

Chemical Combustion

0.1 Quick Review and Motivation

We saw in the previous chapter that rocket performance is fundamentally characterized by effective exhaust velocity, C and its equivalent specific impulse, I_{sp} . And we divided the form of effective exhaust velocities into two mostly independent parameters: c^* which captures the effect of the propellants' thermodynamics on performance and C_f which captures the effects of pressure and nozzle geometry.

For simple non-reacting substances with fixed properties in the gas phase, we can compute all of these parameters in closed form.

$$c^* = \frac{P_t A^*}{\dot{m}} = \sqrt{\frac{R_u T_t}{\gamma M_w}} \left[\frac{\gamma + 1}{2} \right]^{\frac{\gamma + 1}{2(\gamma - 1)}} \quad (1)$$

$$C_f = \frac{T}{P_t A^*} = \frac{\left(\frac{\gamma + 1}{2} \right)^{\frac{\gamma + 1}{-2(\gamma - 1)}}}{M_e \sqrt{1 + \frac{\gamma - 1}{2} M_e^2}} \left[\gamma M_e^2 + 1 - \frac{P_0}{P_e} \right] \quad (2)$$

$$\begin{aligned} C &= \frac{T}{\dot{m}} = C_f c^* \\ &= (P_e - P_0) \frac{A_e}{\dot{m}} + \sqrt{\frac{2\gamma}{\gamma - 1} \frac{R_u T_t}{M_w} \left[1 - \left(\frac{P_e}{P_t} \right)^{(\gamma - 1)/\gamma} \right]} \end{aligned} \quad (3)$$

I've been careful to note that $R = \frac{R_u}{M_w}$ in these equations because as we saw last lecture, the molecular weight of rocket gasses, M_w has a first-order effect on performance.

And I will replay a plot from last lecture that captures how the various parameters impact specific impulse.

The thing that pops out most clearly from Figure 0.1 is that T_t/M_w has the largest influence on specific impulse and exhaust velocity. For purely gasdynamic non-reacting rockets we have little influence on T_t and so our primary knob is M_w . And indeed in the last lecture we saw that Hydrogen and Helium make nice *cold-gas propellants* due to their low molecular weights.

But to get performance useful for space travel, we need to pump T_t up. And increasing T_t requires an energy source of

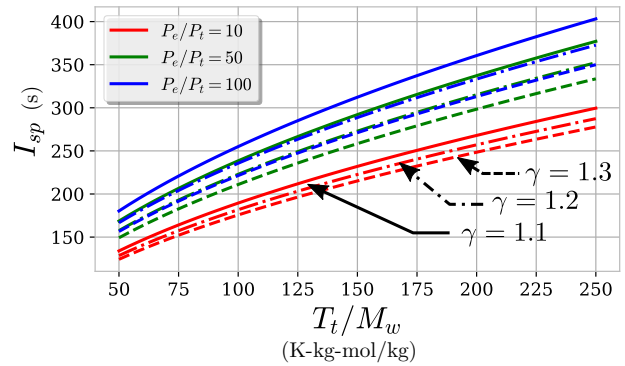


Figure 0.1: How specific impulse varies

which there are fundamentally three: exothermic chemical reactions, some form of external heat input or non-thermal body forces. We will cover the external heat input case and non-thermal body forces later when we get to electric and nuclear propulsion. But today the focus is on the most ubiquitous and versatile source of energy - chemical energy.

Why is chemical energy so useful? It comes down to the combination of energy density and power density. Rockets must release and leverage an enormous amount of energy in a very short period of time and mass is of first-order importance as we saw in the Rocket Equation. Look at how chemical combustion of rocket propellants compare with other sources of energy:

Energy Source	Power Density	Energy Density
SSME H ₂ /O ₂	2.8 MW/kg	19.4 MJ/kg
Nuclear Fission ¹	0.08 MW/kg	68.9 MJ/kg
Lilon Battery	3×10^{-4} MW/kg	0.7 MJ/kg
Triple-junction Solar Panel[1]	7×10^{-5} MW/kg	unlimited

Table 0.1: Comparison of the energy and power density of several energy sources

Table 0.1 demonstrates the unique combination of power and energy density reacting chemical propellants provide. The Hydrogen/Oxygen combination combusted in the Space Shuttle Main Engine provides a useful (exhaust kinetic energy) power density of 2.8 MW/kg. The nuclear fission-powered NERVA rocket of the 1960's is more than $30 \times$ less! Nuclear fission does provide higher energy density (hence the interest for high energy interplanetary missions) but only by a factor of about 3.

And looking at electrical energy sources (batteries and solar arrays) gives an even more dramatic contrast. Lithium ion batteries store $25 \times$ less energy in a given mass and liberate that energy *four orders of magnitude* more slowly than the chemical energy release in hydrogen, oxygen combustion.

Chemical combustion provides a uniquely valuable energy source for a moving vehicle. But where does this energy reside?

0.2 The Origins of Chemical Energy

When looking at the total intrinsic energy of a substance in a closed system, it is composed of the potential and kinetic energy of its particles,

$$E = E_p + E_k \quad (4)$$

where kinetic energy is the motion of particles with respect to the systems center of mass². This internal kinetic energy manifests macroscopically as temperature. The potential piece may consist of several components: body forces from external fields (e.g. electrostatic, magnetic), nuclear potential, chemical potential, intermolecular, etc. For the purposes of this lecture we will only be considering the kinetic and chemical-component of potential energies and we will refer to the kinetic component as *sensible energy*:

$$E = E_{chemical} + E_{sensible} \quad (5)$$

In its most basic form, chemical energy is potential energy stored within the bonds between atoms. The presence and proximity of electrons in orbitals surrounding atomic nuclei with oppositely charged nucleus and electrons in other orbitals or other atoms produce an electrostatic potential field. And particles moving in this field experience a force and gain or lose energy.

In non-reacting mixtures, the association of bonded atoms and their electron orbitals are essentially static. We consider the bond energy *latent* energy as it is hidden and unavailable without reaction. Molecules have anisotropic distribution of charge and so generate inter-molecular forces (and therefore potential fields) that are responsible for many thermodynamic behaviors such as phase states.

The electron configuration around atoms also generate inter-atomic forces. These forces are responsible for chemical bonding of atoms into molecules. At very short separations, the effective inter-atomic forces are strongly repulsive³. At intermediate ranges, the forces transition to attractive and the forces dissipate at long distances, as expected.

The simplest useful model for these inter-atomic forces is the Lennard-Jones (LJ) potential:

$$V_{LJ} = 4\epsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right] \quad (6)$$

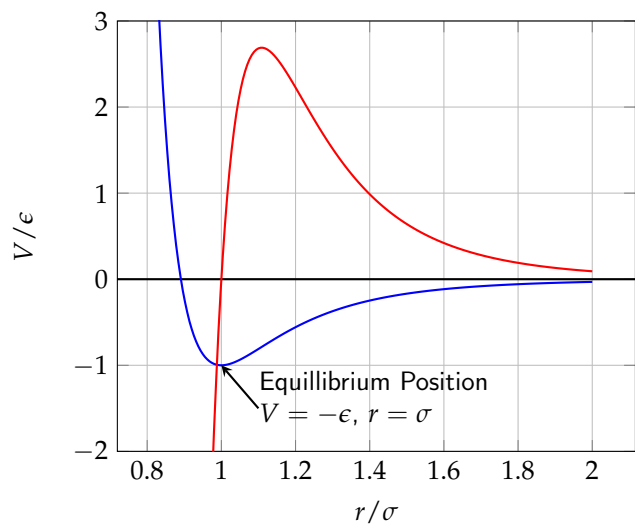


Figure 0.2: The normalized form of the Lennard-Jones potential field (blue) and force field (red).

The force associated with the potential field is $F = \frac{dV}{dr}$. The minimum in the potential field at $r = \sigma$ corresponds with the point of zero force and thus becomes the *equilibrium position* in the system. A perturbation to the left or right will result in a force resisting the perturbation, returning the system to the equilibrium point. In the case of a diatomic system, the distance between the atoms (the bond length) will be roughly defined by this minimum in potential energy.

Furthermore, the depth of the minimum trough represents the equilibrium potential energy associated with a system. Moving particles apart requires work to be performed in the potential field and the limiting value of this work is that required to "climb" out of the potential well, ϵ . And so

¹NERVA flight-weight fission reactor

²for flowing systems with non-zero bulk motion, the relevant energy measure is enthalpy H which we will use later

³In reality this repulsive "force" is just a model for quantum effects such as the Pauli exclusion principle. There is no fundamental force carrier at short distances - instead configurations with small separation are unlikely or forbidden by quantum mechanics and we can model this classically as a strong repulsive force

the depth of the well represents the *bond energy* for atomic interactions⁴.

For real inter-atomic potentials, σ and ϵ are not independent. In general, $\sigma \propto 1/\epsilon$ so that bonds with shorter bond length ($\sim \sigma$) have larger potential wells ($\sim \epsilon$). Figure 0.3 illustrates this trend graphically and Table 0.2 shows it quantitatively.

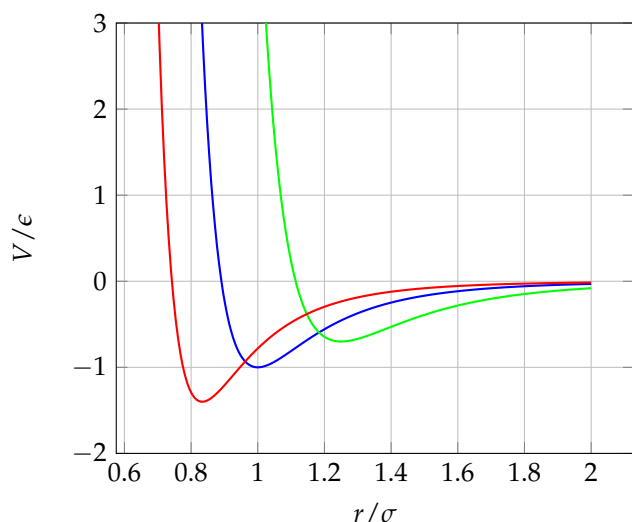


Figure 0.3: Real interatomic potentials show deeper well minimums as the bond length shortens. This results in the observation that bond energy is inversely proportional to bond length.

Note some trends in Table 0.2.

- For a given set of atoms, the inverse trend of energy and bond length holds true. It *does not* hold true when looking at different atom pairs.
- Double and triple bonds have **much larger** bond energies. In fact this is highly non-linear - the N=N double bond has more than twice the energy of the N-N.
- With a couple of exceptions, bond energy tends to be higher for atom pairs further apart on the periodic table. This is related to the concept of *electronegativity* which we will discuss more below.

All chemical energy fundamentally arises from the re-configuration of electrons and atoms in this complex potential space. We speak of making and breaking bonds as a model for how this reconfiguration process occurs. Depending on the totality of these bond changes and their associated energy, the system may transfer some chemical energy (derived from bonds) to sensible or vice-versa. In the

⁴For molecular interactions, moving in and out of the well typically represents a phase change and the depth of the well represents the latent heat associated with the phase change

Bond	Avg. Energy (kJ/mol)	Avg. Length (Å)
H-H	432	0.74
N-N	167	1.45
F-F	155	1.42
O-O	142	1.48
H-F	565	0.92
H-O	459	0.96
H-Cl	428	1.27
H-S	363	1.34
H-C	413	1.09
C-F	485	1.35
C-O	358	1.43
C-C	346	1.54
C=C	602	1.34
C≡C	835	1.20
N=N	418	1.25
N≡N	942	1.10
N=O	607	1.21
O=O	494	1.21
C=O	799	1.20
C≡O	1072	1.13

Table 0.2: Abbreviated bond energy and length table.

cases where the net bond energy before the re-configuration process is *more negative* than the final state we say that the process is *endothermic* and energy is transferred from sensible into chemical energy. Conversely, if the initial state's bond energy is *less negative* than the final state, we call the process *exothermic* and energy is transferred from chemical bond energy to sensible energy. If the direction of movement and magnitudes of energy don't make sense here yet, don't worry we will return to this.

Electronegativity, Oxidizers and Fuels

In the third bullet above, we mentioned the concept of electronegativity. Electronegativity represents an atoms affinity or attraction for a new electron. It is a fundamental characteristic of the electron orbital configuration around atoms and is a large factor driving the strength and character of chemical bonding and reactions.

We mentioned that bond energy tends to be higher for atoms further apart on the periodic table. This is because those atoms have larger difference in electronegativity. Low electronegativity implies that the atom is not especially attached to it's valence (most weakly held) electrons and is willing to donate one in a bond. High electronegativity implies the opposite - that it is looking for another electron to add to its valence band and will gladly except one donated. Atoms with large differences in electronegativity are thus happy (stable) and breaking them apart requires a

great deal of energy.⁵

Here is the periodic table colored by electronegativity showing this effect.

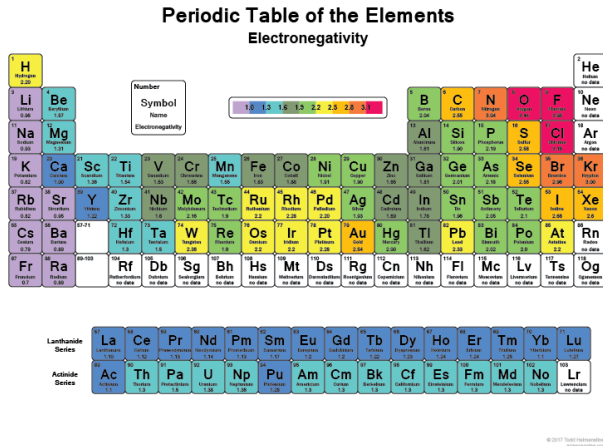


Figure 0.4: Periodic table colored by electronegativity. Note the left-to-right trend and the very high values of the Group 16 and Group 17 (Chalcogens and Halogens respectively) elements.

Notice the very high electronegativity of the elements in the upper right, Group 16 and Group 17 elements and the trend towards lower electronegativity as you proceed to the left. We call the high electronegativity component(s) of a propellant system *oxidizers* and the lower electronegativity component(s) *fuels* out of convention.

In summary, when we speak of chemical energy, we are referring to the potential energy stored in the bonds of molecules. To *release* chemical energy in an *exothermic* reaction, the net potential energy in the totality of bonds in the final state must be *lower* than the net potential energy in the initial state. And this reconfiguration process we call *chemical reaction*.

0.3 First Law of Thermodynamics

Now we will zoom out a bit and discuss all of this bond business at the macro scale of chemical reactions. Remember we are aiming to get to the magic T_i in the specific impulse equation and understand how our choice of propellants influence it. We understand now that the energy that powers this is held in chemical bonds, but how does this quantitatively manifest in our ability to drive T_i up?

But before we go there a bit of nomenclature. We will be going back and forth between *extensive* properties (those

⁵We are glossing over some important subtlety in the interest of expediency regarding bond energy and electronegativity. [See this paper for a more complete explanation.](#)

that depend on the quantity of substance in the system) and *intensive* properties (those that are intrinsic and do not depend on quantity). Extrinsic properties, such as U for internal energy or S for entropy are denoted in capital, while their intrinsic equivalents are in lower case. Later we will want to work in *mass-intensive* units where quantities are in mass but for much of this lecture we will be working in *mole-intensive* units, with mole number being the quantity.

So for instance, the internal energy of a system is composed of its mean intrinsic internal energy times the mole number (quantity) in the system:

$$U = N\bar{u} \quad (7)$$

For a system that is an ideal mixture, internal energy would be

$$U = \sum_i n_i \bar{u}_i \quad (8)$$

noting that for some properties, such as entropy, we will see a more complex *mixing rule*. We will also occasionally use normalized mole number, or *mole fraction*, X_i where

$$X_i = \frac{n_i}{\sum_i n_i} \quad (9)$$

We will be talking a lot about *standard* or *reference* states, denoted with the superscript $^\circ$. Because most of the calculations we will be doing involve *changes* in energy, we need a reference from which to define these changes. And in general it may be impossible (as in the case of enthalpy) or impractical to define an absolute value. So the standard state represents a convenient place to define as zero. And for our purposes the standard thermodynamic state will be $T = 298.15 \text{ K}$, $P = 1 \text{ bar}$.

To complement T and P , we will need a set of standard or reference molecules (or species) for each atom in our reactions. In this case, the reference state is defined such as that the net chemical (bond) energy in the reference molecule is zero at the standard thermodynamic state. The choice of reference molecules is arbitrary but we will use the JANAF/NIST convention of the most stable molecular state for that atom. So in the case of the diatomic gasses (H_2 , N_2 , O_2 , etc) the reference is the diatomic form whereas for Carbon, it is crystalline C(graphite). In summary, a reaction component's thermodynamic state will always be defined in reference to a standard state that has, by definition, zero sensible and chemical energy.

Standard Enthalpy of Reaction

Similarly we can define a *Standard Enthalpy of Reaction*, ΔH_{rxn}° , that represents the ensemble summation of the bond reconfigurations associated with a chemical reaction when held at the standard state.

$$\Delta H_{rxn}^{\circ} = \sum_i n_i \Delta_f H_i^{\circ}(T_{ref})|_{product} - \sum_i n_i \Delta_f H_i^{\circ}(T_{ref})|_{reactant} \quad (10)$$

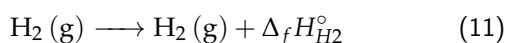
ΔH_{rxn}° represents the amount of energy converted from latent chemical to sensible energy in a chemical reaction and is essentially a statement of the First Law of Thermodynamics (conservation of energy). Because it is defined at the reference state, the sensible energy must be moved in or out of the system such as to keep the temperature at the reference temperature and as such is also commonly called *Standard Heat of Reaction*.

We touched on *exothermic* and *endothermic* reactions in the discussion about bond energy earlier and indeed the same logic applies to Standard Enthalpy of Reaction.

- $\Delta h_{rxn}^{\circ} < 0 \Rightarrow$ Exothermic (heat releasing) Reaction
- $\Delta h_{rxn}^{\circ} > 0 \Rightarrow$ Endothermic (heat absorbing) Reaction

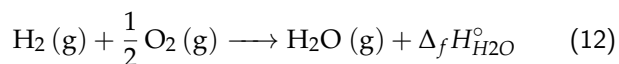
But what are these $\Delta_f H_i^{\circ}$? They are the *Standard Enthalpy of Formation* and capture the latent chemical energy in each molecule at the standard state and relative to the reference species represented in their atomic makeup. State differently, Standard Enthalpy of *Formation* is the Standard Enthalpy of *Reaction* for the elementary chemical reaction that represents the molecule's formation.

A trivial example would be for Hydrogen whose elementary formation reaction is:



where we can see that since H_2 is its own reference molecule, its standard heat of formation, $\Delta_f H_{H_2}^{\circ}$ is, by definition, zero.

A more interesting example is water.



and in this case the standard heat of formation is non-zero. But how do we arrive at a number for $\Delta_f H_{H_2O}^{\circ}$? One method is to carefully measure it in a calorimeter (Figure 0.5). The reactants are introduced, induced to react at the reference temperature and the amount of heat entering or leaving is carefully measured. And indeed this has been done for many many substances and are available in tabular form. One can also infer heat of formation from less direct measurement, such as behavior of gasses in a shock tube. And detailed quantum mechanics simulations may produce good results in certain cases.

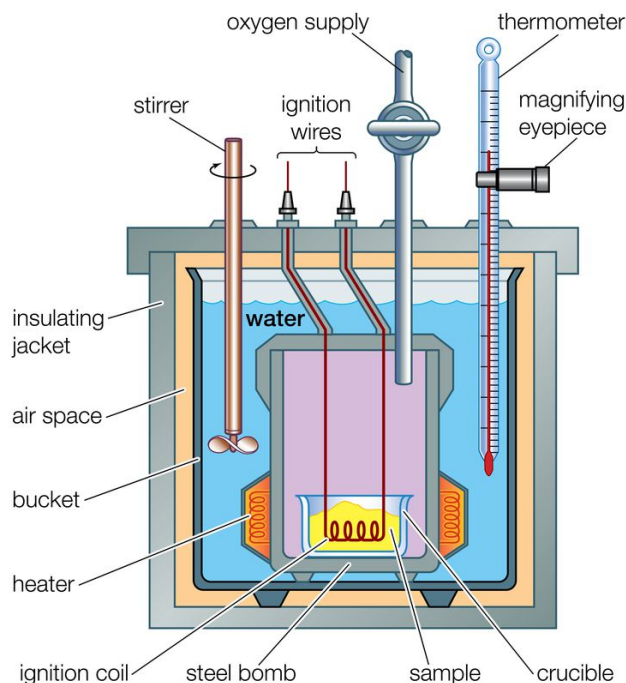


Figure 0.5: A calorimeter can be used to measure heat of reaction for self-sustaining exothermic reactions such as the water formation reaction. From [Britannica Online](#)

Bond Energy Method

We can also take a stab at it ourselves using the bond energy tables we saw earlier. The bond-energy method relies on the assumption that the tabulated average bond energies are a good representation of real molecular bonds. However as discussed before, the potential fields that atoms exist in is complex and there are many molecular configurations that make this assumption partly or wholly invalid.

With those caveats in mind, let's take a shot at water. The method is quite simple - we take a look at the formation reaction and compute the sum of bond energies for each molecule in the reaction.

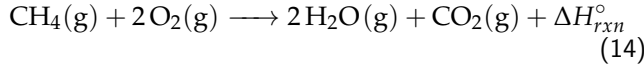
$$\begin{aligned} \Delta_f H_{H_2O}^{\circ} &= 2 \times (H-O) - [1 \times (H-H) + \frac{1}{2} \times (O=O)] \\ &= (2)(459) - (1)(432) - (0.5)494 \\ &= -239 \text{ kJ/mol} \end{aligned} \quad (13)$$

The actual value is around -241 kJ/mol, pretty darn close!! This method will generally work well with bonds that are mostly symmetric and covalent. Highly ionic compounds and covalent compounds with inter-bond effects will fair more poorly. Pratically most people will just use standard tables (such as [JANAF Tables](#)) for standard heat of formation. But the bond energy method can come in handy

if it is difficult to find tabulated data for a more exotic compound.

Adiabatic Combustion

Now let's return to standard enthalpy of reaction by way of example - the stoichiometric oxygen, methane combustion reaction.



where we note the capital H to represent the extensive heat of reaction for the multi-mole product.

In this case we have gaseous methane reacting with molecular oxygen producing water and carbon dioxide. We all know this to be a *highly* exothermic reaction - it is what powers our stoves, hot-water heaters and furnaces. I will use tabular data for the heats of formation

$$\begin{aligned} \Delta H_{rxn}^\circ &= \sum_i n_i \Delta_f H_i^\circ(T_{ref})|_{product} - \sum_i n_i \Delta_f H_i^\circ(T_{ref})|_{reactant} \\ &= 2 \times \Delta_f H_{\text{H}_2\text{O}}^\circ + \Delta_f H_{\text{CO}_2}^\circ - 2 \times \Delta_f H_{\text{O}_2}^\circ - \Delta_f H_{\text{CH}_4}^\circ \\ &= (2)(-240) + (-394) - (-75) \\ &= 800\text{kJ} \end{aligned} \quad (15)$$

remembering that the heat of formation for O_2 is zero as it is a reference molecule. We implicitly assumed that this reaction happens *isothermally* because we used only the enthalpies of formation for the species which is, by definition, the enthalpy at the reference state. In reality typical combustion reactions look a lot more like

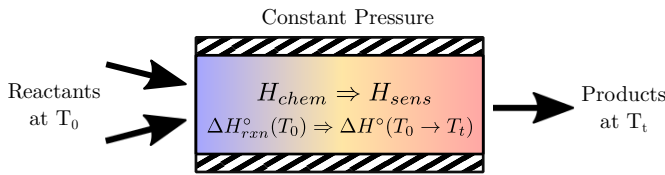


Figure 0.6: *Adiabatic Combustion* is typically considered a constant pressure flow process with no adiabatic (no heat transfer) boundary conditions. Reactants are introduced at some rate in one end, combustion occurs in the reactor and products emerge at the other end

where reactants enter at a constant *flowrate* and the reaction proceeds continuously at constant pressure with products emerging at the other end. In this view, the latent chemical energy liberated in the reaction (ΔH_{rxn}°) are converted to sensible enthalpy in the emerging product stream ($\Delta H^\circ(T_0 \rightarrow T_t)$) raising its temperature from T_0 to T_t .

A view of the constant-pressure combustion problem in enthalpy/temperature space is nicely illustrated in this diagram from the Stanford ME371 lecture notes[2]

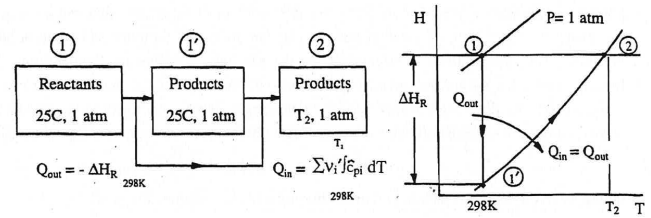


Figure 0.7: Enthalpy-temperature plot for an adiabatic constant-pressure reaction. From [2]

For the methane / oxygen reaction, we have the heat of reaction and a set of assumed reaction products so we should be able to compute the combustion flame temperature, T_t , right? Let's give it a shot. Assuming the reactants start the reaction in the standard state, and that after holding the system at the reference temperature we removing heat and add it to the sensible energy in the products, conservation of energy states:

$$\sum_i n_i h_i^\circ(T_{ref})|_{reactant} = \sum_i n_i h_i^\circ(T_t)|_{product} \quad (16)$$

where h_i° is the *total enthalpy* consisting of both the sensible and latent (chemical) components:

$$\begin{aligned} h_i^\circ(T) &= h_i^{chemical} + h_i^{sensible} \\ &= \Delta_f H_i^\circ(T_{ref}) + \Delta h_i^\circ(T) \\ &= \Delta_f H_i^\circ(T_{ref}) + \int_{T_{ref}}^T C_p(T) dT \end{aligned} \quad (17)$$

$\Delta h_i^\circ(T)$ is the difference in sensible enthalpy of the substance between temperature T and it's reference temperature.

Combining Equation (10), Equation (16) and Equation (17) we can arrive at

$$\begin{aligned} -\Delta H_{rxn}^\circ &= \sum_i n_i \Delta h_i^\circ(T)|_{product} \\ &= \sum_i n_i \int_{T_{ref}}^T C_p(T) dT|_{product} \end{aligned} \quad (18)$$

This can be interpreted as

With adiabatic boundary conditions the latent chemical energy liberated in the combustion reaction is transformed into sensible energy in the form of a temperature rise in the products.

Because of the temperatures involved, constant specific heat is a very bad assumption and so we have to either use tables of specific enthalpy as a function of temperature or integrate with tabulated C_p as a function of temperature. Happily, JANAF tables provide a nice, pre-calculated helper as a function of temperature:

Enthalpy Reference Temperature = $T_r = 298.15\text{ K}$				Standard State Pressure = $p^\circ = 0.1\text{ MPa}$			
T/K	C_p°	S°	$-[G^\circ - H^\circ(T_r)]/T$	$H - H^\circ(T_r)$	$\Delta_f H^\circ$	$\Delta_f G^\circ$	$\log K_f$
0	0.	0.	INFINITE	-9.904	-238.921	-238.921	INFINITE
100	33.299	152.388	218.534	-6.615	-240.083	-236.584	123.579

Figure 0.8: JANAF tables provide a bunch of useful tabulated thermodynamic data. We are interested in the high-lighted value now, but we will touch upon many of the others in the upcoming sections.

Note the boxed parameter is Δh_i° exactly and using it we can plot the right hand side Equation (18) and graphically look for the intersection with ΔH_{rxn}° :

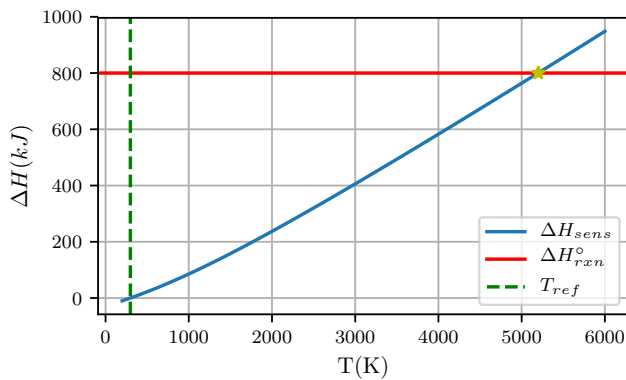


Figure 0.9: We can determine graphically that the predicted adiabatic flame temperature for methane air is $> 5000\text{ K}$. Beware, this is incorrect as we will soon see!

The result is an adiabatic flame temperature $> 5000\text{ K}$. However if you go do the experiment, you will measure a value a little over 3000 K - we're off by 2000 degrees!!! How could this be?

The issue is that at the high temperatures that adiabatic combustion takes place, there are many more species present in the mix than just the products of the reaction we wrote above. At these temperatures, there are non-negligible dissociation reactions that break the products down into species that would not be energetically favorable at low temperatures. I will jump the gun a bit and show a result for these compositions as a function of temperature before we know exactly how to compute them:

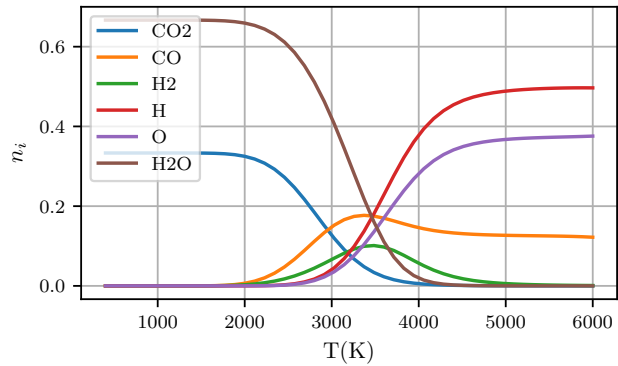
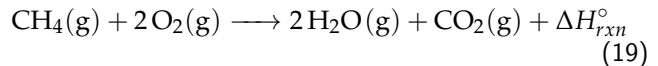


Figure 0.10: A detailed chemical equilibrium result for the adiabatic methane/oxygen combustion reaction. Note that the products are only water and carbon dioxide at lower temperatures. Also note that some products have been removed for clarity here.

So life gets more complicated and we need to move into full equilibrium chemistry to continue.

0.4 Equilibrium Thermodynamics

Let's return to our methane, oxygen reaction and how we thought about heat and temperature.



We presumed that the reaction is *one-directional* and all reactants go solely to the products H_2O and CO_2 . We used the first law of thermodynamics to make sure energy balanced and computed the resulting combustion temperature. It turns out many reactions are two-way streets and can go either direction depending on the thermodynamic conditions. In one way, a combustion is like making soup - we put a bunch of stuff in, release some energy and the result has chunks of ingredients and mixtures of those ingredients.

So what does our soup looks like when we take oxygen and methane and put them in a adiabatic, constant pressure combustor? To answer this we will need to start with the assumption that the soup making is well-approximated by *equilibrium thermodynamics*. Subject to some small caveats, this assumption is a very good one for chemical rockets.

Much of this derivation follows the works of [2-6].

Second Law of Thermodynamics

Equilibrium implies balance - in this case the balance between the forces (or potentials) pushing reactants go to products with those pushing products go to reactants. Note that equilibrium does not imply stasis. In fact there are constant dynamics at the molecular level. But at the macroscopic level, if the ensemble sum of these reactions balance,

we consider the system in *dynamic equilibrium*, a very useful construct. Thermodynamics is also not picky - it doesn't care what reactants and products we wrote down earlier. It will drive towards equilibrium using whatever species it can construct from the atoms and energy we put in the box.

To quantify this behavior, we will invoke the Second Law of thermodynamics which states that for a system in isolation at (no heat, work or mass transfer with the environment or constant U and V), entropy will tend towards its maximum,

$$dS_{U,V} \geq 0$$

and at equilibrium will achieve that maximum

$$dS_{U,V} \equiv 0 \Rightarrow S = S_{max} \quad (20)$$

A quick aside on Statistical Mechanics

I think it is important to pause here for a moment and talk about what the Second Law is saying from the statistical point of view. Most or all of you will have learned classical thermodynamics in which the laws are defined largely empirically by *careful study of the ways matter behaves*. The second law is often derived from the observation that heat tends to flow from hot places to cold places rather than vice-versa. And while these observations led scientists to the correct answers, they don't explain *why* things behave this way.

Statistical mechanics came along a bit later and aspired to describe the way matter works at the microscopic level directly and from first-principles. Of course systems we care about at the macro level consist of a very large number of elements (atoms, molecules) at the micro-level so what we do is develop the *statistics* for how these microscopic particles behavior looks in aggregate (hence the name). And while we don't have the time to go deep here, it is important to point out that statistical mechanics is extremely successful at arriving the laws of thermodynamics (and other results for matter) simply by applying first principles to large ensembles of particles.

The one result from SM I want to present here is the result for entropy

$$S = -k_B \sum_i p_i \ln p_i \quad (21)$$

where k_B is Boltzmann's constant and the p_i are the enumerated probabilities for all of the possible energy micro-states of the system. If we presume that all the energy states for a system are equally likely (not necessarily true, but useful for many problems) we arrive at Boltzmann's famous formula for entropy

$$S = k_B \ln \Omega \quad (22)$$

where Ω is simply the number of possible microstates available to the system. Thus we can interpret maximization of entropy as a statistical phenomenon. Maximal entropy in the macro-state corresponds with maximizing the number of micro states available in the system. Or if we invert this we can say that the configuration of the system with the most available micro-states is *most likely*, or *expected* and in that configuration we would see Entropy maximized!

A simple example might make this a bit more clear. Imagine we take a box connected to the world at constant temperature. Now partition it in the middle and fill one half up with some gas. Remove the barrier in the middle and let the molecules inside move around in the larger volume. After some time, the molecules inside will spread out to roughly fill the volume and, since we are connected to a constant temperature world, will settle into the same kinetic energy distribution (temperature) as before the change.

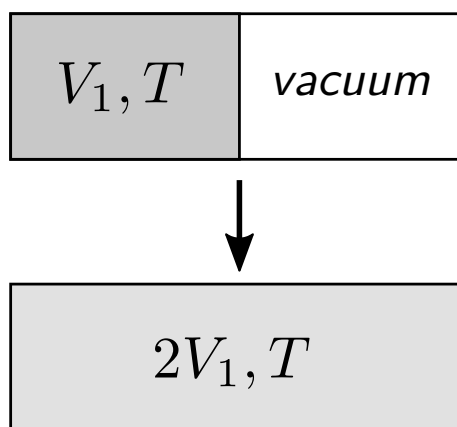


Figure 0.11: Adiabatic expansion problem

The question is, how was the entropy of the system changed? From the SM perspective we will notice that there are more *microstates* available to the gas particles. You can think of microstates as their positions and velocities. We know the velocity distribution is the same because the temperature hasn't changed. But because the volume has doubled, the number of places each particle could be has doubled and thus total number of microstates available to the system has doubled. Or

$$\begin{aligned} \Omega &\propto V \\ \Rightarrow \frac{\Omega_f}{\Omega_0} &= \frac{V_f}{V_0} = 2 \end{aligned}$$

By Boltzmann's equation above, we see that

$$S_2 - S_1 = k_B \ln(2\Omega_1) - k_B \ln(\Omega_1) = k_B \ln(2)$$

We can do this exercise purely using classical thermodynamics and macro state variables as well by leveraging the Gibbs equation which states

$$dS = \frac{1}{T}dU + \frac{P}{T}dV$$

Because T is constant, dU is zero and we can substitute the ideal gas law into the last term to arrive at

$$dS = R \frac{1}{V} dV$$

Integrating both sides

$$\int_{S_0}^{S_f} = R \int_{V_0}^{V_f} \frac{1}{V} dV = S_f - S_0 = R \ln \left(\frac{V_f}{V_0} \right) = R \ln(2)$$

Look familiar?

The important point here is that a system will tend towards equilibrium over time. And at equilibrium, the most micro-states are available to the system. So the if we find the configuration that maximizes microstates, we have found the equilibrium macrostate.

Back to Classical Thermo

Now if we look at the entropy of a system consisting of multiple chemical species

$$S = S(U, V, N_1, \dots, N_I)$$

and taking the differential of this

$$dS \equiv \left(\frac{\partial S}{\partial U} \right)_{V, n_i} dU + \left(\frac{\partial S}{\partial V} \right)_{U, n_i} dV + \sum_{i=1}^I \left(\frac{\partial S}{\partial n_i} \right)_{U, V, N_j \neq n_i} dn_i$$

where

$$\left(\frac{\partial S}{\partial U} \right)_{V, n_i} \equiv \frac{1}{T}$$

$$\left(\frac{\partial S}{\partial V} \right)_{U, n_i} \equiv \frac{P}{T}$$

and by analogy we will define a new parameter, the *chemical potential*, μ_i

$$\left(\frac{\partial S}{\partial n_i} \right)_{P, T, N_j \neq n_i} \equiv \frac{-\mu_i}{T}$$

In the fully isolated (U, V constant) system described above, this means

$$dS_{U, V} = - \sum_{i=1}^I \frac{\mu_i}{T} dn_i.$$

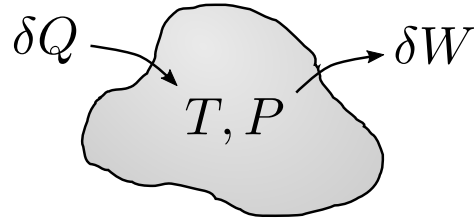
In this form we can see that μ_i captures the direction and magnitude that an incremental change in component

i changes the entropy of the system. And finally we can write the Gibbs equation:

$$dS = \frac{1}{T}dU + \frac{P}{T}dV - \sum_{i=1}^I \frac{\mu_i}{T} dn_i \quad (23)$$

This is helpful but our combustor is a constant-pressure flow reactor, not an isolated control mass. It may exchange work with the environment so instead of internal energy and volume, we must use temperature and pressure as our constraint variables. But wait, *temperature??* - we are trying to *compute* temperature not *impose* it as a constraint! Not to worry, this whole combustion business is a two-step, iterative process - first we assume some temperature and compute the equilibrium composition, then we test whether that temperature and composition are compatible with our First Law energy balance. If not, we pick a different temperature and repeat until we converge.

Looking at a small control mass in the reactor,



we can combine the First Law

$$\delta W - \delta Q + dU = (PdV - VdP) - \sum_{i=1}^I \mu_i dn_i \quad (24)$$

and the Second Law

$$dS - \frac{\delta Q}{T} \geq 0$$

to arrive at

$$TdS - dU - PdV \geq 0 \quad (24)$$

where happily all of the variables are now state variables. Now we recognize that the left hand side of Equation (24) is

$$TdS - dU - PdV = d[TS - (U + PV)]_{P, T} = d[TS - H]_{P, T}$$

and we will define the Gibbs function or Gibbs Energy

$$G \equiv H - TS \quad (25)$$

such that Equation (24) can now be written:

$$dG_{T, P} \leq 0.$$

This equation is the corollary to Equation (20) that we saw for constant U, V and it states

For a constant temperature and pressure process, the Gibbs energy must tend towards a minimum.

It is a result of the Second Law when applied to a constant temperature and pressure system exchanging work and heat with a reservoir.

For a *multi-component* system comprising I chemical species, the Gibbs energy is a function of temperature, pressure and the quantities of the species present:

$$G = G(P, T, N_1, \dots, N_I)$$

If we take the complete differential of the Gibbs energy

$$dG \equiv \left(\frac{\partial G}{\partial T} \right)_{P, n_i} dT + \left(\frac{\partial G}{\partial P} \right)_{T, n_i} dP + \sum_I \left(\frac{\partial G}{\partial n_i} \right)_{P, T, N_j \neq n_i} dn_i \quad (26)$$

Differentiating Equation (25)

$$dG = dH - TdS - SdT$$

and combining with Equation (23), we obtain

$$dG = -SdT + VdP + \sum_I \mu_i dn_i.$$

Recognizing

$$\begin{aligned} \left(\frac{\partial G}{\partial T} \right)_{P, n_i} dT &\equiv -S \\ \left(\frac{\partial G}{\partial P} \right)_{T, n_i} dP &\equiv V \end{aligned}$$

we see this is equivalent to Equation (26) with

$$\left(\frac{\partial G}{\partial n_i} \right)_{P, T, N_j \neq n_i} = \mu_i. \quad (27)$$

But the partial differential $\left(\frac{\partial G}{\partial n_i} \right)_{P, T, N_j \neq n_i}$ is simply how much Gibbs energy an differential number of moles dn_i carry which is, by definition, the partial molal Gibbs energy of species i , g_i . And so finally we have shown that

$$\mu_i = g_i, \quad (28)$$

a *very important and useful result*. At equilibrium we know that

$$dG = 0 = \sum_{\text{Products}} n_i \mu_i - \sum_{\text{Reactants}} n_i \mu_i = \sum_I (N_{ip} - N_{ir}) g_i \quad (29)$$

For an ideal mixture, which is all we will dive into here, the partial molal Gibbs energy of species i , g_i depends on the temperature (which we're holding constant) and the species

partial pressure in the mixture P_i . How does g_i vary with pressure?

For fixed T

$$ds_i = -R \frac{dP_i}{P_i}$$

and because

$$dg_i = -Tds_i(T, P_i)$$

it can be shown that

$$g_i(T, P_i) - g_i(T, P^\circ) = RT \ln \left(\frac{P_i}{P^\circ} \right) \quad (30)$$

Combining with Equation (29) we arrive at

$$\sum_I (N_{ip} - N_{ir}) g_i(T, P^\circ) + RT \sum_I (N_{ip} - N_{ir}) \ln \left(\frac{P_i}{P^\circ} \right) = 0.$$

Note that the standard or reference state Gibbs molal energy, g_i° is only a function of temperature

$$g_i(T, P^\circ) = g_i^\circ(T).$$

Defining

$$\Delta G^\circ(T) = \sum_I (N_{ip} - N_{ir}) g_i^\circ(T)$$

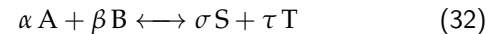
we rearrange the equation above to obtain

$$\prod_I \left[\frac{P_i}{P^\circ} \right]^{N_{ip} - N_{ir}} = e^{\left(\frac{-\Delta G^\circ(T)}{RT} \right)}.$$

With analogy to enthalpy of formation, we can define a standard Gibbs energy of formation, $\Delta_f G_i^\circ(T)$ as the Gibbs energy of reaction for the formation reaction computed in the same way as enthalpy of formation. This leads to the final and very useful form of the equilibrium equation:

$$K_p(T) = \prod_I \left[\frac{P_i}{P^\circ} \right]^{N_{ip} - N_{ir}} = e^{\left(\frac{-\sum_I (N_{ip} - N_{ir}) \Delta_f G_i^\circ(T)}{RT} \right)}. \quad (31)$$

Equation (31) defines the equilibrium constant, K_p which you may remember from chemistry. Historically, this was derived in terms of the so-called *law of mass action* which related the rates of the forward and backward reaction to the stoichiometry and concentration of participating species. Using the model one-step reaction



and setting the rates equal to each other thus would define the dynamic equilibrium condition:

$$k_+[A]^\alpha[B]^\beta = k_-[S]^\sigma[T]^\tau$$

where $[A]$, $[B]$, etc are molar concentrations of the species and k_+ and k_- are the forward and reverse reaction rates.

This leads to the definition of the concentration equilibrium constant, K_c as:

$$K_c = \frac{k_+}{k_-} = \frac{[S]^\sigma [T]^\tau}{[A]^\alpha [B]^\beta}$$

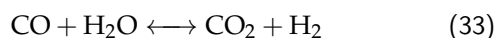
where we note the analogy to the pressure-explicit equilibrium constant, K_p above⁶.

The reasoning (in terms of rates proportional to reaction stoichiometry) is actually not valid in general (minimization of Gibbs energy is the proper interpretation) but does produce the correct form for reaction constant and it holds for most elementary reactions. It is also commonly taught and does provide some useful intuition as to what equilibrium constants represent.

It may not be completely clear yet, but this result combined with thermodynamic property values, gives us all that we need to postulate a set of species, formulate chemical reactions involving them and then solving for the equilibrium composition as a function of temperature and pressure.

Example: Simple Equilibrium

Let's do an example to apply all that we have gone through. The water gas shift reaction is a famous example:



Even though our trusty JANAF table (see Section 0.3) tabulates the Gibbs energy of formation for us, computing ΔG° becomes a bit bothersome to compute by hand. So they also provide another useful set of tabulated values in the form of $\log_{10} K_{pfi}$ where we can show from Equation (31) that

$$\log_{10} K_p = \sum_i (N_{ip} - N_{ir}) \log_{10} K_{pfi} \quad (34)$$

For the water gas shift reaction then

$$\log_{10} \left(\frac{X_{\text{CO}_2} X_{\text{H}_2}}{X_{\text{H}_2\text{O}} X_{\text{CO}}} \right) = \log_{10} K_{pfc\text{O}_2}(T) + \log_{10} K_{pf\text{H}_2}(T) - \log_{10} K_{pf\text{H}_2\text{O}}(T) - \log_{10} K_{pf\text{CO}}(T) \quad (35)$$

And we get an equilibrium constant that looks like this as a function of temperature:

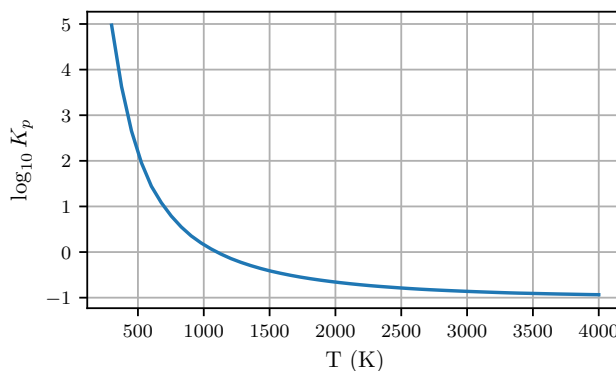


Figure 0.12: \log_{10} of the equilibrium constant for the water-gas shift reaction

To this we add the atom balance (conservation of elements) equations. For conservation of O

$$2X_{\text{CO}_2} + X_{\text{H}_2\text{O}} + X_{\text{CO}} = 2, \quad (36)$$

for conservation of C

$$X_{\text{CO}_2} + X_{\text{CO}} = 1, \quad (37)$$

and for conservation of H

$$X_{\text{H}_2} + X_{\text{H}_2\text{O}} = 2. \quad (38)$$

This provides us four equations in four unknowns and we can solve the system. In this case there is a nice, closed form solution for the mole fractions:

$$\begin{aligned} X_{\text{CO}} &= \frac{1}{\sqrt{K_p} + 1} \\ X_{\text{CO}_2} &= 1 - X_{\text{CO}} \\ X_{\text{H}_2\text{O}} &= X_{\text{CO}} \\ X_{\text{H}_2} &= 1 - X_{\text{CO}} \end{aligned} \quad (39)$$

And finally the resulting equilibrium mole fractions look like:

⁶In fact, K_c and K_p are precisely related by $K_p = K_c(RT)^{\sum N_{ip} - N_{ir}}$

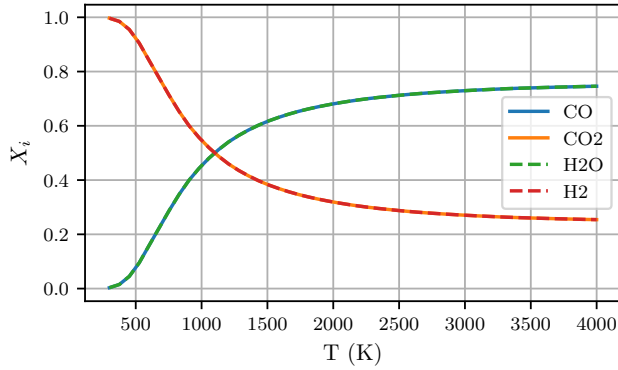


Figure 0.13: Equilibrium mole fractions for the water-gas shift reaction

So now we have all the basic tools needed to solve any gas-phase chemical equilibrium problem at a variety of temperatures. However as we mentioned before, there are likely many more species in the mix than just the four we considered in the water-gas shift reaction. So additional reactions with additional species would need to be written. Each additional reaction will add an equilibrium constant equation and the additional species will show up in the atom balances.

For systems much larger than this one, there will be no closed-form solution and so iterative numerical solvers will be needed and things start to get hairy pretty quick. Fortunately for us we have software tools that do all the dirty work for us. However these tools actually use a slightly different method to solve for equilibrium called the *element potential method* and I want to briefly introduce that for completeness.

Method of Element Potentials

For most combustion processes of practical interest, the number of species and reactions involved in the equilibrium calculations becomes large. In fact, the solution to a combustion problem involving just species including C O and H must consider around 8 species. The atom balances for each element in the product species provide one equation and each chemical reaction considered provides an equation. Thus if we are trying to solve for the composition of M species consisting of N elements, we must consider $M - N$ reaction equilibrium equations (and thus $M - N$ chemical reactions) in order to solve the system. For simple systems like H, O this is practical, but $M - N$ grows non-linearly as species with additional elements are considered. Solving a large non-linear system of equations is inherently problematic and typically requires some prior approximation to initialize from.

Historically, a chemist (or more likely their junior staff) might sit down for days working through the equilibrium math by hand to analyze just one possible combination of

propellants. They would rely on their judgement, analogy to similar reactions or experimental results to "seed" the solution. This all changed with the advent of accessible computers in the 1960's and 1970's. Since that time there have been several generations of software developed to compute complex thermal equilibrium numerically. But the large system size still poses numerical challenges.

In light of these difficulties the so-called *Element Potential* approach was developed. The insight is to recognize that in solving the system, the mole fractions are not independent but are coupled through the atom balance. The element potential method reformulates the problem with the atom balance as constraint. This can then be solved using the Method of Lagrange Multipliers [3]. The atom balance constraint states that

$$\sum_i \eta_{ij} n_i = a_j \quad (40)$$

where η_{ij} represents the number of atoms/mol of element j in species i and a_j is the total number of moles of element j in the system.

Using this as a constraint, the method of Lagrange Multipliers then states that

$$d \left[G + \sum_j \lambda_j \left(\sum_i \eta_{ij} n_i - a_j \right) \right]_{T,P} = 0$$

or

$$dG_{T,P} - \sum_j \lambda_j \sum_i \eta_{ij} dn_i = \sum_i \left(g_i - \sum_j \eta_{ij} \lambda_j \right) dn_i = 0. \quad (41)$$

where λ_j are the Lagrange Multipliers for element j . In the equilibrium state, the coefficients in front of dn_i must vanish such that

$$g_i = \sum_j \eta_{ij} \lambda_j. \quad (42)$$

Because this is very similar to the relationship between partial molal Gibbs energy and chemical potential, the λ_j have been called *element potentials*.

Before we get to the point we need to look at the full form for g_i .

$$g_i = h_i - Ts_i(X_i) \\ \rightarrow \frac{\partial g_i}{\partial X_i} = T \frac{\partial s_i}{\partial X_i} \quad (43)$$

where the important observation is that the component entropy (and thus Gibbs energy) depends on its mole fraction in the mixture. This dependency comes from the *entropy of mixing* for an ideal gas and is derived in most introductory thermodynamics courses. The result is simple:

$$\frac{\partial s_i}{\partial X_i} = R \ln X_i \quad (44)$$

And using this result with Equation (41), we can expand similarly to Equation (31) to arrive at

$$\frac{g_i}{RT} + \ln X_i + \frac{1}{RT} \sum_j \eta_{ij} \lambda_j = 0. \quad (45)$$

Equation (45) provides an equation for *each species, i* rather than having to write out individual chemical reaction equations as we did to arrive at the equilibrium constant method in Equation (31). It does introduce additional variables that must be solved for in the element potentials, λ_j . However as pointed out in [3] the element potential method has the following advantages over the equilibrium constant method:

- There is less book-keeping. In the equilibrium constant method, species must be selected and reactions written to build the system to be solved. In the element potential method, we only need identify the species that we want to consider.
- Solving the element potential method is better behaved numerically. If species are not chosen appropriately, the equilibrium constant method will encounter numerical precision difficulties for species that have very near-zero mole fractions
- If condensed phases are present, the element potential method provides a more robust criteria for phase determination

For these reasons the element potential method is used almost exclusively in modern equilibrium codes.

0.5 Rocket Performance Calculation

We have finally arrived at a place where we have the knowledge to do practical chemical rocket performance calculations. Reviewing, the steps are as follows:

We learned how to do all of the steps in this flow with the one exception of the last box where we compute c^* and C_f using the adiabatic combustion calculation. But wait, you might say, we did learn that last lecture and we even produced equations for them at the beginning of this lecture. This is true but those equations were derived with the following assumptions:

- Constant specific heats
- *Frozen* (unreacting) gasses during the nozzle expansion process

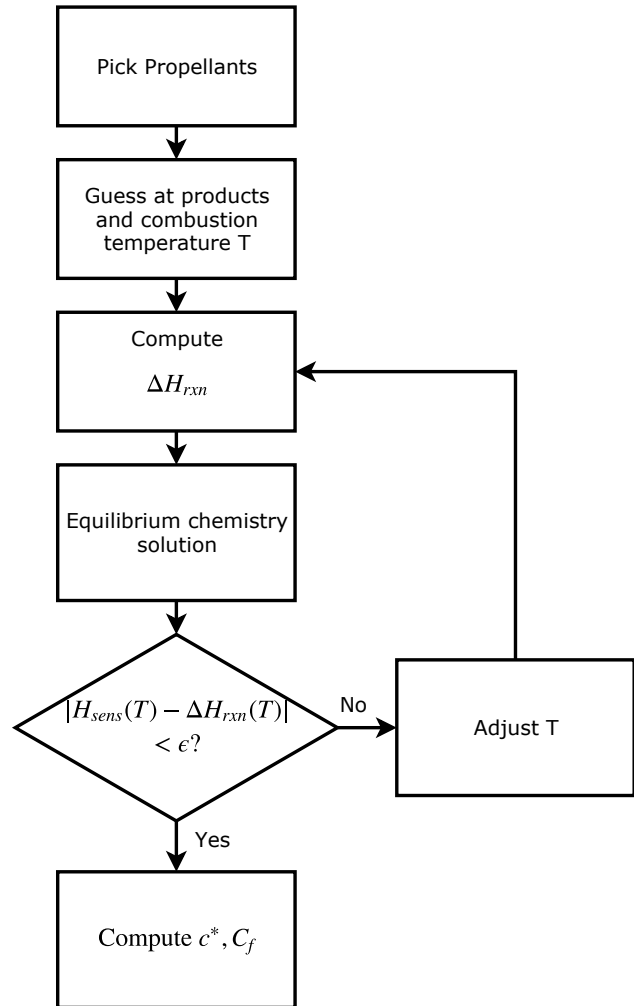


Figure 0.14: Basic flow of the combustion performance calculation process

In reality the properties of the product mixture may be changing dramatically as gasses expand through the nozzle. In one conceptual limit, the gasses stay in thermodynamic equilibrium as they expand. This is called the shifting equilibrium assumption. In the other limit, we assume equilibrium in the chamber and then compute the gas mixture expansion using that composition without re-computing chemical equilibrium in the nozzle. This is called the frozen equilibrium assumption. In reality, the flow will be somewhere in between. Early in the chamber when temperatures are high and velocities low, the rate that chemical reactions proceed (chemical kinetics) will be high enough that the mixture stays very near equilibrium. Later as temperatures fall (slower chemical kinetics) and velocities increase (shorter residency time), the reactions will fail to keep the flow in equilibrium and the frozen assumption will be closer.

Below I've plotted c^* as a function of the oxidizer-to-fuel

mass ratio, often referred to as O/F ratio in the rocket community.

$$O/F = \frac{\dot{m}_{ox}}{\dot{m}_{fuel}} \quad (46)$$

Note of course that the O/F ratio sets the relative mole fractions of reactants in the system and that this is customarily a mass-specific ratio. Mass ratio is used because it is much more common in engineering.⁷

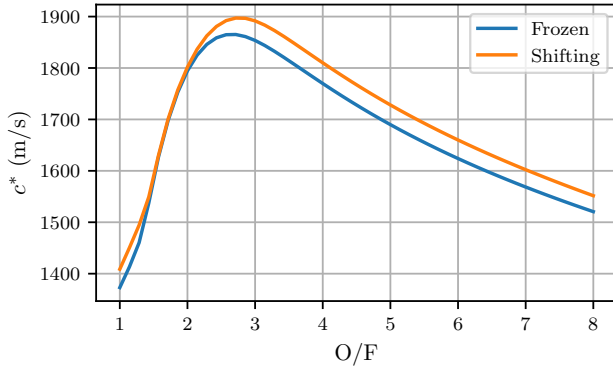


Figure 0.15: c^* as a function of O/F for the CH_4 / O_2 propellant system. Chamber pressure is set at 70 bar

The frozen assumption produces more conservative performance numbers and so is often used as a conservative starting point for design. Later, more sophisticated nozzle models that include the effects of chemical kinetics may be used to provide a more accurate estimate of actual performance although typically the differences will be swamped by things like realized combustion efficiency in a real motor.

In the shifting case where the constant specific heat assumption is not a very good one, the rocket performance can be computed by iteratively reducing the pressure and re-computing equilibrium using the constant entropy and pressure (S, P) constraint rather than constant (T, P). As this iteration proceeds, the local gas velocity at station i can be computed as

$$U_i = \sqrt{2(h_t - h_i)}. \quad (47)$$

To solve for throat conditions (c^*), the iteration is stopped when the local velocity reaches the sound speed computed for the mixture (within some tolerance). To solve for the nozzle exit conditions the iteration is stopped when the pressure reaches the specified exit pressure or the requisite area ratio reaches the specified nozzle area ratio. Once the exit state (T, P) and equilibrium are known, exit velocity, U_e and

pressure P_e can be computed. From these and c^* , C_f may be computed.

Note also that the difference in performance computed by the frozen and shifting assumption is larger for C than c^* because c^* only considers effects up to the nozzle throat:

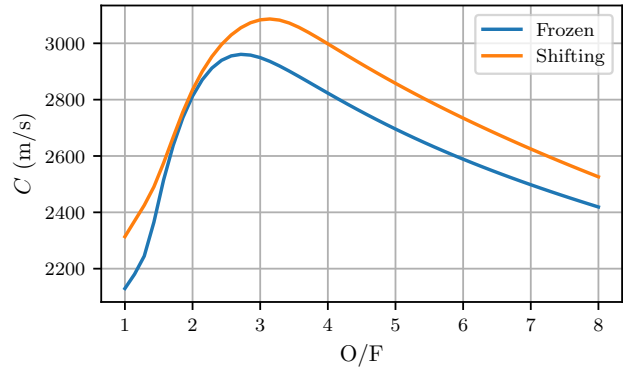
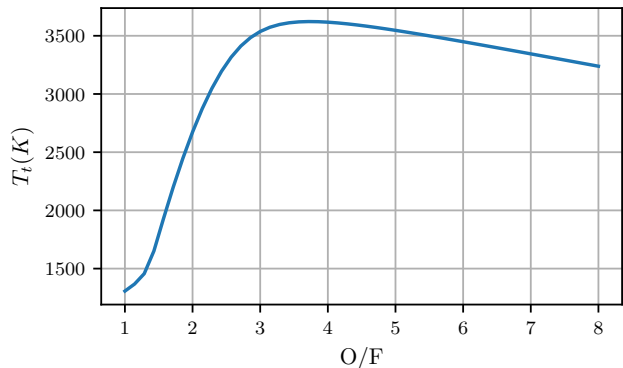


Figure 0.16: C as a function of O/F for the CH_4 / O_2 propellant system. Chamber pressure is set at 70 bar, and the exit condition is set at 1 bar pressure (so-called sea-level performance)

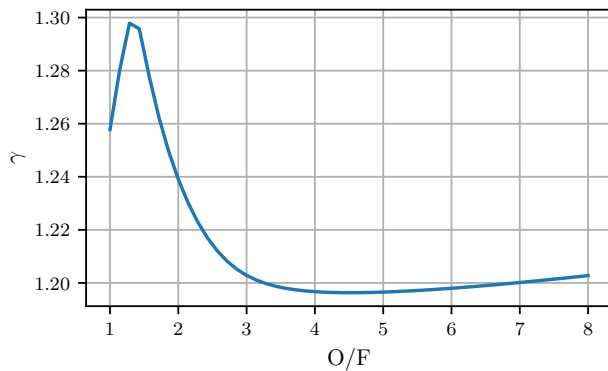
For more details on these computations, I highly recommend the classic [NASA Reference Publication 1311 by Sanford Gordon and Bonnie McBride\[5\]](#) who were pioneers in the field of these calculations.

Another question of interest might be how closely the ideal analytical Equations (1) and (3) compare with the numerical results using variable specific heats? If we perform the full chamber equilibrium calculation to obtain adiabatic flame temperature:

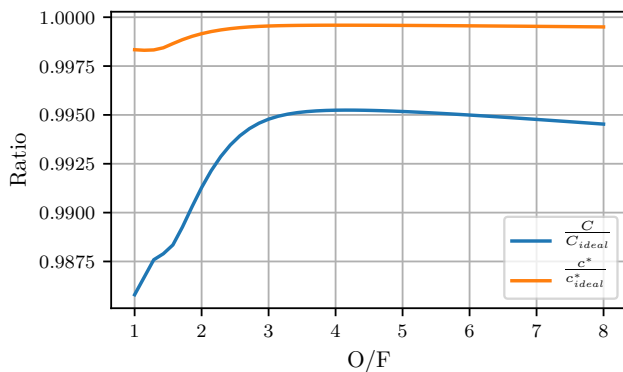


specific heat ratio

⁷Make a HW problem to figure out how to convert O/F to mol ratio



and product gas molecular weight (which I didn't bother to plot), we can plug these into those equations. The resulting ratios are



So the ideal approximations are not bad for methane and oxygen. However, as the chemistry becomes more complicated and we start getting effects like condensed species in the exhaust, the ideal approximations will be less effective.

Tools

There are several tools available to you to do these calculations the most accessible of which are:

- Chemical Equilibrium with Applications (CEA) is a NASA code developed by Gordon and McBride with a long heritage and is considered the defacto standard for these chemical equilibrium calculations in the rocket world. It is located at <https://www.grc.nasa.gov/www/CEAWeb/>. It is not publicly available and you must request access to it at <https://software.nasa.gov/software/LEW-17687-1>. There are binaries for Mac and Windows as well as a JAVA based GUI
- pypropep - Available at <https://github.com/jonnydyer/pypropep>, pypropep is a Python library

that wraps an older open-source called Cpropep (which, in turn, was originally based on a Fortran code developed by the Navy). If you are comfortable with Python, it provides a simple, scriptable interface to run performance calculations

- Rocket Propulsion Analysis (RPA) is a commercial application for both Mac and Windows. It is a paid product but they provide a free limited version that will perform chemical equilibrium and basic rocket performance calculations. It is probably the simplest to get up and running with if you're not a command-line guru or Python user. Available at <http://propulsion-analysis.com/index.htm>

A quick example I used to compute some of the plots above with pypropep is given here

```
import pypropep as ppp
ppp.init()

ch4 = ppp.PROPELLANTS['METHANE']
o2 = ppp.PROPELLANTS['OXYGEN_(GAS)']

Pt = 70.
Pe = 1.

OF = np.linspace(1, 5)
cstar = np.zeros_like(OF)
Cf = np.zeros_like(OF)
C = np.zeros([len(OF), 2])
T = np.zeros_like(OF)
gamma = np.zeros_like(OF)
Mw = np.zeros_like(OF)

for i in range(len(OF)):
    fp = ppp.FrozenPerformance()

    m_o2 = OF[i]
    m_ch4 = 1.0

    fp.add_propellants_by_mass([(ch4, m_ch4),
                                (o2, m_o2)])

    fp.set_state(P=Pt, Pe=Pe)

    T[i] = fp.properties[0].T
    gamma[i] = fp.properties[0].lsex
    Mw[i] = fp.properties[0].M

    cstar[i] = fp.performance.cstar
    Cf[i] = fp.performance.cf
    C[i] = fp.performance.lsp
```

0.6 Some Performance Results for Discussion

Finally I want to talk about the fun stuff, the real smoke and fire if you will. Now that we have the tools to rigorously analyze the performance of propellant combinations, what are some good ones?

The development of liquid propellant chemistry has a long and rich history. Today we have settled on just a few combinations (see Figure 0.17 below) for a variety of mostly practical reasons. If you're interested (and you should be), I highly recommend *Dr. John Clark's classic Ignition!*^[7] which covers the technical history of liquid propellant research through the 1960's and is a very well-written, engaging and funny read.

Not being able to replay that full history, here are some general observations about what combinations make "good" rocket propellants

- Basic fuel and oxidizers that consist of atoms with large differences in electronegativity are good. This is because the electronegativity difference drives strong bonds in the products which means heats of reaction are large. The best oxidizers from this perspective are Fluorine, Oxygen and (to a lesser extent) Chlorine. The best fuels from an energetic perspective are metals - Lithium, Beryllium, Aluminum and, to a lesser extent, Carbon.
- Molecular weight matters a lot. This drives to fuels with lots of hydrogen. Hydrogen is also a good propellant from an energetic perspective, but that 2 g/mol in the denominator is really what does it.
- Nitrogen makes a reasonable pairing with other elements in both fuels and oxidizers. The nitrates (including Nitric Acid HNO_3) are pretty good oxidizers and the nitrogen/hydrogen compounds (like Hydrazine N_2H_4) are respectable fuels.
- Performance (C , I_{sp}) is obviously extremely important for propellant combinations. But other considerations are often deciding factors. For example:
 - The extremely low density and deep cryogenic nature of liquid hydrogen has limited its utility for many applications. In fact, in many applications density impulse, $\frac{C}{\rho}$ may be as or more important than I_{sp}
 - There are some oxidizers, such as ClF_3 that look *FANTASTIC* in performance calculations but are so unbelievably nasty that handling them is nigh impossible.
 - Many tactical applications require *storable* propellants that won't evaporate or freeze under storage

- The inclusion of fuel metals has a long, sordid and ultimately unsuccessful history largely do to the difficulties of incorporating them in liquid engines and their poor combustion performance.

Figure 0.17 is a good table taken from Sutton. It tabulates the performance of some common liquid propellant combinations. Note that "Average Specific Gravity" is called out - this is to capture the importance of impulse density for some missions. As you can see, hydrogen does come out looking awfully good in this table until you look at average specific gravity.

RP-1 is "Rocket Propellant 1" and is essentially a careful cut of jet fuel. It is what powered the first two stages of the Saturn V as well as both Falcon 9 stages and can pretty safely be considered the workhorse of the launch business. O_2 and CH_4 are a good combination for "green" propellants, although Methane's improvement in I_{sp} over RP-1 is not so dramatic (296 s vs. 285 s) when you consider the hit on specific gravity (0.81 vs 1.01). The reason there is so much interest in it now is that makes a good fuel for Staged Combustion Engines (which are all the rage) if you don't want to deal with liquid hydrogen.

Hydrazine, N_2H_4 , unsymmetrical dimethylhydrazine (UDMH), $\text{H}_2\text{NN}(\text{CH}_3)_2$, and monomethylhydrazine (MMH), $\text{CH}_3(\text{NH})\text{NH}_2$, are important because they are storable and hypergolic with Nitric Acid, HNO_3 and Nitrogen Tetroxide, N_2O_4 . They were used in the early ICBM's and are still used in some launch vehicles today, largely on the Russian side. They are not fun to work with - the various hydrazines are highly toxic and likely carcinogens. Nitrogen tetroxide is acutely toxic and nitric acid is obviously very difficult to handle at large scale.

It is worth noting that hydrazine is still commonly used for in-space propulsion. It decomposes exothermically and thus is considered a *monopropellant*. The performance is not terribly high but for small propulsion requirements on satellites and the like, it is a good option.

The specific propellant combinations will be covered in more detail when we get to the liquid rocket lectures but I also want to discuss a few extreme propellant cases just to give a flavor of how far some were willing to go for performance.

I mentioned ClF_3 before which was studied through the 1960's after it's fantastic performance potential was noted as early as the 1930's. But it didn't pan out... quoting John Clark:

Chlorine trifluoride, ClF_3 , or "CTF" as the engineers insist on calling it, is a colorless gas, a greenish liquid, or a white solid. It boils at 12C (so that a trivial pressure will keep it liquid at room temperature) and freezes at a convenient -76C . It also has a nice fat density, about 1.81 at room temperature.

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

Oxidizer	Fuel	Mixture Ratio		Average Specific Gravity	Chamber Temp. (K)	Chamber c^* (m/sec)	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
Fluorine	UDMH	2.56	1.82	1.02	3677	1800	23.3		300	
		1.39	0.96	0.96	3542	1835	19.8		295	1.25
	Hydrazine	1.65	1.14	0.98	3594	1864	21.3	310		
		1.83	1.22	1.29	4553	2128	18.5	334		1.33
	Hydrogen	2.30	1.54	1.31	4713	2208	19.4		365	
		4.54	0.21	0.33	3080	2534	8.9		389	1.33
	RP-1	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
	MMH	2.15	1.30	1.20	3396	1747	22.3	289		
		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 .**Figure 0.17:** The primary liquid propellant systems the world has largely settled into after 70 years of experimentation. Note that this table has the shifting and frozen performance for O₂/RP-1 switched. Reference [8]

It is also quite probably the most vigorous fluorinating agent in existence—much more vigorous than fluorine itself. Gaseous fluorine, of course, is much more dilute than the liquid ClF₃, and liquid fluorine is so cold that its activity is very much reduced.

All this sounds fairly academic and innocuous, but when it is translated into the problem of handling the stuff, the results are horrendous. It is, of course, extremely toxic, but that's the least of the problem. It is hypergolic with every known fuel, and so rapidly hypergolic that no ignition delay has ever been measured. It is also hypergolic with such things as cloth, wood, and test engineers, not to mention asbestos, sand, and water—with which it reacts explosively. It can be kept in some of the ordinary structural metals—steel, copper, aluminum, etc.—because of the formation of a thin film of insoluble metal fluoride which protects the bulk of the metal, just as the invisible coat of oxide on aluminum keeps it from burning up in the atmosphere.

If, however, this coat is melted or scrubbed off, and has no chance to reform, the operator is con-

fronted with the problem of coping with a metal-fluorine fire. For dealing with this situation, I have always recommended a good pair of running shoes. And even if you don't have a fire, the results can be devastating enough when chlorine trifluoride gets loose, as the General Chemical Co. discovered when they had a big spill...

...It happened at their Shreveport, Louisiana, installation, while they were preparing to ship out, for the first time, a one-ton steel cylinder of CTF. The cylinder had been cooled with dry ice to make it easier to load the material into it, and the cold had apparently embrittled the steel. For as they were maneuvering the cylinder onto a dolly, it split and dumped one ton of chlorine trifluoride onto the floor. It chewed its way through twelve inches of concrete and dug a threefoot hole in the gravel underneath, filled the place with fumes which corroded everything in sight, and, in general, made one hell of a mess. Civil Defense turned out, and started to evacuate the neighborhood, and to put it mildly, there was quite a brouhaha before things quieted down. Miraculously, nobody was killed, but there was one casualty—the man who had

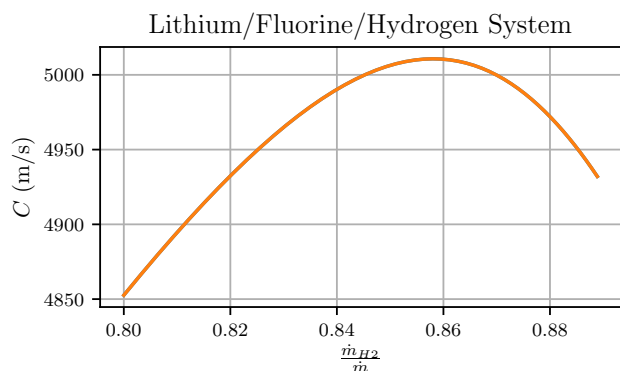


Figure 0.18: The Lithium/Fluorine/Hydrogen system with mass ratio of $2/3 F_2 / Li$ and the rest in hydrogen. Over 500 seconds of I_{sp} !

been steadying the cylinder when it split. He was found some five hundred feet away, where he had reached Mach 2 and was still picking up speed when he was stopped by a heart attack.

This episode was still in the future when the rocket people started working with CTF, but they nevertheless knew enough to be scared to death, and proceeded with a degree of caution appropriate to dental work on a king cobra. And they never had any reason to regret that caution. The stuff consistently lived up to its reputation....

...It was when the stuff got into the motor that the real difficulties began, for a chlorine trifluoride motor operates at a chamber temperature close to 4000 K, where injectors and nozzle throats have a deplorable tendency to wash away, and unless the materials of which they are made are chosen with considerable astuteness, and unless the design is very good, the motor isn't going to last long. The propellant man liked CTF because of its performance, and the engineer hated the beast because it was so rough on motors and so miserable to handle...

Another valiant attempt now confined to the dustbin of history was the Li, F_2 , H_2 system. On paper, this should have about the highest performance that could be assembled from the periodic table: extreme electronegativity difference between the fuels Li, H_2 and the oxidizer F_2 ; plus the very low molecular weight of hydrogen. What does theoretical performance look like?

John Clark had something to say about this as well:

...and in the meantime Rocketdyne went ahead with the other approach, and fired the combination in a true tripropellant motor. They used liquid

lithium and liquid fluorine, but used gaseous hydrogen instead of liquid. I presume that they considered that handling two such hairy liquids as fluorine and lithium at the same time was enough, without adding to their misery by coping with liquid hydrogen. I have described some of the problems associated with liquid fluorine, and liquid lithium has its own collection of headaches. You have to keep it hot, or it will freeze in the propellant lines. You must also keep it from contact with the atmosphere, or it will burst into brilliant and practically inextinguishable flame. Add to this the fact that liquid lithium is highly corrosive to most metals, and that it is incompatible with anything you might want to use for gaskets and sealing materials (it even attacks Teflon with enthusiasm), and you have problems.

But somehow the Rocketdyne crew (H. A. Arbit, R. A. Dickerson, S. D. Clapp, and C. K. Nagai) managed to overcome them, and made their firings. They worked at 500 psi chamber pressure, with a high expansion nozzle (exit area/throat area = 60) designed for space work. Their main problem stemmed from the high surface tension of liquid lithium, orders of magnitude higher than that of ordinary propellants, which made it difficult to design an injector that would produce droplets of lithium small enough to burn completely before going out the nozzle. Once this problem was overcome, their results were spectacular. Using lithium and fluorine alone (no hydrogen) their maximum specific impulse was 458 seconds. But when they proportioned the lithium and fluorine to burn stoichiometrically to LiF , and injected hydrogen to make up 30 percent of the mass flow, they measured 542 seconds—probably the highest measured specific impulse ever attained by anything except a nuclear motor.

Bibliography

- [1] *Lightweight, Flexible, High-efficiency III-V Multijunction Cells*, 2006.
- [2] C.T. Bowman. Course notes on combustion. Reference Material for ME 371 Combustion Fundamentals.
- [3] Sanford Gordon. Kinetics and thermodynamics in high-temperature gases. Special Publication (SP) 239, NASA, 1970.
- [4] Sanford Gordon and Bonnie J. McBride. Computer program for calculation of complex chemical equilibrium compositions, rocket performance, incident and reflected shocks and chapman-jouget detonations. Special Publication (SP) 273, NASA, 1976.
- [5] Sanford Gordon and Bonnie J. McBride. Computer program for calculation of complex chemical equilibrium compositions and applications. Reference Publication (RP) 1311, NASA, 1994.
- [6] Joseph Richard Wrobel. *Application of the Element Potential Method to Gaseous Chemical Equilibrium Calculation*. PhD thesis, California Institute of Technology, 1963.
- [7] John D. Clark. *Ignition! An Informal History of Liquid Rocket Propellants*. Rutgers University Press, 1972.
- [8] George P. Sutton and Oscar Biblarz. *Rocket Propulsion Elements*. John Wiley & Sons, Inc., 7 edition, 2001.