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R. L. Scoria

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On the Thermodynamic Theory of Detonation

R. L. SCORAH, *Department of Mechanical Engineering, Stanford University*

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THE DETONATION WAVE

IN 1881, Berthelot and Vieille¹ and independently Mallard and Le Chatelier² discovered that when an explosive gas mixture is ignited at the end of a uniform tube, the initial slow progress of the combustion process is quickly accelerated to a high velocity which remains constant regardless of the length of the tube. This constant velocity combustion process is called the "detonation wave." These early studies, and those of others³ which followed, show that, once established, the detonation wave proceeds at a constant velocity which depends upon the constituent gases and their proportions in the explosive mixture. On the other hand, the speed of detonation is independent of (1) the method of ignition; (2) the material forming the tube; (3) the diameter of the tube, so long as a certain diameter (6-8 mm) is exceeded; (4) the tube end construction which may be closed or open; (5) the course of the tube which may be straight, coiled, or even zig-zagged. Further, the influence of moderate variations of the initial temperature and pressure is small. It appears, then, that the detonation velocity is a physical constant of the particular explosive gas mixture and as such should be amenable to thermodynamic analysis.

THEORIES OF THE DETONATION WAVE

In 1881, Berthelot and Vieille¹ suggested that the speed of the detonation wave was approximated by the mean translational velocity of the molecules in the burned gases, as calculated from the temperature attained in combustion. For some gas mixtures, it happens that the velocity thus predicted is verified by experiment but for many others, the agreement is unsatisfactory. In 1893, Dixon⁴ combined this idea with a complicated conception of sound waves but again, the

computed velocity agreed with experiment for some mixtures and not for others. Recently, Lewis⁵ has advanced a chain reaction theory in which the detonation velocity for the optimum mixture of the constituent gases is compared to the final velocity of the "carrier" in the reaction chain. This theory has not been extended to various mixtures of the same gases and so, at present, it must be regarded more as an attempt to visualize the reaction occurring within the wave. In 1899, Chapman⁶ approached this problem from the point of view of thermodynamics (including the flow of compressible fluids) and was able to compute detonation velocities in good agreement with those observed for the various detonating mixtures of the same gases. Apparently without knowledge of this earlier work, Jouguet,⁷ in 1905-6, gave an extensive development of this method and achieved a similar success. Using the Chapman-Jouguet theory, Lewis⁸ has recently recalculated the detonation velocity for various mixtures of hydrogen and oxygen using modern thermal data and considering the dissociation of the combustion products. His results, in general, agree very well with experiment.

This Chapman-Jouguet theory depends essentially on the thermodynamic relations for one-dimensional shock waves which were first correctly deduced by Hugoniot⁹ in 1887. It is important to note that these Hugoniot relations fail to define any particular detonation velocity but permit velocities ranging from a certain minimum to infinity. So far as is generally known, no rigorous argument has been made for selecting the velocity at which detonation becomes stable. To meet this difficulty, Chapman simply assumed that the detonation wave would proceed at the minimum velocity and it so happens that the velocities thus computed do agree very well with experiment. Jouguet also postulated

¹ Berthelot and Vieille, *Comptes rendus* **93**, 18 (1881).

² Mallard and Le Chatelier, *Comptes rendus* **93**, 145 (1881).

³ For references, see Bone and Townend, *Flame and Combustion in Gases*, 1927.

⁴ Dixon, *Phil. Trans. Roy. Soc. A* **184**, 97 (1893).

⁵ Lewis, *J. Am. Chem. Soc.* **52**, 3120 (1930).

⁶ Chapman, *Phil. Mag.* **47**, 90 (1899).

⁷ Jouguet, *J. de mathematique* **1905**, 347; **1906**, 6.

⁸ Lewis, *J. Am. Chem. Soc.* **52**, 3905 (1930).

⁹ Hugoniot, *J. de l'ecole polytech.* **57**, 3 (1887); **58**, 1 (1889).

stability at this minimum velocity, basing his arguments for doing so on a physical interpretation of his deduction that, at this speed, the burned gases move from the wave front at their acoustic velocity. Somewhat similar arguments have been advanced by Becker.¹⁰ It is the object of this paper to approach the problem of defining the speed at which detonation is stable by considerations of available energy and, for this purpose, the thermodynamic theory will be briefly outlined.

THE HUGONOT RELATIONS

Suppose that a plane detonation wave is traveling at its characteristic high and constant velocity through a gas mixture that is confined within a uniform tube. At any plane 0 ahead of the wave, the gases are at rest, entirely undisturbed by the approaching wave front which is located between two moving planes, 1 just ahead of the wave front and 2 just behind. The notation used is as follows: velocity u , pressure P , specific volume V , moles of gas mixture N , temperature T , internal energy E , entropy S , available energy A . The unburned gases are fed into the wave front with properties identified by subscript 1 and the burned gases are discharged from the wave front with properties identified by the subscript 2. At any point ahead of the wave, the unburned gases have properties identified by the subscript 0 and are at rest with respect to the tube so that $u_0=0$. Aside from the velocity u and the available energy A , the properties at plane 0 are assumed to have the same values as at plane 1. Since the velocity of detonation is constant, it is assumed that the conditions immediately ahead and behind the wave front do not vary with time, and further, since the speed is high, it is assumed that the effect of heat losses is negligible. The principles of continuity of mass, conservation of energy, and the impulse law, then, provide the following relations:

Continuity,

$$u_1/V_1 = u_2/V_2. \quad (1)$$

Momentum,

$$P_1 + u_1^2/V_1 = P_2 + u_2^2/V_2, \quad (2)$$

¹⁰ Becker, *Zeits. f. Physik* 8, 321 (1922); N. A. C. A. Tech. Memo. 505, 506.

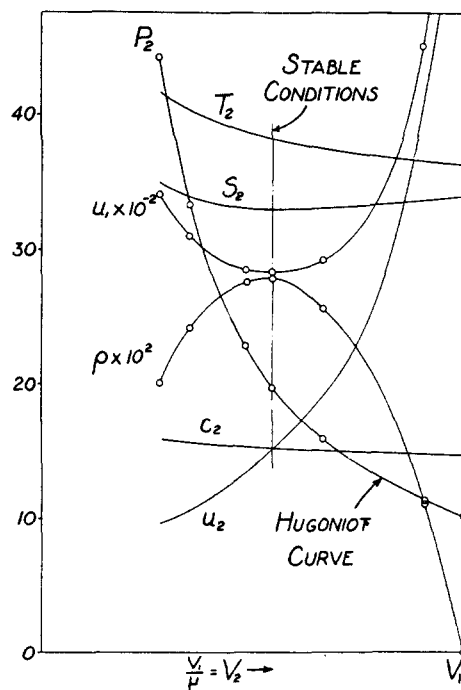


FIG. 1. The variation of properties along the Hugoniot curve.

Energy,

$$E_1 + P_1 V_1 + u_1^2/2 = E_2 + P_2 V_2 + u_2^2/2. \quad (3)$$

The simultaneous solution of Eqs. (1) and (2) gives Hugoniot's expressions for the velocities u_1 and u_2 :

$$u_1/V_1 = u_2/V_2 = [(P_2 - P_1)/(V_1 - V_2)]^{1/2}. \quad (4)$$

These expressions (4) can be used to eliminate the velocity terms in (3) and the result is Hugoniot's equation,

$$\frac{1}{2}(P_1 + P_2)(V_1 - V_2) = (E_2 - E_1). \quad (5)$$

Because of the high temperature attained by combustion within the wave front, the discharged material may be represented as a mixture of perfect gases. Further, the internal energy of these burned gases is assumed to be a function of temperature only. It follows that

$$P_2 V_2 = N_2 R T_2 \quad (6)$$

$$\text{and} \quad E_2 - E_1 = \int_{T_1}^{T_2} C_v dT - \Delta E, \quad (7)$$

where C_v is the instantaneous specific heat at constant volume of the burned gases and ΔE is the energy released during constant volume combustion. The values of N_2 , C_v and ΔE depend on the progress made by the combustion reactions which may be fixed either by assumption or by the requirements of thermodynamic equilibrium. For a given initial mixture, the four independent equations above (exclusive of equilibrium equations) establish relations between the five variables u_1 , u_2 , P_2 , V_2 and T_2 . These relations for compression waves, in which $V_2 < V_1$, are shown in Fig. 1. To reach a solution for the stable detonation velocity u_1 , another independent relation is required. It will be seen from Fig. 1 that the Hugoniot relations admit velocities ranging from a certain minimum to infinity. Chapman assumed this minimum value.

THE JOUGUET RELATIONS

Jouguet has shown that further relations may be obtained from Hugoniot's Eq. (5), the more important of which are conveniently derived in this somewhat different way. Since the conditions ahead of the wave front are regarded as constant, differentiation along the Hugoniot curve provides the equation,

$$(V_1 - V_2)dP_2 - (P_1 + P_2)dV_2 - 2dE_2 = 0.$$

Inasmuch as the composition of the burned gases is known, either by assumption or by the requirements of thermodynamic equilibrium, the entropy S_2 may be introduced by the relation $T_2 dS_2 = dE_2 + P_2 dV_2$ so that the above equation becomes

$$dS_2/dV_2 = [(V_1 - V_2)/2T_2] \times [(P_2 - P_1)/(V_1 - V_2) + dP_2/dV_2].$$

Now at a point where $dS_2/dV_2 = 0$, the derivative dP_2/dV_2 acquires the subscript s and the second derivative is

$$d^2S_2/dV_2^2 = [(V_1 - V_2)/2T_2][d^2P_2/dV_2^2]_s.$$

For a mixture of perfect gases, in which γ is the ratio of specific heats, it follows that

$$[d^2P_2/dV_2^2]_s = (d/dV_2)(-\gamma_2 P_2/V_2)_s = \gamma_2(\gamma_2 + 1)P_2/V_2^2,$$

which is always positive. Consequently, in waves of compression (where $V_2 < V_1$), the second derivative d^2S_2/dV_2^2 is always positive and the equation

$$(P_2 - P_1)/(V_1 - V_2) = -(dP_2/dV_2)_s = \gamma_2 P_2/V_2 \quad (8)$$

defines a point of minimum entropy. By multiplying both sides by V_2^2 , this equation becomes

$$V_2^2(P_2 - P_1)/(V_1 - V_2) = \gamma_2 P_2 V_2 \quad \text{or} \quad u_2 = c_2$$

where c_2 is the velocity of sound in the burned gases at temperature T_2 . The physical significance of this result is not at once clear. Jouguet ingeniously postulated that a sound wave, evidently, pursued the wave front and, by controlling the pressure P_2 , governed the velocity of detonation. He argued that the detonation velocity would be stable when this sound wave was just able to overtake the wave front, that is, when $u_2 = c_2$. So far as is generally known, this physical hypothesis has never been verified. Acting on these ideas, Jouguet chose Eq. (8) as the additional independent relation required to effect a solution for the detonation velocity u_1 . The variation of entropy and acoustic velocity along the Hugoniot curve is shown in Fig. 1. It will be seen that the detonation velocity thus postulated is exactly that assumed by Chapman, namely, the minimum value.

For computation purposes, Jouguet combined Eq. (7) with Eq. (5) and used the equation of state to eliminate the pressure terms in both (5) and (8). Then, if $\mu = V_1/V_2$, Eq. (5) becomes

$$\int_{T_1}^{T_2} C_v dT = \Delta E - (R/2)(\mu - 1)(N_2 T_2 + N_1 T_1/\mu),$$

and Eq. (8) becomes $\gamma_2 \mu^2 - (\gamma_2 + 1)\mu + N_1 T_1/N_2 T_2 = 0$, which are solved simultaneously for μ and T_2 . When combustion is considered to proceed to thermodynamic equilibrium, the additional composition variables may be eliminated by the like number of equilibrium equations. Having found μ and T_2 , the velocity of detonation

can be computed from $u_1 = \mu(\gamma_2 N_2 R T_2)^{1/2}$, which results from Eqs. (4) and (8).

THE AVAILABLE ENERGY OF STEADY FLOW

Suppose that steady flow is established within a rigid channel and that the temperature datum for available energy is T_0 . If this flow is *ideal*, that is frictionless and reversible, the energy equation accounting for any changes of state at thermodynamic equilibrium is $TdS = dE + PdV$, and the energy equation accounting for the mechanical equilibrium of the forces producing motion is $0 = VdP + udu + dL$, where dL represents high grade energy derived from the flow such as work derived by mechanical means.¹¹ The sum of these equations is

$$TdS - dL = dE + d(PV) + udu. \quad (9)$$

In general, the *actual* flow is passing from state 1 at section 1 to state 2 at section 2 involves a loss of available energy. It is possible, however, to measure the actual loss of available energy by substituting for the actual flow process, a series of reversible transformations from which the equivalent change of available energy can be estimated. Following the usual convention of signs for the energy equation, $(1 - T_0/T)TdS = dA + dL$, where $(1 - T_0/T)TdS$ is the available portion of any heat TdS added reversibly to the system, dA is the change of the available energy of the system, and dL is high grade energy as defined above. The change of the available energy of the system is, then $dA = TdS - T_0 dS - dL$. This equation becomes integrable by virtue of (9), that is

$$dA = dE + d(PV) + udu - T_0 dS$$

so

$$A_1 - A_2 = (E_1 + P_1 V_1 + u_1^2/2 - T_0 S_1) - (E_2 + P_2 V_2 + u_2^2/2 - T_0 S_2). \quad (10)$$

These above considerations have been studied by J. Willard Gibbs and others.¹²

¹¹ For the equations of flow of compressible fluids see, among others, Stodola, *Dampf und Gas-turbinen*, 1924, p. 31.

¹² Gibbs, Trans. Conn. Acad. 2, 382 (1873); *Scientific Papers*, Vol. 1, p. 49; Gouy, J. de physique, November (1889); Stodola, Zeits. d. Ver. deutsch. Ing., p. 1088 (1898); Jouguet, Revue de mecanique, March (1906); Darrieus, Revue gen. de l'elect. 27, 963 (1930); Keenan, Mech. Eng. 54, 195 (1932).

AVAILABLE ENERGY CHANGES IN THE DETONATION WAVE

Since the conditions immediately ahead and behind the wave front are assumed not to change with time, the above expression may be used to measure the decrease of available energy suffered by the gases as they stream through the wave front. In this case, Eq. (10), by virtue of Eq. (3), becomes $A_1 - A_2 = T_0(S_2 - S_1)$, the decrease of available energy in calories per mole of gas mixture passed through the wave front. The initial gas mixture is fed into the wave front at the rate of u_1/V_1 moles per second, so that the time rate at which degradation proceeds is $D = T_0(S_2 - S_1)u_1/V_1$ calories per second. When the velocity u_1 attains its minimum (the value verified by experiment) S_2 is likewise at its minimum so that D must also be minimum, that is, normal detonation proceeds at that speed for which the time rate of degradation of available energy is least.

The available energy entering the wave front as measured with respect to the stationary gases ahead of the oncoming wave, that is, the available energy passing the moving plane 1 as measured from the datum state represented by the undisturbed gas mixture at some stationary plane 0 ahead of the wave front, is given by Eq. (10) as follows

$$A_1 - A_0 = (E_1 + P_1 V_1 + u_1^2/2 - T_0 S_1) - (E_0 + P_0 V_0 + u_0^2/2 - T_0 S_0).$$

These parentheses are identical except for the velocity terms, namely, u_1 , which is the velocity of the wave front, and u_0 , which is zero since the gases at plane 0 are at rest; so the above expression reduces to $A_1 = u_1^2/2 + A_0$, the available energy fed into the wave front in calories per mole. The time rate at which available energy enters the wave front, in calories per second, is, then, $F = (u_1^2/2 + A_0)u_1/V_1$, from which it follows that normal detonation proceeds at that speed for which the available energy supplied to the wave front (as measured with respect to the available energy of the stationary gases ahead of the wave) is least.

At any given point along the Hugoniot curve, the extent of the degradation (D) within the

wave front in comparison to the available energy (F) supplied may be estimated from the ratio of these two quantities, that is, by

$$\rho = D/F = T_0(S_2 - S_1)/(u_1^2/2 + A_0). \quad (11)$$

The derivative of ρ with respect to V_2 , along the Hugoniot curve, is

$$\frac{d^2\rho}{dV_2^2} = \frac{T_0}{A_1} \frac{d^2S_2}{dV_2^2} \left[1 - \frac{T_2(S_2 - S_1)}{\frac{1}{2}(P_2 - P_1)(V_1 - V_2) + ((V_1 - V_2)/V_1)^2 A_0} \right]$$

For waves of compression, the several terms of this expression are intrinsically positive. Referring to the denominator of the fraction within the large brackets, it will be observed that the left-hand part is, by virtue of Eq. (5), less than $(E_2 - E_1)$. The value of the available energy A_0 , to have significance here, should be referred to a datum state that is stationary with respect to plane 0 and thermodynamically consistent with the datum used in assigning a value to E_1 . Under such conditions, A_0 will be some fraction of E_1 , and thus, the denominator of the above fraction will be less than E_2 which, on the T - S plane, is a smaller area than the rectangle represented by the numerator $T_2(S_2 - S_1)$ and so, the fraction is greater than 1. Accordingly, the second derivative is negative for waves of compression, and ρ is a maximum at that point on the Hugoniot curve defined by Eq. (8). This is the point defined by Jouguet's postulate, and the corresponding detonation velocity is the minimum allowed by the Hugoniot relations, the same that Chapman had assumed and which experiment has verified. The fact that ρ is a maximum at this point on the Hugoniot curve implies that the normal detonation wave proceeds at that speed which allows the greatest degradation of each unit of energy supplied to the wave.

This result is in accord with the fundamental principle of degradation of energy in all natural processes—a principle that is so universally verified that when the extent of degradation brought about by a natural process is discovered to vary with the speed of the process, it would seem only consistent that the stable speed would be that which allowed the greatest degradation.

$$\frac{d\rho}{dV_2} = \frac{T_0}{A_1} \frac{dS_2}{dV_2} - \frac{T_0}{A_1^2} \frac{V_1}{2} \frac{(S_2 - S_1)}{(V_1 - V_2)} \left[\frac{dP_2}{dV_2} + \frac{P_2 - P_1}{V_1 - V_2} \right]$$

At a point where $dS_2/dV_2 = 0$, the derivative dP_2/dV_2 acquires the subscript s so that, when equated to zero, the above equation reduces to Jouguet's postulate, Eq. (8). The second derivative at this same point is

In the case of detonation, such a statement of the principle of degradation would not only explain the success of Chapman's outright assumption and of Jouguet's physical postulate but would also provide a fundamental starting point from which to derive such stability relations. The velocity of the normal detonation wave may, therefore, be regarded as fixed by arguments within the realm of thermodynamics.

CALCULATED RESULTS

In order to provide a specific illustration of the way in which the function ρ identifies the stable speed of normal detonation from the range of velocities defined by the Hugoniot relations without recourse to either (1) the physical considerations required by Jouguet's postulate or (2) the outright assumption of Chapman, the following calculations have been carried out with a mixture of 1 mole of hydrogen and $\frac{1}{2}$ mole of oxygen; a mixture for which Dixon⁴ found the experimental detonation velocity to be 2821 meters per second when the initial pressure and temperature were 1 atmosphere and 10°C. The leading calculated items are listed in Table I.

TABLE I.

$\mu = V_1/V_2$	P_2 (atmos.)	u_1 (m/sec.)	ρ ($A_0 = 0$)
1.0000	10.09	∞	0.00000
1.1097	11.27	4516.3	.10997
1.4837	15.41	2946.1	.25525
1.8553	19.69	2820.9 min.	.27725 max.
2.0480	21.97	2836.2	.27465
2.8129	31.48	3046.8	.24196
3.7563	44.31	3403.8	.20006

These computations consider the dissociation $H_2=2H$ and $H_2O=H_2+\frac{1}{2}O_2$; all thermal data being taken from Bulletin 139 of the University of Illinois Engineering Experiment Station.¹³ It will be observed that when ρ is maximum, the corresponding velocity u_1 is 2820.9 meters per

¹³ The use of the recent spectroscopic thermal data will entail small modifications in Table I. The merits of the function ρ , of course, are independent of the correctness of the underlying data.

second which agrees with Dixon's experimental value. Referring to Eq. (11), it will be seen that the value of A_0 will influence the magnitude of ρ without changing the position of its maximum on the Hugoniot curve. For the purposes of this example, this constant has been taken as zero. With appropriate values of A_0 , ρ would be smaller and its maximum, although less sharp, would identify the same detonation velocity.

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The Ionization Potential of Acetone Vapor

W. ALBERT NOYES, JR., *Department of Chemistry, Brown University*

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The ionization potential of acetone vapor has been measured with a two-electrode tube. The value found agrees within experimental error with that predicted from spectroscopic data.

THE absorption spectrum of acetone vapor has been investigated recently both in the quartz region and with a vacuum grating to as far as 850A.¹ It consists of a continuous absorption in the neighborhood of 3000A with a faint discrete absorption on the long wave end, a rather complex system of bands extending from about 1960A to about 1800A and finally several other band systems obviously involving several different upper electron states at still shorter wavelengths. Among the latter bands Duncan^{1b} found one series which could be represented by the Rydberg formula

$$\bar{\nu} = 82,767 - R/(n - 0.495)^2 (n = 3, 4, 5 \dots). \quad (1)$$

No other Rydberg series which were convincing from the standpoint of intensity relationships could be found, although it was thought at one time that two others existed. Eq. (1) predicts an ionization potential of 10.20 volts and the present work was undertaken with the object of verifying this value by the electron collision method.

(A) EXPERIMENTAL PROCEDURE

The purification of the acetone has already been described.^{1a} It was stored over calcium chloride.

¹ (a) W. A. Noyes, Jr., A. B. F. Duncan and W. M. Manning, *J. Chem. Phys.* **2**, 717 (1934); (b) A. B. F. Duncan, *ibid.* **3**, 131 (1935).

Fig. 1 shows a diagram of the apparatus. The acetone vapor was admitted through the capillary tube H from a supply bulb kept at one of the following temperatures: -77° (CO_2 -ether); -33° (liquid ammonia); 0° (ice water). At these temperatures the vapor pressures of acetone are approximately 0.15, 7 and 67 mm, respectively. In general the best results were obtained at the lowest vapor pressure, although the rate of evacuation was sufficiently high to permit measurements to be made at the higher temperatures. At B are two diaphragms made of glass perforated by holes about 0.5 mm in diameter. The traps A and C were immersed in liquid air during a run and E was attached to a high speed diffusion pump. Since the vapor pressure of acetone is immeasurable on a McLeod gauge

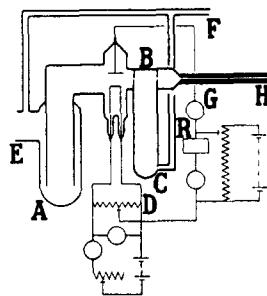


FIG. 1.