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

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

where

$$\left.\frac{dn^{*\prime}}{dt}\right|_{t=t_i}=-\beta pn^* \tag{20}$$

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

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

and

$$\left.\frac{d}{dt}\left(\frac{1}{v_3'-\alpha_3'}\right)\right|_{t=t_i}=\frac{-1}{(v_{i3}'-\alpha_{i3}')^2\left(1-\beta\int_0^{t_i}pdt\right)(m_f+m_c)}\left[A\left.\frac{dy}{dt}\right|_{t=t_i}+\frac{V_0+Ay_i}{1-\beta\int_0^{t_i}pdt}\right]\left.\left(1-\frac{d\alpha_3'}{dv_3'}\right)\right|_{t=t_i}, \tag{22}$$

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 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 $t=t_i$.

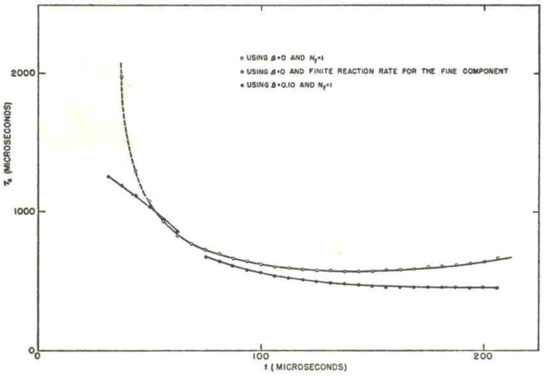

FIG. 7. Typical variation of τ_c (calculated reaction time) with t (elapsed time).

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

$$O=-\tau_{ic}^3\left[m_f\beta p_i+\frac{m_f}{m_f+m_c}G_i\right]+\tau_{ic}^2\left[3m_c\left(1-\beta\int_0^{t_i}pdt\right)-3m_ct_i\beta p_i-\frac{3m_ct_i}{m_f+m_c}G_i\right]+\tau_{ic}\left[-6t_i\left(1-\beta\int_0^{t_i}pdt\right)m_c+3m_ct_i^2\beta p_i+\frac{3m_ct_i^2}{m_f+m_c}G_i\right]+3m_c\left(1-\beta\int_0^{t_i}pdt\right)t_i^2-m_ct_i^3\beta p_i-\frac{m_ct_i^3}{m_f+m_c}G_i, \tag{23}$$

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 $N_f=1$, $\beta\neq0$.

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.