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A NOTE ON THE DETONATION OF T. N. T.

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Introduction

Whenever a non-reactive shock passes through a system which is capable of undergoing an exothermic reaction, the high temperature and pressure in the shock front may start the chemical reaction, and it is possible that the heat evolved, under suitable conditions, may support the wave, and a self sustained stable shock propagate through the system. This shock wave maintained by the heat of the reaction constitutes a stable detonation wave. The equations of conservation of mass, momentum and energy, across the wave give the well known Rankine Huginiot equation. The formulation of an equation of state leaves the conditons behind the pure shock wave undetermined. All that can be determined for example are the wave and particle velocities etc. for arbitrary compressions. For detonation however, another relation becomes available by way of the hypothesis stating that the terminal conditions behind the detonation wave front correspond to the contact point of the tangent to the Rankine Huginiot curve, from the initial point in the *pv* plane. This point corresponds to the minimum entropy content of the product gases, and represents the most probable terminal state. This hypothesis first postulated by Chapman[1] and Jouguet,[2] enables the conditions behind the detonation wave front to be completely determined. These authors determined these conditions for gaseous explosives assuming a perfect gas equation for the products. The detonation velocity so determined was independant of the rate of chemical reaction and solely depended upon the initial and the final states of the reacting molecules.

The pressures developed in the detonation of gaseous explosives are seldom more than a few hundred atmospheres, and hence the perfect gas equation predicts the behaviour of product gases fairly well. The pressures resulting from the detonation of liquid and solid explosives, however amount to several thousand atmospheres, and therefore due account of the gas imperfections has to be taken while formulating and equation of state suited to those conditions. The correct determination of gas composition entails corrections to chemical equilibria as well.

The first application of the theory to condensed explosives, yielding entirely gaseous products was made by Becker[3] using an equation of state developed by himself, by fitting an equation to Amagats experimintal data on compressibility of N_2, upto 3000 atmospheres. He however did not find any unique solution, and only determined different values of VOD for arbitrary temperatures. Later[4] the approximate form of the Van der Waals equation, usually named after Abel, with the assumption of a constant covolume, was used. The temperature developed is mainly fixed by the heat of the explosion, and therefore when the value of the covolume is taken as four times the total molecular volume excluding molecular motion, the calculated values of the VOD by this equation, are overestimated as compared to the measured values. That is because the product gases in the detonation wave front are very highly compressed and the actual volume occupied by them is much less than their total molecular volume excluding molecular motion, four times which is taken as the correction in the application of this equation of state. Attempts have therefore been made by Schmidt[4], Caldirola[5] and Cook[6], to rather use the theory in the reverse way, in order to determine the values of the covolume from experimental data on different high explosives. While Schmidt calculated these values regarding covolume as a constant, the latter took into account its variation with the loading density of the explosive. The values so determined were of course arbitrary without any physical significance.

Considerable attention was paid towards improving the therodynamics of the detonation process in recent years specially during the last war. The work of Jones and Miller [7] in England, and Kistia Kowsky and Breit Wilson [8] in America, deserve special mention. The basis of Jones contribution is the following equation of state, of a very general form namely

$$\frac{pv'}{n'} = \mathrm{RT} + bp + cp^2 + dp^3 \ \ldots\ldots\ldots\ldots\ldots (1)$$

v, n being the volume and the number of moles of the gaseous products only ; b, c and d being constants independent of temperature. With the assumption of the same field of force for all gaseous molecules, Jones determined the values of b, c and d, by comparison with the experimental data on VOD for loading densities $< 1 \cdot 5$ gm/cc., and gave a neat analytical solution of the equations, for oxygen negative explosives, yielding both gaseous and solid products, also taking into account the interaction energy due to the repulsive forces between the product molecules.

The later authors made similar calculations with an equation of state of much wider application namely

$$pv = n\,\mathrm{RT}\left(1 + xe^{0 \cdot 3x}\right) \ \ldots\ldots\ldots\ldots\ldots (1a);$$

$$x = \mathrm{K}/v\,\mathrm{T}^{\frac{1}{4}}$$

K being a constant$=12 \cdot 5$, The assumption of the same field of force for all gaseous molecules is also implicit in this equation.

One of the first attempts taking account of different field of force for different chemical species, seems to be due to Paterson [9]. His is rather an absolute approach to the problem, as distinguished from Jones. He has employed an equation of state in the virial form, with expansion in terms of v. The values of the higher coefficients have been substituted in terms of B, the second virial coefficient, as determined by Boltzman Jeager and Happel. The numerical value of B for gases used is the high temperature value at 3500°K. For the mixture the value of the second coefficient is taken as a linear combination of B's for different gases.

The object of the present attempt is to apply to the detonation process, a slightly modified version of the treatment of Corner [10] as applied to propellants. The basis of his treatment in an equation of state, with expansion in terms of v, upto the third coefficient. He has tabulated values of B and C for different gases at different temperatures, calculating them on the basis of Lennard-Jones potential of molecular interaction.

In order however to extend the validity of this equation of state to higher pressures as met with in high explosives, the expansion has to be carried a step further, to include the coefficient D. In the absence of any tables for D it has been taken to be$=0{\cdot}287\ B^3$.

BASIC EQUATIONS.

Neglecting the effect of viscosity and heat conduction, the laws of conservation of mass, momentum, and energy lead to the following well known equations :—

$$D^2 = v_o^2 \frac{p}{v_o - v} \qquad \ldots\ldots\ldots\ldots\ldots (2)$$

$$E - H = \tfrac{1}{2} p\,(v_o - v) \qquad \ldots\ldots\ldots\ldots\ldots (3)$$

where D is the velocity of detonation, v_o the specific volume ; p and v are the pressure and volume in the detonation wave front (the original pressure p_o of the explosive being entirely negligible as compared to p) ; E is the energy of the products both solid and gaseous, and H is the energy of the reaction. The energy E is in general a function of temperature and pressure (or volume) and can be completely determined if the equation of state and the product composition is known. The knowledge of the composition of the products enables H also to be determined. Thus with E and H known the curve, in p and v given by equation (3) can be constructed. This is known as the Rankine Huginiot curve. This curve represents the infinity of terminal conditions possible, compatible with conservation laws, and hence corresponding to each value of (p, v) given by these points, there corresponds by virtue of the equation (2) a detonation velocity. The value of the velocity of detonation is uniquely fixed however, by the hypothesis of Chapman and Jouguet, and is taken to be the minimum of all the possible values, given by the contact point of the tangent to the Rankine Huginiot curve from the initial point.

Equation of State

In the present calculations the following equation of state has been employed—

$$\frac{p\,v'}{n'} = 1 + \frac{b}{v'} + \frac{n'c}{v'^2} + \frac{n'^2 d}{v'^3} \qquad \ldots\ldots\ldots\ldots\ldots (4)$$

p being the pressure in atmospheres, v', n', the volume and number of moles of gaseous products only, R the gas constant $=82{\cdot}06$ at. cc/gm. mole/degree, T the absolute temperature ; b, c, d being the second, third and fourth virial coefficient for the mixture of gases. Their values in terms of those for individual gases have been taken as $\Sigma n'_i B_i$, $\Sigma n'_i C_i$ and $\Sigma n'_i D_i$, respectively, B_i, C_i and D_i being the respective coefficients for the species i, n_i being the number of its gm. moles. The value of B_i's and C_i's have been taken as tabulated by Corner[10], while D_i has been taken to be$=0{\cdot}287\ B^3_i$.

Calculation of Energy E and Heat of the Reaction H

The internal energy E of the products of explosion, with respect to the value at room temperature is given by $\int_{V}^{\infty}\left[\mathrm{T}\left(\frac{\partial p}{\partial \mathrm{T}}\right)_{v'n}-p\right]dv' + n_s\,\mathrm{Es}$ ....(5)

where Es and n_s refers to the energy and gm. moles of the solid products. Evaluating the integral with the help of equation (4) we have

$$\mathrm{E} = n_i\left[\mathrm{E}_i - \mathrm{RT}^2\left\{\left(\frac{n'}{v'}\right)\mathrm{B}'i + \tfrac{1}{2}\left(\frac{n'}{v'}\right)^2 c_i'\right\}\right. + n_s\,\mathrm{Es} \quad \text{.....(6)}$$

E_i being the temperature dependent part of the internal energy for the product i, and B_i, C_i, the derivative of B_i, C_i, wrt temperature. In the absence of any knowledge of D'_i, D_i has to be regarded as a constant.

In order to find out E completely as also H—the heat of the reaction, the products must be known, which in turn can be worked out on the assumption of chemical equilibria.

For a reaction like

$$\mathrm{A}i + \mathrm{A}j \rightleftharpoons \mathrm{A}ij \quad \text{................(7)}$$

The condition for chemical equilibrium is given by $\Sigma\mu_i = o$ ....(8)
μ_i being the chemical potential of the species i.

$$\mu i = \mu_i^{\times} + \mathrm{RT}\log\frac{p_i}{p^{+}} \quad \text{..............(9)}$$

p^{+} and μ_i^{+} being the values of p_i and μ_i in some standard state, pi being the partial pressure for the product i. At very high pressures we have instead of equation (9).

$$\mu i = \mu_i^{\times} + \mathrm{RT}\log\frac{p_i^{\times}}{p^{+}} \quad \text{..............(10)}$$

$p_i^{\times}$ being the fugacity of the species i in the mixture. Putting the value of μ_i in (8) above we have

$$\frac{\overset{\times}{p}_{ij}}{\overset{\times}{p}_i\,\overset{\times}{p}_j} = \mathrm{K}(\mathrm{T}) \quad \text{..............(11)}$$

where K(T) is purely a temperature function and is called the equilibrium constant of the reaction for the perfect gas condition. $p_i^{\times}$ is given by

$$\mathrm{RT}\ \ln p_i^{\times} = \int_{v'}\left[\left(\frac{\partial p}{\partial n_i}\right)_{v'n_j} - \frac{\mathrm{RT}}{v'}\right]dv' + \mathrm{RT}\ \ln\frac{n_i\mathrm{RT}}{v'} \quad \text{.....(12)}$$

with the help of equation (4)

$$P_i^{\times} = \left(\frac{n'}{v'}\right) RT \;\; exp \left[\left(\frac{n'}{v'}\right) B + \tfrac{1}{2}\left(\frac{n'}{v'}\right)^2 C_i \times \tfrac{1}{3}\left(\frac{n'}{v'}\right)^3 D_i + \frac{b}{v'} + \frac{n'c}{v'^2} + \frac{n'^2 a}{v'^3}\right] \quad \ldots\ldots\ldots\ldots (13)$$

If on the other hand the mixture be considered as one hypothetical gas we have

$$\Sigma\, n_i B_i = n\, Ba\, ;\; \Sigma\, n_i C_i = n\, Ca\, ;\; \Sigma\, n_i D_i = n\, Da \quad \ldots\ldots\ldots\ldots (14)$$

Ba, Ca, Da, being the value of the coefficients averaged out for all the species present, and n the gm. moles of the mixture. With the assumption (14) p_i^{+} reduces to the fugacity of the mixture $p^{\times}$ and the same for all gases given by

$$p^{\times} = \left(\frac{n'}{v'}\right) RT \; exp \left[2\left(\frac{n'}{v'}\right) Ba + \tfrac{3}{2}\left(\frac{n'}{v'}\right)^2 Ca + \tfrac{4}{3}\left(\frac{n'}{v'}\right)^3 Da \right] \quad \ldots\ldots\ldots (15)$$

Equation (*1*3) when substituted in equation (11) gives

$$\frac{n'_{ij}}{n'_i\; n'_i} = K' = K\left(\frac{v'}{RT}\right) e^{\zeta} \quad \ldots\ldots\ldots\ldots (16)$$

$$\zeta = \phi_B + \phi_C + \phi_D + \phi \quad \ldots\ldots\ldots\ldots (16a)$$

$$\phi_B = \left(\frac{n'}{v'}\right)\left(B^{ij} - B_i - B_j\right) \quad \ldots\ldots\ldots\ldots (16b)$$

$$\phi_C = \tfrac{1}{2}\left(\frac{n'}{v'}\right)^2\left(C_{ij} - C - C_j\right) \quad \ldots\ldots\ldots\ldots (16c)$$

$$\phi_D = \tfrac{1}{3}\left(\frac{n'}{v'}\right)^3\left(D_{ij} - D_i - D_j\right) \quad \ldots\ldots\ldots\ldots (16d)$$

$$\phi = \frac{b}{v'} + \frac{n'c}{v'^2} + \frac{n'^2 d}{v'^3} \quad \ldots\ldots\ldots\ldots (16e)$$

Equation (15) and equation (11) however do not give a relation between n_i, n_j and n_{ij}, unless K is defined in terms of the partial pressures. If p is the total pressure and p_i the partial pressure for product i we have

$$\frac{n_{ij}}{n_i\;\; n_j} = K\,(T)\, \frac{\left(\frac{p_i^{\times}}{p_i}\right) \times \left(\frac{p_j^{\times}}{p_j}\right)}{\left(\overset{\times}{p_{ij}} / \overset{\times}{p_{ij}}\right)} \cdot \frac{p}{n} \quad \ldots\ldots\ldots\ldots (17)$$

Assumption in equation (14) implies

$$\frac{\overset{\times}{p}_i}{p_i} = \frac{\overset{\times}{p}_j}{p_j} = \frac{\overset{\times}{p}_{ij}}{p_{ij}} = \frac{\overset{\times}{p}}{p}$$

So that equation (17) reduces to

$$\frac{n'_{ij}}{n'_i \; n'_j} = K(T)\,\frac{p^{\times}}{n'} = K'_0 \qquad \ldots\ldots\ldots\ldots\ldots(18)$$

A few suitable equilibria among the products enables n_i etc. to be determined if K for each of the reactions is known. The correction factor, as is evident from equation (16) involves n' and v', which are known only if the composition becomes known. With the assumption (14) however K'_0 and hence composition from equation (18) gets determined with the knowledge of $p^{\times}$ from equation (15). This composition can be made use of to calculate K′ for the next approximation.

APPLICATION TO T N T

Calculation of the composition

TNT is an example of an explosive with a live oxygen balance so that, carbon is expected to be present among the products of detonation in the solid form. This fact along with the assumption that no nitrogen compounds are formed make it possible to write the decomposition of TNT, as

$$C_7 H_5 N_3 O_6 = 1.5\, N_2 + \alpha\, Co_2 + \beta\, Co + \gamma\, H_2 O + \delta\, H_2 \ldots\ldots(19)$$
$$+ \epsilon\, C H_4 + \eta\, C$$

where α, β, γ, δ, ϵ and η are the no. of gm. moles of Co_2, Co, H_2, O, H_2, CH_4 and of solid carbon respectively. In order to find out α, β etc. the following equilibria are considered :—

$$Co + H_2 O \leftrightarrows Co_2 + H_2 \qquad \ldots\ldots\ldots\ldots(20a)$$

$$C + 2\, H_2 \rightleftarrows C\, H_4 \qquad \ldots\ldots\ldots\ldots(20b)$$

$$Co + \tfrac{1}{2}\, O_2 \leftrightarrows Co_2 \qquad \ldots\ldots\ldots\ldots(20c)$$

$$C + \tfrac{1}{2}\, O_2 \leftrightarrows Co \qquad \ldots\ldots\ldots\ldots(20d)$$

If K_1, K_2, K_3 and K_4 are the respective equilibrium constants applicable to perfect gas condition for these reactions, the following relations immediately emerge by virtue of the equation (16)

$$\frac{\beta\gamma}{\alpha\delta} = K_1\, e^{-\phi_1} = K'_1 \qquad \ldots\ldots\ldots\ldots\ldots(21)$$

$$\frac{\delta^2}{\epsilon} = \frac{v'}{RT}\, K_2 e^{-\phi_2} = K'_2 \qquad \ldots\ldots\ldots\ldots\ldots(22)$$

$$\frac{\beta^2}{\alpha} = \left(\frac{v'}{RT}\right) \frac{K4}{K3}\, e^{\phi_4 - \phi_3} = \frac{K'_3}{K'_4} \qquad \ldots\ldots\ldots\ldots\ldots(23)$$

where

$$\phi_1 = \left(\frac{n'}{v'}\right) \Delta B + \left(\frac{n'}{v'}\right)^2 \frac{\Delta c}{2} + \left(\frac{n'}{v'}\right)^3 \frac{\Delta D}{3} \tag{21a}$$

$$\Delta B = \Sigma Bi \tag{21b}$$

$$\Delta C = \Sigma Ci \tag{21c}$$

$$\Delta D = \Sigma Di \tag{21d}$$

Σ refering to the reactants of the water gas reaction

$$\phi_2 = \left(\frac{n'}{v'}\right) f_2(B) + \left(\frac{n'}{v'}\right)^2 f_2(C) + \left(\frac{n'}{v'}\right)^3 f_2(D) + \phi \tag{22a}$$

in which

$$f_2(B) = (2B_{H_2} - B_{CH_4}) \tag{22b}$$

$$f_2(C) = (C_{H_2} - \tfrac{1}{2} C_{CH_4}) \tag{22c}$$

$$f_2(D) = (\tfrac{2}{3} D_{H_2} - \tfrac{1}{3} D_{CH_4}) \tag{22d}$$

$$\phi = \frac{b}{v'} + \frac{n'c}{v'^2} + \frac{n'^2}{v'^3} d \tag{22e}$$

$$\phi_3 = \left(\frac{n'}{v'}\right) f_3(B) + \left(\frac{n'}{v'}\right)^2 f_3(C) + \left(\frac{n'}{v'}\right)^3 f_3(D) + \tfrac{1}{2}\phi \tag{23a}$$

in which

$$f_3(B) = (B_{CO} + \tfrac{1}{2} B_{O_2} - B_{CO_2}) \tag{23b}$$

$$f_3(C) = (\tfrac{1}{2} C_{CO} + \tfrac{1}{4} C_{O_2} - \tfrac{1}{2} C_{CO_2}) \tag{23c}$$

$$f_3(D) = (\tfrac{1}{3} D_{CO} + \tfrac{1}{6} D_{O_2} - \tfrac{1}{3} D_{CO_2}) \tag{23d}$$

$$\phi_4 = \left(\frac{n'}{v'}\right) f_4(B) + \left(\frac{n'}{v'}\right)^2 f_4(C) + \left(\frac{n'}{v'}\right)^3 f_4(D) - \tfrac{1}{2}\phi \tag{23e}$$

in which

$$f_4(B) = (\tfrac{1}{2} B_{O_2} - B_{CO}) \tag{23f}$$

$$f_4(C) = (\tfrac{1}{4} C_{O_2} - \tfrac{1}{2} C_{CO}) \tag{23g}$$

$$f_4(D) = (\tfrac{1}{6} D_{O_2} - \tfrac{1}{3} D_{CO}) \tag{23h}$$

The equations (21), (22) and (23) alongwith the following

$$\epsilon + \alpha + \beta + \eta = 7 \tag{24}$$

$$2\alpha + 2\delta + 4\epsilon = 5 \tag{25}$$

$$\gamma + 2\alpha + \beta = 6 \tag{26}$$

determine the composition at any temperature.

Calculation of the Detonation Velocity

From the finally calculated composition at a certain assumed temperature, the internal energy E of the mixture of products, and the heat of the reaction H were determined with the help of the tables compiled by Pike and the Huginoit curve constructed, in the usual way, by working backwards till the various quantities involved correspond to a particular loading density. the results of calculations are tabulated below.

TABLE

Loading density gms./cc	Detonation velocity calculated met./sec.	Detonation velocity observed met./sec.	Pressure Atm. $\times 10^{-5}$	Temperature °K.
1.0	4300	4900	·40	3900
1.5	6890	6700	1.12	3940

Discussion

The temperatures obtained are higher than those found by Jones, while the pressures are lower, for the corresponding loading densities. The form of the state equation, which is the basis of these calculations, does not give rise to the interaction energy term, and hence results in higher temperatures The combination of virial coefficients chosen give a lower compressibility factor and therefore lower pressures.

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