The

THERMODYNAMICS

OF FIREARMS

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PREFACE

This book has been produced under the restrictions of wartime regulations in regard to confidential material. There is nothing in it that has not been available in book and periodical form for some years and that is not known by experts in the field of interior ballistics. Nevertheless, there is no equivalent work on the subject in the English language.

The recent great development of the explosives and ammunition industry has created a demand on the part of newcomers into the field for a compilation of this information on a sound theoretical basis. It is hoped that this book will fill this need.

The bibliography was prepared with the assistance of Ruth A. Ogilvie.

<div align="right">CLARK SHOVE ROBINSON.</div>

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TABLE OF SYMBOLS

A = area

a = acceleration

°C. = degrees centigrade

c = heat capacity or specific heat

= radiation coefficient

d = differential

= diameter

E = internal energy

e = web thickness

°F. = degrees Fahrenheit

F = friction

= force

f = coefficient of friction

g = acceleration due to gravity (980.7 cm. per sec.^{2}, or 32.16 ft. per sec.^{2})

H = enthalpy = $E + PV$

I = moment of inertia

K = equilibrium constant

°K. = degrees Kelvin (degrees centigrade + 273.1)

k = proportionality coefficient

= Vieille exponent

= radius of gyration

L = length

ln = logarithm to base $e = 2.303 \times \log_{10}$

log = logarithm to base $10 = \log_{10}$

M = mass (1 slug = 32.16 lb.; 1 g.)

= molal

N = number of molecular weights (moles)

= force normal to sliding surface

n = twist, in calibers

P = pressure

p = partial pressure

= emissivity

Q = heat (external heat effect)

R = gas constant (1546 in foot-pound–Rankine degree units; 0.08206 in liter-atmosphere–Kelvin degree units, 1.987 in heat units)

°R. = degrees Rankine (degrees Fahrenheit + 459.6)

r = radius, or distance from center of rotation

T = absolute temperature, in degrees Kelvin or Rankine

t = temperature in degrees centigrade or Fahrenheit

u = velocity

V = volume, usually molal or specific
W = work
   = weight of powder
x = elevation
z = fraction of web consumed (Kent formula)

SUBSCRIPTS

c = critical value
   = conductive
   = final value
R = reduced value = $\dfrac{\text{actual value}}{\text{critical value}}$
r = radiant
max = maximum value

GREEK LETTERS

α (alpha) = van der Waals's covolume = $\dfrac{V_c}{3}$
        = proportionality constant
β (beta) = constant in Charbonnier's formula
γ (gamma) = ratio of specific heats $\left(\dfrac{c_p}{c_v}\right)$
Δ (delta) = loading density (grams per cubic centimeter)
        = difference of limits, such as $T_2 - T_1$
κ (kappa) = ratio of specific heats
λ (lambda) = Vieille coefficient
μ (mu) = viscosity
     = coefficient in $PV = \mu NRT$
ϕ (phi) = function of
     = angle of twist
π (pi) = ratio of circumference to diameter
     = total pressure
ρ (rho) = density
θ (theta) = time
ω (omega) = angular velocity

CALCULUS SYMBOLS

$\int$ = integral sign (summation)
∂ = partial derivative

THE THERMODYNAMICS OF FIREARMS

CHAPTER I

INTRODUCTION

Thermodynamics is the science of the relationship between heat, work, and other forms of energy in combination with the physical properties of the substances involved.

Firearms are weapons from which projectiles are discharged by the explosion of gunpowder or other propellant.

The gun is a heat engine, used to convert the heat of exploding powder into mechanical energy, and as such is amenable to the fundamental concepts of thermodynamics. It takes propellent powder, rich in stored-up energy, and causes it to explode and produce gases at high temperature and pressure. These hot, highly compressed gases, confined in the powder chamber, expand, pushing the projectile in one direction and the gun in the other, the energy present in the gases being converted by this process into kinetic energy of the moving parts and into friction.

The gun as a heat engine differs only from other types of heat engine in the fact that the firing of the gun is not a cyclic process, in contrast to the steam or internal-combustion engine where all the moving parts return to their original positions at the end of a cycle. But from the thermodynamic viewpoint the three have much in common, the resemblance between the gun and the internal-combustion engine being marked. The basic thermodynamics that applies to the explosion in the internal-combustion engine can be applied to the firing of the gun with but few changes and with much profit.

The present high degree of refinement in steam turbines and gasoline engines is largely due to the fact that scientific study of their functioning is possible with the aid of thermodynamics.

Firearms are susceptible to similar treatment, and it is the purpose of this book to indicate the lines along which this may be carried out. The lack of a complete thermodynamic treatment of firearms at the present time is due, not to the difficulties involved, but to lack of adequate data. It is hoped that such data will be forthcoming.

It is expected that this book will be used to some extent as a textbook in courses relating to the design of firearms and ammunition; therefore, the material has been developed along textbook lines, starting with fundamental thermodynamics and later applying the basic principles to firearms. Readers who are familiar with thermodynamics may find this method elementary. However, many who use this book will have had no previous training in the subject. The arrangement of material is based on the author's experience in teaching both interior ballistics and thermodynamics for many years.

Thermodynamics, as it is now known, is the result of developments over a period of several hundred years, chiefly, however, during the past one hundred and fifty. Numerous engineers and scientists have been interested in these developments—many of them because of their studies of guns and ammunition. For example, the first man to discover what is now known as the first law of thermodynamics, Benjamin Thompson, Count Rumford, investigated the subject while he was inspector general for the Elector of Bavaria in the late eighteenth century. He noticed that heat was liberated when cannon were being bored at the Royal Arsenal at Munich and made measurements of the amount of heat so produced. Another famous name in thermodynamics in the early nineteenth century is that of Carnot, who was trained as an officer of the French army and was thoroughly familiar with ordnance problems. This joint interest has continued all the way from Bernoulli and Newton in the seventeenth and eighteenth centuries to Gibbs and others in the nineteenth and twentieth.

Ballistics is the art of hurling a projectile. It is ordinarily divided into two branches, *interior ballistics*, which deals with the projectile and its accessories while it is within the weapon, and *exterior ballistics*, which deals with the projectile from the gun to the target. Exterior ballistics controls the projectile with its velocity, spin, and angle of flight as it leaves the muzzle of the

gun and subjects it to the several external influences that determine its subsequent course, including gravitational, fluid-frictional, and meteorological effects. Interior ballistics includes all the previous history of the firing from the instant the firing pin or hot wire ignites the primer mixture until the projectile and the hot powder gases have left the muzzle. It involves studies of ignition, the rate of explosion of propellent powder, the temperature, composition, and pressure of the resulting products of the explosion, the travel of the projectile in the bore of the gun together with the fluid flow of the powder gases, and certain external effects such as heat, flash and smoke, and recoil.

The design of propellent powder suitable for a specific weapon falls clearly in the field of interior ballistics. It involves some study of the chemical and physical-chemical relationships of powder and of powder gases.

The possibility of correlating laboratory experiments in interior ballistics, such as closed-chamber, or laboratory, bomb firings, with the actual performance of the same propellent powders in the gun itself is one of the attractive features of this method of presentation.

The mechanical features of gun design and construction are usually grouped under the heading of *ordnance engineering*, and the manufacture of propellent powders and other ammunition materials comes under the subject of *ammunition manufacture*. However, neither ordnance engineer nor ammunition designer can move a step without specifications furnished to them by the *interior ballistician* as to pressures, velocities, charges, rates of explosion, etc.

The primary requirement of the weapon has to do with the functioning of the missile on arrival at its destination, and the gun has the sole purpose of placing it there in working condition at the right time. The gun is therefore a means to an end and is the result of this primary requirement.

It may therefore be presumed that the statement of the problem will specify the primary conditions to be met. This will include the type and size of projectile to be used, the range at which it is to be fired, and the angle at which it is to hit the target. Secondary requirements that will also influence the problem will have to do with the mobility of the gun and the desired rapidity and duration of its fire.

The problem of the flight of the projectile from the gun to its target is one of exterior ballistics and deals with the behavior of the projectile after it has left the gun and is beyond direct control. Exterior ballistics therefore has to do with the effect of natural laws on the projectile while it is in flight. It presupposes that the projectile leaves the gun with an initial velocity and initial spin and at an initial angle of azimuth and of elevation. It is the specific problem of exterior ballistics to figure backward from the target to the gun in order to determine just what these initial conditions must be.

It is the problem of interior ballistics to design the gun and ammunition so that the initial requirements set up by exterior ballistics as to velocity, spin, and angles are met.

CHAPTER II

BASIC THERMODYNAMIC PRINCIPLES

The relationship between the many forms of energy, including heat and work, is simple. The basic principle is that energy can be neither created nor destroyed. This is known as the *first law of thermodynamics* and is based on experiments covering a period of over a hundred years. Energy in the form of work can be converted completely into heat, while that in the form of heat can be converted partly back into work, depending on the temperature. Energy may also be tied up in a substance as latent, or bound, energy and as such is called *internal energy*. If a substance is in motion, it has *kinetic energy*. If it has been raised up above some datum level, it has *potential energy* due to its elevated position. It may be charged with electricity or magnetism and have energy on that account. It may have *chemical energy* on account of its composition. The first law of thermodynamics says simply that the loss or gain of energy by a body is accompanied by an equivalent gain or loss of energy in its surroundings.

The *second law of thermodynamics* is equally simple. It states merely that energy in the form of heat can be more or less completely converted into work or other form of mechanical energy depending on the temperature of the body from which the heat is taken. The system of temperature referred to in this book is the *absolute temperature*, as measured above *absolute zero*, which is $-273°$C. or $-459.5°$F. depending on whether the centigrade or the Fahrenheit system is used. Absolute zero is the lowest possible temperature that can ever be reached.

Work may be mechanical or electrical in character. *Mechanical work* is usually defined as the product of force times distance. For example, a force that lifts a one-pound weight a vertical distance of one foot has done one foot-pound of work on the body so lifted.

Since work can be quantitatively converted into heat, it is often convenient to express work in heat units instead of mechani-

cal units. One *heat unit* in the English system is the heat needed to raise one pound of water one degree Fahrenheit, and is called the *British thermal unit* (B.t.u.); in the metric system, it is the amount of heat needed to raise one gram of water one degree centigrade, being called the *calorie* (cal.). It requires 778.26 foot-pounds of work to be the equivalent of 1 British thermal unit. Since there are 453.6 grams in 1 pound and 1.8 Fahrenheit degrees is the equivalent of 1 centigrade degree, the number of calories of energy equivalent to 1 British thermal unit is 453.6/1.8, or 252 cal. = 1 B.t.u.

It is customary and convenient to express the first law of thermodynamics as a formula, based on the fact that the amount of energy contained in a system at the start of a process plus the net gain or loss of energy during the process from or to the surroundings must be equal to the amount left in the system at the end of the process. In the following equation the subscript 1 refers to the start and the subscript 2 to the end of the process.

$$E_1 + x_1 + \frac{M u_1^2}{2} + Q - W = E_2 + x_2 + \frac{M u_2^2}{2} \qquad (1)$$

This formula is for a batch system where the entire contents of the system remain within it at all times. The meaning of the symbols is as follows:

E = *internal energy* of the material in the system. This energy is represented by the energy content due to the temperature of the body, its chemical composition, its molecular structure, its physical state, whether a liquid, solid, or gas, and similar properties. This form of energy is that stored within the body and is other than that due to its position in space or its mass movement as a whole. It is not practicable to obtain an exact value of E, but its relative value can be obtained by comparison with some other known condition as a point of reference. It does not depend on the previous history of the material in the system.

x = *potential energy*, which is the energy a body possesses due to its position above some datum plane or reference level.

M = *mass* of the body in question. In the English system, the unit of mass is the *slug*, which weighs 32.2 or g lb. In the metric system the unit of mass is the gram.

u = *velocity*, or rate of mass movement of the body as a whole

Q = *heat* received by the body from the surroundings between the start of the process (point 1) and the end of the process (point 2)

W = *work* performed by the system on the surroundings between the beginning and the end of the process

The mechanical work done on a mass of material to force it into a system from the outside may be computed by measuring the force needed to move the mass from the outside to the inside of the system multiplied by the distance the force has to act, since, by *Newton's laws of motion*, mechanical work is equal to force times distance. Since force can be measured as pressure per unit area (pounds per square inch) times the cross-sectional area against which the pressure is applied and the distance which the mass moves times the cross-sectional area is the volume of the mass, the work needed to push it into the system will be

$$\text{Work} = \text{force} \times \text{distance} = \text{pressure} \times \text{area} \times \text{distance} \quad (2)$$

$$\text{Work} = \text{pressure} \times \text{volume} = PV \quad (3)$$

where P = *pressure* acting on the mass in question

V = its volume

In a system in which material is entering continuously at a uniform rate at one point and the same weight of material is leaving the system at another point, the work done by the surroundings on the material so entering is equal to the pressure required to force it into the system times its volume. If the inlet point be designated by the subscript 1, then this work will be P_1V_1. In the same manner, the material leaving the system must do work on the surroundings in order to get out; and if the outlet point be called 2, then this amount of work will be P_2V_2.

A system, therefore, in which material is entering and leaving at a continuous, uniform rate is known as a "flow" system, and the formula for the energy balance on a definite mass of material entering and leaving the system is similar to the one for the batch system with the items P_1V_1 and P_2V_2 added. This is in the form

$$E_1 + P_1V_1 + x_1 + \frac{Mu_1^2}{2} + Q - W = E_2 + P_2V_2 + x_2 + \frac{Mu_2^2}{2} \quad (4)$$

The sum $E + PV$ is called *enthalpy* and is indicated by H.

Therefore, the flow formula becomes

$$H_1 + x_1 + \frac{Mu_1{}^2}{2} + Q - W = H_2 + x_2 + \frac{Mu_2{}^2}{2} \qquad (5)$$

The gun is an example of what might be called a "semiflow" process. At the time it is fired, all the material, powder, and projectile are already in the system and the initial velocity is zero. At the end of the process, the projectile and some of the powder gases are leaving the system and there is a large velocity effect. A special formula of the energy balance for this case would be

$$E_1 + x_1 + Q - W = E_2 + P_2 V_2 + x_2 + \frac{Mu_2{}^2}{2} \qquad (6)$$

For this equation to hold, all terms in it must be expressed in the same units, such as foot-pounds or perhaps calories. It is customary to select the system so that it contains 1 lb. or 1 gm.

The word *system* in thermodynamics refers to a body of matter isolated from its surroundings but able to exchange energy with it in the form of either heat or work. If there is no heat exchange between the system and its surroundings, the process is called *adiabatic*. If a system undergoes a change of such a character that an exact reversal of the process would restore the system to its original state, which might occur if the process were frictionless, the change is called *reversible*.

Heat added to a system is positive and is called Q. When heat is removed, Q is a negative quantity.

Work done by a system on the surroundings is positive and is called W; therefore, in a horizontal batch apparatus with no velocity effects,

$$Q - W = \Delta E \qquad (7)$$

The last formula is commonly used for many cases, particularly in its differential form

$$dQ - dW = dE \qquad (8)$$

Suppose that the system consists of a horizontal cylinder, insulated against external heat effects so that it is adiabatic and equipped at one end with a frictionless piston whose cross-sectional area is A and with its other end closed. The cylinder contains expansible fluid, such as air, at the pressure P. The

force acting on the inside of the piston and attempting to push it out will be pressure times area, or F (force) $= PA$. If the piston moves out a distance dL, which would correspond to an expansion of the fluid dV at zero velocity, so that there is no kinetic-energy effect, then $dW = PA\ dL = P\ dV$, which is the work done by the fluid on the piston and, in this case of a frictionless piston, also equals the work done by the piston on the surroundings. When the piston has moved a finite distance L, the total work will be the sum of all the differential works and will be given by the integrated formula

$$W = \int_{V_1}^{V_2} P\ dV \tag{9}$$

which is good for a frictionless or reversible process only. Therefore the batch energy balance becomes

$$Q = \Delta E + \int_{V_1}^{V_2} P\ dV \tag{10}$$

for a reversible process only, where ΔE represents $E_2 - E_1$.

In the case where the cylinder is not horizontal and the piston moves with an appreciable velocity, the changes in potential energy and kinetic energy must be allowed for. If the cylinder contains a unit weight of fluid and the piston itself has no mass, then the increase in kinetic energy of the moving fluid will be $(Mu_2{}^2/2) - (Mu_1{}^2/2)$; and since, for one unit weight, $M = 1/g$ where g is the acceleration due to gravity, the increase in kinetic energy will be $\Delta\left(\dfrac{u^2}{2g}\right)$. Similarly, the change in potential energy will be $x_2 - x_1$, or Δx. In such a case, u and x represent the average velocity and average elevation, respectively, of the unit weight of fluid at the instant in question.

Example 1.—The work done by a gas supplied to a horizontal cylinder 12 in. inside diameter at a constant average pressure of 2,000 atm., pushing a frictionless piston a distance of 10 ft., is calculated as follows:

$$W = \int_{V_1}^{V_2} P\ dV = P(V_2 - V_1) = PA(L_2 - L_1) = 2,000 \times 14.7$$
$$\times 144\,\frac{\pi(12)^2}{4 \times 144} \times 10 = 33,200,000 \text{ ft.-lb.}$$

The units in this calculation are taken as follows: If W is to come out in foot-pounds (ft.-lb.), then P must be in pounds per square foot (lb. per

sq. ft.), and V must be in cubic feet (cu. ft.), since pounds per square **foot** times cubic feet equals foot-pounds.

$$1 \text{ atm.} = 14.7 \text{ lb. per sq. in.} = 14.7 \times 144 \text{ lb. per sq. ft.}$$

$$\frac{33,200,000 \text{ ft.-lb.}}{778.26} = 42,700 \text{ B.t.u.}$$

Example 2.—Suppose the gas in Example 1 had expanded, not at constant pressure, but under such conditions that the pressure decreased as the volume increased, so that $PV = a$ constant $= P_1 V_1$. Then $P = P_1 V_1 / V$. Since $W = \int_{V_1}^{V_2} P \, dV$, substituting that value for P gives $W = \int_{V_1}^{V_2} P_1 V_1 \frac{dV}{V}$, the value of which, according to calculus, is $P_1 V_1 \log_e (V_2 / V_1)$.

If the original volume of the gas V_1 corresponded to $L_1 = 10$ ft., then V_2 would correspond to $L_2 = 20$ ft. and

$$W = 2,000 \times 14.7 \times 144 \times \frac{\pi}{4} \times \frac{(12)^2}{144} \times 10 \times \log_e \left(\frac{20}{10}\right)$$

Since $\log_e \frac{20}{10} = \log_e 2 = 0.693$,

$$W = 2,000 \times 14.7 \times 144 \times \frac{\pi}{4} \times \frac{(12)^2}{144} \times 10 \times 0.693$$
$$= 23,000,000 \text{ ft.-lb.}$$

This example would approximate a constant-temperature expansion of the gas.

Example 3.—If the gas in Example 2 had expanded adiabatically, without friction, the relation between the pressure and the volume would be given approximately by the formula $PV^n = a$ constant $= P_1 V_1^n$. If the exponent n were 1.4, then the expansion work of the gas would be calculated as follows:

$$W = \int_{V_1}^{V_2} P \, dV = P_1 V_1^{1.4} \int_{V_1}^{V_2} \frac{dV}{V^{1.4}}$$

By calculus,

$$W = \frac{P_1 V_1^{1.4}}{0.4} \left(\frac{1}{V_1^{0.4}} - \frac{1}{V_2^{0.4}} \right)$$

$$W = \frac{P_1}{0.4} \left(\frac{V_1^{1.4}}{V_1^{0.4}} - \frac{V_1^{1.4}}{V_2^{0.4}} \right) = \frac{P_1}{0.4} \left(V_1 - \frac{V_1^{1.4}}{V_2^{0.4}} \right)$$

Since $P_1 = 2,000 \times 14.7 \times 144 = 4,230,000$ lb. per sq. ft.,

$$V_1 = \frac{\pi}{4} \times \frac{(12)^2}{144} \times 10 = 7.85 \text{ cu. ft.}$$

$$V_2 = \frac{\pi}{4} \times \frac{(12)^2}{144} \times 20 = 15.7 \text{ cu. ft.}$$

$$W = \frac{4,230,000}{0.4} \left[7.85 - \frac{(7.85)^{1.4}}{(15.7)^{0.4}} \right] = 19,900,000 \text{ ft.-lb.}$$

Example 4.—Suppose that the tube in Example 3 had been vertical, and the frictionless piston being pushed by the expanding gas had weighed 3220 lb., which would be 100 slugs (the English system unit of mass is the slug, weighing 32.2 lb.); then the energy given up by the gas, whose weight in this example will be neglected, will be used up in raising the piston and giving it kinetic energy due to its velocity.

$$W = 19{,}900{,}000 \text{ ft.-lb.} = \Delta x + \Delta \left(\frac{Mu^2}{2}\right)$$

$$\Delta x = 10 \text{ ft.} \times 3{,}220 \text{ lb.} = 32{,}200 \text{ ft.-lb.}$$

Initial velocity $u_1 = 0$

In order to calculate u_2, the velocity when the piston has traveled 10 ft., make use of the following mechanics relationships:

$$F = Ma$$

where F = force
$\quad\quad M$ = mass
$\quad\quad a$ = acceleration   (11)

$$a = \text{rate of increase of velocity} = \frac{du}{d\theta} \tag{12}$$

where du = velocity increase during the time $d\theta$

$$u \text{ (velocity)} = \frac{dL}{d\theta}$$

where dL = distance traveled during the time $d\theta$ (13)

When energy is added to a body, causing a rise in temperature of that body, that energy is called *sensible heat. Latent heat,* when added to a body, is that energy which causes a change in its physical form such as melting or boiling without rise in temperature

Sensible heat, added to a body under such conditions that the pressure exerted by the body remains constant during the heating process, is called *hea added at constant pressure* and is represented by Q_p. Sensible heat added while the volume of the body remains constant is called *heat added at constant volume* and has the symbol Q_v. The Q_p needed to raise one unit weight of the material in question 1° is called its *specific heat at constant pressure, c_p,* while the corresponding Q_v is called *specific heat at constant volume, c_v.*

Referring to the basic formula $Q - W = \Delta E$, for a *constant-volume* reversible process where the work W is equal to $\int_{V_1}^{V_2} P \, dV$,

since $dV = 0$, therefore, $Q_v = \Delta E$.   However, if Q_v is the sensible heat needed to raise the temperature of a unit weight of the material from T_1 to T_2, then

$$Q_v = \int_{T_1}^{T_2} c_v \, dT = \Delta E \qquad (14)$$

Another way of writing the same thing is

$$\left(\frac{\partial E}{\partial T}\right)_v = c_v \qquad (15)$$

and this is its usual definition.

The sensible heat added at constant pressure, Q_p, must allow, not only for the heating at constant volume, but also for the expansion of the body where it does the reversible work $\int_{V_1}^{V_2} P \, dV$ against the surroundings.   Therefore,

$$Q_p - W = \Delta E \quad \text{or} \quad Q_p - \int_{V_1}^{V_2} P \, dV = \Delta E \qquad (16)$$

$$Q_p = \int_{T_1}^{T_2} c_p \, dT = \Delta E + \int_{V_1}^{V_2} P \, dV \qquad (17)$$

This last equation may be rewritten in differential form as in the previous case, giving

$$\left(\frac{\partial E}{\partial T}\right)_p + P \left(\frac{\partial V}{\partial T}\right)_p = c_p \qquad (18)$$

which is the usual definition for specific heat at constant volume.

If these heat effects are for quantities other than one unit weight, they are called *heat capacities* and the quantity of material must be stated.

In addition to the heat capacities of substances, their pressure-volume-temperature relationships must be known.   There are no accurate simple PVT relations for real gases and vapors.   They must be determined experimentally for each gas.   There are, however, certain approximate PVT relations that are often convenient, if not exact.   The best known is the *perfect-gas law*. This so-called law does not apply accurately to real gases, but some of them come close enough to it so that it may be used for many calculations.   The perfect-gas law has two formulas, both of which must apply for a perfect gas.

$$PV = NRT \tag{19}$$

$$\left(\frac{\partial E}{\partial P}\right)_T = 0 \tag{20}$$

The second formula states that there is no change in the internal energy E of a perfect gas when the temperature is constant, no matter how the pressure P or, for that matter, any other condition such as volume V changes. In $PV = NRT$, for the perfect gas,

P = pressure exerted by the gas, lb. per sq. ft.
V = volume occupied by the gas, cu. ft.
N = number of molecular weights of the gas in question

One molecular weight would be 2 parts by weight of hydrogen (H_2), or 32 parts of oxygen (O_2), or 28 parts of nitrogen (N_2), etc., considering these gases as "perfect."

R = the *gas constant* = 1,546, in ft.-lb.—°F. units
T = absolute temperature of the gas = °F. + 459.6, in °F. units

Since, for a perfect gas, the second formula means that the internal energy is a function of temperature only, then the formula can be rewritten

$$dE = c_v \, dT \tag{21}$$

and, combining it with the $PV = NRT$ for $N = 1$ and with $Q - W = \Delta E$ for a reversible process, it follows that

$$Mc_p = Mc_v + R \tag{22}$$

where Mc_p and Mc_v are *molal heat capacities*, for one molecular weight of the gas.

The ratio of the specific heats c_p/c_v (called κ or γ) is also useful.

For a perfect gas, being compressed or allowed to expand reversibly at constant temperature, since $\Delta E = 0$

$$W_T = Q_T = \int_{V_1}^{V_2} P \, dV$$

Substituting for P its value NRT/V gives

$$Q_T = W_T \int_{V_1}^{V_2} \frac{NRT \, dV}{V} = \int_{V_1}^{V_2} NRT \, d \, (\ln V)$$

$$Q_T = NRT \ln \frac{V_2}{V_1} = NRT \ln \frac{P_1}{P_2} \tag{23}$$

Table 1.—Summary of Formulas for Perfect Gases

Condition of restraint	$V = C$	$P = C$	$T = C$	$Q = 0$ Reversible; adiabatic	$Q = C_n\,\Delta T$ Reversible; polytropic
PV relations	$V_1 = V_2$	$P_1 = P_2$	$P_1V_1 = P_2V_2$ $\dfrac{P_2}{P_1} = \dfrac{V_1}{V_2}$	$P_1V_1^\kappa = P_2V_2^\kappa$ $\dfrac{P_2}{P_1} = \left(\dfrac{V_1}{V_2}\right)^\kappa$	$P_1V_1^n = P_2V_2^n$ $\dfrac{P_2}{P_1} = \left(\dfrac{V_1}{V_2}\right)^n$
PT relations	$\dfrac{P_2}{P_1} = \dfrac{T_2}{T_1}$	....	$T_1 = T_2$	$\dfrac{T_2}{T_1} = \left(\dfrac{P_2}{P_1}\right)^{\frac{\kappa-1}{\kappa}}$	$\dfrac{T_2}{T_1} = \left(\dfrac{P_2}{P_1}\right)^{\frac{n-1}{n}}$
TV relations	....	$\dfrac{V_2}{V_1} = \dfrac{T_2}{T_1}$	....	$\dfrac{T_2}{T_1} = \left(\dfrac{V_1}{V_2}\right)^{\kappa-1}$	$\dfrac{T_2}{T_1} = \left(\dfrac{V_1}{V_2}\right)^{n-1}$
ΔPV	$= V(P_2 - P_1)$	$= P(V_2 - V_1)$ $= PV_1\left(\dfrac{T_2}{T_1} - 1\right)$	$= 0$	$= P_1V_1\left[\left(\dfrac{P_2}{P_1}\right)^{\frac{\kappa-1}{\kappa}} - 1\right]$ $= NRT_1\left[\left(\dfrac{P_2}{P_1}\right)^{\frac{\kappa-1}{\kappa}} - 1\right]$	$= P_1V_1\left[\left(\dfrac{P_2}{P_1}\right)^{\frac{n-1}{n}} - 1\right]$ $= NRT_1\left[\left(\dfrac{P_2}{P_1}\right)^{\frac{n-1}{n}} - 1\right]$
ΔT	$= T_1\left(\dfrac{P_2}{P_1} - 1\right)$	$= T_1\left(\dfrac{V_2}{V_1} - 1\right)$	$= 0$	$= T_1\left[\left(\dfrac{P_2}{P_1}\right)^{\frac{\kappa-1}{\kappa}} - 1\right]$ $= T_1\left[\left(\dfrac{V_1}{V_2}\right)^{\kappa-1} - 1\right]$	$= T_1\left[\left(\dfrac{P_2}{P_1}\right)^{\frac{n-1}{n}} - 1\right]$ $= T_1\left[\left(\dfrac{V_1}{V_2}\right)^{n-1} - 1\right]$
Q	$= \Delta E = NC_v\,\Delta T$ $= \dfrac{\Delta PV}{\kappa - 1}$	$= \Delta H = NC_p\,\Delta T$ $= \dfrac{\kappa}{\kappa - 1}\,\Delta PV$	$= -NRT\ln\dfrac{P_2}{P_1}$ $= -NRT\ln\dfrac{V_1}{V_2}$	$= 0$	$= \dfrac{-(\kappa - n)}{(\kappa - 1)(n - 1)}NR\,\Delta T$ $= \dfrac{-(\kappa - n)(NRT_1)}{(\kappa - 1)(n - 1)}\left[\left(\dfrac{P_2}{P_1}\right)^{\frac{n-1}{n}} - 1\right]$ $= \dfrac{-(\kappa - n)}{(\kappa - 1)(n - 1)}\,\Delta PV$ $= \dfrac{-(\kappa - n)(P_1V_1)}{(\kappa - 1)(n - 1)}\left[\left(\dfrac{P_2}{P_1}\right)^{\frac{n-1}{n}} - 1\right]$

$W_{\text{non-flow}} = \int P\,dV$ Reversible	$= 0$	$= \Delta PV = P(V_2 - V_1)$	$= -NRT\ln\frac{P_2}{P_1}$ $= -NRT\ln\frac{V_1}{V_2}$	$= -\Delta E = -NC_v\,\Delta T$ $= \dfrac{-NRT_1}{\kappa-1}\left[\left(\frac{P_2}{P_1}\right)^{\frac{\kappa-1}{\kappa}} - 1\right]$ $= (-\Delta PV)/(\kappa-1)$ $= \dfrac{-P_1V_1}{\kappa-1}\left[\left(\frac{P_2}{P_1}\right)^{\frac{\kappa-1}{\kappa}} - 1\right]$	$= -NR\,\Delta T/(n-1)$ $= \dfrac{-NRT_1}{n-1}\left[\left(\frac{P_2}{P_1}\right)^{\frac{n-1}{n}} - 1\right]$ $= (-\Delta PV)/(n-1)$ $= \dfrac{-P_1V_1}{n-1}\left[\left(\frac{P_2}{P_1}\right)^{\frac{n-1}{n}} - 1\right]$
$W_{\text{shaft}} = -\int V\,dP = V\,\Delta P = V(P_2 - P_1)$ Reversible		$= 0$	$= -NRT\ln\frac{P_2}{P_1}$ $= -NRT\ln\frac{V_1}{V_2}$	$= -\Delta H = -NC_p\,\Delta T$ $= \dfrac{-\kappa NRT_1}{\kappa-1}\left[\left(\frac{P_2}{P_1}\right)^{\frac{\kappa-1}{\kappa}} - 1\right]$ $= -(\kappa/\kappa-1)(\Delta PV)$ $= \dfrac{-\kappa P_1V_1}{\kappa-1}\left[\left(\frac{P_2}{P_1}\right)^{\frac{\kappa-1}{\kappa}} - 1\right]$	$= -(n/n-1)\,NR\,\Delta T$ $= \dfrac{-nNRT_1}{n-1}\left[\left(\frac{P_2}{P_1}\right)^{\frac{n-1}{n}} - 1\right]$ $= -(n/n-1)(\Delta PV)$ $= \dfrac{-nP_1V_1}{n-1}\left[\left(\frac{P_2}{P_1}\right)^{\frac{n-1}{n}} - 1\right]$
ΔE	$= NC_v\,\Delta T$ $= \dfrac{\Delta PV}{\kappa-1}$		$= 0$	$= -W_{\text{non-flow}} = NC_v\,\Delta T$ $= \dfrac{NRT_1}{\kappa-1}\left[\left(\frac{P_2}{P_1}\right)^{\frac{\kappa-1}{\kappa}} - 1\right]$ $= \dfrac{\Delta PV}{\kappa-1}$ $= \dfrac{P_1V_1}{\kappa-1}\left[\left(\frac{P_2}{P_1}\right)^{\frac{\kappa-1}{\kappa}} - 1\right]$	$= NR\,\Delta T/(\kappa-1)$ $= \dfrac{NRT_1}{\kappa-1}\left[\left(\frac{P_2}{P_1}\right)^{\frac{n-1}{n}} - 1\right]$ $= \dfrac{\Delta PV}{\kappa-1}$ $= \dfrac{P_1V_1}{\kappa-1}\left[\left(\frac{P_2}{P_1}\right)^{\frac{n-1}{n}} - 1\right]$
ΔH	$= NC_p\,\Delta T$ $= \dfrac{\kappa}{\kappa-1}\,\Delta PV$		$= 0$	$= -W_{\text{shaft}} = NC_p\,\Delta T$ $= \dfrac{\kappa NRT_1}{\kappa-1}\left[\left(\frac{P_2}{P_1}\right)^{\frac{\kappa-1}{\kappa}} - 1\right]$ $= \dfrac{\kappa}{\kappa-1}\,\Delta PV$ $= \dfrac{\kappa P_1V_1}{\kappa-1}\left[\left(\frac{P_2}{P_1}\right)^{\frac{\kappa-1}{\kappa}} - 1\right]$	$= \dfrac{\kappa}{\kappa-1}\,NR\,\Delta T$ $= \dfrac{\kappa NRT_1}{\kappa-1}\left[\left(\frac{P_2}{P_1}\right)^{\frac{n-1}{n}} - 1\right]$ $= \dfrac{\kappa}{\kappa-1}\,\Delta PV$ $= \dfrac{\kappa P_1V_1}{\kappa-1}\left[\left(\frac{P_2}{P_1}\right)^{\frac{n-1}{n}} - 1\right]$

Notation: P = absolute pressure, T = absolute temperature, V = volume. C_p = molal heat capacity at constant pressure. C_v = molal heat capacity at constant volume. $\kappa = C_p/C_v$, Δ = final value − initial value.
Subscript: 1 = initial state; 2 = final state. N = number of moles. R = gas constant.
Conditions: $PV = NRT$ for equation of state. C_p and C_v are constant. $C_p - C_v = R$. For flow, $\Delta(U^2/2g)$ and ΔX are assumed negligible.

For a perfect gas in a reversible adiabatic process, $Q = 0$ and therefore

$$-W = \Delta E = -\int_{V_1}^{V_2} P \, dV$$

Since $\Delta E = \int_{T_1}^{T_2} c_v \, dT$, then

$$\int_{T_1}^{T_2} c_v \, dT = \int_{V_1}^{V_2} P \, dV = \int_{V_1}^{V_2} NRT \frac{dV}{V}$$

which, when rearranged, gives

$$\int_{T_1}^{T_2} c_v \, dT = NR \int_{V_1}^{V_2} \frac{dV}{V} = NR \ln \frac{V_2}{V_2} \tag{24}$$

If c_v is called a constant at the average volume over the temperature range involved, this relationship then becomes

$$c_v \int_{T_1}^{T_2} \frac{dT}{T} = c_v \ln \frac{T_2}{T_1} = NR \ln \frac{P_2}{V_1} \tag{25}$$

For one mole, or molecular weight, $N = 1$ and

$$\left(\frac{T_2}{T_1}\right)^{MC_v} = \left(\frac{V_2}{V_1}\right)^{R} = \left(\frac{V_2}{V_1}\right)^{MC_p - MC_v}$$

giving

$$\left(\frac{T_2}{T_1}\right)^{\frac{MC_p}{MC_v} - 1} = \frac{V_2}{V_1} = \left(\frac{T_2}{T_1}\right)^{\kappa - 1} \tag{26}$$

and also the PT relationship

$$\frac{P_2}{P_1} = \left(\frac{V_1}{V_2}\right)^{\kappa} \qquad \text{or} \qquad PV^{\kappa} = \text{a constant} \tag{27}$$

Substituting this in the ΔE value for one mole of a perfect gas,

$$\Delta E = Mc_v \, \Delta T = \frac{RT_1}{\kappa - 1} \left[\left(\frac{P_2}{P_1}\right)^{\frac{\kappa - 1}{\kappa}} - 1 \right] \tag{28}$$

Table 1 is a summary of the thermodynamic formulas for a perfect gas with a constant value of the specific heat.

When it is not safe to call c_v a constant, the $\int_{T_1}^{T_2} c_v \, dT$ should be evaluated graphically, using experimental relationships between c_v and T, as given later in Chap. VII.

At the pressures and temperatures obtained in firearms, the perfect-gas laws fail to give sufficiently accurate results at higher pressures. Various formulas have been developed to allow for these deviations. The best one is that due to van der Waals,

$$\left(P + \frac{b}{V^2}\right)(V - \alpha) = RT \text{ for 1 mole} \tag{29}$$

In this formula b/V^2 is a measure of the mutual attraction of the gas molecules for each other, and α is the so-called "covolume," or the space actually occupied by the gas molecules, and is supposed to be one-third the critical volume V_c of the gas in question. When the pressure P is very high, it is often suitable to omit the b/V^2, and the formula becomes

$$P(V - \alpha) = RT \tag{30}$$

A still better approximation of the PVT relationships is given by the μ chart method. This method uses the formula

$$PV = \mu NRT \tag{31}$$

when μ is an empirical factor that has been found to be the same for all common gases and is based on the critical values for the individual gases. The treatment is as follows:

Divide the actual absolute pressure exerted by the gas by its critical pressure, and call the quotient the *reduced pressure*

$$\frac{P}{P_c} = P_R$$

The *reduced temperature* is obtained in a similar fashion,

$$\frac{T}{T_c} = T_R$$

and the *reduced* volume

$$\frac{V}{V_c} = V_R$$

Table 2 gives critical volume for common gases, the temperatures being in degrees Kelvin (°C.abs. = °C. + 273.2) and the pressures at atmospheres.

TABLE 2

Gas	T_c, °K.	V_c, liters per mole	P_c, atm.	Molecular weight
Acetylene (C_2H_2)............	309.	0.113	62.	26.02
Ammonia (NH_3).............	405.6	0.0724	111.5	17.03
Argon (A)....................	151.	0.0753	48.	39.94
Carbon dioxide (CO_2).........	304.3	0.0957	73.0	44.00
Carbon monoxide (CO).......	133.0	0.0930	35.	28.00
Ethylene (C_2H_4).............	282.8	0.127	50.9	28.03
Helium (He).................	6.3*	0.058	3.26*	4.00
Hydrogen (H_2)..............	41.3*	0.065	20.8*	2.02
Methane (CH_4).............	190.7	0.099	45.8	16.03
Nitric oxide (NO)...........	179.	0.0578	65.	30.01
Nitrogen (N_2)................	126.1	0.0900	33.5	28.02
Oxygen (O_2).................	154.4	0.0744	49.7	32.00
Water vapor (H_2O)..........	647.2	0.0566	217.7	18.02

* The values for hydrogen and helium are not the true critical values but empirical ones selected so that these two gases will fit the same values of μ that other gases fit.

The plots (Figs. 1 and 2) give the values of μ plotted against the reduced pressure P_R for various values of the reduced tem-
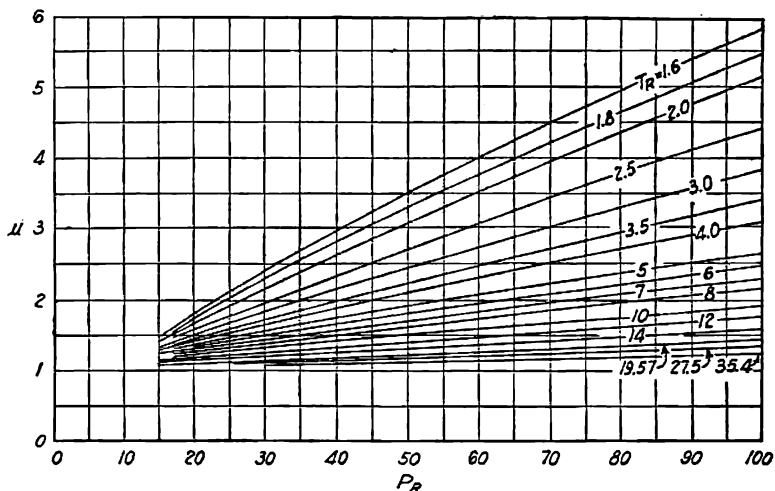

FIG. 1.

perature T_R. The values for T_R up to 14 are based on averages of several gases, while those for higher values of T_R are based on helium alone. For purposes of interpolation, the following helium
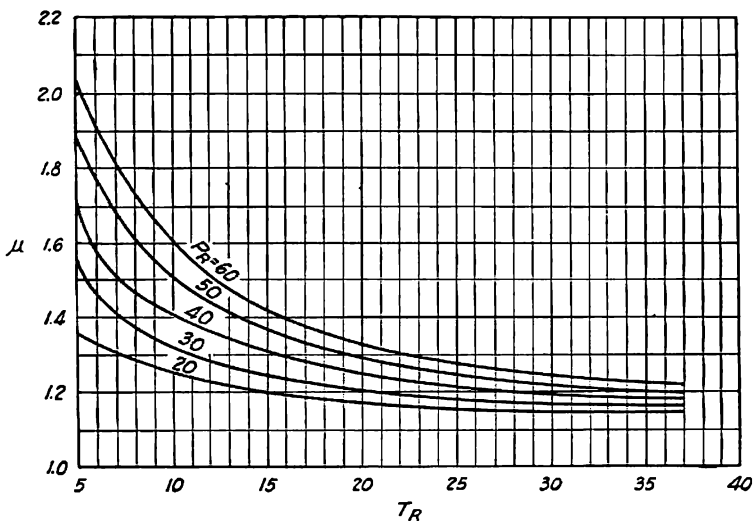
Fig. 2.

data are given from the "International Critical Tables" (vol. III, page 6); $V = 1$ at 0°C. and 1 atm.

$$PV = a + bP + cP^2 + dP^3 \qquad (32)$$

TABLE 3

T, °C.	a	b	c	d
−208	+0.2384	+0.0³5508	+0.0⁵2380	−0.0⁷141
−183	0.3299	6229	0735	
−150	0.4507	5090	0259	
−100	0.6336	5310	0165	
−50	0.8165	5320	0.0⁶0094	
0	0.9994	5290		
+50	1.1824	5240		
+100	1.3654	0.0³5080		

In order to use Figs. 1 and 2, proceed as in the following example:

Determine the volume occupied by 44 g. of CO_2 gas at 2,000 atm. abs. and 335.4°C.

The critical pressure for CO_2 is 73 atm., and the critical temperature is 304.2°K.

$$T_R = \frac{304.2 + 273.2}{304.2} = 2.0$$

$$P_R = \frac{2,000}{73.0} = 27.4$$

Using Fig. 1, $\mu = 2.02$, and therefore

$$PV = 2.02NRT$$

μ being independent of the kind of units used.

In the metric system, with P in atmospheres and T in degrees Kelvin (degrees centigrade + 273.2), R is 0.08206, giving V in liters and N in moles.

$$2,000 \times V = 2.02 \times \tfrac{44}{44} \times 0.08206 \times (335.4 + 273.2)$$
$$V = 0.0504 \text{ l.}$$

Experience indicates that calculations with the μ charts are usually very close to the exact experimental values and, except for very moderate pressures, are much to be preferred to those values calculated from $PV = NRT$.

Using the covolume method, the following results are obtained for the same case:

$$P(V - \alpha) = RT$$
$$\alpha = \frac{V_c}{3} = \frac{0.0957}{3} = 0.0319$$
$$2,000 \times (V - 0.0319) = 0.08206 \times 608.6$$
$$V = 0.0250 + 0.0319 = 0.0569 \text{ l.}$$

which varies by more than 10 per cent from the more reliable μ chart value.

By *Dalton's law*, the total pressure exerted by a gas mixture is the sum of the pressures exerted by each of the constituents, or the sum of the *partial pressures*. By *Amagat's law*, the volume of a gas mixture is the sum of the volumes of the several constituents. Both these rules are approximate only but are usually adequate for ballistic purposes.

For mixtures of gases, data for which at high pressures and temperatures are not yet sufficiently reliable for accurate calculations, it is believed that the most satisfactory method for com-

puting PVT relations is to use the μ charts with weighted average values for the reduced pressure and temperature. As an example, it is required to estimate the volume occupied by two gram-molecular weights of CO mixed with one gram-molecular weight of N_2 at 1000°C. and 1,000 atm. abs. pressure.

From the table of critical values, T_c for N_2 is 134° and for CO is 1261°, while P_c for N_2 is 35 atm. and for CO is 33.5 atm. The general method, for a moles of A, b moles of B, c moles of C, etc., would be

$$T_R = \frac{T}{a + b + c + \cdots}\left(\frac{a}{T_{c_A}} + \frac{b}{T_{c_B}} + \frac{c}{T_{c_d}} + \cdots\right) \quad (33)$$

$$P_R = \frac{1,000}{a + b + c + \cdots}\left(\frac{a}{P_{c_A}} + \frac{b}{P_{c_B}} + \frac{c}{P_{c_d}} + \cdots\right) \quad (34)$$

Thus, in this example,

$$T_R = \frac{(1,000 + 273.2)}{3}\left(\frac{2}{134} + \frac{1}{126.1}\right) = 9.7$$

$$P_R = \frac{1,000}{3}\left(\frac{2}{35} + \frac{1}{33.5}\right) = 29.0$$

From the charts, $\mu = 1.30$ and

$$1,000 \times V = 1.30 \times 3 \times 0.08206 \times 1,273.2$$
$$V = 0.408 \text{ l.}$$

This method checks the volume of known mixtures very closely.

CHAPTER III

BASIC MECHANICS

The basic mechanics of firearms stem from Newton's laws of motion. The basic units are *mass (M)*, *distance (L)*, and *time (θ)*.

Velocity (u) is the rate of change of distance with respect to time and is usually written

$$u = \frac{dL}{d\theta} \tag{35}$$

Acceleration (a) is the rate of change of velocity with respect to time and is written

$$a = \frac{du}{d\theta} = \frac{d^2L}{(d\theta)^2} = g \qquad \text{(when due to gravity)} \tag{36}$$

Force (F) produces acceleration in a mass and is defined as

$$F = Ma \tag{37}$$

Momentum is defined as mass times velocity,

$$\text{Momentum} = M \times u \tag{38}$$

Newton's three *laws of motion* are given as follows:

I. A force *(F)* is necessary to change the direction or velocity of a mass in motion.

II. A change in momentum *(M × u)* of any part of a system must be accompanied by a corresponding change in momentum in the opposite direction in the balance of the system so that the resultant of all the changes in momentum is zero. This is called the principle of the *conservation of momentum*.

III. To every force exerted by one body on another, there is a corresponding force equal to and opposite in direction, exerted by the second body on the first. This is the principle known as *action equals reaction*.

The work *(W)* done on a body by a force *(F)* is the product of the force times the distance over which the force acts, or

$$W = \int_{L_1}^{L_2} F \, dL \tag{39}$$

Since $u = \dfrac{dL}{d\theta}$, $F = Ma$, and $a = \dfrac{du}{d\theta}$,

$$W = \int_{L_1}^{L_2} Ma \, dL = \int_{L_1}^{L_2} M \frac{du}{d\theta} u \, d\theta \qquad (40)$$
$$= \int_{u_1}^{u_2} Mu \, du = \frac{Mu_2^2}{2} - \frac{Mu_1^2}{2} = \Delta \left(\frac{Mu^2}{2} \right)$$

$Mu^2/2$ is called the *kinetic energy* of the moving body.

The mechanical work thus done on a moving body equals its increase in kinetic energy. Force used up in overcoming friction, rather than causing acceleration, does not increase kinetic energy.

In the case of a rigid body rotating about a fixed axis with the angular velocity ω, the change in angular velocity due to the action of an applied force is $\dfrac{d\omega}{d\theta}$ and is called the *angular acceleration*. The linear acceleration a tangential to the line of rotation of any unit particle of the mass M' of the body is

$$a = r \frac{d\omega}{d\theta} \qquad (41)$$

where r is the distance of the particle in question from the center of rotation and the force F acting on that particle is

$$F = M_2' = M'r \frac{d\omega}{d\theta} \qquad (42)$$

The product $F \times r$ is the moment of the force acting on that particle, and therefore the summation of all the moments of force acting on the entire rotating body is

$$\sum_{r=0}^{r=r_1} Fr = \left(\sum M'r^2 \right) \left(\frac{d\omega}{d\theta} \right) = I \frac{d\omega}{d\theta} \qquad (43)$$

where I = moment of inertia of the rotating body

If the entire mass M of the rotating body could be concentrated in a hollow cylindrical shell of radius k such that

$$Mk^2 = I \qquad (44)$$

then k would be called the "radius of gyration" of the rotating body.

The moment of inertia of a non-homogeneous rigid body is the sum of the moments of all the homogeneous portions.

It follows from these formulas that the kinetic energy of a rotating body

$$\text{K.E.} = \frac{I\omega^2}{2} \tag{45}$$

and the work done by the application of a force tangential to the direction of rotation is equal to the increase in this kinetic energy.

It should be remembered that forces used in overcoming friction or in producing acceleration in directions other than those in question are not included in the above discussion, only the resultant forces acting in the direction of motion being used.

In the metric system, the gram is the unit of mass, and the force exerted by gravity on one gram is therefore

$$F = 980.5 \times \text{weight, g.} = \text{force, dynes} \tag{46}$$

where the units are expressed in the centimeter-gram-second system.

In the English system, the pound is the unit of force, and then the value of the mass in this system is

$$M = \frac{\text{weight, lb.}}{32.2} = \text{mass, } slugs \tag{47}$$

where the units are expressed in the foot-pound-second system.

The use of these relations is given in the following examples:

A body weighing 322 lb. and therefore having a mass of $322/32.2 = 10$ slugs is acted on by an unresisted force of 100 lb. for a distance of 100 ft.

$$M = 10 \text{ slugs} \qquad F = 100 \text{ lb.} \qquad F = Ma \qquad 100 = 10a,$$
$$a = 10 \text{ ft. per sec.}^2$$
$$a = \frac{du}{d\theta}$$
$$\therefore u_2 - u_1 = 10(\theta_2 - \theta_1)$$

If, at the start, when $\theta_1 = 0$, $u_1 = 0$, and $L_1 = 0$,

$$u = 10\theta = \frac{dL}{d\theta}$$
$$\int_0^L dL = 10 \int_0^\theta \theta \, d\theta$$
$$\therefore L = 5\theta^2 \qquad \text{or} \qquad \theta = \sqrt{\frac{L}{5}}$$

Since $L_2 = 100$,

$$\theta = \sqrt{100/5} = \sqrt{20} = 4.47 \text{ sec.}$$

and

$$u_2 = 10\sqrt{20} = 44.7 \text{ ft. per sec.}$$
$$\therefore W = F \times L = 100 \times 100 = 10,000 \text{ lb.-ft.}$$

Using the metric system, consider a body weighing 1,000 g. ($M = 1,000$) and acted on by a force of 5,000 dynes for a distance of 300 cm.; initial velocity and time $= 0$.

$$M = 1,000 \qquad F = 5,000 \qquad L = 300$$

$$a = \frac{F}{M} = \frac{5,000}{1,000} = 5 \text{ cm. per sec.}^2$$

$$a = \frac{du}{d\theta} = u = a\theta = 5\theta$$

$$L = \int_0^0 5\theta \, d\theta = 5\frac{\theta^2}{2} = 2.5\theta^2 \qquad \text{or} \qquad \theta = \sqrt{\frac{L}{2.5}}$$

$$\theta = \sqrt{\frac{300}{2.5}} = 10.94 \text{ sec.}$$

$$u = 5 \times 10.94 = 54.7 \text{ cm. per sec.}$$

As an example of the principle of the conservation of momentum, suppose that a projectile weighing 1,000 lb. is fired from a gun mounted on a boat weighing 1,000 tons (2,000,000 lb.) with a muzzle velocity of 2,000 ft. per sec. Since

$$M_A \times u_A = M_B \times u_B$$
$$\frac{1,000}{32.2} \times 2,000 = \frac{2,000,000}{32.2} u_B \qquad (48)$$

the velocity or recoil imparted to the vessel, u_B, will be 1 ft. per sec., in the opposite direction.

The force exerted by a gas under pressure in a closed chamber is the product of the pressure per unit area times the area against which the pressure is acting. Thus a 2,000-lb. projectile 1 ft. in diameter whose base, against which a gas is pressing with a pressure of 1,000 atm., has an area of $\pi/4$ sq. ft. has acting on it a force of

$$1,000 \times 14.7 \times 144 \times \frac{\pi}{4} = 1,660,000 \text{ lb.}$$

If this force is unopposed, the projectile will have an acceleration of a ft. per sec.^{2}

$$1,660,000 = \frac{2,000}{32.2}\, a$$
$$a = 27,600 \text{ ft. per sec.}^2$$

If such a pressure acted for a period of $\frac{1}{10}$ sec. with the projectile starting from rest, the velocity developed would be 2,760 ft. per sec., and the amount of work done on the projectile would equal its kinetic energy, or

$$M\, \frac{u^2}{2} = \frac{2,000}{32.2} \times \frac{(2,760)^2}{2} = 2.36 \times 10^8 \text{ ft.-lb.}$$

and the distance over which it must have acted would be

$$W = F \times L$$
$$2.36 \times 10^8 = 1.66 \times 10^6 \times L$$
$$L = \frac{236}{1.66} = 142.5 \text{ ft.}$$

CHAPTER IV
BASIC STOICHIOMETRY

The application of the principle of the conservation of energy and of material balances to chemical equations is called *stoichiometry*. The sum of the number of atoms of any element present on one side of an equation must be equal to the sum of the number of atoms of that element present on the other side of the equation. Similarly the weights of each element on both sides of an equation must be equal.

The system of symbols used by chemists is very simple. For example, the symbol C stands for the element carbon. It also stands for one *atom* of carbon, which has an *atomic weight* of 12, expressed in pounds, or grams, or any other convenient system. The common chemical elements met with in propellent powders and other explosives are given in Table 4:

TABLE 4

Name	Symbol	Atomic weight
Commonest:		
Hydrogen.....................	H	1.008
Carbon.......................	C	12.01
Nitrogen.....................	N	14.01
Oxygen.......................	O	16.00
Less common:		
Aluminum....................	Al	26.97
Barium.......................	Ba	137.36
Calcium......................	Ca	40.08
Chlorine......................	Cl	35.46
Copper.......................	Cu	63.57
Iron..........................	Fe	55.84
Lead..........................	Pb	207.21
Magnesium...................	Mg	24.32
Mercury......................	Hg	200.61
Phosphorus...................	P	30.98
Potassium....................	K	39.10
Silver........................	Ag	107.88
Sodium.......................	Na	23.00
Sulphur......................	S	32.06
Tin..........................	Sn	118.70
Zinc.........................	Zn	65.38

The equations to describe chemical reactions make use of these symbols, to indicate, first, the proportions of the several elements that go to make up a chemical compound and, second, the ratios in which these chemical compounds react with each other to produce new substances.

For example, water is a compound of hydrogen (H) and oxygen (O) in the proportion of 2 H and 1 O, and so its chemical formula is written H_2O. This also shows that 2 parts of hydrogen, weighing 2.016 lb., combine with 1 part of oxygen, weighing 16.00 lb., to produce 18.016 lb. of water (H_2O).

In a similar manner, 12.01 g. of carbon (C) combine with 32.00 g. of oxygen (O) to produce 44.01 g. of carbon dioxide (CO_2).

To use a less familiar material, the modern very sensitive explosive that is used in detonators, lead azide, is a compound of 1 atom of lead, weighing 207.21, and 6 atoms of nitrogen, weighing $6 \times 14.01 = 84.06$, so that the formula weight of PbN_6 is $207.21 + 84.06 = 291.27$.

One of the principal constituents of smokeless powder is cellulose nitrate, one form of which has the chemical formula $C_{24}H_{30}O_{20}(NO_2)_{10}$, each molecular weight of this substance containing 24 atoms of C, 30 of H, 10 of N, and 40 of O. Its formula weight would therefore be

$$
\begin{aligned}
24 \times 12.01 &= 288.24 \text{ C} \\
30 \times 1.008 &= 30.24 \text{ H} \\
10 \times 14.01 &= 140.1 \text{ N} \\
40 \times 16.00 &= \underline{640.0 \text{ O}} \\
\text{Formula weight} &= 1,098.58
\end{aligned}
$$

and it contains $140.1/1,098.58 \times 100 = 12.76$ per cent N.

When cellulose nitrate explodes, the products of the explosion may be considered to be CO_2, CO (carbon monoxide), H_2O, H_2 (hydrogen gas), and N_2 (nitrogen gas). The chemical equation for this explosion would be as follows, the lower-case letters indicating the number of molecules of each of the explosion products.

$$
C_{24}H_{30}O_{20}(NO_2)_{10} = aCO_2 + bCO + cH_2O + dH_2 + eN_2 \quad (49)
$$

The number of each atom must be the same on both sides of the equation. Therefore,

$$a + b = 24 \text{ C}$$
$$a + \frac{b}{2} + \frac{c}{2} = 20 \text{ O}_2$$
$$c + d = 15 \text{ H}_2$$
$$e = 5 \text{ N}_2$$

Here are five quantities to be evaluated, a, b, c, d, and e, with four equations. Therefore, a fifth relationship is needed. As will be shown in Chap. V on Basic Physical Chemistry, such an additional relation is obtained from the equilibrium constant of the water-gas reaction, which might, for example, show that

$$\frac{a \times d}{b \times c} = 10$$

When these five equations are solved simultaneously for a, b, c, d, and e, there is obtained the following result:

$$C_{24}H_{30}O_{20}(NO_2)_{10} = 14.11CO_2 + 9.89CO + 1.89H_2O$$
$$+ 13.11H_2 + 5N_2 \quad (50)$$
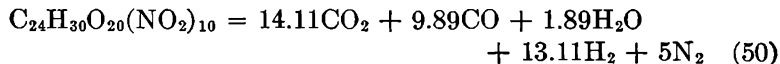
This is therefore the correct equation to fit this explosion when the equilibrium constant is as stated above.

In dealing with gases, it is customary to assume Dalton's and Amagat's laws, although they are not exact for extreme conditions. It is therefore permissible in most cases to assume that the volumes of the gases produced in an explosion like the above are proportional to the number of moles of the individual constituents. Thus, the composition of the products of the explosion in the preceding example may be calculated in per cent by volume in the following manner. Obtain the total moles of gas present and divide the number of moles of each gas by the sum, multiplying the quotient by 100.

$$14.11 + 9.89 + 1.89 + 13.11 + 5 = 44.00$$

Per cent CO_2 by volume $= \dfrac{14.11}{44} \times 100 = \quad 32.1$

$\quad\quad CO \quad\quad\quad\quad = \dfrac{9.89}{44} \times 100 = \quad 22.5$

$\quad\quad H_2O \quad\quad\quad\quad = \dfrac{1.89}{44} \times 100 = \quad\quad 4.3$

$\quad\quad H_2 \quad\quad\quad\quad = \dfrac{13.11}{44} \times 100 = \quad 29.8$

$\quad\quad N_2 \quad\quad\quad\quad = \dfrac{5}{44} \times 100 = \quad 11.3$

$$\overline{\quad 100.0 \quad}$$

In order to calculate the percentage by weight, the number of moles of each gas must be multiplied by its molecular weight, the results added, and each one divided by the sum as before.

$$\text{Per cent } CO_2 \text{ by weight} = \frac{14.11 \times 44}{\Sigma} \times 100 = 56.5$$

$$CO \qquad = \frac{9.89 \times 28}{\Sigma} \times 100 = 25.2$$

$$H_2O \qquad = \frac{1.89 \times 18}{\Sigma} \times 100 = 3.1$$

$$H_2 \qquad = \frac{13.11 \times 2}{\Sigma} \times 100 = 2.4$$

$$N_2 \qquad = \frac{5 \times 28}{\Sigma} \times 100 = 12.8$$

$$\overline{100.0}$$

and, since $\Sigma = 1,098$, the formula weight of the powder, the percentage becomes as indicated above.

The volume of one mole of a perfect gas at standard conditions (normal barometer and the freezing point of water) is 22.4 l. per gram-mole or 359 cu. ft. per lb.-mole.   If the gases deviate appreciably from $PV = NRT$, the best thing to do is to use the μ chart method given in Chap. II.   Where the perfect-gas relation can be used, the volume of a mixture such as that just calculated would be estimated as follows:

The average molecular weight of the gas mixture is obtained by dividing the weight of a given number of moles of the mixture by that number.   Thus in the preceding example the average molecular weight is $1,098 \div 44 = 25.0$.

As an example, calculate the volume occupied by 1 kg. of this gas mixture at 100 atm. abs. pressure and at 2000°C.

$$\frac{1,000}{25} \left| \underset{\text{No. of moles}}{22,400} \right| \underset{\text{Cc. at S.C.}}{\frac{2,000 + 273}{273}} \left| \underset{\text{Cc. at 2,000°C.}}{1} \right| \underset{\text{Cc. at 100 atm.}}{\frac{1}{100}} = 75,000 \text{ cc.}$$

Similarly, calculate the volume occupied by 100 lb. of this gas at 200 atm. abs. pressure and 3000°F.

$$\frac{100}{25} \bigg|\ 359\ \bigg|\ \frac{3{,}000 + 460}{492}\ \bigg|\ \frac{1}{200}\ \bigg|\ = 50.5 \text{ cu. ft.}$$

(with diagonal labels: *Lb.- molecules*, *Cu. ft. at S.C.*, *Cu. ft. at 3,000° F.*, *Cu. ft. at 200 atm.*)

In correcting gas volumes for pressure and temperature, absolute pressures and absolute temperatures must be used. (°F. abs. = 460 + °F.; °C. abs. = 273 + °C.)

These values should then be corrected for deviation from the perfect-gas laws by means of the μ chart given in Chap. II. When this is done, it will be found that the first example should be 77,000 cc. and the second should be 51.9 cu. ft.

BASIC PHYSICAL CHEMISTRY

The rate at which any process takes place may be expressed by a very simple basic rule, that the rate is proportional to the potential, or driving force, and is inversely proportional to the resistance, or retarding effect. This general rule applies to all natural phenomena whether physical or chemical. It applies to the rate at which the projectile travels through the bore of the gun and to the explosion of the propellent powder which is responsible for the movement.

This general rule may be stated in the form of a *rate equation*,

$$\frac{dW}{d\theta} = k \times \frac{\text{potential}}{\text{resistance}} \tag{51}$$

All that is necessary is to evaluate the potential and the resistance of the phenomenon in question and solve this equation. In many cases, this is quite simple.

The explosion of propellent powder in a firearm is a chemical reaction, and it is possible to study its rate. The products of the explosion are mostly gases. It is a characteristic of gaseous mixtures that they frequently react with each other chemically. It is also usual that these gaseous chemical reactions will proceed either backward or forward, depending on the direction of the potential, or driving force. Such reactions are termed *reversible*.

The driving force of a chemical reaction is proportional to the quantities of the reacting substances present. Suppose that a particular reaction takes place between three substances A, B, and C and that the basic stoichiometry indicates that the reaction equation (producing the products D and E) is as follows:

$$aA + bB + cC = dD + eE \tag{52}$$
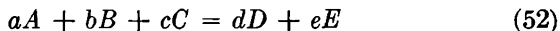
The rate at which this reaction would proceed from left to right would be indicated in the following way:

$$\frac{dW \text{ (either } A, B, \text{ or } C)}{d\theta} = k \frac{[A]^a[B]^b[C]^c}{\text{resistance}} \tag{53}$$

where the brackets [ ] indicate the concentration or amount of the constituent present in the reacting mixture.

If this reaction is reversible, and most gaseous reactions are, as soon as any D and E are formed, then these two products react to form some of the original materials A, B, and C and the rate at which this reverse reaction takes place is given by a similar equation,

$$\frac{dW \text{ (either } D \text{ or } E)}{d\theta} = k' \frac{[D]^d[E]^e}{\text{resistance}} \tag{54}$$

As the original reaction progresses, A, B, and C are being used up, so the rate becomes smaller. At the same time D and E are increasing, and so the reverse reaction has an increasing rate. Finally, the two rates will approach the same value; at this time the net change of any component will become zero, and the reaction is said to have reached equilibrium and the two rates are equal. When this is true, then

$$k \frac{[A]^a[B]^b[C]^c}{\text{resistance}} = k' \frac{[D]^d[E]^e}{\text{resistance}} \tag{55}$$

This equation can be rearranged, combining k, k', and the two resistances into one grand coefficient K, called the *equilibrium constant*.

$$\frac{[D]^d[E]^e}{[A]^a[B]^b[C]^c} = K \tag{56}$$

In many cases in gaseous reactions, the partial pressures of the constituents of the mixture of gases are directly proportional to their concentration in the mixture so that another equilibrium relationship may be written, using partial pressures instead of concentrations, the symbol P_A referring the partial pressure of A, etc., while π indicates the total pressure on the whole mixture.

$$\frac{P_D/\pi \times P_E/\pi}{P_A/\pi \times P_B/\pi \times P_C/\pi} = K \tag{57}$$

If the total pressure π is kept constant, it may be combined with K, and the formula becomes

$$\frac{P_D \times P_E}{P_A \times P_B \times P_C} = K_P \tag{58}$$

and K_P is called the equilibrium constant of the **gas reaction at constant pressure.**

This equilibrium constant K_P changes as the total pressure changes and also is affected by temperature. If the gases in the reaction approximate perfect gases, the following relation holds for the change of K_P with temperature:

$$\frac{d \ln K_P}{dT} = \frac{\Delta H_P}{RT^2} \tag{59}$$

where ΔH_P = external heat effect at constant pressure for one mole.

While the products of the explosion of propellent powders include a large variety of gases, those present in the greatest proportion are CO_2, CO, H_2, H_2O, and N_2. The first four of these are joined in what is called the *water-gas reaction*, which is usually written

$$CO_2 + H_2 = CO + H_2O \tag{60}$$

and which is associated with the manufacture of water gas by the action of steam on hot carbon. Whenever these four gases are present in a gaseous mixture, their relation to each other may be approximated by the equilibrium constant for that reaction, as follows, assuming the perfect-gas laws and constant pressure:

$$\frac{P_{CO} \times P_{H_2O}}{P_{CO_2} \times P_{H_2}} = K_P \tag{61}$$

where P_{CO} = partial pressure of CO, etc.

The values of K_P vary widely with temperature as indicated by Eq. (59), experimental values being found in Table 5.

Suppose, for example, that cellulose deca-nitrate,

$$C_{26}H_{30}O_{20}(NO_2)_{10},$$
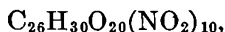
is to explode in the absence of air and that the products of the explosion are in equilibrium at 2000°C., or 2273°K. Since the reaction may be assumed to have the following form

$$C_{24}H_{30}O_{24}(NO_2)_{10} = aCO_2 + bCO + cH_{20} + H_2 + eN_2 \tag{62}$$
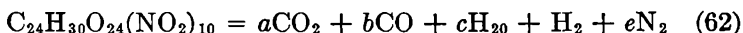
which neglects any other gases such as CH_4, NH_3, or oxides of nitrogen, the stoichiometric values for a, b, c, d, and e may be

TABLE 5.—VALUES FOR THE LOGARITHM (LOG₁₀) OF THE EQUILIBRIUM CONSTANT K_p*

Reaction	ΔE_0°	$\log_{10} K$								
		300°	400°	600°	800°	1000°	1200°	1400°	1600°	1800°
$H_2 \rightleftarrows 2H$	−102,800	−70.9	−52.1	−32.2	−21.7	−17.19	−13.19	−10.52	−8.48	−6.85
$O_2 \rightleftarrows 2O$	−117,300	−80.2	−58.6	−36.9	−26.1	−19.48	−15.10	−11.97	−9.61	−7.77
$N_2 \rightleftarrows 2N$	−168,000	−117.2	−86.2	−55.4	−39.9	−30.6	−24.4	−19.9	−16.6	−13.9
$CO_2 \rightleftarrows CO + \tfrac{1}{2}O_2$	−66,757	−44.72	−32.43	−20.07	−13.89	−10.20	−7.755	−6.00	−4.715	−3.69
$H_2O \rightleftarrows H_2 + \tfrac{1}{2}O_2$	−57,111	−39.77	−29.26	−18.64	−13.28	−10.05	−7.90	−6.34	−5.20	−4.27
$CO_2 + H_2 \rightleftarrows CO + H_2O$	−9,646	−4.947	−3.167	−1.433	−0.610	−0.147	+0.145	+0.341	+0.485	+0.580
$CO \rightleftarrows C + \tfrac{1}{2}O_2$	−27,404	−24.08	−19.23	−14.41	−11.98	−10.52	−9.530	−8.817	−8.277	−7.850
$\tfrac{1}{2}O_2 + \tfrac{1}{2}N_2 \rightleftarrows NO$	−21,400	−15.04	−11.13	−7.194	−5.231	−4.052	−3.207	−2.706	−2.285	−1.959
$NO \rightleftarrows N + O$	−121,000	−83.4	−61.2	−38.9	−27.7	−20.93	−16.42	−13.18	−10.76	−8.87
$CO + 3H_2 \rightleftarrows CH_4 + H_2O$	......		+11.6 at 500°K.						−5.8 at 1500°K.	

Reaction	ΔE_0°	$\log_{10} K$								
		2000°	2200°	2400°	2600°	2800°	3000°	3200°	3500°	4000°	5000°
$H_2 \rightleftarrows 2H$	−102,800	−5.53	−4.46	−3.57	−2.80	−2.13	−1.58	−1.08	−0.434	+0.43	+1.64
$O_2 \rightleftarrows 2O$	−117,300	−6.30	−5.09	−4.08	−3.23	−2.50	−1.86	−1.29	−0.577	+0.379	+2.715
$N_2 \rightleftarrows 2N$	−168,000	−11.9	−10.2	−8.72	−7.50	−6.47	−5.56	−4.77	−3.76	−2.39	−0.472
$CO_2 \rightleftarrows CO + \tfrac{1}{2}O_2$	−66,757	−2.86	−2.19	−1.648	−1.206	−0.811	−0.470				
$H_2O \rightleftarrows H_2 + \tfrac{1}{2}O_2$	−57,111	−3.52	−2.91	−2.41	−2.00	−1.63	−1.31		Data from Cranz (See Bibliography, Ref. 11.)		
$CO_2 + H_2 \rightleftarrows CO + H_2O$	−9,646	+0.658	+0.717	+0.762	+0.794	+0.819	+0.840				
$CO \rightleftarrows C + \tfrac{1}{2}O_2$	−27,404	−7.504	−7.221	−6.980	−6.777	−6.595	−6.440				
$\tfrac{1}{2}O_2 + \tfrac{1}{2}N_2 \rightleftarrows NO$	−21,400	−1.695	−1.479	−1.300	−1.150	−1.019	−0.907	−0.807	−0.680	−0.513	−0.279
$NO \rightleftarrows N + O$	−121,000	−7.35	−6.11	−5.065	−4.194	−3.431	−2.778	−2.203	−1.465	−0.475	−0.924
$CO + 3H_2 \rightleftarrows CH_4 + H_2O$	......	−8.0		−9 at 2300°K.							

* Lewis and von Elbe, *J. Am. Chem. Soc.*, No. 612, p. 57, 1935.

calculated as in Chap. IV, using K_P for 2273°K.   This is found to be

$$\log K_P = 0.73 \qquad \text{or} \qquad K_P = 5.37$$

Write material balances as follows:

Carbon	$a + b = 24$
Oxygen	$a + \dfrac{b}{2} + \dfrac{c}{2} = 20$
Hydrogen	$c + d = 15$
Nitrogen	$e = 5$
Equilibrium value	$\dfrac{b \times c}{a \times d} = 5.37$

This last is correct, since $a + b + c + d + e$ always equals 44 in this reaction, no matter what the proportions are, and, by *Dalton's law,*

$$\frac{P_A}{\pi} = \frac{a}{44} \qquad \text{and} \qquad P_A = \frac{a\pi}{44} \tag{63}$$

Solving these five equations simultaneously gives $a = 6.21$ $b = 17.79$, $c = 9.79$, $d = 5.21$, $e = 5$.   Therefore it may be written that cellulose deca-nitrate explodes and gives the following gaseous mixture at 2000°C.

CO_2	$= 6.21$ moles	$\dfrac{6.21}{44} \times 100 =$	14.1 per cent by volume
CO	$= 17.79$	$\dfrac{17.79}{44} \times 100 =$	40.5
H_2O	$= 9.79$	$\dfrac{9.79}{44} \times 100 =$	22.2
H_2	$= 5.21$	$\dfrac{5.21}{44} \times 100 =$	11.8
N_2	$= 5.00$	$\dfrac{5}{44} \times 100 =$	11.4
Total	$\overline{44.00}$ moles	Total	$\overline{100.0}$ per cent by volume

The example just quoted was for an explosive with insufficient oxygen for complete combustion.   To illustrate a case where the explosive has more than sufficient oxygen for complete combustion, consider nitroglycerin, or, more properly, glycerin tri-

nitrate, $C_3H_5(NO_3)_3$. If possible oxides of nitrogen formation are neglected, the explosion would give

$$C_3H_5(NO_3)_3 = aCO_2 + bCO + cH_2O + dH_2 + eO_2 + fN_2 \quad (64)$$
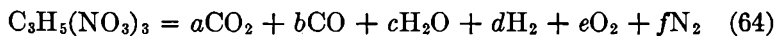
Setting up material balances as before,

Carbon $\qquad\qquad a + b = 3$

Oxygen $\qquad\qquad a + \dfrac{b}{2} + \dfrac{c}{2} + e = \dfrac{9}{2}$

Hydrogen $\qquad\qquad c + d = \dfrac{5}{2}$

Nitrogen $\qquad\qquad f = \dfrac{3}{2}$

Since there are this time six unknowns, two equilibrium constants must be chosen; any two that involve any of the reacting gases will do. Assume that the gases exist at 3000°K., and use the reactions

$$CO_2 = CO + \tfrac{1}{2}O_2$$
$$H_2O = H_2 + \tfrac{1}{2}O_2$$
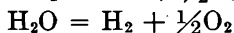
For the first one,

$$\frac{b \times e}{a} = K_P = 0.339 \quad \text{(from Table 5)}$$

For the second,

$$\frac{d \times e}{c} = K_P = 0.049$$

Solve these simultaneously as before.

$$a + b = 3$$
$$a + 0.5b + 0.5c + e = 4.5$$
$$c + d = 2.5$$
$$b \times e = 0.339a$$
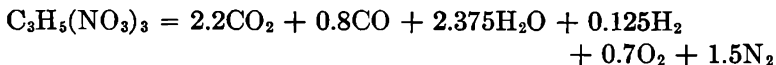$$d \times e = 0.049c$$

The approximate values are as follows:

$$a = 2.2 \qquad d = 0.125$$
$$b = 0.8 \qquad e = 0.7$$
$$c = 2.375 \qquad f = 1.5$$

Thus that the products of the explosion of nitroglycerin at 3000°K. (2727°C.) would be approximately

$$C_3H_5(NO_3)_3 = 2.2CO_2 + 0.8CO + 2.375H_2O + 0.125H_2$$
$$+ 0.7O_2 + 1.5N_2$$

and the gas composition would be

$$CO_2 = \frac{2.2}{7.7} \times 100 = 28.6 \text{ per cent by volume}$$

$$CO = \frac{0.8}{7.7} \times 100 = 10.4$$

$$H_2O = \frac{2.375}{7.7} \times 100 = 30.8$$

$$H_2 = \frac{0.125}{7.7} \times 100 = 1.6$$

$$O_2 = \frac{0.7}{7.7} \times 100 = 9.1$$

$$N_2 = \frac{1.5}{7.7} \times 100 = 19.5$$

$$\overline{100.0} \text{ per cent by volume}$$

The reaction rate increases with rise in temperature. At room temperature the reaction rate of many chemical reactions doubles with a rise in temperature of 10°C. At higher temperatures this temperature interval increases somewhat. Many reactions have rates which are extremely rapid at high temperatures (2000°C. and higher) but which become so slow at room temperature that the reaction appears to be at a standstill. When a gas mixture is cooled from a high to a low temperature, it frequently passes through a point in temperature at which the reaction apparently stops and the composition of the gas mixture becomes "frozen" at that temperature. It is possible to calculate the "freezing" temperature from the composition of the gas as analyzed and from the equilibrium constant of that particular reaction.

A sample of pyro smokeless powder was exploded in a bomb, giving the following gas, analyzed after the removal of water:

$$CO_2 = 14.83 \text{ per cent by volume}$$
$$CO = 46.65$$
$$H_2 = 23.00$$
$$N_2 = 14.84$$
$$O_2 = 0.26$$
$$CH_4 = 0.31$$
$$C_2H_4 = 0.13$$

The original powder had the following composition:

$$C = 27.86 \text{ per cent by weight}$$
$$H = 3.26$$
$$O = 56.86$$
$$N = 12.02$$

Take a basis of 100 parts by weight of the powder.

$$\text{Atoms C} = \frac{27.86}{12} = 2.32$$

$$\text{Moles H}_2 = \frac{3.26}{2} = 1.63$$

$$\text{Moles O}_2 = \frac{56.86}{32} = 1.78$$

$$\text{Moles N}_2 = \frac{12.02}{28} = 0.43$$

Take a basis of 100 moles of dry gas as analyzed.

TABLE 6

Moles	C	O_2	H_2	N_2
CO_2 = 14.83	14.83	14.83		
CO = 46.65	46.65	23.33		
H_2 = 23.00	.....	.....	23.00	
N_2 = 14.84	.....	.....		14.84
O_2 = 0.26	.....	0.26		
CH_4 = 0.31	0.31	.....	0.62	
C_2H_4 = 0.13	0.26	.....	0.26	
Total.........	62.05	38.42	23.88	14.84

Using C as a reference value, the O_2 from the powder must have been

$$62.05 \times \frac{1.78}{2.32} = 47.6 \text{ moles}$$

Similarly, the H_2 must have been

$$62.05 \times \frac{1.63}{2.32} = 43.6$$

Therefore, the O_2 that disappeared is

$$47.6 - 38.42 = 9.18$$

and the H_2 that disappeared is

$$43.6 - 23.88 = 19.72$$

If the H_2 that disappeared all has gone to form H_2O, this amount would have been $9.18 \times 2 = 18.36$ moles, which is in fair agreement with the 19.72 reported.

The N_2 that should be present in the gas is

$$62.05 \times \frac{0.43}{2.32} = 11.5 \text{ moles}$$

14.84 actually appeared, showing that some air was present in the gas as analyzed, probably owing to difficulties of manipulation. The N_2 from the air $= 14.84 - 11.5 = 3.34$ moles. This would correspond to

$$3.34 \times 21\frac{1}{7}9 = 0.89 \text{ moles } O_2 \text{ from air}$$

Therefore, the corrected O_2 from the powder is

$$38.42 - 0.89 = 37.53 \text{ moles}$$

and that to form water is

$$47.6 - 37.53 = 10.07 \text{ moles}$$

which corresponds to $10.07 \times 2 = 20.14$ moles of H_2 as compared with that actually calculated by the H_2 disappearance, or 19.72, a satisfactory agreement. The H_2O present in the gas may therefore be taken as 20 moles. Calculating the value of K for the water-gas reaction,

$$K = \frac{46.65 \times 20}{14.83 \times 23} = 2.74, \qquad \log K = +0.438$$

This corresponds to a temperature of approximately 1520°K. or 1247°C.$\pm$, at which temperature the reaction "froze."

CHAPTER VI

HEAT OF EXPLOSION

While most chemical reactions liberate or absorb heat, it is a characteristic of all explosive chemical reactions that they liberate heat, making the external heat effect Q a positive quantity.

Using the simple form of the batch energy balance

$$Q - W = \Delta E \qquad (7)$$

it appears that in an adiabatic apparatus, where there is no heat interchange with the surroundings and therefore where $Q = 0$,

$$-W = \Delta E$$

If the explosion occurs in a closed-chamber, or laboratory, adiabatic calorimetric bomb, where there can be no external work, then

$$W = 0$$

and ΔE must also equal zero. This means that all the heat liberated by the explosion must be absorbed by the system itself, which means a corresponding rise in temperature. Since, in a constant-volume process,

$$\int_{T_1}^{T_2} C_v \, dT = \Delta E \qquad (14)$$

the rise in temperature may be computed if values of the heat capacity at constant volume of the products of the explosion are known.

By similar reasoning, in a constant-pressure process where there is no external heat effect and any expansion takes place reversibly, *i.e.*, without friction,

$$Q_p - \int_{V_1}^{V_2} P \, dV = \Delta E = Q_p - P \, \Delta V \qquad (16)$$

But in a constant-pressure process $P \, \Delta V = \Delta PV$, and therefore, under this condition, since $\Delta H = \Delta E + \Delta PV$, $Q_p = \Delta H$. If the

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process is also adiabatic so that $Q = 0$, then the heat liberated will all go toward raising the temperature and since

$$\Delta H = \int_{T_1}^{T_2} c_p \, dT \tag{65}$$

if the heat capacity at constant pressure of the explosion products is known, the rise in temperature may be computed.

The relation between the molal heat capacity of a perfect gas at constant pressure and at constant volume is

$$Mc_p - Mc_v = R \tag{66}$$

For a non-perfect gas, the relationship is

$$c_p - c_v = \left[P + \left(\frac{\partial E}{\partial V} \right)_t \right] \left(\frac{\partial V}{\partial T} \right)_p \tag{67}$$

which can be evaluated by use of the μ charts and the critical data for the gases in question.

The relation between the heat effect at constant pressure, Q_p, and that at constant volume, Q_v,

$$Q_v = \Delta E, \qquad Q_p = \Delta H = \Delta E + \Delta PV \tag{68}$$

$$\therefore \; Q_p - Q_v = \Delta PV \tag{69}$$

If the average values of c_p and c_v are taken as constants over the temperature ranges in question, the

$$\int_{T_1}^{T_2} c_p \, dT = c_p(T_2 - T_1) \tag{70}$$

and

$$\int_{T_1}^{T_2} c_v \, dT = c_v(T_2 - T_1) \tag{71}$$

Then

$$Q_p - Q_v = (c_p - c_v)(T_2 - T_1) \tag{72}$$

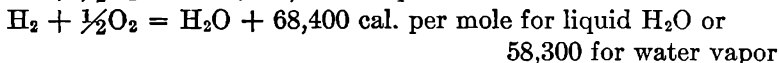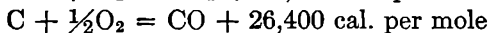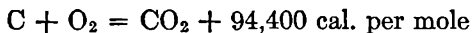and for one mole of a perfect gas, when $Mc_p - Mc_v = R$,

$$Q_p - Q_v = R \, \Delta T \tag{73}$$

Most values for heats of explosion are computed from data on heats of formation. Experimental determinations in the laboratory serve to check the reliability of the data used. Most heats of explosion of solid explosives are measured in calorimetric
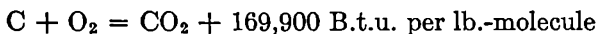
bombs, *i.e.*, at constant volume. Those for gaseous explosions may be carried out at constant pressure if the explosion reaction can be slowed down enough, but the closed-chamber method is much more common.

The technique for computing heat of explosion from heat of formation makes use of the method of Henri Hess, over 100 years old. Hess's law is correct for constant-pressure reactions only as may be shown by thermodynamic manipulation. The usual procedure, making use of a calorimetric bomb, is to explode the material being studied at ordinary temperature, the resulting temperature and pressure being very high. The temperature of the contents of the bomb is then allowed to fall until the initial value is again reached, and the external heat effect, measured by a calorimeter, is called the *heat of explosion*. Since, in such a calorimetric device, the heat passes from the interior, which is at high temperature, to the calorimeter, which is at lower temperature, this heat effect is not reversible and cannot be handled thermodynamically as a point function as can E or H. The correct method for computing such heat effects requires, therefore, the use of ΔE or ΔH, rather than Q. For a constant-pressure process, however, since $Q_p = \Delta H$, the use of Hess's method, with Q effects, is exact.

To illustrate the method of computing heat of reaction, take the case of the water-gas reaction, $CO_2 + H_2 = CO + H_2O$. It is required to calculate the heat of this reaction at ordinary temperature (25°C.) and pressure (normal barometer). In order to do this, the heats of formation of CO_2, CO, and H_2O from their elements, at the same temperature and pressure, are needed. The following gives these values:

$$C + O_2 = CO_2 + 94{,}400 \text{ cal. per mole}$$
$$C + \tfrac{1}{2}O_2 = CO + 26{,}400 \text{ cal. per mole}$$
$$H_2 + \tfrac{1}{2}O_2 = H_2O + 68{,}400 \text{ cal. per mole for liquid } H_2O \text{ or}$$
$$58{,}300 \text{ for water vapor}$$

These values, expressed as gram calories per gram formula weight, may be converted to the English system in B.t.u. per pound formula weight by multiplying by 1.8. Thus,

$$C + O_2 = CO_2 + 169{,}900 \text{ B.t.u. per lb.-molecule}$$

Then proceed as follows:

$$CO_2 + H_2 = CO + N_2O + Q_p(\Delta H)$$

|	
$\frac{1}{2}\cancel{O}_2 + H_2 = H_2O$ (vapor) $+ 58,300$ cal.	
$\cancel{C} + \frac{1}{2}\cancel{O}_2 \quad = \quad CO \quad\quad + 26,400$ cal.	
$-\cancel{C} - \cancel{O}_2 \quad = \quad -CO_2 \quad\quad - 94,400$ cal.	

$$CO_2 + H_2 = CO + H_2O \text{ (vapor)} - 9,700 \text{ cal.}$$
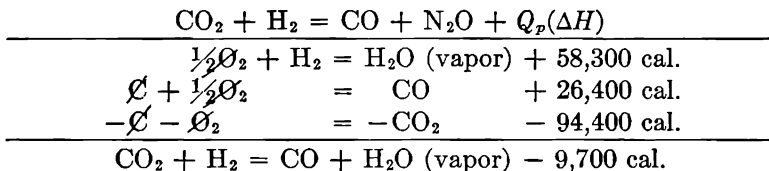
This states that at constant pressure and at 25°C. the water-gas reaction absorbs 9,700 cal. per mole (of any one constituent such as CO_2), being what is called an *endothermic reaction.* (A reaction that liberates heat is called *exothermic.*)

If this reaction were allowed to take place at constant volume, since

$$Q_p = \Delta H = \Delta E + \Delta PV \quad\text{and}\quad Q_v = \Delta E$$

it is necessary to evaluate ΔPV and subtract it from $Q_p = \Delta H$. In this case, since the temperature before and after was the same and the number of moles on each side of the equation
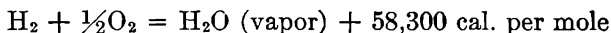
$$CO_2 + H_2 = CO + H_2O$$
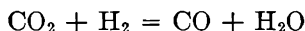
is the same (two), and if the perfect-gas formula $PV = NRT$ is assumed, then

$$\Delta PV = P_2V_2 - P_1V_1 - N_2RT_2 - N_1RT_1$$

and

$$T_2 = T_1 \quad\text{and}\quad N_2 = N_1$$
$$\therefore \Delta PV = 0 \quad\text{and}\quad Q_v = Q_p = \Delta H = \Delta E$$

Where the number of moles of gas on the two sides of a stoichiometrical equation is different, there is a correction, as illustrated in the heat of formation of H_2O vapor.

$$H_2 + \frac{1}{2}O_2 = H_2O \text{ (vapor)} + 58,300 \text{ cal. per mole}$$

at constant temperature and pressure, where $Q_p = \Delta H = 58,300$.

At moderate pressures and temperatures, where $PV = NRT$ is sufficiently close to the correct value, $V_2 = \frac{2}{3}V_1$ since there are $1\frac{1}{2}$ moles on the left-hand side of the equation and 1 mole on the right. Therefore, for each mole of H_2O formed, $N_2 = 1$ and $N_1 = 1\frac{1}{2}$.
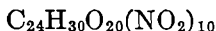
$$\therefore \Delta PV = RT\,\Delta N = 1.985 \times 298 \times (-\tfrac{1}{2})$$
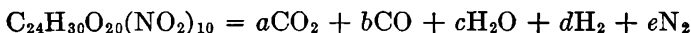$$= 296 \text{ cal. } (300 \text{ cal. approx.})$$

and

$$Q_v = \Delta E = 58,300 - 300 = 58,000 \text{ cal.}$$

Since most interior-ballistic calculations are for processes that are more nearly constant volume than constant pressure, the values given in Table 7 are given for $Q_v = \Delta E$ and must have ΔPV added to them to obtain $Q_p = \Delta H$.

The heat of formation of cellulose deca-nitrate,

$$C_{24}H_{30}O_{20}(NO_2)_{10}$$

at constant volume and room temperature is about 670,000 cal. per mole. It is required to calculate the heat of explosion at constant volume at room temperature. First it is necessary to determine the equilibrium products of the explosion at 25°C. (298°K.), making use of the value of K_P for the water-gas reaction at that temperature and assuming that the value of K_P is not affected by the change in pressure.

$$C_{24}H_{30}O_{20}(NO_2)_{10} = aCO_2 + bCO + cH_2O + dH_2 + eN_2$$
$$a + b = 24$$
$$c + d = 15$$
$$a + \frac{b}{2} + \frac{c}{2} = 20$$
$$e = 5$$

$$\frac{b \times c}{a \times d} = \log^{-1} - 4.947 = 0.0000113 \text{ (from Table 5)}$$

giving $a = 16$, $b = 8$, $c = 0$, $d = 15$, $e = 5$ (approx.).

Solve these five equations simultaneously.

$$C_{24}H_{30}O_{20}(NO_2)_{10} = 16CO_2 + 8CO + 15H_2 + 5N_2$$

$16C + 16O_2 = 16CO_2$	$+ 16 \times 94,400$ cal.
$8C + 4O_2 = 8CO$	$+ 8 \times 26,700$ cal.
$-5N_2 - 15H_2 - 24C - 20O_2 = C_{24}H_{33}O_{20}(NO_2)_{10}$	$- 670,000$ cal.
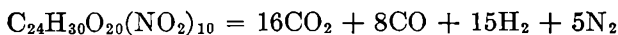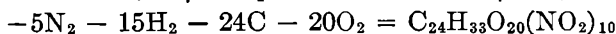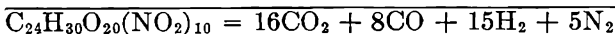
$$C_{24}H_{30}O_{20}(NO_2)_{10} = 16CO_2 + 8CO + 15H_2 + 5N_2$$
$$+ 1,054,000 \text{ cal.}$$

Since the formula weight of cellulose deca-nitrate is 1,098.44, the heat of explosion at constant volume at 25°C. will be

$$\frac{1,054,000}{1,098.44} = 960. \text{ cal. per g.}$$

or

$$960 \times 1.8 = 1,728 \text{ B.t.u. per lb.}$$

TABLE 7.—THERMOCHEMICAL DATA AT CONSTANT VOLUME AND ROOM TEMPERATURE
(Based on Schmidt, Z. ges. Schiess-Sprengstoffw., **29**: 259–266, 296–301, 1934)

Name*	Formulas†	Molecular weight (approx.)	Heat of combustion‡	Heat of formation§
Carbon—Diamond	C	12	7,873	
Graphite	......	......	7,856	
Sugar charcoal	......	......	8,060	
Gas carbon	......	......	8,097	
Carbon monoxide	CO	28	......	26,700
Carbon dioxide	CO_2	44	......	94,400
Hydrogen cyanide (hydrocyanic acid)	HCN	27	5,881	25,400
Formaldehyde	CH_2O	30	......	25,600
Nitromethane	CH_3NO_2	61	2,790	62,700
Nitrourea	$CH_3N_3O_3$ $NH_2{\cdot}CO{\cdot}NH{\cdot}NO_2$	105	1,272	39,900
Methyl nitrate	CH_3NO_3	77	......	77,300
Urea	CH_4N_2O $(NH_2)_2CO$	60	2,535	
Methane	CH_4	16	13,270	
Methyl alcohol	CH_4O CH_3OH	32	......	61,700
Nitroguanidine	$CH_4N_4O_2$ $NH_2{\cdot}C{\cdot}NH{\cdot}NH{\cdot}NO_2$	104	2,032	18,000
Methylamine nitrate	$CH_6N_2O_3$ $CH_3{\cdot}NH_2{\cdot}HNO_3$	94	......	58,000
Guanidine nitrate	$CH_6N_4O_3$ $CNH(NH_2)_2{\cdot}HNO_3$	122	1,715	88,000
Acetylene	C_2H_2	26	12,115	−58,100
Ethylene	C_2H_4	28	12,140	
Ethylene glycol dinitrate	$C_2H_4N_2O_6$ $C_2H_4(ONO_2)_2$	152	1,764	56,000
Acetaldehyde	C_2H_4O $CH_3{\cdot}CHO$	44	......	57,100

Nitroethane	C₂H₅NO₂	75	4,299	35,400
Ethyl nitrate	C₂H₅NO₃	91	3,561	33,700
Ethane	C₂H₆	30	12,360	51,400 (gas)
Methyl ether	C₂H₆O (CH₃)₂O	46	. . . . .	67,000
Methyl alcohol	C₂H₆O C₂H₅·OH	46	4,143	18,400
Ethyl nitramine	C₂H₆N₂O₂ C₂H₅·NH·NO₂	90	1,887	107,000
Ethanol amine dinitrate	C₂H₇N₃O₆ C₂H₅·NH₂·(NO₃)₂	169	2,030	149,000
Ethylene diamine nitrate	C₂H₁₀N₄O₆ C₂H₄(NH₂)₂·(HNO₃)₂	186	5,056	. . . . .
Cyanogen	C₂N₂	52	. . . . .	−65,400
Mercury fulminate	C₂N₂O₂Hg Hg(OCN)₂	284.6	1,631	82,700
Glycerin trinitrate (nitroglycerin)	C₃H₅N₃O₉ C₃H₅(NO₃)₃	227	. . . . .	66,300
Acetone	C₃H₆O (CH₃)₂CO	58	2,285	. . . . .
Cyclic trimethylene trinitramine (hexogen) (cyclonite)	C₃H₆N₆O₆ (CH₂·N·NO₂)₃	222	5,369	−21,300
Nitropropane	C₃H₇NO₂	89	4,312	42,100
Glycerin	C₃H₈O₃ C₃H₅(OH)₃	92	5,360	157,000
Ethyl urea	C₃H₈N₂O CO·NH₂·NH·C₂H₅	88	. . . . .	81,200
Cyanuric triazide	C₃N₁₂	204	. . . . .	−222,000
Erithritol tetranitrate	C₄H₆N₄O₁₂ C₄H₆(NO₃)₄	302	1,546	114,000
Dinitrodimethyl oxamide	C₄H₆N₄O₆ C₂O₂(N·CH₃·NO₂)₂	206	2,485	68,600
Diethylene glycol dinitrate	C₄H₈N₂O₇ O(C₂H₄O·NO₂)₂	196	2,798	99,400
Ethyl acetate	C₄H₈O₂ C₂H₅·CH₃·COO	88	. . . . .	114,900
Erithritol	C₄H₈O₃ C₄H₆(OH)₄	122	4,132	211,000
Ethyl ether	C₄H₁₀O (C₂H₅)₂O	74	. . . . .	70,500

* The usual chemical name, in certain cases followed by the common industrial name.
† The condensed chemical formula is followed by the explanatory formula.
‡ The heat of combustion is in calories per gram
§ The heat of formation is in calories per gram molecular weight (mole).

TABLE 7.—THERMOCHEMICAL DATA AT CONSTANT VOLUME AND ROOM TEMPERATURE.—(Continued)

Name*	Formulas†		Molecular weight (approx.)	Heat of combustion‡	Heat of formation§
Penta erithritol tetranitrate (PETN)	$C_5H_8N_4O_{12}$	$C(CH_2O\cdot NO_2)_4$	316	1,960	123,000
Penta erithritol	$C_5H_{12}O_4$	$C_5H_8(OH)_4$	136	4,132	211,000
Trinitrochlorobenzene	$C_6H_2N_3O_6Cl$	$C_6H_2(NO_2)_3Cl$	247.5	2,609	−11,100
Lead trinitroresorcinate (lead styphnate)	$C_6H_3N_3O_8Pb$	$C_6H(NO_2)_3O\cdot Pb\cdot H_2O$	468	1,111	−107,000
Trinitrobenzene (symmetrical)	$C_6H_3N_3O_6$	$C_6H_3(NO_2)_3$	213	3,126	2,300
Trinitrobenzene (unsymmetrical)	. . . .	. . . .	. . . .	3,195	−12,400
2,4,6 Trinitrophenol (picric acid)	$C_6H_3N_3O_7$	$C_6H_2(OH)(NO_2)_3$	229	2,690	53,500
2,3,4,6 Tetranitroaniline	$C_6H_3N_5O_8$	$C_6H\cdot NH_2\cdot(NO_2)_4$	273	2,411	8,500
2,4,6 Trinitroresorcinol (styphnic acid)	$C_6H_3N_3O_8$	$C_6H(OH)_2(NO_2)_3$	245	2,203	125,000
o-Dinitrobenzene	$C_6H_4N_2O_4$	$C_6H_4(NO_2)_2$	168	4,194	−2,500
m-Dinitrobenzene	. . . .	. . . .	. . . .	4,155	4,000
p-Dinitrobenzene	. . . .	. . . .	. . . .	4,146	5,600
2,4 Dinitrophenol	$C_6H_4N_2O_5$	$C_6H_3OH(NO_2)_2$	184	3,527	53,000
2,4,6 Trinitroaniline	$C_6H_4N_4O_6$	$C_6H_2\cdot NH_2(NO_2)_3$	228	2,962	27,000
Nitrobenzene	$C_6H_5NO_2$		123	6,033	6,200
p-Nitrophenol	$C_6H_5NO_3$	$C_6H_4OH(NO_2)$	139	4,900	54,800
2,4 Dinitroaniline	$C_6H_5N_3O_4$	$C_6H_3\cdot NH_2(NO_2)_2$	183	3,934	15,500
Phenyl azide	$C_6H_5N_3$		119	6,866	−82,000
m-Nitroaniline	$C_6H_6N_2O_2$	$C_6H_4\cdot NH_2\cdot NO_2$	138	5,464	16,000
Ammonium picrate (Explosive D)	$C_6H_6N_4O_7$	$C_6H_2(NO_2)_3O\cdot NH_4$	246	. . . .	81,900

					cal. per gram
Benzene	C_6H_6	C_6H_6	78	10,026	−13,000
Phenol	C_6H_6O	C_6H_5OH	94	7,811	35,000
Resorcinol	$C_6H_6O_2$	$C_6H_4(OH)_2$	110	6,210	86,000
Aniline	C_6H_7N	$C_6H_5NH_2$	93	8,756	−12,000
Mannitol hexanitrate	$C_6H_8N_6O_{18}$	$C_6H_8(O \cdot NO_2)_6$	452	1,515	152,000
Dinitro diethyl oxamide dinitrate	$C_6H_3N_6O_{14}$	$C_2O_4N_2(NO_2)_2(C_2H_4 \cdot NO_3)_2$	356	2,024	116,000
Hexamethylene diamine triperoxide	$C_6H_{12}N_2O_6$	$(CH_2)_6O_6N_2$	208	4,295	80,000
Cellulose	$(C_6H_{10}O_5)_n$		$162n$	4,185	$227,000n$
Nitrocellulose	11.05 per cent N			2,580	754
	11.64			2,515	699
	12.20			2,437	664
	12.81			2,370	605
	13.45			2,280	558
	14.12			2,208	500
Trinitro triazide benzene	$C_6N_{12}O_6$	$C_6(N_3)_3(NO_2)_3$	336	2,500	−272,000
Trinitro benzaldehyde	$C_7H_3N_3O_7$	$C_6H_2 \cdot CHO(NO_2)_3$	241	3,035	31,600
Trinitro anisol	$C_7H_5N_3O_7$	$C_6H_2O(CH_3)(NO_2)_3$	243	3,236	44,200
2,4,6 Trinitrotoluene (TNT)	$C_7H_5N_3O_6$	$C_6H_2 \cdot CH_3(NO_2)_3$	227	3,599	13,000
Trinitrocresol	$C_7H_5N_3O_7$	$C_6H(CH_3)OH(NO_2)_3$	243	3,200	52,700
Trinitro phenyl methyl nitramine (tetryl)	$C_7H_5N_5O_8$	$C_6H_2(NO_2)_3 \cdot N \cdot CH_3 \cdot NO_2$	287	2,925	−9,300
Dinitrotoluene (DNT)	$C_7H_6N_2O_4$	$C_6H_3 \cdot CH_3(NO_2)_2$	182	4,709	6,900
o-Nitrotoluene	$C_7H_7NO_2$	$C_6H_4 \cdot CH_3(NO_2)$	137	6,559	8,400
m-Nitrotoluene				6,527	12,700
p-Nitrotoluene				6,494	17,300
Cresol	C_7H_8O	$C_6H_4 \cdot CH_3 \cdot OH$	108	8,290	36,000
Phenyl urea	$C_7H_8N_2O$	$C_6H_5 \cdot NH \cdot NH_2 \cdot CO$	136	6,469	51,300
Phthalide	$C_8H_6O_2$	$C_6H_4 \cdot CH_2 \cdot COO$	134	6,470	92,000

TABLE 7.—THERMOCHEMICAL DATA AT CONSTANT VOLUME AND ROOM TEMPERATURE.—(*Continued*)

Name*	Formulas†	Molecular weight (approx.)	Heat of combustion‡	Heat of formation§
Trinitro phenyl glycol nitrate ether	$C_8H_6N_4O_{10}$	$C_6H_2(NO_2)_3O\cdot C_2H_4O\cdot NO_2$	318	2,823	61,400
Dinitro phenyl glycol nitrate ether	$C_8H_7N_3O_8$	$C_6H_3(NO_2)_2O\cdot C_2H_4O\cdot NO_2$	273	3,455	49,400
2,4,6 Trinitro xylene	$C_8H_7N_3O_6$	$C_6H(CH_3)_2(NO_2)_3$	241	4,039	19,200
Nitroso ethyl phenylamine	$C_8H_{10}N_2O$	$C_2H_5\cdot C_6H_5\cdot N\cdot NO$	150	7,453	-24,500
Xylene	C_8H_{10}	$C_6H_4(CH_3)_2$	106	10,273	4,000
Tetra methanol cyclopentanone tetranitrate	$C_9H_{12}N_4O_{13}$	$C_4H_4(CH_2\cdot O\cdot NO_2)_4CO$	384	2,870	153,000
Tetra methanol cyclopentanol tetranitrate	$C_9H_{13}N_4O_{15}$	$C_4H_4(CH_2\cdot O\cdot NO_2)_4CHO\cdot NO_2$	431	2,668	140,000
1,5 Dinitronaphthalene	$C_{10}H_6N_2O_4$	$C_{10}H_6(NO_2)_2$	218	5,299	-7,300
1,8 Dinitronaphthalene			.....	5,286	-4,600
Nitronaphthalene	$C_{10}H_7NO_2$		173	6,878	-8,700
Naphthalene	$C_{10}H_8$		128	9,640	
Naphthylamine	$C_{10}H_9N$	$C_{10}H_7\cdot NH_2$	143	8,865	-20,000
Methyl phenyl urethane	$C_{10}H_{13}NO_2$	$CO\cdot N\cdot CH_2\cdot C_6H_5\cdot O\cdot C_2H_5$	179	7,515	36,000
Tetra methylol cyclohexanone tetranitrate	$C_{10}H_{14}N_4O_{15}$	$C_6H_6(CH_2ONO_2)_4CO$	398	3,153	163,000
Tetra methylol cyclohexanol tetranitrate	$C_{10}H_{15}N_6O_{15}$	$C_6H_6(CH_2ONO_2)_4CHO\cdot NO_2$	445	2,921	152,000
Camphor	$C_{10}H_{16}O$		152	9,273	74,900
Ethyl phenyl urethane	$C_{11}H_{15}NO_2$	$CO\cdot N\cdot C_2H_5\cdot C_6H_5(OC_2H_5)$	193	7,561	80,000
Nitroso diphenylamine	$C_{12}H_{10}N_2O$	$(C_6H_5)_2N\cdot NO$	198	7,788	-71,000
Diphenylamine (DPA)	$C_{12}H_{11}N$	$(C_6H_5)_2NH$	169	9,086	-31,000

Diphenyl urea (asymmetrical)	$C_{13}H_{12}N_2O$	$CO \cdot NH_2 \cdot N(C_6H_5)_2$	212	7,700	1,000
Benzoyl peroxide	$C_{14}H_{10}O_4$	$(C_6H_5 \cdot CO)_2O_2$	242	6,417	107,000
Diphenyl urethane	$C_{15}H_{15}NO_2$	$CO \cdot N \cdot (C_6H_5)_2O \cdot C_2H_5$	241	7,697	69,000
Diethyl diphenyl urea (Centralite)	$C_{15}H_{20}N_2O$	$CO \cdot N \cdot (C_6H_5)_2(C_2H_5)_2$	268	8,528	−4,000
Dibutyl phthalate	$C_{16}H_{22}O_4$	$C_6H_4(COOC_4H_9)_2$	278	7,756	100,000

Inorganic Compounds

Aluminum oxide	Al_2O_3		102	.....	392,000
Ammonia (gas)	NH_3		17	.....	10,500
Ammonium azide	NH_4N_3		60	.....	−19,000
Ammonium carbonate	$(NH_4)_2CO_3$		96	.....	221,600 (solution)
Ammonium chloride	NH_4Cl		53.5	.....	75,800
Ammonium nitrate	NH_4NO_3		80	.....	88,100
Ammonium sulphate	$(NH_4)_2SO_4$		132.2	.....	282,000
Antimony sulphide	Sb_2S_3		336.3	.....	34,400
Barium azide	BaN_6		221.4	.....	−13,700
Barium chlorate	$Ba(ClO_3)_2$		304.1	.....	175,200
Barium chloride	$BaCl_2$		208.1	.....	197,100
Barium nitrate	$Ba(NO_3)_2$		261.4	.....	228,000
Carbon disulphide	CS_2		76	.....	−19,000
Copper azide	CuN_3		105.6	.....	−63,700
Copper picrate	$Cu[C_6H_2(NO_2)_3O]_2$		519.3	.....	60,400
Hydrazoic acid	HN_3		43	.....	−55,200
Lead azide	PbN_6		291.2	.....	−107,000
Lead oxide	PbO		221.9	.....	52,900
Lead nitrate	$Pb(NO_3)_2$		330.9	.....	108,100
Lead picrate	$Pb[C_6H_2(NO_2)_3O]_2$		661.9	.....	82,200

TABLE 7.—THERMOCHEMICAL DATA AT CONSTANT VOLUME AND ROOM TEMPERATURE.—(Continued)

Name*	Formulas†	Molecular weight (approx.)	Heat of combustion‡	Heat of formation§
Mercury azide	HgN_3	242.6		-64,500
Mercury oxide	HgO	216		21,500
Mercury nitrate	$Hg(NO_3)_2$	333.6		57,400
Nitric acid	HNO_3	63		41,600
Nitrogen oxide	N_2O	44		-18,000
	NO	30		-21,600
	N_2O_3	76		-21,400
	NO_2	46		-4,100
	N_2O_5	108		-1,200
Potassium carbonate	K_2CO_3	138.2		280,000
Potassium chlorate	$KClO_3$	122.6		93,800
Potassium chloride	KCl	74.6		103,300
Potassium nitrate	KNO_3	101.1		119,500
Potassium oxide	K_2O	94.2		86,800
Potassium perchlorate	$KClO_4$	138.6	......	113,500
Potassium picrate	$K[C_6H_2(NO_2)_3O]$	267.1	......	110,100
Potassium sulphate	K_2SO_4	174.2	......	344,300
Potassium sulphide	K_2S	110.2	......	102,200
Silver azide	AgN_3	149.9	......	-67,800
Silver oxide	Ag_2O	231.8	......	22,200
Silver nitrate	$AgNO_3$	169	......	28,700
Sodium carbonate	Na_2CO_3	106	......	272,000
Sodium chlorate	$NaClO_3$	106.5	......	84,800

Sodium chloride	NaCl	58.5		97,800
Sodium nitrate	NaNO₃	85		111,300
Sodium perchlorate	NaClO₄	122.5		100,300
Sodium picrate	Na[C₆H₂(NO₂)₃O]	251		103,400
Sodium sulphate	Na₂SO₄	142.8		328,600
Sodium sulphide	Na₂S	78		88,400
Strontium oxide	SrO	103.5		141,200
Strontium nitrate	Sr(NO₃)₂	211.6		220,000
Strontium picrate	Sr[C₆H₂(NO₂)₃O]₂	543.5		196,000
Sulphur dioxide	SO₂	64		69,300
Sulphur trioxide	SO₃	80		103,700 (solid)
Sulphuric acid	H₂SO₄	98		193,000
Water	H₂O	18		58,000 (gas) 68,000 (liquid)
Zinc azide	ZnN₆	149.4	....	−52,100
Zinc oxide	ZnO	81	....	85,400
Zinc picrate	Zn[C₆H₂(NO₂)₃O]₂	521	....	102,800

If the heat of explosion at constant pressure is desired, it is necessary to subtract ΔPV which in this case, calling it equal ΔNRT with $R = 1.985$, $T = 298°K.$, and $\Delta N = 44$, paying no attention to the volume occupied by the solid powder as compared with that of the gas,

$$\Delta H = 1,054,000 - 44 \times 1.985 \times 298$$
$$= 1,028,000 \text{ cal. per } 1,098 \text{ g., or } 936 \text{ cal. per g.}$$

The computation of heats of explosion at other than room temperature requires reliable heat-capacity data and will be included in a later chapter after such data have been described.

Table 7 gives the heats of formation for a number of chemical compounds of interest in ballistic calculations. These data give the heat of formation at constant volume, expressed in calories per mole. The first portion of Table 7 contains various *organic substances* of interest to the explosives industry. The arrangement is according to the number of C atoms and then according to the H atoms.

CHAPTER VII

HEAT CAPACITY OF POWDER GASES

As stated in Chap. II on Basic Thermodynamic Principles, the heat capacity, or specific heat, of a gas is defined as

$$\text{Heat capacity at constant volume} = c_v = \left(\frac{\partial E}{\partial T}\right)_v$$

or

$$\text{Heat capacity at constant pressure} = c_p = \left(\frac{\partial H}{\partial T}\right)_p$$

When based on one unit weight of substance, it is called *specific heat*. When based on one mole or molecular weight, it is called *molal heat capacity*. In the English system, specific heat is usually expressed as B.t.u. per pound per degree Fahrenheit; in the metric system, as gram calories per gram per degree centigrade. Since the heat capacity of liquid water in the metric system is approximately 1, the expression specific heat often refers to the ratio of the heat capacity of the substance in question to that of an equal weight of liquid water. Heat capacity, while having the physical dimensions of heat per unit of weight per degree temperature, is independent of the system and has the same numerical value in any consistent system.

The specific heat of liquid water is the highest of any known substance, that of vapors being appreciably less and that of the common so-called "permanent" gases being still less, while most heavy solids are lowest of all. All heat capacities increase with increasing temperature.

As an estimate of the molal heat capacity at constant volume for solids (at constant pressure also), it is usual to assume Kopp's law. This rule adds the atomic heat capacities of the elements making up the compound in their proper proportions. For the atomic heat capacities at constant volume of the elements, use the following:

Carbon   = 1.8
Hydrogen   = 2.3
Oxygen and nitrogen = 4.0
Sulphur   = 5.4
Heavier elements   = 6.4

For example, the specific heat of solid sodium chloride (NaCL), whose molecular weight is 58.5, would have a value of c_v calculated from this rule as follows, there being two atoms in the molecule,

$$\frac{2 \times 6.4}{58.5} = 0.22$$

while the actual value is about 0.21 at room temperature. Similarly cellulose deca-nitrate $C_{24}H_{30}O_{20}(NO_2)_{10}$, which has a formula weight of 1,098, would have its specific heat calculated as follows:

$$
\begin{array}{llll}
C & 24 \times 1.8 = & 43.2 \\
H & 30 \times 2.3 = & 69 \\
O & 40 \times 4.0 = & 160 \\
N & 10 \times 4.0 = & 40 \\
\hline
& & 312.2
\end{array}
$$

$$\text{Estimated specific heat} = \frac{312.2}{1,098} = 0.28$$

It should be remembered that such estimated values are for approximate use only. Accurate laboratory determinations are necessary for more reliable values.

The heat capacity of gases varies with both temperature and pressure, as well as with the variety of the gas.

The molal heat capacity at constant pressure of gases common in explosion products is given in Fig. 3 as a function of temperature. This chart is for zero or low pressures, where the gases behave much like perfect gases. To use this chart, it is necessary to allow for the change in Mc_p due to temperature.

$$Q_p = \Delta H = \int_{T_1}^{T_2} c_p \, dT \tag{65}$$

This is best done by graphical evaluation of the definite integral, as shown in Fig. 4. The shaded area between the limits of T_1 and T_2 represents $\int_{T_1}^{T_2} Mc_p \, dT$.

Another way is to use an average value of Mc_p (called $Mc_{p_{ave}}$).

$$Q_p = Mc_{p_{ave}}(T_2 - T_1) \tag{74}$$

Still another method is to use Fig. 5. This chart gives $Mc_{p_{ave}}$ between 60 and $t°$F. and

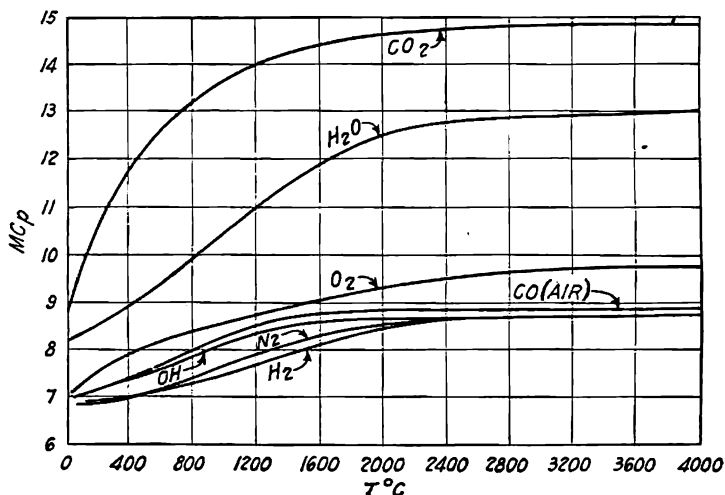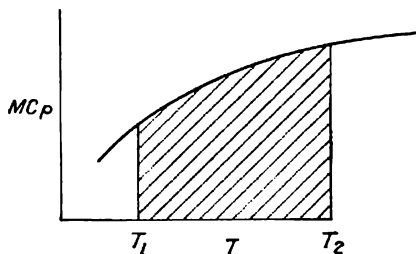$$Q_p = Mc_{p_{ave\,t_2}}(t_2 - 60) = Mc_{p_{ave\,t_1}}(t_1 - 60) \tag{75}$$

Fig. 3.

Fig. 4.

To allow for the change in heat capacity with pressure, the method used by Weber is recommended. It is based on the relation

$$\left(\frac{\partial H}{\partial P}\right)_t = V - T\left(\frac{\partial V}{\partial T}\right)_p \tag{76}$$
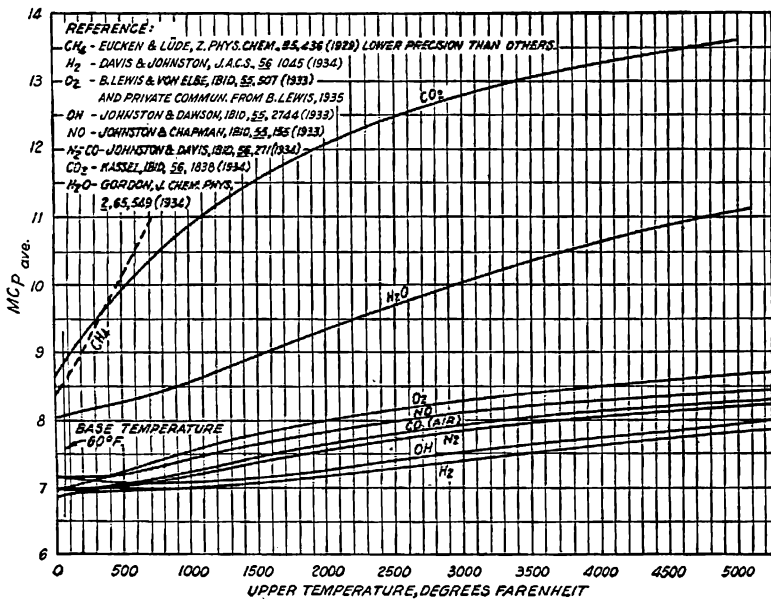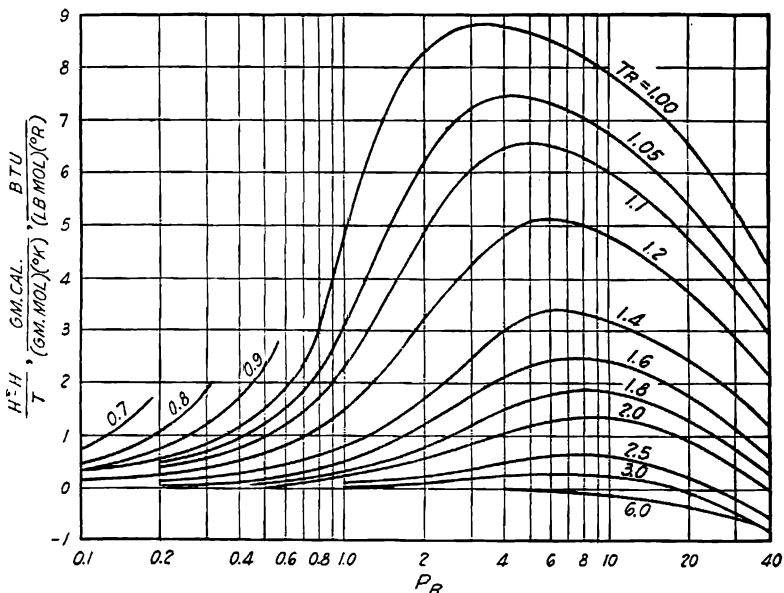
FIG. 5.

FIG. 6.—(From Weber.)

The plot of $(H^* - H)/T$ vs. P_R is shown in Fig. 6. To use this chart, select the temperature T at which the effect of pressure is to be computed, and calculate $T_R = T/T_c$ when T_c is the critical temperature of the gas in question.

H^* represents the enthalpy of the gas at zero pressure where it behaves as a perfect gas and fits the Mc_p chart (Fig. 6), and H is the enthalpy at the desired pressure P, represented on the chart by $P_R = P/P_c$.

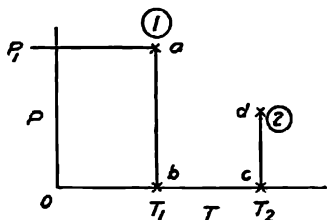
Fig. 7.

To complete the calculation, refer to Fig. 7. Compute $H^* - H$ for T_1 (point a to point b) where P_1 is the initial pressure; then calculate

$$H^*_{T_2} - H^*_{T_1} \int_{T_1}^{T_2} Mc_p \, dT \qquad (77)$$

using the chart, Fig. 7 (point b to point c). Then go from c to d at T_2. The sum of all three ΔH's will be the ΔH required; *i.e.*,

$$H_{(d-a)} = \int_{T_1}^{T_2} Mc_p \, dT$$

and

$$c_{p_{avg}} = \frac{\Delta H(d - a)}{T_2 - T_1} \qquad (78)$$

This method is quite precise for single gases. For mixtures of gases, the best method known at the time of writing is to use a weighted mean, based on the molal composition of the mixture.

CALCULATION OF EXPLOSION TEMPERATURE AND PRESSURE

The chemical reaction that takes place when a propellent powder or similar substance explodes liberates the heat of reaction described in Chap. VI. If the explosion is confined within a closed chamber, such as the calorimetric bomb, the energy thus liberated can do a small amount of external work by causing the bomb to swell, but the bulk of the energy will appear either in the form of heat lost to the surroundings or as an increase in temperature of the contents of the bomb. The first effect due to the expansion of the vessel is usually small enough to be neglected but may be estimated as shown below. The other two effects are complementary. When the final temperature is the same as that at the start, all the heat effect at constant volume goes to the surroundings. If the bomb is strictly adiabatic, the energy must all go toward raising the temperature and the final temperature will be the maximum temperature possible under the circumstances. The pressure produced at the maximum temperature will also be the maximum pressure.

For all practical purposes, the maximum temperature will be independent of the loading density, or quantity of explosive present, but the maximum pressure will vary almost directly with it. For this reason, it is customary to compute the maximum possible temperature by thermochemical means and then use this figure to estimate the corresponding pressure.

While the use of the perfect-gas formula or of the covolume calculation is quite simple, the results of the pressure calculations are not considered sufficiently precise for firearms purposes and recourse is had to the μ chart method, which gives results that appear to be as good as those determined experimentally. The variations of these several methods will be noted below.

Any hot gas confined in a closed vessel will lose heat to that vessel. Therefore, in actual closed-chamber firings of explosives, the maximum temperature obtained and the corresponding pres-

sure will be less than the theoretical "uncooled" temperature. The amount of this heat loss can be predicted and suitable allowance made for it.

The calculation of uncooled maximum temperature requires successive approximation, since it is necessary to know the composition of the explosion gases, and that composition depends on the equilibrium constants, which in turn depend on the temperature. Fortunately, the values of K_P do not change rapidly with respect to temperature at the temperatures reached in firings,
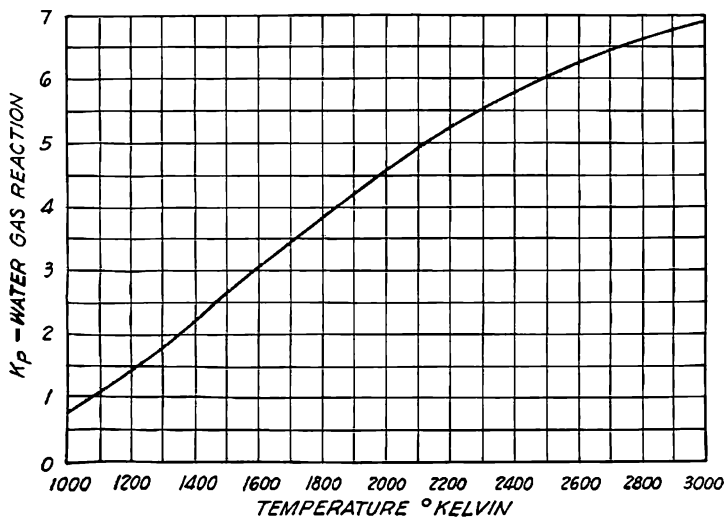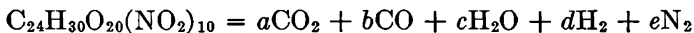

FIG. 8.

and preliminary estimates are usually very near the actual value.

As an example, allow 100 g. of $C_{24}H_{30}O_{20}(NO_2)_{10}$ to explode in a chamber of 1 l. capacity (this is a loading density of 0.1) with no air present and with the initial temperature 15°C. As a first approximation, neglect expansion of the container and any heat losses to it or to the surroundings.

Take as a basis one formula weight of explosive, or 1,098 g. This will not affect the temperature calculation, and it simplifies the stoichiometry. Proceed as in Chap. V.

$$C_{24}H_{30}O_{20}(NO_2)_{10} = aCO_2 + bCO + cH_2O + dH_2 + eN_2$$

$$a + b = 24$$
$$a + \frac{b}{2} + \frac{c}{2} = 20$$
$$c + d = 15$$
$$e = 5$$
$$\frac{b \times c}{a \times d} = K_P \text{ for water-gas reaction (see Table 5)}$$

The plot of K_P vs. temperature in Fig. 8 shows that at the probable high temperature expected—somewhere between 2000 and 3000°K.—the value of K_P is approximately 6; this value will therefore be used as the first approximation.

Solving for a, b, c, d, and e gives the following:

$$C_{24}H_{30}O_{20}(NO_2)_{10} = 6CO_2 + 18CO + 10H_2O + 5H_2 + 5N_2$$
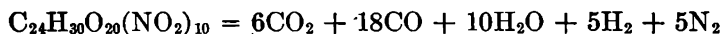
Using this gas composition, then calculate the heat of explosion at constant volume.

$$24C + 30H + 40O + 10N = C_{24}H_{30}O_{20}(NO_2) + 670,000 \text{ cal.}$$
$$6C + 6O_2 = 6CO_2 + 6 + 94,400 = 566,400 \text{ cal.}$$
$$18C + 9O_2 = 18CO + 18 \times 26,700 = 480,600 \text{ cal.}$$
$$10H_2 + 5O_2 = 10H_2O + 10 \times 58,000 = 580,000 \text{ cal.}$$

Combining these heats of formation as before, gives

$$C_{24}H_{30}O_{20}(NO_2)_{10} = 6CO_2 + 18CO + 10H_2O + 5H_2 + 5N_2$$
$$+ 957,000 \text{ cal.}$$
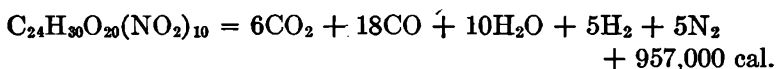
This means that 957,000 cal. is available for heating the explosion gases up to T_2°K.

Continue the approximation by using the chart, Fig. 5, for $Mc_{p_{ave}}$ plotted against t°F., and assuming the perfect-gas relation $Mc_p - R = Mc_v$, when $R = 1.987$.

At 3000°K., t°F. is 4340°, and the values read from the chart for $Mc_{p_{ave}}$ are

$$CO_2 = 13.4$$
$$CO = 8.3$$
$$H_2O = 10.8$$
$$H_2 = 7.7$$
$$N_2 = 8.1$$

Multiply these by the moles of each gas present.

$$\begin{aligned}
CO_2 &= 13.4 \times 6 &&= 80.4 \\
CO &= 8.3 \times 18 &&= 149.4 \\
H_2O &= 10.8 \times 10 &&= 108.0 \\
H_2 &= 7.7 \times 5 &&= 38.5 \\
N_2 &= 8.1 \times 5 &&= \underline{40.5} \\
&\text{Sum for 44 moles} &&\ \ 416.8
\end{aligned}$$

or a weighted average $Mc_p = 416.8/44 = 9.47$.

Then subtract $1.987(R)$ to obtain the perfect-gas value for $Mc_{v_{ave}} = 7.48$.

The rise in temperature that might be expected, therefore, would be

$$\Delta T = T_2 - T_1 = \frac{957,000}{7.48 \times 44} = 2910°$$

which would give T_2 as $2910° + 15°C. = 2925°C.$ or

$$2925°C. + 273° = 3198°K.$$

Referring again to K_P, it is seen that for $3198°K.$, $K_P = 7.15$ (extrapolated above $3000°K.$). Solving again for a, b, c, d, and e, using the new value $(b \times c)/(a \times d) = 7.15$, gives

$$5.65CO_2 + 18.35CO + 10.35H_2O + 4.65H_2 + 5N_2$$
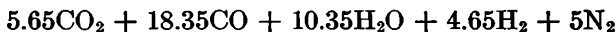
This change in gas composition will make but little change in the computed temperature, and because of the approximations introduced it is considered unnecessary to carry the calculation of T further. It may therefore be stated that the maximum uncooled temperature would be approximately $3200°K.$ or $2900°C.$ (to the nearest $100°$).

It is now possible to calculate the pressure corresponding to the maximum uncooled temperature.

First use the least reliable $PV = NRT$ formula when

P = desired pressure, atm.

V = gas volume, l. $= 1,098/100 = 10.98$ l. (since 100 g. occupies 1 l.)

N = moles of gas present = 44

R = gas constant $= 0.08206$, in l.-atm.

T = uncooled temperature $= 3200°K.$

$P \times 10.98 = 44 \times 0.08206 \times 3,200$

$P_{max} = 1,050$ atm.

Next use the *covolume relation;* since $\alpha = V_c/3$, tabulate α for the constituents of the gas.

<div align="center">TABLE 8</div>

Gas	V_c	α	N	αN	T_c, °K.	P_c, atm.
CO_2	0.0957	0.0319	5.65	0.180	304.26	73.0
CO	0.0930	0.0310	18.35	0.569	132.98	34.53
H_2O	0.0566	0.0189	10.35	0.196	647.30	218.53
H_2	0.0650	0.0217	4.65	0.101	41.3	20.8 (pseudo value)
N_2	0.0900	0.0300	5.00	0.150	126.1	33.5
			44.00	1.196		

$$\alpha \text{ average} = \frac{1.196}{44} = 0.0272$$

$$P(V - \alpha) = RT \qquad \text{(for 1 mole)}$$

$$V = 1. \text{ per mole} = \frac{10.98}{44} = 0.2496$$

$$P(0.2496 - 0.0272) = 0.08206 \times 3,200$$

$$P_{max} = \frac{0.08206 \times 3,200}{0.2224} = 1,180 \text{ atm.}$$

Now to use the μ chart relation (Fig. 1). Calculate first the reduced temperature (T_R) using the critical data given above.

$$T_R = \frac{3,200}{44} \left(\frac{5.65}{304.26} + \frac{18.35}{132.98} + \frac{10.35}{647.30} + \frac{4.65}{41.3} + \frac{5}{126.1} \right)$$

$$T_R = 23.9$$

$$P_R = \frac{P_{max}}{44} \left(\frac{5.65}{73.0} + \frac{18.35}{34.53} + \frac{10.35}{218.53} + \frac{4.65}{20.8} + \frac{5}{33.5} \right)$$

$$P_R = 0.0233 P_{max}$$

$$P_{max} \times 0.2496 = \mu \times 0.08206 \times 3,200$$

$$P_{max} = 1,052\mu$$

To solve for P_{max} by successive approximation, set up Table 9:

<div align="center">TABLE 9</div>

P_{max}	P_R	μ	$1,052\mu = P_{max}$	Deviation
1,000	23.3	1.17	1,233	+233
1,233	28.8	1.16	1,220	− 13

<div align="center">Probable correct $P_{max} = 1,220$ atm.</div>

Summary of calculation of P_{max}.

$$\text{By } \mu \text{ charts} = 1{,}220 \text{ atm.} \quad \text{(most reliable)}$$
$$\text{By covolume} = 1{,}180$$
$$\text{By } PV = NRT = 1{,}053$$

The relative reliability of the μ chart method increases with increasing loading density and therefore with pressure.

The actual temperatures and pressures obtained in a closed chamber or in a gun are less than those calculated by the above method because of the loss of heat to the walls of the container and the resulting drop in temperature and pressure and also because of the work done by the gas in causing the expansion of the container. The latter loss may be calculated quite accurately from the dimensions and physical properties of the container. The heat loss may be estimated approximately by the following method:

Call the rate of heat loss $\dfrac{dQ}{d\theta}$.

$$\frac{dQ}{d\theta} = 0.0001368A \left(\frac{T}{100}\right)^4 + 0.000373c_p T^{1/2} \frac{G^{0.8}}{D^{0.2}} A(T - T_0) \quad (79)$$

where $\dfrac{dQ}{d\theta}$ = cal. per sec.

    A = container surface area, sq. cm.

    T = temperature of gas, °K.

    T_0 = wall temperature, °K.

    D = container diameter, cm.

    G = average mass burning rate, g. per sq. cm. per sec.

    c_p = average specific heat of gas at constant pressure

The loss due to expansion of the container has been found by Crow and Grimshaw (Ref. 69) to be

$$\text{Loss in calories} = kP^2A \quad (80)$$

where k was 8.18×10^{-8} for a chamber of 130.7 cc. and 251.6 sq. cm. surface, and 3.70×10^{-8} for a chamber of 649 cc. and 656.8 sq. cm. surface, P being in kilograms per square centimeter.

The loss of heat from the hot explosion gases to the wall of the chamber and thence to the surroundings depends, not only on the time interval, but also on the respective temperatures. As

the gas cools off and the walls warm up, the rate of loss gradually becomes smaller. It can be calculated for each instant and the total obtained by summation. However, at the start of the cooling-off period, the gas is somewhere near the maximum uncooled temperature and the walls are relatively cold. It is therefore possible to calculate a maximum value for the cooling loss.

Taking the results of the previous calculation,

A = surface of 1-l. sphere = 589 sq. cm.

T = 3200°K.

T_0 = 300°K.

D = sphere diameter = 12.4 cm.

$c_p = \dfrac{Mc_v + 1,987}{44} = \dfrac{7.48 + 1.987}{44} = 0.215$

G = average mass burning rate, g. per sq. cm. of bomb surface per second

Since this is a fictitious example, no rate-of-burning data are available, but from other data a reasonable estimate would be 50 milliseconds, or 0.05 sec. G then would be 100 g. burning in 0.05 sec. in a container whose surface is 589 sq. cm.

$$\therefore G = \frac{100}{589 \times 0.05} = 3.3$$

Substituting these values in the heat-loss formula,

$$\frac{dQ}{d\theta} = 0.0001368(589)\left(\frac{3,200}{100}\right)^4$$

$$+ 0.000373(0.215)(3,200)^{1/2}\left[\frac{(3.3)^{0.8}}{(12.4)^{0.2}}\right](2,900)(589)$$

$$= 84,500 + 12,200 = 96,700 \text{ cal. lost per second}$$

If the elapsed time were 0.05 sec., as assumed above, the calories lost would be

$$96,700 \times 0.05 = 4,830 \text{ cal. lost}$$

The original value of Q_o for 100 g. of powder was

$$\frac{957,000}{10.98} = 87,000 \text{ cal.}$$

As an approximation, therefore, the value of the maximum "cooled" temperature would be

$$2,910 \left(\frac{87,000 - 4,830}{87,000} \right) + 273 = 3000°K.$$

and P_{max} would be

$$1,220 \times \frac{3,000}{3,200} = 1,140 \text{ atm.}$$

The expansion loss is usually negligible. Using the Crow and Grimshaw formula, which fits only the closed chamber they used but which may be used to indicate the relative magnitude of the correction,

$$\text{Loss } (Q) = kP^2A$$

where k = about 4×10^{-8}
$\quad\quad P$ = $1,140 \times 1.033$ (kg. per sq. cm. = 1 atm.) = 1,180
$\quad\quad A$ = 589 sq. cm.
$\quad\quad Q$ = $4 \times 10^{-8} \times (1,180)^2 \times 589$ = 33 cal., which is negligible.

CHAPTER IX

IGNITION OF PROPELLENT POWDERS

With few exceptions, explosives are compounds or mixtures of compounds of nitrogen. This chemical element is unique in its apparent disinclination to form stable chemical compounds, most of them being relatively unstable and therefore likely to decompose on little provocation. The decomposition of an explosive is a chemical reaction; and, as with all chemical reactions, the rate at which it takes place is influenced by potential, resistance, and certain other factors of which temperature is the most important. Physical chemists have known for many years that the rate of chemical reaction increases with rising temperature, doubling in many cases for each rise of 10 centigrade degrees or thereabouts. Since explosive nitrogen compounds exist in an unstable state, it must be assumed that this is possible only because at the temperature in question their decomposition rates are so low that they are negligible or practically zero.

To illustrate the point, certain forms of nitrocellulose, a principal constituent of smokeless powder, and particularly guncotton, will explode instantly when heated to about 185°C., or, to be more precise, within 5 sec. after exposure to that temperature. The same substance, when held at room temperature, will have a life, or "stability," of several years. If pure guncotton, in the absence of any added stabilizer, may be expected to have a stability life of 10 years at 0°C., then doubling its decomposition rate each 7°C. would cause it to increase so that it would explode in 5 sec. at 185°C. If stored in a magazine near a steam radiator that is at 100°C., the guncotton would be expected to explode in

$$(5 \text{ sec.}) \times (2)^{\frac{100°}{70}} = 5 \times (2)^{14.3} = 5 \times 2 \times 10^4 = 10^5 \text{ sec.}$$

or a little over 1 day.

The significance of this temperature effect, which is common to all explosives, lies in the fact that it is necessary to raise the tem-

perature of the explosive to this *instantaneous-ignition temperature* to cause it to explode. This is the problem of ignition in the gun.

Propellent powders may decompose in three ways, *viz.*, by detonation, by explosion, or by combustion.

Combustion occurs when the explosive is burned in the presence of air or other external source of oxygen, just as any combustible material burns in external oxygen. Most propellent powders burn by combustion in a manner similar to celluloid or camera film, quietly, with little flame and no smoke.

Explosion takes place in the absence of additional oxygen and may be a relatively slow process, the speed of which depends on the degree of confinement, or loading density. Explosion is a surface effect, taking place solely on the surface of the powder grain, never beneath the surface. Each layer of the surface must explode away before the next layer underneath can do so. This phenomenon is called an *explosion* because it is usually so confined that the process is rapid as compared with combustion and gives an explosive effect.

Detonation is an extremely rapid phenomenon, as much faster than explosion as explosion is faster than combustion. The whole solid mass detonates almost simultaneously, the detonation wave proceeding through the solid mass with a velocity of several thousand meters per second. Detonation is therefore a violent process. If propellent powders are allowed to detonate, which happens at times, the result is always a burst gun and other serious effects.

The products of explosion and of detonation are the same, while those from combustion are presumably solely CO_2, H_2O, and N_2. There is no sharp line of demarcation between explosion and detonation. There is a long list of explosives whose individual decomposition rates range all the way from very rapid detonation to very slow explosions. Certain high explosives detonate only; at the other end of the list is black powder, which does not detonate. Smokeless powder will either explode or detonate, depending on circumstances; when it detonates, it is a true high explosive. Nitroglycerin, which normally detonates, can be made to explode by blending it with certain other explosives as is done in certain types of smokeless powders like cordite.

From the foregoing discussion, it is evident that the problem of the ignition of propellants consists in raising the temperature

of the surface of the powder grain to above the instantaneous-explosion temperature but doing so under such conditions that explosion and not detonation occurs. A corollary to this statement is that, if, by chance, the powder-grain surface is cooled below this temperature, the explosion will stop because of the slowing up of the decomposition reaction, as when partly burned grains or slivers are blown out of the muzzle of a gun. Another factor in maintaining ignition is that the heat produced by the explosion must be more than sufficient to take care of the energy delivered to the moving projectile and also the heat lost to the gun itself; otherwise, the temperature will fall and the explosion be extinguished before the powder has all been consumed.

One of the most important factors in ignition is the *adiabatic compression* of gas. Suppose, for example, a perfect gas is subjected to reversible adiabatic compression. Using the simple batch energy balance,

$$Q - W = \Delta E = Q + \int_{V_1}^{V_2} P \, dV \tag{81}$$

Since the compression is adiabatic,

$$Q = 0$$

and

$$-\int_{V_1}^{V_2} P \, dV = \Delta E = \int_{T_1}^{T_2} c_v \, dT \tag{82}$$

Since $PV = RT$ for one mole of a perfect gas,

$$-\int_{V_1}^{V_2} P \, dV = -\int_{V_1}^{V_2} RT \frac{dV}{V} = \int c_v \, dT \tag{83}$$

Rearranging gives

$$-R \int_{V_1}^{V_2} \frac{dV}{V} = \int_{T_1}^{T_2} c_v \frac{dT}{T} \tag{84}$$

Then, calling c_v a constant, this becomes

$$R \ln \frac{V_1}{V_2} = c_v \ln \frac{T_2}{T_1} \tag{85}$$

But since, for one mole, $R = c_p - c_v$,

$$(c_p - c_v) \ln \frac{V_1}{V_2} = c_v \ln \frac{T_2}{T_1} \tag{86}$$

$$\left(\frac{V_1}{V_2}\right)^{c_p - c_v} = \left(\frac{T_2}{T_1}\right)^{c_v} \tag{87}$$

and if $c_p/c_v = \gamma$,

$$\left(\frac{V_1}{V_2}\right)^{\gamma-1} = \frac{T_2}{T_1} \qquad (88)$$

But as

$$\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}$$

$$\frac{V_1}{V_2} = \frac{P_2T_1}{P_1T_2} \qquad (89)$$

$$\left(\frac{P_2T_1}{P_1T_2}\right)^{\gamma-1} = \frac{T_2}{T_1} \qquad (90)$$

or

$$\left(\frac{P_2}{P_1}\right)^{\gamma-1} = \left(\frac{T_2}{T_1}\right) \qquad (91)$$

or

$$\frac{P_2}{P_1} = \left(\frac{T_2}{T_1}\right)^{\left(\frac{\gamma}{\gamma-1}\right)} \qquad (92)$$

This gives the compression ratio P_2/P_1 needed to raise the temperature of a perfect gas from T_1 to T_2.

Suppose now that it is required to raise the surface of propellent powder grams to such a temperature that ignition and explosion would take place in 0.001 sec., or 1 millisecond. Using the same rule as before, that explosion will take place in 5 sec. at 185°C. $(185 + 273 = 458°K.)$, the increase in explosion rate $= 5/0.001 = 5,000$ fold.

$$5,000 = (2)^{\frac{T_2-458}{7}}$$

$$\log 5000 = \frac{T_2 - 458}{7} \log 2$$

$$3.699 = 0.301 \left(\frac{T_2 - 458}{7}\right)$$

$$T_2 = 544°K. = 271°C. \qquad (T_1 = 288°K.; 15°C.)$$

In the previous chapter, it was seen that for a specific case, using the average values, $Mc_p = 9.47$, and $Mc_v = 7.48$.

$$\therefore \frac{Mc_p}{Mc_v} = \frac{9.47}{7.48} = 1.266$$

$$\frac{P_2}{P_1} = \left(\frac{544}{288}\right)^{\frac{1.266}{0.266}} = (2.04)^{4.76} = 29.7$$

If the initial pressure were 1 atm., it would appear that a reversible adiabatic compression of the gas surrounding the powder grain to about 30 atm. would raise its temperature, and therefore that of the surface of the grains in contact with it, to such a temperature that ignition of the powder would take place in about 0.001 sec. It is believed that some such process of compression equivalent to that just calculated is responsible for part of the ignition phenomenon.

Propellent powders in firearms are ignited by primers. In small arms, which always have the propellent powder enclosed in a metallic cartridge case, the primer consists of a small cup inserted in the base, or rear end, of the cartridge. This cup contains a sensitive composition that explodes by friction or shock and produces a flame made up of hot gases and incandescent solids which flows through an orifice in the base of the cartridge case into the powder chamber, where it comes into direct contact with the propelling change. In cannon, the primer must ignite a much larger amount of powder and therefore is made up of two parts. The first part is much like that in the small-arms cartridge and contains a sensitive composition that is exploded by friction, shock, or electric heat. This explosion then ignites a much larger mass of black powder, which in turn supplies the heat for igniting the main charge of propellant.

There is no substitute for black powder in cannon primers. The reason for this is well understood. Propellent powders must be ignited by high temperature and not by shock, since the latter will cause detonation. This means that heat must flow from the hot primer flame to the powder grain. This sensible heat plus that due to any adiabatic compression of gases in the vicinity is the sole source of the heat needed.

Heat flows from a hot substance to a cooler substance by a combination of two means, conduction and radiation. The laws governing heat flow have been well developed. The semiempirical formula quoted in Chap. VIII for the rate of heat flow from hot gases to the walls of the chamber is an excellent example of this effect.

Heat flow by radiation is correctly given by the formula

$$\frac{dQ_r}{d\theta} = cpA \left(\frac{T}{100}\right)^4 \qquad (93)$$

where $\dfrac{dQ_r}{d\theta}$ = rate of radiant heat flow, B.t.u. per sec.

    c = radiation coefficient = 0.172, English units

    p = emissivity, or specific radiating ability

    A = area of radiating surface

    T = absolute temperature of radiating surface

In the case where one body more or less surrounds the other, the net radiation between them is given as

$$\frac{dQ_r}{d\theta} = cpA\left[\left(\frac{T_1}{100}\right)^4 - \left(\frac{T_2}{100}\right)^4\right] \tag{94}$$

The emissivity p of most solids is high, from 0.5 to 1.0, while that of most gases is low, not over one-tenth as much. For this reason, luminous flames, which contain large numbers of solid particles in suspension in the flame, radiate much more intensely than non-luminous flames. This accounts in large measure for the superiority of black powder for use in primers, for the products of the explosion contain large amounts of solids such as potassium carbonate and sulphate. These incandescent solids radiate intense heat, in contrast to the non-luminous flames from smokeless powders.

Heat also flows by direct conduction, following Newton's laws of conduction, to the effect that

$$\frac{dQ_c}{d\theta} = k\,\frac{T_2 - T_1}{R} \tag{95}$$

where R = resistance offered to the flow of heat.

Such a formula for flow from a hot gas to a solid surface is typified by the following:

$$\frac{dQ_c}{dT} = kc_pA(T_1)^{0.5}\frac{(G)^{0.8}}{(D)^{0.2}}(T_1 - T_2) \tag{96}$$

where k = conductivity coefficient

    c_p = specific heat at constant pressure of the hot gas

    A = area of the solid in question to which the heat is flowing

    T_1 = temperature of the hot gas

    T_2 = temperature of the cold surface

    G = mass velocity of the gas in contact with the solid,

    D = average diameter of the solid

The example quoted in Chap. VIII indicated that, for that case, the bulk of the heat flow from the hot gas was by radiation. When the radiation from hot gas is enhanced by the presence of incandescent solids, it is believed that radiation effects are more important than conduction.

The usual methods for determining the ignition temperature of explosives are those which depend largely on direct conduction of heat rather than on radiation. For this reason, no great r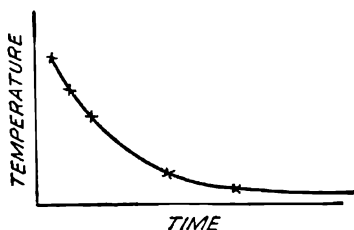eliance is placed on such results. The most common method consists in placing some of the explosive in a copper cup and immersing it in a bath of molten metal. The time for explosion and the bath temperature are recorded.

FIG. 9.

Extrapolation of the curve in Fig. 9 would give the instantaneous ignition temperature. However, it is believed that some other method, based on radiant heating, would be much more likely to represent ignition conditions as they exist in the gun.

Under ideal conditions, each grain of powder in the propelling charge would be ignited at the same instant by being brought into complete contact with the primer flame. It has been found quite difficult to arrange this, particularly in large guns. The use of a large primer requires so much black powder that the firing is no longer smokeless. Powder grains that pack together tightly offer such obstruction to the flow of hot primer flame that ignition is irregular; and it is believed that many of the irregularities in firings can be traced to poor ignition conditions·

From a purely theoretical viewpoint, the most satisfactory primer would consist of an explosive gas which would permeate the entire propellent charge and which, on exploding, would liberate solid particles. It is suggested that a mixture of acetylene and air (or oxygen), with insufficient of the latter for complete combustion to carbon monoxide, would liberate incandescent carbon particles and give ideal ignition conditions. Such a mixture would be an equal-volume mixture of acetylene and oxygen.

CHAPTER X

RATE OF EXPLOSION

The chemical decomposition of smokeless powder at ordinary temperatures is an autocatalytic process. That is, the products formed in the decomposition catalyze, or increase the speed of, the subsequent reaction, the catalytic effect increasing as their amount increases. At ordinary temperatures, it is believed that nitrocellulose does not form the same sort of products as at high temperatures and that the oxides of nitrogen, which are very evident in laboratory experiments at moderate temperatures and which are acid in behavior, are largely responsible for this catalytic effect. This decomposition might be indicated by the following equation:

$$C_{24}H_{30}O_{20}(NO_2)_{10} = 4CO_2 + 17CO + 3C + 15H_2 + 5NO + 5NO_2$$

the last two, the oxides of nitrogen, both being decidedly acidic when in the presence of water.

However, in the successive layer explosion of propellent powder, it is believed that the temperature is too high for these oxides of nitrogen to exist in any appreciable amount, even though their presence is obvious in the gases discharged from some guns. Freak examples even show the presence of free ammonia (NH_3) in the products of the explosion. It is much more likely that the rate of explosion in a confined space is affected chiefly by temperature and to a less degree by pressure. This statement is based on the belief that the rate of explosion is determined by the rate at which heat flows from the hot explosion products to the cold unburned surface of the powder, which is distinctly a temperature phenomenon, pressure having a purely secondary effect. Nevertheless, all current formulas for rate of explosion are on a pressure basis.

The reason for the attempt to explain explosion rate on a pressure basis is historical and experimental. Temperatures of flames of short duration are extremely difficult to measure, particularly when the flame is enclosed in a powder chamber. Gas

pressures, on the other hand, are relatively easy to measure, at least with approximate accuracy. It is only to be expected, therefore, that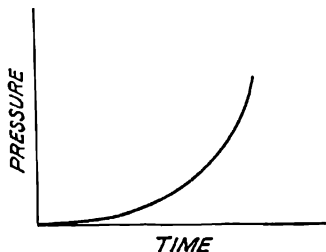 the first studies of explosion rates were made in connection with pressure-time measurements and that the formulas so developed were based on pressure rather than on temperature or heat transfer.

FIG. 10.

Experiments showed very early, both in closed chambers and in guns during the period before the projectile starts to move, that the pressure increases slowly at first, and then more and more rapidly, as shown in Fig. 10. This type of curve strongly resembles a hyperbola of the form

$$y = ax^n \tag{97}$$

This led *Vieille*, in 1893, to offer such a formula, in the differential form

$$dy = d(ax^n) = anx^{n-1} \, dx \tag{98}$$

or

$$\frac{dy}{dx} = anx^{n-1} \tag{99}$$

where $n =$ a quantity greater than unity

His formula is

$$\frac{de}{d\theta} = \lambda P^k \tag{100}$$

where $\frac{de}{d\theta} =$ decrease in web thickness in the time $d\theta$

$\lambda =$ a coefficient
$P =$ pressure at the time θ
$k =$ an exponent that has a value greater than 0

Vieille recognized that k varied with conditions, but others who have attempted to use his formula have tried to fix it at a constant value, using values variously from 0.5 to 1.0. In this formula, the web thickness e is the radial dimension of the powder grain, measured in a direction at right angles to the layers that are successively burning away. In the case of long single-

perforated powder grains, or multiperforated grains, whose burning surface does not change much or increases slightly as the grain burns away, the rate of decrease of web thickness is about proportional to the rate at which the powder burns. Furthermore, if the temperature of the powder gases remains about constant during the firing, which would be true in an ideal adiabatic closed chamber, then the amount of gas produced and therefore the pressure would increase at a rate proportional to that at which the web thickness decreased, or

$$-\alpha \, dp = de \tag{101}$$

Using this substitution in the Vieille formula gives

$$\frac{-\alpha \, dP}{d\theta} = \lambda P^k \tag{102}$$

Separating the variables and integrating between limits gives

$$\int_{P_1}^{P_2} \frac{-\alpha \, dP}{P^k} = \int_{\theta_1}^{\theta_2} \lambda \, d\theta \tag{103}$$

If α and λ are assumed to be constant, this becomes

$$\int_{P_1}^{P_2} \frac{dP}{P^k} = -\frac{\lambda}{\alpha} \int_{\theta_1}^{\theta_2} d\theta \tag{104}$$

This, when solved, gives

$$\frac{1}{1-k} \left(P_2^{1-k} - P_1^{1-k}\right) = \frac{\lambda}{\alpha} \theta_2 \tag{105}$$

when $\theta_1 = 0$.

Except at the beginning of the explosion, P_1 is small compared with P_2 and may therefore be neglected, giving

$$P_2^{1-k} = -\frac{\lambda(1-k)}{\alpha} \theta_2 \tag{106}$$

Perhaps a better way to handle the Vieille formula, as converted to P vs. θ, is to take the logarithm of both sides.

$$\log \frac{dP}{d\theta} = \log \frac{-\lambda}{\alpha} + k \log P \tag{107}$$

A plot of this last equation should give a straight line with the slope equal to k, if it fits experimental data. In using the Vieille

TABLE 10

| Charge = 0.8 kg.		Charge = 0.7 kg.		Charge = 0.4 kg.	
Time	Pressure	Time	Pressure	Time	Pressure
0	0	0	0	0	0
0.8	4	0.9	4	2	2
2.5	12	2.7	8	6	4
4.1	33	4.6	16	10	8
5.8	90	6.4	36	14	20
7.5	159	8.2	77	18	45
9.2	240	10.0	137	22	89
10.8	326	11.5	202	26	146
12.5	440	13.6	274	30	223
14.2	580	15:5	363	34	321
15.8	769	17.3	471	38	435
17.5	1,030	19.1	620	42	587
19.16	1,380	20.9	801	46	792
20.83	1,860	22.73	1,040	50	1,063
22.50	2,580	24.55	1,345	52.6	1,280
23.25	3,010	26.36	1,770		
		28.18	2,360		
		28.61	2,510		
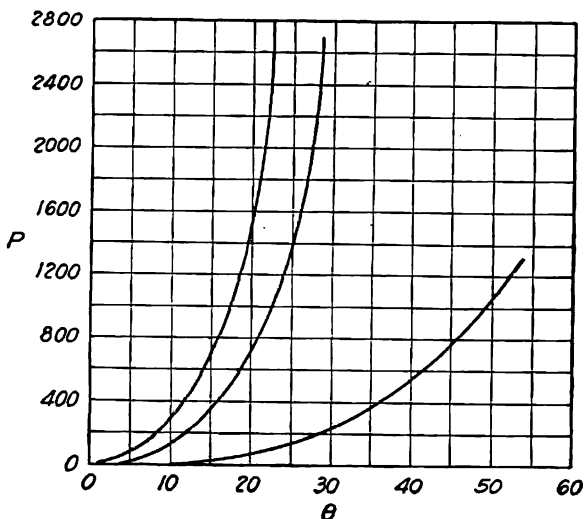
FIG. 11.

formula, λ/α should be the same for any given variety of powder, independent of the loading density.

As a test of this formula, the classic data by Krupp, quoted by Cranz (Ref. 11), are used. These data were obtained on some German S.D. (solventless powder, made with a non-volatile gelatinizing agent) tubular powder, fired in a calorimetric bomb of 3.450 l. capacity. The density of the powder was 1.64 kg. per l. Runs were made on three weights of charge, 0.8, 0.7, and 0.4 kg., the pressures being given in kilograms per square centimeter and the time (elapsed) in milliseconds, the origin being in doubt by about 1.5 milliseconds. Three grams of black powder was used to

TABLE 11

θ	P	$\dfrac{dP}{d\theta}$	$\log \dfrac{dP}{d\theta}$	$\log P$
Charge = 0.8 kg.				
6.2	110	32.7	1.515	2.041
10.0	280	54.3	1.735	2.447
13.8	560	109.5	2.039	2.748
17.9	1,080	178	2.250	3.033
22.0	2,275	435	2.638	3.357
Charge = 0.7 kg.				
6.0	30	15.5	1.190	1.477
10.1	130	30.8	1.489	2.114
14.2	290	51.3	1.710	2.462
18.0	530	80.0	1.903	2.724
21.9	920	122	2.086	2.964
25.8	1,575	226	2.354	3.197
Charge = 0.4 kg.				
10	8	3.64	0.561	0.903
14	20	6.12	0.787	1.201
22	89	12.2	1.086	1.949
28.3	185	18.6	1.270	2.267
31	250	21.4	1.330	2.398
34	320	26.5	1.423	2.505
38	430	32.8	1.516	2.633
42	587	46.5	1.667	2.769
46	792	59.0	1.770	2.899
50	1,063	76.7	1.885	3.027

ignite each charge. The final value in each run is the maximum pressure obtained.

Figure 11 shows these data plotted as pressure against time. The values of the slopes $\frac{dP}{d\theta}$ in Table 11 were then obtained from those curves and tabulated with their logarithms.

These values of $\log \frac{dP}{d\theta}$ and $\log P$ have been plotted in Fig. 12. It will be seen that they fail to give straight lines and that the slopes of straight lines approximating the points are variable, as shown in Table 12.

<div align="center">

TABLE 12

Loading	Slope
0.8	0.92
0.7	0.72
0.4	0.67

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From Figs. 11 and 12, it would appear that the Vieille formula serves as a rough approximation only; for the lines are not straight, and the slopes vary widely with the loading density.
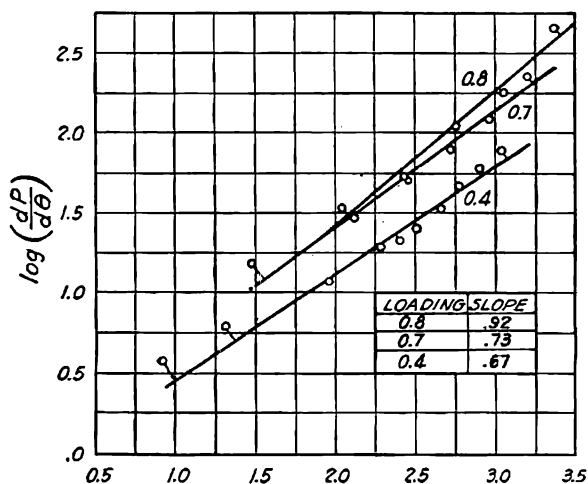

Fig. 12.

Another still more empirical formula, based on pressure relations, is the *Krupp-Schmitz* modification of the Charbonnier formula, as follows:

$$\frac{dy}{d\theta} = \phi(y)P \tag{108}$$

where y is the weight fraction of the powder burned at the time θ and $\phi(y)$ is a purely empirical function of y, which is a function solely of the variety and granulation of the powder and independent of the loading density. Since $\phi(y)$ can be any sort of function whatsoever, the formula can be made to fit any curve exactly, and the only test of its usefulness is to see whether $\phi(y)$ is independent of loading density.

Separating the variables gives

$$\int_0^0 P \, d\theta = \int_0^1 \frac{dy}{\phi(y)} \tag{109}$$

between the initial and final limits. Since for any variety of powder $\phi(y)$ is a definite function,

$$\int_0^1 \frac{dy}{\phi(y)}$$

must be the same, no matter what the loading density.
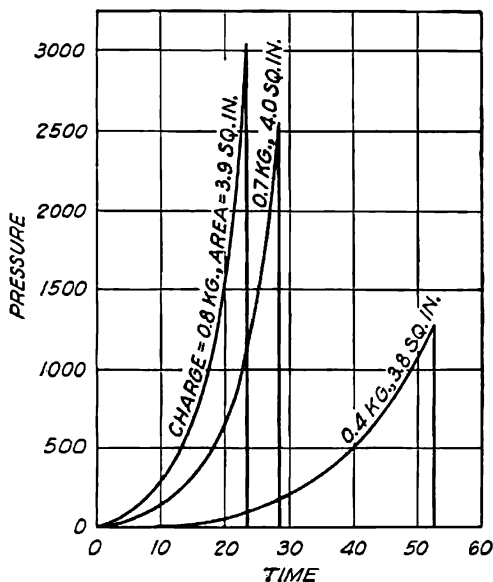

Fig. 13.

Furthermore, since in an ideal adiabatic closed chamber the pressure is directly proportional to the fraction of the powder burned, the final value of P will be P_{max}.

Take the same Krupp data that were used in the Vieille formula, and plot P vs. θ, the area under the curve being equal to $\int_0^\theta P \, d\theta$. If this Charbonnier formula is reasonable, the areas for the three runs should be the same. This has been done in Fig. 13 as indicated, the areas as measured on the original drawing being given in Table 13.

TABLE 13

Weight of Charge, Kg.	Area, Sq. In.
0.8	3.9
0.7	4.0
0.4	3.8

This is considered to be a satisfactory check for these firings. However, it offers no check as to the pressure-time relations, which must be made by determining whether or not the $\phi(y)$ relation is the same for all three loading densities. To do this, proceed as follows:

Making the same simplifying assumptions as in the Vieille formula,

$$P = yP_{max}$$

$P = P_{max}$ when $y = 1$

$$\therefore dP = P_{max} \, dy \tag{110}$$

or

$$dy = \frac{dP}{P_{max}} \tag{111}$$

Substituting this in the Charbonnier formula,

$$P \, d\theta = \frac{\dfrac{dP}{P_{max}}}{\phi(y)} \tag{112}$$

$$P_{max} \, d\theta = \frac{\dfrac{dP}{P}}{\phi(y)} = \frac{d \ln P}{\phi(y)} \tag{113}$$

$$\frac{d \ln P}{d\theta} = P_{max}\phi(y) \tag{114}$$

Thus, to test the formula, plot $\ln P$ vs. θ, measuring the slope $\dfrac{d \ln P}{d\theta}$ for various values of y, as shown in Fig. 14. These slopes,
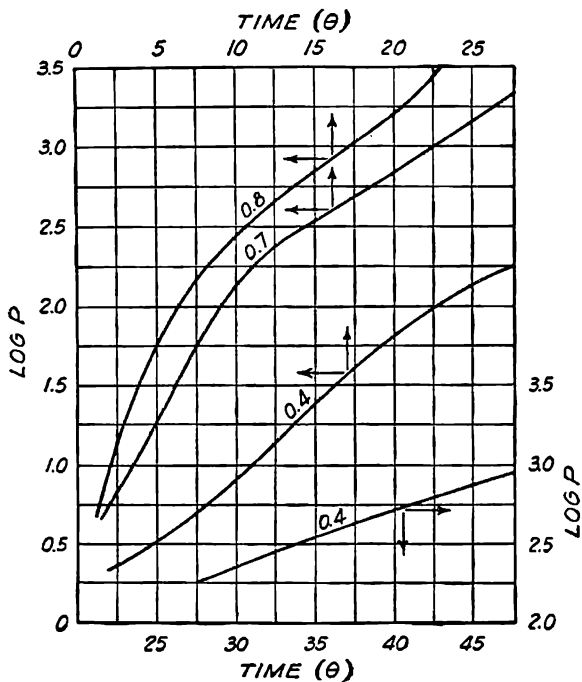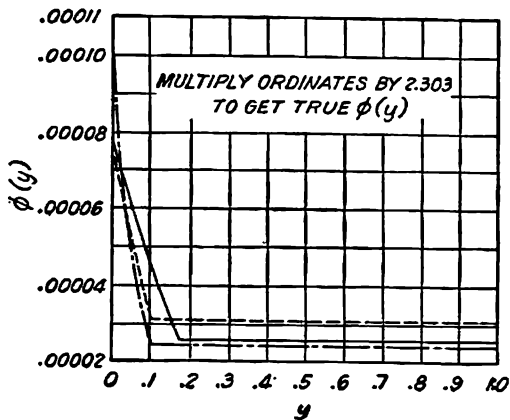
Fig. 14.

Fig. 15.

when divided by P_{max}, will give the corresponding value of $\phi(y)$, samples of which are given in Figs. 15 and 16.

Neither the Vieille nor the Charbonnier formulas recognize the thermal effects involved, the adiabatic compression of the powder gases, and the heat flow from those gases to the unburned grains. It would appear that so far as the latter effect is concerned, since the temperature of each gas molecule is in the vicinity of T_{max}, the heat conveyed from the hot gases to the cold powder surface
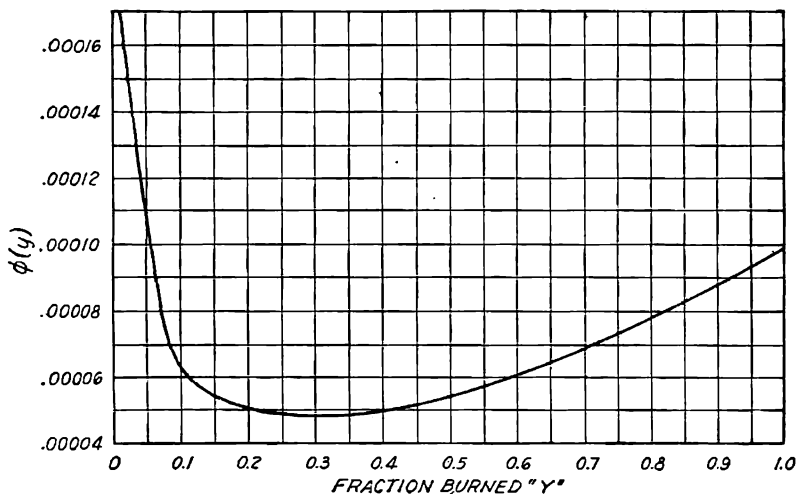

Fig. 16.

by conduction would depend on the number of molecular contacts per unit time, which, in turn, would be some function of the pressure. In addition, the heat flow by radiation would depend on the fourth power of the gas temperature and would also be greater the greater the density of the gas itself. Therefore, if it be assumed that the rate of heating and the corresponding rate of burning depend on the sum of these two effects, there can be written

$$\frac{de}{d\theta} = k[\phi(P)] + k'[\phi'(P)](T)^4 \tag{115}$$

their relative magnitude being determinable analytically from experimental data.

A simplification of this formula was suggested orally to the author some years ago by R. H. Kent, as follows:

$$\frac{dr}{d\theta} = kP + C \tag{116}$$

where dr is the regression of the grain surface [about equal to $d(e/2)$] in the time $d\theta$, kP is an approximation of the term for
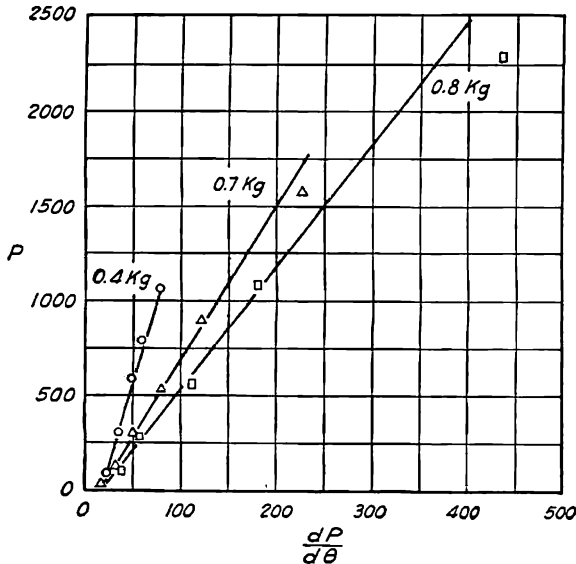
Fig. 17.

heat conduction, and C is the heat flow by radiation, being called constant for simplicity's sake. If

W = weight of solid powder at the time θ
e_0 = original web thickness
z = fraction of web consumed

the formula becomes

$$\frac{dr}{d\theta} = \frac{dP}{d\theta} \times \frac{e_0}{zP_{\text{max}}\left(\dfrac{dW}{dz}\right)} \tag{117}$$

Since in the long tubular powder described by Cranz (Ref. 11) dr is directly proportioned to dP, this formula reduces to the simpler form

$$\frac{dP}{d\theta} = kP + C \tag{118}$$

A plot of $\frac{dP}{d\theta}$ vs. P should give a straight line with the intercept on the $\frac{dP}{d\theta}$ axis equal to C.   Figure 17 shows this plot, and it will be seen that, if the final points are omitted, the three lines have a common intercept, indicating the reliability of the radiation concept.

CHAPTER XI

LOADING DENSITY

The loading density is defined as the weight of powder per unit volume of chamber, grams per cubic centimeter, or kilograms per liter and is given the letter Δ. This quantity has both theoretical and practical importance.

The uncooled gas pressure developed in a chamber by a given weight of explosive varies directly as the loading density for any given temperature. From a theoretical standpoint, in an adiabatic container, this is the chief effect that loading density would have on the ultimate pressure. However, in actual chambers, both gun chambers and closed chambers, the loading density has much greater importance.

Actual powder chambers consist of metal walls which are at a temperature much lower than the powder flame temperatures and which are able to absorb heat from the hot gases just as well as the burning powder itself absorbs heat, with the additional effect that the walls are good conductors of heat and tend to keep cool on that account. The result is that the powder gases lose an appreciable amount of heat to the surrounding walls. When the loading density is small, the percentage loss will be greater than when Δ is large. The effect of increasing Δ is much the same as increasing the value of Q, the heat evolved in the explosion, per unit weight of explosive. The result is higher net temperatures and correspondingly higher chamber pressures. It must be remembered that, when Δ increases, the pressure produced will increase for two reasons. There is a larger amount of explosive per unit volume, and the final temperature is higher.

A still more important effect of increasing Δ is the effect on the rate of explosion, because the temperature difference between the powder gases and the solid powder increases, and the velocity constant of the reaction increases.

Using the data on the closed chamber given in the preceding chapter on Rate of Explosion, it will be interesting to compare

the final maximum pressure with the weight of charge. The values are as follows (chamber = 3.45 l.):

TABLE 14

Weight of charge, kg.	P_2	Δ
0.8	3,010	0.232
0.7	2,510	0.203
0.4	1,280	0.116

It may be assumed that P_2 is a function of Δ and that a function of the type

$$P_2 = a(\Delta)^n$$

may approximate the data. Take the logarithm of both sides

$$\log P_1 = \log a + n \log \Delta$$

and construct a plot of $\log P$ vs. $\log \Delta$.

TABLE 15

P_1	$\log P_1$	Δ	$\log \Delta$
3,010	3.479	0.232	0.614
2,510	3.400	0.203	0.692
1,280	3.1075	0.116	0.935

Plotting $\log P_1$ against $\log \Delta$ gives the line as shown in Fig. 18. The equation of this line is

$$\log P_2 = 4.257 + 1.23 \log \Delta$$

or, written in the original form,

$$P_2 = 18,100(\Delta)^{1.23}$$

This relation has no theoretical significance. It does, however, indicate that the maximum pressure rises faster than Δ.

Table 16 gives the results of purely theoretical calculations on the effect of loading density on the composition of the powder gases obtained on firing an obsolete pyro nitrocellulose powder in a closed chamber.

TABLE 16

Loading density Δ	0.0337	0.1481	0.2577
Maximum pressure, atm. (measured)	340	1,700	3,400
Maximum temperature, °K. (calculated)	2,890	2,905	2,910
Partial pressures (calculated from equilibrium constants):			
CO_2	41.3	206.3	412.9
CO	138.1	691.3	1,382.7
H_2O	82.1	412.8	827.2
H	0.75	1.7	2.5
OH	0.85	2.0	2.9
H_2	40.7	204.6	409.2
N_2	36.3	181.3	362.6

It is well known that a moderate increase in Δ may change the reaction in the chamber from explosion into detonation, with a correspondingly great increase in peak pressures due to pressure
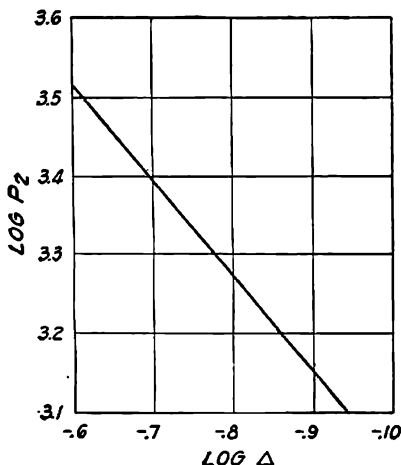

FIG. 18.

wave impulses and excessive gas pressures due to the inability of the projectile to move fast enough in the bore to relieve the chamber pressure.

CHAPTER XII

SURFACE FACTOR

A study of rate of explosion shows that per unit area of powder-grain surface, under given external conditions, the weight of a specific powder burning per unit time is a constant. It follows from this that the total weight of powder burning per unit of time is directly proportional to the total powder surface exposed. This, of course, presupposes that the surface everywhere has the same opportunity to ignite and to free itself of the explosion products.

This fact is utilized to control the explosion rate during the entire explosion to suit the requirements of the gun. Some of the commoner types of powder grains are mentioned below.

Flat sheets of powder, whose width and length are large compared with the thickness, burn with but little change in surface exposed, until the strip becomes very thin, after which the surface decreases. Flat sheets sewed together lose this effect.

Hollow cylinders of considerable length, or so-called "single-perforated" long grains, burn with nearly constant surface, provided that the ignition is uniform inside and out.

Solid rods, solid grains, etc., burn with constantly decreasing surface. These powders are called "degressive" powders.

Rods or grains with a large number of perforations, such as the standard seven-holed grain, have an increase in surface during that part of the burning in which the grain is still in one piece. Such grains finally fall into pieces or slivers, and the surface decreases thereafter. The grain is called "progressive" while the surface area increases.

Certain types of granulation may be changed from degressive to simulated progressive powders by coating the surface with a slow-burning composition, which will give a slow degressive period followed by a fast degressive period.

Figure 19 shows the area in square millimeters of three common grain forms, plotted against the per cent of the powder burned.

By controlling the area of the grain during the explosion, it is possible to exert some control over the rate at which the pressure rises in the gun chamber. The internal surface, the degree of
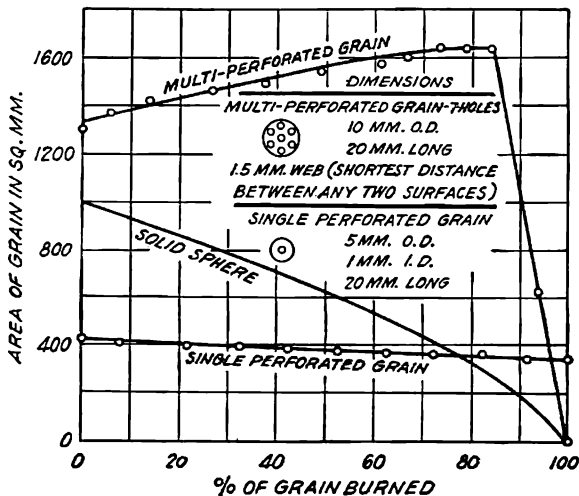

FIG. 19.

progressivity or degressivity, the loading density, and the heat of explosion are the four chief factors with which the powder designer can work to produce the required gun ballistics so far as the propellant is concerned.

PROPELLENT-POWDER COMPOSITION

Propellent powders are divided into groups, the modern smokeless powders and the nearly obsolete smoking powders. Black powder, which is a mechanical mixture of charcoal, sulphur, and potassium or sodium nitrate, the commonest of the obsolete propellants, is still used as a propellant in some of the older sporting rifles; but for military purposes its use is confined to saluting charges, to its use as a priming powder for smokeless powder, for which it is unexcelled, and for use in fuze trains and similar purposes.

Modern smokeless powders consist of nitrated organic compounds, mixed with each other and with small amounts of non-explosive materials in various combinations. These mixtures are made in order to give the powder the desired properties. The factors that must be considered include the following:

Supply of raw materials needed

Problems of manufacture

Safety in handling

Stability in storage

Uniformity in properties

Heat of explosion

Ease of ignition

Corrosion and erosion of rifling in the gun

Smoke production

Flash production

Hydroscopicity

For many years, the standard smokeless powder used by the United States Army and Navy consisted of about 95 per cent nitrocellulose of about 12.6 per cent nitrogen content, which corresponds roughly to the pure compound $C_{24}H_{30}O_{20}(NO_2)_{10}$, with about $\frac{1}{2}$ per cent of diphenylamine added as a stabilizer, the remaining 4 or more per cent consisting of water, alcohol, and ether left behind from the manufacturing process. This so-called "pyro" powder is smokeless in rifles and small guns but is not

smokeless in large ones, owing chiefly to the formation of oxides of nitrogen. Furthermore, in many important weapons it produces a large flash in front of the muzzle of the gun. It also picks up moisture from the air, and, unless manufactured with the greatest care, its stability is not particularly good. On the other hand, it is made out of raw materials that are abundant, it is safe to handle, it can be blended to give uniform charges, it is fairly easy to ignite, and it is not particularly erosive to the rifling in the gun.

The standard smokeless powder used in England, on the other hand, has been of the "cordite" type—the name comes from the shape of grain used, long slender solid rods—which is a mixture of nitrocellulose and nitroglycerin with suitable stabilizers, etc. Sample compositions, including various grades of "cordite," from Crow and Grimshaw (Ref. 69) are given in Table 17.

TABLE 17

Name	Per cent nitro-cellulose	Per cent N content	Per cent nitro-glycerin	Per cent stabilizer	Kind of stabilizer
N.C.	96.90	12.6	.....	0.46	Diphenylamine
M.D.	65.68	13.0	29.53	4.45	Mineral jelly
Mk. 1	37.00	13.0	58.00	5.00	Mineral jelly
H.C.	39.00	12.2	58.00	3.00	Centralite

The first sample, N.C., in Table 17 is obviously similar to the now obsolete United States pyro powder.

Cordite-type powders have superior stability to pyro powders, have a higher heat of explosion, and are probably superior in regard to smoke formation. On the other hand, they cause severe erosion in the gun because of their high temperature, and their manufacture is more hazardous. The supply of raw materials is also less plentiful.

Recently both in the United States and in Europe there have been developed powders that are superior to the ones given above in regard both to hydroscopicity and to flash in front of the muzzle of the gun.

Improvement in non-hydroscopicity may be made by incorporating into the powder substances that are less soluble in water, making the powder more waterproof. Flash reduction is

obtained by cutting down the heat of explosion and the resulting temperature or by improving the ignition in order to move the point of maximum pressure back toward the breech of the gun.

Table 18 shows the effect of the composition of modern powders on their properties.

TABLE 18

Name	Composition, per cent	Chamber temperature, °C. (calculated)	Heat of explosion, cal. per g.
N.C.	Nitrocellulose 95.79 (12.57 per cent N) Diphenylamine 0.49 Volatiles 3.72	2400 This is usually called "pyro" powder	874
N.G.	Nitrocellulose 78.20 (13.15 per cent N) Nitroglycerin 19.80 Diphenylamine 0.99 Volatiles 1.01	3200 This is known as 80–20 cordite	1,150
F.N.H.	Nitrocellulose 83.3 (13.15 per cent N) Dinitrotoluene 9.8 Dibutylphthalate 4.9 Diphenylamine 1.0 K_2SO_4 .0	2200 This is du Pont F.N.H. powder (German Patent, D.R.P. 640,312)	750

The last of the three above powders, F.N.H. (flashless, nonhydroscopic), is in general the type of smokeless powder recommended at the present time because of those two very desirable properties.

Various other combinations of explosive substances have been experimented with. It is quite probable that changes in accepted powder compositions will occur from time to time in accordance with the results obtained.

In general, propellent powders containing nitroglycerin are known as *double-base* powders. Cordite is an example. Powders that contain no nitroglycerin are known as *single-base* powders, even though there may be more than one explosive constituent present.

The composition of propellent powders is of the greatest importance for firearms because, from the interior-ballistics standpoint, it is possible to predict the behavior of the powder when fired if its composition is known. The compositions that have the proper ballistic properties are studied by the powder manufacturer and that one is selected which is most desirable. This phase of the subject is beyond the scope of this book. The patent literature is full of references to powder and explosive compositions, and a study of this will convince the reader that there appears to be no limit to the possibilities of variation.

Cool-burning powders, such as F.N.H. and to a less extent pyro powder, produce much less energy on explosion than does a hot powder such as cordite, and a corresponding larger amount must therefore be used. Furthermore, the presence of flash reducers such as K_2SO_4 tends to increase smoke, especially when coupled with the solid residues from a black-powder primer.

CHAPTER XIV

RECOIL

As will be recalled from Chap. III on Basic Mechanics, New-ton's third law of motion states that, when a force acts in one direction, there is an equal force acting in the opposite direction, or that action equals reaction.

When a propelling charge explodes in the chamber of a gun, the resulting gases under pressure exert a force in all directions. Part of this force is exerted against the base of the projectile. Another force exactly equal in amount must therefore be exerted against the breechblock of the gun in the opposite direction. The first effect of the force is to push the projectile against the rifling in the bore, which prevents the forward motion of the projectile until grooves have been cut in the soft-metal rotating bands on the projectile. As soon as this is done, the projectile starts ahead under increasing velocity.

According to the principle of the conservation of momentum, at any instant the sum of the momenta of the projectile and powder gases moving toward the muzzle of the gun must exactly equal the momentum of the gun and other recoiling parts moving in the opposite direction. If M_P is the mass of the projectile, M_G the mass of the gases, U_P the velocity of projectile, U_G the velocity of the gas, m the mass of all the recoiling parts, and u the velocity of the recoiling parts, then

$$M_P U_P + M_G U_G = mu \qquad (119)$$

The momentum of the projectile and that of the recoiling parts are not difficult to calculate. That of the moving gas must be approximated, however. It is customary to assume that the average velocity of the gas at any instant is equal to half that of the projectile and that it is all in forward motion. This is obviously an approximation since the gas pressure at the breech must be higher than it is on the base of the projectile in order to account for the forward motion of the gas itself. How-

ever, it is believed that the assumption stated does not introduce a serious error

Thus, write

$$U_P = 2U_G \qquad (120)$$

giving

$$M_P U_P + M_G \frac{U_P}{2} = mu \qquad (121)$$

or

$$\left(M_P + \frac{M_G}{2}\right) U_P = mu \qquad (122)$$

$[M_P + (M_G/2)]$ is called the *equivalent mass* of the projectile indicated as M'.

The kinetic energy of the recoiling parts is $mu^2/2$, while that of the equivalent projectile is $M'U_P^2/2$; and since $M'U_P = mu$, the ratio of the kinetic energy of the recoiling parts to that of the equivalent projectile is

$$\frac{\text{K.E (gun)}}{\text{K.E. (projectile)}} = \frac{mu^2}{M'U_P^2} = \frac{u}{U_P} \qquad (123)$$

There are two theoretical limiting cases, the first when the gun has a fixed mount with no possible recoil, and the second when it has a free-recoiling mount with nothing to stop the backward motion. In the case of a rigid mount, since there is no backward motion of the gun, there is no kinetic energy absorbed by the gun and therefore the amount of energy available for giving the projectile motion is a maximum. Such a gun is impracticable, although a mount of this kind has been occasionally approximated. The other extreme of the free-recoiling mount has been used experimentally with some success. In this case the kinetic energy absorbed by the gun is a maximum, leaving a correspondingly smaller amount available for the projectile.

Actual guns make use of a retarded-recoil mechanism, the particular features of which influence the energy absorbed and thus take away from the supply available. The theory and practice of the design of recoil mechanisms are included in ordnance engineering and are outside the scope of this book.

Advantage is frequently taken of the recoil of a weapon to study the travel of the projectile through the bore. Since the projectile is invisible until it reaches the muzzle, the only direct measurement of its travel is by means of electrical contact points

inserted along the bore. This requires a special weapon and ruins it for any other use. On the other hand, a weapon suspended so that it will recoil freely can be fitted with instruments that measure its motion and speed. An infantry rifle that weighs 10 lb. fires a bullet weighing 150 grains (150/7,000, or 0.02, lb.), and therefore the rifle will recoil with a speed only $\frac{1}{500}$ of that of the bullet, making velocity measurements relatively simple. Some of the best work along these lines, using the recoil method, has been carried out by European investigators and is well reported in their literature. In fact, this method is about the only one that can be used to determine projectile friction.

One of the factors that should have some attention in this regard in the actual weapon as fired in the field is the influence of recoil on the muzzle velocity of the projectile. Recoil mechanisms vary because of the temperature effect on the viscosity of the recoil fluid. An unduly slow recoil means that the gun is absorbing less energy for its kinetic energy than if the recoil were faster. Some of this energy difference goes into heat in the recoil fluid, and the rest must go into increased muzzle velocity. To illustrate the point, take a 10-lb. infantry rifle, firing a 150-grain bullet with 40 grains of powder and producing a muzzle velocity of 3,000 ft. per sec. The free recoil of the gun would be calculated as follows:

$$\frac{10}{32.2}\, u = \left(150 + \frac{45}{2}\right)\left(\frac{1}{7,000 \times 32.2}\right) 3,000$$

u (recoil velocity) $= 7\frac{2}{7}$ ft. per sec., and the kinetic energy of the piece would be

$$\frac{10}{2 \times 32.2}\left(7\frac{2}{7}\right)^2 = 82.5 \text{ ft.-lb.} = 0.106 \text{ B.t.u.}$$
$$= 27 \text{ cal.}$$

Since 45 grains of powder with an energy content of 800 cal. per grain would liberate

$$\frac{800 \times 454 \times 45}{7,000} = 2,340 \text{ cal.}$$

the free recoil of the piece would absorb about 1 per cent of the energy available, which is just about on the line so far as precision of measurements is concerned.

CHAPTER XV

ROTATION OF PROJECTILE

Considerations of stability of the projectile in flight after leaving the muzzle require that the projectile be given a spin about its axis parallel to its motion of translation. The action is that of the familiar gyroscope, which when in rapid rotation about its axis tends to maintain the direction of that axis against forces tending to shift the direction. The spin is given by means of helical grooves cut in the bore of the gun into which the rotating bands on the projectile fit.

There are various methods used in the design of the twist. It may be uniform throughout the length of the bore, or the twist may increase as it approaches the muzzle. The raised ridges separating the grooves are called the "lands," and they must resist the pressure of the corresponding ridges in the projectile. The lands gradually wear away, partly by direct abrasion and partly by melting. When they have worn so smooth that they no longer offer a tight seal for the powder gases, the gun has lost its accuracy and must be repaired by renewal of the rifling.

At any time in the bore of a gun the angle of twist of the rifling φ is found from the relation

$$\tan \varphi = \frac{\pi}{n} \tag{124}$$

where n is the twist in calibers, *i.e.*, the number of bore diameters needed for the twist to make one complete turn.

If the projectile velocity at any point in the bore is U_P, with r the radius of the bore and ω the angular velocity of the projectile at that point, then

$$\omega = \frac{U_P \tan \varphi}{r} \tag{125}$$

The kinetic energy of rotation of the projectile, from the section on mechanics, is

$$\text{K.E.} = \frac{I\omega^2}{2} \tag{126}$$

where I = moment of inertia of the rotating body and

$$I = \Sigma M' r^2 \tag{127}$$
$$I = Mk^2 \tag{128}$$

where k = radius of gyration.

$$\therefore \text{K.E.} = \frac{Mk^2\omega^2}{2} \tag{129}$$

which, combined with Eq. 125, gives

$$\text{K.E.} = \frac{Mk^2 U_P^2 \tan^2 \varphi}{2r^2} \tag{130}$$

Tschappat gives the following values for k^2/r^2 for various projectiles:

Type of projectile	$\frac{k^2}{r^2}$
Solid shot	0.50
Shell	0.58

The uniform twist in the .30-caliber Springfield rifle is 1 turn in 10 in., or about 33 calibers.

$$\tan \phi = \frac{\pi}{33} = 0.095$$

In order to compute the kinetic energy of rotation of the .30-caliber bullet at the muzzle with a translational velocity of 2,700 ft. per sec., use Eq. (130). In this

$$M = \frac{150 \text{ grains}}{7,000 \times 32.2} = 0.000665 \text{ slugs}$$
$$\frac{k_2}{r_2} = 0.50$$
$$UP = 2,700 \text{ ft. per sec.}$$
$$\text{K.E.} = \frac{0.000665 \times 0.50 \times (2,700)^2 (0.095)^2}{2}$$
$$= 5.6 \text{ ft.-lb.} = \frac{5.6}{778} = 0.0072 \text{ B.t.u.}$$

Since the kinetic energy of translation of this bullet would be

$$\text{K.E.} = \frac{0.000665 \times (2,700)^2}{2 \times 778} = 3.12 \text{ B.t.u.}$$

this means that neglecting the energy of rotation introduces an error of about 1 part in 400. By way of contrast, the energy liberated by the propellent powder would be about

$$\frac{800}{7,000} \cdot \frac{454}{252} \cdot 45 = 9 \text{ B.t.u.}$$

(Cal. per g.) (Cal. per grain) (B.t.u. per charge)

indicating that the utilization of the energy of the powder by this weapon is about 35 per cent.

The pressure exerted by the rotating projectile on the lands of the rifling is utilized in two ways, in causing angular acceleration and in overcoming friction. Since the kinetic energy of rotation may be calculated at any point from Eq. (130), for any value of U_p and φ, for a particular projectile and gun, the force producing the angular acceleration may be calculated and from a resolution of forces, combined with some knowledge of the coefficient of sliding friction between the bands and the lands, the total pressure required to produce the rotation of the projectile may be calculated. The friction due to motion of translation in the bore of the gun is probably small compared with that due to pressure against the lands. The difference between the total pressure acting on the base of the projectile and that needed to cause the rotation is available for causing acceleration along the bore of the gun.

The rate at which a projectile travels through the bore of a gun depends on the driving force and on the resistance, the basic flow formula being

$$\frac{dL}{d\theta} = \frac{\text{force}}{\text{resistance}} \tag{131}$$

The resistance is the sum of that due to the projectile itself and that due to the gases moving along with it.

In addition to the resistance of travel, most firearms, that is, those of the rifled variety, require the cutting of grooves in the walls or rotating bands of the projectile as well, and this additional resistance must be overcome before the projectile really gets under way.

These resistances are usually classed as friction (F) and are measured by the force necessary to maintain constant velocity applied in the direction of travel. The coefficient of friction (f) is defined as F/N when N is the force normal or at right angles to the surface where the sliding motion is taking place. The force needed to put a body which is at rest into motion is called *static friction.*

Friction in firearms is made up of three parts. The first part has to do with the forces needed to cut the grooves in the rotating bands and put the projectile into motion. Part two consists of the sliding friction overcome as the projectile slides along the bore, and the third part has to do with the friction of the gases in front of and behind the moving projectile. The last one of these can be predicted quite satisfactorily by means of well worked out formulas for fluid flow. The other two are in a less satisfactory condition.

Fluid friction is best predicted by means of the Fanning formula and the Reynolds number. The force needed to produce fluid flow through a tube, F, is given by the formula

$$\frac{dP}{dL} = \frac{2f\rho u^2}{gd} \tag{132}$$

where dP = pressure drop, lb. per sq. in., or pressure needed to overcome fluid friction over a length of tube dL

ρ = density of the fluid

u = average velocity of the fluid at the point in question

d = tube diameter

g = acceleration due to gravity

f = "friction factor," which depends on the Reynolds number

$$\left(\frac{du\rho}{\mu}\right)$$

where μ = viscosity of the fluid

The friction factor f may be estimated with sufficient precision for present purposes by the formula

$$\log f = -0.133 \log\left(\frac{du\rho}{\mu}\right) - 1.641 \qquad (133)$$

This formula is independent of the system of units, provided that the system is consistent.

The viscosity of gases increases with temperature. Pressure has much less effect and, within the precision of these calculations, may be neglected. The Sutherland formula for gas viscosity is

$$\mu = \mu_0\left(\frac{273 + C}{T + C}\right)\left(\frac{T}{273}\right)^{3/2} \qquad (134)$$

where μ = viscosity at the temperature T, °K.

C = a coefficient given in Table 19

TABLE 19

Gas	μ_0*	C
Air	171	124
CO	166	102
CO_2	137	240
H_2	84	72
N_2	166	110

* μ is given in poises times 10^6. To convert poises to English engineering units suitable for use in the Reynolds number, multiply poises by 0.0672.

FRICTION

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To illustrate the use of these formulas, calculate the pressure needed to force compressed air through a gun tube under the following conditions:

Diameter of tube   = 3 in. = 0.25 ft.
Pressure of gas   = 1,000 atm.
Temperature of gas = 3600°R. (°F. abs.)(2000°K.)
Gas velocity   = 1,000 ft. per sec.

$$\mu = 171 \left(\frac{273 + 2,000}{124 + 2,000}\right) \left(\frac{2,000}{273}\right)^{3/2} = 3,600 \times 10^{-6} \text{ poises}$$

$$= 3,600 \times 10^{-6} \times 0.0672 = 0.00024 \text{ English units}$$

$$P_R = \frac{3,000}{36} = 83, \qquad T_R = \frac{2,000}{132} = 15$$

$$\mu(\text{for } PV = \mu NRT) = 1.45$$

$$\rho = \frac{1}{V} = \frac{P}{\mu NRT} = \frac{1,000 \times 14.7 \times 144}{1.45 \times \frac{1}{29} \times 1,546 \times 3,600}$$

$$= 7.6 \text{ lb. per cu. ft.}$$

since P must be expressed in pounds per square foot.

$$N = \frac{\text{weight}}{\text{molecular weight}} = \frac{1}{29} \text{ (for air)}$$

$$R = 1,546 \text{ English ft.-lb., °R. units}$$

$$\text{Reynolds number} = \frac{du\rho}{\mu} = \frac{0.25 \times 1,000 \times 7.6}{0.00024} = 7.6 \times 10^6$$

$$\log f = 0.133 \log (716 \times 10^6) - 1.641$$

$$f = 0.0028$$

$$g = 32.2$$

$$\frac{dP}{dL} = \frac{2 \times 0.0028 \times 7.6 \times (1,000)^2}{32.2 \times 0.25}$$

$$= 5,300 \text{ lb. per sq. ft.}$$

$$= \frac{5,300}{144} = 37 \text{ lb. per sq. in.}$$

which would be the pressure drop due to friction of air moving under these conditions through 1 ft. of length of tube.

The sliding friction of the metal projectile on the metal gun-barrel wall is not nearly so well known. Many experimental data are available for metal-on-metal sliding friction for moderate speeds and pressures, up to about 100 ft. per sec. Gun velocities, however, may exceed 3,000 ft. per sec. It is very difficult to measure friction directly at high speeds, for the friction gener-

ates so much heat that the sliding surfaces start to melt almost instantly, giving a lubricated contact. Incidentally, there is no reason to believe that such melting, or at least plastic flow on the surface of the metal, does not actually take place in the gun.

The most successful direct measurement of friction of metal on metal at high speed has been made by W. K. Woods in his "bouncing-ball" method. This method allows a steel ball to fall vertically on top of a rapidly revolving horizontal metal drum. If the drum is standing still, the ball will rebound vertically. If the drum is revolving, the ball will rebound at an angle, the magnitude of the angle, which is measured photo-
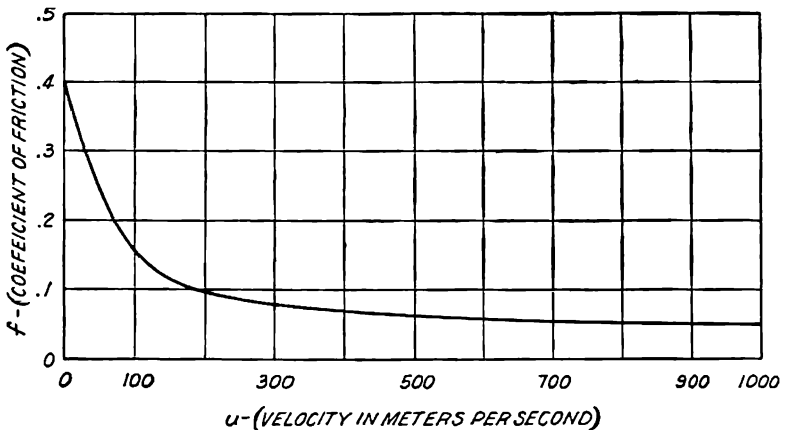

Fig. 20.

graphically, being a simple algebraic function of the coefficient of friction. Experiments by this method indicate that the coefficient decreases slightly with increasing speed up to the limit of the experiments, about 300 ft. per sec.

Indirect ballistic measurements have been made of sliding friction by certain European investigators, giving a relation like Fig. 20. This method of indirect determination appears to be most hopeful, as it is based on actual firings. The weakness in this method is due to the necessity for determining friction by the difference of various ballistic measurements whose precision is not always good.

The coefficient of friction is that fraction of a pressure normal to the surface in question which is necessary to keep the moving surfaces in contact with each other at constant velocity. For

example, Woods found that the coefficient of sliding friction of steel at a speed of 300 ft. per sec. was about 0.11. If, therefore, a steel block with an area of 1 sq. ft. were pressed against a steel plate with a pressure of 1,000 lb. per sq. in. and were sliding at a velocity of 300 ft. per sec., the force needed to overcome friction would be $1,000 \times 144 \times 0.11 = 16,000$ lb.; the energy to overcome this friction for a distance of 1 ft. would be 16,000 ft.-lb., and the power needed to produce this energy would be

$$16,000 \times 300 = \frac{16,000}{300} = \overline{4,800,000} \text{ ft.-lb. per sec.}$$

or

$$\frac{4,800,000}{550} = 8,700 \text{ hp}$$

In order to calculate the friction of the rotating bands against the lands of the rifling, consider Fig. 21, in which the line BA is
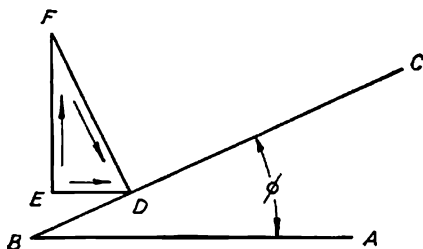

Fig. 21.

parallel to the axis of the bore of the gun, while the angle φ represents the angle of twist of the rifling. A force represented in direction and magnitude by the line ED is forcing the projectile parallel to the axis of the bore. At the same time, a line EF represents the force acting at right angles to the axis of the bore with a radius of gyration equal to k, causing the projectile to rotate. The resultant of these two forces, represented by the line FD, is the force pressing against the lands of the rifling and the cause of the frictional resistance to sliding. The product of this force FD and the coefficient of sliding friction will be the force needed to overcome the friction of the projectile against the lands.

$$dE = F \, dL \tag{135}$$
$$dE = F_R \times r \times \omega \, d\theta \tag{136}$$
$$dE = F_R \times U \times \tan \varphi \, d\theta \tag{137}$$

where F_R = force causing rotation

Since the kinetic energy of rotation is

$$\text{K.E.} = M \left(\frac{k}{r}\right)^2 (\tan^2 \varphi) \frac{U^2}{2} \tag{138}$$

then, differentiating,

$$dE = M \left(\frac{k}{r}\right)^2 \tan^2 \varphi U \, dU \tag{139}$$

whence

$$F_R = M \left(\frac{k}{r}\right)^2 \tan \varphi \frac{dU}{d\theta} \tag{140}$$

If the force FD is called F_f, then

$$F_f = F_R \sec \varphi \tag{141}$$

$$= M \left(\frac{k}{r}\right)^2 \tan \varphi \sec \varphi \frac{dU}{d\theta}$$

and if the coefficient of friction is called f, then the frictional resistance will be

$$= fM \left(\frac{k}{r}\right)^2 \tan \varphi \sec \varphi \frac{dU}{d\theta} \tag{142}$$

where U = velocity of translation of the projectile at the time θ

TABLE 20

VALUES OF STARTING PRESSURE AND MEAN PASSIVE RESISTANCE FOR VARIOUS GUNS*

[Taken from Tschappat (Ref. 57)]

Name of gun	Starting pressure, lb. per sq. in.	Mean resistance, lb. per sq. in.
3-in. field.....................	4,800	3,200
3-in. 15-pounder Seacoast........	4,800	2,450
5-in. Seacoast Model 1897........	5,400	2,100
6-in. Model 1908...............	5,300	1,960
8-in. Model 1888...............	4,800	2,100
10-in. Model 1888 and 1895.......	3,850	1,800
12-in. Model 1888 and 1895.......	3,200	1,640
14-in. Model 1907..............	2,860	1,475
12-in. mortar Model 1890.........	2,500	2,600
16-in. Model 1895..............	2,400	1,200

* These pressures are determined experimentally by ramming a projectile through the gun in question at substantially zero velocity. There are no data as to the effect of velocity on these pressures.

The usual method in the past for estimating friction in guns was based on experiments carried out at Watertown Arsenal many years ago, the results of which are quoted by Tschappat.

In Table 20, it is believed that the values for *starting pressure* are reliable but that those for *mean resistance*, which refers to the average resistance along the bore of the gun, are high. The reason for this is the fact, observed experimentally by DeForest, that the gun barrel swells as the projectile travels along it very much as a boa constrictor swells when swallowing a rabbit. The most suitable method for direct measurement to allow for this swelling effect is to force the projectile through the bore by hydraulic means.

The friction of the projectile in the bore of the gun was studied experimentally by Langweiler (Ref. 73) by measuring the movements of the gun in a free-recoil carriage and at the same time measuring the pressure-time curve by a piezoelectric gauge. It was found that in the case of the standard German army rifle ammunition the average friction of the projectile through the bore amounted to 48 kg. while the starting friction was about four times that value, or 172 kg. (This friction is defined as momentum divided by time and has the dimensions of weight.) The fraction of the charge moving forward was 0.48, and the average pressure difference between the projectile base and the breech was 128 kg. per sq. cm.

CHAPTER XVII

FLASH AND SMOKE

From the practical viewpoint, both flash and smoke are objectionable in firearms. Smoke discloses the location of the gun in daytime, and flash does the same thing at night. Smoke in the daytime hides the target from the gunner; at night, flash may temporarily blind him. Black powder as a propellant was forced out by smoke. Flash is one of the reasons for the discarding of pyro smokeless powder. With present powders, smoke is a minor problem, flash being much more troublesome.

Flash from a gun is of two kinds. The first kind is small and occurs at the muzzle of the gun owing to the incandescent gas leaving the muzzle. The second, which is the objectionable type, is caused by the ignition, out in front of the muzzle, of the explosive mixture *produced by* the mixing of the powder gases with air after leaving the muzzle. In some guns the second type of flash is intense enough to resemble heat lightning in summer and may frequently be seen many miles away.

An analysis of the problem indicates that two factors must be present to produce the second type. The mixture of the gases with air must be explosive, and the temperature must be high enough to ignite the mixture.

It will be recalled that owing to the operation of the mass-action law (see Chap. V on Basic Physical Chemistry) the composition of the gas in the gun depends on its temperature. At low temperatures the value of the equilibrium constant K of the water-gas reaction is small, while at high temperatures K is large. This means that the proportion of carbon monoxide and water vapor is high at high temperatures, while at low temperatures the proportion of carbon dioxide and hydrogen is high. In other words, as the powder gases travel down the length of the bore of the gun, their composition changes as the temperature decreases, so that when they issue from the muzzle into the air their composition will vary according to the length of the gun,

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the amount of work the gases have performed on the projectile, etc. The resulting mixture with the air will therefore have varying explosive properties depending on this composition.

Still more important than the composition, however, is the temperature of the mixture of gases and air. This must be above the ignition point for the particular mixture. The simplest way, therefore, to control the flash for any particular weapon is to control the powder-gas temperature so that it will not ignite after mixing with the air. The best way to do this is to add some substance to the powder which will reduce its net heat of explosion by the absorption of heat. During the First World War it was standard practice to add a small pad of moist salt (NaCl) on top of the regular powder charge, in separately loaded guns, for nighttime firing. Experimentation with various substances indicates that potassium salts seem to be most effective in reducing flash, K_2SO_4 (potassium sulphate) being excellent in this respect.

The principle involved appears to be a chemical dissociation at high temperature with an absorption of heat. This heat is then recovered as the gas cools down but at a lower temperature, so that the net energy loss is not necessarily great, but the cooling effect persists. Cranz (Ref. 11) states that 750°C. is about the critical temperature of the resulting mixture and that the moisture content of the air, either liquid or vapor, has some effect—the higher the moisture, the less the chance of flash.

It is also known that the ignition of the propelling charge has a considerable effect on flash production and that certain guns which have always given severe flashes with certain charges have had the flash entirely removed by improvement in ignition of the powder.

Insofar as smoke is concerned, the smoke is always due to the presence of finely divided solid particles in the gas. Under some conditions, nitric oxide (NO) is one of the constituents of the powder gas, and when this mixes with the oxygen of the air it oxidizes at once to NO_2, which is a dark, reddish-brown gas. In considerable masses this dark gas becomes nearly opaque and has the appearance of true smoke, except that it disappears on diffusion into the air while real smoke persists after diffusion. In the case of black powder, the smoke, which is white, is made up of solid particles of K_2CO_3 and K_2SO_4 and others, the only

color-producing material, the charcoal, being all consumed in the explosion under ordinary conditions. In the case of smokeless powder, however, any solid particles of unburned powder, or any solid organic substances formed as the result of partial burning of the powder may appear as a smoke, varying in color from pale gray to dense black, depending on the amount of free carbonaceous material liberated and the amount of black powder used in the primer. Guns with heavy charges or with a low ratio of length to diameter are likely to offend in this regard. The more nearly finished the burning, the less the smoke. It is an interesting fact that certain guns on the dividing line of flashlessness are known to produce smoke when there is no flash and no smoke when there is flash.

Since the important factor in flash is the gas—air mixture beyond the muzzle and since the temperature of that mixture depends on the amount of air in it, any device attached to the muzzle that gives the issuing gases a wider distribution into the air will increase their dilution and lower their temperature and therefore will reduce flash.

CHAPTER XVIII

STABILITY OF PROPELLANTS

The requirements for propellent powders as to stability include testing by heating the sample of the powder at various temperatures, such as at 135°C. and at 65.5°C. According to Tschappat (Ref. 57), a powder should survive 5 hr. at 135°C. and 60 days at 65.5°C.

The decomposition of powder on standing at an elevated temperature appears to be an autocatalytic reaction in which the products of the reaction catalyze the subsequent reaction. It is known that many chemical reactions of this type are very sensitive to temperature and that a rise in temperature of about 10°C. will double the reaction rate. It is interesting to test this fact against the stability figures given above.

$$60 \text{ days} = 1,440 \text{ hr.}$$

$$\frac{1,440}{5} = 288 \quad \text{and} \quad 135° - 65.5° = 69.5°$$

Therefore, if x is the number of degrees centigrade needed to double the reaction rate,

$$2^{\left(\frac{69.5}{x}\right)} = 288$$

$$\frac{69.5}{x} \log 2 = \log 288$$

$$x = 8.5°$$

This is considered a good check on the theory that the slow decomposition of powder is a chemical reaction of this type.

The decomposition of powder goes on at any temperature, although the rate of decomposition varies as stated above. A statistical analysis of many hundred samples of powders stored at constant temperature gave a curve of the type shown in Fig. 22. From a study of a curve of this sort, it is possible to estimate the probable subsequent life of any particular batch of powder. It is obvious that individual samples deviate widely from the mean in studies of this sort.

One way of writing an autocatalytic reaction is as follows:

Let W_o = weight of original powder

W = weight of powder at time θ

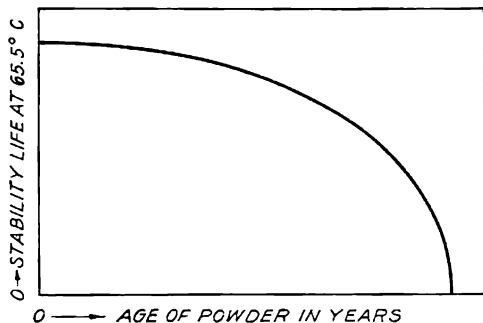$W_o - W$ = weight of decomposed powder

FIG. 22.

Assume that the reaction-rate constant k is directly proportional to the amount of decomposition products present. Then

$$k = k'(W_o - W + \alpha) \tag{143}$$

$$\therefore \frac{dW}{d\theta} = k'(W_o - W + \alpha)W \tag{144}$$

where α is the amount of impurities present at the start of the process, due to imperfections in manufacture. Separation of variables gives on integration

$$\int_{W_o}^{W} \frac{dW}{W_o - W + \alpha} + \int_{W_o}^{W} \frac{dW}{W} = (W_o + \alpha)k' \int_0^\theta d\theta \tag{145}$$

giving

$$\log \frac{\alpha W}{(W_o + \alpha - W)W_o} = \frac{(W_o + \alpha)k'}{2.3} \theta \tag{146}$$

From this equation, it may be seen that the amount of impurities, α, at the start in a sample of powder will influence its life profoundly. This explains the high degree of purity required for military explosives, which must remain in storage fit for use for many years.

CHAPTER XIX

MEASUREMENT OF PRESSURE

The measurement of steady pressures offers few or no difficulties. Variable pressures are increasingly difficult to measure —the greater the rate of change of pressure with respect to time, the greater the difficulty—and in the case of guns and closed chambers, the difficulty becomes very great indeed.

The classical method for measuring the pressure in guns and closed chambers is the copper crusher gauge method. This method makes use of a small copper cylinder of known dimensions; this is placed in a container holding a piston, and the whole is placed in the powder chamber. When the charge is fired, the compressed gas applies pressure to the piston, which in turn compresses the copper cylinder beyond its elastic limit. After firing, the cylinder is measured, and the degree of compression is supposed to be proportional to the maximum pressure in the chamber. The device is calibrated by a static-pressure device to give the proper reading. This method fails to tell the truth, however, for stressing the metal beyond its elastic limit causes plastic flow, and flow of any variety requires time. When the charge is fired in the gun, the time interval is so short that the metal does not have an opportunity to flow so far as it should for the pressure applied and the result is that the gauge records too low a pressure. Recent experiments on the effect of rate of loading on copper crusher gauges have indicated that at a maximum pressure of 30,000 lb. per sq. in. the error in the instantaneous application of load on a gauge calibrated by the static method is 7 per cent, the gauge reading about 27,900 lb. per sq. in. Another difficulty with the crusher gauge is the compression of the wall of the tube through which the piston moves, causing it to stick and thereby reduce the pressure reading still further. It should be remembered, however, that successive gauge readings on similar guns should have values which are correct relative to each other, even if they are in error on an absolute basis.

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The time lag in recording pressure gauges for guns and closed chambers is equally a serious problem. The duration of pressure in a gun is frequently of the order of magnitude of 5/1,000 to 20/1,000 sec., while in a closed chamber the duration of the rise in pressure is often considerably shorter than this. To be of real value in ballistic calculations, the pressure lag should be less than 1/1,000 sec.

There are two satisfactory methods in use at the present time for recording pressures. The first of these is the piezoelectric gauge. This gauge depends on the property of certain crystals, notably quartz, of generating a flow of electricity when pressure is applied to it in a certain direction. The amount of electricity generated is proportional to the rate of application of the pressure; and if this amount is measured by a suitable chronograph, the record should therefore be a function of the pressure-time curve desired. It requires some sort of amplifying device to magnify the reading to make it measurable, the most successful device at present used for this purpose being the cathode-ray oscillograph. Present instruments of this type have very little inertia and a time lag of about one-millionth of a second.

The second method in use is the Petavel mechanical, or spring, gauge. This device makes use of two metal springs in the form of steel tubes, one of which is under compression and the other under tension. These are stressed well within their elastic limits so that the strain is proportional to the pressure. The movement of the end of the spring is recorded by means of a mirror attached to it, which deflects a beam of light. The deflection is recorded on the sensitized paper of a chronograph and is proportional to the pressure. While this device has a certain amount of time lag, it seems possible to build this type so that it is extremely rapid; times of explosion of the order of magnitude of 1.5 milliseconds have been successfully measured by one of these gauges.

CHAPTER XX

MEASUREMENT OF TEMPERATURE

A rational analysis of interior ballistics requires a knowledge of the temperature. At the present time, the only reliable method for determining powder flame temperature is by a calculation by means of a heat and material balance. There are several reasons why it is not an easy matter to measure flame temperature.

In the first place, measuring instruments of the thermometer or thermocouple type consist of solid elements which are immersed in the hot flame and which are supposed to reach the temperature of that flame in order to actuate some sort of indicating device. If the flame is of sufficiently long duration and if the thermometer were to be left in it indefinitely, it might be supposed that the thermometer would reach flame temperature. This is not the case except under very special conditions. The usual result is that the thermometer will reach a final equilibrium temperature between the temperature of the flame and the temperature of the surrounding walls. This is due to radiation effects between hot solids through gases that are transparent to radiant heat. Thus, if the powder gases are at 3000°C. and the surrounding walls are at 1000°C., the thermometer might read in the vicinity of 2000°C. ±, depending on the degree of turbulence of the hot gases. The only case in which the thermometer will read the true gas temperature is the rare one in which the gas and the surrounding walls are all at the same temperature.

But in the case of flames from the explosion of powder the time interval is very short, and, because the thermometer must receive heat in order to become heated up to its final temperature, the time element enters into the picture. The result is that the thermometer never has a chance to reach its theoretical equilibrium temperature, its degree of failure to do so depending on the duration of the flame itself.

Several methods have been used to approximate explosion flame temperatures. One device consists of a rotating disk on the rim of which is placed a thermocouple junction. This disk

is then whirled at known speed through a continuous gas burner flame of known temperature at such a speed that the time interval in contact with the flame corresponds to the duration of an explosion flame. The thermocouple reading under these conditions is an approximate value for the burner flame. Such a device, calibrated in this way, has been used to measure the temperatures of the flames from primers with some success.

Another method for measuring steady flame temperatures of long duration is the sodium-D-line reversal method. In this method the light from a tungsten-filament (or platinum-filament) incandescent lamp is led through the flame in question on the way to the spectroscope. The D line will appear as a bright line on a continuous spectrum if the flame is hotter than the filament and as a dark line if the flame is colder than the filament. The temperature of the filament is then adjusted by electrical means until the D line just disappears, at which point it and the flame have the same temperature. The temperature of the filament is then measured by means of an optical pyrometer, which gives its correct temperature.

This method has been used for flames of short duration by taking a motion-picture film of the spectrum and adjusting the filament temperature by trial and error for successive firings until the proper temperature has been reached.

The results of experiments on powders burning by combustion in the open air by the D-line method are given below:

TABLE 21

Name of Powder	Temperature, °C.
.30-caliber pyro (P.A. 375)	2000
12-in. cannon powder (D.P. 765)	1880
American Powder Mills black powder (FFG)	2700

CHAPTER XXI

CLOSED-CHAMBER EXPERIMENTS

The most useful piece of equipment in the interior-ballistics laboratory is the *closed chamber;* when combined with a calorimeter, this is called a "calorimetric bomb." Such bombs consist of strong vessels fitted with suitable means for opening and closing, drawoff leads for gases, firing connections, and attachments for measuring pressure and sometimes temperature. They have been built in all sizes from about 1 gal. down to minute bombs with but a few cubic centimeters capacity. They are used for two principal purposes, to obtain thermochemical data for checking theoretical calculations and to study rate of explosion. The former use is well developed but the latter has not yet been perfected, particularly in regard to ignition insofar as simulated gun firings are concerned.

While a great mass of experimental closed-chamber data has accumulated in ballistic laboratories of governments and commercial companies, not much has appeared in the literature, and students of this subject depend chiefly on the work of Crow and Grimshaw (Ref. 69), whose work has been unexcelled in quality, superseding all previous published work in reliability. The contents of this chapter are based largely on their work, and all experimental data quoted are taken from their papers.

Two sizes of chambers were used, the larger one having a capacity of 649 cc. and an exposed inside-surface area of 656.8 sq. cm. and the smaller one corresponding values of 130.7 cc. and 251.6 sq. cm. The chambers were equipped with either a spring pressure gauge or a piezoelectric pressure gauge, relief valve, and electrical firing connections.

In order to obtain simultaneous ignition of all the powder, gas ignition was used. After loading, the chamber was filled with a mixture of 2 parts acetylene by volume to 25 parts of air. This gaseous mixture was, in turn, ignited by a small amount of cordite and guncotton threaded on an electrically heated fuze wire. This explosive priming mixture was insufficient alone to

affect the readings on the pressure gauges. It should be noted that this method of ignition is quite different from that used in actual firearms; suitable allowance for this must be made in correlating closed-chamber and gun firings.
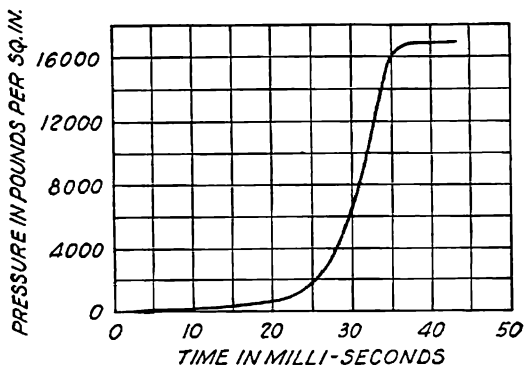

Fig. 23.

The pressure gauges, one of the Petavel spring type and the other of the piezoelectric cathode-ray-tube type, have been mentioned in the chapter on Measurement of Pressure. The original papers should be consulted for details. The apparent precision of the gauges was about 0.2 per cent.

The pressure-time curves obtained were of the type shown in Fig. 23.

Three types of powder were used, all in the form of long cords of the type known as cordite, but of three widely different com-

TABLE 22

Name of powder	Diameter, cm.	N.C., per cent	N con-tent, per cent	N.G., per cent	D.P.A., per cent	Vola-tiles, per cent	Moisture
N(1)	0.071	97.10	12.6	.....	0.47	....	2.43
N(2)	0.215	96.90	12.6	.....	0.46	2.14	0.50
N(3)	0.554	94.80	12.6	.....	0.45	4.25	0.50
C(1)	0.066	71.03	13.2	28.74	....	0.23	
C(2)	0.328	70.16	13.2	28.67	....	1.17	
C(3)	0.890	68.91	13.2	28.79	....	2.30	
B(1)	0.064	40.43	12.6	59.40	....	0.17	
B(2)	0.430	40.49	12.6	59.35	....	0.16	
B(3)	1.200	40.57	12.6	59.26	....	0.17	

positions. One was a single-base pyro powder, the second was a double-base powder resembling M.D. (modified) cordite, and the third was a very hot double-base powder much like Ballistite. Data on the powders used are given in Table 22.

The heat of explosion of these powders was determined separately in a calorimetric bomb; the results are shown in Table 23.

TABLE 23

Expressed as calories per gram, with H_2O as liquid

| Name of Powder	Q_v
N(1)	936
N(2)	896
N(3)	831
C(1)	1250
C(2)	1220
C(3)	1170
B(1)	1470
B(2)	1465
B(3)	1460

Analyses of these experiments indicated the composition of the explosion gases corresponded to a "freezing" temperature such that $K_P = 2.5\pm$.

In order to compute the gas analysis, proceed as in Chap. IV, using powder N(1) as an example.

TABLE 24

Basis = 100 g. of powder

Constituent	Weight	Moles C	Moles O_2	Moles H_2	Moles N_2	Moles of constituent
N.C. (12.6 per cent N)	97.1	2.120	1.767	1.325	0.442	0.0883
D.P.A.	0.47	0.035	.....	0.015	0.001	0.00272
H_2O	2.43	.....	0.068	0.135	.....	0.135
Totals	100.00	2.155	1.835	1.475	0.443	

In this computation, N.C. (12.6 per cent) is presumed to be

$$C_{24}H_{30}O_{20}(NO_2)_{10}$$
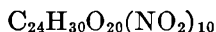
which has a nitrogen content of 12.75 per cent. The D.P.A. is $(C_6H_5)_2NH$ (diphenylamine).

$$(100 \text{ g. powder}) \rightarrow a\text{CO}_2 + b\text{CO} + c\text{H}_2\text{O} + d\text{H}_2 + e\text{N}_2$$
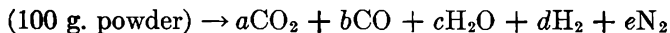
$$a + b = 2.155$$

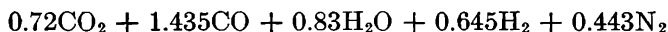$$c + d = 1.475$$

$$a + \frac{b}{2} + \frac{c}{2} = 1.835$$

$$\frac{bc}{ad} = 2.5$$

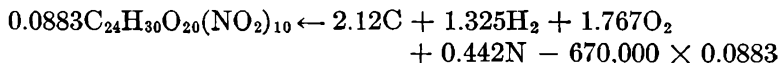$$a = 0.72 \qquad b = 1.435 \qquad c = 0.83 \qquad d = 0.645$$

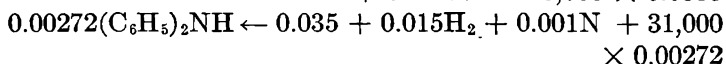Solve simultaneously, for a, b, c, and d. $e = 0.443$
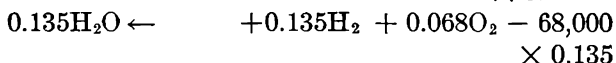Total moles $= 2.598$.
Therefore 100 g. of powder gives

$$0.72\text{CO}_2 + 1.435\text{CO} + 0.83\text{H}_2\text{O} + 0.645\text{H}_2 + 0.443\text{N}_2$$

Computing the heat of explosion at constant volume, Q_v,

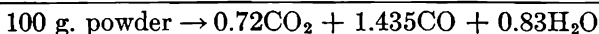$$0.0883\text{C}_{24}\text{H}_{30}\text{O}_{20}(\text{NO}_2)_{10} \leftarrow 2.12\text{C} + 1.325\text{H}_2 + 1.767\text{O}_2$$
$$+ 0.442\text{N} - 670{,}000 \times 0.0883$$

$$0.00272(\text{C}_6\text{H}_5)_2\text{NH} \leftarrow 0.035 + 0.015\text{H}_2 + 0.001\text{N} + 31{,}000$$
$$\times 0.00272$$

$$0.135\text{H}_2\text{O} \leftarrow \qquad +0.135\text{H}_2 + 0.068\text{O}_2 - 68{,}000$$
$$\times 0.135$$

$$0.72\text{C} + 0.72\text{O}_2 \rightarrow 0.72\text{CO}_2 + 0.72 \times 94{,}400$$
$$1.435\text{C} + 0.72\text{O}_2 \rightarrow 1.435\text{CO} + 1.435 \times 26{,}700$$
$$0.83\text{H}_2 + 0.415\text{O}_2 \rightarrow 0.83\text{H}_2\text{O} + 0.83 \times 68{,}000$$
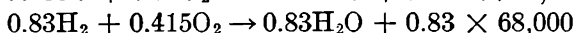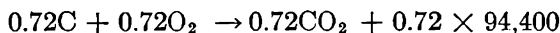
$$100 \text{ g. powder} \rightarrow 0.72\text{CO}_2 + 1.435\text{CO} + 0.83\text{H}_2\text{O}$$
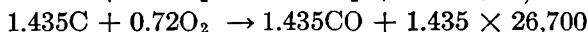$$+ 0.645\text{H}_2 = 0.443\text{N}_2 + 94{,}350 \text{ cal.}$$

or 943.5 cal. per g. This is in fair agreement with the experimental value of 936 as found calorimetrically.

The nine varieties of powder were fired at 11 loading densities, the maximum observed pressure being recorded as well as the time of burning as measured between the point where the recorded pressure was $\frac{1}{50}$ of the maximum and where it was $\frac{49}{50}$ of the maximum. The "uncooled" pressure was then calculated by a method similar to that recommended in earlier chapters of this book. In the following tables,

$\Delta =$ loading density, g. per cc.
$\theta = \frac{48}{50}$ of pressure time, sec.
$P_a =$ maximum recorded pressure in *large* bomb, kg. per sq. cm.

P_b = same for *small* bomb

P_{max} = calculated uncooled pressure, same units

TABLE 25.—N(1) POWDER
Diameter = 0.071

Δ	θ	P_a	P_b	$P_{a_{max}}$	$P_{b_{max}}$
0.2479	0.0054	3,309	3,115	3,395	3,347
0.2211	0.0065	2,862	2,707	2,940	2,909
0.2049	0.0071	2,616	2,523	2,688	2,714
0.1819	0.0081	2,227	2,167	2,296	2,332
0.1546	0.0094	1,857	1,764	1,924	1,911
0.1344	0.0104	1,572	1,507	1,636	1,642
0.1066	0.0119	1,199	1,125	1,261	1,245
0.0755	0.0139	803	762	862	875
0.0585	0.0153	613	583	673	695
0.0420	0.0167	419	397	478	505
0.0263	0.0184	257	228	317	328

The corresponding values for the same loading density (Δ = 0.2479) for the nine varieties of powder are given in Table 26.

TABLE 26

Kind of powder	θ	P_a	P_b	$P_{a_{max}}$	$P_{b_{max}}$
N(1)	0.0054	3,309	3,115	3,395	3,347
N(2)	0.0135	3,284	3,033	3,396	3,306
N(3)	0.0405	3,134	2,906	3,287	3,247
C(1)	0.0031	3,694	3,561	3,781	3,830
C(2)	0.0125	3,722	3,484	3,849	3,819
C(3)	0.0375	3,660	3,377	3,841	3,793
B(1)	0.0016	3,378	3,125	3,448	3,326
B(2)	0.0091	3,271	3,118	3,375	3,391
B(3)	0.0196	3,208	3,079	3,339	3,405

The composition of the gas and the value of the maximum "uncooled temperature," T_{max}, are given in Table 27. These gas compositions were computed by the equilibrium constant of the water-gas reaction at the maximum temperature T_{max}, by a series of successive approximations.

TABLE 27.—MOLES OF GAS PER GRAM OF POWDER

Kind of powder	CO_2	CO	H_2	H_2O	N_2	Total	T_{max}, °K.
N(1)	0.004335	0.017432	0.004463	0.010543	0.004373	0.041146	2998
N(2)	0.003649	0.019174	0.005611	0.009398	0.004363	0.042195	2927
N(3)	0.003200	0.020244	0.006976	0.008827	0.004269	0.043519	2758
C(1)	0.007140	0.011946	0.001370	0.011214	0.005241	0.036911	3781
C(2)	0.006607	0.012771	0.001676	0.011272	0.005195	0.037521	3706
C(3)	0.005964	0.013748	0.002016	0.011367	0.005144	0.038239	3617
B(1)	0.009708	0.007155	0.000546	0.011706	0.005740	0.034855	4172
B(2)	0.009709	0.007155	0.000546	0.011704	0.005739	0.034853	4172
B(3)	0.009699	0.007176	0.000558	0.011698	0.005737	0.034868	4170

It should be noted that the use of five significant figures in some of the columns of Table 27 is not so much a matter of precision of measurements, as of convenience in stoichiometry.

In order to illustrate the calculation of T_{max} and P_{max}, select N(1) as before with a loading density $\Delta = 0.2479$, and to save time in the successive approximation start with the value of T_{max} as given, 2998°K. According to the values given for the water-gas reaction, the value of $K_p = 6.92$.

Take as a basis 100 g. of powder, as before.
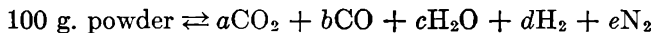
$$100 \text{ g. powder} \rightleftarrows aCO_2 + bCO + cH_2O + dH_2 + eN_2$$
$$a + b = 2.155$$
$$c + d = 1.475$$
$$a + \frac{b}{2} + \frac{c}{2} = 1.835 \qquad e = 0.443$$
$$\frac{bc}{ad} = 6.92$$

Solving these gives

$$b = 2.155 - a$$
$$d = 1.475 - c$$
$$a + \frac{2.155 - a}{2} + \frac{c}{2} = 1.835$$
$$a + c = 1.515$$
$$d = 1.475 - 1.515 + a = a - 0.040$$
$$(2.155 - a)(1.515 - a) = 6.92a(a - 0.040)$$
$$3.263 - 3.670a + a^2 = 6.92a^2 - 2,768a$$

$$5.92a^2 + 3.403a = 3.263$$
$$a^2 + 0.5752a = 0.552$$
$$a^2 + 0.5752a + (0.2876)^2 = 0.552 + 0.0827 = 0.6347$$
$$a + 0.2876 = \pm\sqrt{0.6347} = + 0.796$$

$$a = 0.508$$
$$b = 2.155 - a \quad = 1.647$$
$$c = 1.515 - a \quad = 1.007$$
$$d = a - 0.040 \quad = 0.468$$
$$\frac{bc}{ad} = \frac{1.647 \times 1.007}{0.508 \times 0.468} = 6.98(6.92)$$

To calculate Q_v for room temperature (taken by Crow and Grimshaw as bomb temperature $\doteq 350°$K.) compute the value on the basis of the final T_{max} composition and then allow this heat to raise the explosion products to T_{max}, since in the basic energy balance $Q - W = \Delta E$, $W = 0$, and Q all go toward raising temperature, or

$$Q_v = \int_{T_1}^{T_2} c_v \, dT \text{ (water as water vapor)}$$

$$0.0883C_{24}H_{30}O_{20}(NO_2)_2 \leftarrow 2.12C + 1.325H_2 + 1.767O_2$$
$$+ 0.442N_2 - 670{,}000 \times 0.0883$$
$$0.00272(C_6H_5)_2NH \leftarrow 0.035C + 0.015H_2$$
$$+ 0.001N_2 + 31{,}000 \times 0.00272$$
$$0.135H_2O \leftarrow \quad + 0.135H_2 + 0.068O_2$$
$$- 67{,}000 \times 0.135$$
$$0.508C + 0.508O_2 \rightarrow 0.508CO_2 \quad + 0.508 \times 94{,}400$$
$$1.647C + 0.824O_2 \rightarrow 1.647CO \quad + 1.647 \times 26{,}700$$
$$1.007H_2 + 0.504O_2 \rightarrow 1.007H_2O \text{ (vapor)} + 1.007 \times 67{,}000$$

$$100 \text{ g. powder} \rightarrow 0.508CO_2 + 1.647CO + 1.007H_2O$$
$$+ 0.468H_2 + 0.441N_2 + 91{,}400 \text{ cal.}$$

This heat is now available to heat the gases from T_1 (350°K.) to T_{max} (presumed on first trial to be 2998°K., from Crow and Grimshaw's results). Using the heat-capacity chart, Fig. 5, 0.508 moles of CO_2:

$$Mc_{p_{ave}} \text{ at } 2998°K. \ (4936°F.) = 13.56 \quad Mc_{v_{ave}} = 11.57$$
$$\text{at } 350°K. \ (170°F.) \ = 9.15 \quad Mc_{v_{ave}} = 7.16$$

Heat consumed by CO_2 =
$$0.508[11.57(2{,}998 - 288) - 7.16(350 - 288)] = 15{,}700 \text{ cal.}$$

1.647 moles of CO:

$$Mc_{p\text{ave}} \text{ at } 2998°K. = 8.27 \quad Mc_{v\text{ave}} = 6.28$$
$$\text{at } 350°K. = 7.01 \quad Mc_{v\text{ave}} = 5.02$$

Heat consumed by CO =
$$1.647[6.28(2{,}998 - 288) - 5.02(350 - 288)] = 27{,}500 \text{ cal.}$$

$$\frac{1.007 \text{ moles of } H_2O \text{ vapor}}{Mc_{p\text{ave}} \text{ at } 2998°K.} = 11.05 \quad Mc_{v\text{ave}} = 9.06$$
$$\text{at } 350°K. \quad = 8.11 \quad Mc_{v\text{ave}} = 6.12$$

Heat consumed by H_2O =
$$1.007[9.06(2{,}998 - 288) - 6.12(350 - 288)] = 24{,}350 \text{ cal.}$$

0.468 moles of H_2

$$Mc_{p\text{ave}} \text{ at } 2998°K. = 7.82 \quad Mc_{v\text{ave}} = 5.83$$
$$\text{at } 350°K. = 6.90 \quad Mc_{v\text{ave}} = 4.91$$

Heat consumed by H_2 =
$$0.468[5.83(2{,}998 - 288) - 4.91(300 - 288)] = 7{,}260 \text{ cal.}$$

0.441 moles of N_2

$$Mc_{p\text{ave}} \text{ at } 2998°K. = 8.20 \quad Mc_{v\text{ave}} = 6.21$$
$$\text{at } 350°K. = 6.96 \quad Mc_{v\text{ave}} = 4.97$$

Heat consumed by N_2 =
$$0.441[6.21(2{,}998 - 288) - 4.97(350 - 288)] = \underline{\quad 7{,}280}$$
$$\text{Total} \quad \overline{82{,}090} \text{ cal.}$$

which is a little too low (91,400), indicating that the probable temperature rise is about

$$\frac{91{,}400}{82{,}090} \times \frac{T_{\text{max}} - 288}{2{,}998 - 288} \quad \text{or} \quad T_{\text{max}} = 3370°K.$$

Repeating the previous calculation with $T_{\text{max}} = 3370°K.$ instead of 2998°K., it is found that the heat consumed would be slightly greater than that estimated from the value of Q_v. Therefore, it may be stated that T_{max} is very close to 3300°K.

The next step is to estimate the maximum uncooled pressure P_{max} (which Crow and Grimshaw computed to be about 3,350 kg. per sq. cm.), or 3,240 atm., making use of the μ chart relation $PV = \mu NRT.$

Calculate first the weighted average reduced temperature by the method indicated in Chap. II.

$$T_R = \frac{3{,}300}{4.071}\left(\frac{0.508}{304.3} + \frac{1.647}{133.0} + \frac{1.007}{647.2} + \frac{0.468}{41.3} + \frac{0.441}{126.1}\right)$$
$$= 811(0.001668 + 0.01239 + 0.001556 + 0.01132 + 0.00350)$$
$$= 24.7$$

Then, using Crow and Grimshaw's P_{max} value as a first approximation,

$$P_R = \frac{3{,}240}{4.071}\left(\frac{0.508}{73.0} + \frac{1.647}{35} + \frac{1.007}{217.7} + \frac{0.468}{20.8} + \frac{0.441}{33.5}\right)$$
$$= (0.00696 + 0.0471 + 0.00463 + 0.0225 + 0.01316) = 79.7$$

The value of μ estimated for these values of T_R and P_R is 1.28, indicating that at this high temperature the PVT relations of such a gas do not depart greatly (28 per cent) from the perfect-gas relation in spite of the high pressure.   Put μ into the formula $PV = \mu NRT$, for 100 g. of powder.

Since $\Delta = 0.2479$,

$$V \text{ (liters)} = \frac{100}{0.2479 \times 1{,}000} = 0.404$$
$$N = 2.598 \text{ moles}$$
$$T = 3300°\text{K.}$$
$$R = 0.08206, \text{ l.-atm.}$$
$$P = \frac{1.28 \times 4.071 \times 0.08206 \times 3{,}300}{0.404} = 3{,}390 \text{ atm.}$$

Correcting μ for 3,390 atm. ($P_R = 83.3$) gives a value about 1.29, so that the calculated P_{max} would be 3,410 atm.   The measured pressure, diminished from P_{max} by cooling of the gases and expansion of the larger bomb, was 3,309 kg./sq. cm., or 3,210 atm.

The rate of explosion in the closed chamber was also studied by these investigators, using four types of propellent powders, as follows:

TABLE 28

Name	Cord diameter, cm.	N.C., per cent	N content, per cent	N.G.	Stabilizer, per cent	Volatiles plus moisture
N.C. pyro.........	0.2144	96.90	12.6	.....	0.46	2.64
M.D. cordite......	0.0965	65.68	13.0	29.53	4.45	0.34
Mk. 1 cordite......	0.1340	37.00	13.0	58.00	5.00	Trace
H.C..............	0.2492	39.00	12.2	58.00	3.00	

The stabilizer used in the N.C. pyro was diphenylamine $[(C_6H_5)_2NH]$, that used in the M.D. cordite and the Mk. 1

cordite was mineral jelly or vaseline ($C_{20}H_{42}$), while that used in the H.C. was Centralite ($C_{17}H_{20}N_2O$), which is very commonly used in Europe for that purpose instead of D.P.A. The calculated heats of explosion at room temperature (Q_v) were as follows:

	Cal. per G.
N.C. pyro	891
M.D. cordite	1,051
Mk. 1 cordite	1,253
H.C.	1,323

The specific heats of these powders were estimated from Kopp's law (see Chap. VII) and taken as follows:

N.C. pyro	0.306
M.D. cordite	0.347
Mk. 1 cordite	0.365
H.C.	0.360

The *instantaneous-ignition temperature* was estimated to be as follows:

	°C.
N.C. pyro	303
M.D. cordite	242
Mk. 1 cordite	223
H.C.	263

Using an initial temperature of 26.7°C., the following values of the "uncooled" pressure (P_{max}) were calculated:

TABLE 29

Name of powder	Loading density, g. per cc.	P_{max}, g. per sq. cm.	T_{max}, °K.
N.C. pyro	0.2479	3,385	2927
M.D. cordite	0.2479	3,770	3265
Mk. 1 cordite	0.2211	3,472	3669
H.C.	0.2479	3,953	3898

The explosion products, calculated at T_{max}, are shown in Table 30.

TABLE 30

Based on 100 g. of explosive, expressed in moles

Powder	CO_2	CO	H_2O	H_2	N_2	Total
N.C. pyro........	0.3649	1.9174	0.9398	0.5611	0.4363	4.2195
M.D. cordite....	0.3654	1.7726	1.0738	0.4736	0.5006	4.1860
Mk. 1 cordite....	0.5000	1.4180	1.2339	0.2692	0.5553	3.9764
H.C............	0.7047	1.1305	1.1821	0.1308	0.5643	3.7124

The four powders were then fired in the larger (649 cc.) chambers at two starting temperatures, T_P, to study the effect of
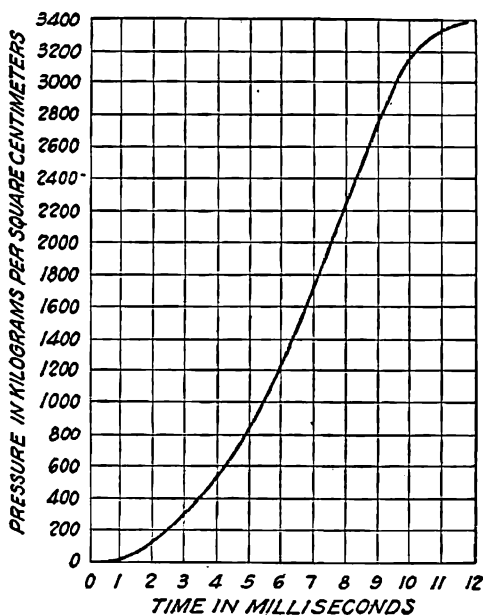
FIG. 24.

powder temperature. The time intervals, expressed in milliseconds ($\frac{1}{1000}$ sec.), are given for each successive 4 per cent of the highest pressure, starting with 2 per cent.

These data for N.C. pyro, for the 26°C. temperature only, using for the highest pressure the calculated "uncooled" pressure, 3,280 atm., have been plotted in Fig. 24.

In order to test rate-of-burning formulas against closed-chamber data, it is permissible to make certain assumptions

in order to avoid too great complications in computation. These will be noted in the following discussion.

The powder used in this experiment was in the form of long cords. If it is assumed that the end effects can be neglected, it then follows that the surface

$$(A) = 2\pi^{1/2}V^{1/2} \tag{147}$$

where V = volume of the cord.

If the density of the powder is ρ, then the weight of powder $W = \rho V$ and

$$A = 2\pi^{1/2}\left(\frac{W}{\rho}\right)^{1/2} \tag{148}$$

since $\rho = 1.58$ g./per cc.,

$$A = 2\left(\frac{\pi}{\rho}\right)^{1/2} W^{1/2} = 2.82W^{1/2} \tag{149}$$

Since in the Charbonnier formula

$$\frac{dy}{d\theta} = \phi(y)P$$

y is the fraction of the powder burned,

$$y = \frac{W_0 - W}{W_0} = 1 - \frac{W}{W_0} \tag{150}$$

and if $P = yP_{max}$,

$$P = \frac{W_0 - W}{W_0}P_{max} \tag{151}$$

Rewrite the Charbonnier formula.

$$\frac{dy}{d\theta} = \phi'(y)AP \tag{152}$$

Then combining these relations gives

$$\frac{dy}{d\theta} = (2.82\sqrt{W_0}\,P_{max})\phi'(y)(1 - y)y \tag{153}$$

where $2.82\sqrt{W_0}\,P_{max}$ is a constant for a particular firing and is called β.

TABLE 31.—TYPICAL TIME-INTERVAL MEASUREMENTS

N.C., $\Delta = 0.2479$ M.D., $\Delta = 0.2479$ Mk. 1, $\Delta = 0.2211$

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
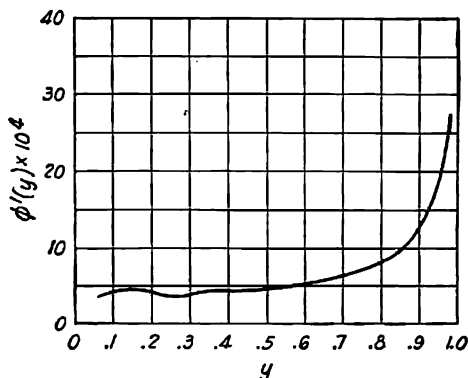
FIG. 25.

Therefore,

$$\phi'(y) = \frac{dy/d\theta}{\beta(y)(1 - y)} \qquad (154)$$

which should be independent of the surface. It is interesting to plot $\phi'(y)$ vs. y for this particular firing.

$$W_0 = 649 \times 0.2479 = 160.7 \text{ g.}$$
$$= 2.82 \sqrt{160.7} \times 3,280 = 117,000$$

This plot in Fig. 25 is quite characteristic of $\phi'(y)$ values from the Charbonnier formula. It indicates that, for the first 80 per cent of the burning, an average value of $\phi'(y)$ may be taken without too great deviation. The last portion, while the remnants of the grains are going, indicates that the relationship is more complex.

TABLE 32

y	Δy	$\Delta \theta$	$\dfrac{\Delta y}{d\theta}$	$1 - y$	$\dfrac{\Delta y/\Delta \theta}{\beta(1 - y)(y)} = \phi'(y)$
0.02	....	.....	......	0.98	
0.06	0.04	1.717	0.0234	0.94	3.53×10^4
0.10	0.04	0.911	0.0439	0.90	4.17
0.14	0.04	0.627	0.0638	0.86	4.53
0.18	0.04	0.556	0.0720	0.82	4.17
0.22	0.04	0.496	0.0807	0.78	4.02
0.26	0.04	0.479	0.0835	0.74	3.71
0.30	0.011	0.403	0.0993	0.70	4.05
0.34	0.04	0.356	0.1122	0.66	4.27
0.38	0.04	0.308	0.1300	0.62	4.71
0.42	0.04	0.313	0.1278	0.58	4.48
0.46	0.04	0.288	0.1388	0.54	4.78
0.50	0.04	0.269	0.1487	0.50	5.08
0.54	0.04	0.268	0.1492	0.46	5.13
0.58	0.04	0.252	0.1587	0.42	5.57
0.62	0.04	0.256	0.1563	0.38	5.67
0.66	0.04	0.255	0.1600	0.34	6.09
0.70	0.04	0.244	0.1638	0.30	6.67
0.74	0.04	0.256	0.1563	0.26	6.93
0.78	0.04	0.260	0.1538	0.22	7.67
0.82	0.04	0.272	0.1470	0.18	8.52
0.86	0.04	0.278	0.1440	0.14	10.23
0.90	0.04	0.284	0.1408	0.10	13.35
0.94	0.04	0.354	0.1130	0.06	17.10
0.98	0.04	0.540	0.0742	0.02	32.4

GRAPHICAL STUDY OF EXPERIMENTAL FIRINGS

Ballistic experiments on actual guns are often of value.

The following are data obtained by firing an experimental gun mounted in such a way as to have virtually frictionless recoil.

Weight of gun and other recoiling parts = 7,700 kg.
Weight of projectile = 162.5 kg.
Weight of propellant = 13.16 kg.
Length of chamber = 74 cm.
Diameter of chamber = 23.9 cm.
Distance from base of projectile to muzzle = 403 cm.

TABLE 33

Time, sec.	Projectile travel, cm. (relative to gun)	Pressure, atm. (piezoelectric gauge)
0.0010	3.1	260
0.0042	12.8	830
0.0069	44.0	1,480
0.0094	74.7	1,530
0.0118	136	1,360
0.0128	212	920
0.0160	302	570
0.0182	393	410

Since this gun was fitted with a free-recoil carriage and the weight of the recoiling parts is known, it is possible to calculate the amount of recoil by the equality of momenta. Taking the equivalent mass of the projectile as that of the projectile plus half that of the charge, then

$$M'U' = mu$$
$$\left(162,500 + \frac{13,160}{2}\right) U' = 7,700,000u$$
$$\frac{u}{U'} = \frac{\left(162,500 + \frac{13,160}{2}\right)}{7,700,000u} = 0.219$$

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but since $u = \dfrac{dl}{d\theta}$ and $U = \dfrac{dL'}{d\theta}$

$$\frac{dl}{dL'} = 0.0219 \quad \text{and} \quad l = 0.0219L' \quad \text{when } l_0 = L_0' = 0,$$

where $M'U'$ and L' are relative to the gun and $U' - u$ equals the projectile velocity relative to the ground.

$L = L' - l =$ projectile travel relative to the ground

By proportion,

$$\frac{L}{L'} = 1 - 0.0219 = 0.9781$$

Therefore calculate the value of the projectile travel relative to the ground. The values obtained are given in Table 34:

TABLE 34

θ, Sec.	Travel Relative to Ground, Cm.
0.0010	3.0
0.0042	12.5
0.0069	45.1
0.0094	73.2
0.0118	133.0
0.0138	207.5
0.0160	296
0.0182	385

See Fig. 26.

Since velocity is the first derivative of distance with respect to time,

$$u = \frac{dL}{d\theta}$$

Therefore construct a derivative curve from curve A; this will be a velocity-time curve, in centimeters per second. This is given in Fig. 26.

The first derivative of the velocity-time curve gives the acceleration-time curve.

$$a = \frac{du}{d\theta}$$

Calling the pressure in excess of that needed to overcome friction P,

$$P \times A = M \times a$$

and $P = (M/A) \times a$. Therefore, multiplying the values of a obtained by differentiating the velocity-time curve by M/A will give values

$$P = \frac{169,080 \times a \times 4}{(23.9)^2 \times \pi \times 980.7 \times 1,033.3} \text{ atm.} = 0.000373a \text{ atm.}$$

The total pressure would be $P + P_f$ when P_f is the pressure needed to overcome friction. Such a pressure curve, not including friction, has been plotted in Fig. 26 as atmospheres.
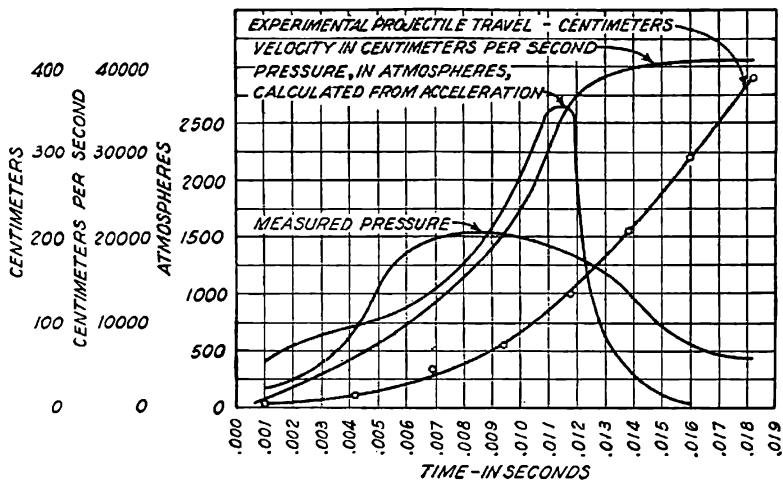
Fig. 26.

Inspection of these curves will show that the pressure needed to overcome friction, which should be the difference between the two, is most irregular, indicating negative friction near the start and at the peak pressure. The difficulty is experimental and illustrates the lack of precision in the determination of friction by differences of quantities that are not sufficiently well measured. This particular set of data is considered very reliable, but analysis of this sort indicates its difficulties.

CHAPTER XXIII

CALCULATION OF INTERIOR-BALLISTIC CURVES

It is possible to predict the relations between time, pressure, velocity, and travel for a definite gun, given suitable data. This makes it possible to estimate the probable performance of firearms before they are constructed, which is of the greatest importance to both the gun designer and the powder maker. It also permits the latter to modify his ammunition on paper in order to attempt to meet changed requirements for guns already in existence. While such predictions are not particularly precise, they are frequently sufficiently accurate as to save much time and effort in firearms development.

There are two methods of attack. One method depends on the use of statistics and empirical relations. The other method depends on physical and chemical data and the application of thermodynamics. The first method is quicker and entirely suitable for interpolation. The second method is more reliable for extrapolation although it is more laborious. The chief object of this book is to emphasize the second method, which while discussed quite completely in the German literature has never been published in English. The first method is largely used in Hayes's "Elements of Ordnance" (Ref. 20) and, earlier, Tschappat's "Text-book of Ordnance and Gunnery" (Ref. 57). A brief outline will be included here:

The velocity-time curve in a gun is usually of the type of curve shown in Fig. 26. If plotted as a velocity-travel curve, its shape becomes the integral curve of the $u\theta$ curve, since

$$u = \frac{dL}{d\theta}$$

$$\int_{L_1}^{L_2} dL = \int_{\theta_1}^{\theta_2} u \, d\theta$$

the area under the $u\theta$ curve between any two values of θ being the distance traveled (L_2 to L_1) during that time (θ_2 to θ_1). When plotted in the usual way, it resembles Fig. 27. On the

other hand, when u is plotted against L, the curve usually resembles Fig. 28. This curve was recognized by Le Duc as a curve of the form $u = aL/(b + L)$. In an equation of this form, as L increases, b becomes less significant and, when $L = $ infinity, $u = a$, which is supposed to be a constant, a practical absurdity since, because of friction and external pressure, u approaches zero as a theoretical limit. However, for reasonable values of L, this is no hardship. The value of b is $2L$ at the point in the travel when the pressure available for increasing velocity is a maximum.
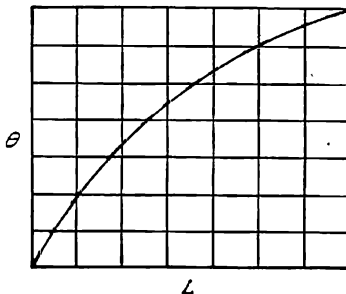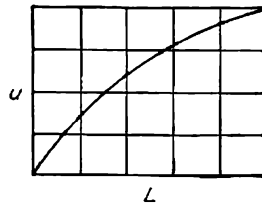
FIG. 27.   FIG. 28.

Note that this is the total pressure minus that needed to overcome friction.

Practically, purely empirical formulas based on statistical evidence are used to determine a and b, and the reader is referred to either of the texts mentioned above for details (Ref. 20 or 57).

As an introduction to the thermodynamic method, consider the example of the classic compressed-air gun of Lieutenant Zalinsky of the United States Army, designed in the late nineteenth century and installed in the abortive U.S.S. "Vesuvius." Data on this weapon are

Length of bore   = 30 ft.
Diameter of bore   = 15 in.
Weight of projectile = 1,300 lb.
Recoil device,   none
Charge   = 48.5 cu. ft. of air at 350 atm. gauge
                         pressure and at 70°F.
Mean pressure needed to overcome friction in the bore assumed
   to be 1,000 lb. per sq. in.
Forcing resistance = zero (smooth bore)

Assume for purposes of this calculation that the air acts as a perfect gas and that the expansion of the air is reversible and adiabatic, **all the friction tak**ing place between the projectile and the bore. **Assume also, as is** customary among ballisticians, that the effective mass of the projectile is that of the actual projectile plus half **that of the charge.**

The problem is to calculate the probable conditions at the muzzle, including velocity, pressure, and temperature.

$$\text{Density of air} = \frac{1}{V} = \frac{P}{NRT}$$

$$\frac{351 \times 14.6 \times 144}{\frac{1}{29} \times 1{,}546 \times 530} = 26.3 \text{ lb. per cu. ft.}$$

$$\text{Weight of air} = 26.3 \times 48.5 = 1{,}275 \text{ lb.}$$

$$\text{Equivalent mass} = \frac{1{,}300 + (1{,}275/2)}{32.2} = 60.2 \text{ slugs,}$$

(English mass units)

$$\text{Kinetic energy} = \frac{Mu^2}{2} = 30.1u^2$$

Energy needed to overcome friction $= F \times L$

$$= P_v \times A \times (L_2 - L_1) = P_f \times (V_2 - V_1)$$

where V_2 and V_1 = final and initial volume of the air, respectively

$$A = (\tfrac{15}{12})^2 \times (\pi/4) \times 1.23 \text{ sq. ft.}$$

$$(V_2 - V_1) = 30 \times 1.23 = 36.9 \text{ cu. ft.} \qquad V_2 = 85.4$$

Frictional energy $= 1{,}000 \times 144 \times 36.9 = 5{,}310{,}000$ ft.-lb.

The energy available from the reversible adiabatic expansion of a perfect gas, from Chap. II, is $-(P_2V_2 - P_1V_1)/(\gamma - 1)$, where γ is the ratio of the specific heats and is about 1.4 for air at this condition. The relation between P and V for this type of expansion is

$$\frac{P_2}{P_1} = \left(\frac{V_1}{V_2}\right)^{\gamma}$$

$$\therefore \frac{P_2}{351} = \left(\frac{48.5}{85.4}\right)^{1.4} = 0.453$$

$$P_2 = 159 \text{ atm.}$$

Total energy of expansion

$$= \frac{159 \times 14.7 \times 144 \times 85.4 - 351 \times 14.7 \times 144 \times 48.5}{1 - 1.4}$$

$$= 18{,}250{,}000 \text{ ft.-lb.}$$

Energy available for producing motion

$$= 18{,}250{,}000 - 5{,}310{,}000 = 12{,}940{,}000 \text{ ft.-lb.}$$
$$30.1u^2 = 12{,}940{,}000$$
$$u = 656 \text{ ft. muzzle velocity}$$

The actual gun had a muzzle velocity of 650 ft. per sec.

The temperature of the air at the instant the projectile leaves the muzzle is calculated from the formula

$$\frac{T_2}{T_1} = \left(\frac{V_1}{V_2}\right)^{\gamma-1}$$
$$\frac{T_2}{70 + 460} = \left(\frac{48.5}{85.4}\right)^{1.4-1}$$
$$T_2 = 422°\text{R.} = -38°\text{F.}$$

The following method may be used to predict the behavior of a specific powder in a specific gun. The powder might be the N.C. pyro powder studied by Crow and Grimshaw (see Chap. XXI) and the gun the 155-mm. G.P.F. Model 1917; it should be realized, however, that that particular powder is not the proper granulation for this weapon. Data on the gun are as follows:

Weight of gun and recoiling parts = 8,795 lb.
Length of chamber = 37.09 in.
Diameter of chamber = 6.69 in.
Volume of powder chambers = 1,329 cu. in.
Travel of projectile = 185 in.
Number of rifling grooves = 48
Twist of rifling (uniform) = 1 turn in 29.89 calibers
Weight of projectile = 95 lb.
Weight of standard pyro charge = 25¼ lb.
Maximum pressure = 31,500 lb. per sq. in.
Muzzle velocity = 2,380 ft. per sec.
Maximum range = 17,700 yd.

It must be emphasized that the Crow and Grimshaw powder differs in several ways from that ordinarily used in this weapon. Some of these differences are listed below:

1. The (Crow and Grimshaw) powder consists of solid rods and is very degressive, while the standard powder is multiperforated and therefore progressive. This will increase the burning rate at the start and give a high maximum pressure.

2. The powder was fired with an explosive gas primer while the standard powder is primed with a pad of black powder at the

base of the charge. This would give more uniform ignition than can be expected with the standard powder.

3. The web thickness is not the same.

The forcing resistance and the friction in the bore are not known, and it will be assumed that the pressures in pounds per square inch needed to overcome these effects are 5,000 and 2,000, respectively.

The relative heat losses to the walls will be considered the same in both gun and closed chamber.

The energy required to produce the retarded recoil will be neglected.

TABLE 35

Δ	θ_c	$\log_e (100\theta_c)$	P_{max}, kg. per sq. cm.
0.2479	0.0135	0.300	3,351
0.2211	0.0160	0.470	2,892
0.2049	0.0176	0.565	2,639
0.1819	0.0194	0.662	2,294
0.1546	0.0232	0.842	1,878
0.1344	0.0260	0.956	1,588
0.1066	0.0303	1.108	1,240
0.0755	0.0362	1.286	863
0.0585	0.0401	1.388	642
0.0420	0.0444	1.495	471
0.0263	0.0489	1.587	292

Using Crow and Grimshaw data for this kind and size of powder to determine the effect of loading density Δ on the total burning time θ_c, and plotting Δ against $\log_e$ (ln) of $(100\theta_c)$ for convenience, as recorded in Table 35, it is seen (Fig. 29) that the points make a straight line. This empirical relation gives an equation of the form

$$\Delta = a \ln \theta_c + b$$

or

$$\theta_c = e^{\frac{\Delta - b}{a}}$$

and applying this to the particular powder gives

$$\Delta = -0.1725 \ln \theta_c + 0.30$$

The relation between Δ and P_{max} is shown in Fig. 30.
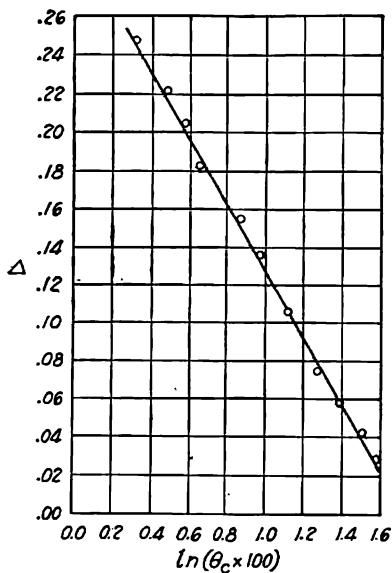
Fig. 29.
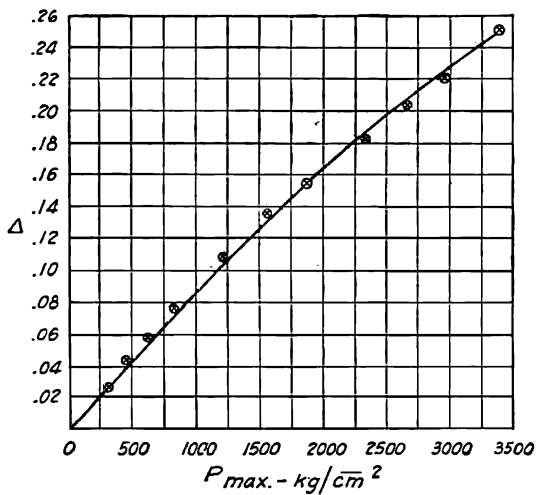
Fig. 30.

The gun data have been converted into the metric system for simplicity.

$$\text{Volume of chamber} = 21.8 \text{ l.}$$
$$\text{Weight of charge} = 11.5 \text{ kg.}$$
$$\text{Loading density} = \frac{11.5}{21.8} = 0.526$$

Since this value of Δ is outside the range of the experimental values, the corresponding value of P_{max} is estimated by the μ chart.

$$T_{max} \text{ (Crow and Grimshaw)} = 2927°K.$$
$$\text{Moles gas per gram} = 0.0422$$

$$T_R = 21.9 \qquad P_R = \frac{P_{max}}{74.8} \quad \text{(74.8 is average } P_c\text{)}$$

$$P_{max} = 21.8\mu \times 0.0422 \times 11,500 \times 0.08206 \times 2,927$$
$$P_{max} = 5,350\mu \text{ atm.}$$

Since this runs off the chart for experimental values of μ, it would appear that P_{max} would be about 8,000 atm. when $\Delta = 0.526$.
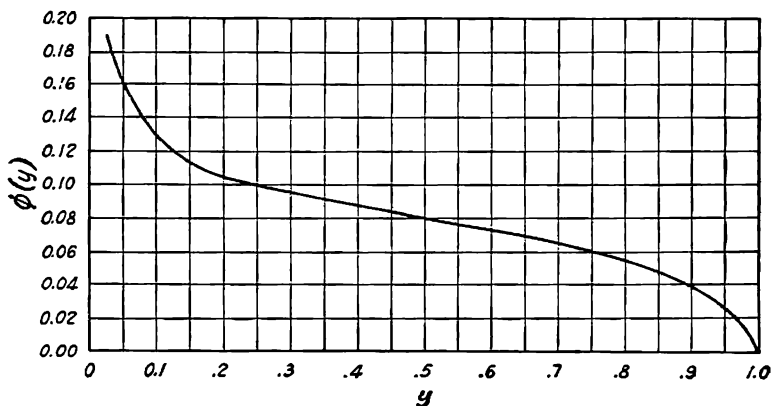
FIG. 31.

Substitute this value in the Charbonnier formula given in Chap. XXI (see Fig. 31).

$$\frac{dy}{d\theta} = \phi(y)P \qquad \text{or} \qquad \frac{d(\ln y)}{d\theta} = \phi(y)P_{max}$$

The value of $\phi(y)$ for the first portion of the burning may be considered as proportional to P_{max}.

The time for the pressure to rise from $y = 0.02$ or 160 atm. to 5,000 lb. per sq. in., or 340 atm., would be estimated by taking the experimental time for $y = 340/8,000 = 0.0425$, or a time about 0.9 milliseconds, and dividing it by this ratio:

$$0.9 \times \frac{3,280}{8,000} = 0.37 \text{ milliseconds}$$

It is therefore estimated that the projectile will start to move when the pressure has risen to 340 atm., which will occur about 0.37 milliseconds after the pressure has reached 160 atm., or $y = 0.02$.

From this point on, the projectile moves down the bore, and the volume of the powder chamber increases in proportion. The equivalent loading density decreases in proportion as does the corresponding value of P_{max}.

The conditions at this instant are summarized as follows:

Pressure   = 340 atm.
Temperature = 2927°K.
y = 0.0425
P_{max} = 8,000 atm.
Δ = 0.526
ΔL = travel of projectile = 0
θ = 0.37 milliseconds after $P = 160$ atm.
V = 21.8 l.
μ = 1.5

The projectile now moves a distance dL and attains a velocity u in the time $d\theta$, the average acceleration during that time being $\frac{du}{d\theta}$, which comes from the applied force. This applied force is the average pressure during that period, P, minus that pressure needed to overcome friction, expressed in suitable units. The kinetic energy delivered to the projectile and moving charge comes from the hot powder gas (N), cooling it a corresponding amount. These several effects can be summarized by the following equations, using *average* values over short increments:

$$\Delta L = u \, \Delta\theta$$

$$F = P'A = M'a = M' \frac{\Delta u}{\Delta\theta}$$

$$\text{K.E.} = F \times \Delta L = N \times c_v \, \Delta T$$

$$\frac{\Delta y}{\Delta\theta} = \phi(y)P$$

In these formulas, use the following values:

$$A = (15.5)^2 \frac{\pi}{4} = 189 \text{ sq. cm.}$$

$$M' = [95 + (25.25/2)]454 = 48,900 \text{ g.}$$

$$F = P' \text{ atm.} \times 1.0133 \times 10^6 \times 189 = 191.5 \times 10^6 P' \text{ dynes}$$

$$N = 25.25 \times 454 \times 0.0422 \times y = 485y \text{ moles}$$

$$P' = P - (2,000/14.7) = P - 136 \text{ atm.}$$

$$c_v = 7.48 \text{ cal. per mole}$$

$$\therefore (P - 136)(189) \times 191.5 \times 10^6 = 48,900 \frac{du}{d\theta}$$

or

$$(P - 136)(0.74 \times 10^6) = \frac{du}{d\theta}$$

$$189 \times 191.5P \, \Delta L = 485y \times 7.48 \, \Delta T$$

or

$$P \, \Delta L = 0.100y \, \Delta T$$

$$\frac{\Delta y}{\Delta \theta} = \phi(y)P \qquad u = \frac{\Delta L}{\Delta \theta} \qquad PV = \mu NRT$$

The simplest method of following the projectile along the bore is to use stepwise integration, taking small finite steps and taking average conditions along the step.

Step 1.—Let $\Delta L = 10$ cm.

$$\therefore L_2 = 10$$

The average P during this interval $= (P_2 + 340)/2$.

$$\therefore P' = P_2 + 170 - 136 = P_2 + 34$$

and

$$(P_2 + 34)(0.74 \times 10^6) = \frac{du}{d\theta}$$

which, on integration, gives

$$\theta \doteq \frac{\Delta u}{0.74 \times 10^6(P_2 + 34)}$$

Since $u_1 = 0$, $\Delta u = u$
and using $\theta_1 = 0$,

$$\therefore \frac{dL}{d\theta} = 0.74 \times 10^6(P_2 + 34)\theta$$

and

$$\Delta L = 0.37 \times 10^6 (P_2 + 34)\theta^2$$

$$\theta = \left(\frac{10}{0.37 \times 10^6 (P_2 + 34)}\right)^{\frac{1}{2}}$$

Since $\phi(y)$ (from Fig. 31) for this case will be about 0.18,

$$\frac{dy}{d\theta} = 0.18 \left(\frac{P_2 + 340}{2}\right) \qquad \text{or} \qquad \theta = \frac{y_2 - 0.0425}{0.18[(P_2 + 340)/2]}$$

These two values for θ are then combined, and the several relations solved simultaneously for the corresponding values of P_2, u_2, T_2, and θ_2.

Step 2.—This is similar to the first step, using a new value of $\Delta L = 10$, with

$$\Delta u = u_3 - u_2, \qquad \Delta T = T_3 - T_2, \qquad \text{and} \qquad P_{\text{ave}} = (P_3 + P_2)/2$$

and a new value of $\phi(y)$ as read from Fig. 31.

A set of values computed for the same gun but for a different powder is given in Table 36.

TABLE 36

L, cm.	P, atm.	T, °K.	θ, sec.	y	u, cm. per sec.
0	367	4,200	0.00358	0.033	0
1	790	4,195	0.00465	0.120	1,860
2	944	4,173	0.00507	0.140	3,007
4	1,280	4,140	0.00592	0.191	6,230
13	1,700	4,073	0.00694	0.266	11,670
43	2,200	3,882	0.00865	0.427	23,880
113	2,485	3,550	0.01081	0.719	42,950
133	2,520	3,477	0.01126	0.797	47,120
185	2,490	3,313	0.01224	1.000	56,240
329	1,400	3,030	0.01424	.....	86,700
470	938	2,810	0.01574	.....	99,800

The final value represents the predicted conditions at the muzzle.

When $y = 1.00$, the powder is completely burned and, from that point to the muzzle, it is sufficiently precise to assume a reversible adiabatic expansion of a perfect gas, *viz.*,

$$\Delta E = \Delta(\text{K.E.}) + F = \frac{\Delta PV}{\kappa - 1} = Nc_v \int_{T_1}^{T_2} dT$$

CHAPTER XXIV

ROCKETS

The use of rockets as a weapon is very old, and the basic principles have remained unchanged, being based on the action-equals-reaction or recoil principle.

The propelling action of the rocket depends on the production of large quantities of gas by a slow-burning propellent powder or other fuel contained within the rocket itself. This gas is formed in the gas chamber of the rocket under moderate pressure and blows out through a nozzle of such design that pressure head is converted to velocity head with but little loss due to friction. This gas, issuing into the atmosphere at high velocity, causes the rocket itself to move in the opposite direction at a velocity such that

$$Mu = M'u'$$

where M and M' = the masses of the rocket and the moving gas, respectively

u and u' = their corresponding velocities referred to a fixed point in the surroundings.

In the usual rocket, it seems preferable to use an outside propellant to give the rocket its initial velocity and to depend on the subsequent reaction effect of the rocket gases for further acceleration and external work, including friction with the air.

The energy available in the rocket gases may be computed if the composition of the fuel is known. Since the gas pressure within the rocket is ordinarily moderate, it is a fair assumption that the propellant burns at constant pressure.

Suppose, for example, that the rocket fuel consists of a petroleum hydrocarbon of the formula C_8H_{18} and compressed oxygen gas, which are allowed to mix gradually in stoichiometric proportions and burn at constant pressure. The heat effect would be computed as follows:

$C_8H_{18} + 12\frac{1}{2}O_2 = 8CO_2 + 9H_2O + Q_p$
$$= 1,300,000 \text{ cal. per mole (114 g.) of } C_8H_{18}$$
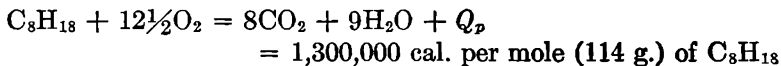
Since the combustion is within the rocket chamber, the process is substantially adiabatic and the result will be the rise in temperature of these combustion gases to T_{max} at constant pressure, which would give $T_{max} = 6000°K.$ approximately. To retain this gas at such a temperature for any length of time would require the use of a ceramic-lined cylinder and a ceramic nozzle.

The energy balance for a flow of a compressible gas through a nozzle is

$$\Delta H + \Delta \frac{u_n^2}{2} + \Delta x = 0$$

when ΔH = enthalpy change of gas

$\Delta \frac{u_n^2}{2}$ = kinetic energy change

Δx = change in elevation

Since in a horizontal, stationary nozzle, $\Delta x = 0$, then

$$\Delta \frac{u_n^2}{2} = -\Delta H$$

But for a perfect gas, and at these high temperatures and low pressures, all gases are nearly perfect.

$$\Delta \frac{u_n^2}{2} = -\frac{\kappa(P_1 V_1)}{\kappa - 1}\left[\left(\frac{P_2}{P_1}\right)^{\frac{\kappa-1}{\kappa}} - 1\right]$$

where κ = ratio of the heat capacities, about 1.2 in this case

P_1 = pressure in the gas chamber

P_2 = pressure in the atmosphere

V_1 = volume occupied by the gas in the gas chamber, per unit mass of gas

It should be remembered that $\Delta \frac{u_n^2}{2}$ refers to the velocity change with respect to the nozzle and not to the surroundings. If the velocity of the rocket is u and that of the gas is u', both with respect to the surroundings, then $u + u' = u_n$. The problem of suitable nozzle design is much the same as that in respect to high-pressure turbine nozzles, to which the reader is referred.

Setting up the momentum balance in differential form, for a differential increase in rocket velocity, du,

$$M\,du = dM'u'$$

where dM' = quantity of gas issuing from the nozzle in the time $d\theta$ with the absolute (referred to the surroundings) velocity u'.

Since the mass of gas flowing is at the expense of the mass of the rocket, then $-dM = dM'$. The relative, or nozzle, velocity may be called a constant, for a constant rocket pressure, and

$$u + u' = u_n,$$

whence

$$du = -du'$$

and

$$+\int_{m_1}^{m_2} \frac{dM}{M} = \int_{u_1}^{u_2} \frac{du}{u}$$

Calling $M_1 = 1$, then

$$\ln \frac{M_2}{1} = \ln M_2 = \ln \frac{u_2}{u_1}$$

Table 37 gives the ratio of propellent weight to rocket weight, p, needed to give velocity u with a jet velocity u_n.

TABLE 37*
From Randolph (Ref. 305)

u	Values of p for various values of U_n			
	$U_n = 6,000$	$U_n = 8,000$	$U_n = 10,000$	$U_n = 12,000$
1,000	0.182	0.133	0.105	0.087
3,000	0.648	0.455	0.35	0.284
5,000	1.3	0.869	0.648	0.516
10,000	4.3	2.49	1.788	1.3
20,000	27	11.2	6.4	4.3

* Velocities are in feet per second. It is stated that rocket velocities of 12,000 ft. per sec. have been obtained experimentally.

The problem of preparing a suitable solid fuel for military use is a matter of control of composition and burning surface such that, under flight conditions, the chamber pressure will remain substantially constant. The nozzle design, both as to shape and size and as to material of construction, is similar to that for the gas turbine, which at the time of writing is still in the experimental stage.

Unit Equivalents

$$1 \text{ inch} = 2.540 \text{ centimeters}$$
$$1 \text{ meter} = 39.37 \text{ inches}$$
$$1 \text{ square inch} = 6.452 \text{ square centimeters}$$
$$1 \text{ square meter} = 1{,}550 \text{ square inches}$$
$$1 \text{ cubic inch} = 16.39 \text{ cubic centimeters}$$
$$1 \text{ liter} = 61.02 \text{ cubic inches}$$
$$1 \text{ pound} = 453.59 \text{ grams} = 7{,}000 \text{ grains}$$
$$1 \text{ kilogram} = 2.205 \text{ pounds}$$
$$1 \text{ slug (English mass unit)} = 32.158 \text{ pounds}$$
$$1 \text{ gram per cubic centimeter} = 62.43 \text{ pounds per cubic foot}$$
$$1 \text{ pound per square inch} = 70.31 \text{ grams per square centimeter}$$
$$1 \text{ atmosphere} = 14.70 \text{ pounds per square inch}$$
$$= 1.0133 \times 10^6 \text{ dynes per square centimeter}$$
$$= 1.0333 \text{ kilograms per square centimeter}$$
$$= 760 \text{ millimeters of mercury}$$
$$= 29.92 \text{ inches of mercury}$$
$$= 1{,}013.3 \text{ millibars}$$
$$1 \text{ gram per square centimeter} = 980.7 \text{ dynes per square centimeter}$$
$$1 \text{ foot per second} = 30.48 \text{ centimeters per second}$$
$$1 \text{ foot-pound} = 0.1383 \text{ kilogram-meters}$$
$$1 \text{ liter-atmosphere} = 74.73 \text{ foot-pounds}$$
$$= 101.33 \text{ joules}$$
$$1 \text{ joule} = 10^7 \text{ ergs} = 10^7 \text{ dyne-centimeters}$$
$$1 \text{ British thermal unit (B.t.u.)} = 777.52 \text{ foot-pounds}$$
$$= 252 \text{ calories}$$
$$1 \text{ calorie} = 4.183 \text{ joules}$$
$$= 0.04129 \text{ liter-atmospheres}$$
$$1 \text{ kilowatt-hour} = 3{,}415 \text{ B.t.u.}$$
$$1 \text{ gram molecular weight (mole)} = 22.4 \text{ liters (standard conditions)}$$
$$1 \text{ pound molecular weight} = 359 \text{ cubic feet (standard conditions)}$$

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PROJECTILES

Patents

127. U.S. 1,742,836. Jan. 7, 1930. Trench mortar projectile. Pieter D. Van Essen, The Hague, Netherlands.
Projectile with short ogival head blending rearward with a portion adapted to fit the muzzle of the mortar; conical tail portion having wind vanes extending to fit muzzle of mortar.

128. U.S. 1,817,377. Aug. 4, 1931. Projectile. Roy Walter James, Covina, Calif.
Projectile with axial bore opening through respective ends and a telescopic rear end. Rear end adapted for rearward axial expansion responsive to air pressure through the bore while the projectile is in flight.

129. U.S. 1,861,522. June 7, 1932. Projectile with automatic driving band. E. W. Brandt, Paris.
Projectile intended to be fired from smooth-bore gun; body portion of lesser diameter than the bore, adapted to slide freely through bore. Body has ring on which powder gases act to expand it outward into engagement between projectile and gun walls to form driving band.

130. U.S. 1,890,175. Dec. 6, 1932. Projectile (with guide tails). William Brandt, Paris, France.

131. U.S. 1,941,590. Jan. 2, 1934. Projectile. Samuel Wiley, Metuchen, N. J.
Projectile comprising body and base plug and including cup-shaped propellent-charge container having an expansible side wall to serve as a gas check and a central fuze container and a cover for the propellent-charge container.

132. U.S. 1,944,885. Jan. 30, 1934. Projectile. Hermann Gerlich, Bexley, England.
Projectile adapted to be fired from a barrel increasing in cross-sectional area from the muzzle toward the breech chamber. Cylindrical body with pointed nose and boat tail.

133. U.S. 2,014,367. Sept. 17, 1935. Projectile. Daniel A. Breegle, Hunkers, Pa.
Elongated projectile with external air-pressure-receiving vanes.

134. U.S. 2,021,685. Nov. 19, 1935. Armor-piercing projectile. Curio Fornaci, Terni, Italy.
Projectile including a body and driving band, with means to fit jacket tightly on body against passage of gases of service charge and to permit jacket to be detached from projectile body only during piercing of armor plate.

135. U.S. 2,062,495. Dec. 1, 1936. Projectile. H. M. Brayton, Teaneck, N.J.

Projectile with radial fins and capsules of impelling powder extending longitudinally between these.

136. U.S. 2,113,313.   Apr. 5, 1938.   Projectile for smooth-bore weapons. Edgar William Brandt, Paris, France.

Includes full-caliber cylindrical guiding part engaging the bore of the weapon; fuze at front end of body adapted to cause bursting of projectile.

137. U.S. 2,115,028.   Projectile and gun.   Orwell Logan, Berkeley, Calif. Apr. 26, 1938.

Subcaliber projectile, with flat rings on body.   Rings fitted so that neither will be driven forward by gas pressure produced in normal operation of gun.

138. U.S. 2,288,604.   July 7, 1942.   Projectile.   Waldemar Born, Stuttgart, Germany.

Projectile suitable for a barrel having a tapered bore portion.

Propellent Powders

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Patents

193. Brit. 494,277. Oct. 24, 1938. Propellent explosives. Western Cartridge Company, East Alton, Ill.

194. Brit. 520,577. Apr. 29, 1940. Double-base propellent powders. Edward Whitworth, Thomas Thomson, and Imperial Chemical Industries Ltd.

195. Brit. 536,096. May 2, 1941. Progressive-burning smokeless powder. Hercules Powder Company, Wilmington, Del.

196. Brit. 537,408. June 20, 1941. Smokeless-powder grains. Bernhart Troxler, assignor to Hercules Powder Company, Wilmington, Del.

197. Can. 308,109. Jan. 27, 1931. Smokeless powder. E. H. Nollau and J. M. R. Linhart, assignors to Canadian Industries, Ltd.
    Nitrocellulose smokeless powder treated with liquid solution, rich in aliphatic nitrocellulose solvent as a softening agent.

198. Can. 314,731. Sept. 1, 1931. Smokeless powder. Arthur Hough.
    Powder composed of diethylene glycol dinitrate, nitrocellulose, and nitroglycerin.

199. Fr. 716,429. May 1, 1931. Ballistic powders. E. I. duPont de Nemours & Company, Inc.
    Contains 0.3 to 2.5, preferably 0.5 to 2 per cent of K_2SO_4 as anti-flash agent. An example contains nitrocellulose (13.15 per cent N) 85, dinitrotoluene 10, dibutyl phthalate 5, diphenylamine 1 and K_2SO_4 1 parts.

200. Ger. 548,427. Jan. 10, 1931. Smokeless powders. Westfälisch-Anhaltische Sprengstoff-Abt.-Ges. Chemische. Fabriken.
    Smokeless powders comprising nitrocellulose and nitrates of glycol condensation products, *e.g.*, of $(OHC_2H_4)_2O$.

201. Ger. 567,878.   June 26, 1930.   Smokeless powder.   E. I. duPont de Nemours & Company, Inc., Wilmington, Del.

> Smokeless powder that causes no flash from the barrel and that contains nitrocellulose, polynitrotoluene, and an ester of an organic acid insoluble in water.

202. Ger. 640,312.   Jan. 5, 1937.   See U.S. 1,838,347.

203. Ger. 691,679.   May 9, 1940.   Smokeless powder.   Wilhelm Rösler, to Westfälisch-Anhaltische Sprengstoff-Akt.-Ges. Chemische Fabriken.

> Smokeless powder sprayed with an aqueous solution of Turkey-red oil with or without the addition of alkali salts.

204. Swed. 69,120.   Mar. 26, 1930.   Progressive smokeless powder.   Antiebolaget Bofors' Nobelkrut (R. Sohlman, inventor).

> Powder composed of several layers of explosives of different compositions and combustion velocity.

205. U.S. 1,752,881.   Apr. 1, 1930.   Smokeless powder, manufacture. C. R. Borland, Concord, Mass.; assignor to American Powder Co.

> Method of treating grains of nitrated cotton to produce smokeless powder.

206. U.S. 1,780,911.   Nov. 11, 1930.   Smokeless powder.   E. I. duPont, Wilmington, Del., assignor to U.S.F. Powder Co., Wilmington, Del.

> Propellent powder containing colloidal nitrocellulose in dominating proportion and a substance substantially non-volatile at normal temperature for the drying of powder.

207. U.S. 1,788,438.   Jan. 13, 1930.   Smokeless powder.   S. G. Norton, assignor to Hercules Powder Company, Wilmington, Del.

> Abietates uch as ethyl, phenyl, or benzyl abietate is used with nitrocellulose and nitroglycerin for improving safety of manufacture and lessening burning temperature and muzzle flash.

208. U.S. 1,808,513.   June 2, 1931.   Propellent powder.   T. F. Werme, assignor to Remington Arms Co.

> Pb dust intermixed in sufficient quantity to form corrosion-preventing coating in bore of gun in which cartridge is fired.

209. U.S. 1,808,613.   June 2, 1931.   Propellent explosive.   W. O. Snelling, Allentown, Pa., assignor to Trojan Powder Company, New York, N.Y.

> Desensitized nitrostarch and a temperature-reducing agent that is an addition product of an amine and a nitric acid.

210. U.S. 1,809,695.   June 9, 1931.   Smokeless powder.   A. S. Hawkesworth.

> $O_2NC_6H_4Me$ used as solvent and stabilizer.

211. U.S. 1,819,458.   Aug. 18, 1931.   Propellent explosive.   W. M. Dehn, Seattle, Wash.

> Comprising a preponderant proportion of ammonium nitrate in an intimate state and molded form with starch and colloided nitrocellulose, the quantity of the starch exceeding that of the nitrocellulose.

212. U.S. 1,838,345. Dec. 29, 1931. Propellent powder. R. G. Woodbridge, assignor to E. I. duPont de Nemours & Company, Inc., Wilmington, Del.

Powder containing a muzzle-flash preventative comprising potassium sulphate.

213. U.S. 1,838,346. Dec. 29, 1931. Propellent powder. R. G. Woodbridge, assignor to E. I. duPont de Nemours & Company, Inc., Wilmington, Del.

Powder containing muzzle-flash preventative, comprising stannous phthalate.

214. U.S. 1,838,347. Dec. 29, 1931. Propellent powder. R. G. Woodbridge, assignor to E. I. duPont de Nemours & Company, Inc., Wilmington, Del.

Powder containing small quantity of a metal salt.

215. U.S. 1,854,776. Apr. 19, 1932. Nitrocellulose propellent powder. R. G. Woodbridge, Wilmington, Del., assignor to E. I. duPont de Nemours & Company, Inc.

Nitrocellulose so incorporated with a deterrent explosive and a flash-eliminating ingredient that each of these when in liquid form has a substantial solvent action on the nitrocellulose.

216. U.S. 1,862,914. June 14, 1932. Propellent powder. W. E. Wagner, assignor to Western Cartridge Company, East Alton, Ill.

Treatment of nitrocellulose grains with a solution of nitroglycerin in a non-solvent for nitrocellulose.

217. U.S. 1,862,915. June 14, 1932. Propellent powder. W. E. Wagner, assignor to Western Cartridge Company, East Alton, Ill.

Process of treating nitrocellulose grains with a solution containing nitrocellulose near its precipitating point.

218. U.S. 1,890,241. Dec. 6, 1932. Double-base powders. W. E. Wagner, assignor to Western Cartridge Company, East Alton, Ill.

Nitroglycerin mixed with the nitrated cellulose in the presence of the nitrating agent.

219. U.S. 1,890,960. Dec. 13, 1932. Smokeless powder. Richard Weingand and H. I. Schulz, Germany.

Submitting nitrocellulose containing at least 12.8 per cent nitrogen to more than 100 atm. pressure in presence of volatile organic liquids.

220. U.S. 1,899,147. Feb. 28, 1933. Propellent powder. G. C. Hale, Dover, N.J.

Powder consisting of nitrocellulose, trinitrotoluene 5 to 15 per cent, mononitrobenzene 2 to 10 per cent.

221. U.S. 1,906,675. May 2, 1933. Propellent powder, double base. W. E. Wagner, assignor to Western Cartridge Company, East Alton, Ill.

Process of treating by partly extracting the more active base from the gelatinized part of a double-base grain.

222. U.S. 1,916,763. July 4, 1933. Smokeless powder. Arthur Hough, Passaic, N.J., assignor to Degn Corp.

Smokeless-powder propellant containing about 85 to 90 per cent of nitrocellulose, together with a small percentage of diethylene glycol dinitrate.

223. U.S. 1,924,464.   Aug. 29, 1933.   Smokeless powder.   J. M. Skilling, Pennsgrove, N.J., and O. J. Teeple, Jr., Cragmere, Del., assignors to E. I. duPont de Nemours & Company, Inc., Wilmington, Del.

Process of preparing nitrocellulose-water mixture, partly colloiding the nitrocellulose with substantially water-insoluble volatile solvent.

224. U.S. 1,924,465.   Aug. 29, 1933.   Propellent powder.   O. J. Teeple, Jr., deceased, assignor to E. I. duPont de Nemours & Company, Inc.

Treating water suspension of nitrocellulose-base grain powder with liquid explosive material.

225. U.S. 1,943,421.   Jan. 16, 1934.   Propellent explosive.   Robert Burns and O. W. Strickland, Stevenson, Scotland, assignors to Imperial Chemical Industries, Ltd.

Containing stable non-volatile organometallic tin compound in which the metal is linked directly to carbon and which has no destabilizing action on constituents of the powder.

226. U.S. 1,955,927.   Apr. 24, 1934.   Propellent powders.   G. A. McBride, Alton, Ill., assignor to Western Cartridge Company, East Alton, Ill.

Suspending deterrent in treating bath and exposing powder grains to action of the suspension.

227. U.S. 1,963,116.   June 19, 1934.   Propellent powder.   Robert Burns, Saltcoats, Oliver Ward Strickland, West Kilbrede, and Edward Whitworth, Saltcoats, Scotland, assignors to Imperial Chemical Industries, Ltd.

Producing antifouling propellent explosive having low erosive power by applying to surface antifouling agent comprising one or more compounds consisting of tin.

228. U.S. 1,963,992.   June 26, 1934.   Propellent powder.   G. C. Hale, Dover, N.J., assignor to Hercules Powder Company, Wilmington, Del.

Colloiding nitrocellulose with liquid nitroderivatives of ethyl benzene.

229. U.S. 1,965,362.   July 3, 1934.   Smokeless powder.   D. R. Wiggam, Kenvil, N.J., assignor to Hercules Powder Company, Wilmington, Del.

Process of wetting nitrocellulose with water, partly dissolving wet nitrocellulose in solvent, and introducing solution into water containing an oxidizing salt in solution.

230. U.S. 1,966,806.   July 17, 1934.   Smokeless powder.   H. M. Spurlin, Kenvil, N.J., assignor to Hercules Powder Company, Wilmington, Del.

Process of dissolving nitrocellulose in solvent, adding nitroglycerin and effecting precipitation of dissolved nitrocellulose with water.

231. U.S. 1,967,913.   July 24, 1934.   Propellent powders.   G. C. Tibbetts and F. R. Seavey, assignors to Western Cartridge Company, East Alton, Ill.

Agitating powder grains in excess of non-solvent.

232. U.S. 2,003,914. June 4, 1935. Propellent explosive. Edward Whitworth, Saltcoats, Scotland, assignor to Imperial Chemical Industries, Ltd.

Process of manufacturing gelatinized propellent explosives containing nitrocellulose and a liquid nitric ester of a polyhydric aliphatic alcohol.

233. U.S. 2,008,889. July 23, 1935. Propellent powder. W. E. Wagner, assignor to Western Cartridge Company, East Alton, Ill.

Nitrocellulose with gelatinizer and sufficient of dialkyl phthalate concentrated near its surface to retard initial combustion rate and render grain progressive burning.

234. U.S. 2,008,888. July 23, 1935. Propellent powder. W. E. Wagner, assignor to Western Cartridge Company, East Alton, Ill.

Ungelatinized nitrocellulose surface treated with diamylphthalate to an extent sufficient to retard initial combustion rate and render grain progressive burning.

235. U.S. 2,024,128. Dec. 10, 1935. Smokeless powder. W. de C. Crater, assignor to Hercules Powder Company, Wilmington, Del.

Double-base smokeless powder containing nitrated flake starch retaining substantially its original flaked form.

236. U.S. 2,026,531. Jan. 7, 1936. Propellent powder. G. C. Hale and D. R. Cameron, Dover, N.J.

Propellent powder consisting of nitrocellulose, trinitrotoluene, and triacetin 2 to 10 per cent.

237. U.S. 2,027,114. Jan. 7, 1936. Smokeless powder. F. Olsen, G. C. Tibbetts, and E. B. W. Kerone, assignors to Western Cartridge Company, East Alton, Ill.

Process of agitating smokeless powder base in non-solvent vehicle with solvent immiscible with vehicle, sufficient to form globules of dissolved base.

238. U.S. 2,028,990. Jan. 28, 1936. Propellent powder. F. Olsen, assignor to Western Cartridge Company, East Alton, Ill.

Treating ungelatinized nitrocellulose powder grain with gelatinizer for nitrocellulose while the grain contains a solvent for the gelatinizer.

239. U.S. 2,031,659. Feb. 25, 1936. Smokeless powder. M. F. Lindsley, Jr., Kings Mill, Ohio, assignor by mesne assignments to E. I. duPont de Nemours & Company, Inc., Wilmington, Del.

Process of forming grains of nitrocellulose suitable for bulk powder from finely divided nitrocellulose.

240. U.S. 2,035,471. Mar. 31, 1936. Propellent powder. G. C. Hale and D. R. Cameron, Dover, N.J.

Powder consisting of nitrocellulose and triacetin 2 to 10 per cent.

241. U.S. 2,038,700. Apr. 28, 1936. Propellent powder. R. G. Woodbridge, Wilmington, Del., assignor to E. I. duPont de Nemours & Company, Inc., Wilmington, Del.

1. Process of suppressing muzzle flash in propellent powder and reducing smoke or fog by incorporating tin compound with inorganic muzzle flash eliminating salt.

2. Powder containing in finely divided condition 0.3 to 2.0 per cent tin oxide and 0.3 to 2.0 per cent potassium sulphate.

242. U.S. 2,050,871. Aug. 11, 1936. Flashless-powder charge. R. G. Woodbridge, assignor to E. I. duPont de Nemours & Company, Inc. Wilmington, Del.

Propellent-powder charge containing central core of cloth impregnated with a flash-suppressing alkali metal salt.

243. U.S. 2,072,671. Mar. 2, 1937. Ammunition and propellent charge. W. B. Foulke, Media, Pa., assignor to Hercules Powder Company, Wilmington, Del.

Propellent charge comprising mass of explosive forming portion of total charge and container formed from a combustible material embedded and freely movable within the mass of material.

244. U.S. 2,076,772. Aug. 13, 1937. Smokeless powder. E. S. Goodyear, assignor to Hercules Powder Company, Wilmington, Del.

Smokeless powder coated with an alkyl phthalyl glycolate.

245. U.S. 2,096,451. Oct. 19, 1937. Propellent powder. Paola Parodi-Delfino, Rome, Italy.

Nitrocellulose propellent powder, containing triacetate of alkyl-trimethylolmethane.

246. U.S. 2,111,075. Mar. 15, 1938. Propellent powder. F. Olsen and G. C. Tibbetts, assignors to Western Cartridge Company, East Alton, Ill.

Process of treating grains with plasticizer and flattening while still soft.

247. U.S. 2,112,256. Mar. 29, 1938. Smokeless powder. Bernhart Troxler, Kenvil, N.J., assignor to Hercules Powder Company, Wilmington, Del.

Method of removing solvent.

248. U.S. 2,112,257. Mar. 29, 1938. Smokeless powder. L. N. Bent, Holly Oak, Del.

Method of removing solvent.

249. U.S. 2,113,418. Apr. 5, 1938. Propellent explosive powder. R. G. Woodbridge, assignor to E. I. duPont de Nemours & Company, Inc.

Double-base powder grain with surface impregnated with diethyl diphenyl urea and capable of maintaining ballistic stability when stored at 55° for about a month.

250. U.S. 2,120,324. June 14, 1938. Smokeless powder. L. D. Dickerman, Hackettstown, N.J., assignor to Hercules Powder Company, Wilmington, Del.

Smokeless double-base powder grain including colloided nitro-cellulose fines agglomerated through the medium of a non-explosive binder.

251. U.S. 2,121,138. June 21, 1938. Smokeless powder. D. R. Wiggam, West Chester, Pa., assignor to Hercules Powder Company, Wilmington, Del.

Method of manufacture that includes admixing nitrocellulose wet with water with nitroglycerin emulsified in water containing a water-soluble hydrophile colloid in solution.

252. U.S. 2,123,517. July 12, 1938. Smokeless powder. R. G. Woodbridge, assignor to E. I. duPont de Nemours & Company, Inc., Wilmington, Del.

Process of restoring chemical stability of diphenylamine stabilized nitrocellulose powder grains while retaining grains in substantially original form.

253. U.S. 2,131,383. Sept. 28, 1938. Propellent explosive. H. N. Marsh, assignor to Hercules Powder Company, Wilmington, Del.

Substance containing 0.25 to 2 per cent of inorganic silicon.

254. U.S. 2,160,626. May 30, 1938. Propellent explosives. H. F. Schaefer, assignor to Western Cartridge Company, East Alton, Ill.

255. U.S. 2,179,330. Nov. 7, 1939. Smokeless powder. E. S. Goodyear, assignor to Hercules Powder Company, Wilmington, Del.

Coating smokeless-powder grains with admixture of non-volatile non-explosive organic material. Breech pressures of this powder at subzero temperatures not much greater than those at ordinary temperatures.

256. U.S. 2,187,866. Jan. 23, 1940. Smokeless powder, manufacture. H. M. Spurlin and G. H. Pfeiffer, assignors to Hercules Powder Company, Wilmington, Del.

Surface coating smokeless-powder grains with non-volatile non-explosive organic deterrent, which is non-solvent for nitrocellulose but compatible with it.

257. U.S. 2,201,640. May 21, 1940. Smokeless powder, progressive burning. L. C. Weldin, assignor to Hercules Powder Company, Wilmington, Del.

Comprises preformed smokeless-powder grains mechanically and loosely admixed with particles, separate from those of the powder grains, of a deterrent selected from the group of carbonaceous materials, consisting of starch, organic esters and ethers thereof, cellulose, organic esters and ethers thereof, gelatin, and coal dust.

258. U.S. 2,206,048. July 2, 1940. Propellent charge. E. R. Rechel and T. Stevenson.

Double-base powder with nitroglycerin as base constituent, with non-corrosive and non-explosive primer including red phosphorus.

259. U.S. 2,206,916. July 9, 1940. Smokeless powder, manufacture. F. Olsen, G. C. Tibbetts, and E. B. W. Kerone, assignors to Western Cartridge Company, East Alton, Ill.

Process of comminuting gelatinized nitrocellulose containing unstable regions so as to form fine particles and treating nitrocellulose with a solvent in presence of protective colloid.

260. U.S. 2,210,871. Aug. 6, 1940. Smokeless powder. F. L. Boddicker, assignor to Hercules Powder Company, Wilmington, Del.

Process of making smokeless powder containing more than 35 per cent by weight of a non-volatile solvent plasticizer.

261. U.S. 2,221,391. Nov. 12, 1940. Propellent powders. E. Whitworth and T. Thomson, Scotland, assignors to Imperial Chemical Industries, Ltd.

Process for manufacture of double-base propellent powder. Agitating sheet material with nitroglycerin in presence of volatile liquid.

Powder comprises rounded masses including nitroglycerin and aggregations of lamellar fragments.

262. U.S. 2,228,309. Jan. 14, 1941. Propellent powder. E. S. Goodyear, assignor to Hercules Powder Company, Wilmington, Del.

Smokeless flashless non-hygroscopic powder consisting essentially of nitrocellulose. Nitrocellulose, 76 to 79 per cent. Dinitrotoluene, 21 to 24 per cent. Diphenylamine, 0.8 to 1.2 per cent.

263. U.S. 2,230,100. Jan. 28, 1941. Smokeless powder. J. H. Aaron and J. J. McIntyre, assignors to E. I. duPont de Nemours & Company, Inc., Wilmington, Del.

Method for producing cellular smokeless powder that involves colloiding nitrocellulose by means of solvent having boiling point of at least 100°C.

264. U.S. 2,230,848. Feb. 4, 1941. Smokeless powder, progressive burning. W. P. Regestein, assignor to E. I. duPont de Nemours & Company, Inc., Wilmington, Del.

Nitrocellulose-base grain, coating with moderant, adding explosive liquid nitric ester.

265. U.S. 2,231,946. Feb. 18, 1941. Propellent powder. E. R. Rechel and T. Stevenson.

Propellant containing 2 to 10 per cent of an agent selected from class consisting of phosphorus and its compounds and yielding phosphoric acid on combustion.

266. U.S. 2,235,298. Mar. 18, 1941. Smokeless powder, manufacture. Frederich Olsen, assignor to Western Cartridge Company, East Alton, Ill.

Process of making grains of powder suitable for use as propellent powder.

267. U.S. 2,131,061. Sept. 27, 1938. Propellent explosive. H. N. Marsh, Wilmington, Del., assignor to Hercules Powder Company, Wilmington, Del.

Smokeless powder composed of about 0.25 to 2 per cent of an inorganic substance selected from group consisting of antimony sulphide, metallic antimony, and antimony oxide.

268. U.S. 2,131,352. Sept. 27, 1938. Propellent explosive. H. N. Marsh, Wilmington, Del., assignor to Hercules Powder Company, Wilmington, Del.

Smokeless powder containing 0.25 to 2 per cent of inorganic cadmium-containing substance.

269. U.S. 2,131,353. Sept. 27, 1938. Propellent explosive. H. N. Marsh, Wilmington, Del., assignor to Hercules Powder Company, Wilmington, Del.

Smokeless powder containing 0.25 to about 2 per cent metallic cobalt.

270. U.S. 2,131,354. Sept. 27, 1938. Propellent explosive. H. N. Marsh, Wilmington, Del., assignor to Hercules Powder Company, Wilmington, Del.

Smokeless powder containing 0.25 to 2 per cent manganese dioxide.

271. U.S. 2,292,469. Aug. 11, 1942. Smokeless powder. F. Olsen, assignor to Western Cartridge Company, East Alton, Ill.

Process of making smokeless powder by dissolving wet nitrocellulose containing some residual spent acid in a solvent to form a lacquer.

272. U.S. 2,302,558. Nov. 17, 1942. Smokeless powder. W. W. Lewers, Drexel Hill, Pa., W. A. Menges, Metuchen, N.J., and E. C. Pitman, Red Bank, N.J., assignors to E. I. duPont de Nemours & Company, Inc., Wilmington, Del.

Process of treating smokeless powder to reduce its viscosity characteristic to a value below 3,300 centipoises and to remove color.

273. U.S. 2,304,037. Dec. 1, 1942. Propellent explosive charge. Thomas Thomson, Kilmarnock, Scotland, and Edward Whitworth, New York, N.Y., assignors to Imperial Chemical Industries, Ltd.

Colloided nitrocellulose propellent-powder gun charge comprising an antimonyl compound free from halogens and containing a combined alkali metal.

ROCKET PROPULSION AND ROCKETS

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