

866. Variation of Detonation Parameters of Silver Azide with Changes in Intermolecular Potential Constants.

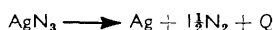
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An attempt has been made to calculate the ideal velocity of detonation in single crystals of silver azide with the help of hydrothermodynamical theory. It is assumed that the Mie-Grüneisen equation of state describes the behaviour of silver at high compression and of nitrogen at densities above 1.03 g./c.c. A three-constant interatomic potential satisfactorily describes the compressibility of silver at high pressures. The behaviour of nitrogen is assumed to be described by a four-constant potential. This potential possesses a good deal of flexibility.

Variation of detonation velocity with loading density has been derived for four sets of values of constants in the intermolecular potential for nitrogen. Change in one particular constant in the intermolecular potential of nitrogen has a pronounced effect on the detonation velocity. On the basis of experimental results it may be said that the ideal velocity of detonation lies within the range given by the values assigned to the constants.

LARGE single crystals of silver azide can be grown easily, and an estimate¹ of the velocity of detonation in them is available. In the present investigations, the ideal velocity of detonation, η , at various loading densities has been estimated, on the assumption that the Mie-Grüneisen equation of state describes the relationship between pressure, temperature, volume, and the Grüneisen constant, γ . In the case of silver, this equation gives good agreement with experimental results. London² showed that, at sufficiently high pressure, the volume available to each molecule is so small that repulsive forces are a decisive factor in determining the molecular arrangement in dense gases. It may, therefore, be reasonable to assume a structure similar to solids for gases like nitrogen at high density. The Mie-Grüneisen³ equation of state may be applicable to gases under these conditions.

Silver azide undergoes irreversible thermal decomposition:



where Q (= 74.17 kcal.) is the heat of detonation.⁴ The Rankine-Hugoniot relationship for the reaction takes the form:

$$E_0 + E'_{\text{Ag}} + 1\frac{1}{2}E'_{\text{N}_2} - Q = \frac{1}{2}P[V_0 - (1\frac{1}{2}V_{\text{N}_2} + V_{\text{Ag}})], \quad (1)$$

where V_0 (= M/ρ_0) is the volume per mole of silver azide, M is its molecular weight, and ρ_0 is the density of single crystals; E_0 (= $E^0_{\text{Ag}} + 1\frac{1}{2}E^0_{\text{N}_2}$) is the sum of excess energies of one gram atom of silver and $1\frac{1}{2}$ moles of nitrogen over their room-temperature values; E' and V (with subscripts) are energies of imperfection and volumes of silver per gram atom and of nitrogen per mole at pressure P , and V is the volume of the reaction products ($1\frac{1}{2}V_{\text{N}_2} + V_{\text{Ag}}$).

The Debye model provides an estimate of thermal energy:

$$(E_T - E_{\text{abs}}) = 3RTD(\theta_s/T), \quad (2)$$

where θ_s is the characteristic temperature and $D(\theta_s/T)$ the Debye function,

$$D(\theta_s/T) = 3(T/\theta_s)^3 \int_0^{\theta_s/T} (x^3/e^x - 1)dx.$$

¹ F. P. Bowden, "Fourth Symposium on Combustion," Williams and Wilkins, Baltimore, 1953, p. 161.

² F. London, *Phys. Rev.*, 1956, **102**, 168.

³ E. Grüneisen, "Handbuch der Physik," Springer, Berlin, 1926, Vol. 10, p. 22.

⁴ P. Gray and T. C. Waddington, *Proc. Roy. Soc.*, 1956, *A*, **235**, 106.

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It has been assumed that, under the conditions obtaining between the shock front and the Chapman–Jouguet surface, silver ($\theta_s = 215$) behaves like a solid.

The energy involved in lattice vibrations of silver can be estimated with the help of expression (2). At temperatures above 2500°K it can be represented by means of expression (3).

$$E_{Ag}^0 = (0.00667T - 1.956) \text{ kcal.} \quad (3)$$

Values of E_{Ag}^0 given by Borelius⁵ are slightly higher than those estimated from the Debye function. This is because, under atmospheric pressure, energy is required not only for increase in vibrational amplitude, but it also goes into the creation of lattice defects such as vacancies. Under detonation pressures the chances of formation of vacancies are low, and the thermal energy goes mainly into lattice vibrations. It is reasonable to assume that the internal energy of silver at atmospheric pressure and above 2500°K is given by expression (3). Above 2500°K this expression approximates to the Debye energy.

Solid nitrogen may be assumed to have a characteristic temperature of 56.0. Energy involved in vibrations of nitrogen molecules within the lattice can be calculated with the help of the Debye expression. To this must be added the energy of internal vibration of the atoms within the molecule, and the energy of molecular rotation within the lattice. The molar energy of nitrogen may be represented by expression (4).

$$E_{N_2} = (0.0105T - 4.82) \text{ kcal.} \quad (4)$$

The total thermal energy of the detonation products, $E^0 (= E_{Ag}^0 + 1\frac{1}{2}E_{N_2}^0)$, is given by expression (5).

$$E^0 = (0.02175T - 9.186) \text{ kcal.} \quad (5)$$

It is assumed in the present investigations that silver and nitrogen at densities near to 10.49 and 1.03 g./c.c., respectively, obey the Mie–Grüneisen equation of state,

$$P = -(\partial\phi/\partial V) + (3\gamma RT/V)D(\theta/T), \quad (6)$$

where ϕ , R , and γ are potential energy, gas constant, and Grüneisen constant, respectively. The energy of imperfection can be calculated by making use of the thermodynamical relationship (7).

$$(\partial E/\partial V)_T = T(\partial P/\partial T)_V - P \quad (7)$$

Since, at high temperatures in the range 3000–5000°K, the function $D(\theta_s/T)$ is almost insensitive to variation in temperature, the energy of imperfection is found to be equal to ϕ . A correction is needed to account for the point of reference in the scale of energy. If the energy of imperfection of silver at the volume occupied at atmospheric pressure and temperature is assumed to be zero, its value E' at any other volume is equal to $(\phi + E)$, where $(-E_0)$ is the minimum value of ϕ , which occurs at an intermolecular distance $r = r_0$. Nitrogen at atmospheric pressure and ambient temperature has zero energy of imperfection because it is gaseous. For this reason E is taken as equal to ϕ .

Methods of estimation of ϕ and γ are given below. Potential energy, u_1 , of a pair of atoms of silver may be assumed to be given by expression (8),

$$u_1 = \epsilon_1 \{ \exp[2\alpha_s(r_0 - r)] - 2 \exp[\alpha_s(r_0 - r)] \}, \quad (8)$$

where r_0 , α_s , and ϵ_1 , are constants and r is the interatomic distance. The potential energy, ϕ , of a mole of silver can be derived on the basis of additivity of pair potentials. By taking into account interaction between nearest neighbours only, the potential energy of a mole of silver is found to be

$$\phi = U_1 \{ \exp[2\alpha_s(r_0 - r)] - 2 \exp[\alpha_s(r_0 - r)] \}, \quad (9)$$

⁵ G. Borelius, "Solid State Physics," Vol. 6, Academic Press, New York, 1958, p. 65.

where $U_1 = \epsilon_1 N/2$ and N is Avogadro's number. The constants in u_1 for silver have been assigned the values:^{6,7} $\alpha_s = 1.4 \text{ \AA}^{-1}$, $r_0 = 2.888 \text{ \AA}$, and $U_1 = 69 \text{ kcal}$. These values of constants fit into experimental results on compressibility (K) of silver at high pressures.

Dugdale and Macdonald⁸ suggested the following expression for the Grüneisen constant:

$$\gamma = -(K/2)(\partial^2 P/\partial V^2) - 1, \quad (10)$$

where $P_1 = -(\partial\phi/\partial V)$. According to Stewart and Swenson,⁹ compressibility is predominantly a function of molar volume. Equations (9) and (10) lead to expression (11) for the Grüneisen constant:

$$\gamma = \frac{(r/6)\{f_1 \exp [2\alpha_s(r_0 - r)] - f_2 \exp [\alpha_s(r_0 - r)]\}}{\{f_3 \exp [2\alpha_s(r_0 - r)] - f_4 \exp [\alpha_s(r_0 - r)]\}}, \quad (11)$$

where f 's are functions of interatomic distance. Values of γ have been calculated for various interatomic distances, and in Fig. 1 is shown its variation with volume, together with results from experimental data.¹⁰

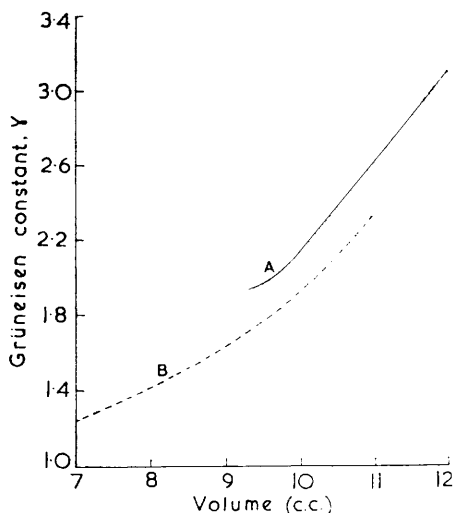


FIG. 1. Variation of the Grüneisen constant, γ , of silver with volume.
A, Experimental; B, calculated.

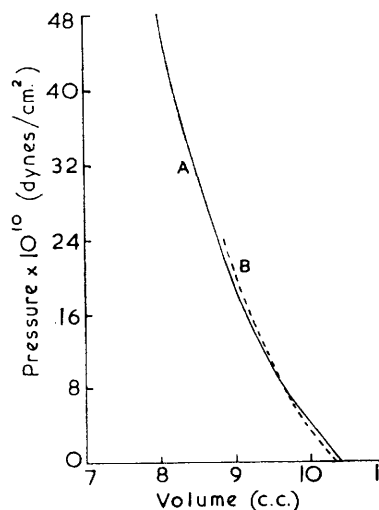


FIG. 2. Variation of volume of silver with pressure at 20° .
A, Theoretical; B, experimental.

The calculated values of γ have been employed in the Mie-Grüneisen equation of state, and the relationship between pressure and volume obtained in this way for silver at 20° is shown in Fig. 2. The three-constant potential may be acceptable for describing the behaviour of metallic silver at high compression.

Because nitrogen is much more compressible than silver, the following four-constant potential has been proposed to describe its behaviour:

$$u_2 = (\epsilon_2 r_0 \cosh \beta x/r)(e^{2y} - 2e^y), \quad (12)$$

where $x = (r_0 - r)$, $y = \alpha_N \sinh \beta x$, and r_0 , α_N , β , and ϵ_2 are constants. A comparison of

⁶ H. Eyring, *Proc. Nat. Acad. Sci. U.S.A.*, 1962, **48**, 502.

⁷ S. S. Mitra, *J. Chem. Phys.*, 1961, **34**, 1462.

⁸ J. S. Dugdale and D. K. C. MacDonald, *Phys. Rev.*, 1953, **89**, 832.

⁹ J. W. Stewart and C. A. Swenson, *Phys. Rev.*, 1954, **94**, 1069.

¹⁰ M. H. Rice, R. G. McQueen, and J. M. Walsh, "Solid State Physics," Vol. 6, Academic Press, New York, 1958, p. 1.

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the behaviour of this potential with the Buckingham–Corner potential, u_3 , for nitrogen is given in Fig. 3.

$$u_3 = \frac{\epsilon_3}{1 - (1/\alpha_b)} \left\{ \frac{6}{\alpha_b} \exp [2\alpha_b(r_0 - r)] - \left(\frac{r_0}{r} \right)^6 \right\} \quad (13)$$

Potential u_2 is less than u_3 at short distances of approach. It may be mentioned at this stage that Paterson and Davidson¹¹ obtained good agreement between theoretically derived results and experimental values of detonation velocity by employing a 9 : 6 instead of a

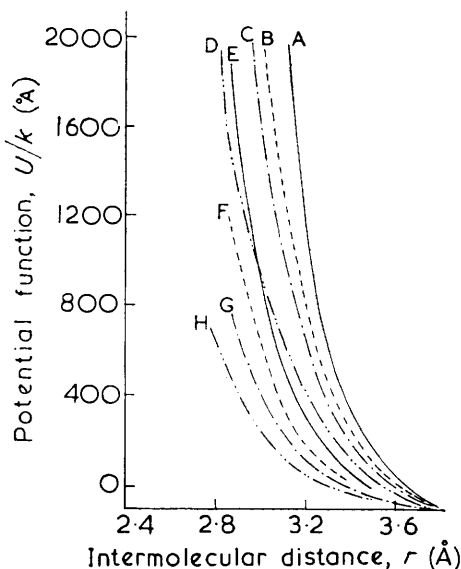


FIG. 3. Variation of potential function for nitrogen with intermolecular distance.

Buckingham–Corner potential (α_b): A, 17; B, 15; C, 14; D, 12 Å⁻¹.

New potential (α_N ; β in parentheses): E, 2.0 (0.6); F, 1.8 (0.6); G, 2.0 (0.5); H, 1.8 (0.5 Å⁻¹).

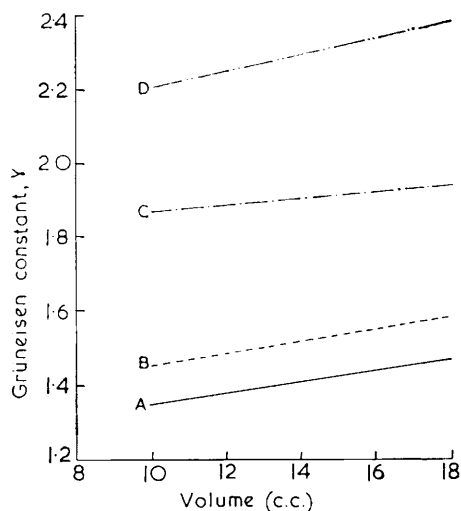


FIG. 4. Variation of Grüneisen constant, γ , of dense nitrogen with volume.

Values of new potential (α_N ; β in parentheses): A, 1.8 (0.5); B, 2.0 (0.5); C, 1.8 (0.6); D, 2.0 (0.6 Å⁻¹).

12 : 6 potential. Potential u_2 possesses greater flexibility than the 9 : 6 potential. It is profitable to make use of this potential in the calculation of detonation parameters.

Potential function u_2 yields the following expressions for pressure, P_i , and γ :

$$P_i = \frac{U_2 r_0}{3V} \left[(\exp 2\alpha \sinh \beta x) \left(\frac{\cosh \beta x}{r} + \beta \sinh \beta x + 2\alpha\beta \cosh^2 \beta x \right) - 2(\exp \alpha \sinh \beta x) \left(\frac{\cosh \beta x}{r} + \beta \sinh \beta x + \alpha\beta \cosh^2 \beta x \right) \right] \quad (14)$$

$\gamma =$

$$\frac{(r/6)[g_1 \exp (2\alpha \sinh \beta x) - 2g_2 \exp (\alpha \sinh \beta x)]}{[g_3 \exp (2\alpha \sinh \beta x) - 2g_4 \exp (\alpha \sinh \beta x)]}, \quad (15)$$

where g 's are functions of intermolecular distance. The values of γ for nitrogen at various volumes have been calculated (Fig. 4).

¹¹ S. Paterson and J. M. Davidson, *J. Chem. Phys.*, 1954, **22**, 150.

The choice of constants in the potential u_2 deserves some mention. On taking into account experimental values of sublimation energy and intermolecular distances in crystalline nitrogen it has been possible to assign to parameters $U_2 (= \epsilon_2 N/2)$ and r_0 values of 1.474 kcal. and 4.007 Å, respectively. Assignment of suitable values to constants α and β involves lengthy calculations. These constants should fit into data on transport, scattering, and equilibrium properties, and should also yield a detonation velocity of the right magnitude. A comprehensive programme of calculations of various properties is in hand. In the present Paper, the effect of changes in the values of α and β on detonation velocity (D) has been investigated. α has been assigned values of 1.8 or 2, and β 0.5 or 0.6 Å⁻¹. These assignments lead to four sets of values for ϕ , γ , P , and η .

By substituting values of γ and ϕ in the Mie-Grüneisen equation of state, the variation of pressure with volume at high temperatures can be determined. A plot of pressure against molar volume for nitrogen at a typical temperature is shown in Fig. 5. Fig. 6

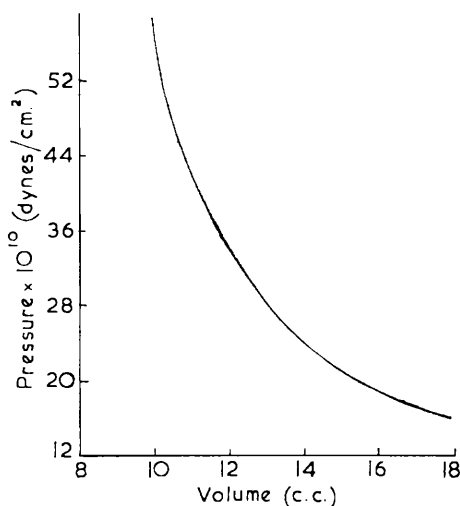


FIG. 5. Variation of volume of nitrogen with pressure at 4400°K. $\alpha_N = 1.8$; $\beta = 0.6 \text{ \AA}^{-1}$.

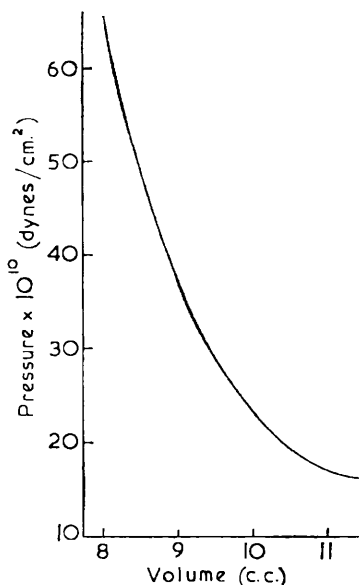


FIG. 6. Variation of volume of silver with pressure at 4200°K.

describes the behaviour of silver. The variations of the energy of imperfection, E' , with volume are shown in Figs. 7 and 8.

The next step is to derive, under Rankine-Hugoniot conditions, the variation of pressure, P , with volume, V , at a given density of loading, $d (= M/V_0')$, where V_0' is the volume occupied by a mole of substance which is in the form of loosely packed crystals. An iterative procedure is used in the derivation of the relationship between P and V . At first a reasonable value of temperature is assumed. For this temperature, internal energy is determined with the help of expressions (3)–(5). Further, a reasonable value is assigned to pressure. From graphs similar to Figs. 5 and 6, values of V_N and V_{AG} corresponding to the assumed value of the pressure are found. E_{AG} and E'_N are determined from the graphs in Figs. 7 and 8. The values of various parameters are substituted in the Rankine-Hugoniot equation to test the acceptability of the value assumed for the pressure. By trial and error, pressure at a given temperature is estimated. The process is repeated for a number of temperatures. The variation of pressure with volume at each loading density is plotted. A typical Rankine-Hugoniot curve is shown in Fig. 9. A tangent is

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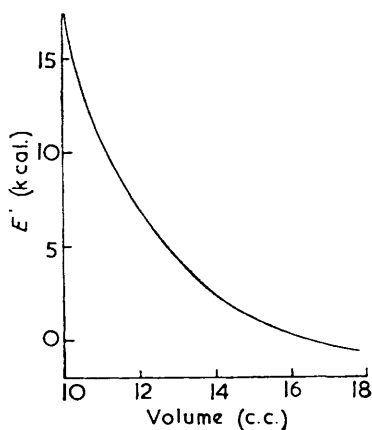


FIG. 7. Variation of energy of imperfection of nitrogen with volume.

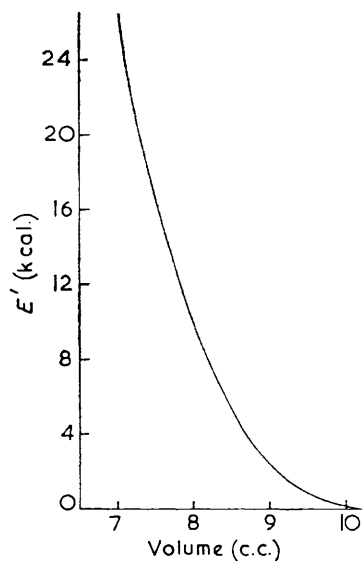


FIG. 8. Variation of energy of imperfection of silver with volume.

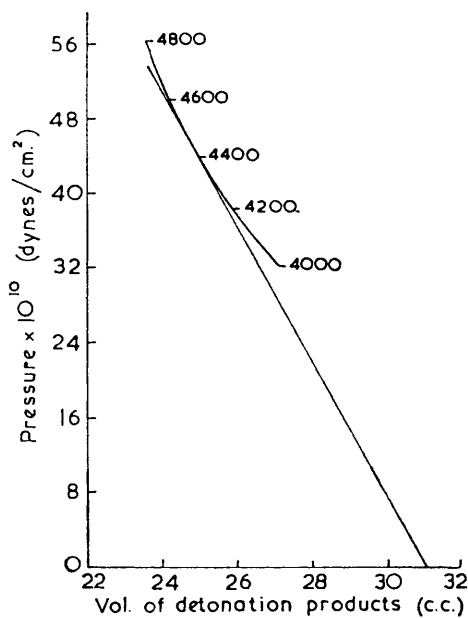
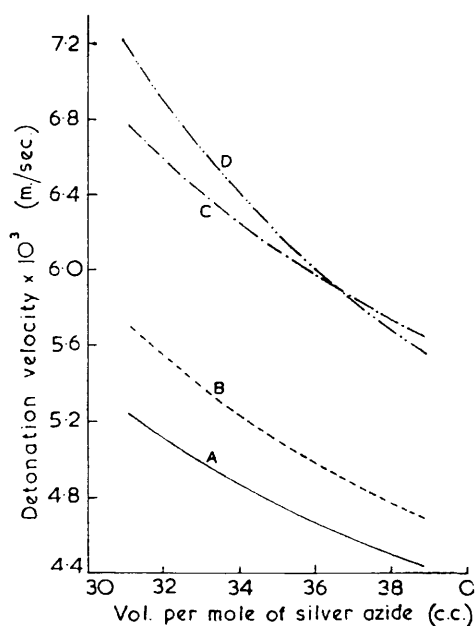


FIG. 9. Rankine-Hugoniot curve for the variation of the volume of detonation products with pressure.

FIG. 10. Variation of detonation velocity with $V_0 \alpha_N$, with β in parentheses: A, 1.8 (0.5); B, 2.0 (0.5); C, 1.8 (0.6); D, 2.0 (0.6 \AA^{-1}).

[1964]

Ibbitson and Sandall.

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drawn from the point representing V_0' to the Rankine–Hugoniot curve. The Chapman–Jouguet condition of tangency yields values for the detonation pressure, P_T , and the volume of the detonation products, V_T , in the detonation front. By making use of the relationship,

$$\eta = V_0'[(P_T - P_0)/(V_0' - V_T)]^{\frac{1}{2}},$$

values of the detonation velocity, η , have been calculated. In the above expression, P_0 is atmospheric pressure. Values of η are given in the Table for various values of α

Variation of detonation velocity with the constants α and β in the nitrogen potential u_2 .

α_N	β (\AA^{-1})	V_0' (c.c.)	P (dynes/cm. ²)	η (m./sec.)
2	0.5	31.16	33.6×10^{10}	5725
2	0.6	31.16	48.0×10^{10}	7192
1.8	0.5	31.16	27.4×10^{10}	5250
1.8	0.6	31.16	45.9×10^{10}	6805

and β . For all these calculations a hand calculating machine was employed. Plots of detonation velocity against V_0' are given in Fig. 10.

Many useful conclusions can be drawn from these data. It is observed that the effect of change in β on detonation velocity is far more pronounced than the change in α . An increase in β by 0.1 increases the detonation velocity by more than 25% whereas an increase in α by 0.2 increases it by only about 6%.

Single crystals of silver azide possess density¹² $\rho = 4.81$ g./c.c. or volume per mole $V_0 = 31.16$ c.c. The detonation velocity in these crystals has been found to be 4400 m./sec. The effect of diameter on the detonation velocity has not been investigated. Owing to the lack of this information it is difficult to assess the exact value of the ideal velocity of detonation. It will be higher than the value of 4400 m./sec., and may reasonably be in the range of values reported above.

The data given in the Table and Fig. 9 lead to another interesting conclusion. For a given velocity of detonation in silver azide, the temperature and pressure of detonation are higher than in secondary explosives. This may be one of the reasons why primary explosives arrive at the point of detonation so rapidly.

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¹² M. M. Bassiere, *Compt. rend.*, 1935, **201**, 735.