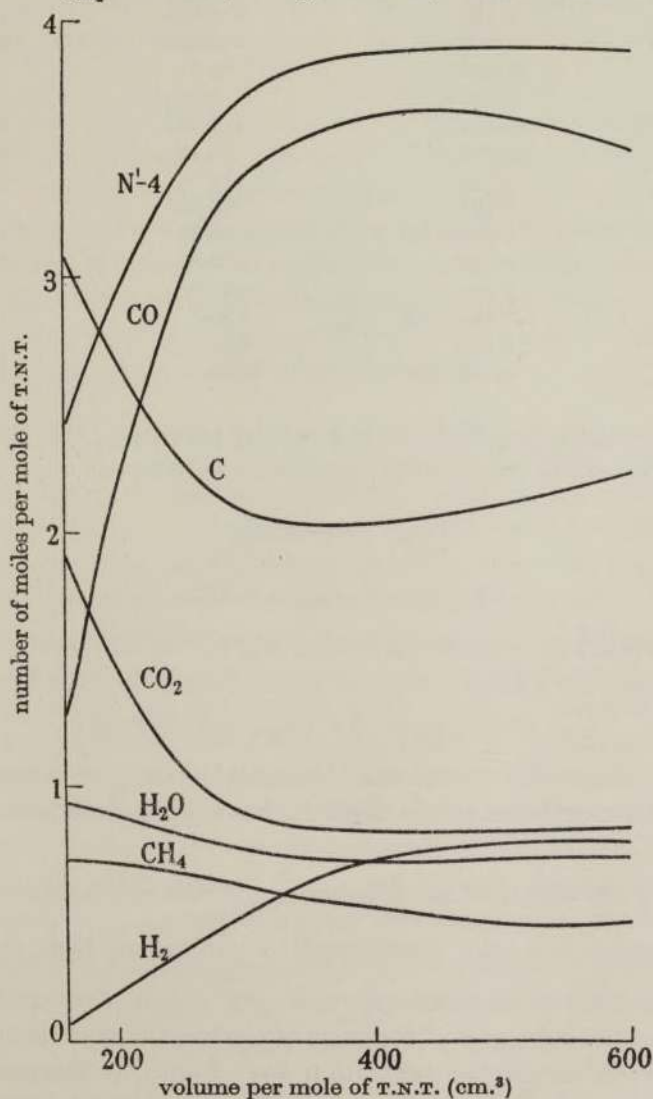


FIGURE 5. Chemical composition of the products of detonation for a loading density of 1.0 g.cm.⁻³.

TABLE 5. TEMPERATURE, PRESSURE AND VOLUME DURING ADIABATIC EXPANSION OF THE DETONATION WAVE-FRONT FOR T.N.T. AT A LOADING DENSITY OF 1.0 G./C.C.

temperature (T° K)	pressure (p dyne/cm ²)	volume (v cm ³ /g.)	γ
3800	8.224×10^{10}	0.7035	2.43
3600	6.905	0.7563	2.54
3400	5.759	0.8123	2.69
3200	4.754	0.8727	2.77
3000	3.851	0.9414	2.91
2800	3.045	1.021	2.98
2600	2.334	1.116	2.97
2400	1.726	1.235	2.88
2200	1.191	1.406	2.62
2000	7.420×10^9	1.684	2.22
1800	3.929	2.242	1.90
1700	2.783	2.688	1.73
1600	1.930	3.322	1.59
1500	1.307	4.245	1.48
1400	8.620×10^8	5.624	1.41
1300	5.511	7.752	1.32
1200	3.400	11.13	1.28
1100	2.011	16.76	1.25
1000	1.131	26.50	1.23
900	5.948×10^7	44.69	1.22
800	2.942	79.57	1.21
700	1.314	155.0	1.20
600	5.184×10^6	335.7	1.20
500	1.725	839.3	1.20
400	4.486×10^5	2580	1.20

For a fixed composition the adiabatic is given by equation (41). Substituting the values (54) for the various parameters, this finally reduces to

$$\left(\frac{dp}{dT}\right)_a = 6.035 \frac{p}{T},$$

whence

$$\log_{10} p = \log_{10} T - 2.57, \quad (55)$$

in which the constant of integration is determined by the temperature and pressure at 2000° K. Further, for a fixed composition, the volume is given by

$$v = 11.01 + 7.897(RT + bp + cp^2 + dp^3)/p, \quad (56)$$

in which the constant term is the volume of the solid phase (free carbon). The entries in table 5 for temperatures below 2000° K have been determined from these equations.

14.3. From the calculated values of pressure and volume, the external work done during the expansion has been determined by evaluating $\int p dv$ from the initial conditions to any point in the adiabatic expansion. This is plotted as the full curve in figure 3 against the cube root of the ratio of the specific volume at that point to the initial specific volume in the detonation wave-front. By comparing this curve with the broken curve in figure 3 it can be seen that the work done for a loading density of 1.0 g.cm.⁻³ is less than for a loading density of 1.5 g.cm.⁻³. The work done

during adiabatic expansion to a given specific volume falls with decreasing loading density on two accounts. First, as the loading density decreases, the specific volume in the detonation wave-front increases so that the ratio v/v_0 falls. Secondly, for a given value of v/v_0 the work done is less for a lower loading density.

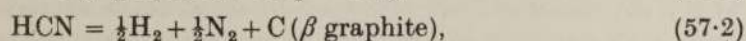
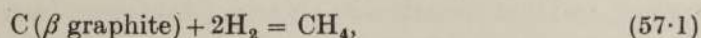
14.4. For the initial conditions the amount of chemical energy released in the detonation wave-front is 263.2 kcal./mole of T.N.T.; some of this is reabsorbed as the amount of carbon monoxide increases and when the chemical equilibrium freezes out the amount of chemical energy available is 212.8 kcal./mole of T.N.T. This final value of the chemical energy released is less than the external work done; as already noted in part B, the difference is the amount of work done on the wave-front by the detonation wave itself. By comparing the figures in this paragraph with those given in § 10.7, it will be seen that the chemical energy released per gram of explosive, and, consequently, the kinetic energy which can be obtained from a given mass of explosive is less for a loading density of 1.0 g.cm.⁻³ than it is for a loading density of 1.5 g.cm.⁻³.

14.5. From the calculated values of pressure and volume, the value of $-(d \log p/d \log v)$, more precisely, the value of the ratio $-\Delta \log p/\Delta \log v$, for each integration interval, has been determined, and is given in column 4 of table 5. It is evident that, as in the case of a high loading density, the effective exponent in the adiabatic law is higher in the initial stages of the adiabatic expansion. The behaviour of $-(d \log p/d \log v)$ is the same for low as for high loading densities, and its maximum occurs at very nearly the same volume. The remarks already made in § 10.6 in this connexion apply also in the case of a low loading density.

15. AMOUNTS OF AMMONIA AND OF HYDROCYANIC ACID

15.1. In calculating the adiabatic both for a high loading density and for a low loading density, not all the molecules which could be formed from carbon, nitrogen, hydrogen and oxygen during the detonation have been considered. In particular, the nitrogen has been treated as chemically inactive during the adiabatic expansion. As various amounts of ammonia and of hydrocyanic acid have been reported in experimental investigations (for example, Robertson & Garner 1923), this point needs further investigation. The purpose of this section is to determine the amounts of ammonia and of hydrocyanic acid which are in equilibrium with the other gases under the conditions at which there is a maximum amount of carbon monoxide and total number of moles of gas and a minimum amount of free carbon. The chemical composition under these conditions, which correspond to the freezing of the chemical equilibrium, should correspond to that which is determined in bomb experiments if no reactions occur in the container after the expansion is completed.

15.2. Ammonia and hydrocyanic acid will be formed at the expense of methane, hydrogen, nitrogen and free carbon. The reactions which have to be considered are



If the equilibrium constants of these reactions at a temperature $T^\circ\text{K}$ be denoted by $K_2(T)$, $K_5(T)$ and $K_6(T)$ respectively then, in our usual notation, the chemical composition is determined by the equations

$$N_{\text{NH}_3} + N_{\text{HCN}} + 2N_{\text{N}_2} = 3, \quad (58.1)$$

$$N_{\text{C}} + N_{\text{CH}_4} + N_{\text{CO}_2} + N_{\text{CO}} + N_{\text{HCN}} = 7, \quad (58.2)$$

$$N_{\text{H}_2\text{O}} + 2N_{\text{CO}_2} + N_{\text{CO}} = 6 \quad (58.3)$$

and
$$2N_{\text{H}_2\text{O}} + 2N_{\text{H}_2} + 4N_{\text{CH}_4} + 3N_{\text{NH}_3} = 5. \quad (58.4)$$

From these equations the values of N_{N_2} , N_{CO_2} , N_{CH_4} , N_{C} and N' can be determined without difficulty in terms of the values of $N_{\text{H}_2\text{O}}$, N_{H_2} , N_{CO} , N_{NH_3} and N_{HCN} . If, following the general equation (16), the equations which express the chemical equilibrium of the reactions (57) be written down and p^*/N' be eliminated from them, simple algebra leads to the equations

$$N_{\text{HCN}}^2 = K_5^2 N_{\text{H}_2} (1.5 - 0.5N_{\text{NH}_3} - 0.5N_{\text{HCN}}) \quad (59.1)$$

and
$$K_5 N_{\text{H}_2} N_{\text{NH}_3} = K_2 K_6 N_{\text{HCN}} (1.25 - 0.5N_{\text{H}_2\text{O}} - 0.5N_{\text{H}_2} - 0.75N_{\text{NH}_3}). \quad (59.2)$$

15.3. Provided that N_{HCN} and N_{NH_3} are small, a first approximation to their values can be obtained by putting them equal to zero in the brackets on the right-hand sides of the equations (59). This gives the approximate relations

$$N_{\text{HCN}} = K_5 (1.5 N_{\text{H}_2})^{\frac{1}{2}}, \quad (60.1)$$

$$N_{\text{NH}_3} = K_2 K_6 \left(\frac{1.5}{N_{\text{H}_2}} \right)^{\frac{1}{2}} (1.25 - 0.5N_{\text{H}_2\text{O}} - 0.5N_{\text{H}_2}). \quad (60.2)$$

At 2000°K , using the values given in (54) and the tabulated values of the equilibrium constants (Lewis & von Elbe 1938), these give the values

$$N_{\text{HCN}} = 0.0209, \quad N_{\text{NH}_3} = 0.0093.$$

These values are so small that it is clear that no appreciable error is introduced by replacing the exact equations (59) by the approximate equations (60). In fact, the error in N_{HCN} is not more than 0.5% and in N_{NH_3} is not more than 3%. It is therefore concluded that only minute amounts of ammonia and hydrocyanic acid are formed during the initial stages of the adiabatic expansion and this would not affect the calculations in this paper. It should also be noted that, in discussing the results of their experiments, Robertson & Garner (1923, p. 549) stated that the action of the permanent gases on the liberated carbon during the cooling process determined the amounts of ammonia and cyanogen compounds formed, and that due to continued reaction with the metallic fragments the amount of hydrocyanic acid depends on the rate of removal of the gases from the bomb. The calculations of this section lend support to this conclusion. It is therefore concluded that during the adiabatic expansion only negligibly small amounts of ammonia and hydrocyanic acid are formed, and that the amounts of these substances which have been found in experimental investigations are produced by reactions between the detonation products while they are cooling to room temperature after the adiabatic expansion is completed.

15.4. This also suggests that the analysis of the products of the detonation experiments carried out at the Chemisch-Technische Reichsanstalt (quoted in table 4) does not give the composition at the completion of the adiabatic expansion precisely. Allowing for the fact that most of the ammonia and hydrocyanic acid reported in these experiments was probably formed after the completion of the adiabatic expansion, it appears that the chemical composition calculated in part B for a loading density of 1.5 g.cm.^{-3} is probably in even better agreement with experiment than would appear at first sight.

16. COMPARISON WITH EXPERIMENT

16.1. It has been pointed out already that the conditions which obtain in closed bomb experiments correspond very nearly to those on which the calculations for the adiabatic expansion have been made. In the light of § 15 of this paper, one should add the proviso that precautions must be taken in the experimental investigation to ensure that the analysis of the products give the result of the expansion and not of subsequent reactions. The ratio of the number of moles of carbon monoxide to the number of moles of carbon dioxide is very sensitive to differences in loading density and to the difference in detonation pressure which arises from this. The relevant data are collected in the second and third columns of table 6, together with the available experimental data.

TABLE 6. DEPENDENCE OF $N_{\text{CO}}/N_{\text{CO}_2}$ ON LOADING DENSITY AND DETONATION PRESSURE

(The unit of pressure is $\text{dyne cm.}^{-2} \times 10^{10}$)

loading density	1.5	1.5	1.0	1.3	1.3
	(experi- mental)	(cal- culated)	(cal- culated)	(inter- polated)	(experi- mental)
pressure when chemical equilibrium freezes out	—	0.888	0.742	—	—
detonation pressure	—	15.9	8.23	—	—
$N_{\text{CO}}/N_{\text{CO}_2}$	1.66	1.33	4.31	2.52	2.93

The figures in columns 2 and 3 of this table show that a difference of about 20 % in the pressure at the point in the expansion at which the maximum amount of carbon monoxide occurs changes the ratio $N_{\text{CO}}/N_{\text{CO}_2}$ by a factor of more than three. The large value of $N_{\text{CO}}/N_{\text{CO}_2}$ at the lower loading density is almost entirely due to the smaller value of the pressure in the detonation wave-front. In fact, if the detonation pressure, for a loading density of 1.5 g.cm.^{-3} , were appreciably less than $15.9 \times 10^{10} \text{ dyne cm.}^{-2}$, the consequent reduction in the value of the activity would lead to a value of $N_{\text{CO}}/N_{\text{CO}_2}$ far in excess of the experimentally observed value of 1.66. Although this result depends on the method of calculating the activity (with its various approximations) it does provide some independent evidence for the high value of the pressure in the detonation wave-front as calculated in part A. The value of nearly $16 \times 10^{10} \text{ dyne cm.}^{-2}$ is appreciably higher than the values obtained with the co-volume method of Schmidt (1935, 1936) and of Langweiler (1938) who give a value of

9.4×10^{10} dyne cm.⁻² for this loading density. The value 2.52 in the fourth column of table 6 has been obtained from those in columns 2 and 3 by linear interpolation (which is possibly somewhat crude), but it is of interest to compare this figure with that (given in column 5 of table 6) which was obtained by Robertson & Garner (1923) for the ratio of N_{CO}/N_{CO_2} in their experiments at this loading density.

16.2. Some work of interest in connexion with these calculations was carried out at the Chemisch-Technische Reichsanstalt (Haid & Schmidt 1929, 1931; Marshall 1932). The experimental arrangement was as indicated in § 11, and two series of experiments were carried out. In one series a plain detonator consisting of 2 g. of lead azide was used to fire the T.N.T., and in the other a composite detonator which consisted of 0.3 g. of lead azide plus 1 g. of tetryl or 2 g. of lead azide was used to fire the T.N.T., and in the other a composite detonator which consisted of 0.3 g. of lead azide plus 1 g. of tetryl or 2 g. of penthrite; this latter provides a much more powerful initiator. The chemical composition of the products of the detonation in the two cases are given in table 7; the figures are the number of moles of the different products per kg. of T.N.T.

TABLE 7. PRODUCTS OF DETONATION OF T.N.T. USING DIFFERENT INITIATORS

detonator	plain	composite
loading density	1.52	1.52
CO ₂	1.78	5.30
CO	18.63	8.79
H ₂ O	4.25	7.05
H ₂	5.34	1.69
CH ₄	0.10	0.03
HCN	1.1	1.43
C ₂ N ₂	1.16	—
NH ₃	0.33	0.93
N ₂	4.74	5.42
C	6.6	15

Although the loading density was the same in the two cases there is an enormous variation in the chemical composition of the products of detonation; in particular, with the plain detonator there is 10.5 times as much carbon monoxide as carbon dioxide, while with the composite detonator this ratio is 1.66. The calculations of this and the preceding part provide an explanation of this. The relatively weak lead azide detonator fails to produce complete decomposition in the shock wave-front of the detonation zone. As a result, the pressure moves ahead of the chemical decomposition, as in the case of a laterally expanding linear charge, and therefore expands the cavity in the lead container enclosing the charge. Thus for a considerable fraction of the charge of T.N.T., the effective loading density at which chemical decomposition takes place is very much reduced. Consequently, on the basis of the calculations in this and the preceding part, a large increase in the value of the ratio of the number of moles of carbon monoxide to the number of moles of carbon dioxide is to be expected; and this is, in fact, observed. It appears that this effect could be made the basis of a means for measuring the effectiveness of initiators, since the value of the ratio N_{CO}/N_{CO_2} , which can be determined experimentally, gives a measure of

the extent to which the pressure can get ahead of the chemical decomposition in the detonation resulting from the use of any particular initiator, which in turn determines the effectiveness of a lightly cased charge.

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