Reprinted from THE JOURNAL OF CHEMICAL PHYSICS, Vol. 24, No. 2, 191–201, February, 1956
Printed in U. S. A.

Rate of Reaction of TNT in Detonation by Direct Pressure Measurements*

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(Received April 27, 1955)

A description of an experimental method of obtaining pressure-time data for the decomposition of coarse TNT following partial detonation is given. This method consisted of photographing (with a streak camera) the displacement of a slug shot from a smooth bore cannon. The velocity and acceleration of the slug were obtained by numerical differentiation of the displacement-time data derived from the photograph. Pressure-time curves were obtained which exhibited pressure maxima at times that were dependent upon the particle size of the TNT detonated in the cannon. Peak pressures for TNT of 4–6 standard mesh particle size occurred between 140–200 μsec, peak pressures for 8–10 mesh occurred between 115–140 μsec, and pressure maxima for "fine" TNT occurred between 50–70 μsec. The pressure-time curves were analyzed, and reaction times of the coarse TNT were calculated by two different methods. One method yielded a value of the reaction time for each pressure-time coordinate and the other a reaction time in terms of the time at which maximum pressure occurred. The results obtained by these two methods were not the same. However, when corrections were made for gas leakage from the cannon, rather good agreement resulted. The most probable value computed (after leakage corrections were made) for the 4–6 TNT was found to be about 300 μsec and for the 8–10 TNT about 200 μsec. On the basis of these reaction times the grain erosion velocity for the TNT in the cannon was evidently much greater than linear burning rates at the same pressure obtained experimentally for explosive deflagration.

APPLICATION of the nozzle[1] and curved front[2] theories to the experimental velocity-diameter curves for various particle sizes of spherically-grained low-density TNT gave the following effective reaction times (in seconds) for detonation (T_2) conditions:

$$\tau = 2.3\times10^{-5}\bar{R}_g \quad \text{(nozzle theory)}$$
$$\tau = 1.07\times10^{-5}\bar{R}_g \quad \text{(curved front theory)}$$

where $\bar{R}_g$ is the average grain radius. Thus the effective reaction time for 4–6 mesh TNT, for example, was 4.6 microseconds and 2.1 microseconds, respectively, according to the nozzle and curved front theories.

Evidence has been found that the total reaction times in detonation may be much longer than the effective times indicated by the "nozzle" and "curved front" theories. This evidence, based on extrapolations of isothermal decomposition data,[3] involves some uncertainties and is far from crucial. However, if it is true, it should be possible to demonstrate this by direct rate-of pressure-development measurements, at least for the most slowly reacting explosives such as 4–6 mesh TNT. To test this possibility the "cannon" method described in this article was designed. The method was not intended to be an accurate one for the measurement of reaction rate, but rather a direct method to determine approximately the total reaction times. While the method may appear somewhat cumbersome, it actually was the only type found suitable for this purpose; the initial pressures and shock intensity were too large for the use of piezoelectric gauge techniques. The procedure consisted of finding the pressure-time curve for an explosive by means of measurements of the acceleration of a slug propelled from the cannon by the explosion following detonation.

Consider a cannon with a cylindrical firing chamber two inches in diameter and two inches long about half-filled with TNT (see Fig. 1). The detonation wave would require roughly 10 μsec to traverse the TNT. (From direct probe measurements in the cannon it was found that about 20 μsec were required for the ionization wave to reach the base of the slug.) If the total reaction zone length were comparable to the predictions of the "curved front" theory or the "nozzle" theory, by the time the detonation wave has traversed the explosive, that explosive in the region A would have completely reacted, and that in the region B would have largely reacted. For such a fast reaction, by the time the shock wave reached the slug the reaction would have reached completion. If, on the other hand, the reaction zone length were large in comparison to the dimensions of the chamber, by the time the detonation wave has

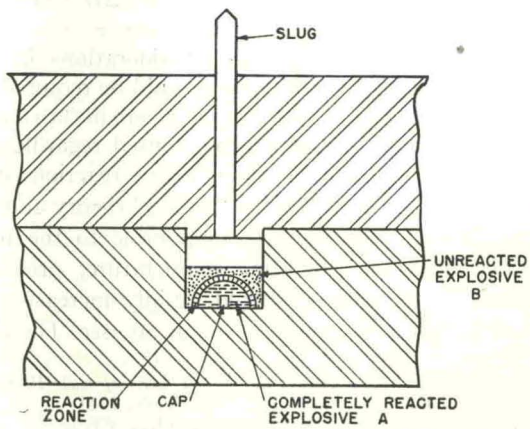

FIG. 1. Cross section of "cannon."

* This project was supported by Office of Naval Research (Contract Number N7–onr–45107, Project Number 357 239).
[1] H. Jones, Proc. Roy. Soc. (London) **A189**, 415 (1947).
[2] Eyring, Powell, Duffey, and Parlin, Chem. Revs. **45**, 16 (1949).
[3] Cook, Horsley, Partridge, and Ursenbach, J. Chem. Phys. **24**, 60 (1956).

traversed the explosive only a small fraction of the explosive would have reacted, and no part of it would have reacted completely in any particular region of the cannon chamber. The detonation wave, however, would have effectively initiated the reaction, and since the explosive would very quickly become distributed throughout the firing chamber, most of the explosive decomposition would therefore take place under temperature and pressure conditions corresponding to uniform filling of the firing chamber.

According to the Eyring absolute reaction rate theory the specific rate constant is given by the equation[4]

$$k_r=\frac{kT}{h}\exp(\Delta S^{\neq}/R)\exp(-\Delta H^{\neq}/RT). \qquad (1)$$

Since the total reaction time is inversely proportional to the rate constant, using Eq. (1) the ratio of the reaction time of a given explosive under "explosion" conditions to the reaction time under "detonation" conditions should be

$$\frac{\tau_3}{\tau_2}=\frac{T_2}{T_3}\exp\left[\frac{\Delta H^{\neq}}{R}(1/T_3-1/T_2)\right] \qquad (2)$$

where T_2 is the detonation temperature, and T_3 is the temperature corresponding to the actual conditions in the chamber. Assuming the Cook $\alpha=\alpha(v)$ equation of state, the detonation temperature of TNT at a density of 1.05 g/cm^3 was calculated to be 3700°K. (For the low densities considered all equations of state which have been applied in detonation theory should give practically the same result.[5] Hence the arguments presented here do not depend significantly on which equation of state one employs. Therefore a relatively simple and convenient one was used.) For detonation of the same product in the cannon at an average loading density of about 0.39 g/cm^3, the temperature T_3 was calculated by the same equation of state to be 2500°K neglecting the initial temperature transient associated with the initial large density change from 1.05 to 0.39 g/cm^3. Using Eq. (2) and the value of $\Delta H=34$ kcal/mole given by Robertson,[6] one calculates $\tau_3/\tau_2=13.6$.

From simple kinetic theory considerations it was concluded that about 40–50 μsec should be required for pressure gradients to reach essentially zero in the cannon firing chamber for the arrangement used regardless of the reaction time. Thus if the effective reaction times in detonation predicted by the "nozzle" theory and the "curved front" theory were comparable to the total reaction times for the same temperature, pressures measured in the cannon should rapidly increase with time and reach a maximum at about 50 μsec. The time of appearance of this peak pressure, moreover, should be quite insensitive to the particle size and the reaction rate of the explosive detonated, because the pressure time curve would not be related at all to the chemical reaction rate but rather to the attainment of pressure equilibrium in the chamber. Experimental verification of these conclusions is given in Fig. 2 which presents a pressure-time curve obtained by detonation of 25 g of fine PETN in the cannon. The peak pressure was measured to be 3300 atmospheres and appeared at 50 μsec, and PETN is known to possess a total reaction time much less than 50 μsec.

On the other hand, if the total reaction time were much longer and the explosive detonated in the cannon were reacting relatively slowly, a pressure-time curve should be measured for which the peak pressure would appear later than 50 μsec. In this case the pressures measured should be associated with the chemical reaction rate, and consequently the time of appearance of the maximum pressure should be dependent upon the particle size of the explosive detonated in the cannon. The maximum pressure should then appear at the time at which the rate of pressure increase due to chemical reaction equaled the rate of pressure decrease due to adiabatic expansion and gas leakage from the firing chamber. Moreover, an analysis of the section of the pressure-time curves for times greater than the time required for the pressure gradient to reach zero should provide a means for studying reaction rates.

It was felt that the "cannon" test would be a desirable one even if the total reaction times were much shorter than one can measure by the cannon method. Although the "cannon" method would then necessarily fail, the negative result would allow one to eliminate models of long reaction time. One would, of course, still be faced with the possibility that an entirely different mecha-

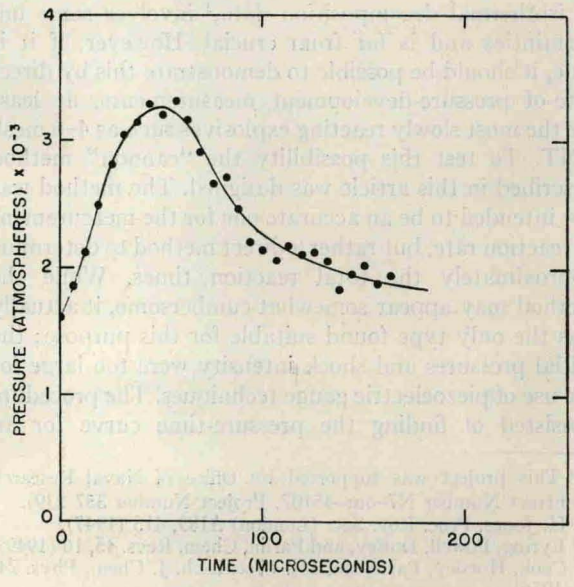

FIG. 2. Pressure-time curve for fine PETN.

[4] Glasstone, Laidler, and Eyring, *The Theory of Rate Processes* (McGraw-Hill Book Company Inc., New York, 1941).

[5] Cook, Keyes, Horsley, and Filler, J. Phys. Chem. **58**, 1114 (1954).

[6] A. J. B. Robertson, Trans. Faraday Soc. **44**, 1677 (1948).

nism of reaction prevails after the explosive passes out of the detonation head. For example, it is obvious that the rate law in ordinary explosive deflagration is quite different than that occurring in detonation; otherwise ideal detonation velocities would be rare. That is, reactions occurring at the rate obtained for explosive deflagration would appear to require very long reaction times and thus long reaction zones. (This point is discussed quantitatively later in this article.)

This article deals with the experimental results obtained from the "cannon" method for the determination of the reaction rate of 4–6 mesh and 8–10 mesh loose-packed TNT, and with a theoretical analysis of these results.

EXPERIMENTAL EQUIPMENT AND PROCEDURE

The cannon used in this study for direct measurements of pressure was constructed in two sections, a barrel and a breech, each being made of a piece of steel 10 in. in diameter. The piece forming the barrel was 4 in. thick, and the one forming the breech was 6 in. thick. A one-half inch hole was drilled through the center of the 4-in. piece to serve as the bore, and a powder chamber about 5 cm diameter and 5 cm deep, having a volume of 103 cm^3, was machined in the center of one side of the 6-in. piece. These two pieces were held together by means of eight $1\frac{1}{2}$-in. diameter heat-treated steel bolts spaced around the circumference of the barrel about $1\frac{1}{2}$ in. from its edge that threaded into the breech parallel to the bore. The projectiles fired from the cannon generally were $\frac{1}{2}$-in. diameter aluminum shafting cut to a length of 6 in. and sharpened to a knife edge in order that the displacement of the leading edge might be accurately measured.

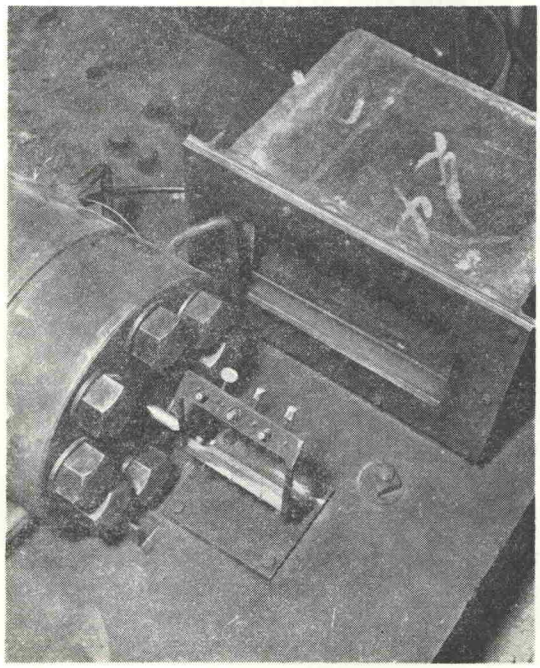

FIG. 3. Cannon and "strobe."

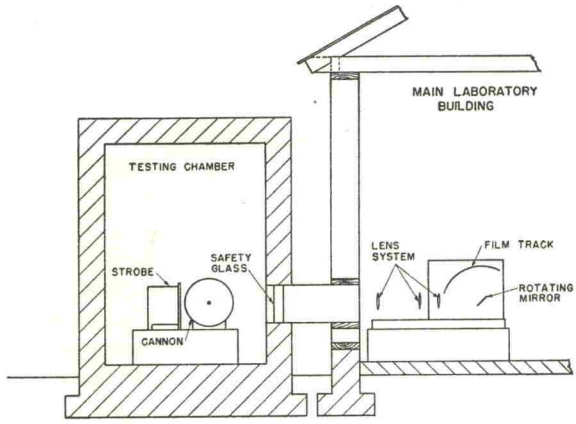

FIG. 4. Experimental arrangement.

The charge was detonated inside the cannon with a special cap of negligible time delay initiated by the discharge of a 1-mfd capacitor charged to 5000 volts. The displacement of the knife edge of the slug was photographed with a rotating mirror streak camera. The camera was mounted inside a dark room in a building adjacent to the test chamber with a short tunnel connecting the chamber and the dark room. The leading edge of the slug was silhouetted by light from a xenon flash tube about 10 inches long, 8 mm inside diameter, and filled to a pressure of about 10 cm of mercury. This strobe was initiated in synchronism with the exploding bridgewire cap and flashed with a 230 mfd capacitor charged to 1000 volts. The tube was mounted with springs inside a steel box with a safety glass window and placed as close to the slug as possible. Adjustable legs were provided on the box in order that the height of the tube could be adjusted conveniently until its image fell along the slit of the camera. Proper distance scale was determined by taking each picture through a wire grid placed about $\frac{1}{8}$ in. behind the slug (see Figs. 3 and 4 for the experimental setup).

With this xenon light source, a 2 mil slit on the camera, Aerographic Super XX film, and a mirror speed of 200 rps corresponding to a writing speed of 0.638 mm/μsec, proper exposure was obtained with the objective lens set at $f/11$ which provided an effective over-all aperture of about $f/22$. The film trace (see Fig. 5) was then read with a Cambridge Universal Measuring Machine having a least count of 0.01 mm.

EXPERIMENTAL DATA

The data obtained from the "cannon" method consisted of a set of distance-time data (X_j, Y_j). The X_j values were proportional to the elapsed time and for convenience were recorded at equally spaced intervals, and the Y_j values taken were proportional to the displacement of the leading edge of the slug. From these data it was required to obtain the velocity and the

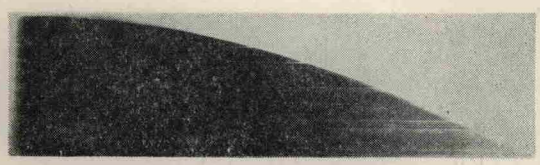

FIG. 5. Typical trace of accelerating slug.

acceleration of the center of gravity of the slug. It is well known that given a set of coordinates one can quite easily perform the mathematical operation of integration, but numerical differentiation is an exceedingly delicate task, and the accurate determination of second derivatives is much more difficult than for first derivatives.

The process of numerical differentiation was further complicated in this problem by the fact that besides the random errors made in setting the cross hairs properly on the film trace and taking the reading, there was a systematic error introduced because of longitudinal vibrations set up in the slug by the initial shock. These vibrations, in other words, were caused by a longitudinal wave which traversed the slug and was reflected at its ends. The film trace thus consisted of the displacement of the center of gravity of the slug superimposed upon which was a rapidly damped oscillation caused by the multiply-reflected longitudinal wave. These oscillations appeared to have about a 60 μsec period in the 6-inch aluminum slug which was in good agreement with the speed of sound in aluminum (5100 m/sec). It was hoped that a material could be found that would be more suitable for slugs than aluminum. Such a material, in addition to being low enough in density that reasonably high accelerations would be experienced, should be rigid enough that the initial amplitude of the vibrations be small and possess a high enough internal viscosity for the vibrations to damp out rapidly. This material should also be sufficiently strong not to shatter under the initial impulse. While various materials were tried, nothing more satisfactory than aluminum was found and since aluminum gave rather good results, no extensive study of projectile materials was undertaken.

Because of the random errors made in reading the film and the oscillations that were set up in the slug by the initial shock of the explosion, it was necessary to apply some kind of smoothing process before any method could profitably be applied to obtain the derivatives. The smoothing was done with an IBM computing unit using a method of least square polynomials over moving arcs outlined by Trimble.[7] Briefly the operation was as follows: A polynomial of chosen degree was fitted to $2n+1$ points by least square methods, and the value of the polynomial at the $n+1$st point was taken as the smoothed ordinate at that point. The arc was then shifted one coordinate each operation, and the process repeated until smoothed ordinates were obtained for all the points except the n points on each extreme end of the data. The calculations were expedited by means of a recursion relation which allows one to calculate conveniently the smoothed ordinate using the preceding polynomial. The data were usually smoothed twice or until the second derivatives were fairly regular.

Any smoothing process must necessarily change the data to some small extent, but it was felt that the above method did justice to the data. The initial oscillations on the film trace appeared to have amplitudes of the order of 0.1 mm, and along this portion of the trace some of the smoothed y's differed from the original Y's as much as this amount. However, these oscillations in general decreased in amplitude fairly rapidly, and then the smoothing process in the main merely added more decimal places to the readings. The derivatives were calculated according to a method of Rutledge.[8] Briefly the process consists of passing a 4th-degree interpolating polynomial, $y(\lambda)$, through five consecutive smoothed points and evaluating the derivatives at the midpoint of the interval by means of the polynomial. The second derivatives were then smoothed by graphical means. An evaluation of the validity of the derivatives thus obtained is given in the Appendix of this article. The results of the evaluation point to the conclusion that in spite of the oscillations of the slug the derivatives obtained are very good, except for the first 10–15 microseconds at the start, and this region is of no interest.

EXPERIMENTAL RESULTS

Pressure-time measurements were first attempted for pure 4–6 mesh TNT at an average loading density of 0.39 liter/kg, but it was found that the pure coarse TNT could not be detonated in the cannon with a cap. This was not surprising since for unconfined charges of this mesh TNT a booster is required for initiation, and propagation failure occurs in charges less than 5 cm in diameter. However, because of the heavy confinement of the cannon, it was found possible to ignite the pure

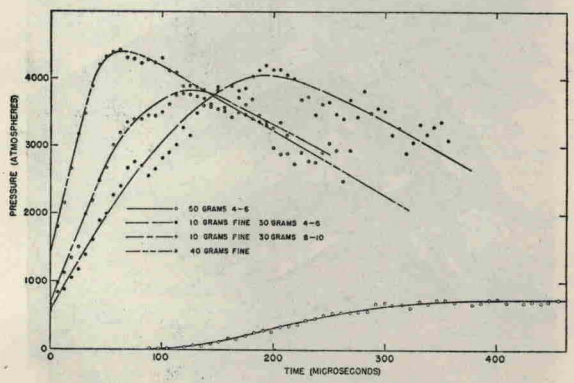

FIG. 6. Typical pressure-time curves.

[7] G. R. Trimble, Jr., Proceedings Computations Seminar, August 1951, p. 93, IBM, New York.

[8] G. Rutledge, Phys. Rev. **40**, 262 (1932).

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(μsec)	p_i(atmos)	τ_c(μsec)
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.

$\rho_1\left(\frac{g}{cm^3}\right)$	T_3(°K)	$\bar{C}_v\left(\frac{kcal}{kgK°}\right)$	$Q\left(\frac{kcal}{kg}\right)$	$n\left(\frac{moles}{kg}\right)$	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

$$pv=nRT+\alpha(v)p \tag{3}$$

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_g/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

[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

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

$$n=N_f n_f^*+N_c n_c^*, \tag{6}$$

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

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

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

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.

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

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

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

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

where

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

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

Eq. (11) with respect to t and equating to zero,

$$0=\left.\frac{dp}{dt}\right|_{t=t_i}=\left[\frac{zn^{*\prime}R}{v_3'-\alpha_3'}\frac{dT_3}{dt}+\frac{zRT_3}{v_3'-\alpha_3'}\frac{dn^{*\prime}}{dt}+\frac{n^{*\prime}RT_3}{v_3'-\alpha_3'}\frac{dz}{dt}+zn^{*\prime}RT_3\frac{d}{dt}\left(\frac{1}{v_3'-\alpha_3'}\right)\right]_{t=t_i}, \quad (19)$$

where

$$\left.\frac{dn^{*\prime}}{dt}\right|_{t=t_i}=-\beta p n^* \quad (20)$$

$$\left.\frac{dz}{dt}\right|_{t=t_i}=\frac{1}{m_f+m_c}\left[m_f\frac{dN_f}{dt}+m_c\frac{dN_c}{dt}\right]_{t=t_i}$$

$$=\frac{1}{m_f+m_c}\left[\frac{3m_f}{\tau_{if}}\left(1-\frac{t_i}{\tau_{if}}\right)^2+\frac{3m_c}{\tau_{ic}}\left(1-\frac{t_i^2}{\tau_{ic}}\right)\right] \quad (21)$$

and

$$\left.\frac{d}{dt}\left(\frac{1}{v_3'-\alpha_3'}\right)\right|_{t=t_i}=\frac{-1}{(v_{i3}'-\alpha_{i3}')^2\left(1-\beta\int_0^{t_i}pdt\right)(m_f+m_c)}$$

$$\left[A\left.\frac{dy}{dt}\right|_{t=t_i}+\frac{V_0+Ay_i}{1-\beta\int_0^{t_i}pdt}\right]\left.\left(1-\frac{d\alpha_3'}{dv_3'}\right)\right|_{t=t_i}, \quad (22)$$

since

$$\frac{d\alpha_3'}{dt}=\frac{d\alpha_3'}{dv_3'}\frac{dv_3'}{dt}.$$

Given values of β, p_i, $dy/dt|_{t=t_i}$, y_i, t_i, and the $\alpha(v)$ curve, Eq. (19) may be solved for the reaction time τ_{ic} of the coarse constituent using Eq. (13) and definitions (20), (21), and (22).

The time at which maximum pressure occurs serves as a good lower limit of the reaction time. In order to obtain an upper limit for the coarse TNT, calculations were made using $\beta=0$ and $N_f=1$. Since the fine material was of very much smaller particle size than the coarse, its reaction time would be much shorter according to Eq. (13), and therefore the assumption $N_f=1$ should be very good for sufficiently large t's. Under these approximations Eq. (15) is not needed, and reaction times may easily be computed for the coarse component at each pressure time point using Eqs. (12), (11), (7), and (14). The results of these calculations are given in Table I. Calculations of ΔT from Eq. (18) substantiated the fact that the reaction was nearly an isothermal one. ΔT seldom exceeded 15 K° during the first 200 μsec of the reaction.

If the above calculations were based on a correct model, and the derivatives were obtained very accurately, the reaction times corresponding to each p, t point should all possess the same value. If, however, the calculated reaction times are plotted against t, the

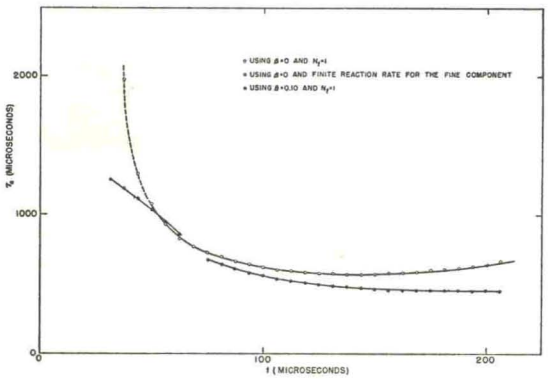

FIG. 7. Typical variation of τ_c (calculated reaction time) with t (elapsed time).

curves all possess the same characteristics. (Figure 7 shows a typical plot of this type.) For small t's the calculated τ_c's are relatively large. As t increases the calculated τ_c's decrease rather rapidly at first, reach a minimum value, and then slowly increase. The most reliable values of τ_c should be those calculated for fairly large t's. Two values of τ_c are listed in Table I, the smaller value being the minimum τ_c calculated, the larger being the value calculated at the p–t point corresponding to $t=t_i$.

The rapid decrease in calculated τ_c's for small t's may be attributed to several factors: (a) The fine component has not completely reacted, and calculations made upon the basis that the fine has completely reacted lead to an overestimation of the reaction times. (b) Insufficient time has elapsed for the gas pressure to reach equilibrium in the chamber. (c) The second derivatives are inaccurate because the smoothing process does not work well at extreme ends of the data.

Calculations made in which $\beta=0$ and N_f was not assumed equal to 1 by means of Eqs. (12), (11), and (15) yielded somewhat smaller values of τ_c for small t's, but the values of τ_c computed by this method for large t's were virtually unchanged (see Fig. 6). It was concluded therefore that the approximation $N_f=1$ was a good one and that probably (b) and (c) were as important sources of error as (a) for small t's.

Thus assuming $N_f=1$ and using Eqs. (20), (21), and (22), Eq. (19) may be written more simply

$$O=-\tau_{ic}^3\left[m_f\beta p_i+\frac{m_f}{m_f+m_c}G_i\right]$$

$$+\tau_{ic}^2\left[3m_c\left(1-\beta\int_0^{t_i}pdt\right)-3m_c t_i\beta p_i-\frac{3m_c t_i}{m_f+m_c}G_i\right]$$

$$+\tau_{ic}\left[-6t_i\left(1-\beta\int_0^{t_i}pdt\right)m_c+3m_c t_i^2\beta p_i+\frac{3m_c t_i^2}{m_f+m_c}G_i\right]$$

$$+3m_c\left(1-\beta\int_0^{t_i}pdt\right)t_i^2-m_c t_i^3\beta p_i-\frac{m_c t_i^3}{m_f+m_c}G_i, \quad (23)$$

where

$$G=\left(1-\frac{d\alpha_3'}{dv_3'}\right)\left[\frac{A}{v_3'-\alpha_3'}\frac{dy}{dt}+\frac{V_0+Ay}{v_3'-\alpha_3'}\frac{\beta p}{1-\beta\int_0^t pdt}\right].$$

[The first term of Eq. (19) has been neglected because it was found by utilizing the ΔT's calculated from Eq. (18) that this term was small in comparison with the other terms.]

Solutions of Eq. (23) under the assumption of no gas leakage ($\beta=0$) in general yielded the result that the reaction time computed by means of maximum pressure was only about 20–30 μsec longer than t_i. Thus one was faced with the fact that the reaction times computed along the p,t curve were much longer than that computed in terms of the maximum pressure (see Table II). This fact along with the consistent slow increase with t in the calculated τ_c's for large times indicated, as was predicted, that gas leakage was an important factor to be considered. The drop in temperature due to adiabatic expansion of the gas in the chamber also contributed a small amount to this effect but the ΔT's were not large enough to be an important factor.

The leakage constant β was then evaluated in order that the consistent increase of the τ_c's calculated along the p,t curve for large t's was eliminated as nearly as possible (see Fig. 7). This was done, using $N_f=1$, by means of Eqs. (12), (11), and (14) using pressure-time data. The results of the calculations of τ_c for three films of 4–6 mesh TNT which had the widest variance of t_i and for one film of 8–10 mesh TNT are shown in Table III. The values of β determined as above were used in Eq. (23), and reaction times of these same shots were calculated in terms of the peak pressures. In these cases the reaction times τ_{ic} calculated in terms of the maximum pressures were in much closer agreement with those calculated along the p,t curve (see Table III).

TABLE III. Calculated reaction times for coarse TNT using $N_f=1$, $\beta\neq 0$.

Film no.	Loading	β	t_i	τ_c (μsec)	τ_{ic} (μsec)	$\frac{\tau_{ic}}{t_i}$
20	10 g fine 30 g (4–6) mesh	0.15	160	370	300	1.84
6	10 g fine 30 g (4–6) mesh	0.10	200	460	350	1.75
24	10 g fine 30 g (4–6) mesh	0.17	144	270	270	1.88
16	10 g fine 30 g (4–6) mesh	...	160	...	(290)[a]	...
7	15 g fine 25 g (4–6) mesh	...	160	...	(290)	...
31	15 g fine 25 g (4–6) mesh	...	160	...	(290)	...
9	20 g fine 20 g (4–6) mesh	...	130	...	(230)	...
36	15 g fine 25 g (8–10) mesh	0.15	115	300	200	1.68
37	10 g fine 30 g (8–10) mesh	...	140	...	[240][b]	...
40	10 g fine 30 g (8–10) mesh	...	120	...	[200]	...

[a] ( ) 1.8 times t_i.
[b] [ ] 1.7 times t_i.

It may be noticed that the value of τ_{ic}/t_i was largest for the case where t_i was the smallest, and τ_{ic}/t_i possessed the smallest value in the case where t_i was the largest. The difference apparently was not great enough to be significant, however, as the values varied only from 1.75 to 1.88. Probably a good average value to use for 4–6 mesh TNT was $\tau_{ic}/t_i=1.8$ and for 8–10 mesh $\tau_{ic}/t_i=1.7$.

The cannon experiment inherently contains errors too numerous to measure reaction times with high precision. The main sources of error were gas leakage from the firing chamber, the fact there existed no unique time $t=0$ at which all of the explosive began to react simultaneously at the explosion temperature T_3, and evaluation of the second derivatives. A time of about 10 μsec was required for the detonation wave to traverse in the explosive and to initiate the reaction, and some of the reaction (depending on the reaction zone length) must necessarily have taken place under detonation conditions. All the data are listed, and the calculations were made on the basis of this, roughly 10 μsec, time lag; that is, the time $t=0$ was taken to be 10μsec after the initiation of the cap.

According to pressure measurements in the cannon, it was concluded that the total reaction time of the 4–7 mesh TNT was between 140 and 640 μsec, and the reaction time of the 8–10 mesh TNT was between 120 and 500 μsec corresponding to the temperature $T_3=2500$°K calculated by the $\alpha=\alpha(v)$ equation of state. On the basis of the model used for leakage calculations (neglecting the amount of reaction which took place under detonation conditions), the best value of the total time reaction time for the 4–6 TNT was concluded to be about 1.8 times t_i or about 300 μsec, and the best value for the 8–10 mesh TNT about 1.7 times t_i or about 200 μsec. These conclusions are not in exact agreement with the surface burning law that the reaction time of the 4–6 mesh should be twice that of the 8–10 mesh, but the discrepancy is within experimental error. The reaction time of the fine TNT was probably too short to be measured in the cannon. Peak pressures for this product occurred at about 60 μsec, but this was about the time required for pressure equilibrium to be attained in the chamber, and therefore it is doubtful that one was measuring in this case pressures which were associated with reaction rates. Also, values of the second derivative obtained in the region of small t's may not be accurate. Peak pressures for coarse TNT were measured at times much longer than the times required for pressure and temperature equilibrium to be attained in the chamber, and the appearance of these peaks was dependent upon the particle size.

It is quite evident that the chemical process taking place in the cannon was not the normal pressure dependent reaction occurring in explosive deflagration.

Rather it is believed to be a mechanism of the higher rate type occurring in detonation. The linear burning rate for TNT in normal explosive deflagration is given by

$$\frac{dR_g}{dt}(\text{cm/sec}) = 2.07 + 1.20 \times 10^{-2} p(\text{atmos}), \quad (24)$$

which has been carried out experimentally for pressures roughly as great as the maximum attained in the cannon.

The average radius of the 4–6 pellets was about 0.2 cm. Thus if one assumes a reaction time of 500 μsec, the burning velocity of the TNT in the cannon would be 400 cm/sec. Using Eq. (24) and a value of 5470 atmos, the calculated maximum pressure that may be obtained in the cannon under conditions of uniform filling of the chamber, one calculates a burning rate of only 68 cm/sec, or about $\frac{1}{6}$ the rate measured in the cannon. The measured pressures, except possibly for a short period at the start of the reaction, were at all times somewhat lower than this; probably due to cannon leakage.

The possibility was considered early in this study that the reaction process observed in the cannon method may be simply normal explosive deflagration in a much finer mesh product resulting from fragmentation of the explosive grains by the initial transient detonation. However, experimental results show that the amount of fragmentation produced by the initial detonation if any is not large. Indeed, the assumption that mechanical fragmentation of the coarse TNT particles should not be appreciable during the interval of time covered by the cannon experiment seems entirely justified from the fact that solids fragment primarily only in tension rather than in compression. Moreover, the fact that particle size effects were observed in the first place, and that these effects were directly related to the particle sizes used argue against appreciable fragmentation; it would be fortuitous indeed if fragmentation were to occur such as to give fragmented particles of sizes reproducibly in direct proportion to the original size. As a matter of fact, the coarse-grained TNT used in this test was not easily fragmented owing to its excellent spherical shape and nonporous character. One should also realize that the general applicability of the Eyring surface burning law in detonation shows that particles are not broken up by the shock front in detonation.

A 40 gram sample of 4–6 mesh TNT was fired in the cannon without the slug, i.e., with the barrel open, using a No. 8 electric blasting cap. Considerable unreacted TNT was blown out of the chamber and could not be recovered, but that (8 grams of the original charge) remaining in the cannon showed very little evidence of breakup. Moreover, when one fires a charge containing both fine and coarse TNT in the cannon without the slug, the drop in pressure and temperature following detonation are sufficiently sharp that reaction cuts off in the early stages. Under these conditions little explosive remains in the chamber, but particles blown out of the cannon have been found and examined; while they were invariably blackened by reaction at the surface, they showed surprisingly little evidence of particle fragmentation despite the drastic conditions to which they were exposed.

TABLE IV. Studies of the fragmentation of inert substances in mixtures with TNT or RDX detonated in the cannon.

Particle size	Fine TNT, 15 grams borax beads (14–20 mesh), 40 grams Percent recovered	Fine RDX, 10 grams quartz (20–28 mesh), 40 grams Percent recovered
− 4+ 6	...	...
−14+20	51	...
−20+28	11	28
−28+35	3	13
−35+48	2	17
−48+65	1	13
−65	4	29
Lost	27	1

Low density mixtures consisting of fine TNT or RDX and inert substances of known initial particle size were detonated in the cannon with a No. 8 cap. In these studies the barrel was plugged to prevent blowout of the solid particles (although some of the material was found to blow out the cap wire openings). The solid residue recovered from the cannon was carefully sized. Table IV presents some of the results of this study. In the case of borax beads more than half of the original material was recovered unfragmented and less than 30% of it was fragmented to less than one-sixth the original size even assuming that the material (27%) lost through the cap wire opening was shattered before hitting these openings, which quite likely is not the case. When quartz was used with RDX, 28% was recovered unfragmented and only 30% was fragmented to less than one-fourth the original size. Unfortunately when larger percentages of explosive were used, it was too difficult to open the cannon owing to binding resulting from detonation against the threaded bolt used to seal the chamber.

In order to test a material of the same particle size and apparent physical texture as the coarse TNT, a shot was made using 15 grams of fine TNT and 40 grams of 4–6 mesh tapioca or ordinary grocery store variety. Examination of the residue showed no evidence of shattering of the tapioca. About one gram of fine material was present which was primarily carbon from the detonated TNT. Although many of the tapioca particles were clumped together by partial fusion at the points of contact, each particle clearly maintained its identity. Tapioca contains considerable moisture as a result of which some of the particles near the center of the chamber swelled and "popped" like popcorn owing to the high temperatures to which they were exposed. Those near the walls of the chamber did not heat and swell, however, apparently because the heat

was dissipated with sufficient rapidity through the walls of the cannon to prevent heating of the tapioca grains. The "popping" of the tapioca grains in the interior of the sample was heard to occur up to several seconds after detonation. Of the initial 40 gram sample, 32 grams of material were recovered, the 20% loss being attributed primarily to the loss of moisture.

The difficulty of fragmenting a solid in compression was shown quite convincingly by the following experiment. A charge of liquid nitroglycerine in a 1-in. diameter tube of length/diameter ratio greater than 6 was surrounded by glass marbles in direct contact with the tube of explosive. The charge was then completely surrounded by a heavy wire screen with openings too small to allow the marbles to pass without fragmentation through the wire screen. The basket did not come closer to the explosive charge than 12 in. at any point. This assembly was then placed under water and fired. Most of the marbles were recovered intact. The only effect of exposure to the detonation which should produce a peak pressure in excess of 100 katmos was that the marbles were no longer transparent.

If it is assumed that even as much as half of the coarse TNT was fragmented by detonation before the time that the cannon begins to measure reaction rate, the p–t curves observed in this study would still be those determined by the coarse unfragmented fraction, since the peak pressures observed were only about 10–15% lower than those for reaction of fine mesh TNT in which reaction is complete within 50 μsec after the initial detonation. Hence it may be concluded that a large part of the reaction even in the unfragmented portion had taken place at the time corresponding to the peak of the p–t curves and that the reaction rates observed were therefore determined by the coarsest fractions. Clearly, therefore, one is dealing with a reaction mechanism even in the after-detonation regime in the cannon experiment which is quite different from the normal pressure sensitive type observed in normal explosive deflagration.

APPENDIX

An evaluation of the accuracy of the numerical method which was used in obtaining the first and second derivatives from the cannon film traces was accomplished as follows. This method of obtaining derivatives was applied to a problem whose derivatives were known, the problem being designed as near in character as possible to the ones encountered in the cannon test. The second derivative was given the form.

$$y''(\lambda)=A\lambda e^{-a\lambda}. \tag{i}$$

[A prime indicates differentiation with respect to λ.] It was felt that an exponential form for Eq. (i) would provide a more valid test than a polynomial form, because polynomials were used in the smoothing process. When the parameters (A) and (a) were assigned the values 0.0004 and 0.04 respectively, a curve for $y''(\lambda)$ was obtained which possessed the same general shape as the experimental curves from the cannon experiment and had a maximum of 3.679×10^{-3} for $\lambda=25$. [$\lambda=25$ refers to 25th interval for X_j.]

Integration of Eq. (i) yields for $y'(\lambda)$ and $y(\lambda)$

$$y'(\lambda)=-\frac{A}{a^2}e^{-a\lambda}(a\lambda+1)+y_0', \tag{ii}$$

$$y(\lambda)=\frac{A}{a^3}e^{-a\lambda}(a\lambda+2)+y_0'\lambda+y_0. \tag{iii}$$

The constant of integration y_0' was given the value A/a^2 and y_0 the value $1-2A/a^3$. In order to simulate the "wiggles" in the film trace caused by the vibration of the slug, a damped sine term was added to Eq. (iii). Equations (iii), (ii), and (i) accordingly may be rewritten

$$\bar{y}(\lambda)=y(\lambda)+Be^{-a\lambda}\sin b\lambda, \tag{iv}$$

$$\bar{y}'(\lambda)=y'(\lambda)+Be^{-a\lambda}(b\cos b\lambda-a\sin b\lambda), \tag{v}$$

$$\bar{y}''(\lambda)=y''(\lambda)+Be^{-a\lambda}\times[(a^2-b^2)\sin b\lambda-2ab\cos b\lambda]. \tag{vi}$$

On the film trace obtained from the cannon experiments the initial amplitude of the "wiggles" was estimated to be less than 0.03 cm, and their maxima were about 4 cm apart or about 10 intervals apart. (Readings were taken on the film at 4 mm intervals.) Thus B was given the value of 0.03 and $b=0.2\pi$ radians.

Values of $y(\lambda)$ were calculated for $(\lambda=0,1,2,\cdots90)$ and rounded off at three decimal points. Then these points were smoothed by the IBM, and the first and second derivatives calculated for 1, 2, and 3 smoothings. Figure 8 contains graphs of Eq. (i), Eq. (vi), and values of $y''(\lambda)_1$, the second derivative calculated after one smoothing. Figure 9 contains a graph of Eq. (i), plotted to a different scale than in Fig. 8, and the second derivatives $y''(\lambda)_1$, $y''(\lambda)_2$, and $y''(\lambda)_3$ obtained by the IBM process after 1, 2, and 3 smoothings.

The degree of effectiveness of the smoothing process

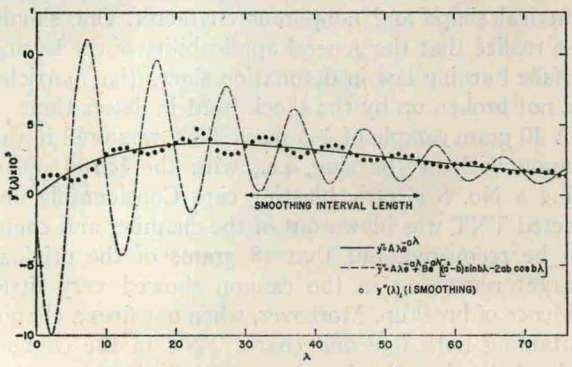

FIG. 8. Comparison of calculated second derivatives with analytical values.

may be judged by the degree to which the derivatives calculated from the smoothed points agree with Eq. (i). Examination of Fig. 8 shows that the first smoothing has a great effect on the value of the calculated derivatives, as the points obtained agree much closer to Eq. (i) than Eq. (vi). [Equation (vi) provides a good indication of the derivatives one would obtain numerically before any smoothing process was applied.] Examination of Fig. 9 shows that except for small λ's the values of $y''(\lambda)_2$ and $y''(\lambda)_3$ agree very well with Eq. (i), and that in general the agreement is a little better in the case of $y''(\lambda)_3$ than $y''(\lambda)_2$. The deviation from Eq. (i) for small λ's was due to a systematic error introduced by the smoothing process in this region since the actual second derivative is discontinuous at $t=0$, and the calculations give an approximation to a continuous function. The error in this case was not large, however, and certainly is not serious in the cannon problem because pressure equilibrium does not exist in the cannon chamber at times corresponding to this region. Except for small λ's Eq. (i) is very nearly the curve of best fit one could drawn through either the points $y''(\lambda)_2$ or $y''(\lambda)_3$. No actual numerical estimate can be made for the error in obtaining the derivatives for the cannon test, but the above problem indicates that the error was in all probability small.

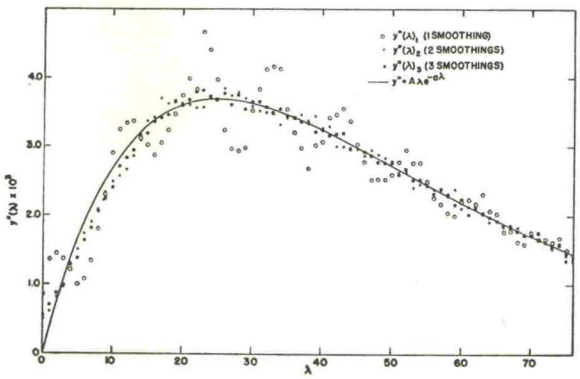

FIG. 9. Comparison of calculated second derivatives with analytical values.