coarse TNT, and pressure-time curves evidently corresponding to normal explosive deflagration were measured. In these cases pressures were developed which increased with time for at least 700 μsec (see Fig. 6). No maxima in the pressure-time curves were found, and the measured pressures never exceeded 900 atmos. Because of this difficulty, it was decided to mix enough fine TNT with the coarse in order to form a mixture that was known to be cap-sensitive, and readily detonates in the cannon; this mixture propagates normally in small diameter, unconfined charges, e.g., less than 1 in. (The fine product used had an average particle diameter of 0.2 mm.) The addition of this fine TNT in sufficient amounts (25% or more) produced a marked change in the character of the pressure-time curves. The measured pressures in the cannon were much higher in these cases, and the curves exhibited pressure maxima that appeared considerably later than the time required for equilibrium to be attained in the chamber. The times at which these maxima appeared were also found to be dependent upon the particle size of the coarse component of the TNT mixture, and therefore it was concluded that these pressures were associated with the chemical reaction rate and not merely with the attainment of equilibrium. Typical pressure-time curves for various TNT particle sizes are given in Fig. 6.

Space limitations do not permit complete presentation of all the pressure-time data here. However, these data are available upon request, including data showing a complete analysis of a typical film and illustrations of the smoothing process. Table I contains values of peak pressure for various mixtures, and the times at which these peaks appeared.

TABLE I. Peak pressure, time of attainment, and calculated reaction times of coarse TNT using $N_f=1$ and $\beta=0$.[a, b]

Film No.	Loading	$t_i(\mu\text{sec})$	p_i(atmos)	$\tau_c(\mu\text{sec})$
10	50 g (4–6) mesh	>600	>900	...
6	10 g fine 30 g (4–6) mesh	200	4060	560–640
16	10 g fine 30 g (4–6) mesh	160	4060	470–530
20	10 g fine 30 g (4–6) mesh	160	4040	510–540
24	10 g fine 30 g (4–6) mesh	144	4110	310–420
7	15 g fine 25 g (4–6) mesh	160	4080	500–600
31	15 g fine 25 g (4–6) mesh	160	3630	590–660
9	20 g fine 20 g (4–6) mesh	130	4180	430–550
37	10 g fine 30 g (8–10) mesh	140	3950	430–500
40	10 g fine 30 g (8–10) mesh	120	3860	390–450
36	15 g fine 25 g (8–10) mesh	115	4080	400–430
18	30 g fine	65	3150	...
22	40 g fine	60	4380	...

[a] $p^*=5470$ atmos assuming $\tau_c=0$.

[b] The values of τ_c listed are the minimum value calculated and the value calculated at $t=t_i$.

TABLE II. Data computed for TNT in the "explosion" state.

$\rho_1\left(\frac{\text{g}}{\text{cm}^3}\right)$	T_3(°K)	$\bar{C}_v\left(\frac{\text{kcal}}{\text{kgK°}}\right)$	$Q\left(\frac{\text{kcal}}{\text{kg}}\right)$	$n\left(\frac{\text{moles}}{\text{kg}}\right)$	p_3(atmos)
0.266	2420	0.289	614	43.1	3230
0.307	2450	0.291	626	42.9	3950
0.342	2480	0.292	635	42.6	4650
0.377	2500	0.293	645	42.2	5380
0.415	2520	0.294	654	41.7	6200
0.450	2550	0.295	665	41.2	7070
0.526	2600	0.297	683	40.3	9110
0.599	2640	0.299	701	39.3	11 350
0.676	2690	0.301	720	38.5	14 360
0.752	2750	0.304	742	37.8	17 440
0.926	2880	0.310	803	35.7	25 940
1.111	3050	0.319	881	33.2	37 440

Before one can apply the pressure *vs* time measurements obtained from the cannon toward calculations of reaction times, it is necessary to carry out the thermohydrodynamic solution of TNT under "explosion" conditions.

Calculations were made using the equivalent of the equation of state

$$pv=nRT+\alpha(v)p \qquad (3)$$

and a fugacity method for the products of detonation[9] using a "universal" $\alpha(v)$ curve described in reference 9. As mentioned above the particular choice of the equation of state in this case is not critical since the pressure is the hydrodynamic variable of most interest in these experiments. Previous studies have shown the pressure to be relatively insensitive to the form of the equation of state.[5] Table II contains the necessary solution for TNT under the appropriate "explosion" conditions applicable in this study.

THEORY OF THE CANNON

The reaction rate determinations were based upon the following model:

(1) The chemical reaction follows the Eyring surface burning mechanism,[2] the rate determining step being the rate of flow of heat which proceeds at a constant radial velocity R_0/τ into the grain. Thermal equilibrium is established in the gas phase right up to the reacting surface, and the surface temperature of the grain is T_3, the "explosion" temperature corresponding to the particular conditions involved. (In the case of explosive deflagration a temperature gradient exists between the grain surface and the surrounding gases.)

(2) The amount of chemical reaction which takes place under "detonation" conditions is very small. The detonation wave merely initiates the reaction. The pressure and temperature in the chamber than reaches equilibrium in a very short time, and the major portion of the reaction proceeds at a temperature T_3.

(3) Defining n as the number of moles of gas produced per kilogram of explosive reacted at a given time t, Q as the chemical energy released per kilogram of

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[9] M. A. Cook, J. Chem. Phys. **15**, (1947); **16**, 1081 (1948).

reacted explosive, and $\bar{C}_v$ the average specific heat between T_1 and T_3 of the gas formed per kilogram of explosive reacted, the quantities n, Q, $\bar{C}_v$, and consequently T_3 are assumed to be constant with time.

Assumption (3) does not mean strictly that the composition is constant with time because the composition may change considerably without producing large variations in n, Q, and $\bar{C}_v$. Also the fugacity factor remains relatively constant with time in the "cannon" test since the specific volume remains substantially constant.

The theory of the cannon was based upon the $\alpha(v)$ equation of state[9] and the Eyring surface burning equation[2] for the extent of reaction N for isothermal decomposition.

$$N=1-\left(1-\frac{t}{\tau}\right)^3. \tag{4}$$

Since it was necessary to mix fine TNT with the coarse in order to detonate it in the cannon, and since it was impossible to build a smooth bore cannon which suffered no gas leakage, the equations were developed for a charge consisting of two particle sizes, and efforts were made to correct for gas leakage.

Let the subscript f refer to the fine particle size, the subscript c refer to the coarse component, and an asterisk refer to complete reaction. Accordingly, one may write

$$n^*=n_f^*+n_c^*, \tag{5}$$

$$n=N_fn_f^*+N_cn_c^*, \tag{6}$$

$$n=zn^* \quad \text{where} \quad z=\frac{m_fN_f+m_cN_c}{m_f+m_c}, \tag{7}$$

where m refers to the mass of explosive loaded in the chamber. If one now makes the reasonable assumption that the leakage rate at any given time is proportional to the pressure, then

$$dn_1/dt=\beta n^*p, \quad \text{and} \quad n_1=\beta n^*\int_0^t pdt, \tag{8}$$

where n_1 is the number of moles per kilogram of reacted explosive which have leaked from the firing chamber at time t. Equation (7) may be rewritten in terms of these leakage corrections.

$$n'=zn^{*\prime}, \tag{9}$$

$$n^{*\prime}=n^*-n_1=n^*\left(1-\beta\int_0^t pdt\right). \tag{10}$$

From Eq. (3) (replacing n by n'), using Eqs. (9) and (10), one finds

$$z=\frac{p(v_3'-\alpha_3')}{n^*\left(1-\beta\int_0^t pdt\right)RT_3}, \tag{11}$$

where

$$v_3'=\frac{Ay+V_0}{\left(1-\beta\int_0^t pdt\right)(m_f+m_c)}. \tag{12}$$

V_0 is the volume of the firing chamber, A is the cross-sectional area of the bore, and y is the slug displacement.

According to assumption (1) one may write

$$\frac{1}{\tau_f}=\frac{R_c}{R_f}\frac{1}{\tau_c} \tag{13}$$

where R refers to the initial grain radius of the explosive. In terms of the fine and coarse components Eq. (4) becomes

$$N_f=1-\left(1-\gamma\frac{R_c}{R_f}\right)^3; \quad N_c=1-(1-\gamma)^3; \quad \gamma=\frac{t}{\tau_c}. \tag{14}$$

Equations (7) and (14) may be combined yielding

$$\gamma^3\left[1+\frac{m_f}{m_c}\left(\frac{R_c}{R_f}\right)^3\right]-3\gamma^2\left[1+\frac{m_f}{m_c}\left(\frac{R_c}{R_f}\right)^2\right] +3\gamma\left[1+\frac{m_f}{m_c}\frac{R_c}{R_f}\right]=\frac{m_f+m_c}{m_c}z. \tag{15}$$

Given pressure-time data, displacement-time data, and the $\alpha(v)$ curve a value of γ and consequently τ_c may be calculated corresponding to each pressure-time coordinate using Eqs. (12), (11), (15), and the computations given in Table II provided that a value of β has been determined.

A good estimation of the temperature drop of the confined gas on the basis of adiabatic expansion may be obtained from the first law of thermodynamics using the measured velocity-time data of the slug. One may accordingly write

$$T_3=\frac{(Q^*/1000)(m_f+m_c)z-(h/1000)}{(\bar{C}_v^*/1000)(m_f+m_c)z} \tag{16}$$

where h is the kinetic energy of the slug expressed in calories, and

$$T_3^*=(Q^*/\bar{C}_v^*)+T_1. \tag{17}$$

Equation (16) may be expressed in terms of Eq. (17) by

$$T_3=T_3^*-\Delta T; \quad \Delta T=\frac{h}{\bar{C}_v^*(m_f+m_f)z}. \tag{18}$$

As a check, a reaction time may also be calculated from each set of data in terms of the time t_i at which the peak pressure was attained. (Let a subscript i refer to the value of a variable at the time $t=t_i$). Differentiating