16.512, Rocket Propulsion
Prof. Manuel Martinez-Sanchez
Lecture 12: Review of Equilibrium Thermochemistry

Thermochemistry of Combustion for Propulsion Devices

12.1.1 Introduction

The general principles that govern chemical reactions (species conservation, enthalpy balance and chemical equilibrium) have been introduced in previous subjects. In the next three Sections we will briefly examine the application of these principles to Propulsion.

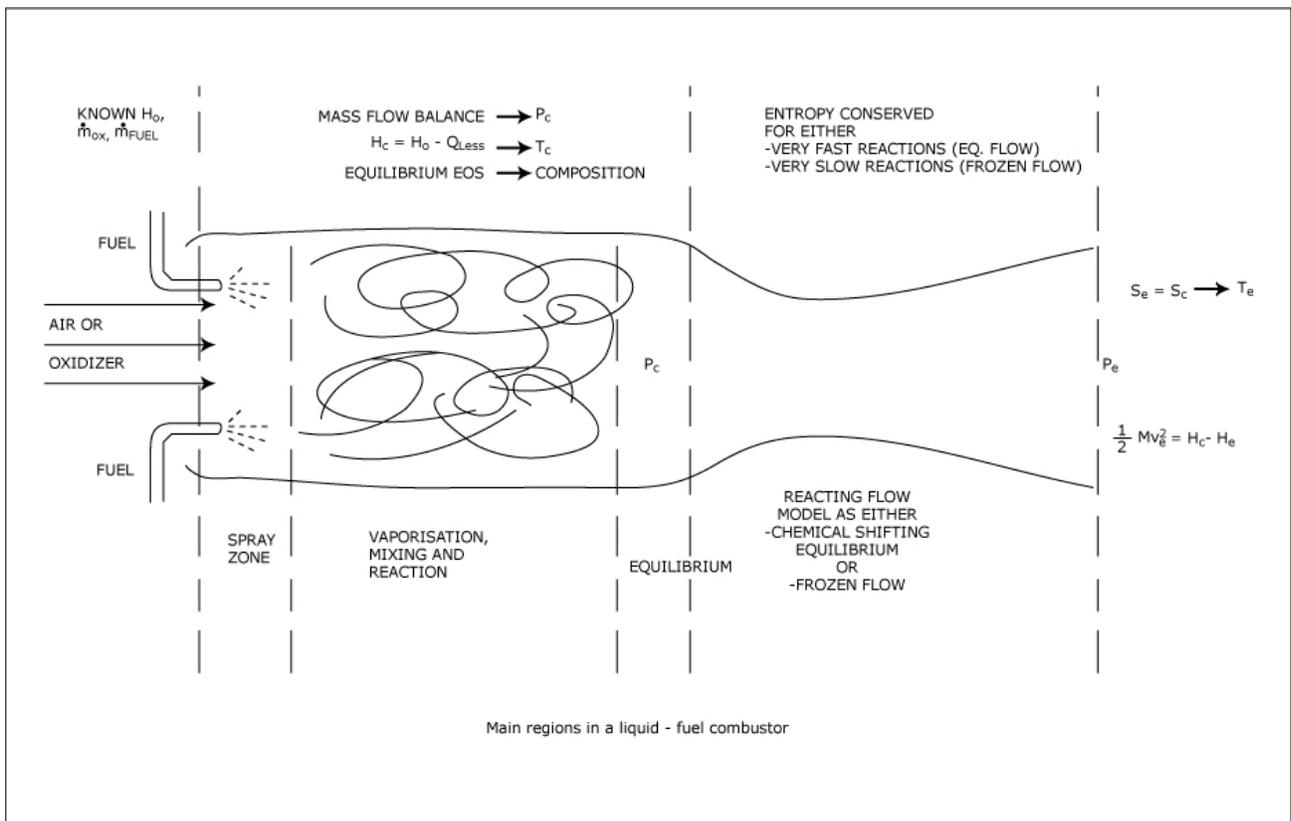The sketch in Fig 12.1 indicates the main regions.

Fig. 12.1. Main regions in a liquid-fuel combustor

In a combustion chamber which could belong to a ramjet or rocket, or, with minor variations, to many other technical devices which utilize hot gas flows. It is frequent to supply fuel (and sometimes oxidizer as well) in liquid form, and so the first region involves a series of colliding liquid jets or sprays, designed to break up these liquids into fine droplets. These now find themselves immersed in the hot combustion gases, and evaporate rapidly, a step which must necessarily precede actual chemical reaction. Mixing of the oxidizer and fuel vapors typically proceeds via the strong turbulence existing in the combustor, and once this mixing has actually

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achieved intimate molecular level interdiffusion within the turbulent eddies, reaction occurs usually on a time scale which is short compared to those for vaporization and mixing.

The combustion chamber design must take into account the kinetics of these steps to arrive at a dimension which guarantees completion of the combustion reactions without waste of volume. If this is so, the last portion of the combustor contains at any time a mixture of combustion products which have reached a state of thermodynamic equilibrium, and which are about to flow into their working devices, be it a simple nozzle, a turbine (also preceded by its nozzles) or other configurations.

Equilibrium does not necessarily mean complete combustion since, at high temperatures, various decomposition reactions are thermodynamically favored. In a high speed Ramjet with a subsonic combustion chamber the incompleteness of the combustion is so extreme –due to the high temperature prevailing- that, beyond a certain flight speed, no net heat release can be obtained.

It is important to distinguish between this kind of combustion incompleteness, which is unavoidable at high temperatures, and is due to the activation of reverse reactions, and a more common but avoidable incompleteness, which occurs when the combustion chamber is inadequately sized and the vaporization-mixing-reaction processes are not completed in the residence time allowed to each fluid particle.

A first objective of our analysis is to determine the actual gas conditions (temperature, composition) at the exit of an equilibrated combustor, for a set of prescribed reactant flow rates. These flow rates, together with the discharge nozzle geometry, also determine a combustor pressure, which we will here assume as an independently prescribed quantity.

Beyond this point the flow typically expands and cools more or less adiabatically. As it does so, there is at least a tendency to shift its chemical composition, usually in the sense of completing the incomplete combustion, since the lower temperature now inhibits decomposition reactions. Thus, there may be a sort of afterburning effect along the nozzle expansion, and this sometimes contributes significantly to increase the performance of rockets or ramjets. It is worth noting here that, even if all the reactions that were not completed in the chamber were completed in the nozzle, thus still releasing all the heat of combustion, the performance level achieved would be lower than if no decomposition had ever occurred in the first place; this is because in any thermodynamic cycle less work can be extracted from heat added at lower than at higher temperatures. In any event, it often happens that the nozzle recombination reactions are too slow (due to their occurring at a reduced temperature, which slows down reaction rates) to keep pace with the rapidity of the nozzle expansion process. In that case the flow is said to be chemically <u>frozen</u>, and it comes out of the nozzle exit in a state of substantial non-equilibrium, maintaining a composition close to what it had in the chamber. This is the opposite extreme to the case when all the recombination reactions actually do occur along the flow (<u>equilibrium</u> expansion). Actual performance always falls between these two extremes (more performance than that for frozen expansion, less than that for equilibrium expansion), and since the spread between them may not be too large, it is useful to bracket the actual result by performing both frozen and equilibrium flow calculations, both of which, as we will see, involve only consideration of the end points of the expansion. Anything in between entails much more complex

calculations, due to the need to follow in detail the kinetics of a variety of chemical reactions.

12.1.2 Combustors Far from Stoichiometry

Stoichiometric proportions of fuel and oxidizer are those for which, if the reaction were complete, no excess of either would ensue. It is clear that this would then ensure maximum heat release per unit mass, and hence highest adiabatic flame temperature. Even under conditions of incomplete reaction, maximum temperature usually does occur near stoichiometric conditions, and falls off for either fuel-rich or fuel-lean conditions.

For some important types of combustors the fuel/air ratio is purposely selected to be very far from stoichiometric, so as to keep the final temperatures below acceptable materials limits. Examples are:

(a) Jet engine combustors (operated fuel/lean)

(b) Gas generators for rocket turbopumps (operated typically very fuel-rich).

In cases such as these the final temperature and other properties of the reacted gases can be obtained from simple mass and energy balances, since their composition can usually be obtained by inspection by assuming complete combustion with excess oxidizer or fuel, as the case may be. This is because decomposition reactions responsible for combustion incompleteness are not very active at these moderate temperatures.

Example

The liquid hydrogen fuel in the Space Shuttle main engine is pressurized to the very high combustion chamber pressure by a turbopump which is driven by a turbine. The gas driving this turbine is generated in a "preburner", into which the flow rates of oxygen and hydrogen are (at maximum power)
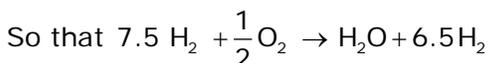
$$\dot{m}_{LOX} = 43 \ Kg/sec \qquad\qquad \dot{m}_{LH} = 40.2 \ Kg/sec$$

Since this is very fuel-rich, we can safely assume all of the O_2 is consumed, and we have the reaction

$$x \ H_2 + \frac{1}{2}O_2 \ \rightarrow \ H_2O + (1-x) \ H_2$$
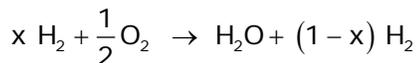
where the x is given by the oxidizer/fuel ratio:

$$\frac{43}{40.2} = \frac{\frac{1}{2} 32}{x.2} = \frac{8}{x} \rightarrow \qquad x = 7.5$$

So that $7.5 \ H_2 \ + \frac{1}{2}O_2 \rightarrow H_2O + 6.5 H_2$

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The adiabatic flame temperature corresponding to this reaction is obtained by stating that the combustion process is adiabatic:

Enthalpy before reaction = Enthalpy after reaction

Before reaction, assuming the H_2 and O_2 enter the preburner very cold (say, for an approximation, at O K), we read in Ref. 12.1,

h_{O_2} = -8682 J/mole, h_{H_2} = -8468 J/mole, for a total enthalpy

$$h_{before} = 7.5 \times (-8468) + \frac{1}{2}(-8682) = -67,850 \text{ J}$$

The temperature after reaction is such as to give this same enthalpy. With some hindsight (we know the turbines are unlikely to be designed for more than 1100-1200K), we try 1000, 1100 K, and using the tables in VW-S (Ref. 12.1), App. A. 11 we obtain

T (K)	1000	1100
h_{H_2O}	-241,827 + 25,978	-241,827 + 30167
h_{H_2}	20,678	23,723
$h = h_{H_2O} + 6.5 h_{H_2}$	-81,390	-57,461

Interpolating linearly gives

$$T = 1000 + 100 \, \frac{13,540}{23,939} = 1057 \text{ K}$$

The mean molecular mass of the gas is simply

$$M = \frac{18 \times 1 + 2 \times 6.5}{1 + 6.5} = 4.13 \text{ g/mole}$$

We can also calculate easily the mean specific heats $\bar{c}_p$ and $\bar{c}_v$ and their ratio, $\bar{\gamma}$.

For each of the components, H_2O and H_2, we can approximate $c_p = \left(\frac{\partial h}{\partial T}\right)$ as

$$c_p \simeq \frac{h(1100) - h(1000)}{100}$$. This gives $(c_p)_{H_2O}$ = 41.89 J/mole K,

$(c_p)_{H_2}$ = 30.37 J/mole K, so that

$$\bar{c}_p = \frac{41.89 \times 1 + 30.37 \times 6.5}{7.5} = 31.91 \text{ J/mole K}$$

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Since for each constituent $c_v = c_p - R$, we also have

$$\bar{c}_v = \bar{c}_p - R = 31.91 - 8.31 = 23.60 \, \text{J/mole K, giving}$$

$$\gamma = \frac{\bar{c}_p}{\bar{c}_v} = \frac{31.91}{23.60} = 1.352$$

(Notice $\bar{\gamma}$ is not the average of the individual γ's)

12.1.3 Reactions Close to Stoichiometry (or with Preheated Reactants)

In other applications, where materials limits are either absent or can be overcome by appropriate cooling of walls, the reactants may be in proportions close to stoichiometric, so as to generate very high gas temperatures. Examples are:

(a) Rocket combustors (operated typically on the fuel-rich side, but only moderately so)
(b) Ramjet combustors (where, in addition, the air is strongly heated by the ram effect)
(c) Piston engines (fuel-lean for gasoline engines, but near-stoichiometric in Diesel engines)
(d) Welding torches

In these cases one cannot easily predict the final composition of the burnt gases, since the relatively complex molecules like H_2O, CO_2 (or even H_2, O_2) tend to break down into simpler ones which are more stable at high temperatures (such as OH, H, O, etc.). Thus, in addition to mass and energy conservation, one needs to use also the laws of chemical equilibrium to determine the temperature and other properties of the gas products. In most real situations, many molecular species may be present at the high temperatures of the flame, and so more than one equilibria are simultaneously to be considered. In these cases, iteration is required to obtain consistent solutions. A procedure which, with some judgment, usually works, is as follows:

(1) Identify the possible molecular species in the products, classify them into major and minor (minor species would be those that are expected to be present in small concentration).

(2) Neglect at first the "minor" species, use procedures similar to those in the previous example to obtain the "major" species concentration and an approximate temperature.

(3) Write chemical reactions which would produce one "minor" species at a time from only "major" ones. Calculate their equilibrium constants at the approximate temperature of step (2), and use the equilibrium laws to calculate the concentrations of the "minors".

(4) Correct the "majors" concentration, and do a new enthalpy balance to obtain an improved temperature.

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(5) Iterate back to step (3) until convergence is obtained.
We illustrate these principles below.

Ref.12.1.1 G. Van Wylen and R. E. Sonntag, <u>Fundamentals of Classical Thermodynamic</u>, Appendix A. 11, 3rd Ed., SI Version, J. Wiley & Sons, 1985.

12.2 Example Calculation of Thermochemical Equilibrium in a Rocket Chamber

12.2.1 Introduction

In the Space Shuttle's Main Engines (SSME'S), the rocket combustion chamber operates at $p = 210$ atm and an oxidizer-to-fuel mass ratio O/F = 6, the reactants being cryogenic H_2 and O_2. The stoichiometric ratio for full combustion $\left(H_2 + \frac{1}{2} O_2 \rightarrow H_2O \right)$ would be O/F = 8, so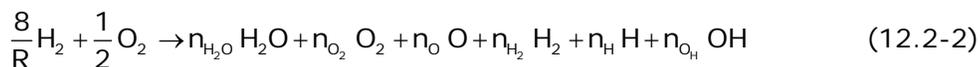 this is now only slightly fuel-rich, and we expect a very high combustion temperature. In the next few sections we will analyze this case step-by-step, in order to bring out the important points of any such calculation. Practical problems of this nature are routinely solved by means of complex computer programs based on the present methods or on more generalized iteration schemes, but, of course, entailing the same basic physics. One such standard code is the so-called CEC, Chemical Equilibrium Code, developed and maintained by NASA (Ref. 12.2), which in its normal configuration, can handle about 200 species simultaneously.

12.2.2 Atomic Species Concentration

In order to more easily keep track of mass conservation, it is useful to work with the numbers of moles, n_i of the various chemical product species in an arbitrary total mass of gas. This same mass of gas originates from a set of numbers of moles n_j of reactants, and we must impose that, no matter what reaction shifts occur, the number of <u>atomic</u> moles for each kind of atom (O, H, N, C, ...) is the same before and after reaction. As an example, suppose we have combustion of hydrogen in oxygen, with unknown amounts of water, molecular and atomic oxygen, molecular and atomic hydrogen and hydroxyl (OH) radicals formed. The oxidizer/fuel ratio is prescribed to be, say, R, so that, if we arbitrarily select $N_{O_2} = 1/2$, then

$$\frac{32 \times 1/2}{2N_{H_2}} = R \qquad ; \qquad N_{H_2} = \frac{8}{R} \qquad (12.2\text{-}1)$$

The reaction is

$$\frac{8}{R} H_2 + \frac{1}{2} O_2 \rightarrow n_{H_2O} H_2O + n_{O_2} O_2 + n_O O + n_{H_2} H_2 + n_H H + n_{O_H} OH \qquad (12.2\text{-}2)$$

Note that the list of candidate reaction products is arrived at from our background knowledge of what species actually do occur in significant quantities. For instance, we might not include O_2 or O if R were low enough to make the mixture fuel-rich, such that under those conditions, oxygen species would be mainly depleted.

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However, if we still did include them, with the proper equilibrium constants, we would still find some small concentrations of these molecules present. We would simply ignore them for practical purposes, as we ignore other exotic, but potentially real species, like HO_2, H_3, etc.

The <u>atomic</u> species are H and O and in order to conserve atoms, we must impose:

H-conservation: $\qquad \dfrac{16}{R} = 2n_{H_2O} + 2n_{H_2} + n_H + n_{OH}$ $\qquad\qquad$ (12.2-3)

O-conservation: $\qquad 1 = n_{H_2O} + 2n_{O_2} + n_O + n_{OH}$ $\qquad\qquad\qquad$ (12.2-4)

12.2.3 Equilibrium Relations

These are two equations involving the six unknown n_i's. Clearly because of the presence of the "decomposition products" O, H and OH, (plus O_2 if fuel-rich or H_2 if lean), conservation alone cannot tell us the composition of the burnt gas. We need four extra relationships, and these are the equilibrium conditions (laws of mass-action) for four elementary reactions selected so as to involve these decomposition products, as well as some of the "major" products, H_2O, CO_2, H_2. These could be, for example,

$$H_2O \rightleftarrows \frac{1}{2} H_2 + OH \qquad\qquad\qquad\qquad\qquad (12.2\text{-}5)$$

$$H_2 \rightleftarrows 2H \qquad\qquad\qquad\qquad\qquad\qquad\qquad (12.2\text{-}6)$$

$$H_2O \rightleftarrows H_2 + \frac{1}{2} O_2 \qquad\qquad\qquad\qquad\qquad (12.2\text{-}7)$$

$$O_2 \rightleftarrows 2O \qquad\qquad\qquad\qquad\qquad\qquad\qquad (12.2\text{-}8)$$

or any linear combination of them.

For each of the elementary reactions above, an equilibrium relationship must be satisfied. According to Ch. 16, these take the form

$$\frac{P_{H_2}^{1/2} P_{OH}}{P_{H_2O}} = K_1(T) \qquad\qquad\qquad\qquad\qquad (12.2\text{-}9)$$

$$\frac{P_H^2}{P_H} = K_2(T) \qquad\qquad\qquad\qquad\qquad\qquad (12.2\text{-}10)$$

$$\frac{P_{H_2} P_{O_2}^{1/2}}{P_{H_2O}} = K_3(T) \qquad\qquad\qquad\qquad\qquad (12.2\text{-}11)$$

$$\frac{P_O^2}{P_{O_2}} = K_4(T) \qquad\qquad (12.2\text{-}12)$$

where each P_i represents a partial pressure. These can be expressed in terms of the given <u>total</u> pressure P and the mole numbers n_i :

$$P_{H_2O} = P\frac{n_{H_2O}}{n} \qquad (n = n_{H_2O} + n_{O_2} + n_{H_2} + n_H + n_{OH})$$

$$P_{O_2} = P\frac{n_{O_2}}{n}$$

$$P_{OH} = P\frac{n_{OH}}{n} \qquad\qquad (12.2\text{-}13)$$

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And therefore the equilibrium relations become

$$\frac{n_{H_2}^{1/2}\, n_{OH}}{n_{H_2O}} = \sqrt{\frac{n}{p}}\ K_1(T) \qquad\qquad (12.2\text{-}14)$$

$$\frac{n_H^2}{n_{H_2}} = \frac{n}{p}\ K_2(T) \qquad\qquad (12.2\text{-}15)$$

$$\frac{n_{H_2}\, n_{O_2}^{1/2}}{n_{H_2O}} = \sqrt{\frac{n}{p}}\ K_3(T) \qquad\qquad (12.2\text{-}16)$$

$$\frac{n_O^2}{n_{O_2}} = \frac{n}{p}\ K_4(T) \qquad\qquad (12.2\text{-}17)$$

The equilibrium constants K_1, K_2, K_3, K_4 still depend on temperature. If temperature is known a-priori (or assumed at some step in an iteration process), are can either look their values up in some compilation of chemical properties (such as Table A.12 of Ref. 12.1), or more rationally, given the many possible combinations of

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elementary reactions, they can be built up from tabulated values of the standard chemical potentials (or Gibbs free energies) of the intervening species. The equilibrium constants are given in our example by

$$K_1 = \exp\left(-\frac{\frac{1}{2}\mu_{H_2}^0 + \mu_{HO}^0 - \mu_{H_2O}^0}{RT}\right) \qquad (12.2\text{-}18)$$

$$K_2 = \exp\left(-\frac{2\mu_{H_2}^0 - \mu_{H_2}^0}{RT}\right) \qquad (12.2\text{-}19)$$

$$K_3 = \exp\left(-\frac{\mu_{H_2}^0 + \frac{1}{2}\mu_{O_2}^0 - \mu_{H_2O}^0}{RT}\right) \qquad (12.2\text{-}20)$$

$$K_4 = \exp\left(-\frac{2\mu_O^0 - \mu_{H_2}^0}{RT}\right) \qquad (12.2\text{-}21)$$

where each $\mu_i^0(T)$ is the chemical potential of species i at 1 atm. pressure (standard chemical potential), at the given temperature T, and R is the universal gas constant in consistent units.

12.2.4 Conservation of Energy

Since the reactions occur at constant pressure, if we assume a well-insulated combustor, the enthalpy of the products must equal that of the reactants. If $h_i(T)$ is the molar enthalpy of the ith species at temperature T, we must have in our example:

$$\frac{8}{R}h_{H_2}(T_i) + \frac{1}{2}h_{O_2}(T_i) = n_{H_2O}\, h_{H_2O}(T) + n_{O_2}\, h_{O_2}(T) + n_O\, h_O(T)$$

$$+ n_{H_2}\, h_{H_2}(T) + n_H\, h_H(T) + n_{OH}\, h_{OH}(T) \qquad (12.2\text{-}22)$$

Notice the left hand side of this equation represents the enthalpy of the reactants ($\frac{8}{R}$ moles of H_2, $\frac{1}{2}$ mole of O_2) at their injection temperature, T_i, whereas the right

hand side represents that of the products, with each h_i evaluated at T, the final equilibration temperature, to be found. This is what is often called the "adiabatic flame temperature" for the given O/F and pressure.