JUL 29 1965

LA-DC-6991 (Full Paper)

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FAILURE OF THE CHAPMAN-JOUGUET THEORY FOR LIQUID AND SOLID EXPLOSIVES

W. C. Davis, B. G. Craig, and J. B. Ramsay

Los Alamos Scientific Laboratory, Los Alamos, N.M.

84796

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The usual treatment of unsupported detonation, often called the Chapman-Jouguet theory, is based on four assumptions: (1) the detonation approaches a steady state, (2) the flow is laminar and one-dimensional, (3) the detonation products approach a state of chemical equilibrium some distance behind the detonation front, and (4) the detonation velocity is the minimum permitted by the conservation conditions. In a recent paper Wood and Fickett (Phys. Fluids 6, 648(1963)) proposed experiments to test the validity of the Chapman-Jouguet "theory", not requiring knowledge or assumptions about the nature of the equation of state of the detonation products, by making variations of the initial state of the explosive. In this paper we report the results of experiments in which (1) the initial state was varied by using mixtures of nitromethane and another liquid made of equal molar parts of nitric acid, acetonitrile, and water, which has the same atomic composition as nitromethane, and (2) the initial state was varied by using TNT as liquid and as solid. These results show that the Chapman-Jouguet theory is violated. The calculated pressures are 15% to 20% below the measured pressures. Results of measurements using other explosives are also presented to support the conclusion that the theory fails. No explanation or alternative theory is offered.

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I. INTRODUCTION

The usual treatment of unsupported detonation, often called the Chapman-Jouguet theory, is based on four assumptions:

(1) The detonation approaches a steady state. All experimental measurements have indicated that the detonation velocity, pressure, light emission, etc., approach a steady limiting value, but of course very rapid oscillations cannot be ruled out.

(2) The flow is laminar and one-dimensional. For comparison with experiment the one-dimensional values must be inferred from extrapolation of experimentally measured values to those for infinite charge size.

(3) Far enough behind the detonation front (i.e., at the end of the reaction zone) the products approach a state of chemical equilibrium, they are described by a true thermodynamic equation of state, and the same equation of state applies to products obtained from different initial states. This implies that the reaction rates for the chemical reactions are reversible and very fast compared with the time of the experiments.

(4) The propagation velocity is determined by the Chapman-Jouguet hypothesis, which is that the actual velocity is the minimum one which is consistent with the conservation conditions. This assumption has been made a plausible consequence of the other assumptions under a wide range of initial conditions by Wood and Salsburg¹, although it can be violated^{2,3}. It is customary, but probably not necessary, to assume that the Rayleigh line crosses any isentrope of the explosive products at most twice, so that there are no extra relative minima in the velocity.

The consequences of these assumptions have been considered by many workers and carefully summarized in a recent paper by Wood and Fickett⁴ in which they

suggest experiments which, if they disagree with the predictions of the theory, will prove that the assumptions are not correct for the real physical systems used for the experiments. Agreement between theory and experiment will support but not prove the theory.

The work of Wood and Fickett will not be reproduced here. They showed that for solid and liquid explosives we can write

$$dD/D = -A dv_0/v_0 + B dE_0/D^2 - C dp_0/\rho_0 D^2 \quad (1)$$

where $A = \frac{\Gamma - 1 - \alpha}{\alpha + 2}$, $B = \frac{\alpha(\Gamma + 1)^2}{\alpha + 2}$, $C = \frac{\Gamma + 1}{\alpha + 2}$.

The symbols are defined as follows: D is the detonation velocity, v is the specific volume, E is the specific internal energy, p is the pressure,

$$\rho_0 = 1/v_0, \quad \Gamma = -(\partial \ln p / \partial \ln v)_S \text{ where } S \text{ is the specific entropy, } \alpha = p(\partial v / \partial E)_p.$$

The subscript zero indicates the initial state. Three variables are used rather than the usual two because in low-density pressed explosive E_0 and v_0 are independent. The differentials in eq. (1) are differentials only of the initial state variables. Therefore, measurement of the changes in the detonation velocity D produced by two independent variations in the initial-state variables v_0 , p_0 , and E_0 , will give two equations for the determination of the two unknowns Γ and α , which are unknown because the equation of state of the products of detonation is unknown. The C-J pressure is then given by

$$p = \rho_0 D^2 / (\Gamma + 1) \quad (2)$$

which follows from the assumptions. Comparison of this value of the pressure with the pressure measured by experiment then provides the test of the theory.

In this paper such experiments are described and their results presented. Most of the experiments were done at this laboratory for this study. The results show that the assumptions are not correct for the explosive systems

used. The pressures calculated from the detonation velocity measurements using the Wood and Fickett analysis are 15% to 20% below the measured pressures for nitromethane, liquid TNT, and solid TNT.

The experimental values of D and p must of course be inferred by extrapolating sets of measurements to infinite diameter in order to satisfy the assumptions of the theory. The extrapolations of D are linear with reciprocal charge radius and are of very small range. The pressure measurements, however, have revealed a structure⁵ which was not predicted and which is not understood. In some cases it is difficult to be sure what point on the pressure-distance curve corresponds to the C-J point. The uncertainty introduced by this unexpected pressure structure is small compared with the difference between theory and experiment and does not affect the conclusion that the theory is violated.

Using theory and measurements it is possible to infer something about the equation of state of the explosive products. Some data are presented which show that if the theory is correct the equation of state must be very peculiar. This result is interpreted in support of the conclusion that the C-J theory is incorrect.

No replacement for the usual theory is offered; no suggestion of the nature of the failure of the assumptions is found in the data. The only conclusion that can be drawn is that the experimental results are inconsistent with the consequences of the theory.

II. NITROMETHANE AND ACENINA

A. Theory

A variation of the initial energy can be made by using two explosives with the same atomic composition but different heats of formation. Nitromethane (CH_3NO_2) and a mixture called Acenina, made from equimolar quantities

of acetonitrile (CH_3CN), nitric acid (HNO_3), and water, are two such explosives. They are miscible to an appreciable extent and so allow the determination of the derivatives with respect to composition. Acenina is used only to determine a first derivative which is to be evaluated for pure nitromethane, and the test of the theory is for nitromethane only.

The experiments with variations of initial state are:

(1) Determination of $(\partial D / \partial T_o)_{p_o}$ by measurement of the variation of D with initial temperature for pure nitromethane.

(2) Determination of $(\partial D^2 / \partial w_o)_{T_o, p_o}$, where w_o is the weight fraction of Acenina, by measurement of the variation of D with composition at constant temperature.

The choice of D as the variable in (1) and D^2 in (2) is dictated by the fact that the dependence on T_o or E_o must be sufficiently linear that the first derivatives can be obtained with sufficient accuracy from measurements at a few values of T_o and E_o . The choice is discussed by Wood and Fickett⁴.

From eq. (1) for the first variation,

$$D^{-1}(\partial D / \partial T_o)_{p_o, w_o} = -A(\partial \ln v_o / \partial T_o)_{p_o, w_o} + (B/D^2)(\partial E_o / \partial T_o)_{p_o, w_o}, \quad (3)$$

and for the second,

$$D^{-1}(\partial D / \partial w_o)_{p_o, T_o} = -A(\partial \ln v_o / \partial w_o)_{p_o, T_o} + (B/D^2)(\partial E_o / \partial w_o)_{p_o, T_o}. \quad (4)$$

Solved for A and B these become

$$A = \frac{\frac{1}{2}C_p^o(\partial D^2 / \partial w_o)_{T_o, p_o} - \bar{E}_o D(\partial D / \partial T_o)_{p_o, w_o}}{D^2(\beta \bar{E}_o - \rho_o \bar{v}_o C_p^o)} \quad (5)$$

$$B = \frac{\frac{1}{2}\beta_o(\partial D^2 / \partial w_o)_{T_o, p_o} - \rho_o \bar{v}_o D(\partial D / \partial T_o)_{p_o, w_o}}{\beta_o \bar{E}_o - \rho_o \bar{v}_o C_p^o} \quad (6)$$

where we set $(\partial E_o / \partial T_o)_{p_o, w_o} = (\partial H_o / \partial T_o)_{p_o, w_o} = C_p^o$, the constant-pressure heat capacity, and use $(\partial \ln v_o / \partial T_o)_{p_o, w_o} = \beta_o$, the thermal expansion

coefficient, with the partial specific quantities $\bar{v}_0 = (\partial v_0 / \partial w_0)_{T_0, p_0}$ and $\bar{E}_0 = (\partial E_0 / \partial w_0)_{T_0, p_0}$. Using experimental quantities in eqs. (5) and (6) to get A and B, we will then use A and B to get Γ . We then substitute this value into eq. (2) to find p, the C-J pressure. Finally we compare this value with the measured value to see whether the theory is in agreement with experiment.

Conclusions drawn from this comparison will depend on the size of the experimental errors, so the experimental technique and the analysis of the errors will be presented in detail. The quantities involved will be taken up one at a time.

B. Detonation Velocity and its Derivatives

A system based on nitromethane was convenient because many data were available. The detonation velocity and the temperature coefficient of velocity have been reported by Malin, Campbell and Holland⁶, and by Campbell⁷. All of the data obtained by these authors have been reexamined for the purpose of this study. This reexamination involved the establishment of the purity of the material used and the analysis of all data as a complete group.

The infinite-diameter velocity for nitromethane was taken from the unpublished work of Campbell. These experiments consisted of 14 shots fired during 1957 and 1958. The confinement material was 0.05-mm Mylar with the diameter ranging from 2.5 cm to 10 cm and lengths up to 1.5 m. The temperature was controlled for all shots at $26 \pm 2^\circ \text{C}$. The material used was specially prepared for these studies by Commercial Solvents Corporation. An analysis of the nitromethane showed 0.16% water with no detectable traces of the higher nitroparaffins. The nitromethane content was in excess of 99%. Electrical discharge pins were located on the axis of the charges and the

transit time between pins was recorded on an electronic chronograph⁸. The velocity of each rate stick was calculated as the reciprocal of the slope of the linear least-squares fit of time as a function of distance. The variance of this fit was used only to determine that the velocity was constant in that shot. The measured velocity was adjusted for the difference between the temperature at the time of firing and 26° using a correction factor of -4 m/sec °C. In no case did this correction amount to more than 5 m/sec. The infinite-diameter velocity was then calculated as the intercept of the least-squares fit of the adjusted velocity as a function of reciprocal diameter. The value obtained was 6286.8 m/sec with 95% confidence limits of ± 7.8 m/sec. This confidence limit was calculated using the shot-to-shot variance, and is not influenced by the (smaller) variance of the fit to the pins of a single shot.

The temperature coefficient of the infinite-diameter velocity was calculated from data obtained by Malin, Campbell, and Holland⁶. The nitromethane used for these experiments was a commercial grade supplied by Commercial Solvents Corporation and contained approximately 97% nitromethane with 0.1% water and the balance higher nitroparaffins. The experiments consisted of a group of shots at each of five temperatures ranging from -26°C to +34°C with the confinement material being either glass or brass. The diameters ranged from 0.6 to 10 cm. The experimental details are given in Ref. 6. Because additional data were obtained after the publication of Ref. 6, the temperature coefficient has been recalculated utilizing all the data. This was done by first making a least-squares fit of the velocities at each temperature as a function of reciprocal diameter to obtain the infinite-diameter velocity for that temperature. In addition, the standard deviation

for each infinite-diameter velocity was calculated from the variance of the fit to the adjusted velocity from each shot. Each value of the infinite-diameter velocity was then weighted by the reciprocal of the square of its standard deviation and a least-squares fit of velocity vs temperature performed. The temperature coefficient obtained was $-3.964 \text{ m/sec } ^\circ\text{C}$ with 95% confidence limits of $\pm 0.18 \text{ m/sec } ^\circ\text{C}$. The value obtained for the velocity of nitromethane from these experiments was lower than the value obtained from the work discussed in the preceding paragraph by approximately 0.7%. This difference is the result of the impurities in the nitromethane. The effect of the impurities on the temperature coefficient is expected to be very small. A plot of the infinite-diameter velocity vs temperature is shown in Fig. 1.

To evaluate $(\partial D^2 / \partial w_o)$ measurements of the detonation velocity of mixtures of nitromethane and Acenina are required. Shots were fired with the mixture containing 50%, 85%, and 100% by weight of Acenina, and the nitromethane velocity measurements give a point corresponding to 0% Acenina. In addition to giving the value for $(\partial D^2 / \partial w_o)$, these data demonstrate that the square of the velocity is indeed a linear function of the energy, as predicted by Wood and Fickett⁴ from calculations.

The Acenina used for the experiments was prepared by first making an equimolar solution of nitric acid and water and then mixing the proper amount of the acid solution with acetonitrile on the firing mound just prior to firing the shot, handling the chemicals by remote control. The concentration of the nitric acid solution was checked by titration with a standardized sodium hydroxide solution and the error in concentration probably did not exceed $\pm 0.05 \text{ wt. } \%$. The acetonitrile used was analyzed spectrophotometrically for other nitriles and a Karl Fisher determination was made for the water content. No nitriles were detected and the water content was

between 0.12 and 0.4 wt % for different lots. The required amounts of nitric acid solution and acetonitrile for a particular shot were measured by weight to ± 0.5 gram. All shots, except one, required amounts of each constituent in excess of 300 grams, which meant that the expected error in concentration was less than 0.5%. The temperature of the shots was controlled by having the remote mixing apparatus and the shot tube immersed in ice water. The actual temperature at the time of firing was monitored by a thermistor in the liquid explosive. Experiments were performed which indicated that there were no phase separations for either Acenina or a 50-50 mixture of Acenina and nitromethane in the temperature range -5° to 30°C .

A major difficulty with the Acenina composition was that the solution was electrically conducting and highly corrosive. This made the use of the usual pin switch impossible. After several attempts to develop a pin switch which would work, it was found that a coaxial pin which was completely incased in gold had been developed by Wasley, et al.⁹ Samples of the pins were obtained and it was found that they would withstand Acenina for several hours. Pins of this kind were generously supplied by Lawrence Radiation Laboratory-Livermore for this study.

The shot geometry used for all shots, except one, consisted of a Type 321 stainless-steel tube with an inside diameter of 5.25 cm and a wall thickness of 0.406 cm. This 5-cm diameter was selected as a compromise between the requirement that the velocity be measured at as large diameter as possible and the restrictions on the size of the remote-mixing apparatus. Seven pins were used for most shots. They were inserted through the wall of the shot tube and centered within 0.5 mm of the axis of the tube. The first pin was located 25 cm from the booster and succeeding pins were placed at 5-cm intervals. The booster system for all shots consisted of a 10-cm diameter

plane-wave lens, 3.8 cm of Composition B, 0.279 cm of steel, and 1.68 cm of the polyester plastic Homolite. The distance between the pins was measured with a height gage and contact between the measuring foot and the pin was detected electrically. The reproducibility among sets of readings was 0.05 mm. The time for the detonation wave to travel between the pins was measured with an electronic chronograph⁸ and the velocity was calculated by a least-squares fit of time as a function of distance.

Despite the fact that the shot assemblies were immersed in ice baths, some difficulty was encountered in obtaining a uniform temperature for all the shots. The range was from 0.8°C to 9.0°C. Therefore, the measured velocities were adjusted to a standard temperature of 4°C. This was done using the same temperature coefficient of velocity as for pure nitromethane. The use of the same coefficient for Acenina as for nitromethane was supported by BKW equation-of-state calculations¹⁰ performed by Lombardi¹¹. The velocities were also corrected for the small amount of water which was introduced as an impurity in the acetonitrile. This correction amounted to less than 2 m/sec for all shots. For one shot it was found that an incorrect amount of acetonitrile had been used. An adjustment was made for this difference. Both the adjustments for the water concentration and for the error in the acetonitrile concentration were made on the basis of coefficients obtained by Lombardi. These adjusted velocities are shown in Table I under the column headed "Corrected Velocity". Also shown for the purpose of comparison is the best estimate of the infinite-diameter velocity of nitromethane.

The velocities which are required for the calculations are the infinite-diameter velocities. If it had been necessary to establish the diameter-effect curve for each composition studied, the project would have required an

Table I

The Detonation Velocity of Acenina and Mixtures of Acenina and Nitromethane

<u>Diameter (mm)</u>	<u>Temperature (°C)</u>	<u>Weight Fraction Acenina</u>	<u>Measured Velocity (m/sec)</u>	<u>Corrected^a Velocity at 4°C (m/sec)</u>	<u>D² m²/sec² x 10⁻⁶</u>
52.5	4.0	1.00	5717.4	5715.9	32.672
52.5	2.0	1.00	5707.2	5697.7	32.464
52.5	0.8	1.00	5721.6	5707.4	32.574
9.5	2.4	1.00	5724.1	5717.7	32.692
52.5	9.0	0.850	5820.8	5840.7	34.114
52.5	1.4	0.493	6080.9	6059.3	36.715
52.5	2.1	0.500	6060.3	6052.1	36.628
∞	26.0	0.00	6286.8	6374.0	40.628

a. See text.

inordinately large number of shots. It was therefore decided to try to estimate the size of the diameter effect. Malin, Campbell and Holland⁶ showed that at 5-cm diameter the detonation velocity of nitromethane confined in glass tubes was only 3 m/sec less than the infinite-diameter velocity. They also showed that the diameter effect was smaller in brass tubes than in glass ones. If the diameter effect in Acenina and in mixtures of Acenina and nitromethane is no larger than in pure nitromethane, then the difference between the velocities measured at 5-cm diameter and the infinite-diameter velocities is less than the expected experimental errors. One shot on Acenina was made at a diameter of 9.5 mm, which is as small as the present techniques permit, and the velocity was indistinguishable from that measured for the larger diameters. If the diameter effect was the same as or larger than that for pure nitromethane, a decrease in velocity of 15 m/sec or more was expected. It was therefore concluded that the diameter effect of Acenina was no larger than for nitromethane. This conclusion is supported by the fact that the failure diameter for Acenina is 0.025 cm compared with 0.25 cm for nitromethane under the same conditions.

C. Physical and Thermochemical Quantities

A search of the literature indicated that the required physical and thermochemical quantities were available for nitromethane,^{6,12} and that the heats of formation were available for the components of Acenina¹². It was therefore only necessary to measure the density of Acenina and to determine the heat of mixing of nitric acid monohydrate with acetonitrile. These measurements were made using standard laboratory procedures, except that the procedure for measuring the heat of mixing was modified to allow remote handling of the explosive. It was possible to determine the density with a small sample

so that remote handling was not required. The relationship between density and temperature for Acenina was found to fit the following equation over the temperature range -2°C to $+22^{\circ}\text{C}$.

$$\rho \text{ (g/cc)} = 1.145 [1 + 0.0012 T (^{\circ}\text{C})]^{-1}$$

The estimated error of this fit is $\pm 0.002 \text{ g/cm}^3$. The heat of mixing $\text{HNO}_3 \cdot \text{H}_2\text{O}$ with an equal molar amount of acetonitrile at 10°C was found to be $-10.6 \pm 0.3 \text{ cal/g}$. The heat of mixing Acenina with nitromethane was also measured for a 60-40 solution. This was found to be -1.7 cal/g of solution (60% Acenina). The estimated error of this measurement is $\pm 1 \text{ cal/g}$.

It is necessary to estimate the error in each quantity used in eqs. (5) and (6). The values of the quantities together with their source references and estimates of the errors are given in Table II. The errors listed are believed to be pessimistic estimates.

Ideal mixing was assumed for the calculation of the partial specific quantities $\bar{E}_0$ and $\bar{v}_0$. This is justified because it was shown that there is only a small heat of mixing of nitromethane and Acenina. The estimated error in the energy term was increased to compensate for this assumption. The absolute value of $\bar{v}_0$ is small and errors arising from non-ideal mixing could not affect the calculations. $(\partial^2 D / \partial w_0)_{p_0, T_0}$ is a measured quantity and does not depend on the assumption of ideal mixing.

D. Results

Substituting the values listed in Table II into eqs. (5) and (6) to get A and B, then using the definitions given with eq. (1) to find Γ , and finally using eq. (2), the calculated C-J pressure can be found. By using

Table II

Physical and thermochemical properties of nitromethane and Acenina at 4°C

<u>Explosive</u>	<u>Property</u>	<u>Value</u>	<u>Reference</u>
Nitromethane	ρ_o	$1.159 \pm 0.001 \text{ g/cm}^3$	6
"	C_p^o	$0.414 \pm 0.01 \text{ cal/g}$	12
"	β_o	$(1.158 \pm 0.01) \times 10^{-3} \text{ }^\circ\text{C}^{-1}$	6
"	ΔH_f^o	$-347.0 \pm 0.5 \text{ cal/g}$	12
"	$(\partial D / \partial T_o)$	$-3.964 \pm 0.18 \text{ m/sec } ^\circ\text{C}$	7 and this paper
"	D	$6374.0 \pm 8.7 \text{ m/sec}$	this paper
Acenina	ρ_o	$1.139 \pm 0.002 \text{ g/cm}^3$	this paper
"	ΔH_{mix}	$-10.6 \pm 0.5 \text{ cal/g}$	this paper
"	$\Delta H_f(\text{HNO}_3 \cdot \text{H}_2\text{O})$	$-112.79 \pm 0.01 \text{ kcal/mole}$	12
"	$\Delta H_f(\text{CH}_3\text{CN})$	$+12.8 \pm 0.2 \text{ kcal/mole}$	12
"	$\Delta H_f(\text{Acenina})$	$-829.8 \pm 3.0 \text{ cal/g}$	
Mixture	$(\partial D^2 / \partial w_o)$	$(-7.983 \pm 0.177) \times 10^6 \text{ (m/sec)}^2$	this paper
"	$\bar{E}_o$	$-482.8 \pm 4.0 \text{ cal/g}$	
"	$\bar{V}_o$	$(+1.5 \pm 0.2) \times 10^{-2} \text{ cm}^3/\text{g}$	

partial differentiation it can be shown that

$$\begin{aligned} dp/p = & 3.184 dD/D - 0.249 d(\partial D^2/\partial w_o)/(\partial D^2/\partial w_o) - 0.93 d(\partial D/\partial T_o)/(\partial D/\partial T_o) \\ & - 0.110 dc_p^o/c_p^o + 1.017 dp_o/p_o + 0.225 d\bar{E}_o/\bar{E}_o \\ & + 1.3 d\beta_o/\beta_o + 0.02 d\bar{v}_o/\bar{v}_o. \end{aligned}$$

With the error values from Table II the rms error of the pressure is found by taking the square root of the sum of the squares of the terms. Although the first three terms are not really independent in principle, in this case each comes from a separate set of experiments. The calculated C-J pressure is 126.5 ± 5.4 kbar, with the $\pm$ term the probable 95% confidence limit. The term in $(\partial D/\partial T_o)$ is responsible for almost all the error.

Extensive experimental measurements of the detonation pressure of nitromethane have been made by Craig⁵. He finds the C-J pressure to be 141 ± 1 kbar at 23°C . Adjusting this value to 4°C either by assuming constant Γ in eq. (2) and using the proper value of ρ_o and D , or by using the BKW calculations of Lombardi¹¹, the experimental pressure is found to be 148 ± 1 kbar. Some of the experimental data are plotted in Fig. 2 to show how charge size influences the measurements. For the measurements to agree with the calculated value of 126 kbar, the intercept would have to be $1.90 \text{ mm}/\mu\text{sec}$.

The calculated C-J pressure, 126.5 ± 5.4 kbar, and the measured pressure, 148 ± 1 kbar, are significantly different. The Chapman-Jouguet theory does not work for nitromethane.

III. LIQUID AND SOLID TNT

A. Theory

Another variation of the initial energy can be made by using liquid and solid forms of the same explosive. The initial energy will be different by

approximately the heat of fusion. This experiment has been done using liquid and solid TNT at the same density.

The experiments with variations of initial state are:

(1a) Determination of $(\partial D / \partial T_o)_{p_o}$ by measurement of the liquid detonation velocity as a function of initial temperature.

(1b) Determination of $(\partial D / \partial \rho_o)_{p_o}$ by measurement of the solid detonation velocity as a function of initial loading density.

(2) Approximate determination of $(\partial D^2 / \partial E_o)_{p_o}$ by the ratio $\Delta D^2 / \Delta E_o$ of the difference between the squares of the solid and liquid detonation velocities and the difference in the solid and liquid initial energies

$$\Delta E_o = H_l - H_s \quad (7)$$

where H_l and H_s are the enthalpies of the liquid and solid at their respective temperatures.

In this experiment we have from eq. (1) with variation (1a)

$$B = \frac{1}{2} (\Delta D^2 / \Delta E_o) \quad (8)$$

$$A = (B/D^2) (C_p^o / \beta_o) - \beta_o^{-1} D^{-1} (\partial D / \partial T_o)_{p_o} \quad (9)$$

If we use variation (1b) we have

$$B = \frac{1}{2} (\Delta D^2 / \Delta E_o) \quad (10)$$

$$A = (\partial \ln D / \partial \ln \rho_o)_{p_o} \quad (11)$$

The value of Γ obtained from variation (1a) will, when substituted into eq. (2), give the theoretical value of p for the liquid, while variation (1b) will give p for the solid.

B. Detonation Velocities and their Derivatives

Very extensive accurate measurements of the detonation velocity of pressed TNT charges have been reported by Urizar et al.¹³ All the

measurements were made with a single lot of TNT manufactured in August, 1944, by the Atlas Powder Company. This lot is estimated to be 99.6 mole percent 2,4,6-TNT. They used several different diameters at each of several densities, and extrapolated their data to infinite diameter. They give an expression for infinite-diameter detonation velocity as a function of initial density. For density 1.4502 g/cm^3 they give $D = 6494.8 \text{ m/sec}$, with the 95% confidence interval given as $\pm 7 \text{ m/sec}$, and $(\partial D / \partial \rho_0) = 3187.2 \pm 27.1 \text{ m/sec per g/cm}^3$, with the $\pm$ value the 95% confidence limit. At a density about 6% higher the value of $(\partial D / \partial \rho_0)$ drops to about one-half its low-density value. We believe that this change is caused by a change in the utilization of the heat of sublimation of the large amount of solid carbon present in the products of high-density TNT, and that the value of $(\partial D / \partial \rho_0)$ in our density range is an accurate value.

The detonation velocity of liquid TNT was measured using the same lot of TNT that Urizar, et al. used to make the pressed TNT charges. This precaution was necessary because the difference between the liquid and solid velocities at the same density is an important item in the test of the theory and small differences in detonation velocity have been noticed between lots of explosive in other experiments.

Each shot was made up from two coaxial stainless steel tubes; the inner tube contained the TNT, and the annular space between the two tubes contained a boiling liquid (water or butyl acetate) and electric heaters. The ends of the tubes were sealed with Teflon gaskets to Dural endplates. The velocity-measuring pins extended through the annular space into the center of the inner tube. The front endplate was made as a re-entrant cone to reduce the cooling

at its center, and contained at its center as an insert a small polished disc of Dural. The free-surface velocity of the small disc was measured to indicate the detonation pressure. Figure 3 shows a diagram of the complete shot.

The design of the pins for the velocity measurement presented some severe problems. The electrical connections to the pins had to be insulated from the two tubes and from the liquid in the annular space, and the arrangement had to allow assembly of the two tubes. The final design, which proved very satisfactory, is shown in Fig. 4. The conical section of the Teflon sleeve is cut to a 59° included angle, and the conical hole in the inner tube into which it fits is cut to 60° . When the assembly is tightened the Teflon contracts against the wire, holding it securely in place.

In assembly, the points of the pins were centered in the tube within 0.25 mm. The pin spacing was measured, with the whole assembly at the temperature at which it would be shot, through the hole in the front plate which would contain the pressure measuring disc. A measuring rod with a foot on it was inserted through the hole and carefully moved into contact with the pin. Contact was determined with an electrical ohmmeter. The position of the rod was determined with a vernier height gage. Repeated measurements with the system cooled and reheated between measurements showed that the pins were stable to about 0.05 mm. The spacings were 140 mm and 70 mm in the two sizes. A correction of about 1 part in 2000 for the expansion of the measuring rod is required. A correction of 3 m/sec has been added to each velocity.

The times were recorded using standard techniques⁸ with electronic chronograph systems. A least-squares fit to the times and distances was used to get the best velocity determinations.

The temperature was controlled by maintaining the liquid in the annular space at its boiling point with electric heaters. Water was used to get a temperature of 93°C (at atmospheric pressure of 59 cm Hg), and technical grade butyl acetate to get 114°C . Measurements with thermocouples showed internal temperatures constant within 1° . The temperature inside the inner tube 0.25 mm from the pressure measuring plate was about 1° or 2° cooler, and the temperature of the plate itself was about 3° below the temperature of the interior TNT. Rapid boiling was necessary to get uniform temperature, and a condenser was used to prevent loss of the liquid.

The explosive was transported from the melting room to the firing site in Dewar flasks. The explosive was molten for periods ranging from 3 to 6 hours. Two identical shots fired at the two extremes of this time range showed velocities differing by only 1 m/sec, which is not a statistically different result. Many other experiments show that no significant decomposition of the TNT takes place in a few hours.

A listing of the shots and all the data are given in Table III. The velocities for each increment of the sticks are given to provide an idea of the stabilities of the pins, but the best values are least-squares fits to the readings of the times. These least-squares values must be corrected for the expansion of the measuring rod by adding 3 m/sec to each. The data are too few for statistical analysis, and the errors must be estimated from experience with other liquid explosives. We have found that the standard deviation is about 1.5 m/sec for a velocity measurement in a rate stick of the type used here. The temperature error may have a standard deviation of about 0.4°C , with a resulting velocity standard deviation of about 1.4 m/sec.

TABLE III

Molten TNT Shots

Diameter (mm)	Length (mm)	Temperature (°C)	Density ^a (g/cm ³)	Segment Velocities (m/sec)	Least-Square Velocities (m/sec)	Free-Surface Velocity (m/sec)	Corrected ^b Velocity (m/sec)
54	629	93	1.450	6555.5	6554.0	2210	6557
				6555.8			
				6547.1			
				6554.2			
				6561.5			
54	629	93	1.450	6556.0	6554.6		6558
				6554.5 ^c			
				6553.3			
122	1238	93	1.450	6568.4	6572.6	2400	6576
				6564.8			
				6569.3			
				6600.5 ^d			
				6552.8 ^d			
54	629	114	1.429	6501.2	6500.6	2195	6504
				6501.4			
				6503.4			
				6497.4			
				6499.4			
122	1238	114	1.429	6503.6	6513.6 6508.3 ^e	2340	6511
				6504.7			
				6515.7			
				6508.6			
				6539.6			

a. Reference 15.

b. Correction for expansion of measuring rod - add 3 m/sec.

c. Segment velocity between pins 2 and 5.

d. Pin 5 out of position.

e. Omitting last segment.

The two errors combine to give a standard deviation of about 2 m/sec. Figure 5 shows the extrapolation of the detonation velocity to infinite diameter at the two temperatures. Every one-component explosive studied has shown a linear dependence of detonation velocity on reciprocal radius. Therefore, although we have only two values of radius at each temperature, we have confidence that the method of extrapolation is correct. The extrapolated values are 6590 m/sec at 93°C, and 6517 m/sec at 114°C, with the standard deviation estimated as 4 m/sec for each. The temperature coefficient of velocity is -3.5 m/sec °C, with the standard deviation estimated to be 0.3 m/sec °C.

The detonation velocity of liquid TNT has also been measured by Seely and Johnson¹⁴. They did experiments in glass, paper-base-phenolic plastic, and brass tubes. The most extensive set of measurements, and the one most applicable to this paper, was done in brass tubes. The temperature was controlled with heated air and measured at several points along the tube with thermocouples. The temperature was known to within about $\frac{1}{2}$ °C. The velocity was measured using only two pin contactors in each shot. The signals were recorded using the standard techniques⁸, although corrections for non-linearity of the oscilloscope sweeps were required. In every case the detonation was allowed to run at least five diameters before reaching the first pin. The pin spacing was constant at about 63 mm. Shots were fired at internal tube diameters of 32 mm, 50 mm, and 101 mm with 6 mm brass wall thickness in each case.

A least-squares fit of detonation velocity versus reciprocal radius to 21 shots at 90°C extrapolates to give the infinite-diameter detonation velocity as 6582.3 ± 7 m/sec, 14 shots at 100°C give 6555.5 ± 8 m/sec, and

13 shots at 120°C give 6489.4 ± 8 m/sec. These extrapolations give $(\partial D/\partial T_0) = -3.13 \pm 0.3$ m/sec °C. The error limits are estimated 95% confidence limits.

The TNT used for these shots was from a different lot than that used for the measurements of the detonation velocity of the solid and for the other liquid measurements. The purity of the TNT was estimated from freezing point measurements to be at least 99.6%, so the difference in detonation velocity must also be small. Perhaps the confidence limits on the velocity should be increased by ± 10 m/sec when finding the difference between liquid and solid velocities.

This work has not been written up by Seely and Johnson, and it is difficult for us to tell whether there may be systematic errors in the measurements. We have no reason to doubt the statistical analysis of the data, but we have too little knowledge of the details of the experiments to feel sure of the results, so we have not used them in the error analysis at the end of this section.

C. Physical and Thermochemical Properties

Especially good measurements of the enthalpy, density, and coefficient of thermal expansion have been reported by Cady and Rogers¹⁵. The TNT they used had a melting point of 80.71°C, which is very slightly different from that of the TNT used for the velocity measurements (80.55°C). Both are estimated to be 99.6 mole percent 2,4,6-trinitrotoluene, and the impurities are presumed to be the other isomers of TNT and the dinitrotoluenes. We believe that the TNT used is identical with that used for the velocity measurements for the purposes of this paper, and that corrections are neither necessary nor possible. Cady and Rogers give the density of TNT as

$$\rho_0 \text{ (g/cm}^3\text{)} = (1.54463 \pm 0.00039) - (1.0156 \pm 0.0043) \times 10^{-3} T \text{ (}^\circ\text{C)}$$

where the $\pm$ values are the 95% confidence limits. They express the enthalpy of the liquid from 83°C to 117°C as

$$H - H_0 = (12.450 + 0.45023 T - 4.0091 \times 10^{-4} T^2) \text{ cal/g}$$

where the 95% confidence limit is ± 0.08 cal/g at 83°C, ± 0.06 cal/g at 96°C, and ± 0.12 cal/g at 117°C. For the solid the enthalpy between 25°C and 68°C is given by

$$H - H_0 = 0.045 + 0.24625 T + 4.205 \times 10^{-4} T^2 \text{ cal/g}$$

where the 95% confidence interval is ± 0.049 cal/g at 25°C, ± 0.035 cal/g at 50°C, and ± 0.041 cal/g at 68°C. For the liquid at 93°C we have

$$C_p^0 = 0.376 \text{ cal/g}^\circ\text{C} \text{ with a 95\% confidence interval of } \pm 0.006 \text{ cal/g}^\circ\text{C}.$$

The confidence intervals given here for the enthalpies are about three times those stated by Cady and Rogers, because their expression for $\pm L_{95}$ contains an error.

D. Pressure Measurements

There are two good independent sets of measurements of the pressure in liquid TNT. The velocity measurement shots described above were fitted with a polished Dural disc 2.57 mm thick for free-surface velocity measurement using the smear camera technique described by Davis and Craig¹⁶. The results are given in Table III. One way to use these data to find the pressure at infinite diameter is to assume that the velocity of a plate of constant thickness varies inversely as the diameter of the charge, in analogy to the known fact that the detonation velocity varies inversely with the charge diameter for a single component explosive. Used in this way, the data, reduced by the method described by Garn¹⁷, give the infinite-diameter pressure as 179 kbar at 93°C and 172 kbar at 114°C, with an uncertainty of about 2% in each case.

Garn¹⁷ made extensive measurements on liquid TNT using the flash-gap technique described by Deal¹⁸. His charges were 203 mm diameter and 304 mm long for most of his measurements. He fired one charge that was 203 mm diameter and 608 mm long, and another that was 203 mm diameter and 229 mm long, as tests to see that steady state had been reached. He found the pressure to be 171.8 ± 1.4 kbar at 92°C .

More recent work, some of which has been discussed by Craig⁵, leads us to believe that in explosives like TNT with long reaction times, on the order of 10^{-8} sec, the pressure at the end of the reaction zone in charges of a size which we can use conveniently, up to a few hundred pounds, depends upon the size of the charge. Small charges give measured pressures much below the pressure for a charge which has reached steady state. This is true even though the detonation velocity is very close to its steady-state value after only a short run. Probably both estimates of the C-J pressure given above are too low, but we do not know what the correct value is. For the purposes of this paper, however, we will find that the lower confidence limit on the pressure is the number we need. We can safely assume that the pressure is certainly higher than 170 kbar, which is Garn's lower limit, so we will write the C-J pressure for liquid TNT at 93°C as 182 ± 12 kbar.

In his paper on the pressure in liquid TNT Garn¹⁷ also gives results of measurements of pressure in solid TNT at a density of 1.455 g/cm^3 . He finds the pressure to be 168 ± 3.4 kbar. We believe that this value is at least 10 kbar low. We know, for example, that for TNT at 1.637 g/cm^3 the same method gives 189.1 kbar, as reported by Deal¹⁸, while newer work⁵ gives about 225 kbar. Again the lower confidence limit is the number of

interest for this paper, and we will assume that it is the lower limit of Garn's value. We will write the pressure for solid TNT at 1.4502 g/cm^3 as $178 \pm 13 \text{ kbar}$.

E. Results

All the necessary data with their 95% confidence limits are tabulated in Table IV, with liquid TNT at 93°C and solid TNT of density 1.4502 g/cm^3 at 25°C taken as initial states. The results of the computations and the experimental values are given in Table V. The errors have been treated by differentiating with respect to the experimentally measured quantity and then finding the rms error. Almost all the error comes from the measurements of detonation velocity of the liquid at the two temperatures and of detonation velocity of the solid, because their differences are used.

Studying the results in Table V we notice immediately that the values of A are significantly different for the solid and the liquid. Since the two values of A are for the same chemical system in only slightly different thermodynamic states, it is very difficult to see why this should be so. One possible hypothesis is to assume that for some reason the derivatives change very rapidly with initial energy in this region. A more reasonable assumption, we think, is to assume that the mode of detonation is not the same in liquid and solid. It is worth noting in passing that the value of A for the liquid is higher than the value for the solid, so that although we could perhaps argue from the sudden change in A found¹³ for the solid at higher density that the A we have taken for the solid might be too high, any change in this direction makes the disagreement larger.

Table IV

Physical and Thermochemical Properties of TNT

Liquid at 93°C

$$\rho_o = 1.4502 \pm 0.0006 \text{ g/cm}^3$$

$$H - H_o = 50.854 \pm 0.06 \text{ cal/g}$$

$$\beta_o = +(7.003 \pm 0.030) \times 10^{-4} / ^\circ\text{C}$$

$$D = 6590 \pm 8 \text{ m/sec}$$

$$C_p^o = 0.376 \pm 0.006 \text{ cal/g}$$

$$(\partial D / \partial T_o)_{p_o} = -3.5 \pm 0.6 \text{ m/sec}$$

Solid at 25°C

$$\rho_o = 1.4502$$

$$H - H_o = 6.464 \pm 0.05 \text{ cal/g}$$

$$D = 6494.8 \pm 7 \text{ m/sec}$$

$$(\partial D / \partial \rho_o)_{p_o, E_o} = 3187.2 \pm 27.1 \text{ m/sec per g/cm}^3$$

Differences

$$\Delta H = 44.390 \pm 0.08 \text{ cal/g}$$

$$\Delta D^2 = (1.246 \pm 0.139) \times 10^6 \text{ (m/sec)}^2$$

Table V

Comparison of Calculated and Experimental Results for TNT

Liquid at 93°C

$$A = 0.9319 \pm 0.112$$

$$B = 3.354 \pm 0.376$$

$$\Gamma = 3.466$$

$$\alpha = 0.340$$

$$P_{\text{calc}} = 137.1 \pm 5.4 \text{ kbar}$$

$$P_{\text{exp}} = 182 \pm 12 \text{ kbar}$$

Solid at 25°C

$$A = 0.7117 \pm 0.0061$$

$$B = 3.354 \pm 0.376$$

$$\Gamma = 3.219$$

$$\alpha = 0.465$$

$$P_{\text{calc}} = 145.0 \pm 2.9 \text{ kbar}$$

$$P_{\text{exp}} = 178 \pm 13 \text{ kbar}$$

If we ignore the fact that the values of A are different, which tells us that we cannot expect our theory to apply, and proceed to calculate the pressures, we find the calculated pressures about 20% lower than the measured pressures. The differences are well outside of the possible experimental errors. The experimental data with the largest errors are the difference ΔD between the two detonation velocities and the change in detonation velocity with temperature ($\partial D / \partial T_0$) for the liquid and with density ($\partial D / \partial \rho_0$) for the solid. The other data do not contribute much to the total uncertainty. In Fig. 6 and Fig. 7 curves of constant calculated pressure are plotted to show the effect of different choices of ΔD and ($\partial D / \partial T_0$) or ($\partial D / \partial \rho_0$). The cross shows the values found experimentally and the error flags on it show the 95% confidence limits. The left-hand pressure curve in each figure is the lower 95% confidence limit for the measured pressure. It is easy to see it is extremely improbable that the disagreement between calculated and measured pressures is due to the statistical errors of the experiments, and it seems very unlikely that systematic errors in these carefully checked and compared experiments can be responsible. There is the possibility that the pressure measurements are being misinterpreted, but it seems impossible that a new interpretation will change them enough to bring them into agreement with the calculated pressures.

The results of these experiments, showing that the values of A are very different for liquid and solid TNT, and that the calculated and observed pressures are different, lead us to conclude that the Chapman-Jouguet theory does not apply to liquid or solid TNT.

IV. INVERSION OF THE JONES FORMULA

In solid explosive charges below crystal density the specific internal energy is almost independent of the density. The very small energies of deformation and fracture are negligible compared with the chemical energy, because the explosive is not compressed but only compacted. Therefore, in eq. (1), for the charges fired at constant initial pressure, we have only the first term on the right-hand side to consider. Rearranging (not integrating) eq. (1) and substituting into eq. (2) we express the C-J pressure as

$$p = \rho_0 D^2 (\alpha + 2)^{-1} [1 + (\partial \ln D / \partial \ln \rho_0)]^{-1}. \quad (12)$$

This expression was given by Jones¹⁹ and has often been used to estimate explosive pressures when experimental data were not available. Some estimate of α must be made in order to use eq. (12), and Jones has given convincing arguments that show that α can be expected to be a positive number between 0 and 0.25.

There are enough data²⁰ available for a few explosives to allow the calculations of α from eq. (12). These data and the resulting values for α are presented in Table VI. The difficulties of interpreting pressure measurements were discussed in section III, and all the pressure values listed in the table are subject to qualification.

It is immediately apparent that α calculated from the experimental values is not within the range that Jones predicted in eight of the ten examples. It is possible that α can be negative in the vicinity of a phase change or certain peculiarities of the chemical equilibrium, so these results cannot be used as a proof that the theory is invalid. However, it is probable that in most cases $0 < \alpha < 0.25$ and that the disagreement reflects the failure

Table VI

Inversion of Jones Formula to Compute α

<u>Explosive</u>	ρ_o (g/cm ³)	p (kbar)	D (m/sec)	$\frac{\partial \ln D}{\partial \ln \rho_o}$	α
TNT (solid)	1.63	225	6948	0.381	+ 0.54
TNT (solid)	1.445	178	6484	0.711	$\approx$ 0.0
TNT (solid)	1.051	115	5188	0.647	- 0.50
TNT (solid)	0.732	59	4206	0.555	- 0.59
TNT (liquid)	1.4502	182	6590	0.932 ^a	- 0.21
Nitromethane (liquid)	1.159	148	6378	0.628 ^a	- 0.04
Composition B	1.714	293	7990	0.686	+ 0.22
9404	1.844	390	8811	0.694	+ 0.16
9404	0.969	92	5905	0.545	+ 0.38
PETN	1.67	310	7975	0.827	- 0.12

a. This is the value of A from eq. (5) and eq. (9).

of the theory. Perhaps the values listed in the table will help the reader to get a feel for the magnitude of the difference between theory and experiment.

V. CROSSING OF TNT ISENTROPES

The derivative α is not as familiar as some other thermodynamic derivatives, but the implications of $\alpha < 0$ for more familiar quantities can easily be found. In the appendix to this paper it is shown that if $\alpha > -1$ then $dS/d\rho_0 < 0$ which means that the isentrope from the C-J point at a given density will pass to the left in the p-v plane of the C-J point for the same explosive at a lower density. It is also shown that if $-1 < \alpha < 0$ then $(\partial S/\partial p)_v < 0$ which implies that if α changes sign the isentropes cross in the p-v plane, and the thermal expansion coefficient $\beta = (1/v)(\partial v/\partial T)_p < 0$. While a negative expansion coefficient is not unknown, it seems unlikely in the detonation products of ordinary explosives.

For solid TNT there are good data for pressure and detonation velocity at four densities, and at the two lowest densities $-1 < \alpha < 0$, so the crossing of isentropes in the p-v plane can be illustrated. Figure 8 is a plot, in the log p vs log v plane, of the Rayleigh lines, $p = \rho_0^2 D^2 (v_0 - v)$, and the constant-gamma isentropes, $p v^\Gamma = \text{const.}$, with Γ found from eq. (2) using the measured pressure and velocity, for three initial densities. The Rayleigh line is the locus of all possible pressure-volume points for the measured detonation velocity, and its slope at the C-J point is the slope of the isentrope. It is easily seen that the isentropes from the C-J points for which the initial density was 1.445 g/cm^3 and 1.63 g/cm^3 will cross the isentrope from the C-J point for initial density 1.051 g/cm^3 , as they are expected to do when $-1 < \alpha < 0$.

All the assumptions of the theory enter into the construction of the graph, and the theory has been shown to fail for TNT, so no conclusions about the real equation of state for TNT can be drawn.

VI. CONCLUSIONS

In Secs. II and III it was shown that the Chapman-Jouguet theory does not agree with experiment for nitromethane, solid TNT, and liquid TNT. The calculated pressures are 15% to 20% below the measured pressures. In Sec. IV it was shown that the Jones formula as it is usually used does not give reliable estimates of the pressure. In Sec. V it was shown that $\alpha < 0$ implies that isentropes cross in the p-v plane and the crossing was illustrated using data for solid TNT interpreted according to the C-J theory.

It is certain that the Chapman-Jouguet theory is not valid for nitromethane, solid TNT and liquid TNT. It is very unlikely that it is valid for others. Probably it should no longer be trusted for any kind of calculations. We can offer no replacement for the theory and can only speculate about why it fails.

Perhaps the failure results from some very rapid oscillation in the flow. Erpenbeck^{21,22} has investigated the stability of the steady-state detonation equations and has found numerous cases of instability. Our ignorance of the details of the reactions in liquid and solid explosives and of the equation of state makes it impossible to tell whether instability can be expected in real explosives. Wood and Fickett²³ and Mader²⁴ have made numerical calculations of the behavior of detonation models and have found instability which manifests itself as a periodic variation of the flow. With input parameters thought to be similar to those of nitromethane and TNT, Mader found that the oscillations were large. We believe that it may be fruitful

to explore all those peculiar observed phenomena of detonations which indicate departure from steady-state, one-dimensional flow.

It is also possible that the assumption that an equation of state exists is false. In order that the application of thermodynamics to the problem be valid, it is necessary that all the chemical reactions be fast in both directions relative to the time of the experiments. There is no information about reaction rates as fast as are of interest here.

ACKNOWLEDGEMENT

Contributions to this work have been made by many members of GMX Division of Los Alamos Scientific Laboratory. We are particularly indebted to Drs. Wildon Fickett and W. W. Wood. This work was performed under the auspices of the United States Atomic Energy Commission.

APPENDIX

In this appendix some relations needed for Sec. V are derived. First we relate α and β . Differentiating the definition of enthalpy $E = H - pv$ with respect to volume at constant pressure we find

$$(\partial E / \partial v)_p = (\partial H / \partial v)_p - p = (\partial H / \partial T)_p (\partial T / \partial v)_p - p.$$

Using the definitions $\alpha = p(\partial v / \partial E)_p$, $C_p = (\partial H / \partial T)_p$, and $\beta = (1/v)(\partial v / \partial T)_p$, we rewrite this as

$$\beta = (C_p / pv) \alpha / (1 + \alpha).$$

Now C_p / pv is necessarily positive, so $-1 < \alpha < 0$ implies $\beta < 0$.

A relationship showing how entropy at the C-J point varies with initial density is also needed. This relationship will apply to pressed explosive in which E_0 is independent of ρ_0 . We write the entropy $S = S(p, v)$ and define $S_p = (\partial S / \partial p)_v$, $S_v = (\partial S / \partial v)_p$, and the square of the sound velocity $c^2 = (\partial p / \partial \rho)_S$, and note that $S_v / S_p = -(\partial p / \partial v)_p$. Then

$$\begin{aligned} dS / d\rho_0 &= S_p dp / d\rho_0 + S_v dv / d\rho_0 = S_p [dp / d\rho_0 + (S_v / S_p) dv / d\rho_0] \\ &= S_p [dp / d\rho_0 - (\partial p / \partial v)_S dv / d\rho_0] = S_p [dp / d\rho_0 + \rho_0^2 c^2 dv / d\rho_0]. \end{aligned}$$

The conservation of mass equation $\rho(D - u) = \rho_0 D$ and the alternative form of the Chapman-Jouguet condition $D - u = c$, where u is the particle velocity, combine to give $\rho c = \rho_0 D$, so

$$dS / d\rho_0 = S_p [dp / d\rho_0 + \rho_0^2 D^2 dv / d\rho_0]. \quad (1A)$$

Writing the logarithm of the Rayleigh line equation $\rho_0^2 D^2 = p / (v_0 - v)$ and differentiating with respect to ρ_0 we find

$$\begin{aligned}
1 + \frac{d \ln D}{d \ln \rho_o} &= \frac{1}{2} \rho_o \left[\frac{1}{p} \frac{dp}{d\rho_o} - \frac{1}{v_o - v} \left(\frac{dv_o}{d\rho_o} - \frac{dv}{d\rho_o} \right) \right] \\
&= \frac{\rho_o}{2p} \left[\frac{dp}{d\rho_o} - \rho_o^2 D^2 \left(-\frac{1}{\rho_o^2} - \frac{dv}{d\rho_o} \right) \right] \\
&= \frac{\rho_o}{2p} \left[\frac{dp}{d\rho_o} + \rho_o^2 D^2 \frac{dv}{d\rho_o} \right] + \frac{\rho_o D^2}{2p} .
\end{aligned} \tag{2A}$$

Also from eq. (1) of Sec. I. with E_o and p_o independent of ρ_o , we have $d \ln D / d \ln \rho_o = (\Gamma - 1 - \alpha) / (\alpha + 2)$. Substituting from eq. (2) for $\Gamma + 1$ and rearranging we have

$$1 + \frac{d \ln D}{d \ln \rho_o} = \frac{\rho_o D^2}{p(\alpha + 2)} . \tag{3A}$$

Substituting eq. (3A) into eq. (2A) and the result into eq. (1A) we find

$$dS/d\rho_o = -S_p D^2 \alpha / (\alpha + 2) . \tag{4A}$$

To eliminate S_p we use $dE = TdS - pdv$ at constant p and find

$$1/\alpha = (1/p)(\partial E / \partial v)_p = (TS_v/p) - 1. \text{ Using, as before}$$

$$S_v/S_p = \rho^2 c^2 = \rho_o^2 D^2 \text{ to eliminate } S_v, \text{ we have}$$

$$S_p = \frac{1 + \alpha}{\alpha} \cdot \frac{p}{T \rho_o^2 D^2} . \tag{5A}$$

Finally combining eq. (4A) with eq. (5A) we find

$$\frac{dS}{d\rho_o} = - \frac{p}{T \rho_o^2} \cdot \frac{\alpha + 1}{\alpha + 2} \tag{6A}$$

which demonstrates that if $\alpha > -1$ then $dS/d\rho_o < 0$.

Captions

- Figure 1. Plot of nitromethane infinite-diameter detonation velocity vs temperature. Error flags show the standard deviation of the velocity.
- Figure 2. Plot of free-surface velocity vs plate thickness showing measurements made to determine C-J pressure for nitromethane. Curve A is for charges 3.81 cm diam and length/ diameter = 16, curve B 3.81 cm diam and $L/d = 10$, curve C 7.62 cm and $L/d = 16$, curve D 20.32 cm and $L/d = 0.5$. All charges were confined with brass.
- Figure 3. Diagram of assembly used to make measurements of the detonation velocity of liquid TNT.
- Figure 4. Diagram showing details of the pin assembly used in the liquid TNT shots.
- Figure 5. Liquid TNT detonation velocity vs reciprocal of charge radius for shots at 93°C and 114°C .
- Figure 6. Lines of constant calculated pressure for liquid TNT plotted on a graph of ΔD vs $(\partial D/\partial T_0)$. The points corresponding to the measured values of ΔD and $(\partial D/\partial T_0)$ are plotted with error flags indicating the 95% confidence intervals. The point plotted with dashed error flags is from the work of Seely and Johnson. The measured pressure is 182 ± 12 kbar, so the 170 kbar line shows the position of the lower 95% confidence limit.

Figure 7. Lines of constant calculated pressure for solid TNT plotted on a graph of ΔD vs $(\partial D / \partial \rho_0)$. The point corresponding to the measured values of ΔD and $(\partial D / \partial \rho_0)$ is plotted with error flags indicating the 95% confidence intervals. The measured pressure is 178 ± 13 kbar, so the 165 kbar line shows the position of the lower 95% confidence limit.

Figure 8. A plot, in the $\log p$ vs $\log v$ plane, of the Rayleigh lines, shown as dashed lines, and the constant-gamma isentropes, shown as solid lines, for solid TNT at three densities. The measured pressure and detonation velocity were used to locate the experimental C-J points.

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Fig. 1. W. C. Davis, et al.

Fig. 2. W. C. Davis, et al.

Fig. 3. W. C. Davis, et al.

DETAIL OF PIN CONSTRUCTION

Fig. 5. W. C. Davis, et al.

Fig. 6. W. C. Davis, et al.

Fig. 7. W. C. Davis, et al.

Fig. 8. W. C. Davis, et al.