Superscripts

G = vapor phase
L = liquid phase
∞ = at physicochemical equilibrium

Subscript

O_2 = for oxygen

Composite symbols

k_{O_2} = Henry's law constant for oxygen
K_x^2 = apparent equilibrium constant in terms of mole fractions

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Single Generalized Chart of Detonation Parameters for Gaseous Mixtures

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There exists a need for simplified methods of determining and visualizing the values of detonation parameters for all gaseous mixtures. Some of the instability phenomena observed in aircraft propulsion systems (turbojet afterburner, ramjet, rocket) are believed to be the result of some form of detonation. Information on detonation parameters may have direct application in the understanding of these instabilities. These instability phenomena and their possible association with detonative combustion have been discussed (*1, 5, 6*).

Information relating to aircraft propulsion system instability phenomena can be applied to analogous situations in chemical and other industries. Thus, fundamental aspects of detonation are likely to find application in many areas.

To provide simplified means for analytically determining values of detonation parameters, the authors rearranged the classical equations of detonation and devised a calculation procedure based on the resulting generalized equations, involving only nondimensional quantities (*2*). During the process of generalizing the detonation equations, it became apparent that it would be extremely useful if the detonation parameters for all gaseous mixtures could be presented in nondimensional form on a Mollier-type diagram. This would aid considerably in the visualization of the relationships among the various detonation parameters. It was found that the generalized detonation equations could be utilized for the graphical presentation of detonation parameters on a small number of Mollier-type diagrams. Three such diagrams were presented (*7*), covering the ranges of detonation parameters normally encountered for gaseous mixtures.

In this report, a single generalized chart of detonation parameters for gaseous mixtures is presented. This chart represents an improvement of the generalized charts previously presented (*7*), in that the detonation parameters for all gaseous mixtures are now on a single diagram rather than on a series of diagrams, thereby eliminating the necessity for interpolation between charts. The chief usefulness of the generalized chart is to provide a means for the visualization of the relationships among the detonation parameters for all gaseous mixtures on a single diagram. The application of the single generalized chart is illustrated by several examples.

EQUATIONS FOR GENERALIZED CHART

It has been shown (*2*) that the following four equations can be derived directly from the classical equations describing the detonation process for gaseous mixtures:

$$B = \frac{1}{\gamma_2^2 - 1}\left[\frac{M_1^2}{2} + \left(\frac{\gamma_2}{\gamma_1}\right)^2\left(\frac{1}{2M_1^2} + \gamma_1\right)\right] - \frac{1}{\gamma_1 - 1} \qquad (1)$$

$$\frac{p_2}{p_1} = \frac{1}{\gamma_2 + 1}\,(\gamma_1 M_1^2 + 1) \qquad (2)$$

$$\frac{\rho_2}{\rho_1} = \frac{\gamma_2 + 1}{\gamma_2}\left(\frac{\gamma_1 M_1^2}{\gamma_1 M_1^2 + 1}\right) \qquad (3)$$

$$\frac{T_2 M_{w_1}}{T_1 M_{w_2}} = \frac{\gamma_2}{(\gamma_2 + 1)^2}\cdot\frac{(\gamma_1 M_1^2 + 1)^2}{\gamma_1 M_1^2} \qquad (4)$$

where B is the energy release function, $B = (Jh/a_1^2)$, and M_1 is the detonative Mach number, $M_1 = (D/a_1)$.

In the derivation of these equations it was assumed that the ideal gas law holds for the reactants and the products at the initial and final conditions, respectively. This is equivalent to the assumption that the actual temperatures and pressures of the initial and final mixtures in all cases are in a region where the use of the ideal gas law results in negligible error. For the final mixture, this is a reasonable assumption in all cases in view of the extremely high temperatures occurring in detonation. For the initial mixture, this is a reasonable assumption if the initial conditions are sufficiently far from the critical conditions of pressure and temperature for each component so that compressibility is a negligible factor. Thus, in all cases where an equation of state has been required for describing the states of the initial and final mixtures at the initial and final conditions, respectively, the ideal gas law has been used. The usual assumption is also made that chemical equilibrium is attained in the detonation wave.

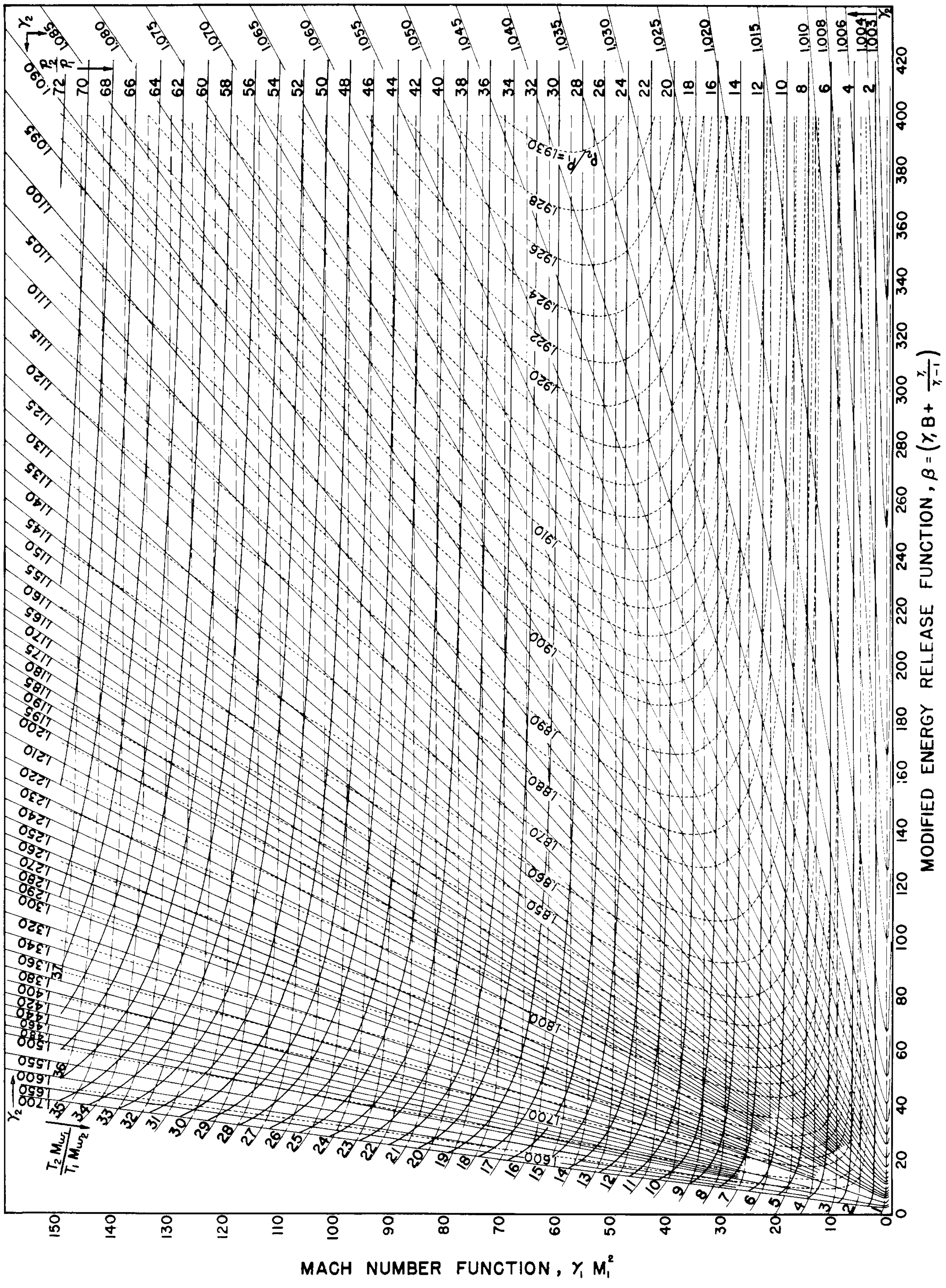

Figure 1. Single generalized chart of detonation parameters for gaseous mixtures

To facilitate generalization of the detonation equations, it was assumed that both the initial and final gaseous mixtures are polytropic (*7*)—that is, the difference in internal energies across the detonation wave is

$$e_2 - e_1 = c_{v_2} T_2 - c_{v_1} T_1$$

It is believed that this assumption did not appreciably affect the accuracy of the final generalized equations.

To permit presentation of the detonation parameters for gaseous mixtures on a single chart, Equation 1 may be utilized in a slightly modified form. Multiplying each side of Equation 1 by γ_1,

$$\gamma_1 B = \frac{1}{\gamma_2^2 - 1}\left[\frac{\gamma_1 M_1^2}{2} + \gamma_2^2\left(\frac{1}{2\gamma_1 M_1^2} + 1\right)\right] - \frac{\gamma_1}{\gamma_1 - 1} \tag{5}$$

$$\gamma_1 B + \frac{\gamma_1}{\gamma_1 - 1} = \frac{1}{\gamma_2^2 - 1}\left[\frac{\gamma_1 M_1^2}{2} + \gamma_2^2\left(\frac{1}{2\gamma_1 M_1^2} + 1\right)\right] \tag{6}$$

Then, introducing the modified energy release function,

$$\beta = \gamma_1 B + \frac{\gamma_1}{\gamma_1 - 1} \tag{7}$$

Equation 6 becomes

$$\beta = \frac{1}{\gamma_2^2 - 1}\left[\frac{\gamma_1 M_1^2}{2} + \gamma_2^2\left(\frac{1}{2\gamma_1 M_1^2} + 1\right)\right] \tag{8}$$

Equations 2, 3, 4, and 8 are the nondimensional equations which form the basis for the single generalized detonation chart presented in this report.

CONSTRUCTION OF GENERALIZED CHART

It was found that all the detonation parameters, applicable to all gaseous mixtures, could be presented on a single generalized chart (Figure 1). This chart is a graphical presentation of the generalized detonation equations (Equations 2, 3, 4, and 8). The chart shows basically the variation of the Mach number function, $\gamma_1 M_1^2$, with the modified energy release function, β, at constant values of the specific heat ratio for the final mixture, γ_2. This relationship (Equation 8) is represented as radial lines (approximately straight) emanating from a region near the origin.

The other detonation parameters—pressure ratio, temperature-molecular weight ratio, and density ratio across the detonation wave—are represented by cross plots on the chart, each of these parameters being dependent only on the Mach number function and γ_2. That is, lines of constant p_2/p_1, lines of constant $T_2 M_{w_1}/T_1 M_{w_2}$, and lines of constant ρ_2/ρ_1 have been cross-plotted on the generalized chart utilizing Equations 2, 3, and 4.

The lines of constant γ_2 (radial lines) shown on the chart are approximately straight. Inspection of Equation 8 shows that for large values of $\gamma_1 M_1^2$, the term $1/(2\gamma_1 M_1^2)$ is negligible. Therefore, for all values of $\gamma_1 M_1^2$ above approximately 15, these lines are straight within the reading accuracy of the chart. Each of these lines is slightly curved at the lower end and reaches a minimum value of β at a value of $\gamma_1 M_1^2$ near unity. The exact coordinates of this minimum point are

$$\beta_{\min} = \frac{\gamma_2}{\gamma_2 - 1} \tag{9}$$

$$\gamma_1 M_1^2 = \gamma_2 \tag{10}$$

and the locus of the $\beta_{\min}$ points is given by the expression

$$\gamma_1 M_1^2 = \frac{\beta_{\min}}{\beta_{\min} - 1} \tag{11}$$

Examination of Equations 2, 3, and 4 shows that this locus (where $\gamma_1 M_1^2 = \gamma_2$) is also the locus of points representing the following theoretical conditions:

$$\frac{p_2}{p_1} = 1 \qquad \frac{T_2 M_{w_1}}{T_1 M_{w_2}} = 1 \qquad \frac{\rho_2}{\rho_1} = 1$$

For the lines of constant density ratio, the point at which β is a minimum is given by the expression

$$\beta_{\min} = \frac{\left[\frac{\rho_2/\rho_1}{2} + \frac{1}{2(\rho_2/\rho_1)} - 1\right](\gamma_1 M_1^2)^2 + \left(\frac{\rho_2/\rho_1}{2} + \frac{1}{2\rho_2/\rho_1}\right)\gamma_1 M_1^2}{(2 - \rho_2/\rho_1)\,\gamma_1 M_1^2 - \rho_2/\rho_1} \tag{12}$$

where the value of $\gamma_1 M_1^2$ at this point is

$$\gamma_1 M_1^2 = \frac{\rho_2/\rho_1}{2 - \rho_2/\rho_1}\left[1 + \frac{\rho_2/\rho_1}{(2 - \rho_2/\rho_1)}\sqrt{\frac{2}{\rho_2/\rho_1}}\right] \tag{13}$$

The range chosen for each of the detonation parameters plotted in the generalized chart was based on theoretical and experimental data obtained from the literature for a number of representative gaseous mixtures. The maximum value found for γ_1 was slightly higher than 1.4 and for M_1, approximately 10; hence, the chart was constructed with values of $\gamma_1 M_1^2$ ranging up to 150. The range of values plotted for β is 0 to 420; for p_2/p_1, 2 to 72; $(T_2 M_{w_1})/(T_1 M_{w_2})$, 1 to 37; and ρ_2/ρ_1, 1.6 to 1.93.

USE OF CHART

The value of the generalized chart (Figure 1) lies principally in the fact that it presents all of the detonation parameters for gaseous mixtures, utilizing only dimensionless quantities, on a single Mollier-type diagram.

The usefulness of the chart in permitting immediate visualization of numerical values of all the detonation parameters may be illustrated by considering two actual gaseous mixtures for which partial detonation data are available in the literature.

For the gaseous mixture $H_2 + \frac{1}{2} O_2$ at 18° C. and a pressure of 1 atm., values reported in the literature (*3*) for detonation velocity and pressure ratio are $D = 2806$ meters per second and $p_2/p_1 = 18.05$, respectively. The molecular weight of this mixture is $M_{w_1} = 12{,}0107$. The Mach number function is, therefore,

$$\gamma_1 M_1^2 = \frac{D^2 M_{w_1}}{JRT} = \frac{(2806 \times 10^2)^2 (12.0107)}{(4.185 \times 10^7)(1.98719)(291.1)} = 39.1$$

If these values of p_2/p_1 and $\gamma_1 M_1^2$ are used, the remaining detonation parameters as obtained from Figure 1 are as follows:

$$\gamma_2 = 1.214$$

$$\rho_2/\rho_1 = 1.78$$

$$\frac{T_2 M_{w_1}}{T_1 M_{w_2}} = 10.2$$

$$\beta = 44.5$$

As an indication of the accuracy of data obtainable from the chart in this manner, calculated values of γ_2 and ρ_2/ρ_1 for this case reported elsewhere (*2*, *4*) are found to be the same as the values given above.

The second example illustrating the use of the generalized detonation chart is for the gaseous mixture, $C_2H_2 + O_2$ at 15° C. and a pressure of 1 atm. For this mixture, Manson (*4*) reported the detonation velocity to be 2960 meters per second and the pressure ratio to be 50.2. The molecular weight of this mixture is 29.008 and the Mach number function is

$$\gamma_1 M_1^2 = \frac{D^2 M_{w_1}}{JRT} = \frac{(2960 \times 10^2)^2 (29.008)}{(4.185 \times 10^7)(1.98719)(291.1)} = 105.0$$

Using these values of p_2/p_1 and $\gamma_1 M_1^2$, the following values of the remaining detonation parameters may be read from Figure 1:

$$\gamma_2 = 1.11 \qquad \frac{T_2 M_{w_1}}{T_1 M_{w_2}} = 26.7$$

$$\rho_2/\rho_1 = 1.88 \qquad \beta = 231$$

In more general applications, the generalized chart can be used to illustrate clearly how all of the detonation parameters vary with initial composition, pressure, and temperature. That is, if data such as $\gamma_1 M_1^2$ and p_2/p_1 are available for a given detonable gaseous mixture at several initial conditions, these data may be plotted directly on the generalized chart. This plot will provide a convenient means of visualizing the change of all detonation parameters under varying initial conditions. The plot may also be used to facilitate accurate interpolation of detonation data, so that values of the detonation parameters may be conveniently obtained for initial conditions where data are not available.

Other practical applications for the generalized chart will become apparent with its use. For example, if the detonation limits for a class of detonable gaseous mixtures can be represented by a single curve on the generalized chart, such information will be extremely valuable in many applications.

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NOMENCLATURE

a = velocity of sound, cm. per second
B = energy release function, dimensionless
c_v = specific heat at constant volume, cal. per gram, °K.
D = detonation velocity—velocity of detonation wave with respect to initial mixture, cm. per second
e = specific internal energy, cal. per gram
h = energy release per unit mass of mixture, cal. per gram
J = mechanical equivalent of heat, dyne-cm./cal. or ergs per cal.
M_1 = detonative Mach number—Mach number of detonation wave with respect to initial mixture, dimensionless
$\gamma_1 M_1^2$ = Mach number function, dimensionless
M_w = molecular weight, grams per gram-mole
p = pressure, atmospheres
R = universal gas constant, cal./gram-mole, °K.
T = absolute temperature, °K.
β = modified energy release function, dimensionless
γ = specific heat ratio, dimensionless
ρ = density, grams per cc.

Subscripts

1 = initial mixture at initial conditions
2 = final mixture immediately behind detonation wave at final conditions

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Explosive Systems Containing Liquid Oxygen

Liquid Oxygen–Liquid Methane Mixtures

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Although the explosive properties of combustible gas-oxygen mixtures have been investigated extensively, little or no work has been done on the explosive properties of the same mixtures in the liquid phase. Liquid systems having densities more than 1000 times as great as the corresponding gas mixture have faster reaction rates. Knowledge of the detonation properties of a mixture in both gas and liquid systems should provide data for testing and extending the classical theory of detonation. Data are being obtained on nine systems (*5,6*).

1. Methane (l)—oxygen (l)
2. Carbon monoxide (l)—oxygen (l)
3. Cyanogen (s)—oxygen (l)
4. Carbon subnitride, C_4N_2 (s)—oxygen (l)
5. Ammonia (s)—oxygen (l)
6. Hydrogen (l)—oxygen (s)
7. Carbon (s)—oxygen (l)
8. Aluminum (s)—oxygen (l)
9. Ozone (l and s)

This article deals with the first system—mixtures of liquid oxygen with liquid methane.

MISCIBILITY OF LIQUID METHANE AND LIQUID OXYGEN

Liquid methane was found to form clear homogeneous solutions with liquid oxygen at 90° K. (-183° C.) over the whole composition range from 0 to 100% oxygen. The solutions are colorless on the methane-rich side and gradually approach the color of liquid oxygen on the oxygen-rich side. Cooling to 77° K., however, caused solid methane to separate in mixtures containing over 50 weight % methane. (Matheson C.P. methane was used in these experiments.) Fastovskiĭ and Krestinskiĭ (*4*) investigated the solubility of solid methane in liquid oxygen between 69° K. (-204° C.) and 74° K. (-199° C.). They found that at 74° K. the weight % of methane in liquid oxygen was 49.35.

EXPLOSIVE RANGE AND EXPLOSIVE FORCE OF LIQUID OXYGEN-LIQUID METHANE SYSTEM

The explosive limits and brisance characteristics of the liquid methane-liquid oxygen system were determined at 90° K. for