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Progress Report on "The Theory of Explosions Initiation"

by
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Princeton University

Report OSRD No. 2026

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Progress Report on "The Theory of Explosion Initiation"
Service Directive OD-02

Endorsement (1) From Dr. J. G. Kirkwood, Member, Division 8 to Dr. G. B. Kistiakowsky, Chief, Division 8.

Forwarding report and noting:

> "This report is concerned with the structure of the reaction zone at the front of a detonation wave. On the hypothesis of thermal initiation and estimates of the absolute rate constant and free energy of activation of the explosion reaction, the authors calculate the width of the reaction zone in a detonation wave, both in the homogeneous case and in the heterogeneous case, in which evaporation is the rate-determining step. Their estimates of the width of the reaction.zone are than those based upon the effect of charge diameter on detonation velocities. However, with a larger value of the grain radius, their estimate would be raised in the heterogeneous case."

(2) From Dr. G. B. Kistiakowsky, Chief, Division 8 to Dr. Irvin Stewart, Executive Secretary of the National Defense Research Committee.

Forwarding report and concurring with the above endorsement.

This is a progress report under Contract No. OEMsr-957 with Princeton University.

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Introduction

All the properties which describe the state of an explosive substance immediately after the passage of a steady-state one-dimensional detonation wave can be calculated with considerable accuracy by the hydrodynamic-thermodynamic theory. This theory determines the five unknown properties

(1) Detonation velocity D
(2) Gas velocity U
(3) Detonation temperature T_2
(4) Detonation pressure P_2
(5) Detonation specific volume v_2

in terms of the known thermal properties of the initial state, with the aid of the five equations

(1) Conservation of mass
(2) Conservation of momentum
(3) Conservation of energy
(4) Equation of state of the substance
(5) The Chapman-Jouguet condition,

$$\frac{P_2-P_1}{v_2-v_1} = \left(\frac{dP_2}{dv_2}\right)_S .$$

These steady-state properties depend only upon the equilibrium conditions in front of the wave and behind the wave, and are completely independent of the detailed structure of the detonation wave and of properties which affect only that structure -- properties like the viscosity, the thermal conductivity, or the specific rate of the chemical reaction.

Various researches on the necessary high-temperature thermal data and on the appropriate equation of state for highly compressed gases (cf. the summaries by Kistiakowsky and Wilson, and by Cook) and on the validity of the Chapman-Jouguet condition (von Neumann) permit calculations of the detonation properties of any chosen explosive to be made with considerable assurance. In the present investigation we shall assume the correctness of the hydrodynamic-thermodynamic theory for steady-state one-dimensional waves, and shall use its results whenever necessary.

The agreement between theory and experiment becomes poor for some explosives under certain conditions -- in particular, for explosives of low energy, loosely confined or in narrow charges, in the cast state or large grains, or insufficiently boosted.

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Under these conditions the explosive may (a) refuse to detonate, or, fail to attain the full theoretical detonation velocity. The problem is to decide whether a particular initial impulse will attenuate and eventually die away, or whether it will grow into a detonation. In other words, a solution of this problem would cover the entire subject of "sensitivity" of explosives (i.e., sensitivity to thermal initiation. The problem of sensitivity to shock involves the additional problem of the conversion of mechanical energy into heat).

Or the explosive may (b) after detonation has been initiated, fail to maintain it. After the explosion, part of the explosive remains unchanged. The solution of this problem requires a study of the rates of the dissipative processes which cause the chemical reaction (and the detonation wave) to come to a stop.

The present investigation has been undertaken to study the theory of the causes of these two kinds of failure. In the course of it we shall study the distribution of temperature and pressure within a detonation wave, and the effect of these variables upon the rate of the chemical decomposition reaction.

The report will be divided into four parts:

Part I. Chemical Reactions in an Explosive Substance.

The effect of temperature, pressure, and the nature of the reacting phase will be discussed.

Part II. Detailed Structure of the Steady-State Detonation Wave.

Numerical integration will be employed to obtain the distribution of temperature and pressure in shock waves with and without chemical reaction.

Part III. Detonation Wave with Radial Losses.

Part IV. Detonation Wave in the Non-Steady State.

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PART I. CHEMICAL REACTIONS IN AN EXPLOSIVE SUBSTANCE.

Time-Temperature Relation in an Explosive Reaction.

It will be useful to have a preliminary idea of the times required to attain various temperatures in the explosive reaction. To obtain this preliminary estimate, we can consider a volume of reactant all of which is brought to the temperature T_o at time $t=0$. We then solve the conservation-of-energy equation with the neglect of all transport terms, obtaining the temperature T as a function of time t. (It is, of course, realized that the neglected transport terms may become important in an actual wave.)

Consider the energy change within this reaction mixture from time $t = 0$ to time $t = t$. Then

$$(E - E_o) + Q - \bar{C}_v(T - T_o) = 0 \qquad \text{.......(1)}$$

where T is the temperature at time t,

$\bar{C}_v$ is the mean heat capacity,

Q is the heat evolved by the reaction to time t,

$(E-E_o)$ includes all other energy terms: radiation, conduction, kinetic energy, adiabatic compression. It will in general be a function of both time and distance.

To the approximation we now require, $(E-E_o)$ may be set equal to zero, giving

$$T - T_o = Q/\bar{C}_v \qquad \text{........(2)}$$

By neglecting all transport terms we have eliminated distance from the equation. In other words, it is assumed that all the heat of the reaction goes to raise the temperature of the reaction mixture.

At infinite time $t = \infty$, the temperature will have attained a terminal value

$$T_\infty - T_o = Q_\infty/\bar{C}_v \qquad \text{......(3)}$$

where Q_∞ is the heat evolved in the complete reaction.

The temperature variation is now given by

$$\frac{dT}{dt} = \frac{1}{\bar{C}_v}\,\frac{dQ}{dt} \qquad \text{......(4)}$$

To proceed farther, we must evaluate dQ/dt in terms of the kinetics of the reaction. For a first order reaction

$$-\frac{dn}{dt} = n\,Z\,e^{-A/T} \qquad \text{......(5)}$$

$$\frac{n}{n_0} = e^{-\int_0^t Z\,e^{-A/T}\,dt} \qquad \text{......(6)}$$

where $\underline{n}$ is the amount of unchanged reactant remaining,
$\underline{Z}$ is the probability factor for the reaction,
$\underline{A}$ is $\Delta H^{\ddagger}/R$, the heat of activation for the reaction divided by the gas constant.

The heat $\underline{Q}$ is then

$$Q = Q_\infty\left(1 - \frac{n}{n_0}\right) = Q_\infty\left(1 - e^{-\int_0^t Z e^{-A/T}\,dt}\right) \qquad \text{......(7)}$$

and its time derivative is

$$\frac{dQ}{dt} = Q_\infty Z\,e^{-A/T}\,e^{-\int_0^t Z e^{-A/T} dt} \qquad \text{......(8)}$$

On combining Eq.(7) and Eq.(8),

$$\frac{dQ}{dt} = (Q_\infty - Q)\,Z\,e^{-A/T} \qquad \text{......(9)}$$

The temperature variation is therefore given by

$$\frac{dT}{dt} = (T_\infty - T)\,Z\,e^{-A/T} \qquad \text{......(10)}$$

which is the basic differential equation to be solved. It is integrated without difficulty to give

$$t = \frac{1}{Z}\,\mathrm{Ei}\,\frac{A}{T} - \frac{1}{Z}\,\mathrm{Ei}\,\frac{A}{T_0} + \frac{e^{A/T_\infty}}{Z}\,\mathrm{Ei}\left(\frac{A}{T_0} - \frac{A}{T_\infty}\right) - \frac{e^{A/T_\infty}}{Z}\,\mathrm{Ei}\left(\frac{A}{T} - \frac{A}{T_\infty}\right) \text{..(11)}$$

where the symbol $\underline{\mathrm{Ei}}$ represents the exponential integral

$$\mathrm{Ei}\,x = \int_{-\infty}^{x} \frac{e^x\,dx}{x}$$

for which tabulated values are available. For all values of temperature except those in the immediate neighborhood of $\underline{T}_\infty$, the exponential integral may be replaced by its approximate value

$$\mathrm{Ei}\, x = \frac{e^x}{x} + \ldots$$

giving as the final result

$$t = \frac{1}{AZ}\left[\frac{T_o^2}{T_\infty - T_o}\, e^{A/T_o} - \frac{T^2}{T_\infty - T}\, e^{A/T}\right] \qquad \ldots\ldots(12)$$

From Eq. (12) -- or, in the neighborhood of $\underline{T}_\infty$, from Eq. (11) -- the time-temperature curve for the entire course of the explosive reaction can be calculated readily. As an illustrative example, this has been done using the following numerical values*

T_o = 1000°K
T_∞ = 6000°K
Z = 10^{15} sec^{-1}
A = 60,000/1.986

and the results are tabulated in Table I. The same results are graphed in Fig. 1, and to a greatly enlarged scale in Fig. 2.

---

*The value of $\underline{Z}$ was taken to be $\underline{kT/h}$ where $\underline{k}$ is Boltzmann's constant, $\underline{T}$ is 3000°K, and $\underline{h}$ is Planck's constant, multiplied into $e^{\Delta S^\ddagger/R}$ with $\underline{\Delta S}^\ddagger$ = 5 cal deg^{-1}. These are reasonable values, for the entropy change of activation in the highly condensed system is probably small.

The value of $\underline{\Delta H}^\ddagger$ was arbitrarily chosen as 60 kcal., or about the strength of a carbon-carbon bond. Experimental values from low-temperature measurements have been reported both higher and lower than this value.

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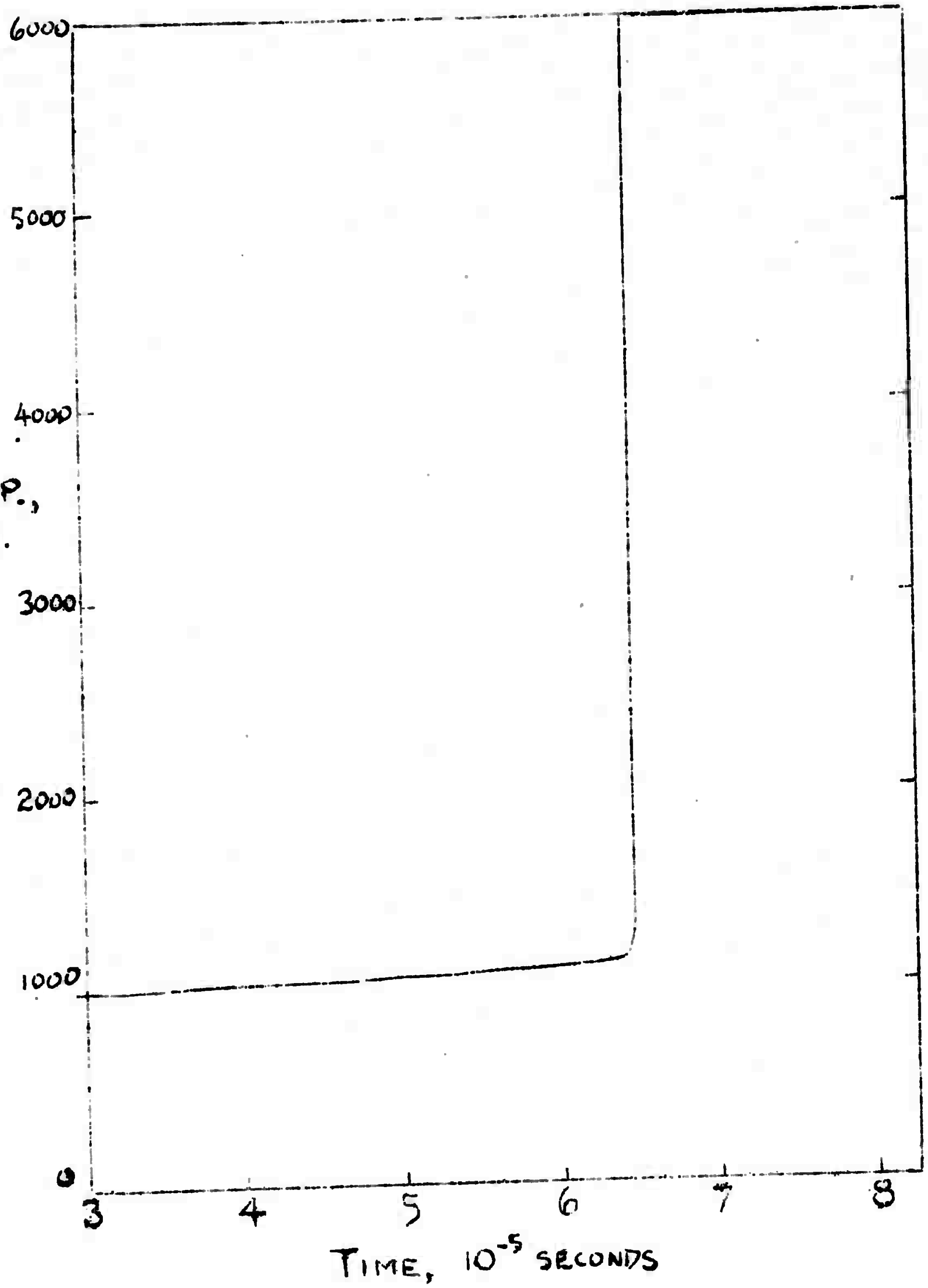
FIGURE 1



Time-temperature relation in an explosive reaction.

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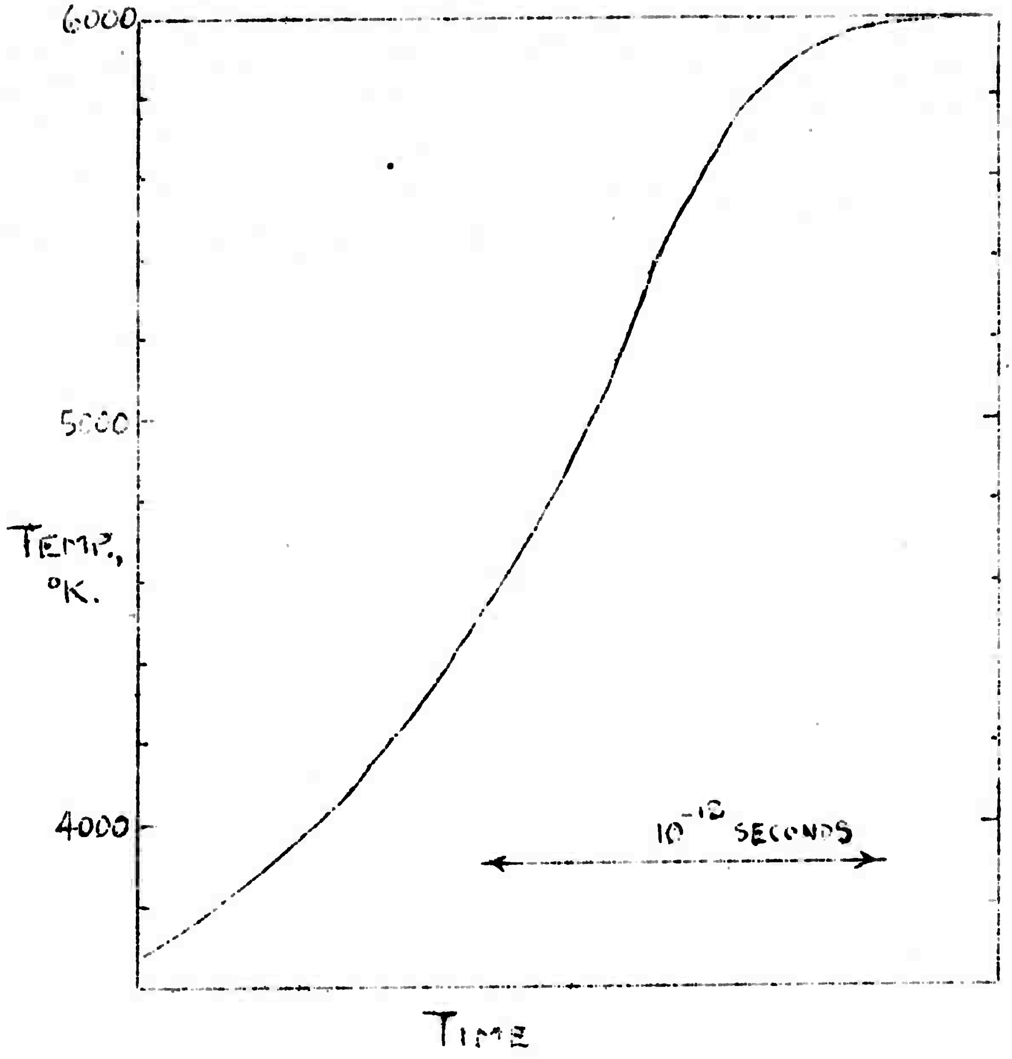
FIGURE 2



Time-temperature relation in an explosive reaction. Enlarged scale.

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Table I

Temperature, °K.	Time, seconds
1000	0
1010	6.46 10^{-5} - 1.88 10^{-5}
1100	" - 5.9 10^{-6}
1200	" - 7.25 10^{-7}
1500	" - 8.1 10^{-9}
2000	" - 1.5 10^{-10}
3000	" - 3.44 10^{-12}
4000	" - 7.58 10^{-13}
5000	" - 1.95 10^{-13}
5500	"
5800	" + 1.96 10^{-13}
5900	" + 3.09 10^{-13}
5950	" + 4.19 10^{-13}
5990	" + 6.65 10^{-13}
5999	" + 9.55 10^{-13}
6000	Infinite

Discussion

(a) The calculated curves will be observed to reproduce the qualitative features of an explosive reaction: a long induction period is followed by an extremely rapid rise of temperature, which does not cease until the reaction is substantially complete.

(b) When the reaction has proceeded to any appreciable extent, the second term on the right of Eq. (12) may be neglected in comparison with the first, giving

$$t = \frac{1}{AZ} \frac{T_0^2}{T_\infty - T_0} e^{A/T_0} \qquad \text{......(13)}$$

The induction period therefore depends exponentially on the reciprocal of the initial absolute temperature.* This is precisely the result found experimentally by various experimenters (Andreev, Garner, Hailes, Harvey, Muraour). The relation is usually written in the form

$$\log t = \frac{A}{T} + B \qquad \text{......(14)}$$

---

*In the illustrative example, the induction period for T_0 = 300°K. is 10^{17} years. The substance would be stable at room temperature!

This agreement with experiment leads us to expect that foregoing time-temperature analysis is not far from correct.

(c) The numerical values of Figs. 1 and 2 are probably sufficiently accurate to provide an order-of-magnitude estimate. It will be observed that the last 75% of the reaction requires only about 10^{-11} seconds. During this time a molecule in the compressed state will undergo some 10 to 100 collisions, which will serve to equalize any local temperature fluctuations.

Even with an initial temperature of 1000^{o}K., (which is a temperature that may reasonably be expected to occur locally from frictional heating) the induction period is only of the order of 10^{-5} seconds. It is a fact that time-lags of ignition of sensitive explosives, as determined from oscillograph records, are about 10^{-5} seconds (quoted by Cook, 1943).

If the reaction does proceed at velocities of the order of those estimated here, there remains no objection to the "thermal" hypothesis of reaction; the only previous objection had been that the reaction would proceed too slowly (e.g., one estimate gave a time-lag of 10^{-3} seconds).

We may therefore make subsequent calculations on the assumption that each individual molecule in the explosion undergoes an ordinary thermal reaction, and that its rate of reaction can be treated by the usual methods of chemical kinetics. In particular, it will not be necessary to assume that the reaction is initiated by any special mechanism involving impact or shock waves, as has sometimes been assumed.

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*Semenov has obtained an equation also of the form of Eq.(14) by assuming that the reaction produces fragments which can later initiate chains -- the so-called "degenerate branching." It is understandable that the equations should be formally similar because in each process something produced by the reaction (heat or chain-starters, respectively) serves to accelerate the reaction. The "degenerate branching" hypothesis seems less likely than the present "thermal" hypothesis for detonation in solid explosives, since the detonation process has not been shown to be sensitized by added chain-initiators.

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Effect of Pressure on an Explosive Reaction

We now proceed to investigate the consequences of our assumption that the elementary rate process in an explosive reaction may be treated by the usual methods of reaction kinetics. The absolute rate of a chemical reaction is given by

$$k_r = \frac{kT}{h} e^{-\Delta F^{\ddagger}/RT} \qquad \text{......(15)}$$

where k_r is the specific reaction rate constant,
k is Boltzmann's constant,
T is the absolute temperature,
h is Planck's constant,
$\Delta F^{\ddagger}$ is the standard free energy change for the formation of a mole of activated complex from the reactants,
R is the gas constant in the same units as F/T.

To investigate the effect of pressure P on the specific reaction rate, we wish to calculate the increase in free energy when the system goes from its normal to its activated state at the pressure P. The thermodynamic relation is

$$\left(\frac{\partial F}{\partial P}\right)_T = V \qquad \text{......(16)}$$

which integrated becomes

$$\Delta F^{\ddagger}_{P=P} = \Delta F^{\ddagger}_{P=0} + \int_0^P \Delta V^{\ddagger}\, dP = P\,\overline{\Delta V^{\ddagger}} + \Delta F^{\ddagger}_{P=0} \qquad \text{......(17)}$$

This is the increase in free energy of activation which results from the work done in the volume change of activation $\Delta V^{\ddagger}$ against the external pressure P. It seems safe to assume that in the decomposition reactions found in explosions the activated state will be more expanded in volume than the reactants. Thus $\Delta V^{\ddagger}$ is always positive, and a reasonable estimate of its magnitude is 10 cm^3 mole^{-1} (cf. Stearn and Eyring). If we take the pressure in an explosion to be 50,000 atmospheres, the increase in free energy is

$$\begin{aligned} P\Delta V^{\ddagger} &= 500{,}000 \text{ cm}^3 \text{ atmospheres} \\ &= 12 \text{ kilocalories} \qquad \text{......(18)} \end{aligned}$$

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Since the volume change of activation of a dilute gas is ze this free energy is also the difference between the free energie of activation in the gas phase and in the liquid (or highly compressed gas) phase:

$$\Delta F^{\ddagger}_{liquid} - \Delta F^{\ddagger}_{gas} = P\Delta V^{\ddagger} = 12 \text{ kcal} \qquad \ldots\ldots(19)$$

At a temperature of 5000°K., this difference in free energy of activation is enough to slow the reaction rate down by a factor of $e^{1.2} = 3$. The effect of pressure on the specific rate at high temperatures is therefore so small that it may safely be ignored in all but the most highly refined calculations.

Since the sign of the volume change of activation will most probably be positive, the effect of high pressure will always be to slow the reaction down if the reaction is unimolecular. An increase of pressure would never be expected to have the effect of markedly increasing the specific reaction rate, as has sometimes been proposed.

Homogeneous Reaction in the Solid State

Suppose the activated state is to be formed in the interior of a solid. Since the reaction has been supposed to require a volume increase on activation, there will be a corresponding increase in the free energy of activation, because of the additional work of compression on the surrounding solid. One way of estimating the increase in free energy is to suppose that the surrounding solid contracts homogeneously. Again making use of the thermodynamic relation

$$\left(\frac{\partial F}{\partial P}\right)_T = V \qquad \ldots\ldots(16)$$

we integrate to obtain

$$F^{\ddagger}_{V_2} - F^{\ddagger}_{V_1} = \int_{V_1}^{V_2} V\,dP = \int_{V_1}^{V_2} V\left(\frac{dP}{dV}\right)_T dV = \int_{V_1}^{V_2} \frac{dV}{\beta} = \frac{\Delta V^{\ddagger}}{\beta} \qquad \ldots\ldots(19)$$

where β is the compressibility of the solid. This is the increase in free energy of activation which results from the work done in the deformation of the solid lattice. The compressibility in $kg^{-1}\ cm^2$ of fats and related compounds is about $50\ 10^{-6}$, and of granite is about $2\ 10^{-6}$. Thus the increase in free energy is

$$\frac{\Delta V^{\ddagger}}{\beta} = 10\ 10^{5}\ \text{kg cm}$$
$$= 10^{6}\ \text{cm}^{3}\ \text{atmospheres}$$
$$= 24\ \text{kilocalories} \qquad \text{......(20)}$$

Since a liquid is sufficiently disordered that its lattice will not be compressed like that of a solid, this free energy is also the difference between the free energies of activation in the solid phase and in the liquid (or compressed gas) phase:

$$\Delta F^{\ddagger}_{\text{solid}} - \Delta F^{\ddagger}_{\text{liquid}} = \frac{\Delta V^{\ddagger}}{\beta} = 24\ \text{kcal} \qquad \text{......(21)}$$

While at room temperature this difference in free energy would cause the rate to be slower in the solid state by a factor of $e^{40} = 10^{17}$, and so cause the solid to be enormously more stable than the liquid or gas, at a temperature of 4000°K. the reaction in the solid will only be slower by a factor of e^{3} or about 20. Thus if the temperature is high enough, the solid will decompose at a rate comparable to that of the liquid or vapor.

Discussion

The parallel between the decomposition reactions of explosives in the gas, liquid, and solid states and diffusion processes in those same states is complete.

In the dilute gas phase, the diffusion process goes without activation energy and does not depend on pressure. The volume change necessary in the decomposition reaction can take place at no expense of free energy, since each molecule has plenty of space already.

In the liquid phase, a diffusing molecule requires a certain amount of additional volume-- or, as it has been called, a "hole" The formation of this hole requires a certain amount of free energy (a fraction of the heat of vaporization) and, in addition, the free energy required to carry out the expansion against any external pressure P. In the decomposition reaction, free energy must similarly be supplied for the volume change $\underline{\Delta V^{\ddagger}}$ against the external pressure P.

In the solid phase, a diffusing molecule also requires extra volume to permit its flow. But where in a liquid such a hole could be introduced without appreciably disturbing the order of the entire liquid (since it was already disordered), in a solid the introduction of such a hole produces a displacement of a considerable number of molecules in the lattice from their previous positions. This requires more energy, consequently diffusion in the solid state is much more difficult than that in the liquid state. The same is true of decomposition in the solid state. It is the requirement that the lattice retains its order -- that a great many molecules in the lattice must move cooperatively when the lattice expands -- that suppresses both diffusion and chemical reaction.

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The Transition Between Reaction Mechanisms

Both from the considerations of the previous section which indicate that reaction should be possible in the solid state, and from the experimental fact that it is possible to detonate cast sticks of explosive, we are led to write the reaction

$$\text{REACTANT} \xrightarrow{k_{solid}} \text{PRODUCTS} \qquad \ldots\ldots(22)$$

It is also known that under conditions where dissipation is possible, detonation velocity is very sensitive to particle size, smaller particles (i.e. more total surface) giving velocities nearer to the theoretical. The conclusion immediately suggests itself that the reaction is a surface (or "topochemical") 2/3 order reaction, evaporation probably being the rate-determining step. The reaction may be formulated

$$\begin{aligned} &\text{REACTANT} \underset{k'_{evap}}{\overset{k_{evap}}{\rightleftarrows}} \text{VAPOR} \\ &\text{VAPOR} \xrightarrow{k_{gas}} \text{PRODUCTS} \end{aligned} \qquad \ldots\ldots(23)$$

We now enquire when reaction (22) will outstrip the system of reactions (23). The kinetics of reactions (23) may be obtained by assuming a steady-state concentration of vapor. Then

$$\frac{d(\text{VAPOR})}{dt} = k_{evap}(\text{SURFACE}) - k'_{evap}(\text{SURFACE})(\text{VAPOR}) - k_{gas}(\text{VAPOR}) = 0 \qquad \ldots\ldots(24)$$

$$k_{gas}(\text{VAPOR}) = \frac{k_{evap}(\text{SURFACE})}{\dfrac{k'_{evap}(\text{SURFACE})}{k_{gas}} + 1} = \frac{d(\text{PRODUCTS})}{dt} \qquad \ldots\ldots(25)$$

The two limiting cases are of most interest: If evaporation is much slower than gas reaction,

$$\frac{d(\text{PRODUCTS})}{dt} = k_{evap}(\text{SURFACE}) \qquad \ldots\ldots(26)$$

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If on the other hand the gas reaction is slower, then

$$\frac{d(\mathrm{PRODUCTS})}{dt} = k_{gas}\,\frac{k_{evap}}{k'_{evap}} \qquad \ldots\ldots(27)$$

Above the temperature at which

$$k_{gas} = k'_{evap}(\mathrm{SURFACE})$$

the rate-determining process is evaporation; below that temperature it is the gas reaction. In order to find the absolute rates of these two processes, we estimate their heats and entropies of activation and apply the absolute rate theory:

$$k_{gas} = \frac{kT}{h}\, e^{-\frac{\Delta F^{\ddagger}_{electronic}}{RT}} \qquad \ldots\ldots(28)$$

The only activation energy for the gas reaction is that necessary for the electronic rearrangement which accompanies the reaction.

$$k'_{evap}(\mathrm{SURFACE}) = 10^{-6}\,\frac{kT}{h}\, e^{-10/R} \qquad \ldots\ldots(29)$$

The fraction of molecules which are in the surface is really variable, since it depends on the 2/3 power of the amount unreacted. The fraction here taken, 10^{-6}, is an estimate which might vary from case to case. Condensation is assumed to go without activation energy, but requires the loss of the entropy of vaporization, which is estimated to be 10 cal deg^{-1} for the compressed gas.

When the two rates are equal,

$$T = \frac{\Delta F^{\ddagger}_{electronic}}{R \ln 6 + \Delta S^{0}_{evap}} \qquad \ldots\ldots(30)$$

$$= \frac{30{,}000}{27.4 + 10} = 800^{\circ}\mathrm{K}.$$

The electronic activation energy is estimated to be 30 kcal. The final result is, of course, subject to considerable error.

The rate of the homogeneous reaction is

$$k_{solid} = \frac{kT}{h}\, e^{-\frac{(\Delta F^{\ddagger}_{electronic} + \Delta F^{\ddagger}_{expansion})}{RT}} \qquad \ldots\ldots(31)$$

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and the rate of evaporation is

$$k_{evap}(\text{SURFACE}) = 10^{-6}\,\frac{kT}{h}\,e^{-\frac{\Delta H^{0}_{evap}}{RT}} \qquad \ldots\ldots(52)$$

where the fraction of surface molecules is taken as before, and evaporation is assumed to require the full heat of evaporation and to proceed without entropy of activation.

Reactions (22) and (26) now have the same rate at a temperature

$$T = \frac{\Delta F^{\ddagger}_{electronic} + \Delta F^{\ddagger}_{expansion} - \Delta H^{0}_{evap}}{R \ln 6} \qquad \ldots\ldots(53)$$

$$= \frac{30{,}000 + 30{,}000 - 10{,}000}{27.4} = 1800^{o}K.$$

The free energy necessary for expansion is estimated to be 30 kcal, the heat of vaporization 10 kcal. This final result also is subject to considerable error.

We may now assemble the results of the above calculations.

(a) Solid reaction

Above a temperature of about 2000°K., reaction will by preference occur in the solid phase, homogeneously. The rate will obey Eq. (51). At high temperatures, the high activation energy is not a particularly serious handicap to the reaction (see Figs. 3 and 4). In fact, at high temperatures the reaction is not markedly temperature-dependent (Fig. 4). However at lower temperatures the reaction becomes highly temperature-dependent and drops out completely. This means that if the reaction is to go in the solid, the temperature must be kept high. The mean length of the reaction zone is 100Å upward (see Figs. 3 and 4).

(b) Evaporation

From about 2000°K. down to about 800°K., the preferred rate-determining step is evaporation. It obeys Eq. (52) and is only mildly temperature-dependent. Since it is proportional to the amount of surface, this reaction rate will be sensitive to particle size. The reaction zone is of the order of 1 to 100 centimeters, so this reaction rate will also be sensitive to the size and form of the explosive charge. If the reaction is to go rapidly by this mechanism, the particle size must be kept small or the charge size large.

(c) Gas reaction

This is the only reaction below about 800°K. It is so temperature-dependent and the reaction zone so long that there is little chance of it going at all. In fact **Belyaev** finds that explosion initiation does not occur until the boili

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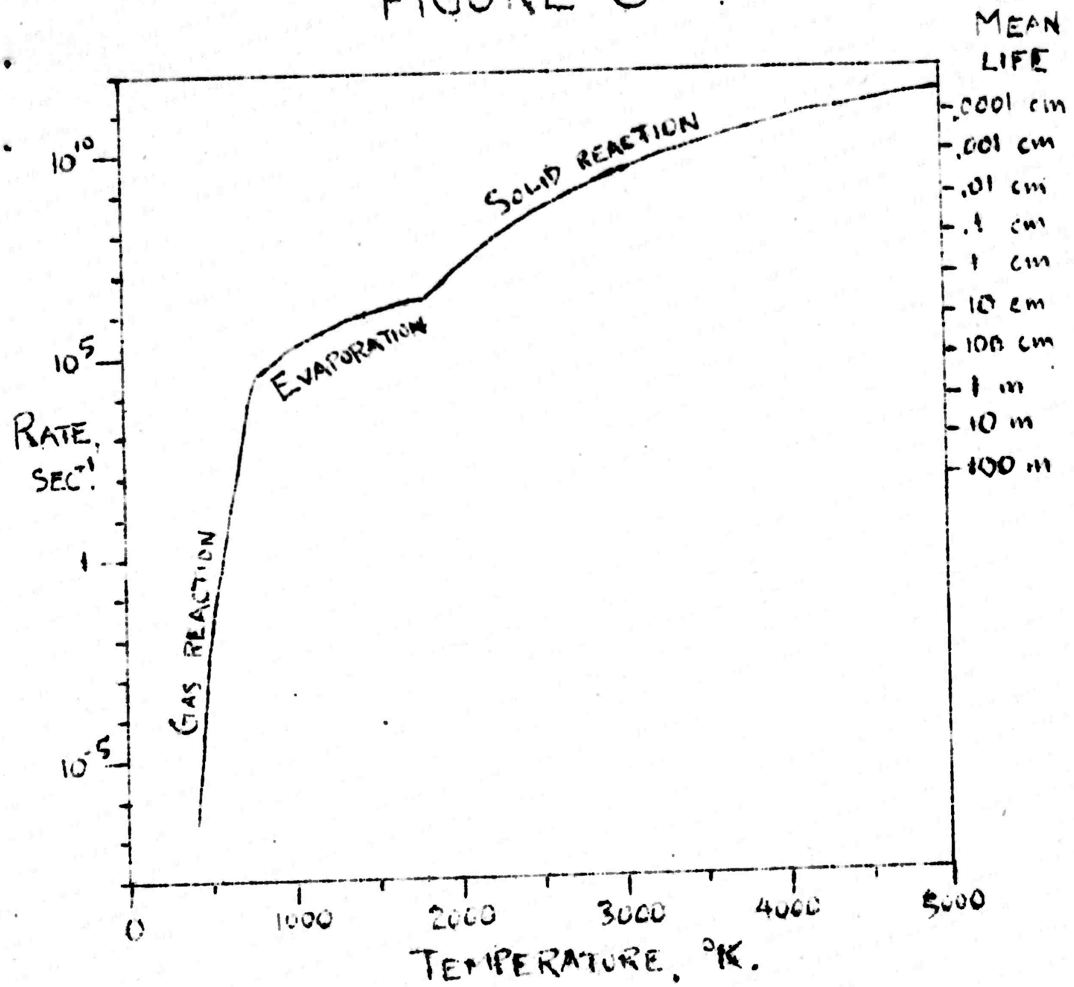
FIGURE 3



Three types of reaction in an explosion. Rate plotted logarithmically against temperature.

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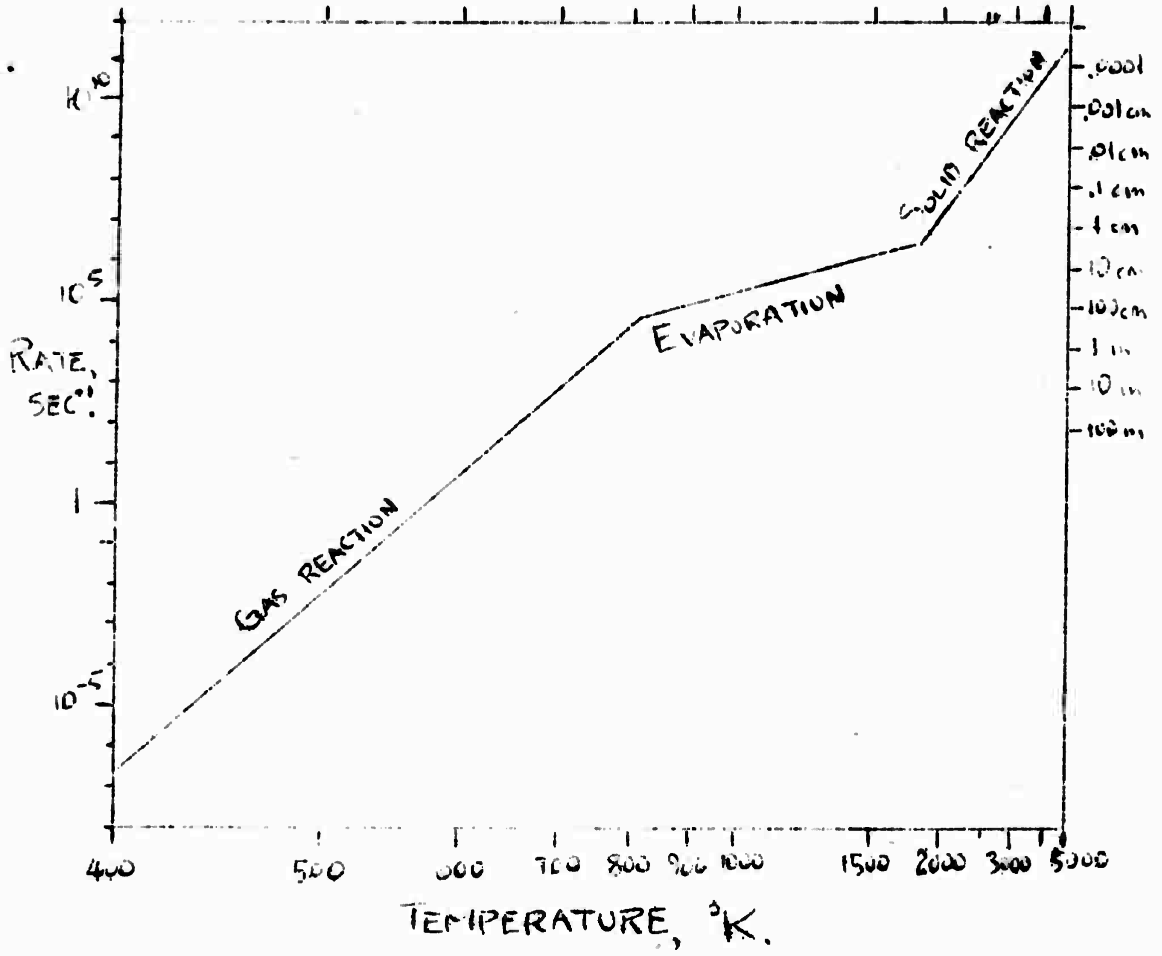
FIGURE 4



Three types of reaction in an explosion. Rate plotted logarithmically against reciprocal absolute temperature.

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PART II. DETAILED STRUCTURE OF THE STEADY-STATE DETONATION WAVE

The Role of Thermal Conduction

It will be of interest to see whether thermal conduction is of any importance in the propagation of the detonation wave. To obtain an approximate answer to this question, we take a semi-infinite medium of thermal conductivity κ, impose on it the boundary condition $\Delta T = \Delta T_1$ at $x=0$ for all time $t > 0$, and follow the temperature within the medium as a function of time and distance.

This is a classical problem and the solution is well known (cf. Carslaw, Conduction of Heat p. 46). If the differential equation for the diffusion of temperature is

$$\frac{\partial T}{\partial t} = \frac{\kappa V}{C_v}\frac{\partial^2 T}{\partial x^2} \qquad \text{......(34)}$$

the required solution is

$$\frac{\Delta T}{\Delta T_1} = 1 - 2\,\mathrm{Erf}\,\frac{x}{\sqrt{2\frac{\kappa V}{C_v}t}} \qquad \text{......(35)}$$

where ΔT is the temperature rise at any x, t,
ΔT_1 is the temperature rise at the boundary $x=0$,
κ is the thermal conductivity,
V is the volume (per gram, mole, or molecule),
C_v is the heat capacity (for the same quantity),
Erf x is the error function $\frac{1}{\sqrt{2\pi}}\int_0^x e^{-y^2/2}dy$
for which values are tabulated.

We now require a numerical value for the parameter $\kappa V/C_v$. A straightforward application of kinetic theory (cf. Jeans, Dynamical Theory of Gases) gives

$$\kappa = 1/3\ N/V\ C_v\bar{C}\,l\ \text{(persistence of velocity factor)} \qquad \text{....(36)}$$

where N/V is the number of molecules per unit volume,
$\bar{C}$ is the mean velocity,
l is the mean free path.

For a liquid this becomes at once (Kincaid and Eyring)

$$\kappa = \frac{(\text{persistence factor})}{3} \, 1/\lambda^3 \; C_v \, u\lambda \qquad \text{......(37)}$$

where $\underline{u}$ is the velocity of sound,
λ is the interatomic distance.

We shall use this expression for the highly compressed gas also. The quantity $\kappa \underline{V}/\underline{C_v}$, which may be called the "thermal diffusivity," is

$$\frac{\kappa V}{C_v} = \frac{(\text{persistence factor})}{3} \, u\lambda \qquad \text{......(38)}$$

For a gas with spherical molecules, the persistence-of-velocity factor is 2.522 (Chapman and Cowling, p. 235). With the high forward velocities existing in the detonation wave, this factor might be somewhat larger. In any event, it will approximately cancel the factor 1/3 so that

$$\frac{\kappa V}{C_v} = u\lambda \qquad \text{......(39)}$$

The diffusion equation and its solution for the problem of the semi-infinite medium now become, respectively

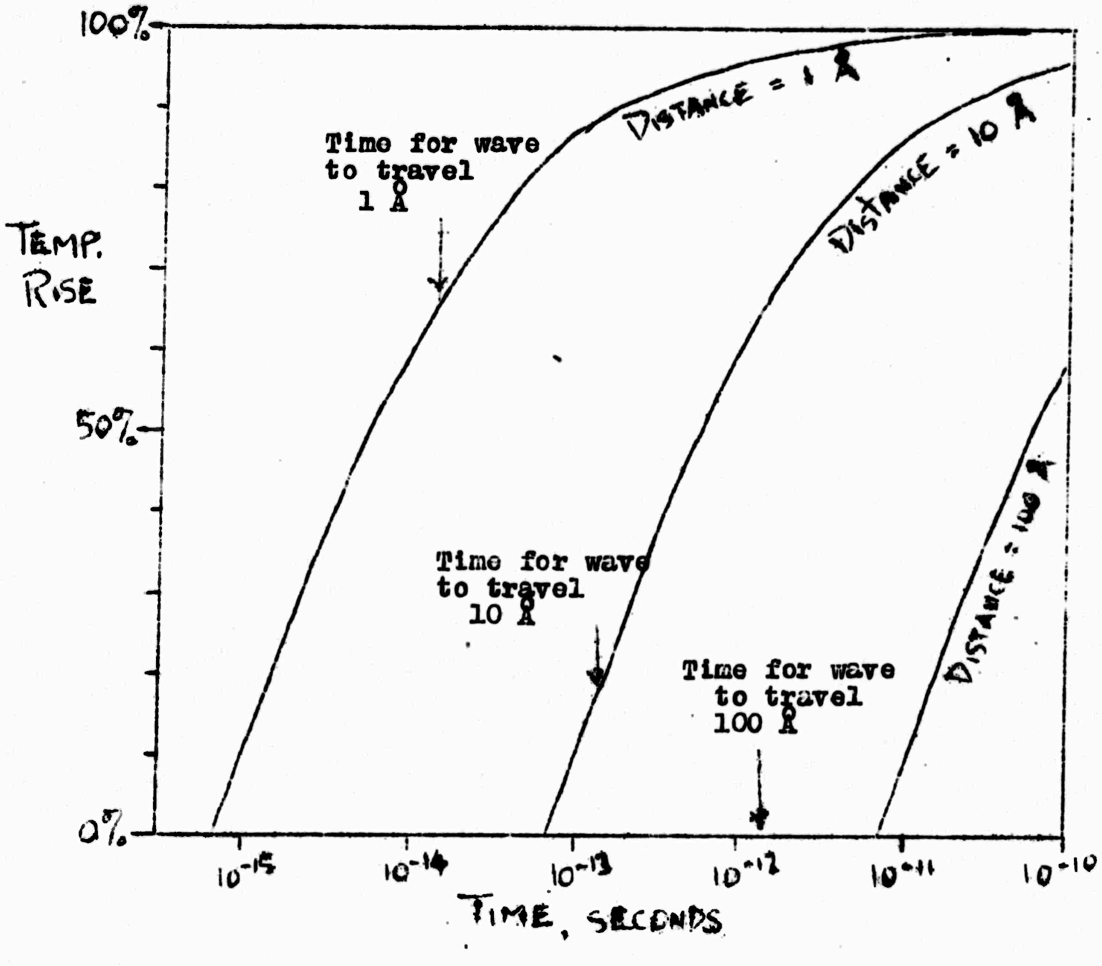
$$\frac{\partial T}{\partial t} = u\lambda \frac{\partial^2 T}{\partial x^2} \qquad \text{......(40)}$$

$$\frac{\Delta T}{\Delta T_1} = 1 - 2 \, \mathrm{Erf} \, \frac{x}{\sqrt{2\, u\lambda \; t}} \qquad \text{......(41)}$$

With the numerical values $\underline{u} = 6 \; 10^5$ cm sec^{-1}
$\lambda = 3 \; 10^{-8}$ cm

the temperature rise has been computed from Eq. (41) for various times and distances. The results for 1 Å, 10 Å, and 100 Å are plotted in Fig. 5, and the numerical results for 10 Å are also given in Table II.

FIGURE 5



The range of effective thermal conduction in a detonation.

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Table II

Time, seconds	$\Delta T/\Delta T_1$
10^{-13}	0.096
10^{-12}	.598
10^{-11}	.868
10^{-10}	.958
10^{-9}	.9867
10^{-8}	.9958

If the detonation wave is traveling with a velocity $D = 8\ 10^5$ cm sec^{-1}, the temperature at 100 Å distance would not have been raised perceptibly by thermal conduction in the time required for the wave to travel 100 Å. Therefore at this distance thermal conduction is of no importance.

At 10 Å, thermal conduction will have raised the temperature about 15% of its total value, in the time the wave would take to travel this far. Therefore at this distance thermal conduction is of a certain importance.

At 1 Å, thermal conduction will have raised the temperature 65% of its total value and is therefore of great importance.

The effect of conduction estimated in this way is probably an upper limit, since in a reacting system the source of temperature would not maintain its high value continuously, nor would the velocity of sound always be so high as that assumed here. This leads us to the conclusion that the conduction of energy (such as that given out by a reacting grain of explosive) in the compressed gas is comparatively short-range...at most, over a distance of a few molecular diameters. Thus the temperature within a reacting system will not be the same throughout. It seems more likely that the temperature in the given region will not be very different from that resulting from the chemical reaction which has taken place in that given region. Those regions in which reaction has proceeded farther will then be at a higher temperature.

If this qualitative result is correct, the temperature distribution in a detonation wave with chemical reaction would more nearly resemble Figure 6a than Figure 6b which is usually assumed:

FIGURE 6a

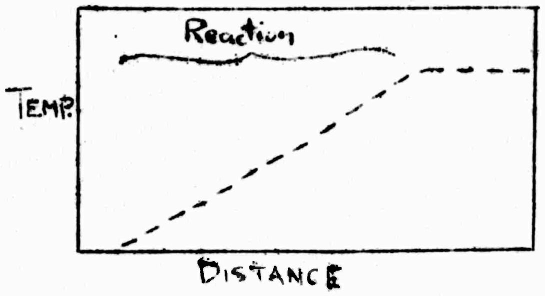
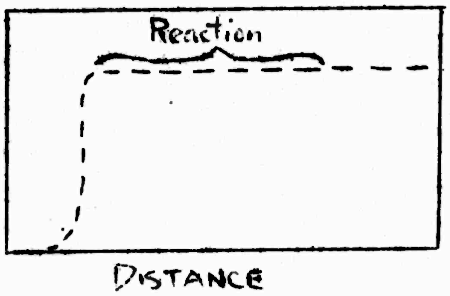


FIGURE 6b



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The Differential Equations for a One-Dimensional Steady-State Detonation Wave

The propagation of a one-dimensional detonation wave is described by the partial differential equations

$$\frac{\partial \rho}{\partial t} + U\frac{\partial \rho}{\partial x} = -\rho\frac{\partial U}{\partial x} \qquad \ldots\ldots(42)$$

for the conservation of mass,

$$\rho\left(\frac{\partial U}{\partial t} + U\frac{\partial U}{\partial x}\right) = -\frac{\partial}{\partial x}\left(P - \mu\frac{\partial U}{\partial x}\right) \qquad \ldots\ldots(43)$$

for the conservation of momentum, and

$$\frac{\partial E}{\partial t} + U\frac{\partial E}{\partial x} = -\frac{1}{\rho}\left(P - \mu\frac{\partial U}{\partial x}\right)\frac{\partial U}{\partial x} + \frac{1}{\rho}\frac{\partial}{\partial x}\left(\kappa\frac{\partial T}{\partial x}\right) \qquad \ldots\ldots(44)$$

for the conservation of energy. Here μ is 4/3 times the viscosity and other symbols have already been defined.

If the detonation wave is moving along at a constant velocity and with a constant shape and magnitude, the transformation to a coordinate system moving with the velocity of the wave permits the conservation equations to be integrated at once (cf. Becker or Kistiakowsky and Wilson) to obtain the total differential equations

$$\rho u = M \qquad \ldots\ldots(45)$$

$$Mu + P - J = \mu\, du/dy \qquad \ldots\ldots(46)$$

$$E + uJ/M - \tfrac{1}{2}u^2 - F = \frac{\kappa}{M}\, dT/dy \qquad \ldots\ldots(47)$$

where u is the velocity in the moving coordinate system,
y is the distance in the moving coordinate system,
M, J, and F are constants of integration to be evaluated from the boundary conditions.

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(a) Structure of shock wave without reaction, perfect gas.

With the assumption that the substance is a perfect gas,

$$P = \rho RT = RMT/u \qquad \text{......(48)}$$

and that no chemical reaction occurs,

$$E = \bar{C}_v T \qquad \text{......(49)}$$

Equations (46) and (47) become

$$Mu + RMT/u - J = \mu \, du/dy \qquad \text{......(50)}$$

$$\bar{C}_v T + uJ/M - \tfrac{1}{2}u^2 - F = \frac{\kappa}{M} dT/dy \qquad \text{......(51)}$$

Equations (50) and (51) are the basic equations for a pure shock wave in a perfect gas -- such a wave as might be initiated and supported by a moving piston.

Since the derivatives on the right sides are equal to zero before the detonation wave and behind the detonation wave, they may be set equal to zero and the two equations solved simultaneously for the temperature and velocity before and after the detonation wave. This is the usual procedure of the hydrodynamic-thermodynamic treatment. On the other hand, Equations (50) and (51) must be solved exactly to find the structure of the wave itself.

For convenience in calculation, we make the following changes of notation:

Reduced temperature $\theta = T\,RM^2/J^2$

Reduced velocity $\omega = u\,M/J$

Reduced distance $z = y\,M/\mu$

$\delta = R/2\bar{C}_v$

$1+a = 2\,M^2F/J^2$

$k = \kappa/\mu\bar{C}_v$

The following differential equations are obtained:

$$d\omega/dz = \omega + \theta/\omega - 1 \qquad \text{......(52)}$$

$$d\theta/dz = 1/k\left[\theta - \delta(1-\omega)^2 - \delta a\right] \qquad \text{......(53)}$$

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If Eq. (53) is divided by Eq. (52) we obtain the temperature-velocity relation for a particle

$$\frac{d\theta}{d\omega} = \frac{1/k\left[\theta - \delta(1-\omega)^2 - \delta a\right]}{\omega + \theta/\omega - 1} \qquad \text{......(54)}$$

For the special case $k = 1+2\delta$, Equations (52)-(54) can be solved in closed form, for if θ is expressed as a power series in ω, the series fortuitously terminates (cf. Becker). The result is

$$\theta = \frac{\delta}{2\delta+1}\,(1+a-\omega^2) \qquad \text{......(55)}$$

$$z = \frac{2\delta+1}{\delta+1}\;\frac{\omega_1 \ln(\omega_1-\omega) - \omega_2 \ln(\omega-\omega_2)}{\omega_1-\omega_2} \qquad \text{......(56)}$$

A computation of the temperature and density within a shock wave has been carried through with the aid of Eqs. (55) and (56) and the assumed numerical values

$\delta = 0.2$ corresponding to $\bar{C}_v = 5$ cal deg^{-1} mole^{-1}.

$k = 1.4$ which is about correct for a dilute gas.

$a = 0$ which means that the detonation velocity is very high or the initial temperature very low, since for low T_0 $a = 2\bar{C}_v T_0/D^2$ approximately.

The results of the computation are plotted in Fig. 7.

In general the conductivity in a shock wave may be expected to be somewhat greater than that corresponding to $\underline{k} = 1.4$. It is therefore desirable to solve Eqs. (52)-(54) for any value of $\underline{k}$. An attempt to solve the equations by setting θ equal to a power series in ω was abandoned because the series did not converge well. Recourse was then had to numerical integration.

The derivative in Eq. (54) is indeterminate at the boundary, since both its numerator and denominator vanish. However, it may be evaluated by the method of L'Hospital, differentiating both with respect to ω and solving the resulting algebraic equation for $d\theta/d\omega$. With this as a starting point, Eq. (54) may be integrated numerically. The values of θ and ω so obtained permit the numerical integration of Eqs. (52) and (53).

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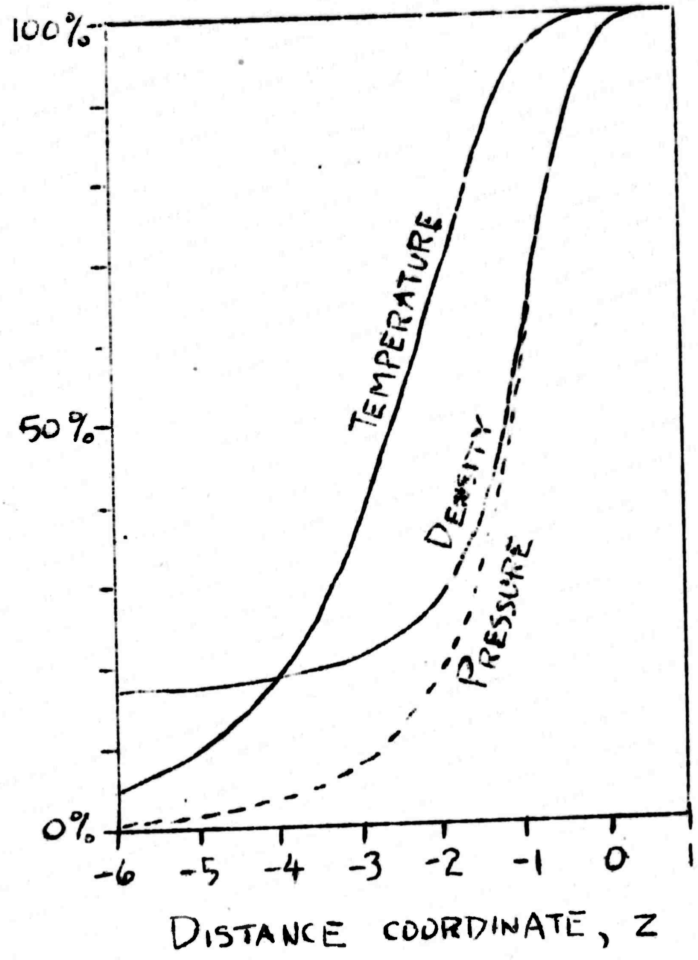
FIGURE 7



Structure of a shock wave without chemical reaction in a perfect gas. One unit of distance z is 0.19/D cm.

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In order to investigate the effect of increased thermal conductivity, the numerical integration was carried through for the numerical values

$$\delta = 0.2$$
$$k = 6$$
$$a = 0$$

and the results appear in Fig. 8. It will be seen that the only effect of the increased thermal conductivity is to spread the temperature-wave farther ahead of the pressure-wave.

In order to investigate the effect of a higher initial temperature, numerical integration was also carried through for the values

$$\delta = 0.2$$
$$k = 6$$
$$a = 0.1$$

and the results appear in Fig. 9. The only effect of the higher initial temperature is to raise the temperature-wave slightly.

Figures 7, 8, and 9 are all drawn to the same scale so they are directly comparable. In each graph temperature, pressure, and density are plotted as percentages of their asymptotic values. In each graph the unit of distance $\underline{z}$ is about 45 Angstrøm units. These shock waves are comparatively wide because the calculations were made for a gas; for a solid, the waves would be much narrower.

Discussion

It is to be noted that in each of the calculated shock waves the temperature-wave precedes the pressure-wave. This appears to be a general phenomenon, and is understandable in the light of the following considerations.

The impulses which form the temperature-wave are transmitted from molecule to molecule by collisions. Because of the short distances between molecules in the highly compressed state, the fraction of the distande through which the signal must be carried by moving molecules is small. The rate of transmission of the thermal impulse can therefore exceed the kinetic-theory velocity of the molecules by a considerable amount.

The density (and pressure)-waves, however, are built up by an increased concentration of molecules themselves. The rate of this process will not exceed that permitted by the kinetic-theory velocity of the molecules.

If the rate of transport of heat always exceeds the rate of transport of molecules, we may safely neglect convective transport of energy in the detonation wave.

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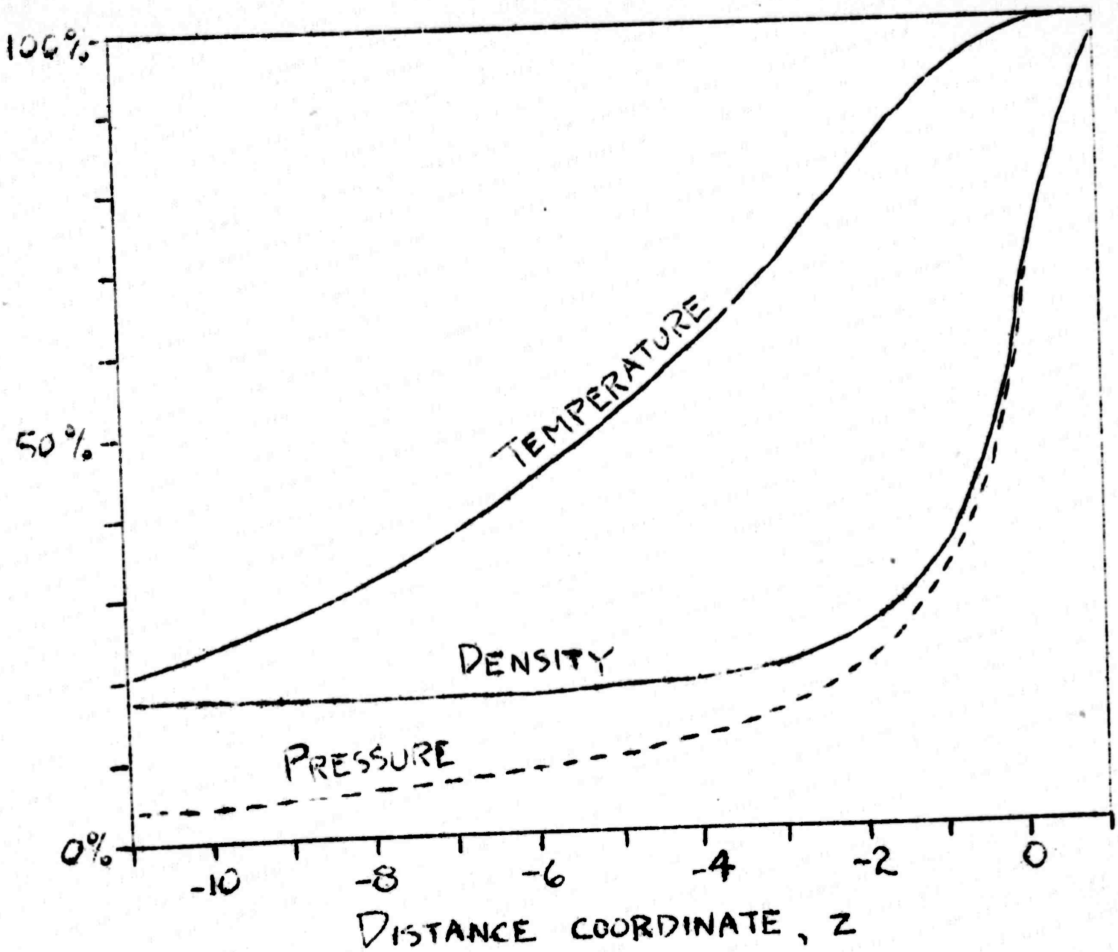
FIGURE 8



Structure of a shock wave without chemical reaction in a perfect gas. Thermal conductivity higher than in Fig. 7. One unit of distance z is 0.19/p cm.

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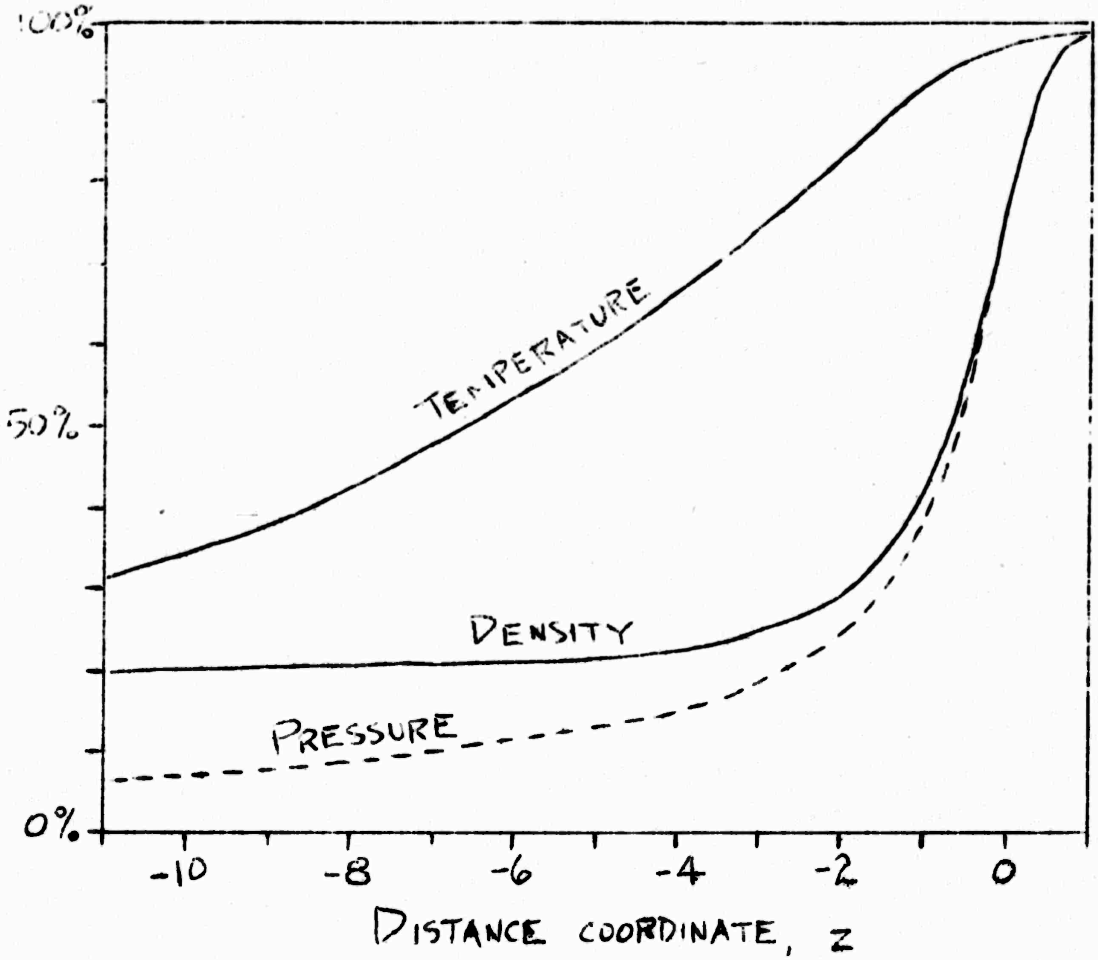
FIGURE 9



Structure of a shock wave without chemical reaction in a perfect gas. Initial temperature higher than in Fig. 8. One unit of distance z is about [illegible] Å.

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(b) Shock wave with chemical reaction, in a perfect gas.

When a chemical reaction is occurring within the shock wave, the basic equations for the steady-state wave become

$$Mu + RMT/u - J = \mu\, du/dy \qquad \text{......(57)}$$

$$C_v T - (1-n)Q + uJ/M - \tfrac{1}{2}u^2 - F = \frac{\kappa}{M}\, dT/dy \qquad \text{......(58)}$$

Eqs. (57) and (58) differ from the equations for the shock wave without reaction only by the inclusion of the term (1-n)Q, where

Q is the heat evolved by the reaction, per unit mass,
n is the fraction of material left unreacted.

In addition there will be an equation for the rate of reaction, which will be for a first-order reaction

$$-\frac{dn}{dt} = n\, Z\, e^{-A/T} \qquad \text{......(59)}$$

The time derivative in Eq. (59) can be changed to the space derivative with the aid of the relation which holds for the steady state

$$\frac{dn}{dt} = u\,\frac{dn}{dy} \qquad \text{......(60)}$$

For convenience in calculation, we make the same changes in notation as before (page 23), with the additional ones

$$Q' = Q\, RM^2/J^2 C_v$$

$$Z' = Z\mu/J$$

$$A' = A\, RM^2/J^2$$

The following three differential equations are obtained:

$$d\omega/dz = \omega + \theta/\omega - 1 \qquad \text{......(61)}$$

$$d\theta/dz = 1/k\left[\theta - Q'(1-n) - \delta(1-\omega)^2 - \delta a\right] \qquad \text{......(62)}$$

$$dn/dz = -\frac{n}{\omega}\, Z'\, e^{-A'/\theta} \qquad \text{......(63)}$$

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Equations (61), (62), (63) must be integrated simultaneously. This can be done by numerical integration.

The result of the integration is given in Fig. 10 for the conditions

$\delta = 0.2$ $a = 0.1$ $k = 6$

$Q' = 0.1435$ $Z' = 10^4$ $A' = 1.735$

which correspond to the boundary conditions

$Z = 2.5\ 10^{15}\ \mathrm{sec}^{-1}$	Probability factor
$A = 60{,}000/1.986$ deg	Heat of activation
$D = 2.15\ 10^{5}\ \mathrm{cm\ sec}^{-1}$	Detonation velocity
$Q = 12.4\ \mathrm{kcal\ mole}^{-1}$	Heat of reaction
$\rho_o = 0.0012\ \mathrm{gm\ cm}^{-3}$	Initial density
$P_o = 1$ atmosphere	Initial pressure
$\mu = 4/3\ \eta = 2.27\ 10^{-4}$ poise	Viscosity

It will be seen from the results of Fig. 10 that a unimolecular gas reaction, even with a high activation energy, will go to completion in a distance less than that required for the system to reach its highest temperature. Under these conditions the rate-determining step will shift to some other process such as evaporation or activation by bimolecular collision for gas reactions (Cf. discussion in Part I).

(c) Shock wave in a solid explosive, with evaporation the rate-determining step.

When a shock wave and its accompanying chemical reaction are taking place in a solid explosive, the equations for the steady-state wave become

$$u/V = M \qquad \ldots\ldots(64)$$

$$Mu + P - J = \mu\, du/dy \qquad \ldots\ldots(65)$$

$$\bar{C}_v T - (1-n)Q + uJ/M - \tfrac{1}{2}u^2 - F = \frac{K}{M}\, dT/dy \qquad \ldots\ldots(66)$$

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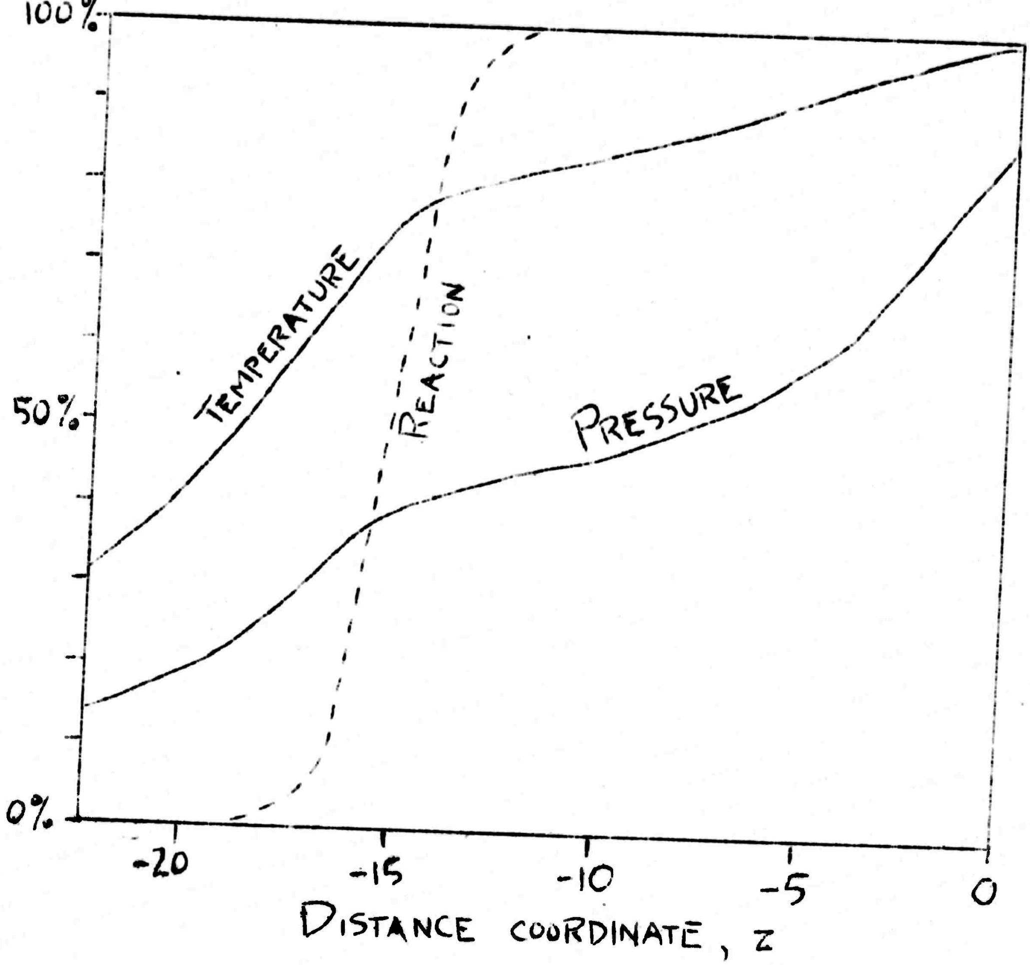
FIGURE 10



Structure of a shock wave in a perfect gas, with chemical reaction. One unit of distance z is equal to 88 Å.

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The pressure P is given by the sum of the pres[illegible] to the gas initially surrounding the grains and that due to th[illegible] evaporated explosive:

$$P = P_1 \frac{V_1 T}{T_1 V} + (1-n) \frac{RT}{V - \alpha} \qquad \text{......(67)}$$

where P_1 is the initial pressure of the residual gas,

V_1 is the initial specific volume,

T_1 is the initial temperature,

n is the fraction of explosive remaining in the solid state,

α is the covolume (assumed constant).

An additional equation is required for the rate of reaction. The solid is supposed to be grains of uniform size, and it is assumed that the reaction rate is given by the rate of evaporation of molecules (or portions of molecules) from the surface. The rate is then given by

$$- dm/dt = g \frac{S}{s} \frac{kT}{h} e^{-4F^{\ddagger}/RT} \qquad \text{......(68)}$$

where m is the number of molecules per gram in the solid state,
g is the number of grains per gram,
S is the surface area of a grain,
s is the area occupied by a molecule.

Upon making the substitutions

$$\begin{aligned} m &= nm_0 \\ g &= 3V_0/4\pi r_0^3 \\ S &= 4\pi r_0^2\, n^{2/3} \\ s &= (V_0/m_0)^{2/3} \end{aligned} \qquad \text{......(69)}$$

where m_0 is the initial number of molecules per gram in the solid,

V_0 is the initial specific volume of a grain,

r_0 is the initial radius of a grain,

the rate equation becomes:

$$- dn/dt = n^{2/3} \frac{3\, v_o^{1/3}}{r_o\, m_o^{1/3}} \frac{kT}{h} e^{\Delta S^{\ddagger}/R} e^{-\Delta H^{\ddagger}/RT} \qquad \text{......(70)}$$

which may be written

$$- dn/dt = n^{2/3}\; Z\, e^{-\Delta H^{\ddagger}/RT} \qquad \text{......(71)}$$

The time derivative is changed to a space derivative with the aid of the steady-state relation

$$\frac{dn}{dt} = u \frac{dn}{dy} = MV \frac{dn}{dy} \qquad \text{......(72)}$$

Upon making the substitution $V' = V - \alpha$, and neglecting $\underline{P_1 V_1 T / V T_1}$, we obtain the three differential equations

$$M\mu\, dV'/dy = V'M^2 + (1-n)RT/V' - J' \qquad \text{......(73)}$$

$$\frac{\kappa}{M}\, dT/dy = \bar{C}_v T - (1-n)Q + J'V' - \tfrac{1}{2}M^2 V'^2 - F' \qquad \text{......(74)}$$

$$- dn/dy = \frac{1}{V' + \alpha}\, Z\, e^{-\Delta H^{\ddagger}/RT}\, n^{2/3} \qquad \text{......(75)}$$

For convenience in calculation we make changes in notation analogous to those used before:

Reduced temperature $\theta = T\, RM^2/J'^2$

Reduced velocity $\omega = V'\, M^2/J'$

Reduced distance $z = y\, M/\mu$

$\delta = R/2\bar{C}_v$

$1 + a = 2M^2 F'/J'^2$

$k = \kappa/\mu \bar{C}_v$

$Q' = Q\, RM^2/J'^2 \bar{C}_v$

$Z' = Z\, \mu/J'$

$A' = \Delta H^{\ddagger}\, M^2/J'^2$

$\alpha' = \alpha\, M^2/J'$

Upon making these substitutions, the three differential equations to be integrated simultaneously become

$$d\omega/dz = \omega + (1-n)\theta/\omega - 1 \qquad \ldots\ldots(76)$$

$$d\theta/dz = 1/k\left[\theta - Q'(1-n) - \delta(1-\omega)^2 - \delta a\right] \qquad \ldots\ldots(77)$$

$$-\,dn/dz = Z'\,e^{-A'/\theta}\,\frac{n^{2/3}}{\omega+\alpha'} \qquad \ldots\ldots(78)$$

While analytic solutions have not been obtained for the system of equations (76), (77), (78) in the general case, it is possible to solve the equations exactly in the front of the wave where the amount of reaction is negligible. The solution is

$$\omega = 1 - c_1\,e^{z} \qquad \ldots\ldots(79)$$

$$\theta = \delta a + \frac{c_1^{\,2}}{1-2k}\,e^{2z} + c_2\,e^{z/k} \qquad \ldots\ldots(80)$$

Solutions over the entire range can be obtained for specific substances by numerical integration. This has been carried through for TNT, the results of the calculations being presented in Fig. 11. The numerical integrations are somewhat tedious because the result of the integration is sensitive to the precise value at which integration is started, so that the integration must be repeated several times before it satisfies all the boundary conditions. The final result in Fig. 11 is believed to be fairly accurate.

The numerical values assumed for TNT in this calculation are:

V_1 = 0.629 $cm^3\ g^{-1}$
D = $6.9\ 10^5$ $cm\ sec^{-1}$
T_1 = $300^{\circ}K$
α = 0.4355 $cm^3\ g^{-1}$
$\bar{C}_v$ = 0.326 cal g^{-1}
Mean molecular weight of products = 25.9
Q = 770 cal g^{-1}
V_2 = 0.5094 $cm^3\ g^{-1}$
T_2 = $3293^{\circ}K$
K = $2.39\ 10^{-4}$ cal $sec^{-1}\ cm^{-2}$ (estimated)
μ = $2\ 10^{-3}$ poise (estimated)

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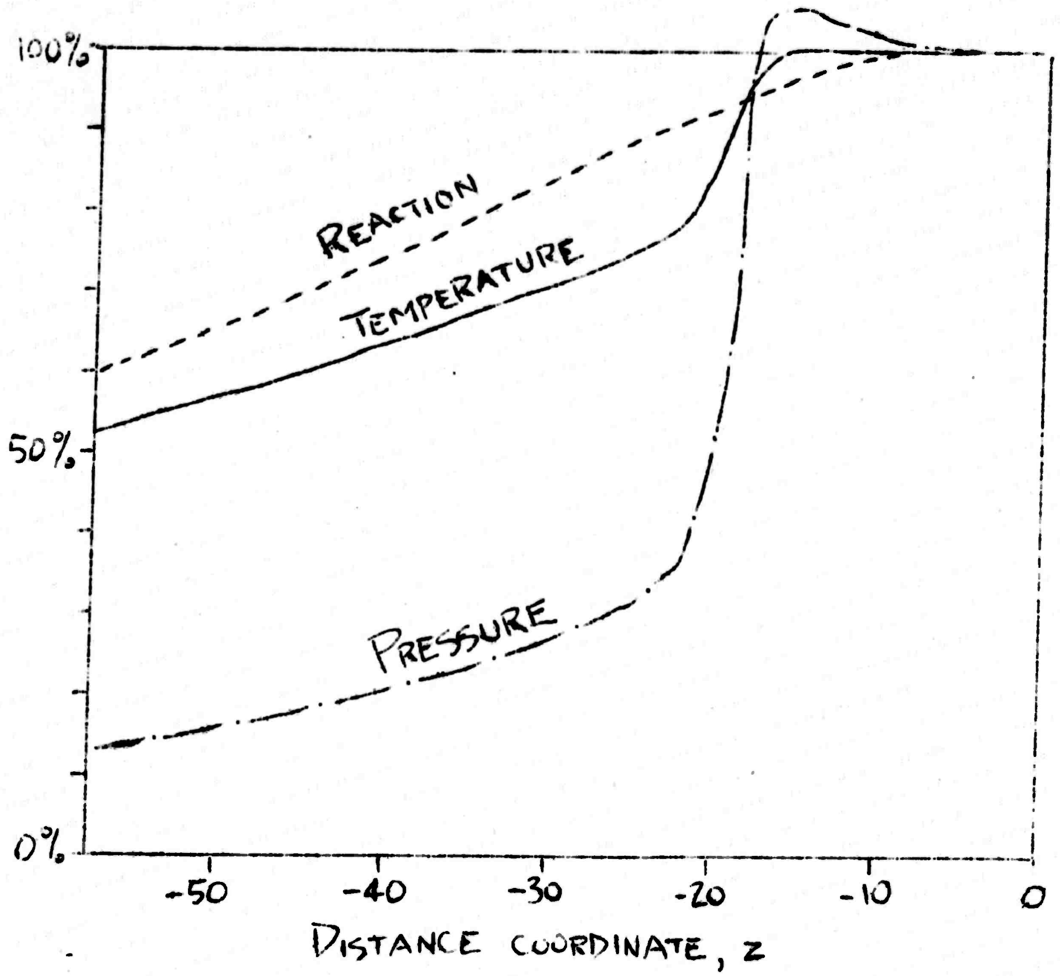
FIGURE 11



Structure of a shock wave in a solid, with chemical reaction. Evaporation is the rate-determining step. One unit of z is 0.2 Å.

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$$V_o = 0.6046 \text{ cm}^3 \text{ g}^{-1}$$
$$kT/h = 0.7553 \; 10^{14} \text{ sec}^{-1} \text{ (estimated)}$$
$$r_o = 10^{-7} \text{ cm (estimated)}$$
$$\Delta H^{\ddagger} = 11 \text{ kcal mole}^{-1} \text{ (estimated)}$$

All of the properties of TNT in the above list except those marked "estimated" were taken from a calculation of the detonation properties of TNT by Cook. The only one of the estimated properties which requires comment is the grain-radius $\underline{r_o}$ which was taken as 10^{-7} cm; this value is surely an extreme lower limit, and since the rate of reaction is inversely proportional to the initial grain size, this calculation represents an extreme upper limit for the rate of reaction by the evaporation mechanism.

One unit of $\underline{z}$ in Fig. 11 is 0.2 Ångstrøm units, which would make the reaction zone (and temperature-wave) about 20 or 30 Ångstrøm units long in all.

Discussion

Several features of these results deserve comment:

(1) The wave-front of the temperature wave is comparatively broad and of a gradual slope, the temperature appearing to rise as the reaction proceeds. See the discussion on page 21.

(2) The pressure-wave, on the contrary, is narrow and steep. Just as in other shock waves, the pressure front lags far behind the temperature front. The effect of pressure changes on the reaction is negligible, and the pressure front is too far behind the temperature front to have any important effect in initiation of the reaction. When the pressure front arrives, it does produce a sudden jump in the temperature.

(3) It has been proposed that detonation reactions should have a wave form like that in Fig. 12, the temperature and pressure passing through an exceedingly high maximum just behind the front of the wave, and approaching their asymptotic values from above. The differential equations do indicate the existence of such a maximum. However, the calculations which Fig. 11 illustrates show that the maximum in pressure is not large, while the maximum in temperature is imperceptible on the graph. These maxima are therefore probably not of sufficient magnitude to be of any great importance.

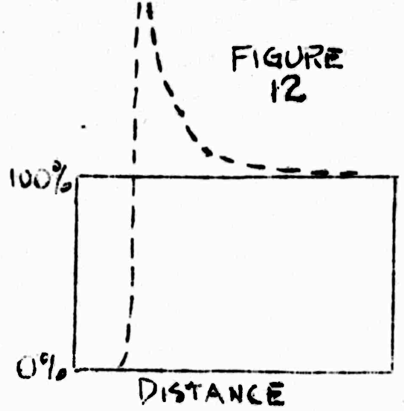
FIGURE 12

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PART III. THE DETONATION WAVE WITH RADIAL LOSSES.

If explosive charges are of sufficient diameter that the wave does resemble closely a one-dimensional wave, it is possible to obtain detonation velocities very close to those theoretically calculated. However, actual explosive charges are often of small enough diameter that a considerable part of the energy of the detonation wave is dissipated laterally -- producing slowing or eventually stopping of the detonation wave. The diameter at which this effect becomes appreciable may be of the order of inches for low-energy explosives.

It may be supposed a priori that the detonation wave ceases because the chemical reaction which was its support has ceased. At a point where there is no detonation, there is no longer any chemical reaction.

As the discussion of Part I indicates, the pressure has little or no effect on the rate of reaction. We therefore suppose that the chemical reaction becomes excessively slow only because the temperature has fallen excessively low. When the explosive is detonated with the aid of a booster, the temperature at the detonator end is sufficiently high (if the booster is supposed to be a high-energy explosive) that the reaction will go in the solid phase. But as the detonation wave proceeds, if heat is lost radially the back part of the detonation wave will be cooled. This will cause the reaction to become slower in this region, which will then cool the region immediately preceding it. The result will be that a region of low pressure and temperature (rarefaction wave) will spread forward until it reaches the front of the detonation wave and the detonation will fail.

The effect of temperature-lowering on the reaction rate will be particularly noticeable if the reaction has to go homogeneously if at all, because it has no surface to permit the heterogeneous reaction. This will be true for cast explosives, and to a lesser extent true for explosives composed of large-sized particles. The high activation energy of the homogeneous reaction will cause the reaction to come to a complete standstill even at moderately high temperatures (cf. Fig. 4).

The complete problem of the rate of dissipative loss in a wave with chemical reaction is a difficult one which has not been solved. However, the magnitude of dissipative loss as a function of the amount of radial expansion can be studied. There are at least three possible ways in which expansion might produce a lowering of temperature:

(1) Effect on the reaction

If the chemical reaction in a particular region has only gone partially to completion when the explosive has expanded, the remaining reaction will take place as if the initial density of loading of the explosive were less. This might effect both the pressure and the temperature which the complete reaction would produce.

The experimental fact is that while the initial density of loading has a marked effect on the detonation velocity (Fig. 13 gives the effect on detonation velocity for some common explosives) and on the detonation pressure (Fig. 14 gives the effect on pressure), it has substantially no effect on the detonation temperature (Fig. 15).

This result should have been expected, for the detonation temperature is determined primarily by the heat evolved by the reaction and the heat capacity of the products, neither of which is particularly sensitive to density. More exactly, the detonation temperature for a solid explosive is given by

$$T_2 = \frac{T_1 + Q/\bar{C}_v}{1 - \dfrac{\frac{1}{2}N}{1 + \dfrac{\bar{C}_v}{R}\left(1 - d\bar{\alpha}/dV_2\right)}} \qquad \ldots\ldots(81)$$

where $\underline{N}$ is the number of molecules produced from a single molecule by the explosion, and the other symbols have their usual meaning (Cook). It will be noted that the density appears explicitly only in the derivative of the covolume. The effect of density would therefore be small.

(2) Effect of adiabatic expansion

If the reacted (or partially reacted) explosive behind the detonation front expands so quickly that heat loss to the surroundings may be neglected, we can calculate the temperature drop caused by the adiabatic expansion.

For a substance which obeys the imperfect gas law

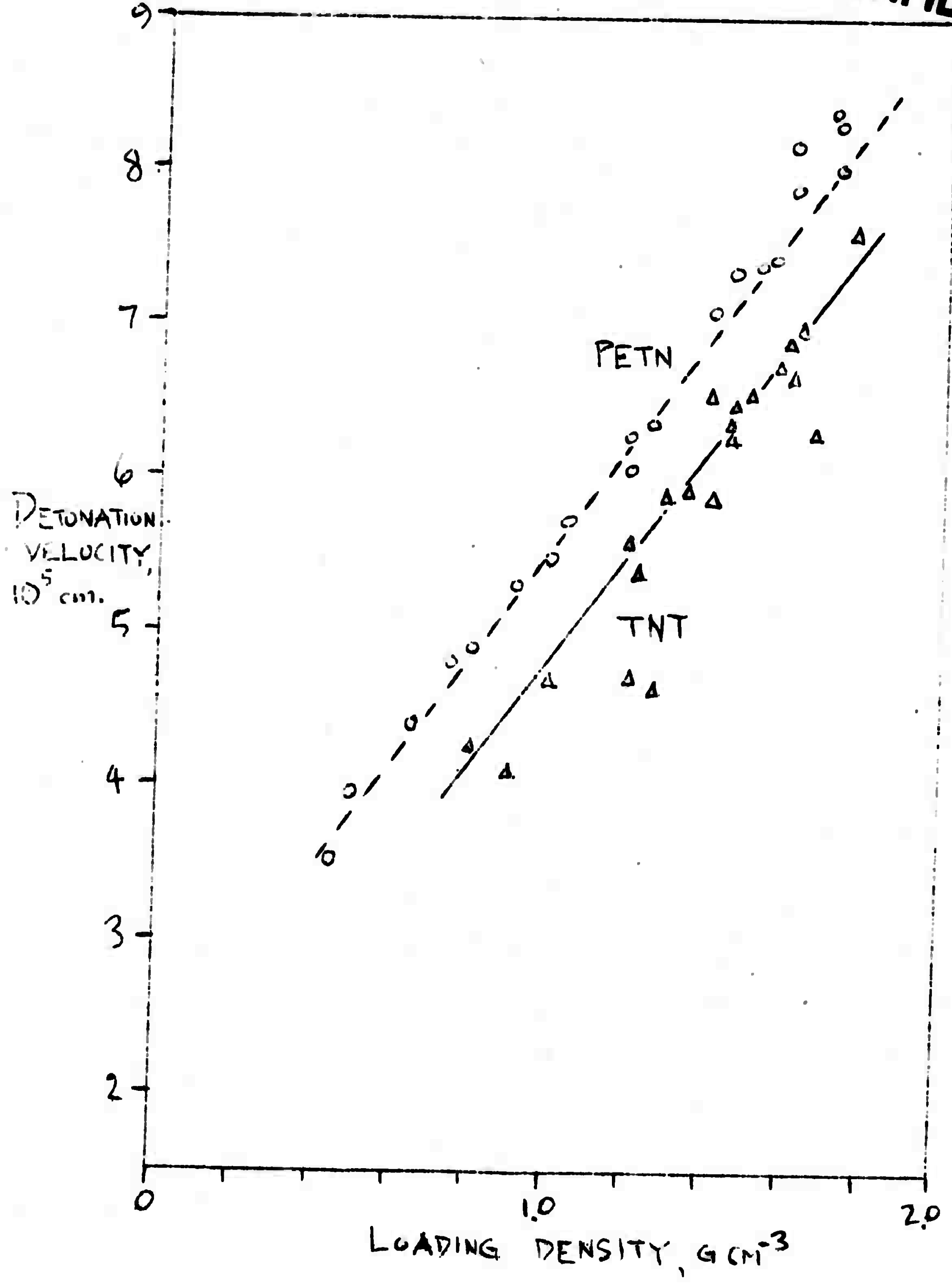
$$P\,(V - \alpha) = RT \qquad \ldots\ldots(82)$$

with the covolume constant, the adiabatic law is

$$\begin{aligned} P\,(V - \alpha)^{C_p/C_v} &= \text{const.} \\ T\,(V - \alpha)^{R/C_v} &= \text{const.} \end{aligned} \qquad \ldots\ldots(83)$$

from which the temperature and pressure after any given expansion may be computed. This has been done, with the assumption that the covolume α is 0.85 of the detonation volume $\underline{V_2}$. The results are plotted in Fig. 16.

FIGURE 13



Effect of loading density on detonation velocity. After various authors.

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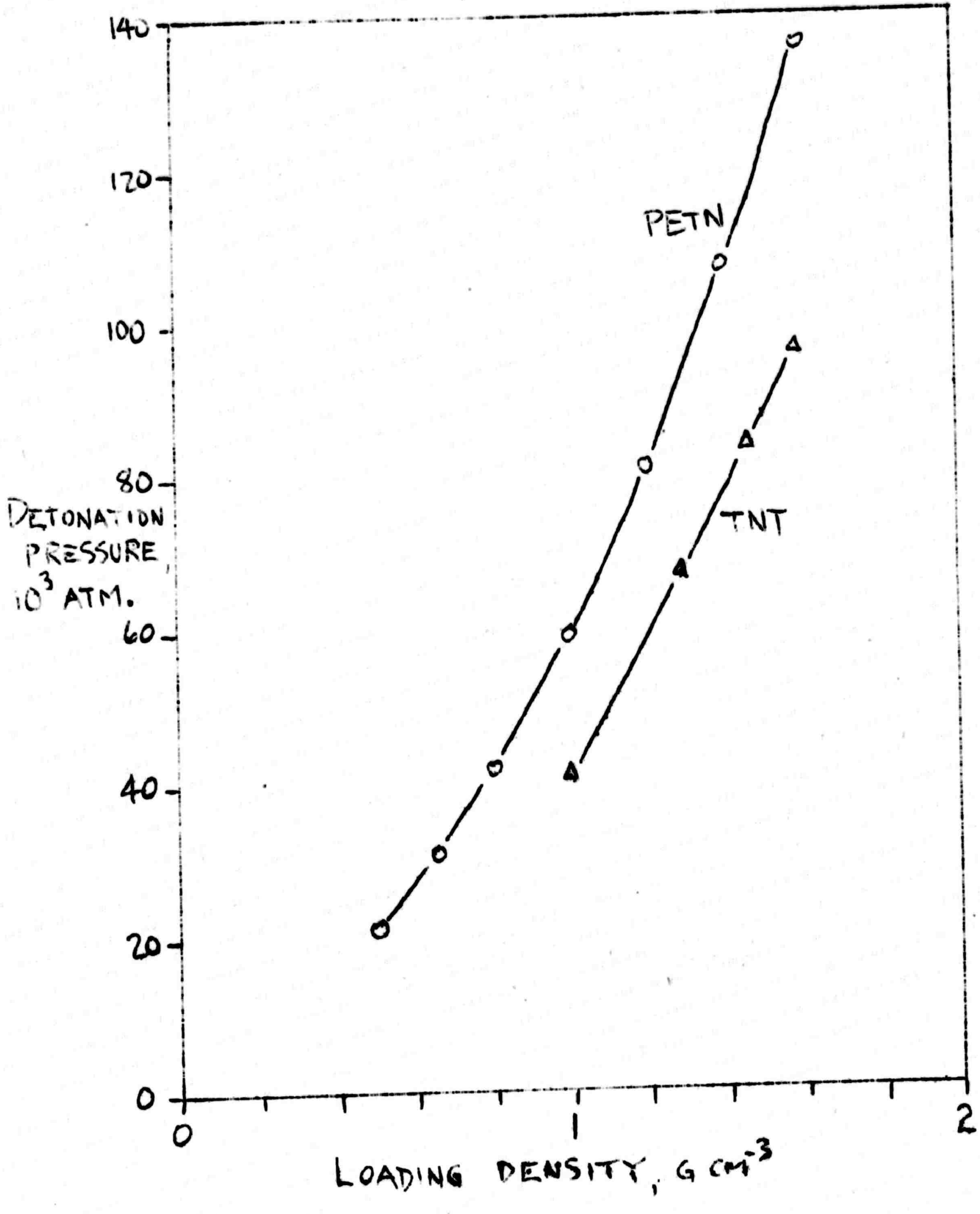
FIGURE 14



Effect of loading density on detonation pressure.

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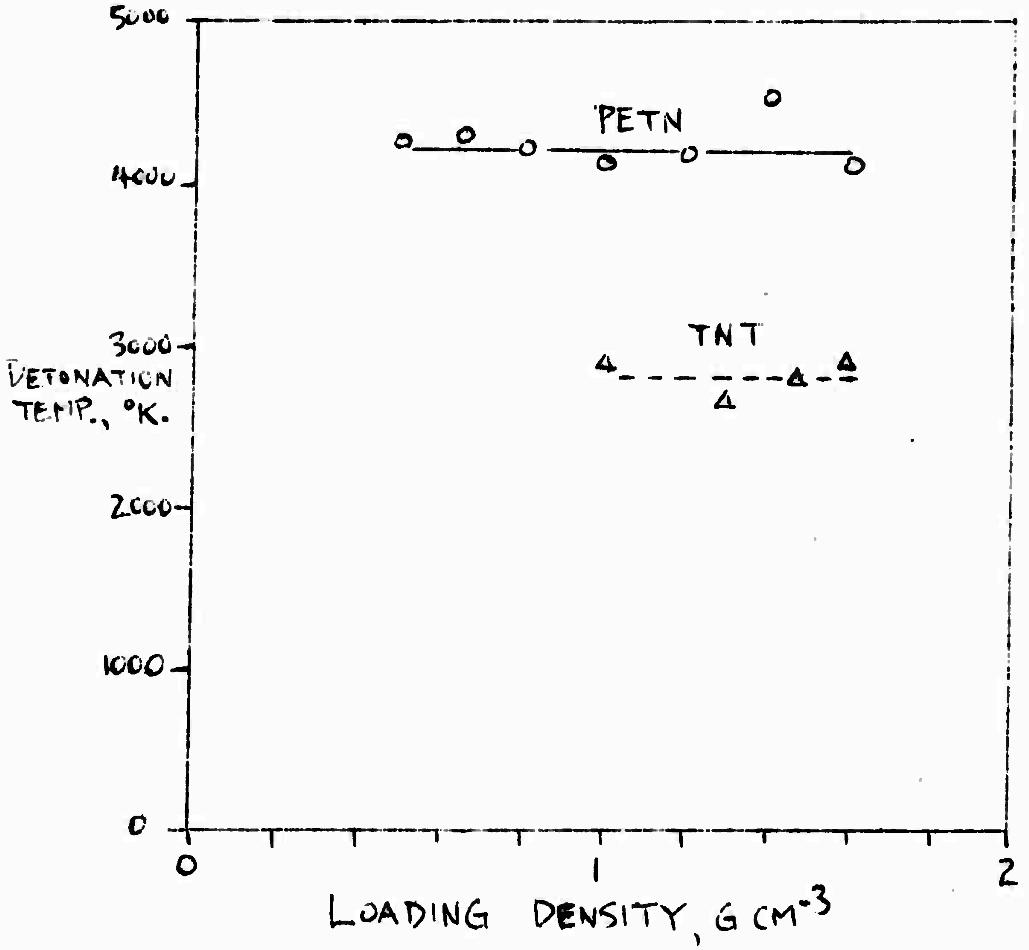
FIGURE 15



Effect of loading density on detonation temperature.

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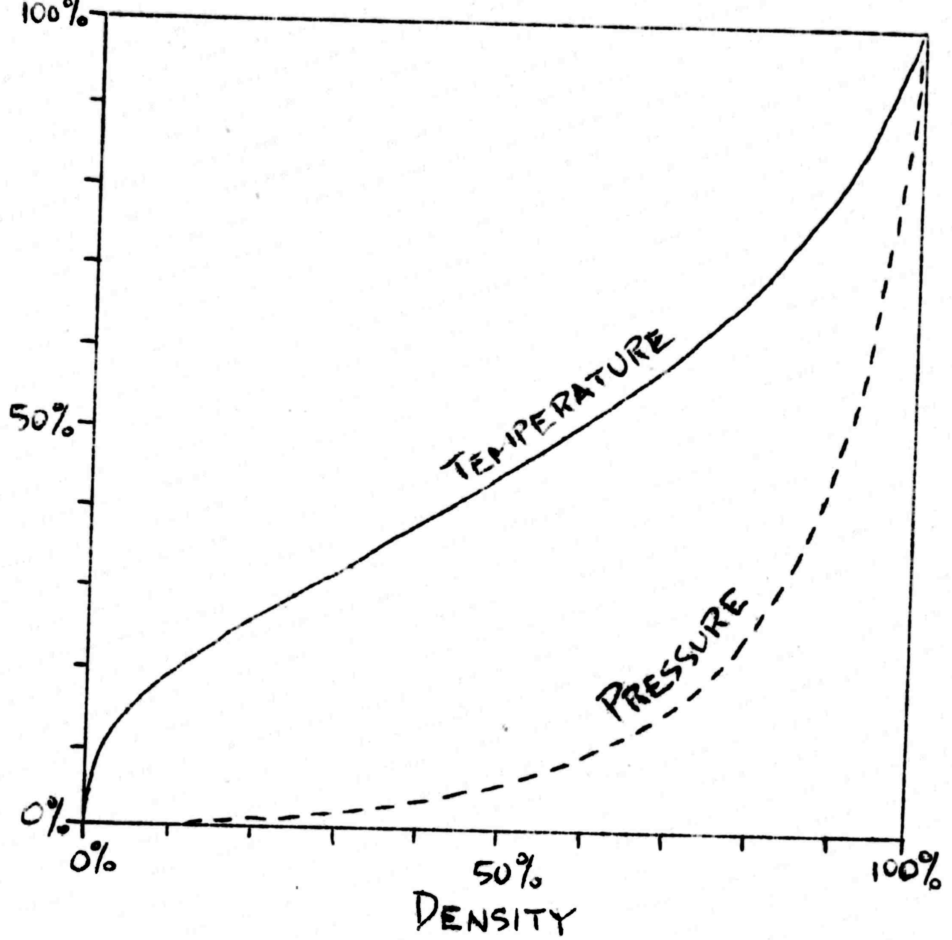
FIGURE 16



Effect of adiabatic expansion.

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(3) Effect of inertia of the case.

If work is done against the inertia forces due to the case surrounding the explosive charge, energy will be dissipated thereby and the temperature will fall.

The results for this process have been calculated by numerical integration by G.I. Taylor, for a cylindrical explosive surrounded by a heavy case, and the case does not begin to expand until the detonation wave has passed and the reaction is over.

The temperature and pressure calculated in this way for various degrees of expansion are plotted in Fig. 17, the data for which were taken from Table I of Taylor's report. The temperature was not given in Taylor's Table I, but was computed from his values of pressure and density with the aid of the equation of state.

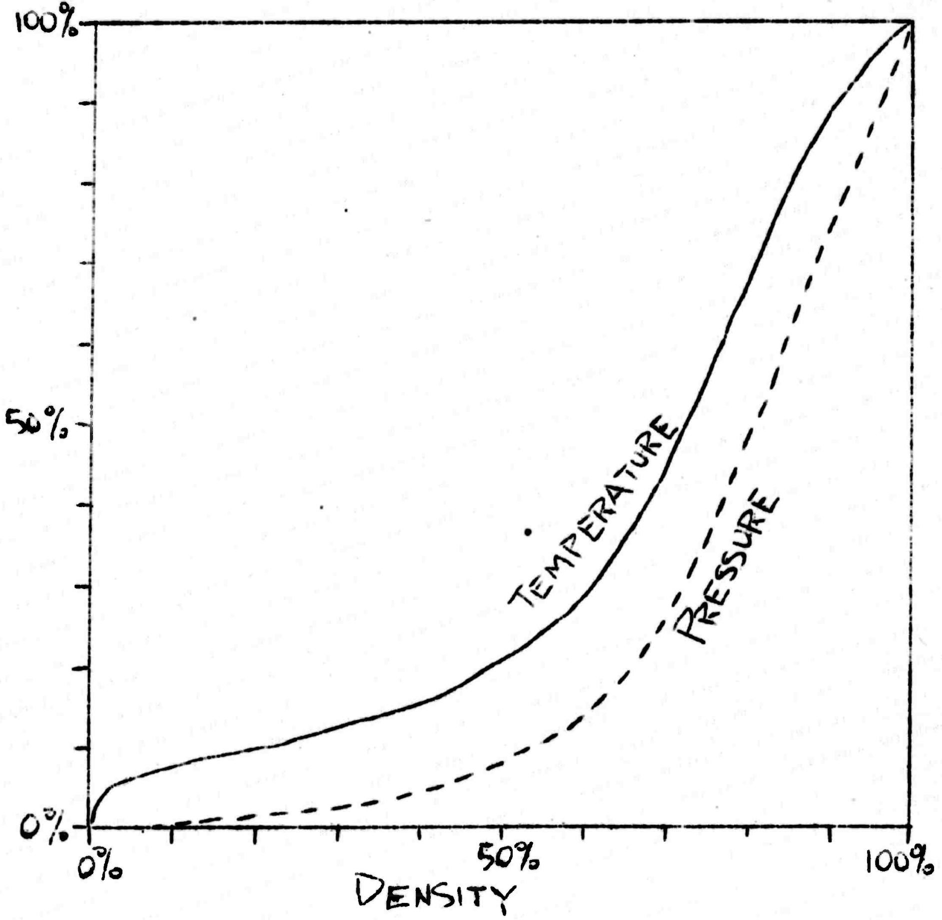
The calculations of Taylor on which Fig. 17 is based include both the effect of inertia and of adiabatic expansion.

Discussion

It is apparent that the effects of radial expansion will lower the temperature behind the front of a detonation wave -- and the magnitude of the temperature effect is large enough to have a major effect on the rate of reaction.

For example, an expansion to twice the initial volume will lower the temperature to about 20% of its initial value (Fig. 17). If the initial temperature was 4000°K, this cooling would be sufficient to bring it to 800°K., which would effectively stop not only the homogeneous (solid) reaction but also the heterogeneous (evaporation) reaction and so bring all decomposition of the explosive to a standstill.

FIGURE 17



Effect of expansion of a cylindrical case.
After G.I. Taylor.

PART IV. THE DETONATION WAVE IN THE NON-STEADY STATE.

Having determined the distribution of pressure, temperature, density and velocity in the steady-state detonation wave, we may wish to determine the same properties for the non-steady state. For example, we may wish to have the wave pass from one medium into another with different properties and follow its progress there.

In principle, it is possible to do this by numerical integration of the general equations of conservation, introducing the chosen conditions discontinuously at some point on the space coordinate. Any given distribution may be differentiated graphically or tabularly to obtain all the necessary terms in the equations

$$\frac{\partial \rho}{\partial t} = -\frac{\partial}{\partial x}(\rho u) \qquad \text{......(84)}$$

$$\frac{\partial u}{\partial t} = -\frac{1}{\rho}\frac{\partial}{\partial x}\left(P - \mu\frac{\partial u}{\partial x}\right) - u\frac{\partial u}{\partial x} \qquad \text{......(85)}$$

$$\frac{\partial T}{\partial t} = \frac{1}{\rho C_v}\left(P - \mu\frac{\partial u}{\partial x}\right)\frac{\partial u}{\partial x} - \frac{\kappa}{\rho C_v}\frac{\partial^2 T}{\partial x^2} - \frac{Q}{C_v}\frac{dn}{dt} - u\frac{\partial T}{\partial x} \qquad \text{......(86)}$$

with the usual auxiliary equations

$$P = f(\rho, T) \qquad \text{(Equation of state)} \qquad \text{......(87)}$$

$$E = C_v T - (1-n)Q \qquad \text{......(88)}$$

$$dn/dt = F(n, T) \qquad \text{(Rate law)} \qquad \text{......(89)}$$

Having obtained the time derivatives, it would be possible to find new values for the variables by relations such as

$$T' = T + \frac{\partial T}{\partial t}\Delta t \qquad \text{etc.} \qquad \text{......(90)}$$

Repetition of this process will then show graphically the effect on a detonation wave of any set of conditions we choose to impose. The wave could be followed from one explosive into another, as for a booster. The method could also follow the thermal initiation of an explosive by a given temperature distribution.

The method has been tried by the writers in a preliminary way, but the calculation involved is excessive and no final results have been obtained in this way. An attempt to evaluate the derivatives by expressing T̲ as a power series in t̲ (see Informal Progress Report 2) was abandoned because it did not converge fast enough to permit any useful calculations.

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On the hypothesis of thermal initiation and estimates of the absolute rate constant and free energy of activation of the explosion reaction, the width of the reaction zone in a detonation wave, both in the homogeneous case and in the heterogeneous case, in which evaporation is the rate-determining step, is calculated. The distribution of temperature and pressure within a detonation wave, and the effect of these variables upon the rate of chemical decomposition reaction, are studied in an investigation of the theory of the causes of the failure of an explosive to detonate, or to maintain an explosive reaction after detonation has been initiated.

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