

## Detonation of Nitromethane

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on rotational transitions in the microwave region for the cases of high barriers. Although they are less accurate at higher  $s$  values, the effect of torsional motion on over-all rotation is greatly reduced at higher barriers. It is the author's hope that the Mathieu functions given in reference 4 will someday soon be extended to higher  $s$  values and smaller intervals.<sup>7</sup> Until this is done it is

<sup>7</sup> Note added in proof.—Mr. R. W. Kilb has just completed tables up to  $s=92$ . The formulas in the present paper are, how-

ever, still a great convenience and have been checked against the new tables.

#### ACKNOWLEDGMENTS

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## Detonation of Nitromethane

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The detonation velocity of nitromethane has been measured for various charge radii and confining materials. A critical diameter of 27 mm for the detonation of unconfined nitromethane has been found. Estimates of the energy of activation, the length of the reaction zone and the reaction time are obtained, according to Eyring's theory.

#### INTRODUCTION

ACCORDING to the theory of Eyring *et al.*,<sup>1</sup> it is possible to determine the energy of activation of an explosive reaction as well as the length of the reaction zone and the reaction time of an explosive substance from the observed relation between its detonation velocity and the diameter of the charge. It seemed interesting to compare the value of the energy of activation thus obtained, with the results of other methods carried out under milder conditions of pressure and temperature. A suitable substance appeared to be nitromethane, which has been known to explode and for which the detonation properties have been measured.<sup>2,3</sup>

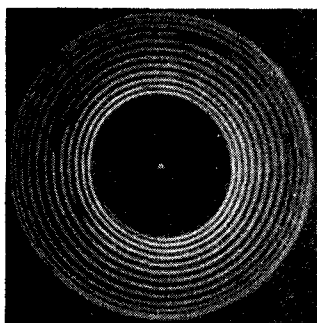


FIG. 1. Oscillogram for determining the detonation velocity of nitromethane. Time base is one turn of spiral in 10  $\mu$ sec.

#### EXPERIMENTAL

In the present experiments the velocity of detonation has been measured with the aid of probes placed in the explosive and a time recording oscillograph with a spiral sweep.<sup>4</sup> The liquid explosive was poured into metal or plastic tubes from 20–40 cm long of various diameters and thicknesses which had probes fitted along their length. The probes were enamelled copper wires, 0.4 mm diameter, cemented together in pairs and threaded across the tube at intervals of a few centimeters apart. When a detonation wave traveled along the tube, the insulation between the wires broke down and a blanking signal was sent to the oscillograph. A typical oscillogram obtained in this fashion is shown in Fig. 1. The estimated error in these measurements is of the order of  $\pm 1\%$ .

TABLE I. Detonation of unconfined nitromethane.

Diam mm	Detonation velocity m/sec	Remarks
44	6280	
34	6260	Mean of two measurements.
29	6150	Mean of four measurements, spread of results $\pm 50$ m/sec.
27	...	Detonation failed in tube with measuring probes; complete detonation with no probes.
26.5	...	Partial detonation with no probes.
25	detonation failed	Result of three measurements.

<sup>1</sup> Eyring, Powell, Duffey, and Parlin, Chem. Revs. **45**, 69 (1949).

<sup>2</sup> Bellinger, Friedman, Bauer, Eastes, and Gross, Ind. Eng. Chem. **40**, 1320 (1948).

<sup>3</sup> L. Medard, Mém. poudres **33**, 125 (1951).

<sup>4</sup> Birk, Erez, Manheimer, and Nahmani, Bull. Research Council Israel **3**, 398 (1954).

TABLE II. Detonation of nitromethane in containers of various materials.

Material	Internal diameter mm	Wall thickness mm	$\frac{W_c^a}{W_e}$	Detonation velocity m/sec
Iron	40	4	2.7	6320
	27	3	3.0	6300
	25	17	18.6	6280
Brass	7	0.8	3.4	6060
Aluminum	6.4	0.5	0.7	Detonation failed after first probe.
	6.4	0.5	0.7	Complete detonation with no probe.
Polyvinyl chloride	7.5	1.0	0.7	No detonation, no probes.
	6.5	2.5	1.9	No detonation, no probes.
Natural rubber	8	2	0.8	No detonation, no probes.
	10	3	1.3	No detonation, no probes.
Polyester	8	7	6.7	No detonation, no probes.

<sup>a</sup>  $W_c$  = Weight of case and  $W_e$  = weight of explosive per unit length.

In order to establish a steady detonation in the explosive in the tube under investigation, an initiation similar to the one shown in Fig. 2 was adopted. This was especially important in charges near their critical diameter in which the detonation was otherwise difficult to initiate.

Experimental results for charges detonated under ordinary conditions of pressure (sea-level) and temperature (18°–22°C) with different confinements are given. The results for unconfined charges, where the explosive was contained in impregnated paper tubes of about 0.25-mm wall thickness are given in Table I; results for confined charges are given in Table II

## DISCUSSION

### The Ideal Velocity of Detonation

The velocity of the detonation of nitromethane, as well as the pressure, temperature, and specific volume, were calculated by the method of Taylor<sup>5</sup> and Jones & Miller.<sup>6</sup> A velocity of 6060 m/sec, a pressure of 89 000 atmos, a temperature of 4000°K, and a specific volume of 0.69 cm<sup>3</sup>/g were thus obtained. Details of the calculation are given in the Appendix.

Medard<sup>3</sup> has measured the velocity of detonation of nitromethane by the Dautriche method using a glass tube of 30-mm diameter and 1.8-mm thickness and an aluminum tube of a similar diameter and 2.5-mm thickness: he found a value of 6600 m/sec  $\pm$  2%. The highest velocity found in the present work was 6320 m/sec. As the ideal detonation velocity is defined for an infinite diameter, it may be somewhat higher than the experimental values obtained; a value of 6350 m/sec is therefore assumed for it, in the following discussion, as a reasonable guess.

<sup>5</sup> J. Taylor, *Detonation In Condensed Explosives* (Oxford University Press, New York, 1952).

<sup>6</sup> H. Jones and A. R. Miller, Proc. Roy. Soc. (London) **A194**, 480 (1948).

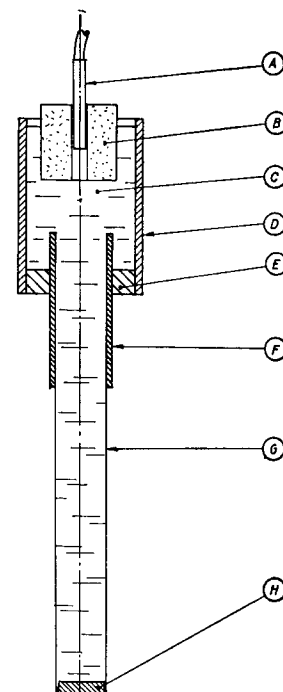


FIG. 2. Initiation of nitromethane near its critical diameter. A Detonator; B Booster (25 g PETN), C Nitromethane; D Pressed paper cylinder (44 mm internal diam, 3 mm thick); E Plug; F Thick metal tube; G Tube under investigation; H Plug.

### Factors Affecting the Detonation Velocity

In many explosives the velocity of detonation is a function of the radius of the charge. This phenomenon is explained according to Jones<sup>7</sup> and Eyring<sup>1</sup> by the assumption that some of the energy released in the reaction zone, behind the detonation front, is dissipated at the sides of the explosive charge and does thus not serve to maintain the detonation velocity. These losses increase when the length of the reaction zone increases, or when the diameter of the charge decreases and are also affected by the confining action of the surrounding medium.

The relation between the detonation velocity  $D$  of a bare charge with radius  $R$  and ideal velocity of detonation  $D_i$  is given by

$$D/D_i = 1 - 0.5a/R, \quad (1)$$

where  $a$  is the length of the reaction zone. The corresponding relation for a cased charge is

$$D/D_i = 1 - 2.17 \frac{(a/R)^2}{W_c/W_e}, \quad (2)$$

where  $W_c$  and  $W_e$  are the weights per unit length of the case and the explosive, respectively.

The length of the reaction zone is not constant, but depends on the reaction time and the velocity of detonation. The reaction time depends on the nature of the explosive and on the temperature. The temperature, in turn, is proportional to the square of the detonation velocity. Thus it is obvious that the size of the reaction

<sup>7</sup> H. Jones, Proc. Roy. Soc. (London) **A189**, 415 (1947).

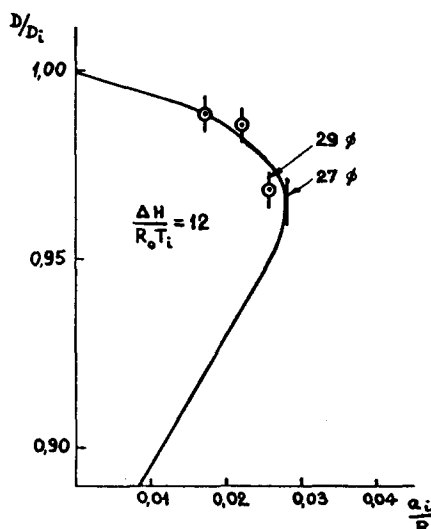


FIG. 3. Failure chart for unconfined nitromethane.

zone will depend on the velocity of detonation. This dependence is given by

$$a/a_i = \exp \left[ \frac{\Delta H^\#}{R_0 T_i} \left( \frac{D_i^2}{D^2} - 1 \right) \right]. \quad (3)$$

Here  $a_i$  is the length of the reaction zone when the velocity is the ideal velocity,  $D_i$ ,  $R_0$  is the gas constant,  $\Delta H^\#$  is the heat of activation for the reaction, cal deg<sup>-1</sup> mole<sup>-1</sup>, and  $T_i$  is the absolute temperature at the end of the reaction zone.

By combining Eq. (3) with 1 or 2, a relation is obtained between the detonation velocity and the radius of the charge, in which the energy of activation appears as a parameter. This relation also shows that there is a critical diameter below which no stable detonation can take place.

#### The Unconfined Charge

The dependence of the detonation velocity on the radius and the energy of activation is obtained for the unconfined charge from Eqs. (1) and (3) as

$$a_i/R = 2D/D_i(1-D/D_i) \exp \left[ -\frac{\Delta H^\#}{R_0 T_i} \left( \frac{D_i^2}{D^2} - 1 \right) \right]. \quad (4)$$

The energy of activation may be calculated from the preceding equations when the values of the ideal detonation velocity and the velocity at the critical diameter are known.

The relation between these velocities and the energy of activation is given in Eq. (5) for the unconfined charge:

$$\frac{\Delta H^\#}{R_0 T_i} = \frac{(2D_c/D_i - 1)(D_c/D_i)^2}{2(1 - D_c/D_i)}, \quad (5)$$

where  $D_c$  is the detonation velocity at the critical diameter. When the critical detonation velocity is not known, the energy of activation may still be determined, according to Eq. (4), if the critical diameter is known, as well as the ideal detonation velocity and some other velocity. While the measurement of the critical detonation velocity was not possible by the present method, because the probes constituted sufficient obstruction to cause the failure of detonation, an estimate of the critical diameter was obtained by detonating the explosive in tubes with no probes. The value obtained for unconfined nitromethane was 27 mm. When the results in Table I were plotted on curves with different values of  $\Delta H^\#/R_0 T_i$ , with the critical diameter taken as 27 mm and the ideal detonation velocity at 6350 m/sec, it was indicated that a reasonable fit is obtained when the value of the parameter lies between 8 and 15, corresponding to an energy of activation of 60–120 kcal/mole (the temperature assumed is 4000°K, as calculated). Figure 3 shows the experimental results fitted, as an illustration, to a curve with  $\Delta H^\#/R_0 T_i = 12$ . The values for the length of the reaction zone and the reaction time corresponding to this range are 0.3–0.6 mm and  $0.6\text{--}1.0 \times 10^{-7}$  sec, respectively. Allowing for experimental errors the results obtained in the present work seem to indicate a higher value for the energy of activation than values obtained by other workers under milder conditions.<sup>8,9-10</sup> This may be interpreted either as evidence of a different mechanism of reaction or as a result of the approximate nature of Eyring's theory used in the present calculations.

#### The Confined Charge

The dependence of the detonation velocity of a confined charge on the radius, the confinement and the energy of activation is obtained from Eqs. (2) and (3), as

$$\frac{a_i}{R} = \frac{D}{D_i} \left[ \frac{W_c/W_e}{2.17} \left( 1 - \frac{D}{D_i} \right) \right]^{\frac{1}{2}} \exp \left[ -\frac{\Delta H^\#}{R_0 T_i} \left( \frac{D_i^2}{D^2} - 1 \right) \right]. \quad (6)$$

This relation is shown graphically in Fig. 4 for  $\Delta H^\#/R_0 T_i = 12$  as before and  $W_c/W_e = 0.7$ . Assuming that the reaction zone, length  $a_i$  is the same both for the confined and unconfined charges, the critical diameter is found from this graph to be 16 mm. Taking the extreme values of  $\Delta H^\#/R_0 T_i$  of 8 and 15 one obtains a critical diameter of 14 to 19 mm. This should be compared with the experimental result of complete detonation in an aluminum tube of 6.4-mm diameter with a wall thickness of 0.5 mm ( $W_c/W_e = 0.7$ ). On the other

<sup>8</sup> Cottrell *et al.*,<sup>8</sup> give 52.7 Kcal/mole, Hillenbrand and Kilpatrick<sup>9</sup> obtained 50.6 Kcal/mole, both by thermochemical methods, while Kandel<sup>10</sup> reports a result of 58 Kcal/mole by mass-spectroscopy.

<sup>9</sup> L. J. Hillenbrand, Graham, and Ried, *Trans Faraday Soc.* **47**, 584 (1951).

<sup>10</sup> L. J. Hillenbrand and M. L. Kilpatrick, *J. Chem. Phys.* **19**, 381 (1951).

<sup>11</sup> R. J. Kandel, *J. Chem. Phys.* **23**, 84 (1955).

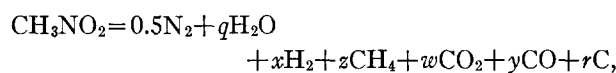
hand more compressible materials, such as rubber or plastics, showed failure of detonation in larger diameter tubes with heavier casing. This effect continued even when these were encased in heavy metal pipes. It seems therefore that Eyring's theory for confined charges does not give quantitative agreement with his theory for unconfined charges.

#### APPENDIX

##### Method for the Calculation of the Detonation Velocity

The methods of Taylor<sup>5</sup> and Jones and Miller<sup>6</sup> are iterative methods and the numerical values given are those obtained in the last step of the iteration.

The first step is to find the composition of the detonation products. Since nitromethane has a negative oxygen balance, we write:



and get 6 equations for the six unknowns  $q, r, x, y, w, z$ ; 3 equations of conservation of matter,

$$\begin{aligned} z + w + y + r &= 1 \\ 2q + 2x + 4z &= 3 \\ q + 2w + y &= 2, \end{aligned}$$

and 3 equations of equilibrium

$$\begin{aligned} yq &= K_1 x w \\ x^2 &= K_2 n' z / p^* \\ y^2 &= K_3 n' w / K_4 p^*, \end{aligned}$$

where

$K_1$  is the equilibrium coefficient of the reaction  
 $\text{CO} + \text{H}_2\text{O} = \text{H}_2 + \text{CO}_2,$

$K_2$  is the equilibrium coefficient of the reaction  
 $\text{C} + 2\text{H}_2 = \text{CH}_4,$

$K_3$  is the equilibrium coefficient of the reaction  
 $\text{CO} + \frac{1}{2}\text{O}_2 = \text{CO}_2,$

$K_4$  is the equilibrium coefficient of the reaction  
 $\text{C} + \frac{1}{2}\text{O}_2 = \text{CO},$

$n'$  gives the number of moles of gaseous products, per gram of explosive, and  $p^*$  stands for the mean fugacity,

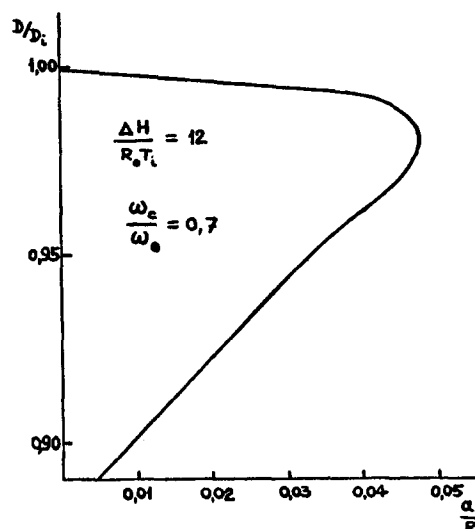


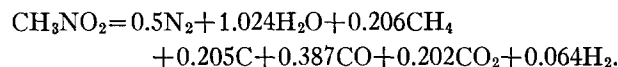
FIG. 4. Failure chart for lightly cased charge.

which substitutes the pressure  $p$  (since the gas is not ideal).

According to Miller and Jones,<sup>6</sup> the ratio  $p^*/p$  is  $2.28 \cdot 10^3$  for  $p = 10^5$  atmos and 98.1 for  $p = 10^4$  atmos. We assume  $p^*/p = 10^3$  for  $p = 89,000$  atmos.

One must also assume a value of the detonation temperature, since the equilibrium coefficients are temperature dependent. After some trials it was found that the fitting value is  $4000^\circ\text{K}$ . The values of the coefficients were taken from the tables of Lewis and Von Elbe<sup>11</sup>; in some cases (as for  $K_2$ ) their tables did not extend to this temperature, and an extrapolation method, as proposed by Miller and Jones, was used.

Our six equations were resolved by iteration; thus (assuming  $T = 4000^\circ\text{K}$ ,  $p^*/n' = 2.10^9$ , and  $p = 89,000$  atmos) the following equation was obtained:



Using this composition of the reaction products, one calculates by iteration, following Taylor,<sup>5</sup> the specific volume and obtains  $V_1 = 0.692 \text{ cm}^3/\text{g}$  and finally the ideal detonation velocity  $D_i = 6060 \text{ m/sec}$  and pressure  $p = 89,000$  atmos. The deviation between the calculated and the measured velocity of detonation is 4%.

<sup>11</sup> B. Lewis and G. Von Elbe, *Combustion, Flames and Explosions of Gases* (Academic Press, Inc., New York, 1951).