Chapter 3

The Thermodynamics of guns

§ 3.0 *Introduction*

There are five thermodynamic equations used in classical internal ballistics. The first is the ideal gas equation, which itself is based on a number of basic laws which are assumed here to be self-evident. The second is the Nobel-Abel equation for non-ideal gasses, which accounts for the space taken up by the gas molecules themselves. The third equation is the relationship between the specific heats of gasses at constant pressure and at constant volume. The forth is the equation for adiabatic expansion of gasses and the fifth equation is Rèsal's energy balance equation. These latter three equations can be derived from the ideal gas equation and that is realised here.

§ 3.1 *The Ideal Gas Equation*

The ideal gas equation is itself a combination of four basic laws for ideal gasses. The first is Boyle's law, which states that for a gas at a constant temperature, the pressure will be inversely proportional to the volume. The second is Charles' law which states that for a gas at constant pressure, the volume will be proportional to the temperature. The third law is Gay-Lussac's law, which states that for a constant volume of gas, the pressure will be proportional to the temperature. And the forth law is that of Avogadro, which states that equal volumes of any gas at the same temperature and pressure will have the same number of molecules. These laws are combined in the ideal gas equation,

$$PV \ = \ m \Re \, T \tag{3.1}$$

Where P is the gas pressure, V is the volume, m is the mass of the gas in the given volume, T is the absolute temperature, and $\Re$ is a constant of proportionality called the gas constant, or more particularly the specific gas constant for the specific gas of interest. Pressure has dimensions of force per unit area, so Eqn. 3.1 could be written as,

$$Force \times Distance \ = \ m \Re \, T$$

Since force times distance is work done, this is an energy equation whose physical meaning can be thought of as the work done to create the space which the gas occupies. If the force (pressure) is constant and the temperature is zero, the (virtual) distance

associated with the force is zero, so that the volume occupied by the gas is zero. This is perfectly acceptable for an ideal gas, where the gas molecules themselves have zero volume and do not occupy any space. An important fact to note is that this energy is a function of temperature alone.

Let v be the specific volume of the gas, the volume occupied by a unit mass of gas at the given pressure P and temperature T then,

$$Pv = \Re T \qquad\qquad 3.2$$

Let the molecular weight M for a gas be the ratio of the mass of a molecule of the given gas to the mass of one atom of hydrogen*. For example, one atom of oxygen is 16 times heavier than a hydrogen atom, so its atomic weight is 16**. A gas molecule of oxygen consists of two atoms of oxygen, so the molecular weight of oxygen in a gas is 32. Hydrogen gas molecules consist of pairs of hydrogen atoms at temperatures below about 3500˚K, so the molecular weight of a hydrogen gas molecule is actually 2. A carbon dioxide gas molecule consists of one atom of carbon (atomic weight 12) and two atoms of oxygen. The molecular weight of carbon dioxide is therefore 44.

From Avogadro's law, the number of molecules in a given volume, at the given pressure P and temperature T will be the same regardless of the type of gas. For oxygen then, the mass of a given volume of gas would be 16 times greater than that for the same volume of an atomic hydrogen gas. The specific volume for a unit mass of oxygen gas will then be 16 times smaller than that for a unit mass of atomic hydrogen gas.

Generally then, the specific volume v for a unit mass of any gas will then be inversely proportional to the molecular weight, M, for that gas. The specific volume v for a given gas can then be related to v_h, the specific volume for an atomic hydrogen gas where, $v = v_h/M$ and Eqn. 3.2 can be written as,

$$Pv_h = M\Re T \qquad\qquad 3.3$$

Let,

$$Pv_h = R T \qquad\qquad 3.4$$

*For historic reasons, atomic weights are actually defined as the ratio of the weight of the atom to one twelfth of that of a carbon 12 atom, which is (very nearly) equivalent to the weight of a hydrogen atom.

**The atomic weights given here are rounded off and the actual values are a fraction of 1% more or less, depending on the number of protons, electrons and neutrons in the atom.

where R is the specific gas constant for an atomic hydrogen gas, then R is defined as a *universal gas constant*, where for any given gas,

$$R = M\Re$$

3.5

and so,

$$Pv = \frac{RT}{M}$$

3.6

Finally, the ideal gas equation for a given volume of gas V can be written as,

$$PV = \frac{mRT}{M}$$

3.7

For the gas products of nitrocellulose powders, the average molecular weight M is about 23.

§ 3.1.1 *The Universal Gas Constant*

By rewriting Eqn. 3.7 as,

$$P = \rho\frac{RT}{M}$$

3.8

where ρ is the density of the gas, then rearranging,

$$R = \frac{PM}{\rho T}$$

3.9

A value of the universal gas constant can be derived using, for example, air at standard temperature and pressure (STP), where the units in Eqn. 3.9 are well defined.

Standard pressure P	14.5038 psi
Standard density ρ	0.0000461 lb in^{-3}
Standard temperature T	273 ˚K
Molecular weight of air M	28.97

Plugging these values into Eqn. 3.9, $R = 33386.18$ psi in^3 lb^{-1} ˚K^{-1}

Of course, the numerical value of the universal gas constant depends upon the units used for weight, for volume and for temperature. But this is the constant for the units used within this book.

The units of $\mathfrak{R}$ can be restated as energy (pressure times volume), per pound of a gas, per degree Kelvin. $\mathfrak{R}$ then is the work done by one pound of gas when it expands at constant pressure, as the temperature is raised in the gas by one degree.

§ 3.2 *The Specific Heats of Ideal Gasses*

Consider a drum with a light, gas tight lid that is able to move within the drum. The lid is at rest on a ledge within the drum and there is a weight of W pounds sitting on the lid. The drum is insulated so that no heat escapes. The initial pressure inside the drum is P_0 and the initial temperature of the gas is T_0. A fire is lit beneath the drum so that the air inside the drum heats up. There is a thermometer to note the temperature. See Fig. 3.1.
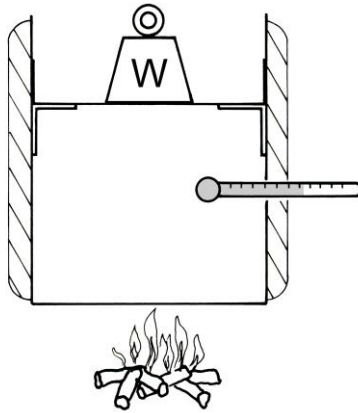

Fig. 3.1 *Airtight drum being heated by a fire beneath it. The gas increases in pressure, but the volume remains constant until the pressure is high enough to lift the lid with the weight on it.*

With the fire heating the bottom of the drum, the thermometer shows the temperature increasing inside the drum, and the pressure inside the drum also increases due to Gay-Lussac's law. Until the pressure is high enough to overcome the weight sitting on the lid, the volume remains constant.

Let C_v be the specific heat of the gas at constant volume, that is the amount of energy that has to be put into the gas to increase the temperature of one pound of gas by one degree Kelvin. While the volume remains constant, the energy put into the gas which is heated up to temperature T can be written as,

$$m\int_{T_0}^{T} C_V\, dT \qquad\qquad 3.10$$

where m is the mass of gas inside the drum and T_0 is the starting temperature of the gas.

Let the pressure P' be the pressure inside the drum where the lid starts to lift, then $P'A = W$ where A is the area of the lid. Let the temperature at which the lid starts to lift be T'
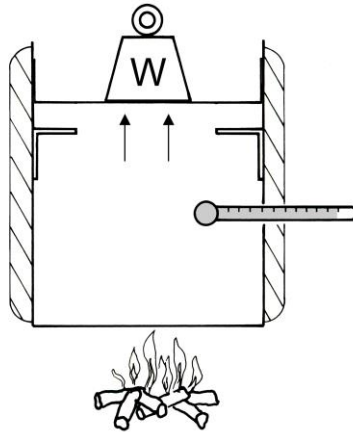

Fig. 3.2 *Airtight drum being heated by a fire beneath it. The gas now increases in volume and the pressure remains constant as the lid lifts.*

Now, the fire continues putting energy into the gas, but also work is also being done in lifting the lid with the weight on top. As a result, it is observed that the rate at which the gas temperature increases (as shown by the thermometer) is slower. Also, it is the volume that now increases according to Charles' law and the pressure remains constant. A specific heat of constant pressure C_P for the gas can now be defined where,

$$m\int_{T'}^{T} C_P\, dT = m\int_{T'}^{T} C_V\, dT + P'\int_{V'}^{V} dV \qquad\qquad 3.11$$

V' is the initial volume of the drum and V is the volume once the temperature has reached a temperature T. This is just an energy balance equation, showing that the energy put into the system equals the energy required to heat the gas, plus the work done (pressure times change in volume) in lifting the weight.

Using Eqn. 3.7, the ideal gas equation, the 'work done' term in Eqn. 3.11 can be written as,

$$P'\int_{V'}^{V} dV = \frac{mR}{M}\int_{T'}^{T} dT \qquad 3.12$$

Substituting into Eqn. 3.11, and assuming the specific heats of the gas are not a function of temperature,

$$mC_P\int_{T'}^{T} dT = mC_V\int_{T'}^{T} dT + \frac{mR}{M}\int_{T'}^{T} dT \qquad 3.13$$

Eqn. 3.13 can now be simplified so that,

$$C_P - C_V = \frac{R}{M} = \Re \qquad 3.14$$

Note that since $C_P - C_V$ is equivalent to the work done (per unit mass, per unit of temperature) while the gas is expanding under constant pressure.

The ratio of the specific heats, C_P/C_V is a very important quantity in thermodynamics and is usually referred to by the gamma symbol.

$$\frac{C_P}{C_V} = \gamma \qquad 3.15$$

Substituting into Eqn. 3.14,

$$C_V(\gamma - 1) = \frac{R}{M} = \Re \qquad 3.16$$

The internal energy of a gas is $mC_V T$ as this is the energy required to heat a gas of mass m of gas to temperature T. However, this is greater than the amount of energy the gas required to establish the space it occupies, which is the fraction $mC_V T(\gamma - 1)$. Also, this fraction of energy is inversely proportional to M the molecular weight of the gas.

§ 3.3 *The Adiabatic Expansion of Gasses*

The word 'adiabatic' means that the thermodynamic system is isolated so that no heat can escape into, or come in from the outside world. The consequence of this is that changes in the energy balance within the system are reversible. Such processes are said to be *isentropic*. That is, that there is no change in the entropy of the system.

Suppose now that the fire beneath the drum in Fig. 3.2 is removed and a layer of insulation is quickly put on the bottom of the drum. (See Fig. 3.3). There will be no more heat being put into the system by the fire, and no heat can escape which would allow the drum to cool down.

In consequence, Eqn. 3.11 can be written as,

$$0 = m\int_{T'}^{T} C_V \, dT + P'\int_{V'}^{V} dV$$

For closed systems, none of the gas laws cited above are valid as for each of them, one variable is held constant which required energy entering or leaving the system. For closed systems then, all three variables in the ideal gas equation have to change at the same time. For a closed system, pressure cannot remain constant if there is a change in temperature in the gas. Pressure must be a function of the volume and is brought inside the integral.

$$m\int_{T''}^{T} C_V \, dT = -\int_{V'}^{V} P \, dV \qquad\qquad 3.17$$

This effectively states that any increase in the internal energy of the gas - the left hand term; must be equivalent to, and balanced by, any work done to the system – the right hand term. So, for example, a bicycle pump gets warm while using it to pump up a tyre as work is being done to the gas to compress it which heats the gas.

The converse is also true. The temperature of the gas will decrease as the gas expands while doing work. In a perfectly insulated system with no friction or other losses, these processes are reversible. That is, the energy expended while doing work to compress a gas can be completely recovered by allowing the gas to expand while doing work.

Suppose now that an additional small weight W' is put on the lid. The lid will sink, reducing the volume inside the drum and increasing the pressure. As work has been done compressing the gas, there will be a rise in temperature, as will be indicated on the thermometer. See Fig. 3.3.

Let V_1 be the volume and T_1 the temperature before the weight W' was added. Let V_2 be the new volume and T_2 be the new temperature after the weight is added. Let the new pressure be P_2 where $P_2 A = W + W'$. By how much will the volume decrease and by how much will the temperature rise?
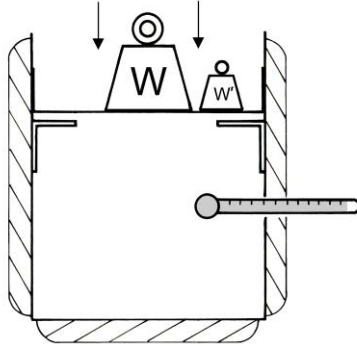

Fig. 3.3 *The fire is removed beneath the drum. The drum is quickly insulated so heat does not escape, and a small weight is put on the lid.*

Substituting for P from the ideal gas equation, Eqn. 3.17 can be restated as,

$$m \int_{T_1}^{T_2} C_V \frac{dT}{T} = -m \frac{R}{M} \int_{V_1}^{V_2} \frac{dV}{V} \qquad 3.18$$

Assume C_V is not a function of temperature, then rearranging and using Eqn. 3.16,

$$C_V \int_{T_1}^{T_2} \frac{dT}{T} = -\frac{R}{M} \int_{V_1}^{V_2} \frac{dV}{V} = -C_V(\gamma - 1) \int_{V_1}^{V_2} \frac{dV}{V} \qquad 3.19$$

Simplifying and integrating,

$$\ln\left(\frac{T_2}{T_1}\right) = (\gamma - 1) \ln\left(\frac{V_1}{V_2}\right) \qquad 3.20$$

Taking antilogs,

$$\left(\frac{T_2}{T_1}\right) = \left(\frac{V_1}{V_2}\right)^{(\gamma - 1)} \qquad 3.21$$

then rearranging,

$$T_1 V_1{}^{(\gamma \text{-}1)} = T_2 V_2{}^{(\gamma \text{-}1)} \hspace{4cm} 3.22$$

Now, it is evident that, $\quad P_1 V_1 = m\dfrac{R}{M}T_1 \;$ and $\; P_2 V_2 = m\dfrac{R}{M}T_2 \;$ so Eqn. 3.22 can be restated in terms of pressure and volume, so that,

$$P_1 V_1{}^{\gamma} = P_2 V_2{}^{\gamma} \hspace{4cm} 3.23$$

This important equation is known as the *adiabatic expansion equation* and is used in almost all analytic systems to describe the trajectory of the projectile down the barrel after the powder has reached 'all-burnt'.

To answer the questions above, the volume change can be related to a known pressure change using Eqn. 3.23, and the temperature change can be determined from the volume change using Eqn. 3.22.

§ 3.4 *Nobel-Abel Equation for Non-Ideal Gasses*

In ideal gasses, the volume taken up by the gas molecules themselves is not considered significant. Also, the gas density is considered low enough that the short range forces between the molecules themselves, called the *Van der Waals forces*, are not significant.

Van der Waals proposed a form of the ideal gas equation which corrected for these factors which can be written as,

$$\left(P + \frac{am^2}{V^2}\right)(V - m\eta) = \frac{mRT}{M} \hspace{3cm} 3.24$$

The term with *a* corrects for the Van der Waals forces between the molecules, and the term with η, called the *covolume*, corrects for the finite volume of the molecules themselves. The covolume has dimension of volume divided by mass and so is an 'inverse density'.

For the propellant gas temperatures (2000˚K to 3000˚K) in a gun, the thermal energy of the molecules is such that the Van der Waals forces are not significant and so the term in *a* is usually dropped. However, the gas densities are such that covolume of the gas molecules is significant. Eqn. 3.24 then reduces to the Nobel-Abel equation [3], sometimes called the Abel equation,

$$P\left(V - m\eta\right) = \frac{mRT}{M} \qquad\qquad 3.25$$

For nitrocellulose propellants, the covolume $\eta \approx 25.5 \text{ in}^3 \text{ lb}^{-1}$.

§ 3.5 *Résal's Equation*

Résal's energy balance equation was published in 1864 [4], a few years after Nobel and Abel published their equation including the covolume term to correct for the finite volume of the gas molecules. It remains to this day the starting point for all classical internal ballistics problems as it enables the description of *polytropic* processes; that is expansion and compression of gasses which includes losses due to heat transfer to (or from) the barrel and friction.

Eqn. 3.17 is restated here more generally to include the losses from the system, which will be the heat loss to the walls of the barrel, and frictional losses as the projectile travels up the barrel, as well as other losses due to gun recoil etc.

$$m\int_{T_0}^{T_1} C_V \, dT + \int_{V_0}^{V_1} P \, dV + \text{Losses} = 0 \qquad\qquad 3.26$$

Here, T_0 and V_0 are the initial temperature and volume, and T_1 and V_1 are the final temperature and volume.

Assuming that the specific heat is independent of temperature, Eqn. 3.26 can be rewritten as,

$$mC_V T_1 - mC_V T_0 + \int_{V_0}^{V_1} P \, dV + \text{Losses} = 0 \qquad\qquad 3.27$$

It is convenient to re-phrase Eqn. 3.27 in terms of quantities that are more measurable than the specific heat and the temperature. A conversion is now made so that instead of Eqn. 3.27 being in terms of a change in the energy put into the system, it is in terms of a change in the energy associated with the pressure and volume of the gas. From the ideal gas equation, $T = PVM/mR$ and from Eqn. 3.16 $C_V = R/M(\gamma - 1)$

Substituting into Eqn. 3.27,

$$\frac{P_1 V_1}{(\gamma-1)} - \frac{P_0 V_0}{(\gamma-1)} + \int_{V_0}^{V_1} P\, dV + \text{Losses} = 0 \qquad\qquad 3.28$$

Rearranging,

$$P_1 V_1 = P_0 V_0 - (\gamma-1)\left(\int_{V_0}^{V_1} P\, dV + \text{Losses}\right) \qquad\qquad 3.29$$

This then is Résal's equation in essence. The energy given up by the gas to change to a pressure and volume $P_1 V_1$ from a pressure and volume $P_0 V_0$ is $(\gamma-1)$ times the sum of the work done and the losses.

§ 3.5.1 *Equivalence of Résal's Equation to the Adiabatic Expansion of Gasses Equation.*

It should be noted that if there are no losses, then Résal's equation is equivalent to the equation for the adiabatic expansion of gasses, Eqn. 3.23. This should be evident since the starting point for the derivation of the equation for the adiabatic expansion of gasses, Eqn. 3.18, is the same as that used to derive Résal's equation if the losses are set to zero.

However, the equivalence can be shown explicitly by deriving the equation for the adiabatic expansion of gasses from Résal's equation.

Starting with Eqn. 3.29, $P_0 V_0$ can be considered as a constant as it is the initial condition. The losses are zero. Differentiating with respect to V, the term $P_0 V_0$ disappears and,

$$P\frac{d}{dV}V + V\frac{dP}{dV} = -(\gamma-1)P \qquad\qquad 3.30$$

Multiplying through by dV,

$$P\, dV + V\, dP = -(\gamma-1)P\, dV \;\rightarrow\; -\gamma P\, dV + P\, dV$$

then,

$$V\, dP = -\gamma P\, dV \quad \text{and so,} \quad \frac{dP}{P} = -\gamma\frac{dV}{V}$$

Integrating,

$$\int_{P_0}^{P_1}\frac{dP}{P} = -\gamma\int_{V_0}^{V_1}\frac{dV}{V} \;\rightarrow\; \ln\left(\frac{P_1}{P_0}\right) = \gamma\ln\left(\frac{V_0}{V_1}\right) \qquad\qquad 3.31$$

Taking antilogs then, Eqn. 3.23 is recovered $P_0 V_0^\gamma = P_1 V_1^\gamma$. Where the losses are zero, Résal's equation and the equation for adiabatic expansion will give the same results for pressure.

§ 3.5.2 *Air Gun Systems*

For an air gun system, energy is initially put into the system by compressing air into a reservoir. The energy is released by allowing the air to expand into the barrel, which accelerates the projectile up the barrel.

Of course, the work done accelerating the projectile up the barrel will just be equal to the kinetic energy of the projectile.

$$\int_{V_0}^{V_1} P \, dV = \frac{w u^2}{2g} \qquad\qquad 3.32$$

where w is the projectile weight and u is the projectile velocity. The term g, the acceleration due to gravity, is present here because in this book the pressure is defined as weight per unit area (pounds per square inch) rather than as force per unit area.

Substituting into Eqn. 3.29 then,

$$P_1 V_1 = P_0 V_0 - (\gamma - 1)\left(\frac{w u^2}{2g} + \text{Losses} \right) \qquad\qquad 3.33$$

If the initial pressure and volume of the gas reservoir P_0 and V_0 are known, then the final volume V_1 is just V_0 plus the volume of the barrel. If adiabatic expansion is assumed, the final pressure P_1 can be determined from Eqn. 3.23, $P_0 V_0^\gamma = P_1 V_1^\gamma$ where for air, $\gamma = 1.4$.

If the losses due to heat loss and friction are approximated to zero in Eqn. 3.33 (adiabatic expansion), the muzzle velocity u can then be determined as it is then the only unknown.

§ 3.5.3 *Propellant Gun Systems*

For most propellant based guns, the energy is stored chemically in the form of powder kernels, usually of nitrocellulose or some variant of it. This propellant burns to create gasses, whose pressure drives the projectile up the barrel.

The temperature T_0 is the flame temperature of the burning nitrocellulose powder kernels. It is assumed that this is also the temperature of the gasses generated by the burning of the powder, before any work is done pushing the projectile up the barrel, or heat is lost into the walls of the chamber and barrel. This is usually referred to as the *adiabatic flame temperature* of the gas - adiabatic because this would be the temperature of the gasses if no work was done and there were no losses. The value of T_0 varies depending on the type of propellant, but it is about 2700°K.

If Q is the chemical energy density of the powder, as determined by burning it in a calorimeter or calorimetric bomb, then it can be defined that,

$$mQ \;=\; mC_V\,T_0 \;=\; \frac{mRT_0}{M(\gamma-1)} \;=\; \frac{mF}{(\gamma-1)} \tag{3.34}$$

Where C_V is the specific heat of the propellant gasses which result from the burning of the propellant. The term F is called the *impetus*, or more commonly, the *Force* of the propellant, where $F = RT_0/M$. The chemical energy density Q is called the *potential* or energy content of the propellant. Note that $F = Q(\gamma-1)$ which is just a restatement of Eqn. 3.16 for the gas. Propellant manufacturers will state the energy of their powders either in terms of the potential Q or the Force F.

Substituting F and the Nobel-Abel equation into Eqn. 3.33,

$$P_1(V_1 - m\eta) \;=\; mF \;-\; (\gamma-1)\!\left(\frac{wv^2}{2g} \;+\; \text{Losses}\right) \tag{3.35}$$

This is recognisably the more usual form of the Résal equation that is used in internal ballistics. As the projectile is being pushed up the barrel, the pressure P_1 at any given moment is a function of the free volume behind the projectile V_1 and the velocity u of the projectile at that moment. All the other constants can be straightforwardly determined, except the losses, which are dealt with in later chapters.

§ 3.6 *The Specific Heats of Real Gasses*

A word should be said about the fact that the propellant gasses in a gun are not perfect gasses. This has consequences for the treatment above that should kept in mind.

It is assumed above that C_V does not change with temperature, whereas in real gasses C_V always increases with temperature. Too, as discussed in § 3.4 above, in real gasses there are attractive forces between the molecules themselves, which effectively increases the pressure, and the molecules themselves occupy a finite volume, which effectively decreases the available volume.

For real gasses then, C_V is not equal to $R/M(\gamma-1)$, with γ defined as C_P/C_V. While it is arguable that a temperature dependent C_V should be used in internal ballistics, in reality the term $R/M(\gamma-1)$ is almost always used instead. But since C_P is never used in internal ballistics and the temperature of the gasses is usually a little below T_0 the adiabatic flame temperature, it is convenient to define C_V in terms of γ, rather than γ in terms of C_V, with the 'gun gamma' for the powder being determined experimentally.

Nomenclature

a = Van der Waals constant

A = bore area: inch^2

C_P = specific heat at constant pressure: inch-pounds/pound/˚K

C_V = specific heat at constant volume: inch-pounds/pound/˚K

F = *Force* or *impetus* of the propellant: inch-pounds/inch^3

g = acceleration due to gravity, which is 386.4 inches/sec^2

m = mass of gas: pounds

M = molecular weight: ratio of gas molecule weight to one twelfth that of carbon atom

P = pressure: pounds/inch^2 or psi.

Q = energy density or *potential* of the propellant: inch-pounds/inch^3

R = ideal gas constant, which here is 33386.18 psi in^3 lb^{-1} ˚K^{-1}

$\mathfrak{R}$ = specific gas constant for any given gas

T = temperature in degrees Kelvin

u = velocity: inches/sec.

v = specific volume, volume occupied by one pound of gas: inch^3/pound

v_h = specific volume of atomic hydrogen gas: inch^3/pound

V = volume: inch^3

w = the weight of the projectile: pounds

γ = the ratio of specific heats for the propellant gasses:

ρ = the density of the gas: pounds/inch^3

η = the covolume of the propellant gasses: inch^3/pound