The Combustion of Colloidal Propellants

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XI. *The Combustion of Colloidal Propellants.*

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I.—*Introductory.*

Scientific treatment of the problems attendant on the combustion of colloidal propellants may be said to have originated with Vieille.* Earlier, Piobert,† in his study of the rate of burning of black powder, had formulated his well-known law of burning by parallel layers, and had further reached the conclusion that the rate of burning was independent of pressure variation during the explosion. Later experimenters with black powder, while accepting Piobert's first law, recognised the dependence of the rate of burning on the pressure, the first attempt to formulate an expression connecting the rate with the pressure being due to De Saint-Robert,‡ who gave the formula $R = \beta p^{\alpha}$, where β is a constant for the powder, and $\alpha = \frac{2}{3}$. In course of time the index α experienced various modifications, being accorded values ranging between $\frac{1}{4}$ and 1 by different investigators.§

Vieille reached the conclusion that the hypothesis of De Saint-Robert was, in general, not true for black powder; but that it could be taken to apply to colloidal explosives, such as gelatinised nitrocellulose, which possess a nearly homogeneous character. Experimenting with a variety of compositions he arrived at a value of α approximating to $\frac{2}{3}$, the value fluctuating slightly with the varying compositions used.

Subsequent investigators, notably Charbonnier,‖ followed by H. Lorenz,¶ Hadcock,** and Henderson and Hassé,†† have taken $\alpha = 1$, an assumption which has

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* 'Mémorial des Poudres et Salpêtres,' vol. 6, pp. 256–391 (1893).

† 'Traité d'Artillerie,' 1839.

‡ *cf.* Berthelot 'Sur la Force des Matières Explosives,' vol. 1, p. 85 (1883).

§ According to Roux and Sarrau, $\alpha = \frac{1}{2}$; Sébert, Hugoniot, and Moisson took $\alpha = 1$. For a very full list of references, *cf.* Cranz, 'Lehrbuch der Ballistik,' vol. 2 (1926).

‖ 'Balistique Intérieure' (1908).

¶ H. Lorenz, 'Ballistik, die mechanischen Grundlagen der Lehre vom Schuss' (1917).

** 'Proc. Roy. Soc.,' A, vol. 94 (1918).

†† 'Proc. Roy. Soc.,' A, vol. 100 (1922).

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formed the basis of by far the larger part of modern ballistic investigations ; a slight modification to the law, namely $R = A + \beta p$, where A is small, has been assumed by MANSELL,* LEES and PETAVEL,† PROUDMAN,‡ and MURAOUR.§ GOSSOT and LIOUVILLE|| accept a pressure index law, and adhere to the value of α originally ascertained by VIEILLE.

Formulæ of the types instanced above can be utilised to interpret the features of propellant explosion with reasonable accuracy over a relatively wide range of experimental conditions, although as shown by WOLFF,¶ the value of β for a given propellant composition varies with the loading conditions. No attempt was made, however, before the work of LÉTANG** to give a physical justification, either of the form of the assumed law or of the values of the constants. LÉTANG investigated the problem from the standpoint of the kinetic theory of gases, along the lines of argument normally followed for the consideration of collision effects between free moving molecules, the respective total energies of the colliding molecules as well as temperature being accepted as the dominant quantities, and the distribution being specified as MAXWELLIAN. He arrived at a formal expression for the rate of burning, as a function of relevant kinetic and thermodynamic quantities, which lent considerable support to the law adopted and utilised by CHARBONNIER.

LÉTANG's work marked a definite advance in the mode of treatment of propellant combustion problems ; and though the deductions from his hypothesis were found in several respects to be not in accord with the results of experiment, the general indications as to comparative magnitudes were usually of the right order. SCHWEIKERT's treatment†† in certain aspects parallels that of LÉTANG, and particularly with regard to the acceptance of the total energy of the impinging molecules as being operative and dominant. Both arrived at expressions for the mode of combustion of propellants, in which the rate of burning under constant temperature conditions included, amongst other things, a factor directly proportional to the pressure ; and it would seem that any hypothesis based on the kinetic theory of gases must necessarily lead to the same conclusion.

During the past few years MURAOUR, assuming the rate of burning to be a linear function of the pressure, has carried out a series of investigations of the effect on the value of $\int p\,dt$ (which by his hypothesis should be inversely proportional to the rate-of-burning constant) of varying the loading conditions, for a variety of propellants of

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* 'Phil. Trans.,' A, vol. 207 (1907).

† 'Proc. Roy. Soc., A, vol. 79 (1907).

‡ 'Proc. Roy. Soc.,' A, vol. 100 (1922).

§ 'Bulletin de la Société Chimique de France,' vol. xli, p. 1451, (1927) ; vol. xlvii, p. 261 (1930).

|| GOSSOT and LIOUVILLE, 'Traité des Effets des Explosifs' (1919).

¶ 'Kriegstechnische Zeitschrift,' vol. 6 (1903).

** 'Mémorial de l'Artillerie Française,' vol. 1, pp. 955–999 (1922).

†† SCHWEIKERT, 'Innere Ballistik' (1923).

different composition. He found that for a given propellant composition the value of the integral is relatively unaffected by the loading conditions in the closed vessel, but that when the maximum pressures realised are less than 1000 kg./cm.^{2}, the value of $\int p\,dt$ falls progressively with decreasing maximum pressure.

The assembly of his experimental results led MURAOUR to the conclusion* that the propellant burns by reason of being brought to the temperature of decomposition by the shock of the gaseous molecules already liberated; that the temperature of the layer immediately in contact with the propellant surface (which he assumes to be lower than the temperature of explosion, on the ground that the reactions are not completed) governs for a given pressure the rate of burning of the powder; that at high pressures, on account of the high gas density, the adjacent hotter layers do not intermix with the layer immediately in contact with the propellant surface, while at low pressures such intermingling takes place, with the result that at low densities of loading† the powder burns faster than would be indicated by a law of direct proportionality to the pressure. He proceeds to argue that since the reactions in the successive gas layers are more rapid the higher the gas temperature, the difference between the temperature of the layer in immediate contact with the propellant surface and that of a layer further away will decrease with increasing temperatures of explosion. The comparative rates of burning of two propellants of differing chemical composition will on this hypothesis be not simply proportional to the respective temperatures of explosion, but will increase more rapidly than would be indicated by the direct ratio.

Reviewing the foregoing the inference is that the phenomenon under investigation is of the nature of mass action, in the main, temperature influences entering to an appreciable degree. Where temperature variations during the explosion are comparatively slight little inaccuracy numerically results from the assumption of a mean gas temperature, lower than the temperature of explosion, obtaining over the duration of the explosion. On general grounds it is known that increase of temperature has a marked influence in accelerating the rate of chemical reaction, and provision for this must be implicit in any formal statement of the rate-of-burning law. The general features of the experimental results obtained by MURAOUR are in agreement with our own observations; as regards the physical interpretation of the mechanism underlying the phenomena, however, it has been thought desirable to re-examine the problem from the standpoint of the quantum theory, to formulate on rational grounds an expression for the rate of burning of stabilised colloidal propellants, in terms of kinetic and thermodynamic quantities, and to submit the law so derived to experimental test.

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* 'Comptes Rendus de l'Académie des Sciences,' vol. 192, p. 227 (1931).

† The density of loading is defined as the ratio of the charge weight in gms. to the volume of the enclosure in cm^3, and is expressed by the symbol Δ.

II.—*Formulation of the Rate-of-Burning Law.*

For the purpose in view a propellant is taken to be a homogeneous isotropic colloid, thoroughly gelatinised during the process of manufacture, and composed basically of a mixture of nitrocellulose, nitroglycerine, and a stabiliser, such as symmetrical diethyl-diphenylurea (centralite) or mineral jelly (vaseline), together with traces of water and solvent. Subject to its physical consistency being such that neither fissuring nor desquamation occurs during combustion, the propellant must burn by parallel layers away from the ignited surface, there being no bias. The conversion of the solid propellant into gas is an exothermic reaction, and impulsive dissociation at any instant takes place under the influence of the incident molecules of the gas already liberated. All the gases under discussion are subject to the requirements of dissociative equilibrium, the constituents being CO_2, CO, H_2, H_2O, and N_2. Further, the temperatures are in every case so high that equilibrium readjustment of the constituents to temperature changes can be regarded as instantaneous, so that there can be no question of the occurrence of lag, consequent on any one type of molecule interfering with any other.

The burning of a propellant results from the action of a gas complex of molecules in a state of high thermal agitation. At low temperatures the main energy of a gas is found in the translational molecular motion; as the temperature increases molecular rotation sets in, and the molecules effectively attain full spin at normal temperatures. Further increase in temperature entails the setting up of internal vibrations. The consequences of the respective influences are manifested in the variation of mean molecular heats with temperature. When, therefore, molecules under high temperature conditions impinge on a solid at a comparatively low temperature, the tendency will be towards reversal of thermal flow, the vibrational part of the energy escaping first, followed by the rotational part, and finally by the translational part.

If a propellant be subjected to extremely high pressures in a surround, at a temperature below that of impulsive decomposition (subsequently referred to as the touch-off temperature)*, it experiences compression only, and, provided that conditions are not prolonged sufficiently for the effects of slow heating to come into operation, it returns to its normal state on release of the pressure, which as such therefore plays no part in the mechanism of ignition. The effect of the translational molecular motion is manifested through momentum as incident energy, operative on the propellant surface, giving rise to pressure, so that, following the preceding argument, although pressure imposes stress in the propellant material, it cannot of itself influence to any extent the chemical breakdown of the propellant at the surface. In this effect is included also the influence of the rotational energy, which may be expected to keep pace exactly with changes in

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* This is not the ignition temperature as ordinarily understood in connection with chemical stability tests, but corresponds to the low limit of the temperature of the surround giving rise to instantaneous inflammation of the propellant surface.

the translational energy.* There remains, therefore, only the vibrational part of the energy to be considered, as regards actual decomposition phenomena.

That many explosive substances are found among the compounds of carbon may be attributed to the chemical inertness of the carbon bond, which admits the existence of molecules whose arrangement only slightly conforms to the requirements of molecular equilibrium. A feeble mechanical impulse is often sufficient to overcome the internal atomic tensions, and to bring about the transition to a more stable arrangement and aggregation of the atoms. Other atomic groups are similarly characterised by the greater or less ease with which they break down, for example, nitrogen-oxygen radicals. A propellant may be visualised, therefore, as a structure in a state of unstable equilibrium, held in position by control struts. On their removal the structure collapses with liberation of the potential energy. Simultaneous removal of the struts causes immediate total collapse; partial removal causes partial collapse, with a tendency towards demolition of the remaining strutted portions. The model may be taken to illustrate the comparative effects of slow and of rapid heating, slow heating corresponding to partial demolitions, and rapid heating to simultaneous breakdown of the entire structure. The expectation is, therefore, that the more rapid the application of heat the higher will be the ignition temperature.

By reason of the presence of the chemical bonds the propellant may be accepted as an assembly of linear oscillators, the frequencies of which, owing to the occurrence of breakdown, are of the same orders as the frequencies of the impinging molecules. JEANS† examines the question of transfer of energy and the vibrations set up by molecular collisions. The argument is quite general and demonstrates that vibrations excited by collisions are small in comparison with the energy of the exciting agency, except in the case of resonance. Where, therefore, resonance is unlikely to occur, as, for example, between the frequencies of the translational and rotational molecular energy and propellant vibrational energy, little or no energy transfer takes place. The problem then is reduced to the consideration of the transfer of vibrational energy from the incident molecules to vibrational energy in the propellant, a transfer manifesting itself in the increase of the propellant temperature at the grain surface to the touch-off point.

The vibrational energy is quantized, and where a number of oscillators are available the *a priori* chance of transfer of a quantum is independent of the quantum, and of the number and energy conditions of the oscillators. Where transfer occurs, however, the actual chance may be and probably is influenced by the orientations of the oscillator axes, and by the phases of the vibrations. In considering the incidence of a number of molecular vibrators impinging on the vibrators in the surface of the propellant, the integrated effect comes into play, and this will be the same for all constituents of the

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* *cf.* JEANS, 'The Dynamical Theory of Gases,' p. 374.

† *Ibid.*, p. 364.

gas complex. Attached, therefore, to any vibrational quantum incident on the propellant surface will be a weighting factor Z, and as the transfer can only be in quanta, Z will weight the total vibrational energy incident on the propellant surface. It follows that if the weighted amount of incident vibrational energy per unit time be computed, it may be equated to the corresponding amount of energy required to raise the temperature of the propellant to the touch-off point, and this equation must yield the rate-of-burning law.

In the present state of knowledge the structure of a colloidal propellant, comprising a variety of ingredients, cannot be specified in a manner analogous to that for crystal structures. We are led, therefore, to consider the propellant as an entity with an intrinsic specific heat, and to state the amount of heat required to raise the temperature of the propellant per unit mass as the product of the specific heat into the temperature increase. If then in time dt an amount dx be burnt away along the normal to the surface of the propellant grain, the quantity of heat required per unit area to raise the temperature of the portion of the propellant affected from the initial temperature T_p to the touch-off temperature T_i is given by

$$dx \, . \, \sigma \, (T_i - T_p) \, \delta,$$

where σ is the specific heat of the solid propellant and δ is the density. The justification for the acceptance of the constancy of T_p during the combustion rests in the fact that colloidal propellants are extremely bad conductors of heat, and, further, that when unconsumed pieces of propellant are recovered after gun firing no difference from standard can be detected in their chemical and physical properties. During the process of combustion, therefore, conditions are repeated from layer to layer, precisely as if there had been no preliminary combustion of intervening layers. Each layer may be regarded as possessing the temperature T_p, and requiring the temperature T_i for decomposition at the surface. T_i in consequence is invariant during the explosion, having a value peculiar to the propellant composition under the special conditions.

We have previously shown* that, within the limits of measurement, no systematic difference is observable in the closed vessel between total combustion times for corresponding loading conditions in different enclosures, although variations in energy losses may be appreciable. The inference is that the rate of burning is essentially an intrinsic phenomenon depending solely on the propellant composition, and the detailed nature and condition of the gas immediately adjacent to the grain surface, and on the uncooled temperature of explosion. As the molecules are released at the grain surface they rush towards the walls of the explosion vessel, impulsive actions in collisions tending to equalise matters, so that the gas already given off during combustion acts as a mechanism for transferring excess action at the grain surface to the walls, where

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* 'Phil. Trans,' A, 682, vol. 230, p. 55 (1931). Subsequent references to this paper will be designated E.S., and the page or equation number quoted.

energy losses actually occur. We may picture, therefore, the gas in the vessel as distributed into three main zones, a narrow zone contiguous to the grain surface at the uncooled temperature of explosion T_0, the main gas body at a temperature T, and a third narrow zone comprising a layer at the wall surface, the temperature of which during the combustion phase being, by reason of convection, very nearly that of the main gas body.

If during the course of the combustion there should happen to be in the vessel any space unoccupied by the molecules, the tendency will clearly be for molecules to rush there from the surround, irrespective of the adjacent temperatures. It follows, therefore, that the immediate consequence of impulsive reactions will be a tendency towards equalisation of density throughout the enclosure, accompanied by a tendency towards equalisation of temperature. Thus no serious error is involved in assuming that the gas density at any instant is uniform within the enclosure, having the same value for all three zones.

Considering now the conditions obtaining within the narrow zone adjacent to the propellant surface, we can follow MURAOUR in accepting that the temperature must increase outwards from the propellant surface to a closely adjacent region, where the absolute uncooled temperature of explosion is attained. Molecules moving from this region towards the propellant surface will tend to drop in velocity, consequent on temperature drop. On the other hand, collision effects, and the fact that the molecules are of finite size, will tend to increase the effective molecular velocity in the direction specified. The two effects are of a compensatory nature, and to allow for this the conditions within the zone are assumed to be uncooled temperature T_0 and a gas obeying the normal BOYLE-CHARLES law. A more rigorous treatment, if practicable, would lead to the derivation of the molecular velocity in the form of a series, the first and most important term of which would be given by the foregoing simplified assumptions.

In usual molecular collision problems the molecules are free-moving and MAXWELLIAN distribution may be postulated. The problem here is not strictly analogous, as the collisions as regards effects at the surface of the propellant occur between free-moving molecules and those embedded in the surface. In the T_0 zone any attempt to specify the detailed nature of the gas complex from the standpoint of MAXWELLIAN distribution leads to formulæ unnecessarily complicated, for the immediate purpose in view, since mass effects are required. JOULE's simplification, therefore, has been taken, namely, that the molecular motion may be regarded as comprising six streams moving perpendicularly to the six faces of a cube, one stream towards each face, all possibilities of molecular collisions being neglected.

Consideration of molecular impact on an interface leads for a simple gas to the relationship

$$v^2 = \frac{3p_{0'}}{\Delta'},$$

where v is the velocity of the impinging molecules, p_0 is the uncooled pressure, and Δ' is the gas density. The equation of state of a simple gas is :—

$$p_0 = 8 \cdot 3155 \times 10^7 \,.\, \frac{1}{\mathrm{M}} \,.\, \Delta' \,.\, \mathrm{T}_0 \,, \quad \ldots\ldots\ldots\ldots \quad (1)$$

where p_0 is in dynes/cm.², and M is the molecular weight of the gas, T_0 being measured in °K. Substituting for p_0 there results :—

$$v = 1 \cdot 57945 \times 10^4 \sqrt{\frac{\mathrm{T}_0}{\mathrm{M}}} \,, \quad \ldots\ldots\ldots\ldots \quad (2)$$

v being measured in cm./sec., a relationship connecting the mean velocity of the gas molecule with the temperature and the molecular weight.

Considering one constituent of the gas complex of concentration g_1 gm. mols./gm. and molecular weight M_1, then the number of gm. mols. of the constituent gas per unit volume is $g_1 \Delta'$. One-sixth of this is streaming towards the propellant surface with velocity $v_1 = 1 \cdot 57945 \times 10^4 \sqrt{\frac{\mathrm{T}_0}{\mathrm{M}_1}}$. The quantity of gas impinging on the propellant surface, per unit area per unit time, is therefore $2 \cdot 6324 \times 10^3 \, g_1 \, \Delta' . \sqrt{\frac{\mathrm{T}_0}{\mathrm{M}_1}}$ gm.mols.

Denoting the mean molecular heat of any gas constituent between 0 °C. and t °C. by $\overline{\mathrm{C}}_v$, and the vibrational contribution to $\overline{\mathrm{C}}_v$ by $\tilde{\mathrm{C}}_v$, we have

$$\tilde{\mathrm{C}}_v = \overline{\mathrm{C}}_v - a, \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (3)$$

where a takes the values 5·961, 4·9675, and 6·0, for CO_2 ; CO, N_2 and H_2 ; and $\mathrm{H}_2\mathrm{O}$ respectively. The total vibrational heat above 0° C. available per gm. mol. is therefore

$$[\tilde{\mathrm{C}}_v]_{t^\circ} \,.\, t^\circ,$$

where $[\tilde{\mathrm{C}}_v]_{t^\circ}$ is determined from the value of $\overline{\mathrm{C}}_v$ corresponding to t° C.* The amount of vibrational heat in consequence available for transfer to the propellant per gm. mol. is

$$[\tilde{\mathrm{C}}_v]_{t^\circ} \, t^\circ - [\tilde{\mathrm{C}}_v]_{t_i^\circ} \,.\, t_i^\circ .$$

Applying the weighting factor Z, and extending the summation over all the constituents of the gas complex, the total amount of vibrational energy transferred in time dt is

$$2 \cdot 6324 \times 10^3 \, \mathrm{Z} \,.\, \Delta' \,.\, \sqrt{\mathrm{T}_0} \,.\, \tilde{\Sigma} \,.\, dt,$$

where

$$\tilde{\Sigma} = \Sigma \left[\frac{g_1}{\sqrt{\mathrm{M}_1}} \{ [\tilde{\mathrm{C}}_v]_{t^\circ} \,.\, t^\circ - [\tilde{\mathrm{C}}_v]_{t_i^\circ} \,.\, t_i^\circ \} \right].$$

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* The values of $\overline{\mathrm{C}}_v$ used in the present investigation are those given in E.S., Table V, p. 62.

This heat is communicated to the propellant, and raises its temperature to the touch-off point. The rate of burning under any surface is consequently given by

$$\frac{dx}{dt} = \frac{2 \cdot 6324 \times 10^3\, \mathrm{Z} \,.\, \Delta' \,.\, \sqrt{\mathrm{T}_0} \,.\, \tilde{\Sigma}}{\sigma\delta\,(\mathrm{T}_i - \mathrm{T}_p)} \quad \ldots\ldots\ldots\ldots \quad (4)$$

Assuming burning to take place by parallel layers, and defining the *size* D of the propellant to be such that D/2 is the greatest depth burnt away below any receding surface before the whole of the grain is consumed; then, if $\phi(f)$ be the fraction of propellant burnt off at any instant corresponding to a remaining thickness Df, for all normal shapes of grain

$$\phi(f) = (1 - f)(1 + \theta f) \quad \ldots\ldots\ldots\ldots \quad (5)$$

where $|\theta| \ngtr 1$, end effects being neglected.

With this definition $x = (1 - f)\,\mathrm{D}/2$, so that

$$\frac{dx}{dt} = -\frac{\mathrm{D}}{2}\frac{df}{dt}. \quad \ldots\ldots\ldots\ldots \quad (6)$$

So far the equations obtained refer to conditions in the immediate vicinity of the propellant surface. To refer matters to the position in the vessel at which observations can be made, resort may be had to the equation of state of the main body of the liberated gas, namely,*

$$p = \frac{84 \cdot 80\,\{(\Sigma \text{ gm. mols.})/\text{gm.}\} \,.\, \mathrm{T}}{\frac{1}{\Delta'} - \eta}, \quad \ldots\ldots\ldots\ldots \quad (7)$$

where p is the pressure at the instant t, T the mean temperature, and η the co-volume of the gas-complex.

Eliminating x and Δ' between equations (4), (6) and (7), there results for the rate of burning along the least dimension of the grain :—

$$-\mathrm{D}\frac{df}{dt} = \frac{\mathrm{BT}_0}{\mathrm{T}} \,.\, \frac{p}{1 + \frac{\eta}{\lambda} \cdot \frac{\mathrm{T}_0}{\mathrm{T}} \cdot p} \quad \ldots\ldots\ldots\ldots \quad (8)$$

where

$$\lambda = 84 \cdot 80\,\{(\Sigma \text{ gm. mols.})/\text{gm.}\} \,.\, \mathrm{T}_0, \quad \ldots\ldots\ldots\ldots \quad (9)$$

and

$$\mathrm{B} = \frac{5 \cdot 2648 \times 10^3\, \mathrm{Z}\, \sqrt{\mathrm{T}_0} \,.\, \tilde{\Sigma}}{\lambda\sigma\delta\,(\mathrm{T}_i - \mathrm{T}_p)}. \quad \ldots\ldots\ldots\ldots \quad (10)$$

Expressed intrinsically, equation (8) takes the form

$$-\mathrm{D}\frac{df}{dt} = \mathrm{B}\lambda\,\Delta'. \quad \ldots\ldots\ldots\ldots \quad (8)\,(\mathrm{i})$$

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* E.S., equation (19).

In arriving at equation (8) ideal conditions have been postulated, and only that stream of the gas molecules incident on the surface of the propellant has been taken to be operative. This stream falling on the propellant breaks down the surface molecules, which are assumed to stream away immediately from the surface, taking no further part in the reaction until they reach the walls of the containing vessel, are reflected, and then become merged into the streams parallel to the propellant surface and into the incident stream, acquiring again the conditions appropriate to the temperature T_0 on passing into the zone immediately adjacent to the grain surface. The amount of heat required to raise 1 gm. of the propellant to the touch-off point is in the region of 80 calories, and the calorimetric value of most propellants is seldom less than 750 cals./gm. The propellant in consequence provides energy ample for its own disintegration once combustion has properly started. Presuming, therefore, that the propellant is properly stabilised, and burns in consonance with the model taken, it is to be anticipated that Z will be substantially independent of the propellant composition, having a value less than unity, since it is a measure of the fraction of the incident vibrational energy operative.

Departures from the model may take place in a variety of ways. For example, there may be fissuring under pressure, if the propellant be of a brittle nature. Moreover, if no stabiliser be present, there may be selective ignition in the sense, for example, that nitroglycerine molecules may ignite and break down more rapidly than nitrocellulose molecules (the touch-off temperature of nitroglycerine has been determined by SNELLING and STORM* to lie between 215° C. and 222° C., and the touch-off temperature for nitrocellulose is given by STOKES and WEBER† as 300° C.). These conditions, if operative, will result in an effectively increased burning surface, and the rates of burning observed experimentally will in such cases be greater than those that would be derived from equation (8), the departures becoming more pronounced the more brittle the propellant, the greater the percentage of nitroglycerine available, and the larger the size of the propellant grain, the total time of burning being more prolonged.

The nature of the vibrational heat summation term throws light on the problem of primary ignition. If the temperature of the igniting gases never attains the touch-off temperature of the propellant, ignition will not take place. Should, however, the temperature only slightly exceed the touch-off value, conditions become very sensitive, as the prime operating factor is essentially the excess of the temperature of the igniting gases over the touch-off temperature of the propellant. This condition only affects the start of burning, for as disintegration of the propellant proceeds the emanating gases take control. The point, however, is of considerable consequence as regards standardisation of ignition conditions, and more so in the gun than in the closed vessel.

The various algebraic forms, quoted in Section I, of the rate-of-burning law in terms of the pressure, are in their separate ways particular methods for fitting numerically

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* U.S. Bureau of Mines, Tech. Paper No. 12 (1912).

† U.S. Bureau of Standards, Tech. Paper No. 98 (1917).

the general expression (8). For example, if a mean value be taken for the terms in the denominator the expression

$$-\mathrm{D}\frac{df}{dt}=\beta p$$

is immediately derived. If T be assumed constant, the equation takes approximately the form

$$-\mathrm{D}\frac{df}{dt}=\frac{\beta p}{1+\mathrm{A}p},$$

a form which numerically can be closely fitted by a pressure-index law.* If allowance be made for the fact that under closed vessel conditions the temperature at the start is lower than the mean gas temperature during the explosion, the values so derived can be made to conform to numerical values given by the expression

$$-\mathrm{D}\frac{df}{dt}=\mathrm{A}+\beta p,$$

where A is small. The quantity usually written β in the first of these three approximations (the form in most general use) is in effect equal to

$$\frac{\mathrm{BT}_0}{\mathrm{T}\left(1+\frac{\eta}{\lambda}\cdot\frac{\mathrm{T}_0}{\mathrm{T}}\cdot p\right)},$$

and it will be seen that this quantity, other things being equal, increases with decreases in T and in p. The experimentally derived value of β, assuming the law of direct proportionality to hold, is known in closed vessel observations to increase with increase of propellant size and with decrease in the density of loading, in both of which cases the mean value of T decreases.

The occurrence of the term $(\mathrm{T}_i-\mathrm{T}_p)$ in the denominator of B is in accordance with the known fact that the rate of burning increases with T_p†; if T_p closely approaches T_i a small amount of incident energy only is required to cause breakdown.‡ It will be shown later that $\tilde{\Sigma}$ increases more rapidly than would be indicated by a law of direct proportionality with T_0.

III.—*Analysis of Closed Vessel Pressure-Time Curves.*

The analytical scheme for obtaining numerical values from pressure-time curves under closed vessel conditions rests basically on equations (5), (7) and (8).

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* The consequences of this form as regards the theory of burning in the gun have been investigated by CLEMMOW, 'Phil. Trans.,' A, vol. 227, pp. 345–382 (1928).

† MANSELL, *loc. cit.*

‡ BRUNSWIG, 'Explosives,' p. 21 (1909).

Let V be the volume of the vessel in cm.^{3}, and C the charge weight fired in gms. At the instant t the amount of charge burnt is $C\phi(f)$, and the amount of solid propellant remaining is $C\{1-\phi(f)\}$. The amount of charge unburnt occupies a volume $C\{1-\phi(f)\}/\delta$, and the free volume available for the gas is in consequence

$$[V - C\{1-\phi(f)\}/\delta].$$

We have therefore

$$\Delta' = \frac{C\,\phi(f)}{V - \dfrac{C\{1-\phi(f)\}}{\delta}} = \frac{\Delta\,\phi(f)}{1-\dfrac{\Delta}{\delta}\{1-\phi(f)\}}. \qquad (11)$$

Substituting in equation (7), the equation of state becomes :—

$$p = \frac{\dfrac{\lambda T}{T_0}\,.\,\Delta\phi(f)}{1-\dfrac{\Delta}{\delta}\{1-\phi(f)\}-\eta\,\Delta\phi(f)} \qquad (12)$$

From equation 8 (i) there results

$$-D\frac{df}{dt} = \frac{B\lambda\,\Delta\phi(f)}{1-\dfrac{\Delta}{\delta}\{1-\phi(f)\}}. \qquad (13)$$

Eliminating λ between equations (12) and (13)

$$-\int\left[\frac{1-\dfrac{\Delta}{\delta}\{1-\phi(f)\}}{1-\dfrac{\Delta}{\delta}\{1-\phi(f)\}-\eta\,\Delta\phi(f)}\right]df = \frac{BT_0}{D}\int\frac{p}{T}\,dt \qquad (14)$$

Integration of the left-hand side of equation (14) is a matter of quadratures. The integration of the right-hand side can be carried out when both p and T are known to a time basis. The pressure-time curve furnishes the first requisite, but so far experimental methods have not been fully developed for ascertaining the temperature at any moment during the explosion.

To turn the difficulty, the procedure adopted has been to arrange experimental conditions, so that cooling and energy losses are reduced to a minimum, not exceeding 4 per cent. in the worst case considered, and the temperature in consequence remains practically constant throughout the explosion. The desired conditions are realised by firing the smallest practicable propellant size, at a high density of loading, in the largest closed vessel volume available. If the value assigned to the temperature during combustion be that obtaining at the instant of maximum pressure (T_m), little error will result from the terms in the summation making the greatest contribution to the total integral, the main chance of error occurring at the start of the time rise; the order of error magnitude being

$$\Sigma \left\{ \frac{p\,(\mathrm{T}_m - \mathrm{T})}{\mathrm{T}_m \mathrm{T}}\, dt \right\},$$

where the summation extends over a relatively short period of time at the start, T being the temperature realised at the instant t. In the conditions it is known that T very rapidly approaches the value T_m, and p itself within the interval of time considered is small, so that the error occurring through evaluating the integral as $\frac{1}{\mathrm{T}_m}\int p\,dt$ in place of $\int \frac{p}{\mathrm{T}}\,dt$ is at most of the order of 1 per cent.*

With an assumed constancy of T, writing $p_m/p_0 = \mathrm{T}_m/\mathrm{T}_0$, where the suffix m refers to conditions at maximum and the suffix o to uncooled conditions, equation (14) may be recast into the form

$$\int_0^t p\,dt = \frac{\mathrm{D}}{\mathrm{B}} \cdot \frac{p_m}{p_0} \cdot \mathrm{I}_{(1,\,f)}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (14)\ (\mathrm{i})$$

where

$$\mathrm{I}_{(1,\,f)} = \int_f^1 \left[\frac{\delta\eta\left(1 - \frac{\Delta}{\delta}\right)}{(\delta\eta - 1)\left[1 - \frac{\Delta}{\delta}\{1 + (\delta\eta - 1)\,\phi\,(f)\}\right]} - \frac{1}{\delta\eta - 1} \right] df$$

Considering the part of the integrand

$$\mathrm{F} = \frac{1 - \frac{\Delta}{\delta}}{1 - \frac{\Delta}{\delta}\{1 + (\delta\eta - 1)\,\phi\,(f)\}}$$

both numerator and denominator are positive. Also, since $\delta\eta > 1$ and $\phi\,(f)$ is always positive, F always increases with Δ for any given value of f, since

$$\frac{d\mathrm{F}}{d\Delta} = \frac{(\delta\eta - 1)\,\phi\,(f)}{\left[1 - \frac{\Delta}{\delta}\{1 + (\delta\eta - 1)\,\phi\,(f)\}\right]^2},$$

and is therefore always positive. Thus, for any range of f, $\mathrm{I}_{(1,\,f)}$ always increases or

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* The immediate object here is the development of an analysis for the verification of the constancy of Z for the propellant compositions under investigation, these possessing values of B having a total spread of 66 per cent. about the mean. For this specific purpose the occurrence of an error of the order of 1 per cent. at most in the assessment of B is unimportant, and particularly so as the order of the spread in the deduced values of Z is unaffected, the error in B being always in the same direction.

decreases with Δ, and it follows that $\int_0^{t_m} p\,dt$ decreases with Δ. Further, for charges of the same size of propellant at the same density of loading, if p_m decreases through increased cooling conditions, $\int_0^{t_m} p\,dt$ also decreases. This is verified by experiment, since the duration of the explosion is unaffected by increased cooling, pressure values diminishing (*cf.* E.S., p. 55).

The main term in the integrand may be written:—

$$\frac{\delta^2\eta\left(1-\frac{\Delta}{\delta}\right)}{(\delta\eta-1)^2\,\theta\,\Delta}\cdot\frac{1}{f^2+\frac{1-\theta}{\theta}f+\frac{(1-\eta\Delta)\,\delta}{(\delta\eta-1)\,\theta\,\Delta}}=\frac{\delta^2\eta\left(1-\frac{\Delta}{\delta}\right)}{(\delta\eta-1)^2\,\theta\,\Delta}\cdot\frac{1}{(f+p+iq)\,(f+p-iq)},$$

where

$$2p=\frac{1-\theta}{\theta},\quad p^2+q^2=\frac{(1-\eta\Delta)\,\delta}{(\delta\eta-1)\,\theta\,\Delta},$$

therefore

$$\mathrm{I}_{(1,f)}=\frac{\delta^2\eta\left(1-\frac{\Delta}{\delta}\right)}{(\delta\eta-1)^2\,\theta\,\Delta}\cdot\frac{1}{2iq}\log\left\{\frac{1+p-iq}{1+p+iq}\cdot\frac{f+p+iq}{f+p-iq}\right\}-\frac{1}{\delta\eta-1}(1-f)$$

$$=\frac{\delta^2\eta\left(1-\frac{\Delta}{\delta}\right)}{(\delta\eta-1)^2\,\theta\,\Delta}\cdot\frac{1}{q}\tan^{-1}\frac{q\,(1-f)}{p+p^2+q^2+f\,(1+p)}-\frac{1}{\delta\eta-1}(1-f).$$

With this form p and q have been assumed real (as, for example, when $\theta=1$, where $p=0$). The term q vanishes when

$$\frac{(1-\eta\Delta)\,\delta}{(\delta\eta-1)\,\theta\,\Delta}=p^2=\left(\frac{1-\theta}{2\theta}\right)^2.$$

Values of θ less than the positive fractional root of this equation make q^2 negative. In this case the expression for $\mathrm{I}_{(1,f)}$ takes the $\tanh^{-1}$ or logarithmic form, as can otherwise be seen by considering the case of $\theta=0$.

All the propellant compositions used in the present investigation have been pressed in the shape of long cylindrical cords, this being the shape best suited to unimpeded gas delivery. $\phi\,(f)$ in consequence takes the form $(1-f^2)$, and the value of the left-hand side of equation (14) between the limits 1 and 0 becomes

$$\mathrm{I}_{(1,0)}=\frac{\eta\,(\delta-\Delta)}{\delta\,\Delta\left(\eta-\frac{1}{\delta}\right)^2}\sqrt{\frac{\left(\eta-\frac{1}{\delta}\right)\Delta}{1-\eta\Delta}}\,.\tan^{-1}\sqrt{\frac{\left(\eta-\frac{1}{\delta}\right)\Delta}{1-\eta\Delta}}-\frac{1}{\delta\eta-1}\,.\;.\;.\quad(15)$$

The value of B may therefore be experimentally determined from the relationship

$$B = \frac{I_{(1,0)} \cdot D}{p_0 \int_0^{t_m} \frac{p}{p_m} dt} . \qquad (16)$$

The procedure that has been adopted for measuring pressure-time curves is as follows :—The maximum pressure p_m is first ascertained, and time intervals are measured corresponding to $p_m/50$, $3p_m/50$, $5p_m/50$ . . . $49\,p_m/50$, the end conditions being computed separately. At the start of the time-rise it follows from the equations that $\int p\,dt$ is very nearly directly proportional to p, so that the value of the integral up to $p_m/50$ is one-half of the value of the integral between $p_m/50$ and $3\,p_m/50$. The theory indicates approximate constancy of the contributions to $\int \frac{p}{p_m} dt$ corresponding to the intervals at the early stages, and measurements show that this is in general true. On these grounds the effect of the starting pressure has been neglected explicitly, being included in the pressure as measured.

There is a practical difficulty in assessing with the accuracy required the precise instant at which maximum pressure is reached. To overcome this a relationship intrinsic to the time-rise is used, connecting pressures and times in the neighbourhood of maximum. The temperature here may be assumed to be constant and the equations underlying the phenomenon may be written :—

$$-\frac{df}{dt} = Ap, \text{ where A is a constant, and } \frac{p}{p_m} = 1 - f^2.$$

Combining the two expressions,

$$-\frac{1}{1-f^2}\frac{df}{dt} = \frac{A}{p_m}, \text{ with } f \longrightarrow 0.$$

This may be written

$$(1 + f^2 + f^4 + f^6 + \ldots)\, df = -\frac{A}{p_m} dt,$$

leading to

$$\left[f + \frac{f^3}{3} + \frac{f^5}{5} + \ldots\right]_f^0 = -\frac{A}{p_m}\Big[t\Big]_{-t}^0$$

time being measured from the instant of maximum pressure.

Denoting p_a and p_b as the pressure corresponding to $-t_{(a,0)}$ and $-t_{(b,0)}$, and eliminating A, there results :—

$$\sqrt{p_m - p_a} \cdot \left[1 + \tfrac{1}{3}\left(\frac{p_m - p_a}{p_m}\right) + \ldots\right] = \frac{t_{(a,0)}}{t_{(b,0)}} \sqrt{p_m - p_b} \cdot \left[1 + \tfrac{1}{3}\left(\frac{p_m - p_b}{p_m}\right) + \ldots\right].$$

(This intrinsic relationship should be true to within ± 1 per cent. even if the temperature varies slightly over the time period considered, since a ratio only is involved.)

The relationship leads to :—

$$t_{(a,0)} = \frac{t_{(b,a)}}{\sqrt{\dfrac{p_m - p_b}{p_m - p_a}} \cdot \left\{ \dfrac{1 + \frac{1}{3}\left(\dfrac{p_m - p_b}{p_m}\right) + \ldots}{1 + \frac{1}{3}\left(\dfrac{p_m - p_a}{p_m}\right) + \ldots} \right\} - 1} . \quad . \quad . \quad . \quad . \qquad (17)$$

All the quantities on the right-hand side of this expression are ascertainable from the observed pressure-time curve, and give $t_{(a,m)}$, the interval between p_a and p_m. Taking $p_a = 49\ p_m/50$ and $p_b = 47\ p_m/50$, we have

$$t_{(a,m)} = 1 \cdot 3226\ t_{(b,a)},$$

where $t_{(b,a)}$ is the time interval measured between $47\ p_m/50$ and $49\ p_m/50$.

The foregoing treatment applies provided that the conditions of the explosion are such that $f = 0$ when $p = p_m$. Where the circumstances lead to the chance of the occurrence of maximum pressure before complete combustion, an estimate of the value of f corresponding to p_m may be made in two ways :—

I. Generalising for conditions near maximum the equation for energy losses previously obtained,* we have :—

$$C\,(1 - f^2)\,(T_0 - T)\,s = bp^2 S + (T - T_w)\,aS\sqrt{t}, \quad . \quad . \quad . \quad . \quad . \quad . \qquad (18)$$

where C is the charge weight fired in gms., s is the mean specific heat of the gas complex over the temperature range concerned, a and b are constants of the vessel, S is the wall surface, T_w is the initial wall temperature, and T is the temperature of the gases at any instant t. We may take also as sufficiently accurate :—

$$\frac{p}{p_0} = \frac{T}{T_0}\,(1 - f^2). \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (19)$$

Further,

$$-\,D\,\frac{df}{dt} = \frac{BT_0 p}{T + \frac{\eta}{\lambda}\,T_0 p}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (8)$$

Differentiating equations (18) and (19), with respect to t, putting $dp/dt = 0$ for conditions at maximum pressure, and eliminating with the help of equation (8) df/dt and dT/dt, there results :—

$$\frac{2BT_0 p_m f_m}{D\left(T_m + \frac{\eta}{\lambda}\,T_0 p_m\right)} \left\{ CsT_0 + \frac{aST_m\sqrt{t_m}}{1 - f_m^{\,2}} \right\} = (T_m - T_w)\,aS \cdot \frac{1}{2\sqrt{t_m}},$$

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* E.S., equation (5).

and approximating, by writing $(1 - f_m{}^2) = 1$ in the denominator of the second term on the left-hand side, we have :—

$$f_m = \frac{a\mathrm{SD}\,(\mathrm{T}_m - \mathrm{T}_w)\left(\mathrm{T}_m + \frac{\eta}{\lambda}\,\mathrm{T}_0 p_m\right)}{4\mathrm{BT}_0 p_m \sqrt{t_m}\,.\,(\mathrm{C}s\mathrm{T}_0 + a\mathrm{ST}_m\sqrt{t_m})}. \quad \ldots \ldots \ldots \quad (20)$$

II. Alternately, a method intrinsic to the pressure-time rise may be adopted, and as f at the instant of maximum pressure cannot be assumed to be zero, three values of the pressure must be considered. Denote them by p_1, p_2, p_3, and let them represent, for example, 41/50ths, 45/50ths, and 49/50ths of p_m respectively. Over this region the temperature is assumed uniform, and to a first order $f_1{}^2 = {\cdot}18, f_2{}^2 = {\cdot}10, f_3{}^2 = {\cdot}02$. Expanding the right-hand side of equation (13), and rejecting powers higher than f^5, we have after one integration :—

$$f + \left(1 - \frac{\Delta}{\delta}\right)\frac{f^3}{3} + \left(1 - \frac{\Delta}{\delta}\right)\frac{f^5}{5} = \frac{\mathrm{B}\lambda\Delta}{\mathrm{D}}\,t_{(f,\,0)}, \quad \ldots \ldots \quad (21)$$

where $t_{(f,\,0)}$ is the interval between the instants corresponding to f and to $f = 0$.

From equation (12), neglecting $\Delta^2 f^4$ and higher powers,

$$p = \frac{\lambda\mathrm{T}\Delta}{\mathrm{T}_0\,(1 - \eta\Delta)}\left\{1 - \frac{1 - \frac{\Delta}{\delta}}{1 - \eta\Delta}\,f^2 + \frac{\Delta\left(\eta - \frac{1}{\delta}\right)}{1 - \eta\Delta}\,f^4\right\}. \quad \ldots \quad (22)$$

There follows :—

$$\frac{p_1 - p_2}{p_2 - p_3} = 1 = \frac{f_1{}^2 - f_2{}^2}{f_2{}^2 - f_3{}^2}\,.\left[\frac{1 - \dfrac{\Delta\left(\eta - \frac{1}{\delta}\right)}{1 - \frac{\Delta}{\delta}}\,.\,(f_1{}^2 + f_2{}^2)}{1 - \dfrac{\Delta\left(\eta - \frac{1}{\delta}\right)}{1 - \frac{\Delta}{\delta}}\,.\,(f_2{}^2 + f_3{}^2)}\right]$$

Giving f_1, f_2, and f_3 their approximate values for the term in parentheses,

$$\frac{f_1{}^2 - f_2{}^2}{f_2{}^2 - f_3{}^2} = \mathrm{R} = \frac{1 - 0{\cdot}88\,\frac{\Delta}{\delta} - 0{\cdot}12\eta\,\Delta}{1 - 0{\cdot}72\,\frac{\Delta}{\delta} - 0{\cdot}28\eta\,\Delta}. \quad \ldots \ldots \ldots \quad (23)$$

From equation (21), following a similar procedure,

$$\frac{f_1 - f_2}{f_2 - f_3} = \mathrm{S} = \frac{1{\cdot}05846 - 0{\cdot}05846\,\frac{\Delta}{\delta}}{1{\cdot}15765 - 0{\cdot}15765\,\frac{\Delta}{\delta}}\,.\,\frac{t_{(1,\,2)}}{t_{(2,\,3)}}. \quad \ldots \ldots \ldots \quad (24)$$

From equations (23) and (24) the following relationships exist :—

$$\left.\begin{aligned} &\frac{f_1}{\kappa_1} = \frac{f_2}{\kappa_2} = \frac{f_3}{\kappa_3} \\ \text{where} \quad &\kappa_1 = 2\text{R} - \text{S} + \frac{\text{R}}{\text{S}} \\ &\kappa_2 = \text{S} + \frac{\text{R}}{\text{S}} \\ &\kappa_3 = 2 + \text{S} - \frac{\text{R}}{\text{S}} \end{aligned}\right\} \quad \ldots\ldots\ldots\ldots \quad (25)$$

Using these relationships, there results from equation (22), considering (p_2, f_2) and (p_3, f_3),

$$f_2^4 \cdot \frac{\Delta\left(\eta - \frac{1}{\delta}\right)}{1 - \eta\Delta}\left\{49 - 45\left(\frac{\kappa_3}{\kappa_2}\right)^4\right\} - f_2^2\left\{1 + \frac{\Delta\left(\eta - \frac{1}{\delta}\right)}{1 - \eta\Delta}\right\}\left\{49 - 45\left(\frac{\kappa_3}{\kappa_2}\right)^2\right\} + 4 = 0, \quad (26)$$

the solution of which yields a second approximation to the value of f_2, the corresponding values of f_1 and f_3 following from equations (25).

From equation (21),

$$\frac{t_{(1,0)}}{t_{(2,0)}} = \frac{f_1 + \left(1 - \frac{\Delta}{\delta}\right)\frac{f_1^3}{3} + \left(1 - \frac{\Delta}{\delta}\right)\frac{f_1^5}{5}}{f_2 + \left(1 - \frac{\Delta}{\delta}\right)\frac{f_2^3}{3} + \left(1 - \frac{\Delta}{\delta}\right)\frac{f_2^5}{5}} = t_{(1/2)}, \text{ say} \quad \ldots\ldots \quad (27)$$

The difference $t_{(1,2)}$ is known from the pressure-time curve, and therefore :—

$$t_{(2,0)} = \frac{t_{(1,2)}}{t_{(1/2)} - 1}. \quad \ldots\ldots\ldots\ldots \quad (28)$$

Knowing $t_{(2,0)}$ and the measured interval between p_2 and p_m, the time interval $t_{(m,0)}$ between the occurrence of maximum pressure and the point of complete combustion follows, whence the value f_m at maximum may be computed.

Where there is relatively little cooling method I may be adopted, but in cases where there is a chance of appreciable unconsumed at the instant of recorded maximum pressure the use of method II is advisable, as it involves solely quantities intrinsic to the pressure-time curve, and does not demand a preliminary knowledge of the nature of the propellant. For the propellant charges fired in the present investigation, the indication from both methods is that in every case $\phi(f)$ at maximum may be taken as unity.

IV. *Propellants Specification and Relevant Thermodynamic Data.*

The propellant compositions used in the investigation were selected to give as wide a range of conditions as practicable. They comprise a straight nitrocellulose propellant, stabilised with diphenylamine ; Service Cordite M.D. (a cool nitrocellulose-nitroglycerine mixture, with mineral jelly as stabiliser); Service Cordite Mk. I (a hot nitrocellulose-nitroglycerine mixture, again with mineral jelly as stabiliser); and a hot nitrocellulose nitroglycerine mixture stabilised with centralite. The compositions cover the practicable spread in T_0 with stabilised propellants, and are so arranged that the relative proportions of the various simple gases occurring in the gas complex are widely different. The percentage compositions and the water-liquid calorimetric values are set out in Table I.

TABLE I.—Propellant Compositions and Calorimetric Values (Water-Liquid).

Propellant.	Cord Diameter (cm.).	Nitro-cellulose.[*]	N-content per cent.	Nitro-glycerine ($C_3H_5N_3O_9$).	Stabiliser.	Volatile matter (C_3H_6O) and Moisture (H_2O).	Cal. val. (w.l.) in cals./gm.[‖]
N.C.	0·2144	96·90	12·6	—	0·46[†]	2·64	891
M.D.	0·0965	65·68	13·0	29·53	4·45[‡]	0·34	1051
Mk. I	0·1340	37·00	13·0	58·00	5·00[‡]	Trace	1253
H.C.	0·2492	39·00	12·2	58·00	3·00[§]	—	1323

[*] The nitrocellulose is composed of a mixture of guncotton ($C_{24}H_{29}N_{11}O_{42}$) and collodion ($C_{24}H_{31}N_9O_{38}$), the N-content depending on the proportions used.

[†] Diphenylamine ($C_{12}H_{11}N$).

[‡] Mineral jelly ($C_{20}H_{42}$).

[§] Centralite ($C_{17}H_{20}N_2O$).

[‖] The heats of formation for calculating the calorimetric values are given in E.S., Table III, p. 59, with the exception of centralite (for which the heats of formation at 15° C. have been taken as 250 calories per gram and 67,000 calories per gm. mol.), and of mineral jelly (for which the corresponding values are 465 calories per gram and 131,130 calories per gm. mol.). In this connection we are indebted to Dr. G. ROTTER for drawing our attention to the fact that the figures quoted in E.S., Table III, for diphenylamine should read + 32·5 calories per gram and + 5490 calories per gm. mol. in place of − 325 and − 54,900 respectively as there entered.

The gas compositions and calculated temperatures of explosion for the various propellants are shown in Table II.

TABLE II.—Gas Composition and Temperature of Explosion (T_0).

Propellant.	Gas (gm. mols.)/gm.						T_0 (°K).
	CO_2.	CO.	H_2.	H_2O.	N_2.	(Σgm. mols.)/gm.	
N.C. ...	0·003649	0·019174	0·005611	0·009398	0·004363	0·042195	2927
M.D. ...	0·003654	0·017726	0·004736	0·010738	0·005006	0·041860	3265
Mk. I ...	0·005000	0·014180	0·002692	0·012339	0·005553	0·039764	3669
H.C. ...	0·007047	0·011305	0·001308	0·011821	0·005643	0·037124	3898

Evaluation of $\tilde{\Sigma}$.—In calculating the vibrational energy contribution, the amount deriving from $[\tilde{C}_v]_{t_i^\circ} \,.\, t_i^\circ$ may be neglected numerically in comparison with the amount from $[\tilde{C}_v]_{t^\circ} . t^\circ$ and the quantity $\tilde{\Sigma}$ may be evaluated as if it consisted of the latter term only. The calculation may best be illustrated by a numerical example, say, in the case of N.C. Here $T_0 = 2927$, so that $t^\circ = 2654$. We have :—

	Gas.			
	CO_2.	$CO + N_2$.	H_2.	H_2O.
g (gm. mols./gm.) …………	0·003649	0·023537	0·005611	0·009398
M (molecular weight) ………	44	28	2	18
$g/\sqrt{M}$ …………………………	0·00055012	0·0044480	0·0039676	0·0022151
$[\bar{C}_v]_{t^\circ}$ …………………………	10·27	5·912	5·762	9·74
$[\tilde{C}_v]_{t^\circ}$ …………………………	4·31	0·945	0·795	3·74
$\frac{g}{\sqrt{M}}[\tilde{C}_v]_{t^\circ}t^\circ$ …………………	6·293	11·156	8·371	21·987

Summing the values in the last line of the table, $\tilde{\Sigma} = 47 \cdot 807$, the assembly of the values of $\tilde{\Sigma}$ for all four propellants being entered in Table III, together with the values of λ, η, and $\sqrt{T_0}$, δ being taken as 1·58 gms./cm.^{3} for all four compositions.

TABLE III.—Thermodynamic Data.

Propellant.	λ*	η†	$\sqrt{T_0}$	$\tilde{\Sigma}$
N.C. …………………	10473	0·94	54·102	47·807
M.D. …………………	11590	0·96	57·140	63·928
Mk. I…………………	12372	0·96	60·572	88·238
H.C. …………………	12271	0·93	62·434	95·647

* λ is obtained from E.S. equation (15).
† η is obtained from E.S. equation (18).

It follows from the table that $\tilde{\Sigma}$ increases more rapidly than direct proportionality with T_0 would indicate; as between N.C. and H.C., for example, for a 33 per cent. increase in T_0 the value of $\tilde{\Sigma}$ is doubled.

The Specific Heat of the Solid Propellant σ.—The accurate determination of σ is by no means an easy matter (particularly in the case of the nitrocellulose), by reason of the low conductivity of the colloids, and reliable experimental data are scanty. The specific heats of M.D. and Mk. I compositions have been given by ROBERTSON as 0·347 and 0·365 respectively,* and that for liquid nitroglycerine at 10° C. by CHALON as 0·4248.† No direct evidence is available as regards N.C. and H.C., and in the circumstances appeal is made to KOPP's law for calculating the specific heats of the solid ingredients, the indications being referred to the experimental evidence as datum.

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* *Cf.* HENDERSON and HASSÉ, 'Proc. Roy. Soc.,' A, vol. 100, p. 467 (1922).

† CHALON, 'Les Explosifs Modernes,' p. 195.

The molecular heat of a solid compound, by KOPP'S law, is taken as equal to the sum of the atomic heats of the constituent elements, the values for C, H, N and O being 1·8, 2·3, 6·4 and 4·0 respectively; any slight increase in the specific heats due to temperature increment being neglected over the region concerned.* The values of the specific heats arrived at in this way for nitrocellulose, mineral jelly and centralite are 0·306, 0·470 and 0·324 respectively. Using these values for nitrocellulose and mineral jelly, from ROBERTSON'S figures the best mean value of the specific heat for nitroglycerine in the mixture comes out at 0·404, giving calculated values of σ for M.D. and Mk. I of 0·344 and 0·371 respectively, the differences from the values observed being $-$ 0·003 and $+$ 0·006 in the two cases. The value for nitroglycerine so derived is less than the value found experimentally for nitroglycerine in the liquid form, a result conforming to expectation as the ingredient is in a less mobile condition when incorporated in the propellant composition. The value, however, is well above the figure that would be indicated by KOPP'S law if the nitroglycerine were a solid.

Accepting the figure 0·306 for the N.C. propellant, the value of σ for H.C. can be computed either directly from KOPP'S law,† resulting in the figure 0·363, or on differences from the observed value of Mk. I, regarding 5 per cent. of mineral jelly as being replaced by 3 per cent. of centralite and 2 per cent. of nitrocellulose in the case of H.C., the contribution of the nitroglycerine remaining unaltered. This process leads to the figure 0·357, so that a mean value for σ of 0·360 cannot be far removed from the truth. The figures taken for σ for the various propellants used are, therefore: N.C., 0·306; M.D., 0·347; Mk. I, 0·365; H.C., 0·360.

The Touch-off Temperature, T_i.—At certain fairly well-defined temperatures, different for different explosives, propellants explode, the explosion temperatures depending very much upon experimental conditions, which must be kept strictly identical in comparative determinations.

STOKES and WEBER‡ carried out a series of experiments with various celluloid articles, also with smokeless and black powder, to determine the effect of variation of rate of heating on the explosion temperature registered. They employed a number of small glass test-tubes, kept in an oil-bath of constant temperature, a small piece of the material under investigation, weighing approximately 0·05 gm., being dropped into the tube, and a stop-watch started. A stopper was inserted loosely in the test-tube, and the time elapsing until explosion took place was noted. The procedure was carried out at temperatures of 170° C., 180° C., 200° C., and 220° C. The data from the experiments give a time-temperature explosion curve which yields considerable information concerning

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* If operative this is in the same direction for all four compositions, and does not affect comparative figures for Z.

† It is worth noting that by this method a mixture of 60·7 per cent. nitrocellulose, 25·3 per cent. nitroglycerine, and 14 per cent. centralite would give a calculated value of $\sigma = 0{\cdot}333$, as compared with the value 0·337 stated by MURAOUR, 'Comptes Rendus de l'Académie des Sciences,' vol. 191, p. 713 (1930).

‡ *Loc. cit.*

the behaviour of the samples in question. They found that the results could readily be duplicated, particular determinations being made at widely different periods.

As a result of their experiments STOKES and WEBER were led to define the ignition point of an explosive substance as the lowest temperature at which a sample would instantaneously burst into flame under conditions favourable to combustion. This temperature was determined for the various substances in the following manner. Small strips of the material were touched with a narrow porcelain tube containing a thermocouple, the tube being heated in an electric furnace, the temperature of which was maintained at the temperature of the test. The experimental procedure consisted in rapidly withdrawing the tube from the furnace and momentarily touching it with the edge of the sample under test, the fact being noted whether the sample burst into flame or not. The temperature of the furnace was then reduced and the samples re-tested. In this way they arrived at a lower limit to the temperature of instantaneous decomposition.

The observations of STOKES and WEBER for collodion cotton (nitrocellulose), smokeless powder and black powder are shown in Table IV.

TABLE IV.—STOKES and WEBER'S Observations.

Sample.	Time of heating to explosive decomposition (seconds).					Ignition temperature (° C.) (porcelain tube).
	170° C.	180° C.	190° C.	200° C.	220° C.	
Collodion cotton	870	165	67	56	18	300
Smokeless powder A	600	195	130	45	23	300
Smokeless powder B	190	130	—	90	25	
Black powder*	*n*	*n*	*n*	*n*	*n*	440

* The symbol *n* signifies failure to explode in less than 20 minutes.

The important conclusion may be drawn from the data assembled in Table IV that the shapes of the temperature-time cuves differ widely, so that the values obtained for time of heating to explosive decomposition at any given temperature yield an approximate indication only of the value of T_i. For our present purpose, therefore, we have been led to avoid resort to ordinary experimental methods of determining explosion temperatures, such as the bar or the oven method,* and to determine values of T_i appropriate to the conditions in the closed vessel from the experiments themselves.

The values of T_i for the various propellants must clearly lie between approximately

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* In the bar method the explosive is placed in recesses of constant temperature, and the temperature taken at which ignition occurs within 5 seconds. In the oven method the explosive is heated at the rate of 5° C. per minute, and the temperature noted at which ignition takes place. The values given by the oven method are of the order of 70° C. less than those given by the bar method.

220° C. (the value for nitroglycerine) and 300° C. (the value for nitrocellulose).* Varying T_p then between 26·7° C. (the standard charge temperature in closed vessel firings) and 0° C. will result in a variation of the order of 10 per cent. in the value of $(T_i - T_p)$, a quantity which, other things being equal, is directly proportional to the observed value of $\int_0^{t_m} \frac{p}{p_m} dt$ (slight variations in $\tilde{\Sigma}$ being neglected). An effect of this magnitude is readily detectable in the experimental conditions.

V.—*Experimental Values and Ascertainment of* T_i *and* Z.

A full description of the general experimental conditions for ascertaining the variation of pressure with time has been given in E.S. (pp. 39–45), the chamber employed in the present determinations having a length of 25·5 cm. and capacity 649 cm.^{3}, the surface exposed to the gases being 656·8 cm.^{2}. Charges of each of the propellants were fired at a density of loading 0·2479 in the case of N.C., M.D. and H.C., and 0·2211 in the case of Mk. I, two values of T_p being employed for each propellant. Measurements of typical records are shown in Table V, arranged in the form of time intervals

TABLE V.—Typical Time Interval Measurements. (10^{-3} sec.)

N.C., $\Delta = 0·2479$.		M.D., $\Delta = 0·2479$.		Mk. I, $\Delta = 0·2211$.		H.C., $\Delta = 0·2479$.	
$T_p = 26·7°$ C.	$T_p = -0·55°$ C.	$T_p = 26·0°$ C.	$T_p = 1·67°$ C.	$T_p = 26·0°$ C.	$T_p = 0·55°$ C.	$T_p = 26·7°$ C.	$T_p = 0·3°$ C.
1·717	3·233	1·371	1·470	1·322	1·606	1·234	1·054
0·911	1·083	0·383	0·455	0·386	0·462	0·558	0·605
0·627	0·731	0·253	0·281	0·220	0·297	0·432	0·458
0·556	0·634	0·188	0·188	0·207	0·193	0·348	0·367
0·496	0·502	0·162	0·181	0·139	0·159	0·297	0·305
0·479	0·451	0·136	0·157	0·131	0·165	0·234	0·253
0·403	0·405	0·111	0·121	0·121	0·127	0·196	0·221
0·356	0·359	0·106	0·119	0·093	0·107	0·183	0·212
0·308	0·349	0·096	0·109	0·091	0·095	0·173	0·187
0·313	0·314	0·093	0·099	0·089	0·093	0·157	0·173
0·288	0·307	0·082	0·089	0·081	0·084	0·154	0·168
0·269	0·280	0·075	0·085	0·072	0·080	0·133	0·160
0·268	0·278	0·071	0·083	0·072	0·075	0·146	0·143
0·252	0·268	0·064	0·079	0·072	0·072	0·121	0·132
0·256	0·266	0·066	0·076	0·070	0·075	0·125	0·145
0·255	0·251	0·067	0·071	0·070	0·077	0·124	0·140
0·244	0·264	0·068	0·069	0·075	0·078	0·121	0·127
0·256	0·254	0·065	0·071	0·075	0·076	0·124	0·131
0·260	0·276	0·067	0·077	0·072	0·071	0·114	0·129
0·272	0·278	0·068	0·076	0·072	0·078	0·137	0·154
0·278	0·312	0·070	0·080	0·079	0·089	0·134	0·154
0·284	0·327	0·082	0·095	0·086	0·091	0·154	0·161
0·354	0·395	0·093	0·100	0·108	0·114	0·190	0·214
0·540	0·563	0·133	0·148	0·136	0·174	0·281	0·284

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* The effect of the stabiliser in general is to act as a brake on the nitroglycerine, and thus prevent the propellant igniting at the touch-off temperature of nitroglycerine. Mineral jelly, however, owing to its relatively low flash point would not be expected to have a restraining influence of this nature as marked as that of, for example, centralite.

corresponding to the pressure stages intervals adopted. $(0·02\ p_m,\ 0·06\ p_m,\ 0·10\ p_m,\ \ldots\ 0·98\ p_m.)$

The table illustrates the general tendency for the time intervals to increase in magnitude with a reduction in the value of T_p. The mean values for $\frac{10^3}{p_m}\int_0^{t_m} pdt$ and the corresponding values of T_i found by the application of equation (16) are entered in Table VI for the various compositions.

TABLE VI.—Values of $\frac{10^3}{p_m}\int_0^{t_m} pdt$ and T_i.

Propellant.	T_p (° C.).	$\frac{10^3}{p_m}\int_0^{m} pdt$	T_i (° C.).
N.C.	26·7	4·6842	303
	—0·55	5·1463	
M.D.	26·0	1·3194	242
	1·67	1·4678	
Mk. I	26·0	1·3639	223
	0·55	1·5400	
H.C.	26·7	2·4072	263
	0·30	2·6764	

Using equations (7), (15), (16) and (10) for the calculation of p_0, $I_{(1,\,0)}$, B, and Z respectively, the values resulting are assembled in Table VII.

TABLE VII.—Values of p_0, $I_{(1,\,0)}$, B, and Z.

Propellant.	Δ	T_p.	p_0.	$I_{(1,\,0)}$.	B.	Z.
N.C.	0·2479	26·7	3385	1·201	0·01624	0·00167
M.D.	0·2479	26·0	3770	1·205	0·02338	0·00167
Mk. I	0·2211	26·0	3472	1·175	0·03325	0·00166
H.C..................	0·2479	26·7	3953	1·199	0·03140	0·00165

The values obtained for Z are quoted to three significant figures, the last of which must be taken as representative rather than exact in view of the small percentage uncertainties occurring in the quantities employed in the derivation.

Summary.

A rate-of-burning law for colloidal propellants has been deduced on formal grounds, following the hypothesis that the factor primarily operative in causing breakdown at the propellant grain surface is the vibrational energy of the incident gas molecules. The consequences of the law have been submitted to the test of experiment over a wide range of conditions for stabilised propellants, and the main supposition on which the derivation depends, namely, the constancy of the weighting factor (Z) for the incident vibrational energy, has been confirmed.

Accepting the constancy of Z, the law demonstrates that the rate of burning is directly proportional to the gas density at any instant, and to a function of the uncooled temperature of explosion, the gas surround, and the nature of the propellant. That the temperature of the gas surround enters, as well as the pressure, follows from the density factor, and affords an explanation of the tendency of the apparent rate-of-burning constant in empirical laws (assuming variation with pressure only) to increase with reduction in the density of loading, increase of propellant size, and conditions giving rise to increased cooling generally.

The investigation indicates that further progress rests in a more accurate knowledge and detailed specification of the nature of propellant colloids. Discussion has been restricted to combustion problems in closed vessels, no attempt being made to deal with the important deductions that derive from the application of the law to general ballistic conditions.

In conclusion, we wish to extend our thanks to Mr. J. G. Madden and Mr. C. M. Balfour for their help in the experimental side of the investigation, and to Commander A. C. Goolden for affording us facilities for carrying out the work and his interest in it. We desire also to acknowledge the courtesy of the Director of Artillery, the Director of Naval Ordnance, and the Ordnance Committee in approving publication.