

CHAPTER 5

CHEMICAL ROCKET PROPELLANT PERFORMANCE ANALYSIS

In Chapter 3, simplified one-dimensional performance relations were developed. They require a knowledge of the composition of the hot rocket gas and the properties of the propellant reaction products, such as their combustion temperature T_1 , average molecular mass \mathfrak{M} , the specific heat ratio or the enthalpy change ($h_1 - h_2$). This chapter discusses several theoretical approaches to determine these thermochemical properties for a given composition of propellant, chamber pressure, nozzle shape, and nozzle exit pressure. This then allows the determination of performance parameters, such as theoretical specific impulse or exhaust velocity values for chemical rockets.

By knowing the calculated gas temperature, pressure, and gas composition (e.g., whether reducing or oxidizing species) it is possible to calculate other gas properties. This knowledge also allows a more intelligent analysis and selection of materials for chamber and nozzle structures. Heat transfer analyses require the determination of the specific heats, thermal conductivity, and specific heat ratio for the gas mixture. The calculated exhaust gas composition forms the basis for estimating environmental effects, such as the potential spreading of a toxic cloud near a launch site, as discussed in Chapter 20. The exhaust gas parameters also form the basis for the analysis of exhaust plumes (Chapter 18) or flames external to the nozzle.

With the advent of digital computers it has been possible to solve the set of equations involving mass balance, energy balance, or thermodynamic and chemical equilibria of complex systems with a variety of propellant ingredients. This chapter is intended to introduce the basic approach to this theoretical analysis, so the reader can understand the thermodynamic and chemical basis of the several computer programs that are in use today. This chapter does not

describe any specific computer analysis programs. However, it discusses which of the physical phenomena or chemical reactions can or cannot be adequately simulated by computer analysis.

The reader is referred to Refs. 5-1 to 5-5 for general chemical and thermodynamic background and principles. For a detailed description of the properties of each of the possible reactant and reaction products, see Refs. 5-6 to 5-12.

All of these theoretical analyses are only approximations of what really happens in rocket combustion and nozzle flow, and they all require some simplifying assumptions. As more of the different phenomena are understood and mathematically simulated, the analysis approach and the computer implementation become more sophisticated, but also more complex. The 11 assumptions made in Section 3.1 for an ideal rocket are valid here also, but only for a quasi-one-dimensional flow. However, some of the more sophisticated analyses can make one or more of these assumptions unnecessary. The analysis is usually divided into two somewhat separate sets of calculations:

1. The *combustion process* is the first part. It usually occurs in the combustion chamber at essentially constant chamber pressure (isobaric) and the resulting gases follow Dalton's law. The chemical reactions or the combustions occur very rapidly. The chamber volume is assumed to be large enough and the residence time in the chamber long enough for attaining chemical equilibrium in the chamber.
2. The *nozzle gas expansion process* constitutes the second set of calculations. The fully reacted, equilibrated gas combustion products enter the nozzle and undergo an adiabatic expansion in the nozzle. The entropy remains constant during a reversible (isentropic) nozzle expansion, but in real nozzle flows it increases slightly.

The principal chemical reactions occur inside the combustion chamber of a liquid propellant rocket engine or inside the grain cavity of a solid propellant rocket motor, usually within a short distance from the burning surface. These chamber combustion analyses are discussed further in Chapters 9 and 13. However, some chemical reactions also occur in the nozzle as the gases expand; the composition of the reaction products can therefore change in the nozzle, as described in this chapter. A further set of chemical reactions can occur in the exhaust plume outside the nozzle, as described in Chapter 18; many of the same basic thermochemical analysis approaches described in this chapter also apply to exhaust plumes.

5.1. BACKGROUND AND FUNDAMENTALS

The principle of chemical reaction or combustion of one or more fuels with one or more oxidizing reactants is the basis of chemical rocket propulsion. The heat

liberated in this reaction transforms the propellants (reactants) into hot gaseous reaction products, which in turn are thermodynamically expanded in a nozzle to produce thrust.

The chemical reactants or propellants can initially be either liquid or solid and occasionally also gaseous. The reaction products are usually gaseous, but with some propellants one or more reactant species remain in the solid or liquid phase. For example, with aluminized solid propellants, the chamber reaction gases contain liquid aluminum oxide and the colder gases in the nozzle exhaust contain solid, condensed aluminum oxide particles. For some of the chemical species, therefore, the analysis must consider as many as all three phases and the energy changes for the phase transitions must be included. If the amount of solid or liquid in the exhaust is small and the particles are small, then to assume a perfect gas introduces only small errors.

It is necessary to accurately know the chemical composition of the propellants and their relative proportion. In liquid propellant this means the mixture ratio and the major propellant impurities; in gelled or slurried liquid propellants it also includes suspended or dissolved solid materials; and in solid propellants it means all the ingredients, their proportions and impurities and phase (some ingredients, such as plasticizers, can be in a liquid state).

Dalton's law applies to the gas resulting from the combustion. It states that a mixture of gases at equilibrium exerts a pressure that is the sum of the partial pressures of the individual gases, all at the same temperature. The subscripts a , b , c , etc. refer to individual gas constituents.

$$p = p_a + p_b + p_c + \dots \quad (5-1)$$

$$T = T_a = T_b = T_c = \dots \quad (5-2)$$

The perfect gas equation $pV = RT$ applies very closely to high temperature gases. Here V is the specific volume or the volume per unit mass of gas mixture, and the gas constant R for the mixture is obtained by dividing the universal gas constant R' (8314.3 J/kg-mol-K) by the average molecular mass \mathfrak{M} (often erroneously called the molecular weight) of the gas mixture. Using Dalton's law, Eq. 5-1 can be rewritten

$$p = R_a T/V_a + R_b T/V_b + R_c T/V_c + \dots = R' T/(\mathfrak{M} V_{\text{mix}}) \quad (5-3)$$

The volumetric proportions of gas species in a gas mixture are determined from the *molar concentration* or *molar fractions*, n_j , expressed as kg-mol for a particular species j per kg of mixture. If n is the total number of kg-mol of species j per kilogram of uniform gas mixture, then

$$n = \sum_{j=1}^{j=m} n_j \quad (5-4)$$

where n_j is the kg-mol of species j per kilogram of mixture, m is the number of different gaseous species present in the equilibrium combustion gas products. The effective average molecular mass \mathfrak{M} of a gas mixture is then

$$\mathfrak{M} = \frac{\sum_{j=1}^m n_j \mathfrak{M}_j}{\sum_{j=1}^m n_j} \quad (5-5)$$

There are n possible species which enter into the relationship and of these only m are gases, so $n - m$ represents the number of condensed species. The *molar specific heat* for a gas mixture at constant pressure C_p can be determined from the individual gas molar fractions n_j and their molar specific heats as shown by Eq. 5-6. The specific heat ratio k of the mixture can be determined by a similar summation or from Eq. 5-7.

$$(C_p)_{\text{mix}} = \frac{\sum_{j=1}^m n_j (C_p)_j}{\sum_{j=1}^m n_j} \quad (5-6)$$

$$k_{\text{mix}} = \frac{(C_p)_{\text{mix}}}{(C_p)_{\text{mix}} - R'} \quad (5-7)$$

When a chemical reaction goes to completion, that is, all of the reactants are consumed and transformed into reaction products, the reactants are in *stoichiometric* proportions. For example, consider this reaction:



All the hydrogen and oxygen are fully consumed to form the single product—water vapor—without any reactant residue of either hydrogen or oxygen. In this case it requires 1 mol of the H_2 and $\frac{1}{2}$ mole of the O_2 to obtain 1 mol of H_2O . On a mass basis this *stoichiometric mixture* requires half of 32.0 kg of O_2 and 2 kg of H_2 , which are in the stoichiometric mixture mass ratio of 8:1. The release of energy per unit mass of propellant mixture and the combustion temperature are highest at or near the stoichiometric mixture.

Rocket propulsion systems usually do not operate with the proportion of their oxidizer and fuel in the stoichiometric mixture ratio. Instead, they usually operate fuel-rich because this allows lightweight molecules such as hydrogen to remain unreacted; this reduces the average molecular mass of the reaction products, which in turn increases the specific impulse (see Eq. 3-16). For rockets using H_2 and O_2 propellants the best operating mixture mass ratio for high-performance rocket engines is typically between 4.5 and 6.0, not at the stoichiometric value of 8.0.

Equation 5-8 is a reversible chemical reaction; by adding energy to the H_2O the reaction can be made to go backward to create H_2 and O_2 and the arrow in the equation would be reversed. The decompositions of solid propellants into reaction product gases are irreversible chemical reactions, as is the reaction of liquid propellants burning to create gases. However, reactions among combustion product gases are usually reversible.

Chemical equilibrium exists in reversible chemical reactions when the rate of forming products is exactly equal to the reverse reaction of forming reactants from the products. Once this equilibrium is reached, no further changes in concentration can take place. In Equation 5-8 all three gases would be present and their relative proportions would depend on the pressure, temperature, and initial mixture.

The *heat of formation* $\Delta_f H^0$ is the energy released (or absorbed), or the value of enthalpy change, when 1 mole of a chemical compound is formed from its constituent atoms or elements at 1 bar (100,000 Pa) and isothermally at 298.15 K or 25°C. The Δ implies that it is an energy change. The subscript f refers to formation and the superscript 0 means that each product or reactant substance is at its thermodynamic standard state and at the reference pressure and temperature. By convention, the heat of formation of the gaseous elements (e.g., H_2 , O_2 , Ar, Xe, etc.) is set to zero at these standard conditions of temperature and pressure. Typical values of $\Delta_f H^0$ and other properties are given in Table 5-1 for selected species. When heat is absorbed in the formation of a product, then $\Delta_f H^0$ has a negative value. Earlier analyses have been made with the standard temperature at other values, such as 273.15 K and a slightly higher standard reference pressure of 1 atm (101,325 Pa).

The *heat of reaction* $\Delta_r H^0$ is the energy released or absorbed when products are formed from its reactants at standard reference conditions, namely at 1 bar and 25°C. The heat of reaction can be negative or positive, depending on whether the reaction is *exothermic* or *endothermic*. The heat of reaction at other temperatures or pressures has to be corrected in accordance with the change in enthalpy. When a species changes from one state to another (e.g., liquid becomes gas or vice versa), it may lose or gain energy. In most rocket propulsion the heat of reaction is determined for a constant-pressure combustion process. In general the heat of reaction can be determined from sums of the heats of formation of the products and the reactants, namely

$$\Delta_r H^0 = \sum [n_j(\Delta_f H^0)_j]_{\text{products}} - \sum [n_j(\Delta_f H^0)_j]_{\text{reactants}} \quad (5-9)$$

Here n_j is the molar fraction of each particular species j . In a typical rocket propellant there are a number of different chemical reactions going on simultaneously; Equation 5-9 provides the heat of reaction for all of these simultaneous reactions. For data on heats of formation and heats of reaction, see Refs. 5-7 to 5-13.

TABLE 5-1. Chemical Thermodynamic Properties of Selected Substances at 298.15 K (25°C) and 0.1 MPa (1 bar)

| Substance | Phase* | Molar Mass (g/mol) | $\Delta_f H^0$ (kJ/mol) | $\Delta_f G^0$ (kJ/mol) | $\log K_f$ | S^0 (J/mol-K) | C_p (J/mol-K) |
|----------------------------------|--------|-----------------------|----------------------------|----------------------------|------------|--------------------|--------------------|
| Al (crystal) | s | 29.9815 | 0 | 0 | 0 | 28.275 | 24.204 |
| Al ₂ O ₃ | l | 101.9612 | -1620.567 | -1532.025 | 268.404 | 67.298 | 79.015 |
| C (graphite) | s | 12.011 | 0 | 0 | 0 | 5.740 | 8.517 |
| CH ₄ | g | 16.0476 | -74.873 | -50.768 | 8.894 | 186.251 | 35.639 |
| CO | g | 28.0106 | -110.527 | -137.163 | 24.030 | 197.653 | 29.142 |
| CO ₂ | g | 44.010 | -393.522 | -394.389 | 69.095 | 213.795 | 37.129 |
| H ₂ | g | 2.01583 | 0 | 0 | 0 | 130.680 | 28.836 |
| HCl | g | 36.4610 | -92.312 | -95.300 | 16.696 | 186.901 | 29.136 |
| HF | g | 20.0063 | -272.546 | -274.646 | 48.117 | 172.780 | 29.138 |
| H ₂ O | l | 18.01528 | -285.830 | -237.141 | 41.546 | 69.950 | 75.351 |
| H ₂ O | g | 18.01528 | -241.826 | -228.582 | 40.047 | 188.834 | 33.590 |
| N ₂ H ₄ | l | 32.0451 | +50.626 | 149.440 | -28.181 | 121.544 | 98.840 |
| N ₂ H ₄ | g | 32.0451 | +95.353 | +159.232 | -27.897 | 238.719 | 50.813 |
| NH ₄ ClO ₄ | s | 117.485 | -295.767 | -88.607 | 15.524 | 184.180 | 128.072 |
| ClF ₅ | g | 130.4450 | -238.488 | -146.725 | 25.706 | 310.739 | 97.165 |
| ClF ₃ | g | 92.442 | -158.866 | -118.877 | 20.827 | 281.600 | 63.845 |
| N ₂ O ₄ | l | 92.011 | -19.564 | +97.521 | -17.085 | 209.198 | 142.509 |
| N ₂ O ₄ | g | 92.011 | 9.079 | 97.787 | -17.132 | 304.376 | 77.256 |
| NO ₂ | g | 46.0055 | 33.095 | 51.258 | -8.980 | 240.034 | 36.974 |
| HNO ₃ | g | 63.0128 | -134.306 | -73.941 | 12.954 | 266.400 | 53.326 |
| N ₂ | g | 28.0134 | 0 | 0 | 0 | 191.609 | 29.125 |
| O ₂ | g | 31.9988 | 0 | 0 | 0 | 205.147 | 29.376 |
| NH ₃ | g | 17.0305 | -45.898 | -16.367 | 2.867 | 192.774 | 35.652 |

*s = solid, l = liquid, g = gas. Several species are listed twice, as a liquid and as a gas; the difference is due to evaporation or condensation.

The molar mass can be in g/g-mol or kg/kg-mol and C_p can be in J/g-mol-K or kJ/kg-mol-K.

Source: Refs. 5-8 and 5-9.

Various thermodynamic criteria that represent the necessary and sufficient conditions for an equilibrium to be stable were first advanced by J. W. Gibbs early in the 20th century; they are based on minimizing the free energy. The Gibbs *free energy* G (often called the *chemical potential*) is a convenient derived function or property of the state of a chemical material describing its thermodynamic potential and is directly related to the internal energy U , the pressure p , molar volume V , enthalpy h , temperature T , and entropy S . For a single species j the free energy is defined as G_j ; it can be determined for specific thermodynamic conditions, for mixtures of gas as well as an individual gas species.

$$G = U + pV - TS = h - TS \quad (5-10)$$

For most materials used as rocket propellant the free energy has been determined and tabulated as a function of temperature. It can be corrected for pressure. Its units are J/kg-mol. For a series of different species the mixture free energy G is

$$G = \sum_{j=1}^n G_j n_j \quad (5-11)$$

The *free energy* is a function of temperature and pressure. It is another property of a material, just like enthalpy or density; only two such independent parameters are required to characterize a gas condition. The free energy may be thought of as the tendency or driving force for a chemical material to enter into a chemical (or physical) change. Although it cannot be measured directly, differences in chemical potential can be measured. When the chemical potential of the reactants is higher than that of the likely products, a chemical reaction can occur and the chemical composition can change. The change in free energy ΔG for reactions at constant temperature and pressure is the chemical potential of the products less that of the reactants.

$$\Delta G = \sum_{j=1}^m [n_j(\Delta_f G^0)_j]_{\text{products}} - \sum_{j=1}^n [n_j(\Delta_f G^0)_j]_{\text{reactants}} \quad (5-12)$$

Here the superscript m gives the number of gas species in the combustion products, the superscript n gives the number of gas species in the reactants, and the ΔG represents the maximum energy that can be “freed” to do work on an “open” system where mass enters and leaves the system. At equilibrium the free energy is a minimum; at its minimum a small change in mixture fractions causes almost no change in ΔG and the free energies of the products and the reactants are essentially equal. Then

$$d \Delta G / dn = 0 \quad (5-13)$$

and a curve of molar concentration n versus ΔG would have a minimum.

If reacting propellants are liquid or solid materials, energy will be needed to change phase, vaporize them, or break them down into other gaseous species. This energy has to be subtracted from the heat or the energy available to heat the gases from the reference temperature to the combustion temperature. Therefore, the values of ΔH^0 and ΔG^0 for liquid and solid species are different from those of the same species in a gaseous state. The standard *free energy of formation* $\Delta_f G^0$ is the increment in free energy associated with the reaction of forming a given compound or species from its elements at their reference state. Table 5-2 gives values of $\Delta_f H^0$ and $\Delta_f G^0$ and other properties of carbon monoxide as a function of temperature. Similar data for other species can be obtained from Refs. 5-7 and 5-13. The *entropy* is another thermodynamic property of matter that is relative, which means that it is determined as a change in entropy. In the analysis of isentropic nozzle flow, it is assumed that the entropy remains constant. It is defined as

$$dS = \frac{dU}{T} + \frac{p dV}{T} = C_p \frac{dT}{T} - R \frac{dp}{p} \quad (5-14)$$

and the corresponding integral is

$$S - S_0 = C_p \ln \frac{T}{T_0} - R \ln \frac{p}{p_0} \quad (5-15)$$

where the zero applies to the reference state. In an isentropic process, entropy is constant. For a mixture the entropy is

TABLE 5-2. Variation of Thermochemical Data with Temperature for Carbon Monoxide (CO) as an Ideal Gas

| Temp. (K) | C_p^0 (J/mol-K) | S^0 | $H^0 - H^0(T)$ | $\Delta_f H^0$ (kJ/mol) | $\Delta_f G^0$ (kJ/mol) | log K_f |
|--------------|----------------------|---------|----------------|----------------------------|----------------------------|-----------|
| 0 | 0 | 0 | -8.671 | -113.805 | -113.805 | ∞ |
| 298.15 | 29.142 | 197.653 | 0 | -110.527 | -137.163 | 24.030 |
| 500 | 29.794 | 212.831 | 5.931 | -110.003 | -155.414 | 16.236 |
| 1000 | 33.183 | 234.538 | 21.690 | -111.983 | -200.275 | 10.461 |
| 1500 | 35.217 | 248.426 | 38.850 | -115.229 | -243.740 | 8.488 |
| 2000 | 36.250 | 258.714 | 56.744 | -118.896 | -286.034 | 7.470 |
| 2500 | 36.838 | 266.854 | 74.985 | -122.994 | -327.356 | 6.840 |
| 3000 | 37.217 | 273.605 | 93.504 | -127.457 | -367.816 | 6.404 |
| 3500 | 37.493 | 279.364 | 112.185 | -132.313 | -407.497 | 6.082 |
| 4000 | 37.715 | 284.386 | 130.989 | -137.537 | -446.457 | 5.830 |

Source: Refs. 5-8 and 5-9.

$$S = \sum_{j=1}^n S_j n_j \quad (5-16)$$

Here entropy is in J/kg-mol-K. The entropy for each gaseous species is

$$S_j = (S_T^0)_j - R \ln \frac{n_j}{n} - R \ln p \quad (5-17)$$

For solid and liquid species the last two terms are zero. Here (S_T^0) refers to the standard state entropy at temperature T . Typical values for entropy are listed in Tables 5-1 and 5-2.

When a chemical reaction is in equilibrium, an *equilibrium constant* has been devised which relates the partial pressures and the molar fractions of the species. For example, in the general reaction



a , b , c , and d are the stoichiometric molar concentration coefficients of the chemical molecules (or atoms) A, B, C, and D. The equilibrium constant K , when expressed as partial pressures, is a function of temperature.

$$K_p = \frac{p_C^c p_D^d}{p_A^a p_B^b} p_0^{-c-d+a+b} \quad (5-19)$$

Here p_0 is the reference pressure. All pressures are in bars or 10^5 Pa. When $a + b = c + d$, then K_p is independent of pressure. This condition is not valid for a reaction like Eq. 5-8. In this case the pressure increase will drive the equilibrium reaction into the direction of fewer moles and in the direction of absorbing heat if the temperature is increased. For Eq. 5-8 the hydrogen and oxygen equilibrium relation would be

$$K_p = \frac{p_{\text{H}_2\text{O}}}{p_{\text{H}_2} p_{\text{O}_2}^{0.5}} p_0^{-1+1+0.5} \quad (5-20)$$

The equilibrium constant can also be expressed as a function of the molar fractions n_j because each partial pressure p_{n_j} is equal to the actual pressure p at which the reaction occurs multiplied by its molar fraction ($p_j = p n_j$). From Equation 5-19 the equilibrium constant K can also be expressed as

$$K_n = \frac{n_C^c n_D^d}{n_A^a n_B^b} \left(\frac{p}{p_0} \right)^{c+d-a-b} \quad (5-21)$$

The equilibrium constant for the chemical formation of a given species from its elements is K_f . Typical values of K_f are shown in Tables 5-1 and 5-2. The free

energy and the equilibrium constant for the formation of a particular species at standard conditions from its atomic elements are related, namely

$$\Delta G^0 = -RT \ln K_f \quad (5-22)$$

Equations 5-19, 5-20, and 5-22 are often used together with mass balance and energy balance relations to solve the simultaneous equations; the equilibrium constant K is primarily used when chemical compounds are formed from their elements.

5.2. ANALYSIS OF CHAMBER OR MOTOR CASE CONDITIONS

The objectives here are to determine the theoretical combustion temperature and the theoretical composition of the resulting reaction products, which in turn will allow the determination of the physical properties of the combustion gases (C_p , k , or ρ). Before we can make this analysis, some basic data (e.g., propellants, their ingredients, desired chamber pressure, or all likely reaction products) have to be known or postulated. Although the combustion process really consists of a series of different chemical reactions that occur almost simultaneously and includes the breakdown of chemical compounds into intermediate and subsequently into final products, the analysis is only concerned with the initial and final conditions, before and after combustion. We will mention several approaches to the analysis of chamber conditions. In this section we will first give some definitions of key terms and explain some concepts and principles. The first principle concerns the *conservation of energy*. The heat created by the combustion is equal to the heat necessary to raise the resulting gases adiabatically to their final combustion temperature. The heat of reaction of the combustion $\Delta_r H$ has to equal the enthalpy change ΔH of the gases.

The *energy balance* can be thought of as a two-step process. The chemical reaction occurs instantaneously but isothermally at the reference temperature, and the resulting energy release then heats the gases from this reference temperature to the final combustion temperature. The heat of reaction is

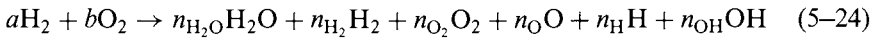
$$\Delta_r H = \sum_1^n n_j \int_{T_{\text{ref}}}^{T_1} C_p dT = \sum_1^n n_j \Delta h_j \Big|_{T_{\text{ref}}}^{T_1} \quad (5-23)$$

Here Δh is the increase in enthalpy for each species multiplied by its molar fraction, and C_p is the molar specific heat at constant pressure.

The second principle is the *conservation of mass*. The mass of any of the atomic species present in the reactants before the chemical reaction must be equal to the mass of the same species in the products. This can be illustrated by

a more general case of the reaction of Equation 5-8. In this case the reactants are not in stoichiometric proportion.

In the combustion of hydrogen with oxygen it is possible to form six products: water, hydrogen, oxygen, hydroxyl, atomic oxygen, and atomic hydrogen. In this case all the reactants and products are gaseous. Theoretically, there could be two additional products: ozone O_3 and hydrogen peroxide H_2O_2 ; however, these are unstable materials that do not readily exist at high temperature, and they can be ignored. In chemical notation this can be stated by



The left side shows the condition before and the right side after the reaction. Since H_2 and O_2 can be found on both sides, it means that not all of these species are consumed and a portion, namely n_{H_2} and n_{O_2} , will remain unreacted. With chemical equilibrium at a particular temperature and pressure the molar concentrations on the right side will remain fixed. Here a , b , n_{H_2O} , n_{H_2} , n_{O_2} , n_O , n_H , and n_{OH} are the respective molar fractions or molar quantities of these substances before and after the reaction, and they can be expressed in kg-mol per kilogram of propellant reactants or reaction products. The initial proportions of a and b are usually known. The number of kg-mol per kilogram of mixture of each element can be established from this initial mix of oxidizer and fuel ingredients. For the hydrogen-oxygen relation above, the mass balances would be

$$\left. \begin{array}{l} \text{for hydrogen: } 2a = 2n_{H_2O} + 2n_{H_2} + n_H + n_{OH} \\ \text{for oxygen: } 2b = n_{H_2O} + 2n_{O_2} + n_O + n_{OH} \end{array} \right\} \quad (5-25)$$

The *mass balance* of Eq. 5-25 provides two more equations for this reaction (one for each atomic species) in addition to the energy balance equation. There are six unknown product percentages and an unknown combustion or equilibrium temperature. However, three equations provide a solution for only three unknowns, say the combustion temperature and the molar fractions of two of the species. If, for example, it is known that the initial mass mixture ratio of b/a is fuel rich, so that the combustion temperature will be relatively low, the percentage of remaining O_2 and the percentage of the dissociation products (O, H, and OH) would all be very low and can be neglected. Thus n_O , n_H , n_{OH} , and n_{O_2} are set to be zero. The solution requires knowledge of the enthalpy change of each of the species, and that information can be obtained from existing tables, such as Table 5-2 or Refs. 5-8 and 5-9.

In more general form, the mass for any given element must be the same before and after the reaction. The number of kg-mol of a given element per kilogram of reactants and product is equal, or their difference is zero. For any one atomic species, such as the H or the O in Eq. 5-25,

$$\left[\sum_{j=1}^m a_{ij} n_j \right]_{\text{products}} - \left[\sum_{j=1}^n a_{ij} n_j \right]_{\text{propellants}} = 0 \quad (5-26)$$

Here the atomic coefficients a_{ij} are the number of kilogram atoms of element i per kg-mol of species j , and m and n are as defined above. The average molecular mass of the products in Eq. 5-5 would be

$$\bar{m} = \frac{2n_{\text{H}_2} + 32n_{\text{O}_2} + 18n_{\text{H}_2\text{O}} + 16n_{\text{O}} + n_{\text{H}} + 17n_{\text{OH}}}{n_{\text{H}_2} + n_{\text{O}_2} + n_{\text{H}_2\text{O}} + n_{\text{O}} + n_{\text{H}} + n_{\text{OH}}} \quad (5-27)$$

Another way to determine the molar fractions for the equilibrium composition is to use a factor λ that represents the degree of advancement of the chemical reaction. This factor λ has the value of zero for the initial conditions before the reaction starts and 1.0 for the final conditions, when the reaction is completed and all the reaction gases are converted to product gases. For the reaction described by Eq. 5-24, λ can be used in this way:

$$\text{Number of moles of A: } n_{\text{A}} = a\lambda \quad (5-28)$$

$$\text{Number of moles of B: } n_{\text{B}} = b\lambda$$

$$\text{Number of moles of C: } n_{\text{C}} = c(1 - \lambda) \quad (5-29)$$

$$\text{Number of moles of D: } n_{\text{D}} = d(1 - \lambda)$$

By substituting these molar fractions into the Gibbs free energy equation (Eq. 5-12), then differentiating the expression with respect to λ and setting the derivative $dG/d\lambda = 0$, one can determine the value of λ at which G is a minimum for the gas mixture. The degree of advancement λ then determines the values of n_{A} , n_{B} , n_{C} , and n_{D} at equilibrium.

The approach used in Ref. 5-13 is commonly used today for thermochemical analysis. It relies on the minimization of the Gibbs free energy and on mass balance and energy balance equations. As was explained in Eq. 5-12, the change in the Gibbs free energy function is zero at equilibrium ($\Delta G = 0$): the chemical potential of the gaseous propellants has to equal that of the gaseous reaction products, which is Eq. 5-12:

$$\Delta G = \sum (n_j \Delta G_j)_{\text{products}} - \sum (n_j \Delta G_j)_{\text{reactants}} = 0 \quad (5-30)$$

To assist in solving this equation a Lagrangian multiplier or a factor of the degree of the completion of the reaction is often used. An alternative method for solving for the gas composition, temperature, and gas properties is to use the energy balance (Eq. 5-23) together with several mass balances (Eq. 5-26) and equilibrium relationships (Eq. 5-21).

After assuming a chamber pressure and setting up the energy balance, mass balances, and equilibrium relations, one method of solving all the equations is

to estimate a combustion temperature and then solve for the various values of n_j . Then a balance has to be achieved between the heat of reaction $\Delta_r H^0$ and the heat absorbed by the gases, $H_T^0 - H_0^0$, to go from the reference temperature to the combustion temperature. If they do not balance, another value of the combustion temperature is chosen until there is convergence and the energy balances.

The *energy release efficiency*, sometimes called the *combustion efficiency*, can now be defined as the ratio of the actual change in enthalpy per unit propellant mixture to the calculated change in enthalpy necessary to transform the propellants from the initial conditions to the products at the chamber temperature and pressure. The actual enthalpy change can be evaluated if the initial propellant condition and the actual composition and the temperature of the combustion gases are measured. Experimental measurements of combustion temperature and gas composition are difficult to perform accurately, and the combustion efficiency is therefore actually evaluated only in rare instances. The combustion efficiency in liquid propellant rocket thrust chambers depends on the method of injection and mixing and increases with increased combustion temperature. In solid propellants the combustion efficiency is a function of the grain design, the propellant, and the degree of mixing between the several solid constituents. Actual measurements on well designed rocket propulsion systems indicate efficiency values of 94 to 99%. These high values indicate that the combustion is essentially complete, that very little, if any, unreacted propellant remains, and that chemical equilibrium is indeed established.

The number of compounds or species in the exhaust can be 50 or more with solid propellants or with liquid propellants that have certain additives. The number of nearly simultaneous chemical reactions that have to be considered can easily exceed 150. Fortunately, many of these chemical species are present only in very small amounts and can usually be neglected.

5.3. ANALYSIS OF NOZZLE EXPANSION PROCESSES

There are several methods for analyzing the nozzle flow, depending on the assumptions made for chemical equilibrium, nozzle expansion, particulates, or energy losses. Several are outlined in Table 5-3.

Once the gases reach the nozzle, they experience an adiabatic, reversible expansion process which is accompanied by a drop in temperature and pressure and a conversion of thermal energy into kinetic energy. Several increasingly more complicated methods have been used for the analysis of the process. For the simple case of frozen equilibrium and one-dimensional flow the state of the gas throughout expansion in the nozzle is fixed by the entropy of the system, which is presumed to be invariant as the pressure is reduced to the value assigned to the nozzle exit plane. All the assumptions listed in Chapter 3 for an ideal rocket are also valid here. Again, the effects of friction, divergence angle, heat exchange, shock waves, or nonequilibrium are neglected in the

simple cases, but are considered in the more sophisticated solutions. The condensed (liquid or solid) phases are again assumed to have zero volume and to be in kinetic as well as thermal equilibrium with the gas flow. This implies that particles or droplets are very small in size, move at the same velocity as the gas stream, and have the same temperature as the gas at all places in the nozzle.

The chemical equilibrium during expansion in the nozzle can be analytically regarded in the following ways:

1. When the composition is invariant throughout the nozzle, there are no chemical reactions or phase changes and the product composition at the nozzle exit is identical to that of its chamber condition. The results are known as *frozen equilibrium* rocket performance. This method usually is simple, but underestimates the performance, typically by 1 to 4%.
2. Instantaneous chemical equilibrium among all molecular species is maintained under the continuously variable pressure and temperature conditions of the nozzle expansion process. Thus the product composition shifts; similarly, instantaneous chemical reactions, phase changes or equilibria occur between gaseous and condensed phases of all species in the exhaust gas. The results so calculated are called *shifting equilibrium* performance. The gas composition mass percentages are different in the chamber and the nozzle exit. This method usually overstates the performance values, such as c^* or I_s , typically by 1 to 4%. Here the analysis is more complex.
3. The chemical reactions do not occur instantaneously, but even though the reactions occur rapidly they require a finite time. The reaction rates of specific reactions can be estimated; the rates are usually a function of temperature, the magnitude of deviation from the equilibrium molar composition, and the nature of the chemicals or reactions involved. The values of T , c^* , or I_s for these types of equilibrium analysis usually are between those of frozen and instantaneously shifting equilibria. This approach is almost never used, because of the lack of good data on reaction rates with multiple simultaneous chemical reactions.

For an axisymmetric nozzle, both one- and two-dimensional analyses can be used. The simplest nozzle flow analysis is one-dimensional, which means that all velocities and temperatures or pressures are equal at any normal cross section of an axisymmetric nozzle. It is often satisfactory for preliminary estimates. In a two-dimensional analysis the velocity, temperature, density, and/or Mach number do not have a flat profile and vary somewhat over the cross sections. For nozzle shapes that are not bodies of revolution (e.g., rectangular, scarfed, or elliptic) a three-dimensional analysis can be performed.

If solid particles or liquid droplets are present in the nozzle flow and if the particles are larger than about $0.1 \mu\text{m}$ average diameter, there will be a thermal lag and velocity lag. The solid particles or liquid droplets do not expand like a

TABLE 5-3. Typical Steps and Alternatives in the Analysis of Rocket Thermochemical Processes in Nozzles

| Step | Process | Method/Implication/Assumption |
|------------------------|---|---|
| Nozzle inlet condition | Same as chamber exit; need to know $T_1, p_1, v_1, H, c^*, \rho_1$, etc. | For simpler analyses assume the flow to be uniformly mixed and steady. |
| Nozzle expansion | An adiabatic process, where flow is accelerated and thermal energy is converted into kinetic energy. Temperature and pressure drop drastically. Several different analyses have been used with different specific effects. Can use one-, two-, or three-dimensional flow pattern. | <ol style="list-style-type: none"> 1. Simplest method is inviscid isentropic expansion flow with constant entropy. 2. Include internal weak shock waves; no longer a truly isentropic process. 3. If solid particles are present, they will create drag, thermal lag, and a hotter exhaust gas. Must assume an average particle size and optical surface properties of the particulates. Flow is no longer isentropic. 4. Include viscous boundary layer effects and/or non-uniform velocity profile. |

Often a simple single correction factor is used with one-dimensional analyses to correct the nozzle exit condition for items 2, 3, and/or 4 above. Computational fluid dynamic codes with finite element analyses have been used with two- and three-dimensional nozzle flow.

| | | |
|--|---|---|
| Chemical equilibrium during nozzle expansion | Due to rapid decrease in T and p , the equilibrium composition can change from that in the chamber. The four processes listed in the next column allow progressively more realistic simulation and require more sophisticated techniques. | <ol style="list-style-type: none"> 1. Frozen equilibrium; no change in gas composition; usually gives low performance. 2. Shifting equilibrium or instantaneous change in composition; usually overstates the performance slightly. 3. Use reaction time rate analysis to estimate the time to reach equilibrium for each of the several chemical reactions; some rate constants are not well known; analysis is more complex. 4. Use different equilibrium analysis for boundary layer and main inviscid flow; will have nonuniform gas temperature, composition, and velocity profiles. |
|--|---|---|

TABLE 5-3. (Continued)

| Step | Process | Method/Implication/Assumption |
|----------------------------|---|--|
| Heat release in nozzle | Recombination of dissociated molecules (e.g., $H + H = H_2$) and exothermic reactions due to changes in equilibrium composition cause an internal heating of the expanding gases. Particulates release heat to the gas. | Heat released in subsonic portion of nozzle will increase the exit velocity. Heating in the supersonic flow portion of nozzle can increase the exit temperature but reduce the exit Mach number. |
| Nozzle shape and size | Can use straight cone, bell-shaped, or other nozzle contour; bell can give slightly lower losses. Make correction for divergence losses and nonuniformity of velocity profile. | Must know or assume a particular nozzle configuration. Calculate bell contour by method of characteristics. Use Eq. 3-34 for divergence losses in conical nozzle. Most analysis programs are one- or two-dimensional. Unsymmetrical non-round nozzles may need three-dimensional analysis. |
| Gas properties | The relationships governing the behavior of the gases apply to both nozzle and chamber conditions. As gases cool in expansion, some species may condense. | Either use perfect gas laws or, if some of the gas species come close to being condensed, use real gas properties. |
| Nozzle exit conditions | Will depend on the assumptions made above for chemical equilibrium, nozzle expansion, and nozzle shape/contour. Assume no jet separation. Determine velocity profile and the pressure profile at the nozzle exit plane. If pressure is not uniform across a section it will have some cross flow. | Need to know the nozzle area ratio or nozzle pressure ratio. For quasi-one-dimensional and uniform nozzle flow, see Eqs. 3-25 and 3-26. If v_2 is not constant over the exit area, determine effective average values of v_2 and p_2 . Then calculate profiles of T , ρ , etc. For nonuniform velocity profile, the solution requires an iterative approach. Can calculate the gas conditions (T , p , etc.) at any point in the nozzle. |
| Calculate specific impulse | Can be determined for different altitudes, pressure ratios, mixture ratios, nozzle area ratios, etc. | Can be determined for average values of v_2 , p_2 , and p_3 based on Eqs. 2-6, 3-35, and/or 2-14. |

gas; their temperature decrease depends on losing energy by convection or radiation, and their velocity depends on the drag forces exerted on the particle. Larger-diameter droplets or particles are not accelerated as rapidly as the smaller ones and flow at a velocity lower than that of the adjacent accelerating gas. Also, the particulates are hotter than the gas and provide heat to the gas. While these particles contribute to the momentum of the exhaust mass, they are not as efficient as an all-gaseous exhaust flow. For composite solid propellants with aluminum oxide particles in the exhaust gas, the loss due to particles could typically be 1 to 3%. The analysis of a two- or three-phase flow requires knowledge of or an assumption about the nongaseous matter, the sizes (diameters), size distribution, shape (usually assumed to be spherical), optical surface properties (for determining the emission/absorption or scattering of radiant energy), and their condensation or freezing temperatures. Some of these parameters are not well known. Performance estimates of flows with particles are explained in Section 3–5.

The viscous boundary layer next to the nozzle wall has velocities substantially lower than that of the inviscid free stream. The slowing down of the gas flow near the wall due to the viscous drag actually causes the conversion of kinetic energy into thermal energy, and thus some parts of the boundary layer can be hotter than the local free-stream static temperature. A diagram of a two-dimensional boundary layer is shown in Figure 3–16. With turbulence this boundary layer can be relatively thick in large-diameter nozzles. The boundary layer is also dependent on the axial pressure gradient in the nozzle, the nozzle geometry, particularly in the throat region, the surface roughness, or the heat losses to the nozzle walls. Today, theoretical boundary layer analyses with unsteady flow are only approximations, but are expected to improve in the future as our understanding of the phenomena and computational fluid dynamics (CFD) techniques are validated. The net effect is a nonuniform velocity and temperature profile, an irreversible friction process in the viscous layers, and therefore an increase in entropy and a slight reduction (usually less than 5%) of the kinetic exhaust energy. The slower moving layers adjacent to the nozzle walls have laminar and subsonic flow.

At the high combustion temperatures a small portion of the combustion gas molecules dissociate (split into simpler species); in this *dissociation* process some energy is absorbed. When energy is released during reassociation (at lower pressures and temperatures in the nozzle), this reduces the kinetic energy of the exhaust gas at the nozzle exit. This is discussed further in the next section.

For propellants that yield only gaseous products, extra energy is released in the nozzle, primarily from the recombination of free-radical and atomic species, which become unstable as the temperature is decreased in the nozzle expansion process. Some propellant products include species that condense as the temperature drops in the nozzle expansion. If the heat release on condensation is large, the difference between frozen and shifting equilibrium performance can be substantial.

In the simplest method the exit temperature T_2 is determined for an isentropic process (frozen equilibrium) by considering the entropy to be constant. The entropy at the exit is the same as the entropy in the chamber. This determines the temperature at the exit and thus the gas condition at the exit. From the corresponding change in enthalpy it is then possible to obtain the exhaust velocity and the specific impulse. For those analysis methods where the nozzle flow is not really isentropic and the expansion process is only partly reversible, it is necessary to include the losses due to friction, shock waves, turbulence, and so on. The result is a somewhat higher average nozzle exit temperature and a slight loss in I_s . A possible set of steps used for the analysis of nozzle processes is given in Table 5-3.

When the contraction between the combustion chamber (or the port area) and the throat area is small ($A_p/A_t \leq 3$), the acceleration of the gases in the chamber causes a drop in the effective chamber pressure at the nozzle entrance. This pressure loss in the chamber causes a slight reduction of the values of c and I_s . The analysis of this chamber configuration is treated in Ref. 5-14 and some data are briefly shown in Tables 3-2 and 6-4.

Example 5-1. Various experiments have been conducted with a liquid monopropellant called nitromethane (CH_3NO_2), which can be decomposed into gaseous reaction products. Determine the values of T , \mathfrak{M} , k , c^* , C_F , and I_s using the water-gas equilibrium conditions. Assume no dissociations and no O_2 .

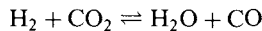
SOLUTION. The chemical reaction for 1 mol of reactant can be described as



Neglect other minor products. The mass balances are obtained for each atomic element.

$$\begin{aligned} \text{C} \quad 1 &= n_{\text{CO}} + n_{\text{CO}_2} \\ \text{H} \quad 3 &= 2n_{\text{H}_2} + 2n_{\text{H}_2\text{O}} \\ \text{O} \quad 2 &= n_{\text{CO}} + 2n_{\text{CO}_2} + n_{\text{H}_2\text{O}} \\ \text{N} \quad 1 &= 2n_{\text{N}_2} \quad \text{or} \quad n_{\text{N}_2} = 0.5 \end{aligned}$$

The reaction commonly known as the water-gas reaction is



Its equilibrium constant K , expressed as molar concentrations, is a function of temperature.

$$K = \frac{n_{\text{H}_2\text{O}}n_{\text{CO}}}{n_{\text{H}_2}n_{\text{CO}_2}}$$

The five equations above have six unknowns: namely, the five molar concentrations and K , which is a function of temperature. Solving for n_{H_2} and K :

$$(K - 1)n_{\text{H}_2}^2 + (3 - K/2)n_{\text{H}_2} = 2.25$$

K can be obtained from a table of the water-gas reaction as a function of temperature. Try $T = 2500\text{ K}$ and $K = 6.440$ and substitute above.

$$5.440n_{\text{H}_2}^2 - 0.220n_{\text{H}_2} - 2.25 = 0$$

then

$$\begin{aligned} n_{\text{H}_2} &= 0.664 \\ n_{\text{H}_2\text{O}} &= 1.500 - n_{\text{H}_2} = 0.836 \\ n_{\text{CO}_2} &= 0.164 \quad n_{\text{CO}} = 0.836 \end{aligned}$$

The heats of formation $\Delta_f H^0$ for the various species are listed in the table below [from the JANAF thermochemical tables (Refs. 5-7 and 5-9)]. The heat of reaction is obtained from Eq. 5-9 in kilojoules per mole. By definition, the heat of formation of H_2 or N_2 is zero. From Eq. 5-9,

$$\begin{aligned} \Delta_r H^0 &= \sum (n\Delta_f H)_{\text{products}} - (\Delta_f H^0)_{\text{reactant}} \\ &= 0.836(-241.8) + 0.164(-393.5) + 0.836(-110.5) - 1.0(-113.1) \\ &= -246 \text{ kJ/mol} \end{aligned}$$

The enthalpy change of the gases going from the reference conditions to the combustion temperature can also be obtained from tables in Refs. 5-7 and 5-8 and is again listed below.

| Species | $\Delta_f H^0$ | Δh_j^{2500} | Molecular Weight | n_j |
|--------------------------|----------------|---------------------|------------------|-------|
| N_2 | 0 | 74.296 | 28 | 0.500 |
| H_2O | -241.826 | 99.108 | 18 | 0.836 |
| H_2 | 0 | 70.498 | 2 | 0.664 |
| CO | -110.53 | 74.985 | 28 | 0.836 |
| CO_2 | -393.522 | 121.917 | 44 | 0.164 |
| CH_3NO_2 | -113.1 | | 61 | 1.000 |

The gas enthalpy change of the hot gas in the combustion chamber is numerically equal to the heat of formation. Using data from the table,

$$\Delta H_{298}^{2500} = \sum n_j \Delta h_j = 249.5 \text{ kJ/mol}$$

This is not identical to the 246 kJ/mol obtained previously, and therefore a lower temperature is to be tried. After one or two iterations the final combustion temperature of 2470 K will be found where the heat of reaction balances the enthalpy rise. The above-mentioned composition will be approximately the same at the new temperature. The molecular weight can then be obtained from Eq. 5-5:

$$\mathfrak{M} = \frac{\sum n_j \mathfrak{M}_j}{\sum n_j} = \frac{28 \times 0.5 + 18 \times 0.836 + 2 \times 0.664 + 28 \times 0.836 + 44 \times 0.164}{2 \times (0.836) + 0.664 + 0.164 + 0.500} = 20.3$$

The specific heat varies with temperature, and average specific heat values \bar{c}_p can be obtained from each species by integrating

$$\bar{c}_p = \frac{\int_{298}^{2470} c_p dT}{\int_{298}^{2470} dT}$$

Values of \bar{c}_p can be obtained from tables in Ref. 5-7 and, if not done by computer, the integration can be done graphically. The result is

$$\begin{aligned}\bar{c}_p &= 41,440 \text{ kJ/K-kg-mol/20.3} \\ &= 2040 \text{ kJ/kg-K}\end{aligned}$$

The specific heat ratio is, from Eq. 5-7,

$$k = \frac{C_p}{C_p - R'} = \frac{41,440}{41440 - 8314} = 1.25$$

With \mathfrak{M} , k , and T_1 now determined, the ideal performance of a nitromethane rocket engine can be established from Eqs. 3-16, 3-30, and 3-32 for $p_1 = 69 \text{ atm}$ and $p_2 = 1.0 \text{ atm}$. The results are

$$\begin{aligned}c^* &= 1525 \text{ m/sec} \\ C_F &= 1.57 \text{ (from Fig. 3-6)} \\ c &= 1.57 \times 1525 = 2394 \text{ m/sec} \\ I_s &= 2394/9.80 = 244 \text{ sec}\end{aligned}$$

5.4. COMPUTER ANALYSIS

All the analysis discussed in this chapter is done today by computer programs. Most are based on minimizing the free energy. This is a simpler approach than relying on equilibrium constants, which was used some years ago. Once the values of n_j and T_1 are determined, it is possible to calculate the molecular mass of the gases (Eq. 5-5), the average molar specific heats C_p by a similar formula, and the specific heat ratio k from Eqs. 3-6 and 5-7. This then characterizes the thermodynamic conditions in the combustion chamber. With these data we can calculate c^* , R , and other parameters of the chamber combustion. The nozzle expansion process simulated by computer gives the performance (such as I_s , c , or A_2/A_1) and the gas conditions in the nozzle; it usually includes several of the corrections mentioned in Chapter 3. Programs exist for one-, two-, and three-dimensional flow patterns.

More sophisticated solutions include a supplementary analysis of combustion chamber conditions where the chamber velocities are high (see Ref. 5-14), a boundary layer analysis, a heat transfer analysis, or a two-dimensional axisymmetric flow with nonuniform flow properties across any cross section of the nozzle. Time-dependent chemical reactions in the chamber are usually neglected, but they can be analyzed by estimating the time rate at which the reaction occurs; one way is to calculate the time derivative of the degree of advancement $d\lambda/dt$ and then to set this derivative to zero. This is described in Ref. 5-3.

An example of a commonly used computer program, based on chemical equilibrium compositions, was developed at the NASA Lewis Laboratory. It is described in Ref. 5-13, Vols. 1 and 2. The key assumptions for this program are one-dimensional forms of the continuity, energy, and momentum equations, zero velocity at the forward end of the chamber, isentropic expansion in the nozzle, using ideal gas laws, and chemical equilibrium in the combustion chamber. It includes options to use frozen equilibrium and narrow chambers (for liquid propellant combustion) or port areas with small cross sections (for solid propellant grains), where the chamber flow velocities are high, causing an extra pressure loss and a slight loss in performance.

Table 5-4 shows calculated data for a liquid oxygen, liquid hydrogen thrust chamber taken from an example of this reference. It has shifting equilibrium in the nozzle flow. The narrow chamber has a cross section that is only a little larger than the throat area. The large pressure drop in the chamber (approximately 126 psi) is due to the energy needed to accelerate the gas, as discussed in Section 3.3 and Table 3-2.

5.5. RESULTS OF THERMOCHEMICAL CALCULATIONS

Voluminous results of these machine calculations are available and only a few samples are indicated here to illustrate typical effects of the variations of various parameters. In general, high specific impulse or high values of c^* can be obtained if the average molecular weight of the reaction products is low (usually this implies a formulation rich in hydrogen) or if the available chemical energy (heat of reaction) is large, which means high combustion temperatures (see Eq. 3-16).

Values of calculated specific impulse will be higher than those obtained from firing actual propellants in rocket units. In practice it has been found that the experimental values are, in general, 3 to 12% lower than those calculated by the method explained in this chapter. Because the nozzle inefficiencies explained in Chapter 3 must be considered, only a portion of this correction (perhaps 1 to 4%) is due to combustion inefficiencies.

Figures 5-1 to 5-6 indicate the results of performance calculations for the liquid propellant combination, liquid oxygen-RP-1. These data are taken from

TABLE 5-4. Calculated Parameters for Liquid Oxygen and Liquid Hydrogen Rocket Engine for Four Different Nozzle Expansions

Chamber pressure at injector 773.3 psia or 53.317 bar; $c^* = 2332.1$ m/sec; shifting equilibrium nozzle flow mixture ratio $O_2/H_2 = 5.551$; chamber to throat area ratio $A_1/A_t = 1.580$.

| Location | <i>Parameters</i> | | | | | | |
|-------------------------------|--------------------------------------|--------------------|-------------------|---------|---------|---------|---------|
| | Injector face | Comb. end | Throat | Exit | Exit | Exit | Exit |
| p_{inj}/p | 1.00 | 1.195 | 1.886 | 10.000 | 100.000 | 282.15 | 709.71 |
| T (K) | 3389 | 3346 | 3184 | 2569 | 1786 | 1468 | 1219 |
| \mathcal{M} (molec. mass) | 12.7 | 12.7 | 12.8 | 13.1 | 13.2 | 13.2 | 13.2 |
| k (spec. heat ratio) | 1.14 | 1.14 | 1.15 | 1.17 | 1.22 | 1.24 | 1.26 |
| C_p (spec. heat, kJ/kg-K) | 8.284 | 8.250 | 7.530 | 4.986 | 3.457 | 3.224 | 3.042 |
| M (Mach number) | 0.00 | 0.413 | 1.000 | 2.105 | 3.289 | 3.848 | 4.379 |
| A_2/A_t | 1.580 ^a | 1.580 ^a | 1.000 | 2.227 | 11.52 | 25.00 | 50.00 |
| c (m/sec) | NA | NA | 2879 ^b | 3485 | 4150 | 4348 | 4487 |
| v_2 (m/sec) | NA | NA | 1537 ^b | 2922 | 3859 | 4124 | 4309 |
| | <i>Mole fractions of gas mixture</i> | | | | | | |
| H | 0.03390 | 0.03336 | 0.02747 | 0.00893 | 0.00024 | 0.00002 | 0.00000 |
| HO ₂ | 0.00002 | 0.00001 | 0.00001 | 0.00000 | 0.00000 | 0.00000 | 0.00000 |
| H ₂ | 0.29410 | 0.29384 | 0.29358 | 0.29659 | 0.30037 | 0.30050 | 0.30052 |
| H ₂ O | 0.63643 | 0.63858 | 0.65337 | 0.68952 | 0.69935 | 0.69948 | 0.69948 |
| H ₂ O ₂ | 0.00001 | 0.00001 | 0.00000 | 0.00000 | 0.00000 | 0.00000 | 0.00000 |
| O | 0.00214 | 0.00204 | 0.00130 | 0.00009 | 0.00000 | 0.00000 | 0.00000 |
| OH | 0.03162 | 0.03045 | 0.02314 | 0.00477 | 0.00004 | 0.00000 | 0.00000 |
| O ₂ | 0.00179 | 0.00172 | 0.00113 | 0.00009 | 0.00000 | 0.00000 | 0.00000 |

^aChamber contraction ratio A_1/A_t .

^bIf cut off at throat.

c is the effective exhaust velocity in a vacuum.

v_2 is the nozzle exit velocity at optimum nozzle expansion.

NA means not applicable.

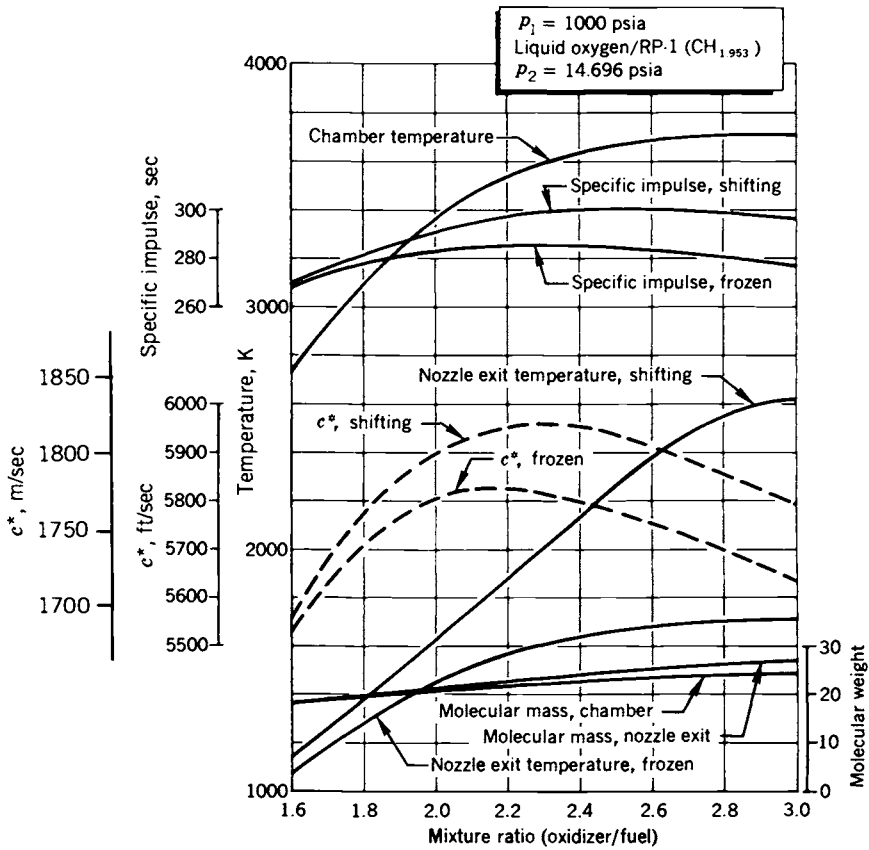


FIGURE 5-1. Calculated performance analysis of liquid oxygen and hydrocarbon fuel as a function of mixture ratio.

Refs. 5-7 and 5-8. The RP-1 fuel is a narrow-cut hydrocarbon similar to kerosene with an average of 1.953 mol of hydrogen for each mole of carbon; thus it has a nominal formula of $CH_{1.953}$. The calculation is limited to a chamber pressure of 1000 psia. Most of the curves are for optimum area ratio expansion to atmospheric pressure, namely, 1 atm or 14.696 psia, and a limited range of oxidizer-to-fuel mixture ratios.

For maximum specific impulse, Figs. 5-1 and 5-4 show an optimum mixture ratio of approximately 2.3 (kg/sec of oxidizer flow divided by kg/sec of fuel flow) for frozen equilibrium expansion and 2.5 for shifting equilibrium with gas expansion to sea level pressure. The maximum values of c^* are at slightly different mixture ratios. This optimum mixture ratio is not the value for highest temperature, which is usually fairly close to the stoichiometric value. The stoichiometric mixture ratio is more than 3.0; much of the carbon is burned to CO_2 and almost all of the hydrogen to H_2O .

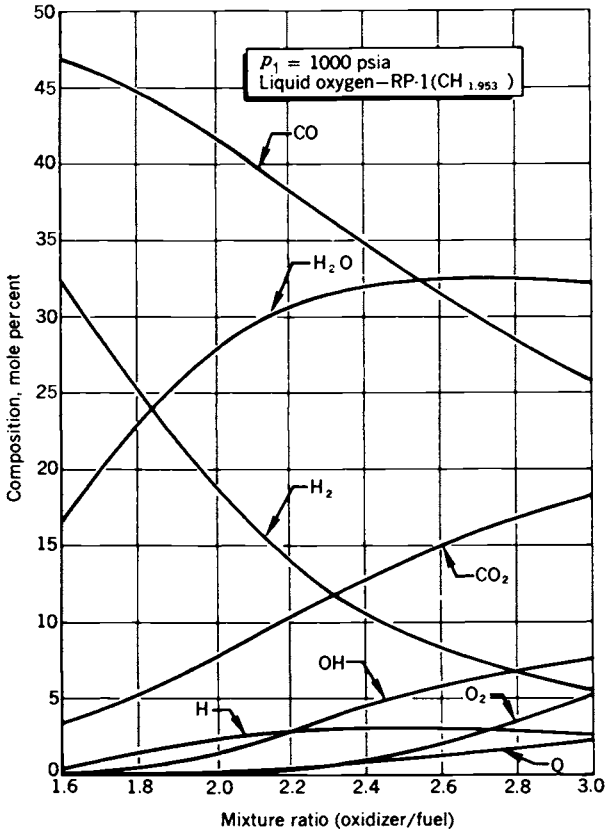


FIGURE 5-2. Calculated chamber gas composition for liquid oxygen and hydrocarbon fuel as a function of mixture ratio. Aggressive gases, such as O₂, O, or OH, can cause oxidation of the wall materials in the chamber and the nozzle.

Because shifting equilibrium makes more enthalpy available for conversion to kinetic energy, it gives higher values of performance (higher I_s or c^*) and higher values of nozzle exit temperature for the same exit pressure (see Fig. 5-1). The influence of mixture ratio on chamber gas composition is evident from Fig. 5-2. A comparison with Fig. 5-3 indicates the marked changes in the gas composition as the gases are expanded under shifting equilibrium conditions. The influence of the degree of expansion, or of the nozzle exit pressure on the gas composition, is shown in Fig. 5-6. As the gases are expanded to higher area ratios and lower exit pressure (or higher pressure ratios) the performance increases; however, the relative increase diminishes as the pressure ratio is further increased (see Figs. 5-5 and 5-6).

Dissociation of molecules requires considerable energy and causes a decrease in the combustion temperature, which in turn can reduce the specific impulse.

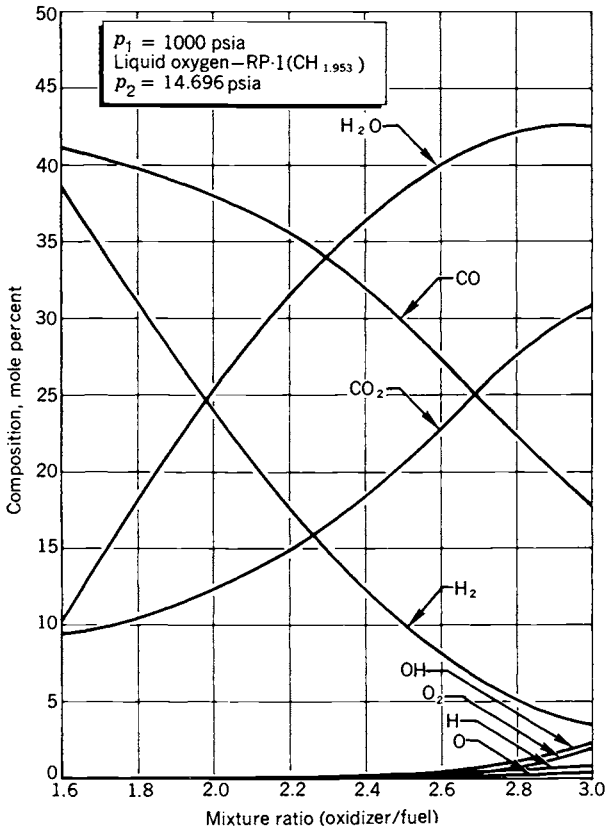


FIGURE 5-3. Calculated nozzle exit gas composition for shifting equilibrium conditions as a function of mixture ratio. Breakdown into O, OH, or H and free O₂ occurs only at the higher temperatures or higher mixture ratios.

Dissociation of the reaction products increases as the chamber temperature rises, and decreases with increasing chamber pressure. Atoms or radicals such as monatomic O or H and OH are formed, as can be seen from Fig. 5-2; some unreacted O₂ also remains at the higher mixture ratios and very high combustion temperatures. As the gases are cooled in the nozzle expansion, the dissociated species react again to form molecules and release heat into the flowing gases. As can be seen from Fig. 5-3, only a small percentage of dissociated species persists at the nozzle exit and only at the high mixture ratio, where the exit temperature is relatively high. (See Fig. 5-1 for exit temperatures with shifting equilibria). Heat released in a supersonic flow actually reduces the Mach number.

Results of calculations for several different liquid and solid propellant combinations are given in Tables 5-5 and 5-6. For the liquid propellant combinations, the listed mixture ratios are optimum and their performance is a

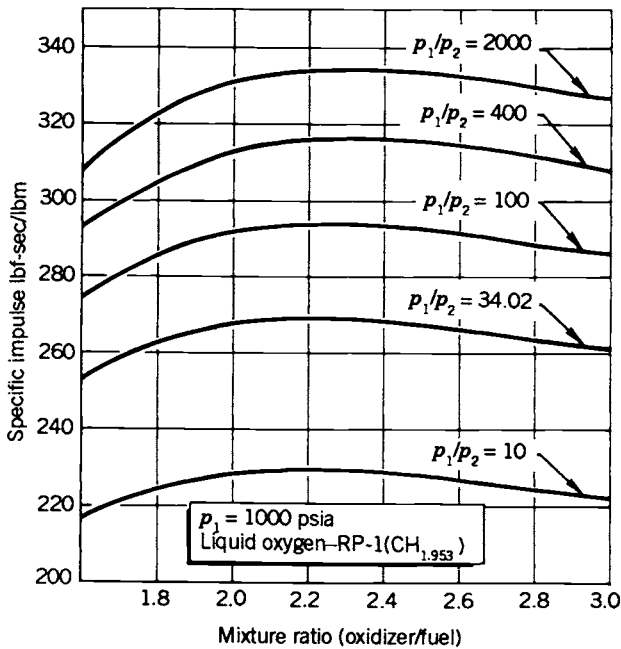


FIGURE 5-4. Variation of theoretical specific impulse with mixture ratio and pressure ratio, calculated for frozen equilibrium.

maximum. For solid propellants, practical considerations (such as propellant physical properties) do not always permit the development of a satisfactory propellant grain when the ingredients are mixed in optimum performance proportions (insufficient binder); therefore the values listed for solid propellants in Table 5-6 correspond in part to practical formulations with reasonable physical and ballistic properties.

Calculated data obtained from Ref. 5-13 are presented in Tables 5-7 to 5-9 for a specific solid propellant to indicate typical variations in performance or gas composition. This particular propellant consists of 60% ammonium perchlorate (NH_4ClO_4), 20% pure aluminum powder, and 20% of an organic polymer of an assumed chemical composition, namely, $\text{C}_{3.1}\text{ON}_{0.84}\text{H}_{5.8}$. Table 5-7 shows the variation of several performance parameters with different chamber pressures expanding to atmospheric exit pressure. The area ratios listed are optimum for this expansion with shifting equilibrium. The exit enthalpy, exit entropy, thrust coefficient, and the specific impulse also consider shifting equilibrium conditions. The characteristic velocity c^* and the chamber molecular mass are functions of chamber conditions only. Table 5-8 shows the variation of gas composition with chamber pressure. Some of the reaction products are in the liquid phase, such as Al_2O_3 . Table 5-9 shows the variation of nozzle exit characteristics and composition for shifting equilibria as a func-

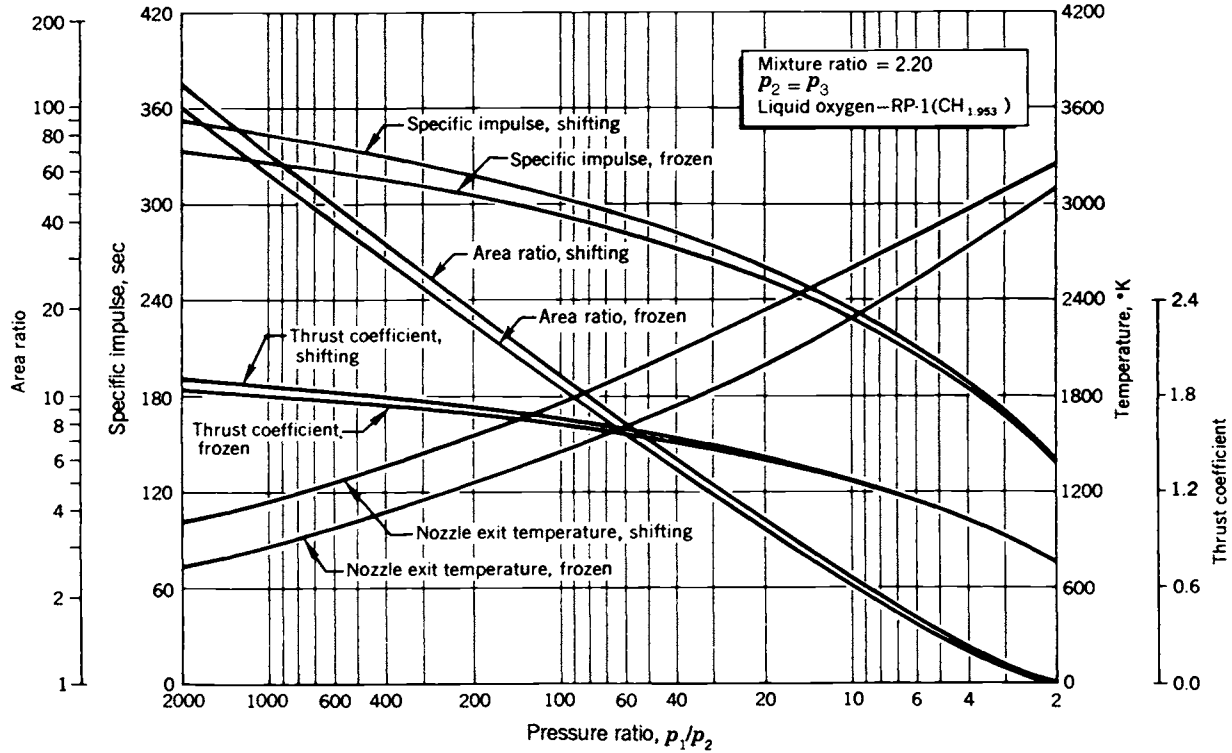


FIGURE 5-5. Variation of calculated parameters with pressure ratio for liquid oxygen-hydrocarbon propellant at a mixture ratio of 2.20. An increase in pressure ratio is due to an increase in chamber pressure, a decrease of nozzle exit pressure (larger area ratio and higher altitude), or both.

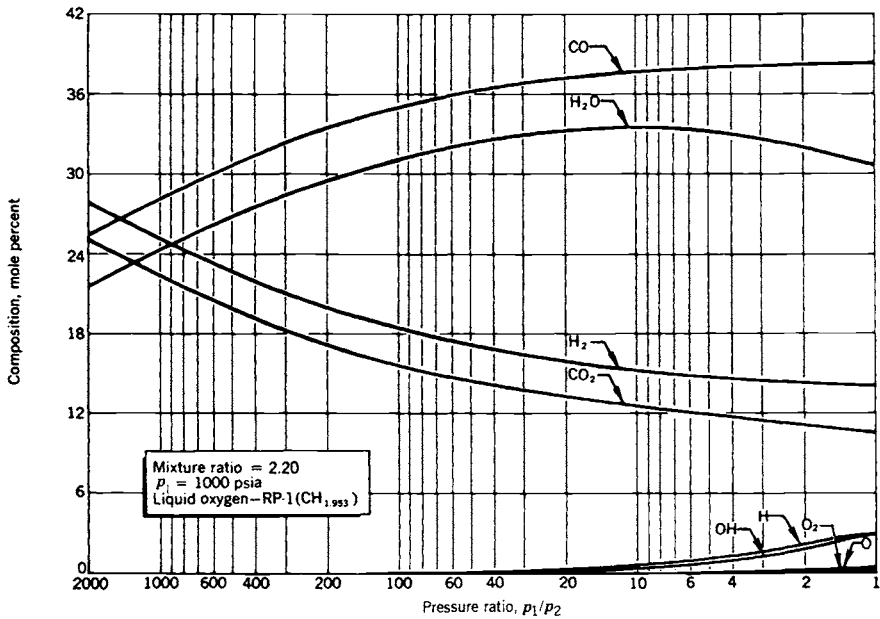


FIGURE 5-6. Variation of exhaust gas composition at nozzle exit with pressure ratio at a fixed mixture ratio and for shifting equilibrium. For frozen equilibrium the composition would be the same as in the chamber, as shown in Fig. 5-2.

tion of exit pressure or pressure ratio for a fixed value of chamber pressure. Table 5-9 shows how the composition is shifted during expansion in the nozzle and how several of the species present in the chamber have disappeared at the nozzle exit. These three tables show theoretical results calculated on a computer; some of the thermodynamic properties of the reactants and reaction products probably do not warrant the indicated high accuracy of five significant figures which are obtained from the computer. In the analysis for chemical ingredients of this solid propellant, approximately 76 additional reaction products were considered in addition to the major product species. This includes, for example, CN, CH, CCl, Cl, NO, and so on. Their calculated mole fractions were very small and therefore they have been neglected and are not included in Table 5-8 or 5-9.

Calculations of this type are useful in estimating performance (I_s , c^* , C_F , ϵ , etc.) for a particular chamber pressure and nozzle exit pressure, and knowledge of the gas composition, as indicated by the previous figures and tables, permits a more detailed estimate of other design parameters, such as gas-film properties for heat transfer determination, radiation characteristics of the flame inside and outside the thrust chambers, and the acoustic characteristics of the gases. Performance data calculated for hybrid propellants are presented briefly in Chapter 15.

TABLE 5-5. Theoretical Performance of Liquid Rocket Propellant Combinations

| Oxidizer | Fuel | Mixture Ratio | | Average Specific Gravity | Chamber Temp. (K) | Chamber c^* (m/sec) | \overline{M} (kg/mol) | I_s (sec) | | k |
|-------------------------|----------------------------|---------------|-----------|--------------------------|-------------------|-----------------------|-------------------------|-------------|--------|------|
| | | By Mass | By Volume | | | | | Shifting | Frozen | |
| Oxygen | Methane | 3.20 | 1.19 | 0.81 | 3526 | 1835 | | | 296 | |
| | | 3.00 | 1.11 | 0.80 | 3526 | 1853 | | 311 | | |
| | Hydrazine | 0.74 | 0.66 | 1.06 | 3285 | 1871 | 18.3 | | 301 | 1.25 |
| | | 0.90 | 0.80 | 1.07 | 3404 | 1892 | 19.3 | 313 | | |
| | Hydrogen | 3.40 | 0.21 | 0.26 | 2959 | 2428 | 8.9 | | 386 | 1.26 |
| | | 4.02 | 0.25 | 0.28 | 2999 | 2432 | 10.0 | 389.5 | | |
| | RP-1 | 2.24 | 1.59 | 1.01 | 3571 | 1774 | 21.9 | 285.4 | | 1.24 |
| | | 2.56 | 1.82 | 1.02 | 3677 | 1800 | 23.3 | | 300 | |
| | UDMH | 1.39 | 0.96 | 0.96 | 3542 | 1835 | 19.8 | | 295 | 1.25 |
| | | 1.65 | 1.14 | 0.98 | 3594 | 1864 | 21.3 | 310 | | |
| Fluorine | Hydrazine | 1.83 | 1.22 | 1.29 | 4553 | 2128 | 18.5 | 334 | | 1.33 |
| | | 2.30 | 1.54 | 1.31 | 4713 | 2208 | 19.4 | | 365 | |
| | Hydrogen | 4.54 | 0.21 | 0.33 | 3080 | 2534 | 8.9 | | 389 | 1.33 |
| | | 7.60 | 0.35 | 0.45 | 3900 | 2549 | 11.8 | 410 | | |
| Nitrogen tetroxide | Hydrazine | 1.08 | 0.75 | 1.20 | 3258 | 1765 | 19.5 | | 283 | 1.26 |
| | | 1.34 | 0.93 | 1.22 | 3152 | 1782 | 20.9 | 292 | | |
| | 50% UDMH- 50% hydrazine | 1.62 | 1.01 | 1.18 | 3242 | 1652 | 21.0 | | 278 | 1.24 |
| | | 2.00 | 1.24 | 1.21 | 3372 | 1711 | 22.6 | 289 | | |
| | RP-1 | 3.4 | 1.05 | 1.23 | 3290 | | 24.1 | | 297 | 1.23 |
| | | 2.15 | 1.30 | 1.20 | 3396 | 1747 | 22.3 | 289 | | |
| | MMH | 1.65 | 1.00 | 1.16 | 3200 | 1591 | 21.7 | | 278 | 1.23 |
| Red fuming nitric acid | RP-1 | 4.1 | 2.12 | 1.35 | 3175 | 1594 | 24.6 | | 258 | 1.22 |
| | | 4.8 | 2.48 | 1.33 | 3230 | 1609 | 25.8 | 269 | | |
| | 50% UDMH- 50% hydrazine | 1.73 | 1.00 | 1.23 | 2997 | 1682 | 20.6 | | 272 | 1.22 |
| | | 2.20 | 1.26 | 1.27 | 3172 | 1701 | 22.4 | 279 | | |
| Hydrogen peroxide (90%) | RP-1 | 7.0 | 4.01 | 1.29 | 2760 | | 21.7 | | 297 | 1.19 |

Notes:

Combustion chamber pressure—1000 psia (6895 kN/m²); nozzle exit pressure—14.7 psia (1 atm); optimum expansion.

Adiabatic combustion and isentropic expansion of ideal gas

The specific gravity at the boiling point was used for those oxidizers or fuels that boil below 20°C at 1 atm pressure.

Mixture ratios are for approximate maximum value of I_s .

TABLE 5-6. Theoretical Performance of Typical Solid Rocket Propellant Combinations

| Oxidizer | Fuel | ρ_b (g/cm ³) ^a | T_1 (K) | c^* (m/sec) ^b | \mathfrak{M} (kg/kg-mol) | I_s (sec) ^b | k |
|--------------------------------|---|---|--------------|-------------------------------|-------------------------------|-----------------------------|------|
| Ammonium nitrate | 11% binder and 7% additives | 1.51 | 1282 | 1209 | 20.1 | 192 | 1.26 |
| Ammonium perchlorate 78-66% | 18% organic polymer binder and 4-20% aluminum | 1.69 | 2816 | 1590 | 25.0 | 262 | 1.21 |
| Ammonium perchlorate 84 to 68% | 12% polymer binder and 4 to 20% aluminum | 1.74 | 3371 | 1577 | 29.3 | 266 | 1.17 |

^a Average specific gravity of solid propellant.

^b Conditions for I_s and c^* :
 Combustion chamber pressure: 1000 psia
 Nozzle exit pressure: 14.7 psia
 Optimum nozzle expansion ratio
 Frozen equilibrium

In gas generators and preburners (see Section 10.5), for staged combustion cycle rocket engines (explained in Section 6.5) the gas temperatures are much lower, to avoid damage to the turbine blades. Typically, the combustion reaction gases are at 900 to 1200 K, which is lower than the gas in the thrust chamber (2900 to 3600 K). The thermochemical analysis of this chapter can also be applied to gas generators; the results (such as gas temperature T_1 , the specific heat c_p , specific heat ratio k , or composition) are used for estimating turbine inlet conditions or turbine power. Examples are listed in Table 5-10 for a chamber pressure of 1000 psia. Some species in the gases will not be present (such as atomic oxygen or hydroxyl), and often real gas properties will need to be used because some of these gases do not behave as a perfect gas at these temperatures.

TABLE 5-7. Variation of Calculated Performance Parameters for an Alumined Ammonium Perchlorate Propellant as a Function of Chamber Pressure for Expansion to Sea Level (1 atm) with Shifting Equilibrium

| | | | | | |
|--|----------|----------|----------|---------|---------|
| Chamber pressure (psia) | 1500 | 1000 | 750 | 500 | 200 |
| Chamber pressure (atm) or pressure ratio p_1/p_2 | 102.07 | 68.046 | 51.034 | 34.023 | 13.609 |
| Chamber temperature (K) | 3346.9 | 3322.7 | 3304.2 | 3276.6 | 3207.7 |
| Nozzle exit temperature (K) | 2007.7 | 2135.6 | 2226.8 | 2327.0 | 2433.6 |
| Chamber enthalpy (cal/g) | -572.17 | -572.17 | -572.17 | -572.17 | -572.17 |
| Exit enthalpy (cal/g) | -1382.19 | -1325.15 | -1282.42 | -1219.8 | -1071.2 |
| Entropy (cal/g-K) | 2.1826 | 2.2101 | 2.2297 | 2.2574 | 2.320 |
| Chamber molecular mass (kg/mol) | 29.303 | 29.215 | 29.149 | 29.050 | 28.908 |
| Exit molecular mass (kg/mol) | 29.879 | 29.853 | 29.820 | 29.763 | 29.668 |
| Exit Mach number | 3.20 | 3.00 | 2.86 | 2.89 | 2.32 |
| Specific heat ratio—chamber, k | 1.1369 | 1.1351 | 1.1337 | 1.1318 | 1.1272 |
| Specific impulse, vacuum (sec) | 287.4 | 280.1 | 274.6 | 265.7 | 242.4 |
| Specific impulse, sea level expansion (sec) | 265.5 | 256.0 | 248.6 | 237.3 | 208.4 |
| Characteristic velocity, c^* (m/sec) | 1532 | 1529 | 1527 | 1525 | 1517 |
| Nozzle area ratio, A_2/A_t^a | 14.297 | 10.541 | 8.507 | 8.531 | 6.300 |
| Thrust coefficient, C_F^a | 1.700 | 1.641 | 1.596 | 1.597 | 1.529 |

^aAt optimum expansion.

TABLE 5-8. Mole Fraction Variation of Chamber Gas Composition with Combustion Chamber Pressure for a Solid Propellant

| Pressure (psia) | 1500 | 1000 | 750 | 500 | 200 |
|---|---------|---------|---------|---------|---------|
| Pressure (atm) or pressure ratio | 102.07 | 68.046 | 51.034 | 34.023 | 13.609 |
| Ingredient | | | | | |
| Al | 0.00007 | 0.00009 | 0.00010 | 0.00012 | 0.00018 |
| AlCl | 0.00454 | 0.00499 | 0.00530 | 0.00572 | 0.00655 |
| AlCl ₂ | 0.00181 | 0.00167 | 0.00157 | 0.00142 | 0.00112 |
| AlCl ₃ | 0.00029 | 0.00023 | 0.00019 | 0.00015 | 0.00009 |
| AlH | 0.00002 | 0.00002 | 0.00002 | 0.00002 | 0.00002 |
| AlO | 0.00007 | 0.00009 | 0.00011 | 0.00013 | 0.00019 |
| AlOCl | 0.00086 | 0.00095 | 0.00102 | 0.00112 | 0.00132 |
| AlOH | 0.00029 | 0.00032 | 0.00034 | 0.00036 | 0.00041 |
| AlO ₂ H | 0.00024 | 0.00026 | 0.00028 | 0.00031 | 0.00036 |
| Al ₂ O | 0.00003 | 0.00004 | 0.00004 | 0.00005 | 0.00006 |
| Al ₂ O ₃ (solid) | 0.00000 | 0.00000 | 0.00000 | 0.00000 | 0.00000 |
| Al ₂ O ₃ (liquid) | 0.09425 | 0.09378 | 0.09343 | 0.09293 | 0.09178 |
| CO | 0.22434 | 0.22374 | 0.22328 | 0.22259 | 0.22085 |
| COCl | 0.00001 | 0.00001 | 0.00001 | 0.00001 | 0.00000 |
| CO ₂ | 0.00785 | 0.00790 | 0.00793 | 0.00799 | 0.00810 |
| Cl | 0.00541 | 0.00620 | 0.00681 | 0.00772 | 0.01002 |
| Cl ₂ | 0.00001 | 0.00001 | 0.00001 | 0.00001 | 0.00001 |
| H | 0.02197 | 0.02525 | 0.02776 | 0.03157 | 0.04125 |
| HCl | 0.12021 | 0.11900 | 0.11808 | 0.11668 | 0.11321 |
| HCN | 0.00003 | 0.00002 | 0.00001 | 0.00001 | 0.00000 |
| HCO | 0.00003 | 0.00002 | 0.00002 | 0.00002 | 0.00001 |
| H ₂ | 0.32599 | 0.32380 | 0.32215 | 0.31968 | 0.31362 |
| H ₂ O | 0.08960 | 0.08937 | 0.08916 | 0.08886 | 0.08787 |
| NH ₂ | 0.00001 | 0.00001 | 0.00001 | 0.00000 | 0.00000 |
| NH ₃ | 0.00004 | 0.00003 | 0.00002 | 0.00001 | 0.00001 |
| NO | 0.00019 | 0.00021 | 0.00023 | 0.00025 | 0.00030 |
| N ₂ | 0.09910 | 0.09886 | 0.09867 | 0.09839 | 0.09767 |
| O | 0.00010 | 0.00014 | 0.00016 | 0.00021 | 0.00036 |
| OH | 0.00262 | 0.00297 | 0.00324 | 0.00364 | 0.00458 |
| O ₂ | 0.00001 | 0.00001 | 0.00002 | 0.00002 | 0.00004 |

TABLE 5-9. Calculated Variation of Thermodynamic Properties and Exit Gas Composition for an Aluminized Perchlorate Propellant with $p_1 = 1500$ psia and Various Exit Pressures at Shifting Equilibrium and Optimum Expansion

| | Chamber | Throat | Nozzle Exit | | | | |
|---|---------|---------|-------------|---------|---------|---------|---------|
| Pressure (atm) | 102.07 | 58.860 | 2.000 | 1.000 | 0.5103 | 0.2552 | 0.1276 |
| Pressure (MPa) | 10.556 | 5.964 | 0.2064 | 0.1032 | 0.0527 | 0.0264 | 0.0132 |
| Nozzle area ratio | > 0.2 | 1.000 | 3.471 | 14.297 | 23.972 | 41.111 | 70.888 |
| Temperature (K) | 3346.9 | 3147.3 | 2228.5 | 2007.7 | 1806.9 | 1616.4 | 1443.1 |
| Ratio chamber pressure/local pressure | 1.000 | 1.7341 | 51.034 | 102.07 | 200.00 | 400.00 | 800.00 |
| Molecular mass (kg/mol) | 29.303 | 29.453 | 29.843 | 29.879 | 29.894 | 29.899 | 29.900 |
| Composition (mol %) | | | | | | | |
| Al | 0.00007 | 0.00003 | 0.00000 | 0.00000 | 0.00000 | 0.00000 | 0.00000 |
| AlCl | 0.00454 | 0.00284 | 0.00014 | 0.00008 | 0.00000 | 0.00000 | 0.00000 |
| AlCl ₂ | 0.00181 | 0.00120 | 0.00002 | 0.00000 | 0.00000 | 0.00000 | 0.00000 |
| AlCl ₃ | 0.00029 | 0.00023 | 0.00002 | 0.00000 | 0.00000 | 0.00000 | 0.00000 |
| AlOCl | 0.00086 | 0.00055 | 0.00001 | 0.00000 | 0.00000 | 0.00000 | 0.00000 |
| AlOH | 0.00029 | 0.00016 | 0.00000 | 0.00000 | 0.00000 | 0.00000 | 0.00000 |
| AlO ₂ H | 0.00024 | 0.00013 | 0.00000 | 0.00000 | 0.00000 | 0.00000 | 0.00000 |
| Al ₂ O | 0.00003 | 0.00001 | 0.00000 | 0.00000 | 0.00000 | 0.00000 | 0.00000 |
| Al ₂ O ₃ (solid) | 0.00000 | 0.00000 | 0.09955 | 0.09969 | 0.09974 | 0.09976 | 0.09976 |
| Al ₂ O ₃ (liquid) | 0.09425 | 0.09608 | 0.00000 | 0.00000 | 0.00000 | 0.00000 | 0.00000 |
| CO | 0.22434 | 0.22511 | 0.22553 | 0.22416 | 0.22008 | 0.21824 | 0.21671 |
| CO ₂ | 0.00785 | 0.00787 | 0.00994 | 0.01126 | 0.01220 | 0.01548 | 0.01885 |
| Cl | 0.00541 | 0.00441 | 0.00074 | 0.00028 | 0.00009 | 0.00002 | 0.00000 |
| H | 0.02197 | 0.01722 | 0.00258 | 0.00095 | 0.00030 | 0.00007 | 0.00001 |
| HCl | 0.12021 | 0.12505 | 0.13635 | 0.13707 | 0.13734 | 0.13743 | 0.13746 |
| H ₂ | 0.32599 | 0.33067 | 0.34403 | 0.34630 | 0.34842 | 0.35288 | 0.35442 |
| H ₂ O | 0.08960 | 0.08704 | 0.08091 | 0.07967 | 0.07796 | 0.07551 | 0.07214 |
| NO | 0.00019 | 0.00011 | 0.00001 | 0.00000 | 0.00000 | 0.00000 | 0.00000 |
| N ₂ | 0.09910 | 0.09950 | 0.10048 | 0.10058 | 0.10063 | 0.10064 | 0.10065 |
| O | 0.00010 | 0.00005 | 0.00000 | 0.00000 | 0.00000 | 0.00000 | 0.00000 |
| OH | 0.00262 | 0.00172 | 0.00009 | 0.00005 | 0.00002 | 0.00000 | 0.00000 |

TABLE 5-10. Typical Gas Characteristics for Fuel-rich Liquid Propellant Gas Generators

| Propellant | T_1 (K) | k | Gas Constant R (ft-lbf/lbm-R) | Oxidizer-to-fuel ratio | Specific heat c_p (kcal/kg-K) |
|---|-----------|-------|-------------------------------|------------------------|---------------------------------|
| Liquid oxygen and liquid hydrogen | 900 | 1.370 | 421 | 0.919 | 1.99 |
| | 1050 | 1.357 | 375 | 1.065 | 1.85 |
| | 1200 | 1.338 | 347 | 1.208 | 1.78 |
| Liquid oxygen and kerosene | 900 | 1.101 | 45.5 | 0.322 | 0.639 |
| | 1050 | 1.127 | 55.3 | 0.423 | 0.654 |
| | 1200 | 1.148 | 64.0 | 0.516 | 0.662 |
| Nitrogen tetroxide and dimethyl hydrazine | 1050 | 1.420 | 87.8 | 0.126 | 0.386 |
| | 1200 | 1.420 | 99.9 | 0.274 | 0.434 |

PROBLEMS

1. Explain the physical or chemical reasons for a maximum value of specific impulse at a particular mixture ratio of oxidizer to fuel.
2. Explain why, in Table 5-8, the relative proportion of monatomic hydrogen and monatomic oxygen changes markedly with different chamber pressures and exit pressures.
3. This chapter contains several charts for the performance of liquid oxygen and RP-1 hydrocarbon fuel. By mistake the next shipment of cryogenic oxidizer contains at least 15% liquid nitrogen. Explain what general trends should be expected in the results of the next test in the performance values, the composition of the exhaust gas under chamber and nozzle conditions, and the optimum mixture ratio.
4. A mixture of perfect gases consists of 3 kg of carbon monoxide and 1.5 kg of nitrogen at a pressure of 0.1 MPa and a temperature of 298.15 K. Using Table 5-1, find (a) the effective molecular mass of the mixture, (b) its gas constant, (c) specific heat ratio, (d) partial pressures, and (e) density.

Answers: (a) 28 kg/kg-mol, (b) 297 J/kg-K, (c) 1.40, (d) 0.0666 and 0.0333 MPa, (e) 1.13 kg/m³.

5. Using information from Table 5-2, plot the value of the specific heat ratio for carbon monoxide (CO) as a function of temperature. Notice the trend of this curve; it is typical of the temperature behavior of other diatomic gases.

Answers: $k = 1.28$ at 3500 K, 1.30 at 2000 K, 1.39 at 500 K.

6. Modify and tabulate two entries in Table 5-5 for operation in the vacuum of space, namely oxygen/hydrogen and nitrogen tetroxide/hydrazine. Assume the data in the table represents the design condition.

7. The figures in this chapter show several parameters and gas compositions of liquid oxygen burning with RP-1, which is a kerosene-type material. For a mixture ratio of 2.0, use the compositions to verify the molecular mass in the chamber and the specific impulse (frozen equilibrium flow in nozzle) in Fig. 5-1.

SYMBOLS

(Symbols referring to chemical elements, compounds, or mathematical operators are not included in this list.)

| | |
|----------------|---|
| a | number of kilogram atoms |
| A_t | throat area, m^2 |
| c^* | characteristic velocity, m/sec |
| c_p | specific heat per unit mass, J/kg-K |
| C_p | molar specific heat at constant pressure of gas mixture, J/kg-mol-K |
| g_0 | acceleration of gravity at sea level, 9.8066 m/sec^2 |
| G | Gibbs free energy for a propellant combustion gas mixture, J/kg |
| $\Delta_f G^0$ | change in free energy of formation at 298.15 K and 1 bar |
| G_j | free energy for a particular species j , J/kg |
| ΔH | overall enthalpy change, J/kg or J/kg-mol |
| ΔH_j | enthalpy change for a particular species j , J/kg |
| $\Delta_r H^0$ | heat of reaction at reference 298.15 K and 1 bar, J/kg |
| $\Delta_f H^0$ | heat of formation at reference 298.15 K and 1 bar, J/kg |
| h | enthalpy for a particular species, J/kg or J/kg-mol |
| I_s | specific impulse, $\text{N-sec}^3/\text{kg}\cdot\text{m}^2$ (lbf-sec/lbm) |
| k | specific heat ratio |
| K_f | equilibrium constant when a compound is formed from its elements |
| K_n | equilibrium constant as a function of molar fractions |
| K_p | equilibrium constant as a function of partial pressure |
| m | number of gaseous species |
| \dot{m} | mass flow rate, kg/sec |
| \mathfrak{M} | molecular mass (also called molecular weight) of gas mixture, kg/mol |
| n | total number of species or moles per unit mass (kg-mol/kg) of mixture |
| n_j | mole fraction or volume percent of species j , kg-mol/kg-mixture |
| p | pressure of gas mixture, N/m^2 |
| R | gas constant, J/kg-K |
| R' | universal gas constant, $8314.3 \text{ J/kg mol-K}$ |
| S | entropy, J/kg mol-K |
| T | absolute temperature, K |
| U | internal energy, J/kg-mol |
| v | gas velocity, m/sec |
| V | specific volume, m^3/kg |

Greek Letters

| | |
|------------|---|
| ϵ | nozzle exit area ratio (exit/throat area) |
| λ | Lagrange multiplier, or factor for the degree of advancement of a chemical reaction |
| ρ | density, kg/m ³ |

Subscripts

| | |
|--------|---|
| a, b | molar fractions of reactant species A or B |
| c, d | molar fractions of product species C or D |
| i | atomic species in a specific propellant |
| j | constituents or species in reactants or products |
| mix | mixture of gases |
| ref | at reference condition (also superscript ⁰) |
| 1 | chamber condition |
| 2 | nozzle exit condition |
| 3 | ambient atmospheric condition |

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