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Chapter 1

Propulsion Thermodynamics

1.1 Introduction

The Figure below shows a cross-section of a Pratt and Whitney JT9D-7 high bypass ratio turbofan engine. The engine is depicted without any inlet, nacelle or nozzle.

Figure 1.1: Cross-section of the Pratt and Whitney JT9D-7 turbofan engine
Two gas streams are indicated in the Figure. The air mass flow rate of the bypass stream is $\dot{m}_{\text{fan}}$ and that of the engine core stream is $\dot{m}_{\text{core}}$. The bypass ratio of the engine is defined as

$$ \beta = \frac{\dot{m}_{\text{fan}}}{\dot{m}_{\text{core}}}. \quad (1.1) $$

The fuel is injected as a liquid; atomized, mixed, and burned with the core air. The exhaust mass flow rate of the core is equal to the sum of core air mass flow rate and fuel mass flow rate $\dot{m}_{\text{core}} + \dot{m}_f$.

This engine was among the first generation of high thrust jet engines designed in the 1960’s to power a new class of wide body aircraft. It was the engine that powered the Boeing 747 when it was introduced into service in 1968. This engine is capable of generating 46,500 pounds of thrust at sea level static conditions typical of the initiation of aircraft takeoff roll. Derivatives of this engine as well as competitors offered by General Electric and Rolls Royce continue to power the 747 today as well as the 767, A300, A310 and DC10. At cruise the engine generates about 10,000 pounds of thrust.

Figure 1.1 is particularly useful in that it shows the pressures and temperatures at various stations in the engine and it presents a powerful reminder that to understand modern propulsion systems we will need to employ the full range of thermodynamic and gasdynamic tools available to us. The total air weight flow at take-off is 1508 pounds per second (685.5 kg/sec) and the bypass ratio is 4.8 with 260 pounds of air per second (118.2 kg/sec) passing through the core of the engine. The thrust to weight ratio of the engine at takeoff thrust is 5.15.

You will notice that I used English units to describe the mass flow. It is an unfortunate fact that in spite of the now generally accepted use of the metric system by the vast majority of the scientific and engineering community, US propulsion companies are still stuck on English units to a large extent (although the British are not). That does not mean that we have to slavishly accept this use and in fact we will generally use metric units throughout this text although quite often the English equivalent will be quoted as well.

The ability of this sort of engine to generate power is remarkable. In metric units the heat capacity of air at room temperature is $C_p = 1005 \, m^2 / (\text{sec}^2 - K)$. The stagnation temperature change of the gas that passes through the core is $T_{t5} - T_{t2} = (5/9) (1035 - 59) = 542 \, K$ and that across the fan is $T_{t13} - T_{t2} = (5/9) (140 - 59) = 45 \, K$. The total power generated is the enthalpy change of the gas times the mass flow.

$$ W = \dot{m}_{\text{core}} C_p (T_{t5} - T_{t2}) + \dot{m}_{\text{fan}} C_p (T_{t13} - T_{t2}) = 
118.2 \times 1005 \times 542 + 567.3 \times 1005 \times 45 = 9 \times 10^7 \, J / \text{sec} \quad (1.2) $$
In English units this is equivalent to approximately 120,000 horsepower (1 horsepower=746 Watts, 1 Watt = 1 Joule/sec). Note that the engine is designed so that the static pressure of the core exhaust flow is nearly equal to the static pressure of the fan exhaust to avoid large changes in flow direction where the two streams meet. The overall engine stagnation pressure ratio is approximately 1.5.

Now let’s examine the work done per second across some of the components. The work done by the gas on the high pressure turbine is

\[ W_{hpt} = 118.2 \times 1005 \times (5/9) \times (2325 - 1525) = 5.28 \times 10^7 \text{ J/sec} \] (1.3)

where the added fuel mass flow is neglected. The high pressure turbine drives the high pressure compressor through a shaft that connects the two components. The work per second done by the high pressure compressor on the core air is

\[ W_{hpc} = 118.2 \times 1005 \times (5/9) \times (940 - 220) = 4.75 \times 10^7 \text{ J/sec} \] (1.4)

Note that the work per second done by the gas on the turbine is very close to but slightly larger than that done by the compressor on the gas. If the shaft connecting the compressor and turbine has no frictional losses and if the mass flow through both components is indeed the same and if both components are adiabatic then the work terms would be identical. The system is not quite adiabatic due to heat loss to the surroundings. The mass flow is not precisely the same because of the added fuel and because some of the relatively cooler compressor flow is bled off to be used for power generation and to internally cool the high temperature components of the turbine.

Since the work output of the turbine and compressor is practically the same across both components why does the compressor have so many more stages than the turbine? The answer comes from the viscous nature of fluid flow. In the compressor, the flow is in the direction of increasing pressure and so the boundary layers on the compressor blades and in the compressor passages encounter an adverse pressure gradient that increases the tendency for flow separation and blade stall. The pressure rise achievable in a single compressor stage is limited by this effect. In the turbine the opposite is the case, the flow is in the direction of decreasing pressure which tends to stabilize the boundary layers on the turbine airfoils reducing the tendency for blade stall. As a result the work output of a single turbine stage is several times larger than that possible in a single compressor stage. If there was no such thing as flow separation all compressors and turbines would have the same number of stages. At the level of an individual blade, turbine blades are much more highly loaded (have much higher lift) than compressor blades. The difference in lift and the requirement that the turbine blades be cooled is reflected in significant differences in the blade profiles as illustrated in Figure 1.2. Cooling of the turbine blades is required because of the very
high temperature of the gas entering the turbine from the combustor. In modern engines the turbine inlet temperature may be several hundred degrees higher than the melting temperature of the turbine blade material and complex cooling schemes are needed to enable the turbine to operate for tens of thousands of hours before overhaul.

In general turbine blades are thicker and have much more camber than compressor blades. The extra thickness allows the turbine blades to be fabricated with internal cooling air passages and the combination of thickness and camber is responsible for the high lift generated by a turbine blade. In a modern turbofan engine the fan operates at blade tip Mach numbers approaching, or slightly above, one. As a result the profile of a typical fan blade tends to be quite slender with a relatively sharp leading edge as illustrated in Figure 1.2.

Let’s take a look at the entropy change per unit mass of the gas as it passes from one engine component to another. The Gibbs equation for an ideal gas is

\[
\frac{ds}{C_p} = \frac{dT}{T} - \left(\frac{\gamma - 1}{\gamma}\right) \frac{dP}{P}.
\] (1.5)

For air \( \gamma = 1.4 \). Throughout our study of air breathing propulsion systems we will assume the gas to be calorically perfect (heat capacities are assumed constant). From a pedagogical standpoint this is the most appropriate approach for learning how air breathing engines work and for a preliminary analysis of engine performance. A designer would use aero-thermodynamic software that would incorporate the temperature dependence of the heat capacities as well as detailed semi-empirical flow models of the various engine components. Occasionally, it may be useful to use different values of the heat capacities in the cold and hot sections of the engine.

Between any two points \( a \) and \( b \) the Gibbs equation integrates to
\[
\frac{s_b - s_a}{C_p} = Ln \left( \frac{T_b}{T_a} \right) - \left( \frac{\gamma - 1}{\gamma} \right) Ln \left( \frac{P_b}{P_a} \right).
\] (1.6)

Integrating between the various stations of the engine shown in Figure 1.1 leads to the following. Note that station 0 is in the free stream and station 1 is at the entrance to the inlet. Neither station is shown in Figure 1.1.

**Station 2** - Sea level static conditions from Figure 1.1 are

\[P_{t2} = 14.7 \text{ psia}\]
\[T_{t2} = 519 \text{ R}\] (1.7)

where the inlet (not shown) is assumed to be adiabatic and isentropic.

**Station 3** - At the outlet of the high pressure compressor

\[P_{t3} = 335 \text{ psia}\]
\[T_{t3} = 1400 \text{ R}\] (1.8)

The non-dimensional entropy change per unit mass across the inlet compression system is

\[
\frac{s_b - s_a}{C_p} = Ln \left( \frac{1400}{519} \right) - \left( \frac{0.4}{1.4} \right) Ln \left( \frac{335}{14.7} \right) = 0.992 - 0.893 = 0.099.
\] (1.9)

**Station 4** - The heat put into the cycle is equal to the stagnation enthalpy change across the burner.

\[
\dot{m}_f h_f = (\dot{m}_{a, cor} + \dot{m}_f) h_{t4} - \dot{m}_{a, cor} h_{t3}
\] (1.10)

The thermodynamic heat of combustion of a fuel is calculated as the heat that must be removed to bring all the products of combustion back to the original pre-combustion temperature. The enthalpy of combustion for fuels is usually expressed as a higher or lower heating value. The higher heating value is realized if the original temperature is below the condensation temperature of water and any water vapor is condensed giving up its vaporization energy as heat. The lower heating value is calculated by subtracting the heat of vaporization of the water in the combustion products from the higher heating value. In this case any water formed is treated as a gas.
The enthalpy of combustion of a typical jet fuel such as JP-4 is generally taken to be the lower heating value since the water vapor in the combustion products does not condense before leaving the nozzle. The value we will use is
\[ h_f|_{JP-4} = 4.28 \times 10^7 \text{ J/sec}. \] (1.11)

The higher heating value of JP-4 is about \( 4.6 \times 10^7 \text{ J/kg} \) and can be calculated from a knowledge of the water vapor content in the combustion products. The higher and lower heating values of most other hydrocarbon fuels are within about 10\% of these values. At the outlet of the burner
\[ P_{t4} = 315 \text{ psia} \] (1.12)
\[ T_{t4} = 2785 \text{ R}. \]

Note the very small stagnation pressure loss across the burner. The stagnation pressure drop across any segment of a channel flow is proportional to the Mach number squared.
\[ \frac{dP_t}{P_t} = -\frac{\gamma M^2}{2} \left( \frac{dT_t}{T_t} + 4C_f \frac{dx}{D} \right) \] (1.13)

A key feature of virtually all propulsion systems is that the heat addition is carried out at very low Mach number in part to keep stagnation pressure losses across the burner as small as possible. The exception to this is the scramjet concept used in hypersonic flight where the heat addition inside the engine occurs at supersonic Mach numbers that are well below the flight Mach number.

The non-dimensional entropy change per unit mass across the burner of the JT9D-7 is
\[ \frac{s_4 - s_3}{C_p} = \ln \left( \frac{2785}{1400} \right) - \left( \frac{0.4}{1.4} \right) \ln \left( \frac{315}{335} \right) = 0.688 + 0.0176 = 0.706. \] (1.14)

**Station 5 - At the outlet of the turbine**
\[ P_{t5} = 22 \text{ psia} \] (1.15)
\[ T_{t5} = 1495 \text{ R}. \]

The non-dimensional entropy change per unit mass across the turbine is
\[
\frac{s_5 - s_4}{C_p} = \ln \left( \frac{1495}{2785} \right) - \left( \frac{0.4}{1.4} \right) \ln \left( \frac{22}{315} \right) = -0.622 + 0.760 = 0.138. \quad (1.16)
\]

Station 0 - The exhaust gas returns to the reference state through nozzle expansion to ambient pressure and thermal mixing with the surrounding atmosphere.

\[P_{t0} = 14.7 \text{ psia} \quad (1.17)\]

\[T_{t0} = 519 \text{ R} \]

The non-dimensional entropy change back to the reference state is

\[
\frac{s_0 - s_5}{C_p} = \ln \left( \frac{519}{1495} \right) - \left( \frac{0.4}{1.4} \right) \ln \left( \frac{14.7}{22} \right) = -1.058 + 0.115 = -0.943. \quad (1.18)
\]

The net change in entropy around the cycle is zero as would be expected. That is \( \Delta s = 0.099 + 0.706 + 0.138 - 0.943 = 0. \)

Note that the entropy changes across the compressor and turbine are much smaller than across the burner where substantial heat is added with only a very small change in pressure. Similarly there is a large temperature and entropy decrease of the exhaust gases as they mix with the surrounding air. Figure 1.3 shows the fully expanded exhaust from an engine.

As the exhaust gas emerges from the nozzle and mixes with the surroundings, heat is conducted from the hot gases to the ambient air.

![Figure 1.3: Constant pressure heat transfer from the engine exhaust to the surroundings.](image)

Through mixing, the exhaust gas eventually returns to the temperature and pressure of the reference state entering the engine. One can think of this as a two step process. In the first step viscosity is neglected and the exhaust flow is treated using the 1-D equations.
of motion. In this approximation, the flow in the stream-tube within the dashed lines in Figure 1.3 is governed by the 1-D momentum equation (the Euler equation).

\[ dP + \rho UdU = 0 \]  \hspace{1cm} \text{(1.19)}

According to (1.19) since the pressure is constant along this stream-tube, the velocity must also be constant \((dP = 0, dU = 0)\) and the flow velocity at the end of the stream-tube must be the same as at the nozzle exit \(U_\infty = U_e\). The 1-D energy equation for the flow in the stream tube is

\[ \delta q = dh \]  \hspace{1cm} \text{(1.20)}

and so the heat rejected to the surroundings per unit mass flow is given by

\[ q = h_e - h_t \infty = h_e + \frac{1}{2} U_e^2 - h_\infty - \frac{1}{2} U_\infty^2 = h_e - h_\infty. \]  \hspace{1cm} \text{(1.21)}

The heat rejected through conduction to the surrounding air in the wake of the engine is equal to the change in static enthalpy of the exhaust gas as it returns to the initial state. At this point the cycle is complete.

In the second step, viscosity is turned on and the kinetic energy of the exhaust gas is eventually lost through viscous dissipation. The temperature of the atmosphere is raised by an infinitesimal amount in the process. In actual fact both processes occur simultaneously through a complex process of nearly constant pressure heat transfer and turbulent mixing in the engine wake.

The process of constant pressure heat addition and rejection illustrated by this example is known as the Brayton cycle.

1.2 Thermodynamic cycles

1.2.1 The Carnot cycle

Using the Second Law one can show that heat and work, are not equivalent though each is a form of energy. All work can be converted to heat but not all heat can be converted to work. The most efficient thermodynamic cycle, the Carnot cycle which involves heat interaction at constant temperature, can be used to illustrate this point. Consider the piston cylinder combination shown in Figure 1.4 and the sequence of piston strokes representing the four basic states in the Carnot cycle.
In the ideal Carnot cycle the adiabatic compression and expansion strokes are carried out isentropically. A concrete example in the P-V plane and T-S plane is shown in Figure 1.5 and Figure 1.6. The working fluid is Nitrogen cycling between the temperatures of 300 and 500 Kelvin with the compression stroke moving between one and six atmospheres. The entropy of the compression leg comes from tabulated data for nitrogen. The entropy of the expansion leg is specified to be 7300 J/(kg − K).

The thermodynamic efficiency of the cycle is

\[
\eta = \frac{\text{work output during the cycle}}{\text{heat added to the system during the cycle}} = \frac{W}{Q_2}. \tag{1.22}
\]

According to the first law of thermodynamics

\[
\delta Q = dE + \delta W. \tag{1.23}
\]

Over the cycle, the change in internal energy which is a state variable is zero and the work done is

\[
W = Q_2 - Q_1 \tag{1.24}
\]
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Figure 1.5: P-V diagram of a Carnot cycle working between the temperatures of 300K and 500K. The working fluid is nitrogen.

Figure 1.6: T-S diagram for the Carnot cycle shown above.
and so the efficiency is

\[ \eta = 1 - \frac{Q_1}{Q_2}. \]  \hspace{1cm} (1.25)

The change in entropy over the cycle is also zero and so from the Second Law

\[ \oint ds = \oint \frac{\delta Q}{T} = 0. \]  \hspace{1cm} (1.26)

Since the temperature is constant during the heat interaction we can use this result to write

\[ \frac{Q_1}{T_1} = \frac{Q_2}{T_2}. \]  \hspace{1cm} (1.27)

Thus the efficiency of the Carnot cycle is

\[ \eta_C = 1 - \frac{T_1}{T_2} < 1. \]  \hspace{1cm} (1.28)

For the example shown \( \eta_C = 0.4 \). At most only 40% of the heat added to the system can be converted to work. The maximum work that can be generated by a heat engine working between two finite temperatures is limited by the temperature ratio of the system and is always less than the heat put into the system.

### 1.2.2 The Brayton cycle

As illustrated by the JT9D example, the Brayton cycle involves heat interaction at constant pressure. Now consider the piston cylinder combination shown below and the sequence of piston strokes representing the four basic states of the Brayton cycle. The piston motion is similar to the Carnot cycle except that the heat interaction occurs at constant pressure.

In the ideal Brayton cycle the adiabatic compression and expansion strokes are carried out isentropically. The corresponding behavior of the ideal Brayton cycle in the P-V plane and T-S plane is shown in Figures 1.8 and 1.9.

In the case of the Brayton cycle the work done is still \( W = Q_2 - Q_1 \). The first law can be written
Figure 1.7: The Brayton cycle heat engine

Figure 1.8: P-V diagram of a Brayton cycle working between the pressures of one and six atmospheres. Nitrogen is the working fluid.
\( \delta Q = dE + PdV = dH - VdP. \) 

The heat interaction occurs at constant pressure, \( dP = 0 \) and so the heat added and removed is equal to the enthalpy change.

\[ Q_2 = H_2 - H_1 \]
\[ Q_1 = H_3 - H_0 \]  

The efficiency of the Brayton cycle is

\[ \eta_B = 1 - \frac{H_3 - H_0}{H_2 - H_1}. \]

If the working fluid is an ideal gas with constant heat capacity then we can write for the ideal Brayton cycle

\[ \frac{H_0}{H_1} = \frac{T_0}{T_1} = \left( \frac{P_0}{P_1} \right)^{\frac{1}{\gamma}} = \left( \frac{P_3}{P_2} \right)^{\frac{1}{\gamma}} = \frac{T_3}{T_2} = \frac{H_3}{H_2}. \]

Using (1.32) the Brayton efficiency can be written

\[ \eta_B = 1 - \frac{T_0}{T_1} \left( \frac{T_2}{T_1} - 1 \right). \]
From (1.32) the term in parentheses is one and so the efficiency of the ideal Brayton cycle is finally

$$\eta_B = 1 - \frac{T_0}{T_1}.$$  \hfill (1.34)

The important point to realize here is that the efficiency of a Brayton process is determined entirely by the temperature increase during the compression step of the cycle (or equivalently the temperature decrease during the expansion step).

### 1.3 The standard atmosphere

Figure 1.10 below shows the distribution of temperature and density in the atmosphere with comparisons with isothermal and isentropic models of the atmosphere. The scale height of the atmosphere is

$$H = \frac{a_0^2}{\gamma g} = \frac{RT_0}{g}.$$ \hfill (1.35)

![Figure 1.10: Isothermal and isentropic models of the standard atmosphere.](image-url)

Figure 1.10: Isothermal and isentropic models of the standard atmosphere.
The speed of sound, temperature, and gravitational acceleration in (1.35) are evaluated at zero altitude. For air at 288.15 K the scale height is 8,435 meters (27,674 feet). At this altitude the thermal and potential energy of the atmosphere are of the same order. Below a scale height of one the atmosphere is approximately isentropic and the temperature falls off almost linearly. Above a scale height of about 1.5 the temperature is almost constant. In order to standardize aircraft performance calculations Diehl (Ref. W. S. Diehl, *Some Approximate Equations for the Standard Atmosphere* N.A.C.A. Technical Report No. 375, 1930) defined a standard atmosphere which was widely adopted by the aeronautics community. According to this standard the atmospheric values at sea level in Figure 1.11 are assumed.

### 1.4 Problems

**Problem 1** - Consider the JT9D-7 turbofan cross-section discussed above. Plot the state of the gas which passes through the core of the engine on a temperature versus entropy diagram and on a pressure versus specific volume diagram. Assume constant specific heat throughout the engine with $\gamma = 1.4$. Do the same for the gas which passes through the fan. Determine the efficiency of the cycle. Assume the fan, compressor and turbine are adiabatic, the inlet is isentropic and the exhaust gas of the JT9D passes through an isentropic nozzle where it is expanded to atmospheric pressure before mixing with the surrounding air. Assume pressures and temperatures within the engine are stagnation values.

**Problem 2** - An accurate approximation to the specific heat of air as a function of temperature is
\[
\frac{C_p}{R} = \frac{7}{2} + \left( \frac{\theta_v}{2T} \right)^2 \sinh \left( \frac{\theta_v}{2T} \right) \tag{1.36}
\]

where the vibrational reference temperature for air, \( \theta_v = 3060 \, K \). Plot \( C_p, C_v, \gamma \) and the enthalpy, \( h \), of air as a function of \( T/\theta_v \) over the range 300 \( K \) to 4000 \( K \).

**Problem 3** - Review quasi-one-dimensional gas dynamics. Carefully derive the mass, momentum and energy equations for stationary 1-D flow

\[
d (\rho U A) = \delta m
\]

\[
d (P - \tau_{xx}) + \rho UdU = -\tau_w \left( \frac{\pi Ddx}{A} \right) + \frac{(U_{xm} - U) \delta m}{A} - \frac{\delta F_x}{A} \tag{1.37}
\]

\[
d \left( h_t - \frac{\tau_{xx}}{\rho} + \frac{Q_x}{\rho U} \right) = \frac{\delta Q}{\rho UA} - \frac{\delta W}{\rho UA} + \left( h_{tm} - \left( h_t - \frac{\tau_{xx}}{\rho} + \frac{Q_x}{\rho U} \right) \right) \delta m
\]

where \( U_{mx} \) is the stream-wise component of the velocity and \( h_{tm} \) is the enthalpy of the injected mass \( \delta m \). Explain the assumptions used to get from the full equations of motion to (1.37).
Chapter 2

Engine performance parameters

2.1 The definition of thrust

One might be surprised to learn that there is no direct way to determine the thrust generated by a propulsion system. The reason for this is that the flow over and through an installed engine on an aircraft or an engine attached to a test stand is responsible for the total force on the engine and its nacelle. On any part of the propulsion surface the combination of pressure and viscous stress forces produced by the flow may contribute to the thrust or to the drag and there is no practical way to extricate one force component from the other. Even the most sophisticated test facility can measure the thrust produced by an engine only up to an accuracy of about 0.5%. Wind and weather conditions during the test, inaccuracies in measurement, poorly known flow characteristics in the entrance flow and exhaust and a variety of minor effects limit the ability of a test engineer to precisely measure or predict the thrust of an engine. Thus as a practical matter we must be satisfied with a thrust formula that is purely a definition. Such a definition is only useful to the extent that it reflects the actual thrust force produced by an engine up to some reasonable level of accuracy. In the following, we will use mass and momentum conservation over an Eulerian control volume surrounding a ramjet to motivate a definition of thrust. The control volume is indicated as the dashed line shown in Figure 2.1.

The control volume is in the shape of a cylinder centered about the ramjet. Note that the control volume is simply connected. That is, by suitable distortions without tearing, it is developable into a sphere. The surface of the control volume runs along the entire wetted surface of the ramjet and encloses the inside of the engine. The upstream surface is far enough upstream so that flow variables there correspond to free-stream values. The downstream surface of the control volume coincides with the nozzle exit. The reason for positioning the downstream surface this way is that we need a definition of thrust that
Figure 2.1: Ramjet control volume for developing a definition of thrust

is expressed in terms of flow variables that can be determined relatively easily in terms of the thermodynamic and geometrical properties of the engine internal gas flow. Note that the velocity profile in the wake cannot be used to determine thrust since the profile is momentum-less. An integral over the wake profile is proportional to the sum of thrust plus drag and since the engine is not accelerating this sum is zero. We will assume that within the engine all flow variables are area averaged (averaged in the $y$-$z$ plane) and that the flow is steady. Fuel from an onboard tank is injected through the control volume surface. The mass flows through the engine are

$$ m_a = \text{air mass flow rate} $$

$$ \dot{m}_f = \text{fuel mass flow rate.} \quad (2.1) $$

The fuel mixes and reacts with the incoming air flow releasing heat and the heat is assumed to be uniformly distributed over the engine cross section downstream of the region of combustion. The integrated form of the conservation equations for steady flow with no body forces on an Eulerian control volume is
\[
\int_{A} \rho \bar{U} \cdot \bar{n} dA = 0 \\
\int_{A} \left( \rho \bar{U} \bar{U} + P \bar{T} - \bar{P} \right) \cdot \bar{n} dA = 0 \\
\int_{A} \left( \rho h_{t} \bar{U} - \bar{P} \cdot \bar{U} + Q \right) \cdot \bar{n} dA = 0.
\]

(2.2)

where \( h_{t} \) is the stagnation enthalpy of the gas flow.

\[
h_{t} = e + P v + k
\]

(2.3)

**Mass Balance**

The continuity equation integrated over the control volume leads to

\[
\int_{A} \rho \bar{U} \cdot \bar{n} dA = \\
\int_{A_2} \rho \bar{U} \bar{U} dA + \rho c U c A c - \rho_0 U_0 (A_2 + A_e) - \dot{m}_f + \int_{A_1} \rho_1 V_1 dA = 0.
\]

(2.4)

The first integral in (2.4) involving a flux of mass out of the control volume is carried out over the annular area labeled \( A_2 \) in Figure 2.1. It is a complicated integral in that it involves the wake velocity profile which is not accurately known without a direct measurement. In fact the nozzle exit flow is assumed to be an area averaged plug flow and so all the complexity of the wake profile is thrown into this integral. The last integral in (2.4) is carried out over the outer surrounding surface of the control volume and involves a flux of mass leaving the control volume due to the outward displacement of air produced by the blockage effect of the engine. It too is a complicated integral but one we will be able to easily approximate. Note that this part of the control volume is taken to be straight. It does not follow a streamline. Thus the area of the upstream face of the control volume is equal to \( A_2 + A_e \).

**Momentum Balance**

Now integrate the \( x \)-momentum equation over the control volume.
\[ \int_{A} \left( \rho \bar{U} + P \bar{U} - \bar{F} \right) \cdot ar{n} dA \bigg|_{x} = \]

\[ \int_{A_2} \left( \rho_2 U_2^2 + P_2 \right) dA + (\rho_e U_e^2 A_e + P_e A_e) - (\rho_0 U_0^2 + P_0) (A_2 + A_e) + \]

\[ \int_{A_1} \rho_1 U_1 V_1 dA + \int_{A_w} \left( P \bar{U} - \bar{F} \right) \cdot ar{n} dA \bigg|_{x} = 0 \quad (2.5) \]

Note that the \( x \)-momentum of the injected fuel mass has been neglected. The first integral involves a complicated distribution of pressure and momentum over the area \( A_2 \) and there is little we can do with it. The last integral involves the pressure and stress forces acting over the entire wetted surface of the engine and although the kernel of this integral may be an incredibly complicated function, the integral itself must be zero since the engine is not accelerating or decelerating (the free stream speed is not a function of time).

\[ \int_{A_w} \left( P \bar{U} - \bar{F} \right) \cdot ar{n} dA \bigg|_{x} = Thrust - Drag = 0 \quad (2.6) \]

The second to last integral in (2.5) can be approximated as follows.

\[ \int_{A_1} \rho_1 U_1 V_1 dA \cong \int_{A_1} \rho_1 U_0 V_1 dA \quad (2.7) \]

The argument for this approximation is that at the outside surface of the control volume the \( x \)-component of the fluid velocity is very close to the free stream value. This is a good approximation as long as the control volume surface is reasonably far away from the engine. This approximation allows us to use the mass balance to get rid of this integral. Multiply (2.4) by \( U_0 \), \( \bar{U} \), and subtract from (2.5). The result is

\[ \rho_e U_e (U_e - U_0) A_e + (P_e - P_0) A_e + \dot{m}_f U_0 + \int_{A_2} \left( \rho_2 U_2 (U_2 - U_0) + (P_2 - P_0) \right) dA = 0. \quad (2.8) \]

This is as far as we can go with our analysis and at this point we have to make an arbitrary choice. We will define the drag of the engine as
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\[ Drag = \int_{A_2} (\rho_2 U_2 (U_0 - U_2) + (P_0 - P_2)) \, dA \]  

(2.9)

and the thrust as

\[ Thrust = \rho_e U_e (U_e - U_0) A_e + (P_e - P_0) A_e + \dot{m}_f U_0. \]  

(2.10)

This is a purely practical choice where the thrust is defined in terms of flow variables that can be determined from a thermo-gas-dynamic analysis of the area-averaged engine internal flow. All the complexity of the flow over the engine has been thrown into the drag integral (2.9) which of course could very well have contributions that could be negative. This would be the case, for example, if some part of the pressure profile had \( P_2 - P_0 > 0 \).

The exit mass flow is the sum of the air mass flow plus the fuel mass flow.

\[ \rho_e U_e A_e = \dot{m}_a + \dot{m}_f \]  

(2.11)

Using (2.11) the thrust definition (2.10) can be written in the form

\[ T = \dot{m}_a (U_e - U_0) + (P_e - P_0) A_e + \dot{m}_f U_e. \]  

(2.12)

In this form the thrust definition can be interpreted as the momentum change of the air mass flow across the engine plus the momentum change of the fuel mass flow. The pressure term reflects the acceleration of the exit flow that occurs as the jet exhaust eventually matches the free stream pressure in the far wake. Keep in mind that the fuel is carried on board the aircraft, and in the frame of reference attached to the engine, the fuel has zero velocity before it is injected and mixed with the air.

The thrust definition (2.12) is very general and applies to much more complex systems. If the selected engine was a turbojet the control volume would look like that shown in Figure 2.2.

The surface of the control volume covers the entire wetted surface of the engine including the struts that hold the rotating components in place as well as the rotating compressor, shaft and turbine. In this case the control volume is of mixed Eulerian-Lagrangian type with part of the control volume surface attached to and moving with the rotating parts. The cut on the engine centerline comes from the wrapping of the control volume about the supports and rotating components. All fluxes cancel on the surface of the cut, which is really a line on the engine axis. The terms arising from the pressure-viscous stress forces on the rotating components are just part of the total surface force integral (2.6) that is still
zero. A mass and momentum balance over the control volume shown in Figure 2.2 would lead to the same result (2.12).

### 2.2 Energy balance

The energy balance across the engine is very simple. The energy equation integrates to

\[
\int_A \left( \rho h \overline{U} - \overline{\tau} \cdot \overline{U} + \overline{Q} \right) \cdot \overline{n} dA = 0
\]

\[
\int_{A_2} \left( \rho_2 h_2 U_2 \right) dA + \rho_e h_{e} U_e A_e - \rho_0 h_{00} U_0 (A_2 + A_e) - \dot{m}_f h_f + \int_{A_1} \rho_1 h_{11} V_1 dA = 0.
\]

(2.13)

Here the viscous and heat conduction terms across the boundaries of the control volume have been neglected and the flow over the inside and outside surface of the ramjet is assumed to be adiabatic (or at least the temperature of the engine is assumed to be at steady state where any heat conducted into the engine is conducted out elsewhere). This is a very reasonable though not an exact assumption. Some heat is always lost through the engine nacelle but this is a tiny fraction of the enthalpy flow in the exhaust. The viscous power term on the wetted surface is zero due to the no-slip condition. The only contribution over the wetted surface is from the flux of fuel which carries with it its fuel enthalpy \( h_f \).
A typical value of fuel enthalpy for JP-4 jet fuel is

\[ h_{f|JP-4} = 4.28 \times 10^7 \, J/kg. \]  
(2.14)

As a comparison, the enthalpy of Air at sea level static conditions is

\[ h|_{\text{Air at } 288.15K} = C_p T_{SL} = 1005 \times 288.15 = 2.896 \times 10^5 \, J/kg. \]  
(2.15)

The ratio is

\[ \frac{h_{f|JP-4}}{h|_{\text{Air at } 288.15K}} = 148. \]  
(2.16)

The energy content of a kilogram of hydrocarbon fuel is remarkably large and constitutes one of the important facts of nature that makes extended powered flight possible.

If the flow over the outside of the engine is adiabatic then the stagnation enthalpy of flow over the outside control volume surfaces is equal to the free-stream value and we can write the energy balance as

\[
\int_{A_2} (\rho_2 h_{t0} U_2) dA + \rho_e h_{te} U_e A_e - \rho_0 h_{t0} U_0 (A_2 + A_e) - \dot{m}_f h_f + \int_{A_1} \rho_1 h_{t0} V_1 dA = 0. 
\]  
(2.17)

Now multiply the continuity equation (2.4) by \( h_{t0} \) and subtract from (2.17). The result is

\[ \rho_e h_{te} U_e A_e - \rho_e h_{t0} U_e A_e - \dot{m}_f (h_f - h_{t0}) = 0. \]  
(2.18)

Using (2.11) the energy balance across the engine can be written as

\[ (\dot{m}_a + \dot{m}_f) h_{te} = \dot{m}_a h_{t0} + \dot{m}_f h_f. \]  
(2.19)

The energy balance boils down to a simple algebraic relationship that states that the change in the stagnation enthalpy per second of the gas flow between the exit and entrance of the engine is equal to the added chemical enthalpy per second of the injected fuel flow.
2.3 Capture area

As the operating point of an engine changes, the amount of air passing through the engine may also vary. This is typically the case for an engine operating at subsonic Mach numbers. The capture area of the engine $A_0$ is defined in terms of the air mass flow rate.

$$\dot{m}_a = \rho_0 U_0 A_0$$  \hspace{1cm} (2.20)

The sketches below depict the variation in capture area that can occur as the engine flight Mach number changes from low subsonic to near sonic flight. The geometric entrance area of the engine is $A_1$. Similar changes can occur at a fixed flight Mach number, for example as the engine throttle is changed leading to changes in the demand of the engine for air. More will be said on this topic in a later chapter when we examine how a jet engine operates.

![Variation of inlet capture area with engine operating point.](image)

Figure 2.3: Variation of inlet capture area with engine operating point.

2.4 Overall efficiency

The overall efficiency of a propulsion system is defined as
\[
\eta_{ov} = \frac{\text{The power delivered to the vehicle}}{\text{The total energy released per second through combustion}}. \tag{2.21}
\]

That is
\[
\eta_{ov} = \frac{T U_0}{m_f h_f}. \tag{2.22}
\]

It may not be so obvious but the definition of overall efficiency embodies a certain choice of the frame of reference in which the engine is viewed. In particular we have selected a frame in which the thrust generated by the engine \( T \) acts at a speed \( U_0 \). This is a frame in which the surrounding air is at rest and the engine moves to the left at the given speed. This idea is illustrated in Figure 2.4.

![Frame of reference used to define efficiencies.](image)

**Figure 2.4:** Frame of reference used to define efficiencies.

Note that in the frame of reference depicted in Figure 2.1 and Figure 2.2 the power generated by the engine thrust is zero.

To the children observing the engine from the ground in Figure 2.4 a parcel of still air is engulfed by the engine moving to the left and exits the engine as a mixture of air and combustion products with a speed to the right equal to \( U_e - U_0 \).
2.5 Breguet aircraft range equation

There are a number of models of aircraft range. The simplest assumes that the aircraft flies at a constant value of lift to drag ratio and constant engine overall efficiency. The range is

\[ R = \int U_0 dt = \int \frac{\dot{m}_f h_f \eta_{ov}}{T} dt. \]  
(2.23)

The fuel mass flow is directly related to the change in aircraft weight, \( w \), per second.

\[ \dot{m}_f = -\frac{1}{g} \frac{dw}{dt} \]  
(2.24)

Since thrust equals drag and aircraft weight equals lift we can write

\[ T = D = \left( \frac{D}{L} \right) L = \left( \frac{D}{L} \right) w. \]  
(2.25)

Now the range integral becomes

\[ R = -\eta_{ov} \frac{h_f}{g} \left( \frac{L}{D} \right) \int_{w_{initial}}^{w_{final}} \frac{dw}{w}. \]  
(2.26)

The result is

\[ R = \eta_{ov} \frac{h_f}{g} \left( \frac{L}{D} \right) \ln \left( \frac{w_{initial}}{w_{final}} \right). \]  
(2.27)

The range formula (2.27) is generally attributed to the great French aircraft pioneer Louis Charles Breguet who in 1919 founded a commercial airline company that would eventually become Air France. This result highlights the key role played by the engine overall efficiency in determining aircraft range. Note that as the aircraft burns fuel it must increase altitude to maintain constant \( L/D \) and the required thrust decreases. The small, time dependent effects due to the upward acceleration are neglected.
2.6 Propulsive efficiency

It is instructive to decompose the overall efficiency into an aerodynamic factor and a thermal factor. To accomplish this, the overall efficiency is written as the product of a propulsive and thermal efficiency.

\[ \eta_{ov} = \eta_{pr} \times \eta_{th} \]

The propulsive efficiency is

\[ \eta_{pr} = \frac{\text{Power delivered to the vehicle}}{\text{Power delivered to the vehicle} + \Delta \text{kinetic energy of air} + \Delta \text{kinetic energy of fuel}} \] (2.29)

or

\[ \eta_{pr} = \frac{TU_0}{TU_0 + \left( \frac{m_a(U_e-U_0)^2}{2} - \frac{m_a(0)^2}{2} \right) + \left( \frac{m_f(U_e-U_0)^2}{2} - \frac{m_f(U_0)^2}{2} \right)} \] (2.30)

If the exhaust is fully expanded so that \( P_e = P_0 \) and the fuel mass flow is much less than the air mass flow \( \dot{m}_f \ll \dot{m}_a \), the propulsive efficiency reduces to

\[ \eta_{pr} = \frac{2U_0}{U_e + U_0} \] (2.31)

This is quite a general result and shows the fundamentally aerodynamic nature of the propulsive efficiency. It indicates that for maximum propulsive efficiency we want to generate thrust by moving as much air as possible with as little a change in velocity across the engine as possible. We shall see later that this is the basis for the increased efficiency of a turbofan over a turbojet with the same thrust. This is also the basis for comparison of a wide variety of thrusters. For example, the larger the area of a helicopter rotor the more efficient the lift system tends to be.

2.7 Thermal efficiency

The thermal efficiency is defined as
\[ \eta_{th} = \frac{\text{Power delivered to the vehicle} + \Delta \text{kinetic energy of air} + \Delta \text{kinetic energy of fuel}}{\dot{m}_f h_f} \]  

or

\[ \eta_{th} = \frac{T U_0 + \left( \frac{\dot{m}_a (U_e - U_0)^2}{2} - \frac{\dot{m}_a (0)^2}{2} \right) + \left( \frac{\dot{m}_f (U_e - U_0)^2}{2} - \frac{\dot{m}_f (U_0)^2}{2} \right)}{\dot{m}_f h_f}. \]  

If the exhaust is fully expanded so that \( P_e = P_0 \) the thermal efficiency reduces to

\[ \eta_{th} = \frac{(\dot{m}_a + \dot{m}_f) \frac{U_e^2}{2} - \dot{m}_a \frac{U_0^2}{2}}{\dot{m}_f h_f}. \]  

The thermal efficiency directly compares the change in gas kinetic energy across the engine to the energy released through combustion.

The thermal efficiency of a thermodynamic cycle compares the work out of the cycle to the heat added to the cycle.

\[ \eta_{th} = \frac{W}{Q_{\text{input during the cycle}}} = \frac{Q_{\text{input during the cycle}} - Q_{\text{rejected during the cycle}}}{Q_{\text{input during the cycle}}} = 1 - \frac{Q_{\text{rejected during the cycle}}}{Q_{\text{input during the cycle}}}. \]  

We can compare (2.34) and (2.35) by rewriting (2.34) as

\[ \eta_{th} = 1 - \left( \frac{\dot{m}_f h_f + \dot{m}_a \frac{U_0^2}{2} - (\dot{m}_a + \dot{m}_f) \frac{U_e^2}{2}}{\dot{m}_f h_f} \right). \]  

This equation for the thermal efficiency can also be expressed in terms of the gas enthalpies. Recall that

\[ h_{te} = h_e + \frac{U_e^2}{2}, \]

\[ h_{t0} = h_0 + \frac{U_0^2}{2}. \]
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Replace the velocities in (2.36).

\[ \eta_{th} = 1 - \left( \frac{\dot{m}_f h_f + \dot{m}_a (h_{t0} - h_0) - (\dot{m}_a + \dot{m}_f) (h_{t_e} - h_e)}{\dot{m}_f h_f} \right) \]  
\[ (2.38) \]

Use (2.19) to replace \( \dot{m}_f h_f \) in (2.38). The result is

\[ \eta_{th} = 1 - \frac{Q_{\text{rejected during the cycle}}}{Q_{\text{input during the cycle}}} = 1 - \left( \frac{(\dot{m}_a + \dot{m}_f) (h_{t_e} - h_0) + \dot{m}_f h_0}{\dot{m}_f h_f} \right). \]  
\[ (2.39) \]

According to (2.39) the heat rejected during the cycle is

\[ Q_{\text{rejected during the cycle}} = (\dot{m}_a + \dot{m}_f) (h_{t_e} - h_0) + \dot{m}_f h_0. \]  
\[ (2.40) \]

This expression deserves some discussion. Strictly speaking the engine is not a closed system because of the fuel mass addition across the burner. So the question is; How does the definition of thermal efficiency account for this mass exchange within the concept of the thermodynamic cycle? The answer is that the heat rejected from the exhaust is comprised of two distinct parts. There is the heat rejected by conduction from the nozzle flow to the surrounding atmosphere plus physical removal from the thermally equilibrated nozzle flow of a portion equal to the added fuel mass flow. From this perspective, the fuel mass flow carries its fuel enthalpy into the system by injection in the burner and the exhaust fuel mass flow carries its ambient enthalpy out of the system by mixing with the surroundings. There is no net mass increase or decrease to the system.

Note that there is no assumption that the compression or expansion process operates isentropically, only that the exhaust is fully expanded.

2.8 Specific impulse, specific fuel consumption

An important measure of engine performance is the amount of thrust produced for a given amount of fuel burned. This leads to the definition of specific impulse

\[ I_{sp} = \frac{\text{Thrust force}}{\text{Weight flow of fuel burned}} = \frac{T}{\dot{m}_f g} \]  
\[ (2.41) \]

with units of seconds. The specific fuel consumption is essentially the inverse of the specific impulse.
CHAPTER 2. ENGINE PERFORMANCE PARAMETERS

\[ SFC = \frac{Pounds \ of \ fuel \ burned \ per \ hour}{Pounds \ of \ thrust} = \frac{3600}{I_{sp}} \]  

(2.42)

The specific fuel consumption is a relatively easy to remember number of order one. Some typical values are

\[ SFC|_{JT9D-\text{takeoff}} \approx 0.35 \]
\[ SFC|_{JT9D-\text{cruise}} \approx 0.6 \]  

(2.43)
\[ SFC|_{\text{military engine}} \approx 0.9 \text{to} 1.2 \]
\[ SFC|_{\text{military engine with afterburning}} \approx 2. \]

The \( SFC \) generally goes up as an engine moves from takeoff to cruise, as the energy required to produce a pound of thrust goes up with increased percentage of stagnation pressure losses and with the increased momentum of the incoming air.

2.9 Dimensionless forms

We have already noted the tendency to use both Metric and English units in dealing with propulsion systems. Unfortunately, despite great effort, the US propulsion industry has been unable to move away from the clumsy system of English units. Whereas the rest of the world, including the British, has gone fully metric. This is a real headache and something we will just have to live with, but the problem is vastly reduced by expressing all of our equations in dimensionless form.

**Dimensionless forms of the Thrust.**

\[ \frac{T}{P_0 A_0} = \gamma M_0^2 \left( (1 + f) \frac{U_e}{U_0} - 1 \right) + \frac{A_e}{A_0} \left( \frac{P_e}{P_0} - 1 \right) \]  

(2.44)

\[ \frac{T}{\dot{m}_a a_0} = \left( \frac{1}{\gamma M_0} \right) \frac{T}{P_0 A_0} \]

Normalizing the thrust by \( P_0 A_0 \) produces a number that compares the thrust to a force equal to the ambient pressure multiplied by the capture area. In order to overcome drag it is essential that this be a number considerably larger than one.

**Dimensionless Specific impulse.**
\[ \frac{I_{sp}g}{a_0} = \left( \frac{1}{f} \right) \frac{T}{\dot{m}_a a_0} \quad (2.45) \]

The quantity \( f \) is the fuel/air ratio defined as

\[ f = \frac{\dot{m}_f}{\dot{m}_a}. \quad (2.46) \]

**Overall efficiency.**

\[ \eta_{ov} = \left( \frac{\gamma - 1}{\gamma} \right) \left( \frac{1}{f \tau_f} \right) \left( \frac{T}{P_0 A_0} \right) \quad (2.47) \]

The ratio of fuel to ambient enthalpy appears in this definition.

\[ \tau_f = \frac{h_f}{C_p T_0} \quad (2.48) \]

And \( T_0 \) is the temperature of the ambient air. Note that the fuel/air ratio is relatively small whereas \( \tau_f \) is rather large (See (2.16)). Thus \( 1/(f \tau_f) \) is generally a fraction somewhat less than one.

### 2.10 Engine notation

An important part of analyzing the performance of a propulsion system has to do with being able to determine how each component of the engine contributes to the overall thrust and specific impulse. To accomplish this, we will use a standard notation widely used in industry for characterizing the pressure and temperature change across each component.

First we need to adopt a standard system for numbering the engine components. Consider the generic engine cross sections shown in Figure 2.5.

The performance of each component is defined in terms of the stagnation pressure and temperature entering and leaving the component. A widely accepted notation is

\[ \tau = \frac{\text{The stagnation temperature leaving the component}}{\text{The stagnation temperature entering the component}} \]

\[ \pi = \frac{\text{The stagnation pressure leaving the component}}{\text{The stagnation pressure entering the component}}. \quad (2.49) \]
The various stations are defined as follows.

Station 0 - This is the reference state of the gas well upstream of the engine entrance. The temperature/pressure parameters are

\[
\tau_p = \frac{T_{r0}}{T_0} = 1 + \frac{\gamma - 1}{2} M_0^2
\]

\[
\pi_p = \frac{P_{r0}}{P_0} = \left(1 + \frac{\gamma - 1}{2} M_0^2\right)^{\frac{\gamma}{\gamma-1}}.
\]  

(2.50)

Note that these definitions are exceptional in that the denominator is the static temperature and pressure of the free stream.

Station 1 - Entrance to the engine inlet. The purpose of the inlet is to reduce the Mach number of the incoming flow to a low subsonic value with as small a stagnation pressure loss as possible. From the entrance to the end of the inlet there is always an increase in area and so the component is appropriately called a diffuser.

Station 1.5 - The inlet throat.

Station 2 - The fan or compressor face. The temperature/pressure parameters across the diffuser are
\[ \tau_d = \frac{T_{t2}}{T_{t1}} \]
\[ \pi_d = \frac{P_{t2}}{P_{t1}}. \]

In the absence of an upstream shock wave the flow from the reference state is regarded as adiabatic and isentropic so that

\[ T_{t1} = T_{t0} \]
\[ P_{t1} = P_{t0}. \]

The inlet is usually modeled as an adiabatic flow so the stagnation temperature is approximately constant, however the stagnation pressure decreases due to the presence of viscous boundary layers and possibly shock waves.

**Station 2.5** - All turbofan engines comprise at least two spools. The fan is usually accompanied by a low pressure compressor driven by a low pressure turbine through a shaft along the centerline of the engine. A concentric shaft connects the high pressure turbine and high pressure compressor. Station 2.5 is generally taken at the interface between the low and high pressure compressor. Roll Royce turbofans commonly employ three spools with the high pressure compressor broken into two spools.

**Station 13** - This is a station in the bypass stream corresponding to the fan exit ahead of the entrance to the fan exhaust nozzle. The temperature/pressure parameters across the fan are

\[ \tau_{1c} = \frac{T_{113}}{T_{t2}} \]
\[ \pi_{1c} = \frac{P_{113}}{P_{t2}}. \]

**Station 18** - The fan nozzle throat.

**Station 1e** - The fan nozzle exit. The temperature/pressure parameters across the fan nozzle are
\( \tau_{1n} = \frac{T_{t1e}}{T_{t13}} \)

\( \pi_{1n} = \frac{P_{t1e}}{P_{t13}} \).

\( \tau_{c} = \frac{T_{t3}}{T_{t2}} \)

\( \pi_{c} = \frac{P_{t3}}{P_{t2}} \).

Station 3 - The exit of the high pressure compressor. The temperature/pressure parameters across the compressor are

Note that the compression includes that due to the fan. From a cycle perspective it is usually not necessary to distinguish the high and low pressure sections of the compressor. The goal of the designer is to produce a compression system that is as near to isentropic as possible.

Station 4 - The exit of the burner. The temperature/pressure parameters across the burner are

\( \tau_{b} = \frac{T_{t4}}{T_{t3}} \)

\( \pi_{b} = \frac{P_{t4}}{P_{t3}} \).

The temperature at the exit of the burner is regarded as the highest temperature in the Brayton cycle although generally higher temperatures do occur at the upstream end of the burner where combustion takes place. The burner is designed to allow an influx of cooler compressor air to mix with the combustion gases bringing the temperature down to a level that the high pressure turbine structure can tolerate. Modern engines use sophisticated cooling methods to enable operation at values of \( T_{t4} \) that approach 3700\( R \) (2050K), well above the melting temperature of the turbine materials.

Station 4.5 - This station is at the interface of the high and low pressure turbines.

Station 5 - The exit of the turbine. The temperature/pressure parameters across the turbine are
As with the compressor the goal of the designer is to produce a turbine system that operates as isentropically as possible.

**Station 6** - The exit of the afterburner if there is one. The temperature/pressure parameters across the afterburner are

\[
\tau_a = \frac{T_{t6}}{T_{t5}}, \quad \pi_a = \frac{P_{t6}}{P_{t5}}.
\]

(2.58)

The Mach number entering the afterburner is fairly low and so the stagnation pressure ratio of the afterburner is fairly close to, and always less than, one.

**Station 7** - The entrance to the nozzle.

**Station 8** - The nozzle throat. Over the vast range of operating conditions of modern engines the nozzle throat is choked or very nearly so.

**Station e** - The nozzle exit. The temperature/pressure component parameters across the nozzle are

\[
\tau_n = \frac{T_{te}}{T_{t7}}, \quad \pi_n = \frac{P_{te}}{P_{t7}}.
\]

(2.59)

In the absence of the afterburner, the nozzle parameters are generally referenced to the turbine exit condition so that

\[
\tau_n = \frac{T_{te}}{T_{t5}}, \quad \pi_n = \frac{P_{te}}{P_{t5}}.
\]

(2.60)
In general the goal of the designer is to minimize heat loss and stagnation pressure loss through the inlet, burner and nozzle.

There are two more very important parameters that need to be defined. The first is one we encountered before when we compared the fuel enthalpy to the ambient air enthalpy.

\[ \tau_f = \frac{h_f}{C_p T_0} \tag{2.61} \]

The second parameter is, in a sense, the most important quantity needed to characterize the performance of an engine.

\[ \tau_\lambda = \frac{T_{t4}}{T_0} \tag{2.62} \]

In general every performance measure of the engine gets better as \( \tau_\lambda \) is increased and a tremendous investment has been made over the years to devise turbine cooling and ceramic coating schemes that permit ever higher turbine inlet temperatures, \( T_{t4} \).

### 2.11 Problems

**Problem 1** - Suppose 10% of the heat generated in a ramjet combustor is lost through conduction to the surroundings. How would this change the energy balance (2.19)? How would it affect the thrust?

**Problem 2** - Write down the appropriate form of the thrust definition (2.12) for a turbofan engine with two independent streams. Suppose 5% of the air from the high pressure compressor is to be used to power aircraft systems. What would be the appropriate thrust formula?

**Problem 3** - Consider the flow through a turbojet. The energy balance across the burner is

\[ (\dot{m}_a + \dot{m}_f) h_{t4} = \dot{m}_a h_{t3} + \dot{m}_f h_f. \tag{2.63} \]

The enthalpy rise across the compressor is equal to the enthalpy decrease across the turbine. Show that the energy balance (2.63) can also be written

\[ (\dot{m}_a + \dot{m}_f) h_{t5} = \dot{m}_a h_{t2} + \dot{m}_f h_f. \tag{2.64} \]
The inlet and nozzle are usually assumed to operate adiabatically. Show that (2.64) can be expressed as

\[(\dot{m}_a + \dot{m}_f) h_{te} = \dot{m}_a h_{t0} + \dot{m}_f h_f\]  

which is the same as the overall enthalpy balance for a ramjet (2.19).

**Problem 4** - Work out the dimensionless forms in Section 2.9.
Chapter 3

The ramjet cycle

3.1 Ramjet flow field

Before we begin to analyze the ramjet cycle we will consider an example that can help us understand how the flow through a ramjet comes about. The key to understanding the flow field is the intelligent use of the relationship for mass flow conservation. In this connection there are two equations that we will rely upon. The first is the expression for 1-D mass flow in terms of the stagnation pressure and temperature.

\[
\dot{m} = \rho U A = \frac{\gamma}{\left(\frac{\gamma+1}{2}\right)^{\frac{\gamma+1}{2(\gamma-1)}}} \left(\frac{P_t A}{\sqrt{\gamma R T_t}}\right) f(M) \tag{3.1}
\]

The second is the all-important area-Mach number function.

\[
f(M) = \frac{A^*}{A} = \left(\frac{\gamma + 1}{2}\right)^{\frac{\gamma+1}{2(\gamma-1)}} \frac{M}{\left(1 + \frac{\gamma-1}{2} M^2\right)^{\frac{\gamma+1}{2(\gamma-1)}}} \tag{3.2}
\]

This function is plotted in Figure 3.1 for three values of \(\gamma\).

For adiabatic, isentropic flow of a calorically perfect gas along a channel Equation (3.1) provides a direct connection between the local channel cross sectional area and Mach number.

In addition to the mass flow relations there are two relationships from Rayleigh line theory that are also very helpful in guiding our understanding of the effect of heat addition on
CHAPTER 3. THE RAMJET CYCLE

3-2

Figure 3.1: Area - Mach number relation.

These are the equations that describe the effect of heat addition on the Mach number and stagnation pressure of the flow.

\[
\frac{T_t^*}{T_t} = \frac{(1 + \gamma M^2)^2}{2 (1 + \gamma) M^2 \left(1 + \frac{\gamma - 1}{2} M^2\right)}
\]

\[
\frac{P_t^*}{P_t} = \left(\frac{1 + \gamma M^2}{1 + \gamma}\right) \left(\frac{\gamma + 1}{2} \frac{\gamma - 1}{2} M^2\right)^{\frac{\gamma}{\gamma - 1}}
\]

These equations are plotted in Figure 3.2.

Figure 3.2: Effects of heat exchange on Mach number and stagnation pressure.

There are several features shown in these plots that have important implications for the ramjet flow. The first is that much more heat can be added to a subsonic flow than to a supersonic flow before thermal choking occurs; that is, before the flow is brought to Mach one. The second is that stagnation pressure losses due to heat addition in subsonic flow are relatively small and cannot exceed about 20% of the stagnation pressure of the flow.
entering the region of heat addition. In contrast stagnation pressure losses due to heat addition can be quite large in a supersonic flow.

With this background we will now construct a ramjet flow field beginning with supersonic flow through a straight, infinitely thin tube. For definiteness let the free stream Mach number be three and the ambient temperature $T_0 = 216 \text{ K}$. Throughout this example we will assume that the friction along the channel wall is negligible.

![Figure 3.3](image1)

Figure 3.3: Step 1 - Initially uniform Mach three flow.

Add an inlet convergence and divergence.

![Figure 3.4](image2)

Figure 3.4: Step 2 - Inlet convergence and divergence with $f(M)$ shown.

Let the throat Mach number be two ($M_{1,5} = 2.0$). In Figure 3.4 the Mach number decreases to the inlet throat ($f(M)$ increases), then increases again to the inlet value of three, ($f(M) = 0.236$). The thrust of this system is clearly zero since the x-directed component of the pressure force on the inlet is exactly balanced on the upstream and downstream sides of the inlet.

In Figure 3.5 heat is added to the supersonic flow inside the engine. Neglect the mass flow of fuel added compared to the air mass flow. As the heat is added the mass flow is conserved. Thus, neglecting the fuel added, the mass balance is
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3-4

Figure 3.5: Step 2 - Introduce a burner and add heat to the flow.

\[ \dot{m} = \frac{\gamma}{(\gamma + 1)} \left( \frac{P_{i0} A_3}{\sqrt{\gamma R T_{i0}}} \right)^{\gamma+1} \frac{f(3)}{2(\gamma - 1)} \left( \frac{P_{i4} A_4}{\sqrt{\gamma R T_{i4}}} \right)^{\gamma+1} f(M_4). \] (3.4)

As the heat is added, \( T_{i4} \) goes up and \( P_{i4} \) goes down while the following equality must be maintained

\[ \frac{P_{i0}}{\sqrt{T_{i0}}} f(3) = \frac{P_{i4}}{\sqrt{T_{i4}}} f(M_4). \] (3.5)

Conservation of mass (3.5) implies that \( f(M_4) \) must increase and the Mach number downstream of the burner decreases. There is a limit to the amount of heat that can be added to this flow and the limit occurs when \( f(M_4) \) attains its maximum value of one. At this point the flow looks like Figure 3.6.

The Rayleigh line relations tell us that the temperature rise across the burner that produces this flow is

\[ \frac{T_{i4}}{T_{i3}} \bigg|_{M_4=1} = 1.53. \] (3.6)

The corresponding stagnation pressure ratio across the system is
Figure 3.6: Step 3 - Introduce sufficient heat to bring the exit Mach number to a value slightly greater than one.

\[
\left( \frac{P_{t4}}{P_{t3}} \right)_{M_4=1 \ before \ unstart} = 0.292. \tag{3.7}
\]

Now, suppose the temperature at station 4 is increased very slightly. We have a problem; \( T_{t4} \) is up slightly, \( P_{t4} \) is down slightly but \( f(M_4) \) cannot increase. To preserve the mass flow rate imposed at the inlet, the supersonic flow in the interior of the engine must undergo an un-start. The flow must switch to the configuration shown in Figure 3.7. The mass flow equation (3.5) can only be satisfied by a flow between the inlet throat and the burner that achieves the same stagnation pressure loss (3.7), since \( f(M_4) \) cannot exceed one and the stagnation temperature ratio is essentially the same.

As a result of the un-start, a shock wave now sits at the end of the diffuser section of the inlet. Notice that the engine internal pressure is still very large and the exit Mach number must remain one. The stagnation temperature has not changed and so, as was just pointed out, the mass balance tells us that the stagnation pressure of the exit flow must be the same as before the un-start. Thus

\[
\left( \frac{P_{t4}}{P_{t0}} \right)_{M_4=1 \ after \ unstart} = 0.292. \tag{3.8}
\]

Now, the stagnation pressure loss is divided between two mechanisms, the loss across the
Figure 3.7: Step 4 - Increase the heat added very slightly to unstart the flow.

shock wave, and the loss due to heat addition across the burner. The stagnation pressure ratio across a Mach three shock wave is

\[
\frac{P_{t3}}{P_{t0}} \bigg|_{M=3} = 0.3285. \tag{3.9}
\]

The burner inlet Mach number is \( M_3 = 0.475 \), and the stagnation loss due to thermal choking across the burner is

\[
\frac{P_{t4}}{P_{t3}} \bigg|_{M=0.475} = 0.889. \tag{3.10}
\]

The product of (3.9), and (3.10) is 0.292.

Now let’s look at the thrust generated by the flow depicted in Figure 3.7. The thrust definition, neglecting the fuel/air ratio, is

\[
\frac{T}{P_0 A_0} = \gamma M_0^2 \left( \frac{U_e}{U_0} - 1 \right) + \frac{A_e}{A_0} \left( \frac{P_e}{P_0} - 1 \right). \tag{3.11}
\]

The pressure ratio across the engine is
CHAPTER 3. THE RAMJET CYCLE

\[ \frac{P_e}{P_0} = \frac{P_{te}}{P_{t0}} \left( \frac{1 + \frac{\gamma-1}{2}M_0^2}{1 + \frac{\gamma-1}{2}M_e^2} \right)^{\frac{\gamma-1}{\gamma}} = 0.292 \left( \frac{2.8}{1.2} \right)^{3.5} = 5.66 \quad (3.12) \]

and the temperature ratio is

\[ \frac{T_e}{T_0} = \frac{T_{te}}{T_{t0}} \left( \frac{1 + \frac{\gamma-1}{2}M_0^2}{1 + \frac{\gamma-1}{2}M_e^2} \right) = 1.53 \left( \frac{2.8}{1.2} \right) = 3.5667. \quad (3.13) \]

This produces the velocity ratio

\[ \frac{U_e}{U_0} = \frac{M_e}{M_0} \sqrt{\frac{T_e}{T_0}} = 0.6295. \quad (3.14) \]

Now substitute into (3.11).

\[ \frac{T}{P_0A_0} = 1.4 \times 9 \times (0.6295 - 1) + 1 \times (5.66 - 1) = -4.66 + 4.66 = 0 \quad (3.15) \]

The thrust is zero. We would expect this from the symmetry of the upstream and downstream distribution of pressure on the inlet. Now let’s see if we can produce some thrust. First adjust the inlet so that the throat area is reduced until the throat Mach number is just slightly larger than one. This will only effect the flow in the inlet and all flow variables in the rest of the engine will remain the same.

With the flow in the engine subsonic, and the shock positioned at the end of the diffuser, we have a great deal of margin for further heat addition. If we increase the heat addition across the burner the mass balance (3.5) is still preserved and the exit Mach number remains one. Let the burner outlet temperature be increased to \( T_{t4} = 1814.4K \). The flow now looks something like Figure 3.8.

The stagnation temperature at the exit is up, the stagnation pressure is up, and the shock has moved to the left to a lower upstream Mach number (higher \( f(M) \)), while the mass flow (3.5) is preserved. Note that we now have some thrust arising from the x-component of the high pressure force behind the shock that acts to the left on an outer portion of the inlet surface. This pressure exceeds the inlet pressure on the corresponding upstream portion of the inlet surface. The stagnation pressure ratio across the engine is determined from the mass balance (3.5).

\[ \frac{P_{te}}{P_{t0}} = f(3) \sqrt{\frac{T_{te}}{T_{t0}}} = 0.263\sqrt{3} = 0.409 \quad (3.16) \]
Let’s check the thrust. The pressure ratio across the engine is

\[ \frac{P_e}{P_0} = 0.409 \left( \frac{2.8}{1.2} \right)^3 = 7.94. \]  

(3.17)

The temperature ratio is

\[ \frac{T_e}{T_0} = \frac{T_{te}}{T_{t0}} \left( \frac{1 + \frac{\gamma - 1}{2} M_0^2}{1 + \frac{\gamma - 1}{2} M_e^2} \right) = 3 \left( \frac{2.8}{1.2} \right) = 7 \]  

(3.18)

and the velocity ratio is now

\[ \frac{U_e}{U_0} = \frac{M_e}{M_0} \sqrt{\frac{T_e}{T_0}} = \frac{\sqrt{7}}{3} = 0.882. \]  

(3.19)

The thrust is

\[ \frac{T}{P_0 A_0} = 1.4 \times 9 \times (0.882 - 1) + 1 \times (7.94 - 1) = -1.49 + 6.94 = 5.45. \]  

(3.20)

This is a pretty substantial amount of thrust. Note that, so far, the pressure term in the thrust definition is the important thrust component in this design.
3.2 The role of the nozzle

Let’s see if we can improve the design. Add a convergent nozzle to the engine as shown in Figure 3.9. The mass balance is

$$P_{t0}A_{1.5} \sqrt{604.8} = P_{te}A_e \sqrt{1814.4}.$$  \hspace{1cm} (3.21)

How much can we decrease $A_e$? Begin with Figure 3.8. As the exit area is decreased the exit Mach number remains one due to the high internal pressure in the engine. The shock moves upstream toward the inlet throat, the exit stagnation pressure increases and the product $P_{te}A_e$ remains constant. The minimum exit area that can be reached without un-starting the inlet flow is when the inlet shock is very close to the throat, becoming vanishingly weak. At this condition, the only mechanism for stagnation pressure loss is the heat addition across the burner. The Mach number entering the burner is $M_3 = 0.138$ as shown in Figure 3.9. The stagnation pressure loss across the burner is proportional to the square of the entering Mach number.

$$\frac{dP_t}{P_t} = -\gamma M^2 \frac{dT_t}{T_t}.$$ \hspace{1.5cm} (3.22)

To a reasonable approximation the stagnation loss across the burner can be neglected and we can take $P_{te} \approx P_{t0}$. In this approximation, the area ratio that leads to the flow depicted...
in Figure 3.9 is

\[
\frac{A_e}{A_{1.5\text{ ideal}}} = \sqrt{\frac{1814.4}{604.8}} = 1.732. \tag{3.23}
\]

This relatively large area ratio is expected considering the greatly increased temperature and lower density of the exhaust gases compared to the gas that passes through the upstream throat. What about the thrust? Now the static pressure ratio across the engine is

\[
\frac{P_e}{P_0} = \left(\frac{2.8}{1.2}\right)^{3.5} = 19.41. \tag{3.24}
\]

The temperatures and Mach numbers at the nozzle exit are the same as before so the velocity ratio does not change between Figure 3.8 and Figure 3.9. The dimensionless thrust is

\[
\frac{T}{P_0A_0} = 1.4 \times 9 \times (0.882 - 1) + 1.732 \times 0.236 \times (19.41 - 1) = -1.49 + 7.53 = 6.034. \tag{3.25}
\]

That’s pretty good; just by adding a convergent nozzle and reducing the shock strength we have increased the thrust by about 20%. Where does the thrust come from in this ramjet design? The figure below schematically shows the pressure distribution through the engine. The pressure forces on the inlet and nozzle surfaces marked "a" roughly balance, although the forward pressure is slightly larger compared to the rearward pressure on the nozzle due to the heat addition. But the pressure on the inlet surfaces marked "b" are not balanced by any force on the nozzle. These pressures substantially exceed the pressure on the upstream face of the inlet and so net thrust is produced.

### 3.3 The ideal ramjet cycle

But we can do better still! The gas that exits the engine is at a very high pressure compared to the ambient and it should be possible to gain thrust from this by adding a divergent section to the nozzle as shown below.

The area ratio of the nozzle is chosen so that the flow is fully expanded, \( P_e = P_0 \). The stagnation pressure is constant through the engine and so we can conclude from
Figure 3.10: Imbalance of pressure forces leading to net thrust.

Figure 3.11: Ideal ramjet with a fully expanded nozzle.
\[
\frac{P_e}{P_0} = \frac{P_{te}}{P_{t0}} \left( \frac{1 + \frac{\gamma-1}{2} M_0^2}{1 + \frac{\gamma-1}{2} M_e^2} \right)^{\frac{\gamma}{\gamma-1}}
\]
\[
1 = 1 \times \left( \frac{1 + \frac{\gamma-1}{2} M_0^2}{1 + \frac{\gamma-1}{2} M_e^2} \right)^{\frac{\gamma}{\gamma-1}}
\] (3.26)

that \(M_e = M_0\). The temperature ratio is
\[
\frac{T_e}{T_0} = \frac{T_{te}}{T_{t0}} \left( \frac{1 + \frac{\gamma-1}{2} M_0^2}{1 + \frac{\gamma-1}{2} M_e^2} \right)^{\frac{\gamma}{\gamma-1}} = \frac{T_{te}}{T_{t0}} = 3.
\] (3.27)

Finally, the dimensionless thrust is
\[
\frac{T}{P_0 A_0} = \gamma M_0^2 \left( \frac{M_e}{M_0} \sqrt{\frac{T_e}{T_0}} - 1 \right) = 1.4 \times 9 \times \left( \sqrt{3} - 1 \right) = 9.22.
\] (3.28)

Adding a divergent section to the nozzle at this relatively high Mach number increases the thrust by 50%.

Now work out the other engine parameters. The fuel/air ratio is determined from
\[
\dot{m}_f h_f = (\dot{m}_a + \dot{m}_f) h_{t4} - \dot{m}_a h_{t3}.
\] (3.29)

Assume the fuel added is JP-4 with \(h_f = 4.28 \times 10^7 J/kg\). Equation (3.29) becomes
\[
f = \frac{\frac{\dot{m}_f}{\dot{m}_a} \frac{T_{t4}}{T_{t3}} - 1}{\frac{h_f}{c_p T_{t3}} - \frac{T_{t4}}{T_{t3}}} = \frac{1814.4}{691.8} - \frac{1}{70.41 - \frac{1814.4}{691.8}} = 0.0297.
\] (3.30)

The relatively small value of fuel/air ratio is the a posteriori justification of our earlier neglect of the fuel mass flow compared to the air mass flow. If we include the fuel/air ratio in the thrust calculation (but still ignore the effect of mass addition on the stagnation pressure change across the burner) the result is
\[
\frac{T}{P_0 A_0} = \gamma M_0^2 \left( 1 + f \frac{M_e}{M_0} \sqrt{\frac{T_e}{T_0}} - 1 \right) = 1.4 \times 9 \times \left( 1.0297 \times \sqrt{3} - 1 \right) = 9.872.
\] (3.31)
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3-13

The error in the thrust is about 7\% when the fuel contribution is neglected. The dimensionless specific impulse is

$$I_{spg} = \left( \frac{1}{f} \right) \left( \frac{1}{\gamma M_0} \right) \frac{T}{P_0 A_0} = \frac{9.872}{0.0297 \times 1.4 \times 3} = 79.14$$

(3.32)

and the overall efficiency is, \((\tau_f = h_f/C_p T_0 = 197.2)\),

$$\eta_{ov} = \left( \frac{\gamma - 1}{\gamma} \right) \left( \frac{1}{f \tau_f} \right) \frac{T}{P_0 A_0} = \left( \frac{0.4}{1.4} \right) \left( \frac{9.872}{0.0297 \times 197.2} \right) = 0.482.$$ \hspace{1cm} (3.33)

The propulsive efficiency is

$$\eta_{pr} = \frac{2U_0}{U_e + U_0} = \frac{2}{1 + \sqrt{3}} = 0.732.$$ \hspace{1cm} (3.34)

The thermal efficiency of the engine shown in Figure 3.11 can be expressed as follows

$$\eta_{th} = \frac{(\dot{m}_a + \dot{m}_f) \frac{U_e^2}{2} - \dot{m}_a U_0^2}{\dot{m}_f h_f} = \frac{(\dot{m}_a + \dot{m}_f) (h_{te} - h_e) - \dot{m}_a (h_{t0} - h_0)}{(\dot{m}_a + \dot{m}_f) h_{te} - \dot{m}_a h_{t0}}$$

$$\eta_{th} = 1 - \frac{Q_{\text{rejected during the cycle}}}{Q_{\text{input during the cycle}}} = 1 - \frac{(\dot{m}_a + \dot{m}_f) h_e - \dot{m}_a h_0}{(\dot{m}_a + \dot{m}_f) h_{te} - \dot{m}_a h_{t0}}$$ \hspace{1cm} (3.35)

$$\eta_{th} = 1 - \frac{T_0}{T_{t0}} \left( \frac{(1 + f) \frac{T_e}{T_{t0}} - 1}{(1 + f) \frac{T_e}{T_{t0}} - 1} \right).$$

The heat rejection is accomplished by mixing of the hot exhaust stream with surrounding air at constant pressure. Noting (3.27) for the ideal ramjet, the last term in brackets is one and the thermal efficiency becomes

$$\eta_{th \text{ ideal ramjet}} = 1 - \frac{T_0}{T_{t0}}.$$ \hspace{1cm} (3.36)

For the ramjet conditions of this example the thermal efficiency is \(2/3\). The Brayton cycle efficiency is

$$\eta_B = 1 - \frac{T_0}{T_3}$$ \hspace{1cm} (3.37)
In the ideal cycle approximation, the Mach number at station 3 is very small thus \( T_3 \approx T_{t0} \) and the thermal and Brayton efficiencies are identical. Note that, characteristically for a Brayton process, the thermal efficiency is determined entirely by the inlet compression process. The ramjet design shown in Figure 3.11 represents the best we can do at this Mach number. In fact the final design is what we would call the ideal ramjet. The ideal cycle will be the basis for comparison with other engine cycles but it is not a practically useful design. The problem is that the inlet is extremely sensitive to small disturbances in the engine. A slight increase in burner exit temperature or decrease in nozzle exit area or a slight decrease in the flight Mach number will cause the inlet to un-start. This would produce a strong normal shock in front of the engine, a large decrease in air mass flow through the engine and a consequent decrease in thrust. A practical ramjet design for supersonic flight requires the presence of a finite amplitude inlet shock for stable operation.

### 3.4 Optimization of the ideal ramjet cycle

For a fully expanded nozzle the thrust equation reduces to

\[
\frac{T}{P_0 A_0} = \gamma M_0^2 \left( (1 + f) \frac{M_e}{M_0} \sqrt{\frac{T_e}{T_0}} - 1 \right).
\]

For the ideal cycle, where \( P_{te} = P_{t0} \), \( M_e = M_0 \) and \( T_{te}/T_{t0} = T_e/T_0 \), the thrust equation using \( (1 + f) = (\tau_f - \tau_r) / (\tau_f - \tau_\lambda) \) becomes

\[
\frac{T}{P_0 A_0} = \frac{2\gamma}{\gamma - 1} \left( \frac{\tau_r - 1}{\tau_f - \tau_r} \right) \left( \frac{\tau_f - \tau_r}{\tau_f - \tau_\lambda} \sqrt{\frac{\tau_\lambda}{\tau_r}} - 1 \right).
\]

(3.39)

This form of the thrust equation is useful because it expresses the thrust in terms of cycle parameters that we can rationalize. The parameter \( \tau_r \) is fixed by the flight Mach number. At a given altitude \( \tau_\lambda \) is determined by maximum temperature constraints on the hot section materials of the engine, as well as fuel chemistry, and gas dissociation. If the flight Mach number goes to zero the thrust also goes to zero. As the flight Mach number increases for fixed \( \tau_\lambda \) the fuel flow must decrease until \( \tau_\lambda = \tau_r \) when fuel shut-off occurs and the thrust is again zero. A typical thrust plot is shown below.

The optimization question is; at what Mach number should the ramjet operate for maximum thrust at a fixed \( \tau_\lambda \)? Differentiate (3.39) with respect to \( \tau_r \) and set the result to zero.
The value of $\tau_r$ for maximum thrust is determined from

$$
\frac{\partial}{\partial \tau_r} \left( \frac{T}{P_0 A_0} \right) = \frac{2\gamma}{\gamma - 1} \left( \tau_\lambda \tau_r \left( 1 - 3\tau_r + 2\tau_r \sqrt{\frac{\tau_\lambda}{\tau_r}} \right) + \tau_f \left( \tau_\lambda + \tau_\lambda \tau_r - 2\tau_r^2 \sqrt{\frac{\tau_\lambda}{\tau_r}} \right) \right) = 0
$$

(3.40)

The quantity $\tau_f$ is quite large and so the second term in parentheses in (3.41) clearly dominates the first term. For $f \ll 1$ the maximum thrust Mach number of a ramjet is found from

$$
\tau_\lambda \tau_r \left( 1 - 3\tau_r + 2\tau_r \sqrt{\frac{\tau_\lambda}{\tau_r}} \right) + \tau_f \left( \tau_\lambda + \tau_\lambda \tau_r - 2\tau_r^2 \sqrt{\frac{\tau_\lambda}{\tau_r}} \right) = 0.
$$

(3.41)

For the case shown above, with $\tau_\lambda = 8.4$, the optimum value of $\tau_r$ is 3.5 corresponding to a Mach number of 3.53. The ramjet is clearly best suited for high Mach number flight and the optimum Mach number increases as the maximum engine temperature increases.
The specific impulse also has an optimum but it is much more gentle than the thrust optimum, as shown in Figure 3.13.

![Figure 3.13: Ramjet specific impulse.](image)

Optimizing the cycle with respect to thrust essentially gives close to optimal specific impulse. Notice that the specific impulse of the ideal cycle has a finite limit as the fuel flow reaches shut-off.

### 3.5 The non-ideal ramjet

The major non-ideal effects come from the stagnation pressure losses due to the inlet shock and the burner heat addition. We have already studied those effects fairly thoroughly. In addition there are stagnation pressure losses due to burner drag and skin friction losses in the inlet and nozzle where the Mach numbers tend to be quite high. A reasonable rule of thumb is that the stagnation pressure losses due to burner drag are comparable to the losses due to heat addition.

### 3.6 Ramjet control

Let’s examine what happens when we apply some control to the ramjet. The two main control mechanisms at our disposal are the fuel flow and the nozzle exit area. The engine we will use for illustration is a stable ramjet with an inlet shock and simple convergent nozzle shown below. The inlet throat is designed to have a Mach number well above one so that it is not so sensitive to un-start if the free stream conditions, burner temperature
or nozzle area change. Changes are assumed to take place slowly so that unsteady changes in the mass, momentum, and energy contained in the ramjet are negligible.

![Image: Ramjet control model.](image)

**Figure 3.14: Ramjet control model.**

The mass balance is

\[
\dot{m}_e = \frac{\gamma}{(\gamma + 1)^{\frac{\gamma + 1}{2}}} \frac{P_{te} A_e}{\sqrt{\gamma R T_{te}}} f (M_e) = (1 + f) \dot{m}_a. \tag{3.44}
\]

The pressure in the engine is virtually certain to be very high at this free stream Mach number, and so the nozzle is surely choked, and we can write

\[
\dot{m}_a = \frac{1}{(1 + f)^{\frac{\gamma + 1}{2}}} \frac{P_{te} A_e}{\sqrt{\gamma R T_{te}}}. \tag{3.45}
\]

The thrust equation is

\[
\frac{T}{P_0 A_0} = \gamma M_0^2 \left( 1 + f \frac{U_e}{U_0} - 1 \right) + \frac{A_e}{A_0} \left( \frac{P_e}{P_0} - 1 \right). \tag{3.46}
\]

Our main concern is to figure out what happens to the velocity ratio and pressure ratio as we control the fuel flow and nozzle exit area.

**Nozzle exit area control**

First, suppose \( A_e \) is increased with \( T_{te} \) constant. In order for (3.45) to be satisfied \( P_{te} \) must drop keeping \( P_{te} A_e \) constant. The shock moves downstream to a higher shock Mach
number. The velocity ratio remains the same and, since the exit Mach number does not change, the product $P_e A_e$ remains constant. Note that the thrust decreases. This can be seen by writing the second term in (3.46) as

$$\frac{A_e P_e}{A_0 P_0} - \frac{A_e}{A_0}. \quad (3.47)$$

The left term in (3.47) is constant but the right term increases leading to a decrease in thrust. If $A_e$ is decreased, the reverse happens, the inlet operates more efficiently and the thrust goes up. But remember, the amount by which the area can be decreased is limited by the Mach number of the inlet throat.

Fuel flow control

Now, suppose $T_{te}$ is decreased with $A_e$ constant. In order for (3.45) to be satisfied, $P_{te}$ must drop keeping $P_{te}/\sqrt{T_{te}}$ constant. Once again the shock moves downstream to a higher shock Mach number. The velocity ratio goes down since the exit stagnation temperature is down and the Mach numbers do not change. The pressure ratio also decreases since the exit stagnation pressure is down. The thrust clearly decreases in this case. If $T_{te}$ is increased, the reverse happens, the inlet operates more efficiently and the thrust goes up. The amount by which the burner exit temperature can be increased is again limited by the Mach number of the inlet throat.

3.7 Example - Ramjet with un-started inlet

For simplicity, assume constant heat capacity with $\gamma = 1.4$, $C_p = 1005 \, M^2 / (sec^2 - K)$. The gas constant is $R = 287 \, M^2 / (sec^2 - K)$. The ambient temperature and pressure are $T_0 = 216K$ and $P_0 = 2 \times 10^4 N/M^2$. The fuel heating value is $h_f = 4.28 \times 10^7 J/kg$. The sketch below shows a ramjet operating at a free stream Mach number of 3.0. A normal shock stands in front of the inlet. Heat is added between stations 3 and 4.

![Figure 3.15: Ramjet with normal shock ahead of the inlet.](image)
The stagnation temperature at station 4 is $T_t^4 = 2000 \text{ K}$. Relevant areas are $A_3/A_{1,5} = 8$, $A_1 = A_3 = A_4$ and $A_4/A_e = 3$. Determine the dimensionless thrust $T/(P_0A_1)$. Do not assume $f \ll 1$. Neglect stagnation pressure losses due to wall friction and burner drag. Assume that the static pressure outside the nozzle has recovered to the ambient value. Suppose $A_{1,5}$ can be increased until $A_1 = A_{1,5} = A_3$. By what proportion would the air mass flow change?

Solution

The first point to recognize is that the stagnation pressure at station 4 exceeds the ambient by more than a factor of two - note the pressure outside the nozzle is assumed to have recovered to the ambient value. Thus the exit Mach number is one and the Mach number at station 4 is $M_4 = 0.1975$. The stagnation temperature at station 3 is $T_t^3 = 604.8 \text{ K}$. The fuel-air ratio is determined from the enthalpy balance

$$\dot{m}_f h_f = (\dot{m}_a + \dot{m}_f) h_{te} - \dot{m}_a h_{t0}. \quad (3.48)$$

For constant heat capacity

$$f = \frac{T_t^4}{T_t^*} - 1 \left( \frac{\dot{m}_f}{\dot{m}_a} \right) h_{te} - \dot{m}_a h_{t0} \quad (3.49)$$

Now we need to determine the flow between stations 1 and 3. To get started we will neglect the fuel addition for the moment. Knowing the Mach number at 4 and the stagnation temperatures at 3 and 4 we can use Rayleigh line results to estimate the Mach number at station 3. The stagnation temperature ratio across the burner is

$$\frac{T_t^4}{T_t^*} = \frac{T_t^4}{T_t^*} \left|_{M=0.1975} \right. = \frac{2000}{604.8} = 3.3069 \quad (3.50)$$

The Rayleigh line tables give

$$\frac{T_t^*}{T_t^3} \left|_{M=0.2066} \right. = \frac{3.3069}{0.2066} = 16.006 \Rightarrow M_3 = 0.103. \quad (3.51)$$

This is a reasonable approximation to the Mach number at station 3. The stagnation pressure ratio across the burner is
The subsonic critical Mach number for an area ratio of 8 is 0.0725. The fact that the Mach number at station 3 is higher than this value implies that there is a shock in the diverging part of the inlet and the inlet throat Mach number is equal to one. The stagnation pressure ratio between the inlet throat and the exit can be determined from a mass balance between stations 1.5 and e.

\[
\frac{P_{t1.5}}{P_{t3}} = \frac{P_{t1.5} A_{1.5} (1 + f)}{\sqrt{T_{t1.5}}} = \frac{P_{te} A_e}{\sqrt{T_{te}}} = \frac{P_{te}}{P_{t1.5}} = \frac{1.0344 \times 3}{8} \sqrt{\frac{2000}{604.8}} = 0.7054
\]

(3.53)

The results (3.52) and (3.53) determine the stagnation pressure ratio across the inlet shock and this determines the Mach number of the inlet shock.

\[
\pi_{shock} = \frac{0.7054}{0.981} = 0.719 \Rightarrow M_{shock} = 2.004
\]

(3.54)

Thus far the ramjet flow looks as shown in Figure 3.16.

Figure 3.16: State I.

The stagnation pressure ratio across the external shock is
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\[
\frac{P_{t1}}{P_{t0}}|_{M=3} = 0.3283 \quad (3.55)
\]

and so the overall stagnation pressure ratio is

\[
\frac{P_{te}}{P_{t0}} = \frac{P_{t1}}{P_{t0}} \frac{P_{te}}{P_{t1.5}} = 0.3283 \times 0.7054 = 0.2316. \quad (3.56)
\]

The static pressure ratio is

\[
P_e \frac{P_0}{P_e} = \frac{P_{te}}{P_{t0}^\gamma} \left(1 + \frac{\gamma - 1}{2} M_0^2 \right)^{-\frac{\gamma}{\gamma - 1}} = 0.2316 \times \left(\frac{2.8}{1.2}\right)^{3.5} = 4.494. \quad (3.57)
\]

The temperature ratio is

\[
\frac{T_e}{T_0} = \frac{T_{te}}{T_{t0}} \left(1 + \frac{\gamma - 1}{2} M_0^2 \right)^{-\frac{1}{\gamma - 1}} = \frac{2000}{604.8} \times \left(\frac{2.8}{1.2}\right) = 7.72. \quad (3.58)
\]

The velocity ratio is

\[
\frac{U_e}{U_0} = \frac{M_e}{M_0} \sqrt{\frac{T_e}{T_0}} = \frac{\sqrt{7.72}}{3} = 0.926. \quad (3.59)
\]

Across the inlet, the mass balance is

\[
P_{t1.5} A_{1.5} = P_{t0} A_0 f(M_0) \quad (3.60)
\]

and so

\[
\frac{A_0}{A_{1.5}} = \frac{P_{t1.5}}{P_{t0} f(M_0)} = 0.3283 \times 4.235 = 1.39. \quad (3.61)
\]

Finally the thrust is

\[
\frac{T}{P_0 A_1} = \gamma M_0^2 \frac{A_0}{A_{1.5}} \frac{A_{1.5}}{A_1} \left(1 + f \frac{U_e}{U_0} - 1\right) + \frac{A_e}{A_1} \left(\frac{P_e}{P_0} - 1\right) \quad (3.62)
\]

and
\[
\frac{T}{P_0 A_1}_{\text{State I}} = 1.4 \times 9 \times 1.39 \times \left(\frac{1}{8}\right) \times (1.0344 \times 0.926 - 1) + \left(\frac{1}{3}\right) \times (4.494 - 1) = \\
-0.0923 + 1.165 = 1.0724.
\] (3.63)

**State II**

Now increase the inlet throat area to the point where the inlet un-chokes. As the inlet throat area is increased the Mach number at station 3 will remain the same since it is determined by the choking at the nozzle exit and the fixed enthalpy rise across the burner. The mass balance between the inlet throat and the nozzle exit is again

\[
\frac{P_{1.5} A_{1.5} \left(1 + f\right)}{\sqrt{T_{1.5}}} = \frac{P_{te} A_e}{\sqrt{T_{te}}}.
\] (3.64)

The stagnation pressure at station 1.5 is fixed by the loss across the external shock. The fuel-air ratio is fixed as are the temperatures in (3.64). As \(A_{1.5}\) is increased, the equality (3.64) is maintained and the inlet shock moves to the left increasing \(P_{te}\). At the point where the the inlet throat un-chokes the shock is infinitely weak and the only stagnation pressure loss between station 1.5 and the nozzle exit is across the burner.

\[
\frac{A_{1.5 \text{ State II}}}{A_e} = \frac{1}{1 + f} \frac{P_{te \text{ State II}}}{P_{1.5}} \sqrt{\frac{T_{1.5}}{T_{te}}} = \frac{0.982}{1.0344} \sqrt{\frac{604.8}{2000}} = 0.522
\] (3.65)

This corresponds to

\[
\frac{A_1}{A_{1.5 \text{ State II}}} = \left(\frac{A_1}{A_e}\right) \left(\frac{A_e}{A_{1.5 \text{ State II}}}\right) = \frac{3}{0.522} = 5.747.
\] (3.66)

The mass flow through the engine has increased by the ratio

\[
\frac{\dot{m}_{a \text{ State II}}}{\dot{m}_{a \text{ State I}}} = \frac{A_{1.5 \text{ State II}}}{A_{1.5 \text{ State I}}} = \left(\frac{A_{1.5 \text{ State II}}}{A_1}\right) \left(\frac{A_1}{A_{1.5 \text{ State I}}}\right) = \frac{8}{5.747} = 1.392 \frac{A_{0 \text{ State II}}}{A_{0 \text{ State I}}}. \tag{3.67}
\]

At this condition the stagnation pressure ratio across the system is

\[
\frac{P_{te \text{ State II}}}{P_0} = \left(\frac{P_{1.5}}{P_0}\right) \left(\frac{P_{te \text{ State II}}}{P_{1.5}}\right) = 0.3283 \times 0.982 = 0.3224. \tag{3.68}
\]
The static pressure ratio is

\[
\frac{P_{e\text{State II}}}{P_0} = \frac{P_{te\text{State II}}}{P_{t0}} \left( \frac{1 + \frac{\gamma - 1}{2} M_0^2}{1 + \frac{\gamma - 1}{2} M_e^2} \right)^{\frac{\gamma}{\gamma - 1}} = 0.3224 \left( \frac{2.8}{1.2} \right)^{3.5} = 6.256. \quad (3.69)
\]

The Mach number at station 1 increases as \(A_{1.5}\) increases and at the condition where the inlet is just about to un-choke reaches the same Mach number as station 3. At this condition the ramjet flow field looks like that shown in Figure 3.17.

![Figure 3.17: State II.](image)

The inlet shock is gone, the inlet Mach number has increased to \(M_1 = M_3\) and the external shock has moved somewhat closer to the inlet. Note that the capture area to throat area ratio is still

\[
\frac{A_{0\text{State II}}}{A_{1.5\text{State II}}} = \frac{P_{t1.5}}{P_{t0} f(M_0)} = 0.3283 \times 4.235 = 1.39 \quad (3.70)
\]

although both \(A_{1.5}\) and \(A_0\) have increased. Also

\[
\frac{A_{0\text{State II}}}{A_1} = \frac{A_{0\text{State II}}}{A_{1.5\text{State II}}} \frac{A_{1.5\text{State II}}}{A_1} = \frac{1.39}{5.747} = 0.242. \quad (3.71)
\]

The thrust formula is
The velocity ratio across the engine is unchanged by the increase in inlet throat area. The thrust of state II is

\[
\frac{T}{P_0 A_1}_{state II} = \gamma M_0^2 \left( \frac{A_{0, state II}}{A_{1.5, state II}} \right) \left( \frac{A_{1.5, state II}}{A_1} \right) \left( 1 + f \right) \frac{U_e}{U_0} - 1 + \frac{A_e}{A_1} \left( \frac{P_{e, state II}}{P_0} - 1 \right). \tag{3.72}
\]

The reduced loss of stagnation pressure leads to almost a 60% increase in thrust at this condition.

**State III**

Now remove the inlet throat altogether.

Now, suppose \( A_{1.5} \) is increased until \( A_1 = A_{1.5} = A_3 \). The ramjet flow field looks like Figure 3.18.

![Figure 3.18: State III.](image)

With the inlet throat absent, the Mach number is constant between 1 and 3. There is no change in mass flow, fuel-air ratio, stagnation pressure, or the position of the upstream shock. The capture area remains
Therefore the thrust is the same as the thrust for State II, equation (3.74). If we want to position the upstream shock very near the entrance to the engine we have to increase the nozzle exit area and reduce the heat addition.

**State IV**

Open the nozzle exit fully.

First increase the exit area to the point where \( A_1 = A_3 = A_4 = A_e \). If we maintain \( T_{t4} = 2000 \text{ K} \) the Mach number at station 4 becomes one and the Mach number between 1 and 3 is, from the Rayleigh solution, \( M_1 = M_3 = 0.276 \). The ramjet flow at this condition is sketched in Figure 3.19.

![Figure 3.19: State IV.](image)

The velocity ratio is still

\[
\frac{U_e}{U_0} = \frac{M_e}{M_0} \sqrt{\frac{T_e}{T_0}} = \frac{\sqrt{7.72}}{3} = 0.926. \tag{3.75}
\]

The stagnation pressure ratio across the burner is, from the Rayleigh solution,

\[
\left. \frac{P_{te}}{P_{t1}} \right|_{State\ IV} = 0.8278. \tag{3.76}
\]

Across the whole system
and the static pressure ratio is

\[
\frac{P_{e, State IV}}{P_0} = \frac{P_{e, State IV}}{P_{e, State III}} \left( \frac{1 + \frac{\gamma-1}{2} M_0^2}{1 + \frac{\gamma-1}{2} M_e^2} \right)^{\frac{\gamma}{\gamma-1}} = 2.8 \left( \frac{1.2}{1.2} \right)^{3.5} = 5.274. \tag{3.78}
\]

The area ratio is

\[
\frac{A_{0, State IV}}{A_1} = \frac{P_{11} f (M_1)}{P_{10} f (M_0)} = 0.3283 \times \frac{0.4558}{0.2362} = 0.634. \tag{3.79}
\]

The thrust formula for state IV is

\[
\frac{T}{P_0 A_1} \bigg|_{State IV} = \gamma M_0^2 \left( \frac{A_{0, State IV}}{A_1} \right) \left( 1 + f \frac{U_e}{U_0} - 1 \right) + \frac{A_e}{A_1} \left( \frac{P_{e, State IV}}{P_0} - 1 \right) \tag{3.80}
\]

which evaluates to

\[
\frac{T}{P_0 A_1} \bigg|_{State IV} = 1.4 \times 9 \times 0.634 \times (1.0344 \times 0.926 - 1) + 1 \times (5.274 - 1) =
\]

\[-0.3367 + 4.274 = 3.937. \tag{3.81}\]

Note the considerable increase in mass flow for state IV compared to state III. From (3.74)

\[
\frac{\dot{m}_{a, State IV}}{\dot{m}_{a, State III}} = \left( \frac{A_{0, State IV}}{A_1} \right) \left( \frac{A_1}{A_{0, State III}} \right) = \frac{0.634}{0.242} = 2.62 \tag{3.82}
\]

which accounts for much of the increased thrust in spite of the increase in stagnation pressure loss across the burner.

**State V**

Reduce the burner outlet temperature until the shock is very close to station 1.
Now reduce $T_{te}$ until the Mach number at station 3 matches the Mach number behind the shock. From the Rayleigh solution, this occurs when $T_{te} = 924.8$. At this condition the ramjet flow field looks like Figure 3.20.

\[
\frac{T_e}{T_0} = \frac{T_{te}}{T_{t0}} \left( \frac{1 + \frac{\gamma - 1}{2} M_0^2}{1 + \frac{\gamma - 1}{2} M_e^2} \right) = \frac{924.8}{604.8} \times \left( \frac{2.8}{1.2} \right) = 3.57. \tag{3.83}
\]

The velocity ratio at this temperature is

\[
\frac{U_e}{U_0} = \frac{M_e}{M_0} \sqrt{\frac{T_e}{T_0}} = \frac{\sqrt{3.57}}{3} = 0.630. \tag{3.84}
\]

The stagnation pressure ratio across the burner at this condition is

\[
\frac{P_{te}}{P_{t3}} = 0.889 \tag{3.85}
\]

and across the system

\[
\frac{P_{te}}{P_{t0}} = 0.889 \times 0.3283 = 0.292. \tag{3.86}
\]

The static pressure ratio is
\[
\frac{P_e}{P_0} = \frac{P_{te}}{P_{to}} \left( \frac{1 + \gamma - \frac{1}{2} M_0^2}{1 + \gamma - \frac{1}{2} M_e^2} \right)^{\frac{\gamma}{\gamma - 1}} = 0.292 \times \left( \frac{2.8}{1.2} \right)^{3.5} = 5.67. \tag{3.87}
\]

Neglecting the fuel flow, the thrust is (Note that at this condition \( A_0 = A_1 = A_e \)).

\[
\frac{T}{P_0 A_1} = \gamma M_0^2 \left( \frac{U_e}{U_0} - 1 \right) + \left( \frac{P_e}{P_0} - 1 \right) = 1.4 \times 9 \times (0.629 - 1) + (5.67 - 1) = -4.67 + 4.67 = 0 \tag{3.88}
\]

**State VI**

Reduce the burner temperature slightly to establish supersonic flow up to the burner.

If the temperature at station 4 is decreased by an infinitesimal amount then supersonic flow will be established through the engine. Finally the flow is as shown in Figure 3.21.

The mass flow, velocity ratio, pressure ratio and thrust all remain the same as in state V. If we were to reduce the fuel flow to the burner to zero we would be back to the state of undisturbed Mach three flow through a straight tube.

### 3.8 Very high speed flight - scramjets

As the Mach number reaches values above 5 or so the ramjet cycle begins to become unusable and a new design has to be considered where the heat addition across the burner is carried out at supersonic Mach numbers. There are several reasons why this is so, all related to the very high stagnation temperature and stagnation pressure of high Mach number flight. To get started let’s recall the thrust equation for the ramjet with a fully expanded nozzle.
\[
\frac{T}{P_0 A_1} = \gamma M_0^2 \left( (1 + f) \frac{M_e}{M_0} \sqrt{\frac{T_e}{T_0}} - 1 \right) \tag{3.89}
\]

Define the thrust coefficient as

\[
C_{thrust} = \frac{Thrust}{\frac{1}{2} \rho_0 U_0^2 A_0} = \frac{T}{\frac{1}{2} M_0^2 P_0 A_0}. \tag{3.90}
\]

If we assume ideal behavior \((M_e = M_0)\) the thrust coefficient becomes

\[
C_{thrust} = 2 \left( (1 + f) \sqrt{\frac{T_e}{T_0}} - 1 \right). \tag{3.91}
\]

When we carried out the energy balance across the burner

\[
\dot{m}_f h_f = (\dot{m}_a + \dot{m}_f) h_{t4} - \dot{m}_a h_{t3} \tag{3.92}
\]

we assumed that the fuel enthalpy was simply added to the flow without regard to the chemistry of the process. In fact the chemistry highly limits the range of fuel-air ratios that are possible. The stoichiometric reaction of JP-4 with air where the fuel and oxygen are completely consumed is

\[
CH_{1.94} + 1.485O_2 + 5.536N_2 \rightarrow CO_2 + 0.97H_2O + 5.536N_2. \tag{3.93}
\]

corresponding to a fuel-air ratio

\[
f = \frac{12.01 + 1.94 \times 1.008}{1.485 \times 32.00 + 5.536 \times 28.02} = 0.0689. \tag{3.94}
\]

This is roughly the value of the fuel-air ratio that produces the maximum outlet temperature from the burner. If we choose the much more energetic hydrogen fuel, the reaction is

\[
H_2 + 0.5O_2 + 1.864N_2 \rightarrow H_2O + 1.864N_2 \tag{3.95}
\]

corresponding to a fuel-air ratio
The fuel enthalpies are generally taken to be

\[ h_{fJP_{-4}} = 4.28 \times 10^7 \text{ J/kg} \]
\[ h_{fH_2} = 12.1 \times 10^7 \text{ J/kg}. \]  

(3.97)

In the earlier discussion, we took the perspective that the ramjet cycle was limited by a red line temperature in the hot part of the engine. Let’s relax this assumption and allow the maximum temperature to be free while keeping the fuel-air ratio constant. Furthermore let’s continue to retain the assumption of constant heat capacities even at high Mach numbers. We will correct this eventually in Chapter 9, but for now we just want to see what happens to the ideal thrust coefficient (3.91) as we increase the free stream Mach number at constant fuel-air ratio. Using (3.92), constant heat capacities, and assuming adiabatic flow in the inlet and nozzle we can express the stagnation temperature ratio across the engine as

\[ \frac{T_{te}}{T_{t0}} = \left( \frac{f \tau_f}{1 + f} \right) \left( \frac{1}{1 + \frac{\gamma - 1}{2} M_0^2} \right) + \frac{1}{1 + f} \]  

(3.98)

where we recall that \( \tau_f = h_f / (C_p T_0) \). Now the thrust coefficient becomes

\[ C_{\text{thrust}} = 2 \left( \left( \frac{f (1 + f) \tau_f}{1 + \frac{\gamma - 1}{2} M_0^2} + (1 + f) \right)^{1/2} - 1 \right). \]  

(3.99)

The temperature ratio and thrust coefficient are plotted in Figures 3.22 and 3.23. The drag coefficient is defined as

\[ C_{\text{drag}} = \frac{D_{\text{drag}}}{\frac{1}{2} \rho_0 U_0^2 A_0} = \frac{D}{\frac{1}{2} M_0^2 P_0 A_0}. \]  

(3.100)

At high Mach numbers the drag coefficient of a body tends toward a constant value. For a sphere the drag coefficient tends toward a constant slightly less than one, about 0.95. More streamlined bodies have lower drag and coefficients as low as 0.2 can be achieved. This observation together with Figure 3.23 indicates that as the Mach number increases it becomes harder and harder to produce thrust that exceeds drag. The thrust coefficient
Figure 3.22: Temperature ratio of an ideal ramjet at constant fuel-air ratio.

Figure 3.23: Thrust coefficient of an ideal ramjet at constant fuel-air ratio.
drops below one at a Mach number of about 7 to 8 for both fuels. As the Mach number increases a conventional ramjet (even an ideal one) simply cannot produce enough thrust to overcome drag. The limiting thrust coefficient at infinite Mach number is

\[
\lim_{M_0 \to \infty} C_{\text{thrust}} = f.
\]  

(3.101)

This last result suggests that a scramjet can benefit from the choice of a fuel-rich mixture ratio as long as it does not exceed the flammability limit of the fuel. This would also provide additional fuel for cooling the vehicle. An advantage of a hydrogen system is that it can operate quite fuel rich. In addition, hydrogen has a higher heat capacity than any other fuel enabling it to be used to provide cooling for the vehicle that, in contrast to a re-entry body, has to operate in a very high temperature environment for long periods of time. The downside of hydrogen is that liquid hydrogen has to be stored at very low temperatures and the liquid density is only about 1/10 of that of JP-4. It is clear that small effects can be important. For example when we developed the thrust formula we neglected the momentum of the injected fuel. In a realistic scramjet analysis that would have to be taken into account.

### 3.8.1 Real chemistry effects

The real chemistry of combustion shows that the problem is even worse than just discussed. The plot points in Figure 3.21 are derived from an equilibrium chemistry computation of the combustion of JP-4 with air. Notice that the temperature reached by the combustion gases is substantially less than the ideal, and for high Mach numbers the temperature rise from the reaction is actually less than one due to the cooling effect of the added fuel.

The solution to this problem, which has been pursued since the 1960s, is to try to add heat with the burner operating with a supersonic Mach number on the order of two or so thereby cutting the static temperature of the air flowing into the combustor by almost a factor of two. This is the concept of a supersonically burning ramjet or scramjet. A generic sketch of such a system is shown in Figure 3.24. Two Homework problems are used to illustrate basic concepts.

### 3.8.2 Scramjet operating envelope

Figure 3.25 shows a widely circulated plot showing the altitude and Mach number regime where a scramjet might be expected to operate. Contours of constant free stream stagnation temperature and flow dynamic pressure are indicated on the plot.
CHAPTER 3. THE RAMJET CYCLE

Figure 3.24: Conceptual figure of a ramjet.

Figure 3.25: Conceptual operating envelope of a scramjet.
CHAPTER 3. THE RAMJET CYCLE

This figure somewhat accurately illustrates the challenges of scramjet flight. These can be listed as follows.

1) At high Mach numbers the vehicle is enveloped in an extremely high temperature gas for a long period of time perhaps more than an hour.

2) At high altitude, combustion is hard to sustain even at high Mach numbers because of the low atmospheric density and long chemical times. This defines the combustor blowout limit.

3) At lower altitude and high Mach number the free stream dynamic pressure increases to the point where the structural loads on the vehicle become untenable.

Let’s take a look at the vehicle structural limit (item 3) in a little more detail. This limit is presented as a line of constant dynamic pressure coinciding with increasing Mach number and altitude. But in supersonic flow, the free stream dynamic pressure is really not a sufficient measure of the actual loads that are likely to act on the vehicle. Again let’s make a constant heat capacity assumption and compare the free stream stagnation pressure to the free stream dynamic pressure as follows. Form the pressure coefficient

\[
\frac{P_{\infty} - P_{\infty}}{q_{\infty}} = \frac{P_{\infty}}{\frac{\gamma}{2} P_{\infty} M_{\infty}^2} \left( \left( 1 + \frac{\gamma - 1}{2} M_{\infty}^2 \right)^{\frac{\gamma}{\gamma - 1}} - 1 \right) = \frac{\left( 1 + \frac{\gamma - 1}{2} M_{\infty}^2 \right)^{\frac{\gamma}{\gamma - 1}} - 1}{\frac{\gamma}{2} M_{\infty}^2}.
\]

(3.102)

This function is plotted in Figure 3.26.

Figure 3.26: Comparison of stagnation pressure and dynamic pressure in supersonic flow.

If one repeats this calculation with real gas effects the stagnation pressures one calculates are even larger because of reduced values of \( \gamma \).

Consider the downstream end of the inlet where the flow enters the combustor. According to Figure 3.26 if, at a free stream Mach number of 8, the internal flow is brought isentropically
to low Mach number at the entrance to the combustor, the combustor will experience a pressure 218 times the free stream dynamic pressure. For example, at an altitude of about 26 kilometers and \( M_0 = 8.0 \) a low Mach number combustor would operate at about 3200 psia (10,000 times the ambient atmospheric pressure at that altitude). This would require a very heavy structure making the whole idea impractical.

If instead, the flow Mach number entering the combustor can be maintained at about Mach 2 then the combustor will operate at a much more feasible value of 28 bar or about 410 psia (somewhat higher with real gas effects accounted for). This structural issue is at least as important as the thermochemistry issue in forcing the designer to consider operating the combustor at supersonic Mach numbers in order to attain hypersonic flight.

### 3.9 Problems

**Problem 1** - Review 1-D gas dynamics with heat addition and area change. Consider the flow of a combustible gas mixture through a sudden expansion in a pipe shown in Figure 3.27.

![Figure 3.27: Dump combustor.](image)

Combustion occurs between section 1 at the exit of the small pipe and section 2 in the large pipe where the flow is uniform. Wall friction may be assumed to be negligible throughout. The flow at station 1 has stagnation properties \( P_{I1} \) and \( T_{I1} \). The Mach number at station 1, \( M_1 \) is subsonic and the pressure on the annular step is approximately equal to \( P_1 \). The heat of reaction is denoted by \( Q \).

(i) Show that the exit Mach number is given by
\[
\frac{M_2^2 \left(1 + \frac{\gamma-1}{2} M_2^2\right)}{(1 + \gamma M_2^2)^2} = \left(1 + \frac{Q}{C_p T_{t1}}\right) \frac{M_1^2 \left(1 + \frac{\gamma-1}{2} M_1^2\right)}{(\frac{A_2}{A_1} + \gamma M_1^2)^2}.
\]

(ii) Show that when \(Q = 0\) and \(A_2/A_1\) goes to infinity
\[
\frac{P_{t1}}{P_{t2}} = \left(1 + \frac{\gamma - 1}{2} M_1^2\right)^{\frac{\gamma-1}{\gamma}}.
\]

This limit is the case of a simple jet coming from an orifice in an infinite plane.

**Problem 2** - Show that for an ideal ramjet
\[
\eta_{th} = \frac{\frac{\gamma-1}{2} M_0^2}{1 + \frac{\gamma-1}{2} M_0^2}.
\]

Do not assume \(f \ll 1\).

**Problem 3** - Figure 3.28 shows a ramjet operating at a free stream Mach number of 0.7. Heat is added between stations 3 and 4 and the stagnation temperature at station 4 is \(T_{t4} = 1000K\). The Mach number at station 3 is very low. The ambient temperature and pressure are \(T_0 = 216K\) and \(P_0 = 2 \times 10^4 N/M^2\). Assume that \(f \ll 1\).

![Ramjet in subsonic flow](image)

Using appropriate assumptions, estimate the dimensionless thrust \(T/(P_0 A_0)\) and the area ratio \(A_0/A_e\).

**Problem 4** - Figure 3.29 shows a ramjet operating at a free stream Mach number \(M_0 = 1.5\), with a normal shock in front of the engine. Heat is added between stations 3 and 4 and the stagnation temperature at station 4 is \(T_{t4} = 1400K\). The Mach number at station 3
is very low. There is no shock in the inlet. The ambient temperature and pressure are $T_0 = 216 K$ and $P_0 = 2 \times 10^4 N/M^2$. Assume that $f \ll 1$.

Using appropriate assumptions, estimate the dimensionless thrust $T/(P_0A_0)$ and the area ratio $A_0/A_e$.

**Problem 5** - In Figure 3.30 a ramjet operates at a freestream Mach number of 3. The inlet is a straight duct and the Mach number of the flow entering the burner at station 3 is three. Heat is added across the burner such that the Mach number of the flow exiting the burner at station 4 is two. The ambient temperature and pressure are $T_0 = 216 K$ and $P_0 = 2 \times 10^4 N/M^2$. Assume that $f \ll 1$.

The exit flow is expanded to $P_e = P_0$. Determine the dimensionless thrust, $T/(P_0A_0)$.

**Problem 6** - In Figure 3.31 a ramjet operates at a freestream Mach number of 2.5. The ambient temperature and pressure are $T_0 = 216 K$ and $P_0 = 2 \times 10^4 N/M^2$. The engine operates with a straight duct after the burner, $A_1/A_e = 1$. Supersonic flow is established at the entrance of the inlet and a normal shock is stabilized somewhere in the diverging part of the inlet. The stagnation temperature exiting the burner is $T_{t4} = 1800 K$. Neglect
wall friction. Determine the dimensionless thrust, $T/(P_0 A_0)$.

\begin{figure}[h]
\centering
\includegraphics[width=0.8\textwidth]{figure3.31.png}
\caption{Ramjet with a constant area nozzle.}
\end{figure}

**Problem 7** - Figure 3.32 shows a ramjet test facility. A very large plenum contains Air at constant stagnation pressure and temperature, $P_{t0}$, $T_{t0}$. Jet fuel ($h_f = 4.28 \times 10^7 \text{ J/kg}$) is added between stations 3 and 4 ($A_3 = A_4$) where combustion takes place. The flow exhausts to a large tank which is maintained at pressure $P_0$. Let $P_{t0}/P_0 = 100$. The upstream nozzle area ratio is $A_3/A_{1.5} = 8$. The exit area, $A_e$ can be varied in order to change the flow conditions in the engine. The gas temperature in the plenum is $T_{t0} = 805.2 \text{ K}$. To simplify the analysis, assume adiabatic flow, neglect wall friction and assume constant specific heat throughout with $\gamma = 1.4$.

\begin{figure}[h]
\centering
\includegraphics[width=0.8\textwidth]{figure3.32.png}
\caption{Ramjet test facility.}
\end{figure}

Initially, the valve controlling $A_e$ is closed, $A_e = 0$ and the fuel mass flow is shut off. Consider a test procedure where the nozzle area is opened, then closed. In the process $A_e/A_{1.5}$ is slowly increased from zero causing Air to start flowing. The nozzle is opened until $A_e = A_3$. Then the nozzle area is slowly reduced until $A_e/A_{1.5} = 0$ once again. Plot the thrust normalized by the plenum pressure and upstream throat area, $T/(P_{t0} A_{1.5})$ and the fuel-Air ratio $f$ as a function of $A_e/A_{1.5}$. Distinguish points corresponding to increasing and decreasing $A_e$. The fuel flow is adjusted to maintain the stagnation temperature at 4
at a constant value. Plot the results for three cases.

\[ T_{t4} = 805.2 \, K \text{ (zero fuel flow)} \]
\[ T_{t4} = 1200 \, K \quad \text{(3.106)} \]
\[ T_{t4} = 2700 \, K \]

Neglect stagnation pressure loss across the burner due to aerodynamic drag of the burner, retain the loss due to heat addition. Do not assume \( f \ll 1 \). What flight Mach number and altitude are being simulated at this condition?

**Problem 8** - In Figure 3.33 a ramjet operates at a free-stream Mach number of 3. The area ratio across the engine is \( A_1/A_e = 2 \). Supersonic flow is established at the entrance of the inlet and a normal shock is stabilized in the diverging part of the inlet. The inlet throat Mach number is 1.01. The stagnation temperature exiting the burner is \( T_{t4} = 1944 \, K \). Assume \( \gamma = 1.4 \), \( R = 287 \, M^2/(\text{sec}^2 - K) \), \( C_p = 1005 \, M^2/(\text{sec}^2 - K) \). The ambient temperature and pressure are \( T_0 = 216 \, K \) and \( P_0 = 2 \times 10^4 \, N/M^2 \). Assume throughout that \( f \ll 1 \).

![Figure 3.33: Ramjet with a simple convergent nozzle.](image)

i) Suppose the fuel flow is increased with the geometry of the engine held fixed. Estimate the value of \( f \) that would cause the inlet to unstart. Plot the dimensionless thrust, \( T/(P_0 A_{1.5}) \), specific impulse, and overall efficiency of the engine as a function of \( f \). Plot your result beyond the point where the inlet un-starts and assume the engine does not flame out. Assume the fuel flow is throttled so as to keep the fuel/air ratio constant. Note that the thrust is normalized by a fixed geometric area rather than the capture area \( A_0 \) that changes when the engine un-starts.

ii) With \( T_{t4} = 1944 \, K \), suppose \( A_e \) is reduced keeping the fuel flow the same. Estimate the value of \( A_1/A_e \) that would cause the inlet to un-start? Plot the dimensionless thrust, \( T/(P_0 A_{1.5}) \) specific impulse and overall efficiency of the engine as a function of \( A_1/A_e \). As in part (i), plot your result beyond the point where the inlet un-starts and assume the engine does not flame out.
Problem 9 - In Figure 3.34 a ramjet operates at a free-stream Mach number of 3. The area ratio across the engine is $A_1/A_e = 2$. Supersonic flow is established at the entrance of the inlet and a normal shock is stabilized in the diverging part of the inlet. The stagnation temperature exiting the burner is $T_{t4} = 1944$ K. The ambient temperature and pressure are $T_0 = 216$ K and $P_0 = 2 \times 10^4$ N/M². Do not assume that $f \ll 1$. Do not neglect the effects of wall friction.

Figure 3.34: Ramjet with a convergent nozzle and inlet shock.

i) Determine the fuel-air ratio, $f$.

ii) Determine the dimensionless thrust, $T/(P_0 A_0)$.

Problem 10 - Assume $\gamma = 1.4$, $R = 287 M^2/ (sec^2 - K)$, $C_p = 1005 M^2/ (sec^2 - K)$. The ambient temperature and pressure are $T_0 = 216$ K and $P_0 = 2 \times 10^4$ N/M². Figure 3.35 shows a ramjet operating at a free stream Mach number of 3.0. The incoming air is decelerated to a Mach number of 2.0 at station 3.

Figure 3.35: A scramjet concept.

Heat is added between 3 and 4 bringing the Mach number at station 4 to one. The flow is then ideally expanded to $P_e = P_0$. This type of engine with the combustion of fuel occurring in a supersonic stream is called a SCRAMJET (supersonic combustion ramjet). Determine the dimensionless thrust $T/(P_0 A_0)$. Assume $f \ll 1$ if you wish and neglect stagnation pressure losses due to friction.

Problem 11 - A ramjet operates in the upper atmosphere at a high supersonic Mach number as shown in Figure 3.36. Supersonic flow is established at the entrance of the
CHAPTER 3. THE RAMJET CYCLE

inlet and a normal shock is stabilized in the diverging part of the inlet. The stagnation temperature exiting the burner is sufficient to produce substantial positive thrust. A small flat plate is placed downstream of the burner as shown, causing a small drop in stagnation pressure between station "a" and station "b". The plate can be positioned so as to produce high drag as shown, or it can be rotated 90° so that the long dimension is aligned with the flow, producing lower drag. The engine operates with a convergent-divergent nozzle. The nozzle throat is choked and the nozzle exit is fully expanded.

Figure 3.36: Ramjet with variable drag loss.

Suppose the plate is rotated from the high drag position to the low drag position. State whether each of the following area-averaged quantities increases, decreases or remains the same.

1) \( M_3 \)
   5) \( T_e \)

2) \( M_a \)
   6) \( P_e \)

3) \( M_b \)
   7) \( U_e \)

4) \( M_c \)
   8) Engine thrust

Explain the answer to part 8) in terms of the drag force on the plate and the pressure forces that act on the engine inlet and nozzle.

Problem 12 - In Figure 3.37 a ramjet operates at a freestream Mach number of 3. The area ratio across the engine is \( A_1/A_e = 2 \). Supersonic flow is established at the entrance of the inlet and a normal shock is stabilized in the diverging part of the inlet. The stagnation temperature exiting the burner is \( T_{t4} = 1512 \text{ K} \). The ambient temperature and pressure are \( T_0 = 216 \text{ K} \) and \( P_0 = 2 \times 10^4 \text{ N/M}^2 \).

Do not neglect wall friction.

i) Determine the dimensionless thrust, \( T/(P_0 A_0) \).

ii) Suppose the wall friction is increased slightly. Determine if each of the following increases, decreases or remains the same.
a) The Mach number at station 4
b) The Mach number at station 1.5
c) The shock Mach number
d) The dimensionless thrust \( T/(P_0 A_0) \)

Assume the inlet does not un-start.

**Problem 13** - In Figure 3.38 a ramjet operates at a freestream Mach number of 3. The area ratio across the engine is \( A_1/A_8 = 1.75 \). Supersonic flow is established at the entrance of the inlet and a normal shock is stabilized in the diverging part of the inlet. The stagnation temperature exiting the burner is \( T_{t4} = 1512 K \). The nozzle is fully expanded \( P_e = P_0 \). The fuel enthalpy is \( h_f = 4.28 \times 10^7 J/kg \). The ambient temperature and pressure are \( T_0 = 216 K \) and \( P_0 = 2 \times 10^4 N/M^2 \).

i) Determine the dimensionless thrust, \( T/(P_0 A_0) \).

ii) Suppose \( T_{t4} \) is decreased slightly. Determine if each of the following increases, decreases or remains the same.

a) The Mach number at station 4
b) The Mach number at station 3
c) The shock Mach number
d) The nozzle exit pressure \( P_e \)
Chapter 4

The Turbojet cycle

4.1 Thermal efficiency of the ideal turbojet

Recalling our discussion in Chapter 2, the thermal efficiency of a jet engine propulsion system is defined as

\[
\eta_{th} = \frac{\text{power to the vehicle} + \frac{\Delta \text{kinetic energy of air}}{\text{second}} + \frac{\Delta \text{kinetic energy of fuel}}{\text{second}}}{\dot{m}_f h_f} \tag{4.1}
\]

or

\[
\eta_{th} = \frac{\text{TU}_0 + \left[ \frac{\dot{m}_a (U_e - U_0)^2}{2} - \frac{\dot{m}_a (0)^2}{2} \right] + \left[ \frac{\dot{m}_f (U_e - U_0)^2}{2} - \frac{\dot{m}_f (U_0)^2}{2} \right]}{\dot{m}_f h_f}. \tag{4.2}
\]

If the exhaust is fully expanded so that \( P_e = P_0 \) the thermal efficiency reduces to

\[
\eta_{th} = \frac{\frac{(\dot{m}_a + \dot{m}_f) U_e^2}{2} - \frac{\dot{m}_a U_0^2}{2}}{\dot{m}_f h_f}. \tag{4.3}
\]

For the ideal ramjet we were able to rearrange the thermal efficiency as follows.
\[ \eta_{th} = \frac{(\dot{m}_a+\dot{m}_f)U_e^2 - \dot{m}_aU_0^2}{\dot{m}_f h_f} = \frac{(\dot{m}_a + \dot{m}_f) (h_{te} - h_e) - \dot{m}_a (h_{t0} - h_0)}{(\dot{m}_a + \dot{m}_f) h_{te} - \dot{m}_a h_{t0}} \]

\[ \eta_{th} = 1 - \frac{Q_{\text{rejected during the cycle}}}{Q_{\text{input during the cycle}}} = 1 - \frac{(\dot{m}_a + \dot{m}_f) h_e - \dot{m}_a h_0}{(\dot{m}_a + \dot{m}_f) h_{te} - \dot{m}_a h_{t0}} \] (4.4)

\[ \eta_{th} = 1 - \left( \frac{T_0}{T_{t0}} \right) \left( \frac{(1 + f) \frac{T_e}{T_0} - 1}{(1 + f) \frac{T_{te}}{T_{t0}} - 1} \right) \]

Noting that for the ideal ramjet \( T_e/T_0 = T_{te}/T_{t0} \), the term in brackets is one, and the thermal efficiency of the ideal ramjet becomes

\[ \eta_{th} = 1 - \frac{T_0}{T_{t0}} = 1 - \frac{1}{\tau} = \frac{\left( \frac{\gamma - 1}{2} \right) M_0^2}{1 + \left( \frac{\gamma - 1}{2} \right) M_0^2}. \] (4.5)

The thermal efficiency of the ideal ramjet is entirely determined by the flight Mach number. As the Mach number goes to zero the thermal efficiency goes to zero and the engine produces no thrust.

To overcome this, we need an engine cycle that produces its own compression at zero Mach number. This is achieved through the use of a compressor driven by a turbine. A sketch of a turbojet engine is shown in Figure 4.1.

Figure 4.1: Turbojet engine and compressor-turbine blade diagram.
In an adiabatic system with no shaft bearing losses the work done by the gas on the turbine matches the work done by the compressor on the gas. This is expressed as a simple enthalpy balance.

\[(\dot{m}_a + \dot{m}_f) (h_{t4} - h_{t5}) = \dot{m}_a (h_{t3} - h_{t2})\]  (4.6)

The enthalpy balance across the burner is

\[(\dot{m}_a + \dot{m}_f) h_{t4} = \dot{m}_a h_{t3} + \dot{m}_f h_f.\]  (4.7)

Subtract (4.6) from (4.7). The enthalpy balance across the engine is

\[(\dot{m}_a + \dot{m}_f) h_{t5} = \dot{m}_a h_{t2} + \dot{m}_f h_f.\]  (4.8)

Assume that the inlet and nozzle flow are adiabatic. Then (4.8) is equivalent to

\[(\dot{m}_a + \dot{m}_f) h_{te} = \dot{m}_a h_{t0} + \dot{m}_f h_f.\]  (4.9)

Now the thermal efficiency (4.3) can be written as

\[\eta_{th} = \frac{(\dot{m}_a + \dot{m}_f) (h_{te} - h_e) - \dot{m}_a (h_{t0} - h_0)}{(\dot{m}_a + \dot{m}_f) h_{t4} - \dot{m}_a h_{t3}}.\]  (4.10)

Using (4.9) and (4.7), equation (4.10) becomes

\[\eta_{th} = \frac{(\dot{m}_a + \dot{m}_f) h_{t4} - \dot{m}_a h_{t3} - (\dot{m}_a + \dot{m}_f) h_e + \dot{m}_a h_0}{(\dot{m}_a + \dot{m}_f) h_{t4} - \dot{m}_a h_{t3}}\]  (4.11)

or

\[\eta_{th} = 1 - \frac{Q_{rejected during the cycle}}{Q_{input during the cycle}} = 1 - \left( \frac{(\dot{m}_a + \dot{m}_f) h_e - \dot{m}_a h_0}{(\dot{m}_a + \dot{m}_f) h_{t4} - \dot{m}_a h_{t3}} \right)\]  (4.12)

or

\[\eta_{th} = 1 - \frac{h_0}{h_{t0}} \left( \frac{1 + f}{1 + f} \frac{h_{t4}}{h_{t3}} - 1 \right).\]

If the gas is calorically perfect then (4.12) can be expressed in terms of the temperature.
CHAPTER 4. THE TURBOJET CYCLE

\[ \eta_{th} = 1 - \frac{T_0}{T_{t3}} \left( \frac{1 + f}{1 + f} \frac{T_e}{T_{t3}} - 1 \right) \]  \hspace{1cm} (4.13)

In the ideal Brayton cycle the compression process from the free stream to station 3 is assumed to be adiabatic and isentropic. Similarly the expansion from station 4 to the exit is assumed to be isentropic. Thus

\[ \frac{T_{t3}}{T_0} = \left( \frac{P_{t3}}{P_0} \right)^{\frac{\gamma-1}{\gamma}} \]  \hspace{1cm} (4.14)

\[ \frac{T_{t4}}{T_e} = \left( \frac{P_{t4}}{P_e} \right)^{\frac{\gamma-1}{\gamma}}. \]

Also in the ideal Brayton cycle the heat addition and removal is assumed to occur at constant pressure. Therefore \( P_{t4} = P_{t3} \), \( P_e = P_0 \) and we can write

\[ \frac{T_{t4}}{T_e} = \frac{T_{t3}}{T_0}. \]  \hspace{1cm} (4.15)

Therefore the expression in brackets in (4.13) is equal to one for the ideal turbojet cycle and the thermal efficiency is

\[ \eta_{th, idealturbojet} = 1 - \frac{T_0}{T_{t3}} = 1 - \frac{1}{\tau_r \tau_c}. \]  \hspace{1cm} (4.16)

When the Mach number is zero (\( \tau_r = 1 \)), the thermal efficiency is positive and determined by the stagnation temperature ratio \( \tau_c = T_{t3}/T_{t2} \) of the compressor. Thermodynamic diagrams of the turbojet cycle are shown in Figures 4.2 and 4.3.

The important impact of the compression process on thermal efficiency is a major factor behind the historical trend toward higher compression engines for both commercial and military applications.

4.2 Thrust of an ideal turbojet engine

The thrust equation for a fully expanded nozzle is

\[ \frac{T}{P_0 A_0} = \gamma M_0^2 \left( (1 + f) \frac{U_e}{U_0} - 1 \right). \]  \hspace{1cm} (4.17)
Figure 4.2: P-V diagram of the ideal turbojet cycle. Station number with a "t" refers to the stagnation state of the gas at that point.

Figure 4.3: T-S diagram of the ideal turbojet cycle.
To determine the thrust we need to work out the velocity ratio.

\[
\frac{U_e}{U_0} = \frac{M_e}{M_0} \sqrt{\frac{T_e}{T_0}}
\]  

(4.18)

To determine the Mach numbers we focus on the variation of stagnation pressure through the engine. Begin with the following identity.

\[
P_{te} = P_0 \left( \frac{P_{t0}}{P_0} \right) \left( \frac{P_{t2}}{P_{t0}} \right) \left( \frac{P_{t3}}{P_{t2}} \right) \left( \frac{P_{t4}}{P_{t3}} \right) \left( \frac{P_{t5}}{P_{t4}} \right) \left( \frac{P_{te}}{P_{t5}} \right)
\]  

(4.19)

Using our engine parameters this would be written as

\[
P_{te} = P_0 \pi_r \pi_d \pi_c \pi_b \pi_t \pi_n.
\]  

(4.20)

Under the assumptions of the ideal cycle the stagnation pressure losses in the diffuser and nozzle are negligible. In other words, skin friction and shock losses are negligible.

\[
\pi_d = 1
\]  

(4.21)

\[
\pi_n = 1
\]  

Similarly, the Mach number through the burner is assumed to be so low that the stagnation pressure losses due to heat addition and aerodynamic drag are assumed to be negligible.

\[
\pi_b = 1
\]  

(4.22)

Therefore

\[
P_{te} = P_0 \pi_r \pi_c \pi_t = P_e \left( 1 + \frac{\gamma - 1}{2} M_e^2 \right)^{-\frac{\gamma}{\gamma - 1}}.
\]  

(4.23)

Another assumption of the ideal cycle is that the nozzle is fully expanded.

\[
\pi_r \pi_c \pi_t = \left( 1 + \frac{\gamma - 1}{2} M_e^2 \right)^{-\frac{\gamma}{\gamma - 1}}
\]  

(4.24)
The final assumption of the ideal turbojet is that the compressor and turbine behave isentropically.

\[
\pi_c = \tau_c^{\frac{\gamma}{\gamma-1}} \\
\pi_t = \tau_t^{\frac{\gamma}{\gamma-1}}
\] (4.25)

Using (4.25) in (4.24) and the relation \( \pi_r = \tau_r^{\gamma/(\gamma-1)} \), the exit Mach number can be determined from

\[
M_e^2 = \frac{2}{\gamma - 1} (\tau_r \tau_c \tau_t - 1)
\] (4.26)

and the Mach number ratio is

\[
\frac{M_e^2}{M_0^2} = \left( \frac{\tau_r \tau_c \tau_t - 1}{\tau_r - 1} \right).
\] (4.27)

We take a similar approach to determining the temperature ratio across the engine. Begin with the identity

\[
T_{te} = T_0 \left( \frac{T_{i0}}{T_0} \right) \left( \frac{T_{i2}}{T_{i0}} \right) \left( \frac{T_{i3}}{T_{i2}} \right) \left( \frac{T_{i4}}{T_{i3}} \right) \left( \frac{T_{i5}}{T_{i4}} \right) \left( \frac{T_{te}}{T_{i5}} \right)
\] (4.28)

or, in terms of component temperature parameters

\[
T_{te} = T_0 \tau_r \tau_d \tau_c \tau_b \tau_t \tau_n.
\] (4.29)

In the ideal turbojet we assume that the diffuser and nozzle flows are adiabatic and so

\[
T_{te} = T_0 \tau_r \tau_c \tau_b \tau_t = T_e \left( 1 + \frac{\gamma - 1}{2} M_e^2 \right) = T_e \tau_r \tau_c \tau_t.
\] (4.30)

From (4.30) we have the result

\[
\frac{T_e}{T_0} = \tau_b = \frac{T_{i4}}{T_{i3}}.
\] (4.31)
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This is the same result we deduced earlier in (4.15) when we analyzed the thermal efficiency. Actually it is more convenient to express the temperature ratio in terms of the all-important parameter \( \tau_\lambda = T_{t4}/T_0 \).

\[
\frac{T_e}{T_0} = \frac{\tau_\lambda}{\tau_r \tau_c}
\]  

(4.32)

The reason is that \( \tau_\lambda \) is a parameter that we would like to make as large as possible, but is limited by the highest temperature that can be tolerated by the turbine materials before they begin to lose strength and undergo creep. The maximum allowable turbine inlet temperature (and therefore the maximum design operating temperature) is one of the cycle variables that is essentially fixed when an engine manufacturer begins the development of a new engine. Enormous sums of money have been invested in turbine materials technology and turbine cooling schemes in an effort to enable jet engines to operate with as high a turbine inlet temperature as possible.

Our thrust formula is now

\[
\frac{T}{P_0 A_0} = \frac{2\gamma}{\gamma - 1} \left( \tau_r - 1 \right) \left( 1 + f \right) \left( \frac{\tau_r \tau_c \tau_t - 1}{\tau_r - 1} \right) \frac{\tau_\lambda}{\tau_r \tau_c}^{1/2} - 1 \right).
\]  

(4.33)

The fuel/air ratio is found from

\[
f = \frac{\tau_\lambda - \tau_r \tau_c}{\tau_f - \tau_\lambda}.
\]  

(4.34)

At this point it would appear that for fixed \( \gamma \), and \( \tau_f \) the thrust is a function of four variables.

\[
\frac{T}{P_0 A_0} = F(\tau_r, \tau_c, \tau_\lambda, \tau_t)
\]  

(4.35)

But the turbine and compressor are not independent components. They are connected by a shaft and the work done across the compressor is the same as the work done across the turbine. They are related by the work matching condition (4.6) repeated here in terms of the temperatures.

\[
(\dot{m}_a + \dot{m}_f) C_P (T_{t4} - T_{t5}) = \dot{m}_a C_P (T_{t3} - T_{t2})
\]  

(4.36)

For simplicity we have assumed the same value of \( C_P \) for the compressor and turbine. If we divide (4.36) by \( C_P T_0 \) then it becomes
\[(1 + f) \tau_\lambda (1 - \tau_t) = \tau_r (\tau_c - 1) \quad (4.37)\]

or

\[\tau_t = 1 - \frac{\tau_r (\tau_c - 1)}{(1 + f) \tau_\lambda} \quad (4.38)\]

where we have assumed \(T_{t2} = T_{t0}\). The result (4.38) only assumes adiabatic flow in the inlet and no shaft losses. It is not tied to the other assumptions of the ideal cycle. The velocity ratio across the engine is now

\[\left(\frac{U_e}{U_0}\right)^2 = \frac{1}{(\tau_r - 1)} \left( \tau_\lambda - \tau_r (\tau_c - 1) - \frac{\tau_\lambda}{\tau_r \tau_c} \right) \quad (4.39)\]

where the fuel/air ratio has been neglected.

### 4.3 Maximum thrust ideal turbojet

How much compression should we use? If there is too little the engine is like a ramjet and may not produce enough thrust at low Mach number. If we use too much then the fuel flow has to be reduced to avoid raising the temperature above the "do not exceed" (redline) value of \(T_{t4}\). The thrust and specific impulse of a typical ideal turbojet is shown in Figure 4.4. Recall that

\[\frac{I_{sp}}{a_0} = \left( \frac{1}{f} \right) \left( \frac{1}{\gamma M_0} \right) \left( \frac{T}{P_0 A_0} \right) \quad (4.40)\]

It is clear from the upper left graph in Figure 4.4 that there is a choice of \(\tau_c\) that maximizes the thrust for fixed values of the other three engine parameters. We can determine this compression ratio by maximizing \((U_e/U_0)^2\).

\[\frac{\partial}{\partial \tau_c} \left(\frac{U_e}{U_0}\right)^2 = \frac{1}{(\tau_r - 1)} \left( -\tau_r + \frac{\tau_\lambda}{\tau_r \tau_c^2} \right) = 0 \quad (4.41)\]

The maximum velocity ratio for the ideal turbojet occurs when

\[\tau_{c_{\text{maxthrust}}} = \frac{\sqrt{\tau_\lambda}}{\tau_r} \quad (4.42)\]
Note that fuel shut-off and zero thrust occurs when $\tau_c = \tau_\lambda/\tau_r$. The relation (4.42) tells us a great deal about why engines look the way they do. An engine designed to cruise at low Mach number (a low value of $\tau_r$) will be designed with a relatively large compressor generating a relatively high value of $\tau_c$ as indicated by (4.42). But as the flight Mach number increases the optimum compression decreases until at $\tau_r = \sqrt{\tau_\lambda}$ one would like to get rid of the compressor altogether and convert the engine to a ramjet. This also tells us something about the general trend of engine design with history. As higher temperature turbine materials and better cooling schemes have been developed over the years, newer engines tend to be designed with correspondingly higher compression ratios leading to higher specific impulse and better fuel efficiency. Over the 40 year period since the introduction of the JT9D, allowable turbine inlet temperatures have increased over 1000°F.

One should note that (4.42) is not a particularly useful relationship for the design of an actual engine. This is partly because, strictly speaking, it only applies to the ideal cycle but mostly due to the fact that any real engine must operate effectively from take-off to cruise. If the compressor is rigorously designed to satisfy (4.42) at cruise then the engine will be seriously underpowered and inefficient at take-off when the desired compression is much larger. On the other hand if the compressor is too large, then the engine will tend to be over-designed and over-weight for cruise.

As (4.42) would indicate, this problem becomes more and more difficult to solve as the cruise Mach number of the engine increases. The J58 powered SR71 Blackbird cruises at
Mach numbers greater than 3.

The engine is designed to be a variable cycle system so that at cruise a large fraction of the inlet air bypasses the rotating machinery and enters the afterburner directly as it would in a ramjet. Despite this design the aircraft cannot take-off with a full load of fuel and has to be refueled in flight before beginning a mission. Another, unrelated reason for the partial fuel load at takeoff is that the braking power of the landing gear is too small for an emergency take-off abort with a full fuel load.

Designing a high Mach number engine for a supersonic transport faces the same problem. In an engine out situation the aircraft must be able to cruise subsonically to the nearest landing field and so the engine must be able to supply adequate thrust for long distances at subsonic Mach numbers.

4.4 Turbine-nozzle mass flow matching

The mass balance between the entrance of the turbine and the nozzle throat is

\[ \dot{m}_4 = \dot{m}_e \]

\[ \frac{P_tA_4}{\sqrt{\gamma RT_4}} f(M_4) = \frac{P_tA_8}{\sqrt{\gamma RT_8}} f(M_8). \]  

(4.43)

In general, the turbine is designed to provide a large pressure drop per stage. This is possible because of the favorable pressure gradient that stabilizes the boundary layers on the turbine airfoils. The result is a large amount of work per stage and this can be seen in the highly cambered, high lift shape of typical turbine airfoils shown in Figure 4.1. The
large pressure drop across each stage implies that at some point near the entrance to the
first stage turbine stator (also called the turbine nozzle) the flow is choked as indicated in
Figure 4.1. At this point $A_4 f (M_4) = A_4^*$. The choked area occurs somewhere in the stator
passage. Similarly for the vast range of practical engine operations the nozzle throat is
also choked. Therefore the mass balance (4.43) can be written

$$\frac{P_{t4} A_4^*}{\sqrt{T_{t4}}} = \frac{P_{t8} A_8}{\sqrt{T_{t8}}}.$$ (4.44)

Under the assumption of an ideal cycle the turbine operates isentropically.

$$\frac{P_{t5}}{P_{t4}} = \left(\frac{T_{t5}}{T_{t4}}\right)^{\frac{\gamma-1}{\gamma}}$$ (4.45)

The skin friction losses in the nozzle duct are assumed to be negligible and the duct is
adiabatic ($P_{t5} = P_{t8}$) and ($T_{t5} = T_{t8}$). Therefore

$$\tau_t = \frac{T_{t5}}{T_{t4}} = \left(\frac{A_4^*}{A_8}\right)^{\frac{2(\gamma-1)}{\gamma+1}}.$$ (4.46)

The temperature and pressure ratio across the turbine is determined entirely by the area
ratio from the turbine inlet to the nozzle throat. As the fuel flow to the engine is increased
or decreased with the areas fixed, the temperature drop across the turbine may increase or
decrease changing the amount of work done while the temperature ratio remains constant.
The turbine inlet and nozzle throat are choked over almost the entire practical range of
engine operating conditions except during brief transients at start-up and shut-down.

4.5 Free-stream-compressor inlet flow matching

The mass balance between the free stream and the compressor face is

$$\dot{m}_a = \dot{m}_2$$

$$\frac{P_{t0} A_0}{\sqrt{T_{t0}}} f (M_0) = \frac{P_{t2} A_2}{\sqrt{T_{t2}}} f (M_2).$$ (4.47)

The flow from the free-stream to the compressor face is assumed to be adiabatic so that
$T_{t2} = T_{t0}$. Thus the mass balance is
\( P_0 A_0 f (M_0) = P_{t2} A_2 f (M_2) \)  

which we write as follows

\[ f (M_2) = \frac{P_0 A_0 f (M_0)}{P_{t2} A_2}. \]  

In terms of our engine parameters (4.49) is

\[ f (M_2) = \left( \frac{1}{\pi_d} \right) \left( \frac{A_0}{A_2} \right) f (M_0). \]  

We shall see that the fuel setting and nozzle throat area determine the value of \( f (M_2) \) independently of what is happening in the free stream and inlet. In other words the engine demands a certain value of \( f (M_2) \) and the gas dynamics of the inlet adjust \( A_0 \) and/or \( \pi_d \) in (4.50) to supply this value.

### 4.6 Compressor-turbine mass flow matching

The mass balance between the compressor face and the turbine inlet is

\[ \dot{m}_2 (1 + f) = \dot{m}_4 \]

\[ (1 + f) \frac{P_{t2} A_2}{\sqrt{T_{t2}}} f (M_2) = \frac{P_{t4} A_4^*}{\sqrt{T_{t4}}}. \]  

We can write (4.51) in terms of our flow parameters as follows.

\[ f (M_2) = \left( \frac{1}{1 + f} \right) \frac{\pi_c \pi_b}{\sqrt{\tau_e/\tau_s}} \left( \frac{A_4^*}{A_2} \right) \]  

Under the ideal cycle assumption \( \pi_b = 1 \). Neglecting the fuel-air ratio, (4.52) becomes

\[ f (M_2) = \frac{\pi_c}{\sqrt{\tau_e/\tau_s}} \left( \frac{A_4^*}{A_2} \right). \]  

Notice that we have written \( f (M_2) \) on the left hand side of (4.53). In this point of view \( f (M_2) \) is an outcome of the interaction of the nozzle with the turbine and compressor. The inlet behavior is then determined from (4.50).
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4.7 Summary - engine matching conditions

In summary, the various component matching conditions needed to understand the operation of the turbojet in order, from the nozzle to the inlet are as follows.

\[
\tau_t = \left( \frac{A_4^*}{A_8} \right)^{2(\gamma - 1)/\gamma + 1} \tag{4.54}
\]

\[
\tau_c - 1 = \frac{\tau_{\lambda}}{\tau_r} (1 - \tau_t) \tag{4.55}
\]

\[
f(M_2) = \frac{\pi_c}{\sqrt{\tau_{\lambda}/\tau_r}} \left( \frac{A_4^*}{A_2} \right) \tag{4.56}
\]

\[
f(M_2) = \left( \frac{1}{\pi_d} \right) \left( \frac{A_0}{A_2} \right) f(M_0) \tag{4.57}
\]

The quantity \( A_0 \) in (4.57) is the area of the external stream tube of air captured by the engine. At first this seems like a vaguely defined quantity. In fact it is precisely determined by the engine pumping characteristics as we shall see shortly.

4.7.1 Example - turbojet in supersonic flow with an inlet shock

A turbojet operates supersonically at \( M_0 = 3 \) and \( T_{t4} = 1944 \, K \). The compressor and turbine polytropic efficiencies are \( \eta_{pc} = \eta_{pt} = 1 \). At the condition shown, the engine operates semi-ideally with \( \pi_b = \pi_n = 1 \) but \( \pi_d \neq 1 \) and with a simple convergent nozzle. The relevant areas are \( A_1/A_2 = 2, \ A_2/A_4^* = 14 \) and \( A_e/A_4^* = 4 \). Supersonic flow is established at the entrance to the inlet with a normal shock downstream of the inlet throat. This type of inlet operation is called supercritical and will be discussed further in a later section.

Figure 4.6: Supersonic turbojet with inlet shock.
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1) Sketch the distribution of stagnation pressure, $P_t/P_{t0}$ and stagnation temperature, $T_t/T_{t0}$ through the engine. Assign numerical values at each station.

**Solution** - Note that $f(3) = 0.236$, $T_{t0} = 605\, K$ and

$$
\frac{A_e}{A_1} = \left(\frac{A_e}{A_1^*}\right) \left(\frac{A_4^*}{A_2}\right) = \frac{4}{14} \left(\frac{1}{2}\right) = 0.143. \quad (4.58)
$$

We need to determine $\pi_c$, $f(M_2)$ and $\pi_d$. The analysis begins at the nozzle where the flow is choked. Choking at the turbine inlet and nozzle determines the turbine temperature and pressure ratio.

$$
\tau_t = \left(\frac{A_4^*}{A_e}\right)^{\frac{2(\gamma-1)}{\gamma+1}} = \left(\frac{1}{4}\right)^{\frac{1}{2}} = 0.63 \quad (4.59)
$$

$$
\pi_t = \tau_t^{\frac{\gamma}{\gamma-1}} = 0.63^{\frac{3}{2}} = 0.198 \quad (4.60)
$$

Matching turbine and compressor work gives the compressor temperature and pressure ratio.

$$
\tau_c = 1 + \frac{\tau_\lambda}{\tau_r} (1 - \tau_t) = 1 + \frac{1944}{605} (1 - 0.63) = 2.19 \quad (4.61)
$$

$$
\pi_c = \tau_c^{\frac{\gamma}{\gamma-1}} = 2.19^{\frac{3}{2}} = 15.54 \quad (4.62)
$$

Now the Mach number at the compressor face is determined.

$$
f(M_2) = A_4^* \left(\frac{\tau_r}{\tau_\lambda}\right)^{1/2} \pi_c \pi_b = A_4^* \left(\frac{605}{1944}\right)^{1/2} 15.54 = A_4^* \frac{8.67}{14} = 0.62 \quad (4.63)
$$

Use free-stream-compressor-mass-flow matching to determine the stagnation pressure loss across the inlet.

$$
\pi_d = \frac{A_0 f(M_0)}{A_2 f(M_2)} = 2 \times \frac{0.236}{0.62} = 0.76 \quad (4.64)
$$

Now determine the stagnation pressure ratio across the engine.

$$
\frac{P_{te}}{P_{t0}} = \pi_d \pi_c \pi_t = 0.76 (15.54) (0.198) = 2.34 \quad (4.65)
$$
Now the exit static pressure ratio is determined

\[
\frac{P_e}{P_0} = \frac{P_{te}}{P_{t0}} \left( \frac{1 + \frac{\gamma^{-1} M_0^2}{2}}{1 + \frac{\gamma^{-1} M_e^2}{2}} \right)^{\frac{\gamma}{\gamma-1}} = 2.34 \left( \frac{2.8}{1.2} \right)^{3.5} = 45.4
\]  \hspace{1cm} (4.66)

as is the stagnation temperature ratio,

\[
\frac{T_{te}}{T_{t0}} = \frac{\tau_{\lambda}}{\tau_e} = \frac{1944}{605} 0.63 = 2.02
\]  \hspace{1cm} (4.67)

static temperature ratio,

\[
\frac{T_e}{T_0} = \frac{T_{te}}{T_{t0}} \left( \frac{1 + \frac{\gamma^{-1} M_0^2}{2}}{1 + \frac{\gamma^{-1} M_e^2}{2}} \right) = 2.02 \left( \frac{2.8}{1.2} \right) = 4.71
\]  \hspace{1cm} (4.68)

velocity ratio,

\[
\frac{U_e}{U_0} = \frac{M_e}{M_0} \left( \frac{T_e}{T_0} \right)^{1/2} = \frac{1}{3} (4.71)^{1/2} = 0.723
\]  \hspace{1cm} (4.69)

and thrust

\[
\frac{T}{P_0 A_0} = \gamma M_0^2 \left( \frac{U_e}{U_0} - 1 \right) + \frac{A_e}{A_0} \left( \frac{P_e}{P_0} - 1 \right)
\]

\[
\frac{T}{P_0 A_0} = 1.4 \times 9 \times (0.723 - 1) + 0.143 (45.4 - 1) = -3.49 + 6.35 = 2.86.
\]

At this point we have all the information we need (and then some) to answer the problem. The pressure ratios are
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\[ \frac{P_{t2}}{P_{t0}} = \pi_d = 0.76 \]
\[ \frac{P_{t3}}{P_{t0}} = \pi_d \pi_c = 11.8 \]
\[ \frac{P_{t4}}{P_{t0}} = \pi_d \pi_c \pi_b = 11.8 \]
\[ \frac{P_{te}}{P_{t0}} = \pi_d \pi_c \pi_b \pi_t = 2.34 \] (4.71)

and the relevant temperature ratios are

\[ \frac{T_{t2}}{T_{t0}} = \tau_d = 1 \]
\[ \frac{T_{t3}}{T_{t0}} = \tau_d \tau_c = 2.19 \] (4.72)
\[ \frac{T_{t4}}{T_{t0}} = \tau_d \tau_c \tau_b = \frac{1944}{605} = 3.21 \]
\[ \frac{T_{te}}{T_{t0}} = \tau_d \tau_c \tau_b \tau_t = 2.02. \]

The stagnation pressure and temperature ratios through the engine are sketched in Figure 4.7.

At this relatively high Mach number, the nozzle exit pressure is far higher than the ambient pressure. That suggests that it should be possible to increase the thrust by adding an expansion section to the nozzle. Let’s see how much improvement might be possible. The thrust is

\[ \frac{T}{P_0 A_0} = \gamma M_0^2 \left( \frac{M_e}{M_0} \sqrt{\frac{T_e}{T_0}} - 1 \right) + \frac{A_e}{A_0} \left( \frac{P_e}{P_0} - 1 \right). \] (4.73)

Let’s express (4.73) in terms of the nozzle exit Mach number assuming isentropic flow in the nozzle.
Figure 4.7: Stagnation temperature and pressure through a supersonic turbojet.

\[
\frac{T}{P_0 A_0} = \gamma M_0^2 \left( \frac{M_e}{M_0} \sqrt{\frac{T_{te}}{T_0} \left( \frac{T_e}{T_{te}} \right)} - 1 \right) + A_8 \frac{A_e}{A_0} A_8 \left( \frac{P_{te}}{P_0} \frac{P_e}{P_{te}} - 1 \right)
\]

or

\[
\frac{T}{P_0 A_0} (M_e) = \gamma M_0^2 \left( \frac{M_e}{M_0} \sqrt{\frac{T_{te}}{T_0} \left( \frac{1}{1 + \frac{\gamma - 1}{2} M_e^2} \right)} - 1 \right) + \frac{A_8}{A_0} \frac{1}{f(M_e)} \left( \frac{P_{te}}{P_0} \left( \frac{1}{1 + \frac{\gamma - 1}{2} M_e^2} \right)^{\gamma - 1} - 1 \right)
\]  

(4.74)

The latter version of the thrust equation in (4.74) can be considered to be just a function of the Mach number for fixed stagnation pressure and temperature leaving the turbine. Equation (4.74) is plotted in Figure 4.8 for selected values of pressure, temperature, and area ratio.

At this flight Mach number the thrust can be nearly doubled using the nozzle. The maximum thrust occurs when the nozzle is fully expanded to \( P_e = P_0 \). The corresponding exit Mach number is \( M_e = 3.585 \) at a nozzle area ratio of \( A_e/A_8 = 7.34 \). The overall engine area ratio is \( A_e/A_1 = (A_e/A_8) (A_8/A_0) = 1.05 \) which suggests that the expansion could be added without much increase in the frontal area that the engine presents to the flow and therefore without much drag penalty.
For an engine designed for a lower flight Mach number the performance gain by fully expanding the nozzle is relatively less. For a commercial engine designed to fly at subsonic Mach numbers the improvement is quite small and usually not worth the additional weight required to fully expand the nozzle.

4.8 How does a turbojet work?

The answer to this question lies in the various matching conditions that must be satisfied between engine components. These are mainly the requirements that the mass flow in and out of a component must be accommodated by the neighboring components and the work taken out of the flow by the turbine must equal the work done on the flow by the compressor. The analysis is simplified by the fact that under most practical operating conditions the nozzle and turbine inlet are choked. The rule of thumb, when trying to understand engine behavior, is to begin at the nozzle and work forward finishing with the inlet.

The total temperature ratio across the turbine is fixed by the turbine and nozzle choked areas. As a result, the turbine tends to operate at a single point. For example, if the pilot pushes the throttle forward, the turbine inlet temperature will go up and the temperature exiting the turbine will go up, but not as much. This leads to an increase in the temperature drop across the turbine. More work is taken out of the flow and the engine revs up while $\tau_t$ remains fixed. There are some variable cycle engine concepts that use a variable area turbine (VAT) to improve performance but the temperature and materials problems associated with movement of the turbine inlet vane make this very difficult to implement.
Many engines, especially military engines, designed to operate over a wide altitude and Mach number flight envelope, do incorporate variable area nozzles.

### 4.8.1 The compressor operating line

Now eliminate $\tau/\tau_r$ between (4.55) and (4.56), using

$$\pi_c = \pi_c^{\frac{1}{\gamma-1}}. \tag{4.75}$$

The result is

$$\frac{\pi_c}{(\pi_c^{\frac{1}{\gamma-1}} - 1)^{1/2}} = \left(\frac{1}{1 - \left(\frac{A_1}{A_4}\right)^{\frac{2(\gamma-1)}{\gamma+1}} f(M_2)}\right)^{1/2}. \tag{4.76}$$

Equation (4.76) defines the compressor operating line on a plot of $\pi_c$ versus $f(M_2)$. Note that the denominator on the left hand side represents a relatively weak dependence on $\pi_c$ except at unrealistically low values of $\pi_c$ where the denominator can become singular. So, to a rough approximation (4.76) defines a nearly straight line relationship between $\pi_c$ and $f(M_2)$. Equation (4.76) is sketched below.

![Figure 4.9: Schematic of the compressor operating line Equation (4.76).](image)

Still missing from our understanding of turbojet operation is the relationship between the compressor temperature and pressure rise and the actual compressor speed. To determine this we will need to develop a model of the compressor aerodynamics.
4.8.2 The gas generator

The combination of compressor, burner and turbine shown below is called the gas generator.

![Gas generator with imbedded station numbers.](image)

Compressor performance is characterized in terms of the compressor map which describes the functional relationship between compressor pressure ratio, mass flow and compressor speed. The compressor map from a J85 turbojet is shown below.

![Compressor map from a J-85 turbojet.](image)

In general the pressure ratio increases with increasing compressor rotation speed. At a given rotation speed the pressure ratio goes up as $f(M_2)$ is decreased. This latter behavior can be understood in terms of increasing relative angle of attack of the air flowing over the compressor blades leading to increased blade lift as the axial speed of the flow decreases.
More will be said on this point later.

### 4.8.3 Corrected weight flow is related to $f(M_2)$.

Industry practice is to correct the mass flow for the effects of altitude and flight speed. One defines the corrected weight flow as

$$\dot{w}_c = \dot{m}_a g \sqrt{\theta} \delta$$  \hspace{1cm} (4.77)

where

$$\theta = \frac{T_{t2}}{T_{SL}}$$  \hspace{1cm} (4.78)

$$\delta = \frac{P_{t2}}{P_{SL}}.$$  

The quantities $T_{SL}$ and $P_{SL}$ refer to sea level standard pressure and temperature. In English units

$$T_{SL} = 518.67R$$  \hspace{1cm} (4.79)

$$P_{SL} = 2116.22\text{pounds/ft}^2.$$  

The gas constant for air is

$$R_{air} = 1710.2\text{ft}^2 / (\sec^2 - R).$$  \hspace{1cm} (4.80)

We can write (4.77) as

$$\dot{w}_c = \dot{m} g \sqrt{\theta} \delta = \left( \frac{1}{\frac{(\gamma+1)}{2}} \frac{\gamma g P_{SL}}{\sqrt{\gamma R T_{SL}}} \right) A f(M).$$  \hspace{1cm} (4.81)

Note that the quantity in parentheses is a constant. Thus the corrected mass flow is proportional to $f(M_2)$. At the compressor face
\[
\dot{w}_c = 49.459 A_2 f(M_2) \text{ pounds/sec (4.82)}
\]

where \( A_2 \) is expressed in terms of square feet. Throughout this course \( f(M_2) \) will be the preferred measure of reduced mass flow through the compressor instead of the usual corrected weight flow. This quantity has several significant advantages. It is dimensionless, independent of compressor size and for practical purposes lies in a fairly narrow range of values that is more or less the same for all engines. The compressor entrance Mach number, \( M_2 \), is generally restricted to lie in the range between 0.2 and 0.6. Unusually low values of \( f(M_2) \) imply that the engine diameter is too large. If \( f(M_2) \) gets too large (\( f(M_2) \) approaches one), the compressor blade passages begin to choke and stagnation pressure losses increase dramatically.

The compressor map can be regarded as a cross plot of three independent functions. The first is determined by the compressor-turbine inlet matching function (4.52). Rearranging variables (4.52) becomes

\[
\pi_c = F_1 \left( \frac{\tau_\lambda}{\tau_r}, f(M_2) \right) = \left( \frac{1 + f}{\pi_b} \frac{A_2}{A_4^*} \right) \sqrt{\frac{\tau_\lambda}{\tau_r}} f(M_2) \quad (4.83)
\]

where the contribution of the fuel/air ratio and burner pressure loss has been included. The factor in parentheses in (4.83) is approximately constant.

The second function relates the compressor efficiency to the pressure ratio and mass flow.

\[
\eta_c = F_2(\pi_c, f(M_2)) \quad (4.84)
\]

This is a function that can only be determined empirically through extensive compressor testing. The contours of constant efficiency in Figure 4.11 illustrate a typical case.

The third function relates the pressure ratio and mass flow to the rotational speed of the compressor. This function is of the form

\[
\pi_c = F_3 \left( \frac{M_{b0}}{\sqrt{\tau_r}}, f(M_2) \right) \quad (4.85)
\]

where

\[
M_{b0} = \frac{U_{\text{blade}}}{\sqrt{\gamma R T_0}} \quad (4.86)
\]
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is the compressor blade Mach number based on the free stream speed of sound and $U_{blade}$ is the blade speed. Equation (4.85) is shown as lines of constant percent corrected speed in Figure 4.11.

4.8.4 A simple model of compressor blade aerodynamics

An accurate model of (4.85) can be derived from a detailed computation of the aerodynamics of the flow over the individual compressor blade elements. This is beyond the scope of this course but we can develop a simplified model of blade aerodynamics that reproduces the most important features of the relation between pressure ratio, mass flow and blade speed illustrated by the family of speed curves in Figure 4.11. Figure 4.12 shows the flow through a typical compressor stage called an imbedded stage. The stations labeled in Figure 4.12 are 2a (the space just ahead of the compressor rotor), 2b (the space between the rotor and stator) and 3a (the space after the stator and just ahead of the next rotor). The velocity vectors at various points in the stage are indicated in Figure 4.12. The vector relationships are

\[ W_{2a} = C_{2a} - U_{blade} \]
\[ W_{2b} = C_{2b} - U_{blade}. \]  

(4.87)

The axial velocity component is $c_z$. Tangential components are $c_{2a\theta}$ and $c_{2b\theta}$. Flow angles in non-moving coordinates are $\alpha_{2a}$, $\alpha_{2b}$ and $\alpha_{3a}$. Flow angles in moving coordinates are $\beta_{2a}$, $\beta_{2b}$ and $\beta_{3a}$. The assumptions of the model are

\begin{align*}
\text{c}_z \text{ is constant through the engine} \\
\text{All stages are identical} \\
\alpha_{2a} = \alpha_{3a} \text{ and } C_{2a} = C_{3a}. 
\end{align*}

(4.88)

In addition, radial variations in the flow along the compressor blade elements are ignored ($c_r$ is negligible). This is called a strip model of the compressor where the blades are approximated by an infinite 2-D cascade.

The basic aerodynamic principle utilized in this model is that the flow coming off the trailing edge of the compressor airfoils is guided by the wing surface and leaves the wing at the angle of the trailing edge. In contrast, the flow angle at the leading edge varies with the axial flow speed and blade speed while the airfoil lift varies accordingly as suggested in Figure 4.13.

When the airfoil is one element of a cascade the guiding effect of the trailing edge is enhanced. One of the design parameters of a compressor cascade is the solidity which
Figure 4.12: Flow geometry in an imbedded stage.

Figure 4.13: Effect of angle of attack on airfoil lift.
is defined as the blade chord divided by the vertical distance between compressor blade trailing edges. If the solidity is low (blades far apart) then the guiding effect of the cascade on the flow is reduced, the trailing edge flow is susceptible to stall (flow separation) and the work capability of the compressor is reduced. If the solidity gets too high then the drag losses of the compressor become excessive as does the compressor weight. A solidity of approximately one is fairly typical.

The tangential velocity components are

\[ c_{2a\theta} = c_z \tan(\alpha_{2a}) \]  
\[ c_{2b\theta} = U_{blade} - c_z \tan(\beta_{2b}) . \]  

The tangential velocity change of the flow induced by the tangential component of the lift force acting on the compressor blades is

\[ \Delta c_{\theta} = c_{2b\theta} - c_{2a\theta} = U_{blade} - c_z \tan(\beta_{2b}) - c_z \tan(\alpha_{2a}) . \]  

Note that there is a considerable axial force component on the stage due to the pressure rise that the flow experiences as the stator removes the tangential velocity change. An energy balance on a control volume that encloses the rotor can be used to show that the work done across the rotor is

\[ \dot{m}_a (h_{t2b} - h_{t2a}) = \bar{F} \cdot \bar{U}_{blade}. \]  

In terms of the tangential velocity change

\[ \dot{m}_a (h_{t2b} - h_{t2a}) = \dot{m}_a \Delta c_{\theta} U_{blade} . \]  

This is a key equation that connects the work done across a cascade with the speed of the blade and the tangential velocity change. Note that all of the stage work is done by the rotor and so we can write

\[ (h_{t3a} - h_{t2a}) = \Delta c_{\theta} U_{blade} . \]  

Assume there are \( n \) identical stages. Then the enthalpy rise across the compressor is

\[ (h_{t3} - h_{t2}) = n (\Delta c_{\theta}) U_{blade} . \]
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Assume constant heat capacity and divide (4.94) by $C_p T_0$.

$$
\tau_r (\tau_c - 1) = n (\gamma - 1) \frac{U_{blade}^2}{\gamma R T_0} \left( \frac{\Delta c_\theta}{U_{blade}} \right) \quad (4.95)
$$

Solve for $\tau_c$

$$
\tau_c = 1 + n (\gamma - 1) \left( \frac{M_{b0}}{\sqrt{\tau_r}} \right)^2 \psi \quad (4.96)
$$

where the stage load factor

$$
\psi = \frac{\Delta c_\theta}{U_{blade}} \quad (4.97)
$$

is introduced. The stage load factor compares the tangential velocity change of the flow across the rotor to the rotor speed. The upper limit of this parameter is about 1/4 and is a measure of the maximum pressure rise achievable in a stage. Equation (4.96) is expressed in terms of the basic compressor speed parameter introduced in (4.85). Now we need to express the stage load factor in terms of this speed parameter and $f(M)$. From (4.90).

$$
\psi = 1 - \frac{c_z}{U_{blade}} (Tan (\beta_{2b}) + Tan (\alpha_{2a})) \quad (4.98)
$$

Equation (4.98) brings into play a second dimensionless velocity ratio, the flow coefficient which compares the flow axial speed to the blade speed.

$$
\phi = \frac{c_z}{U_{blade}} \quad (4.99)
$$

The basic aerodynamic design of the compressor boils down to two dimensionless velocity ratios, the flow coefficient and the stage load factor. Note that (4.98) is written in terms of the trailing edge flow angles. In our simple model these angles are assumed to be constant and so the stage load factor is a simple linear function of the flow coefficient. Now

$$
\tau_c = 1 + n (\gamma - 1) \left( \frac{M_{b0}}{\sqrt{\tau_r}} \right)^2 (1 - \phi (Tan (\beta_{2b}) + Tan (\alpha_{2a}))) \quad (4.100)
$$

At station 2 where the Mach number is relatively low $f(M_2)$ can be approximated by
\[ f(M_2) \approx \left( \frac{\gamma + 1}{2} \right)^{\frac{\gamma + 1}{\gamma - 1}} \frac{c_s}{\sqrt{\gamma R T_2}} \approx \left( \frac{\gamma + 1}{2} \right)^{\frac{\gamma + 1}{2(\gamma - 1)}} \frac{U_{\text{blade}}}{\sqrt{\gamma R T_2}} \left( \frac{c_s}{U_{\text{blade}}} \right). \] (4.101)

So to a reasonable approximation

\[ \phi = \frac{1}{\left( \frac{\gamma + 1}{2} \right)^{\frac{\gamma + 1}{2(\gamma - 1)}} \left( \frac{M_{b0}}{\sqrt{\tau_r}} \right)} \cdot f(M_2). \] (4.102)

Finally our aerodynamic model of the compressor is

\[ \tau_c = 1 + n (\gamma - 1) \left( \frac{M_{b0}}{\sqrt{\tau_r}} \right)^2 - \frac{n (\gamma - 1)}{\left( \frac{\gamma + 1}{2} \right)^{\frac{\gamma + 1}{2(\gamma - 1)}}} (\tan(\beta_{2b}) + \tan(\alpha_{2a})) \left( \frac{M_{b0}}{\sqrt{\tau_r}} \right) f(M_2). \] (4.103)

The pressure ratio is generated from (4.103) using \( \pi_c = \tau_c^{\gamma/(\gamma - 1)} \). A polytropic efficiency of compression (defined below) can also be included. Figure 4.14 shows a cross plot of (4.83) and (4.103) for a typical case.

![Compressor map generated by the strip model.](image)

The model does a reasonable job of reproducing the inverse relationship between pressure ratio and blade speed although the curvature of the speed characteristics (lines of constant \( M_{b0}/\sqrt{\tau_r} \)) is opposite to that observed in Figure 4.9. This is because the model does not include viscous effects at all. Such effects as the deviation in trailing edge flow angle due
to boundary layer thickening at high pressure ratio are not accounted for. At high pressure ratio and low flow speed the trailing edge flow eventually separates and the compressor stalls. This is indicated in Figure 4.11 as the estimated stall line. Modern engine control systems are designed to prevent the engine from stalling although some trailing edge separation can be tolerated. Substantial stall can lead to a condition called surge where large flow oscillations can do substantial damage to the engine. In the most extreme case the high pressure in the engine cannot be maintained and the internal gas may be released in an nearly explosive manner similar to the release from a burst pressure vessel with gas (and possibly engine parts) coming out of the inlet.

4.8.5 Turbojet engine control

The two main inputs to the control of the engine are:

1) The throttle, which we can regard as controlling $T_{t4}$, or equivalently at a fixed altitude, $\tau_\lambda$ and,

2) the nozzle throat area $A_8$.

The logic of the engine operation is as follows.

Case 1 - Increase $A_8$ keeping $\tau_\lambda$ constant. Equation (4.54) determines $\tau_t$ which is used in (4.55) to determine $\tau_c$. This determines $\pi_c$ through (4.75) and $f(M_2)$ through (4.56). Given $f(M_2)$, the combination $(1/\pi_d) (A_0/A_2)$ is now known. This quantity completely specifies the inlet operation. The increase of $A_8$ leads to an increase in both $f(M_2)$ and $\pi_c$ due to an increase in compressor speed as indicated on the compressor map. The compressor operating point moves along a constant $\tau_\lambda/\tau_r$ characteristic.

Case 2 - Increase $\tau_\lambda$ keeping $A_8$ constant. The logic in this case is very similar to case 1 except that the compressor-turbine work matching condition, has $\tau_t = constant$. This determines $\pi_c$ through (4.75) and $f(M_2)$ through the (in this case fixed) compressor operating line (4.76). Given $f(M_2)$ then $(1/\pi_d) (A_0/A_2)$ is known and the inlet operation is defined. As in case 1 the change of $f(M_2)$ and $\pi_c$ is achieved by an increase in compressor speed according to the compressor map. The compressor operating point moves along the operating line (4.76) which crosses the constant $\tau_\lambda/\tau_r$ characteristics as shown in Figure 4.12.

4.8.6 Inlet operation

There are two main points to take away from the previous discussion of engine control. The first is that to understand engine operation one begins at the nozzle and works forward. The other is that the inlet flow is essentially defined by the engine operating point through
the value of \( f(M_2) \). In effect, the engine sets the back pressure for the inlet. This is the fundamental purpose of the inlet; to provide the air mass flow to the engine at the Mach number dictated by the engine operating point with as small a stagnation pressure loss as possible. This whole mechanism is referred to as the pumping characteristic of the engine.

Let's look at the various possible modes of inlet operation recalling the discussion of capture area in Chapter 2. Figure 4.15 depicts an engine in subsonic flow. Shown is the variation in inlet flow as the nozzle throat \( A_8 \) area is increased with \( \tau \lambda \) held constant.

![Diagram](image)

**Figure 4.15:** Inlet behavior with increasing nozzle throat area in subsonic flow.

The Mach number at station 2 entering the compressor increases from top to bottom in Figure 4.15. In the top four figures (a, b, c, d) there is no inlet shock and so, neglecting skin friction, the only way the increase in the Mach number at station 2 can be accommodated according to the matching condition (4.57) is for the capture area \( A_0 \) to increase leading to an increase in the air mass flow through the engine with \( \pi_d = 1 \).

As \( A_8 \) is increased further the inlet eventually chokes (this is the situation shown as case d). The condition for inlet choking is determined from the mass balance between the inlet throat \( A_{1.5} \) and compressor face \( A_2 \).
Neglecting skin friction and heat transfer, the flow from $A_{1.5}$ to $A_2$ is adiabatic and isentropic. The mass balance (4.104) becomes

$$ A_2 f(M_2) = A_{1.5} f(M_{1.5}). \quad (4.105) $$

The inlet chokes when $f(M_{1.5}) = 1$. This occurs when

$$ f(M_2)|_{inlet\ choking} = \frac{A_{1.5}}{A_2}. \quad (4.106) $$

If the nozzle area is increased beyond this point there is no change in $A_0$, the air mass flow remains fixed and a shock wave forms downstream of the inlet throat (this is depicted as case $e$ in Figure 4.15). The matching condition (4.57) is satisfied by increasing stagnation pressure loss across the shock ($\pi_d < 1$). The shock becomes stronger as the Mach number at the compressor face is further increased. This whole mechanism is referred to as the pumping characteristic of the engine. Once a shock begins to form in the inlet, the engine performance (thrust and efficiency) begins to drop off rather rapidly. A well designed system is designed to avoid shock formation.

In supersonic flow the inlet is routinely designed to accommodate an inlet shock and/or a system of external shocks that may be needed to decelerate a high Mach number flow to the subsonic value at the compressor face dictated by the engine pumping characteristics. The basic operation of the inlet throat in supersonic flow is similar to that shown in Figure 4.15. Stagnation pressure losses may include fixed losses due to the external shock system as well as variable losses, due to the movement of the inlet shock. The figure below depicts the effect of increasing $A_8$ on the inlet flow for an engine operating in a supersonic stream.

In case $a$ the Mach number at station 2 is low enough so that the Mach number at station 1 is less than the Mach number behind the normal shock ahead of the inlet as determined by $A_2/A_1$. The inlet operation is said to be sub-critical and after the system of oblique and normal shocks over the center body, the flow into the inlet is all subsonic. The inlet pressure ratio $\pi_d$ is less than one due to the oblique and normal shocks. As the nozzle is opened up, the air mass flow into the engine increases with $\pi_d$ approximately constant (exactly constant if the inlet is planar as opposed to axisymmetric). When the Mach number at station 2 has increased to the point where the Mach number at station 1 is just slightly less than the Mach number behind the normal shock, the normal shock will
be positioned just ahead of the inlet lip and the inlet operation is said to be critical. The Mach number between stations 1 and 2 is all subsonic.

Further increasing $A_8$ leads to starting of the inlet flow and shock formation downstream of $A_{1.5}$. If the nozzle is opened up still more the engine will demand increasing values of $f (M_2)$. In this case the mass flow through the inlet can no longer increase and the mass flow balance between the free stream and compressor face (4.57) is satisfied through decreasing values of $\pi_d$ (supercritical operation) due to downstream movement of the shock to higher shock Mach numbers. Similar inlet behavior occurs with fuel throttling. The shadowgraph photos in Figure 4.17 illustrate sub and supercritical flow on an axisymmetric spike inlet.

A final point to be made here is to remind ourselves of the artificial nature of the ideal turbojet cycle which assumes $\pi_d = 1$. The first step toward a more realistic supersonic engine is to allow the inlet the freedom to accommodate some stagnation pressure loss. Just as in the ramjet cycle the inlet plays a crucial role in the stable operation of the engine.

Figure 4.16: Inlet behavior with increasing nozzle throat area in supersonic flow.
Figure 4.17: Flow over a Mach 3 spike inlet, left photo subcritical behavior, right photo supercritical behavior.

4.9 The non-ideal turbojet cycle

We have already studied one of the most important mechanisms for non-ideal behavior; namely the formation of an inlet shock.

Less than full expansion of the nozzle $P_e < P_0$ generally leads to less than maximum thrust. The loss in performance of a nozzle is a strong function of flight Mach number and becomes less important as the flight Mach number falls below one. Most military engines employ a converging-diverging nozzle for good supersonic performance whereas most commercial engines use a purely convergent nozzle for subsonic flight where the emphasis is on reducing weight and complexity. Most nozzle stagnation pressure losses are associated with viscous skin friction although some shock loss can occur at off design conditions. The nozzle operates in a strongly favorable pressure gradient environment and so stagnation pressure losses tend to be small and flow separation usually does not occur unless the nozzle becomes highly over-expanded. Flow separation can be an important issue in rocket nozzles when operating in the lower atmosphere but the problem is less severe in jet engines.

Stagnation pressure losses across the burner due to heat addition cause $\pi_b$ to be always less than one. Additional reduction of $\pi_b$ occurs due to wall friction and injector drag. Recall that the stagnation pressure loss due to heat addition and friction is proportional to $\gamma M^2/2$. A rule of thumb is

$$\pi_b = 1 - \text{constant} \times \gamma M^2$$

(4.107)

where the constant is between one and two. In addition to the loss of stagnation pressure it is necessary to account for incomplete combustion as well as radiation and conduction of
heat to the combustor walls. The combustor efficiency is defined directly from the energy balance across the burner.

\[ \eta_b = \frac{(1 + f) h_{t4} - h_{t3}}{f h_f} \]  

(4.108)

The burner efficiency in a modern gas turbine engine is generally very close to one; Typically the efficiency is 0.99 or better.

The shaft that connects the turbine and compressor is subject to frictional losses in the bearings that support the shaft and a shaft mechanical efficiency is defined using the work balance across the compressor and turbine.

\[ \eta_m = \frac{h_{t3} - h_{t2}}{(1 + f) (h_{t4} - h_{t5})} \]  

(4.109)

Typical shaft efficiencies are also very close to one.

### 4.9.1 The polytropic efficiency of compression

In the ideal turbojet cycle the compressor is assumed to operate isentropically. But this ignores the viscous frictional losses that are always present. An \( h - s \) diagram illustrating the non-ideal operation of the compressor and turbine in an otherwise ideal turbojet cycle is shown in Figure 4.18.

![Figure 4.18: Path of a turbojet in h-s coordinates with non-ideal compressor and turbine.](image-url)
The diagram shows the thermodynamic path of the gas flowing through a turbojet with ideal inlet, burner and nozzle but non-ideal compressor and turbine. As we consider the non-ideal cycle it is well to keep in mind that the engine is designed to produce thrust first and be efficient second. As an engine ages and various components begin to degrade, the engine control system is designed to increase fuel flow and the turbine inlet temperature so as to maintain the design thrust at the expense of efficiency.

A compressor is expected to reach the design pressure ratio regardless of its efficiency, and the same goes for the turbine. With this in mind Figure 4.18 suggests a reasonable definition of compressor and turbine efficiency

\[
\eta_c = \frac{\text{The work input needed to reach } P_{t3}/P_{t2} \text{ in an isentropic compression process}}{\text{The work input needed to reach } P_{t3}/P_{t2} \text{ in the real compression process}}
\]

\[
\eta_c = \frac{h_{t3s} - h_{t2}}{h_{t3} - h_{t2}}
\]

(4.110)

and

\[
\eta_e = \frac{\text{The work output needed to reach } P_{t5}/P_{t4} \text{ in the real expansion process}}{\text{The work output needed to reach } P_{t5}/P_{t4} \text{ in an isentropic expansion process}}
\]

\[
\eta_e = \frac{h_{t5} - h_{t4}}{h_{t5s} - h_{t4}}
\]

(4.111)

In terms of the temperature for a calorically perfect gas these definitions become

\[
\eta_c = \frac{T_{t3s} - T_{t2}}{T_{t3} - T_{t2}}
\]

(4.112)

These definitions are useful but a little hard to interpret when comparing one compressor with another if the compression ratios are not the same. We can use the approach suggested by Figure 4.18 to define an efficiency that characterizes the compression process itself. Consider an infinitesimal compression process defined by the \( T - s \) diagram shown in Figure 4.19.
Define the polytropic efficiency of compression as the efficiency of an infinitesimal compression process.

\[
\eta_{pc} = \left( \frac{T_{t3s} - T_{t2}}{T_{t3} - T_{t2}} \right)_{\text{infinitesimal compression}} = \frac{dT_{ts}}{dT_t} \tag{4.113}
\]

For an isentropic process of a calorically perfect gas the Gibbs equation is

\[
\frac{dT_{ts}}{T_t} = \left( \frac{\gamma - 1}{\gamma} \right) \frac{dP_t}{P_t}. \tag{4.114}
\]

Using (4.113) the differential change in stagnation temperature for the real process is

\[
\frac{dT_t}{T_t} = \left( \frac{\gamma - 1}{\gamma \eta_{pc}} \right) \frac{dP_t}{P_t}. \tag{4.115}
\]

Now assume the polytropic efficiency is constant over the real finite compression from station 2 to station 3. Integrating (4.115) from 2 to 3 we get

\[
\frac{P_{t3}}{P_{t2}} = \left( \frac{T_{t3}}{T_{t2}} \right)^{\frac{\gamma \eta_{pc}}{\gamma - 1}}. \tag{4.116}
\]

The polytropic efficiency of compression allows us to analyze the flow through the compressor in terms of a relation that retains the simplicity of the isentropic relation. A lot of poorly understood physics is buried in the specification of \( \eta_{pc} \). Modern compressors are designed to have values of \( \eta_{pc} \) in the range 0.88 to 0.92. Now the overall compressor efficiency becomes
\[ \eta_c = \frac{\frac{T_{t3}}{T_{t2}} - 1}{\frac{T_{t3}}{T_{t2}} - 1} = \left( \frac{P_{t3}}{P_{t2}} \right)^{\frac{\gamma - 1}{\gamma}} - 1 \]  
\[ \text{(4.117)} \]

Note that for pressure ratios close to one \( \eta_c \approx \eta_{pc} \). The polytropic efficiency is a fundamental measure of the degree to which the compression process is isentropic. Given \( \eta_{pc} \) the overall compression efficiency is determined for any given pressure ratio.

### 4.10 The polytropic efficiency of expansion

Consider an infinitesimal expansion process defined by the \( T - s \) diagram shown in Figure 4.20.

\[ \eta_{pe} = \left( \frac{T_{t5} - T_{t4}}{T_{t5s} - T_{t4}} \right)^{\text{infinitesimal expansion}} = \frac{dT_t}{dT_{ts}}. \]  
\[ \text{(4.118)} \]

For an isentropic process the Gibbs equation for an ideal, calorically perfect gas is

\[ \frac{dT_{ts}}{T_t} = \left( \frac{\gamma - 1}{\gamma} \right) \frac{dP_t}{P_t}. \]  
\[ \text{(4.119)} \]

Using (4.118) the differential change in stagnation temperature for the real process is
\[
\frac{dT_t}{T_t} = \left(\frac{\gamma - 1}{\gamma}\right) \frac{\eta_{pe}}{\eta_e} \frac{dP_t}{P_t}.
\] (4.120)

Now if we assume the polytropic efficiency is constant over the real finite expansion from station 4 to station 5, then integrating (4.115) from 4 to 5

\[
\frac{P_{t5}}{P_{t4}} = \left(\frac{T_{t5}}{T_{t4}}\right)^{\frac{\gamma}{\gamma - 1}\eta_{pe}}.
\] (4.121)

The polytropic efficiency of expansion allows us to analyze the flow through the turbine in terms of a relation that retains the simplicity of the isentropic relation. Similar to the compression case, a lot of ignorance regarding the viscous turbulent flow through the turbine is buried in the specification of \(\eta_{pe}\). Modern turbines are designed to values of \(\eta_{pe}\) in the range 0.91 to 0.94. The overall turbine efficiency is

\[
\eta_e = \frac{T_{t5} - 1}{T_{t5} - 1} = \frac{\left(\frac{P_{t5}}{P_{t4}}\right)^{\frac{\gamma - 1}{\gamma}\eta_{pe}} - 1}{\left(\frac{P_{t5}}{P_{t4}}\right)^{\frac{\gamma - 1}{\gamma} - 1}}.
\] (4.122)

Note that for pressure ratios close to one \(\eta_e \approx \eta_{pe}\). Generally speaking turbine efficiencies are somewhat greater than compressor efficiencies because of the strongly favorable pressure gradient in the turbine.

### 4.11 The effect of afterburning

Figure 4.21 depicts a turbojet with an afterburner (also called an augmentor). The afterburner is a relatively simple device that includes a spray bar where fuel is injected and a flame holder designed to provide a low speed wake where combustion takes place. Note my drawing is not to scale. Usually the afterburner is considerably longer than the engine itself to permit complete mixing and combustion between the injected fuel and the vitiated air coming out of the turbine, before the flow reaches the exhaust nozzle.

The main effect of the afterburner is to add a lot of heat to the turbine exhaust gases while producing relatively little stagnation loss since the heat addition is at relatively low Mach number. The exhaust Mach number is determined by the nozzle area ratio and for the same exit Mach number the exit velocity is increased in proportion to the increase in the square root of exhaust temperature. In terms of engine parameters
The fact that the nozzle area ratio is fixed ($M_e$ is constant) and the stagnation pressure is the same, implies that the pressure contribution to the thrust is the same. The velocity ratio is

$$\frac{U_e}{U_0} = \frac{M_e}{M_0} \sqrt{\frac{T_e}{T_0}} = \frac{M_e}{M_0} \sqrt{\frac{1}{T_0} \left( \frac{T_e}{1 + \left(\frac{\gamma - 1}{2}\right) M_e^2} \right)^{1/2}}.$$  \hfill (4.124)  

The exit stagnation temperature is

$$T_{te} = T_{t5} \left( \frac{T_{te}}{T_{t5}} \right) = T_{t5} \tau_a.$$  \hfill (4.125)  

The bottom line is that $U_e \approx \sqrt{\tau_a}$. The afterburner provides a rapid increase in thrust on demand allowing the aircraft to respond quickly to changing mission circumstances; perhaps to escape a suddenly emerging threat. The price is a substantial increase in fuel burn rate. Most military engines only spend a few hundred hours in the after-burning mode over a typical engine lifetime of $3 - 4000$ hours before a major overhaul.

### 4.12 Nozzle operation

Commercial engines generally operate with fixed, purely convergent nozzles. There is a penalty for not fully expanding the flow but at low Mach numbers the performance loss is relatively small and the saving in weight and complexity is well worth it. For a commercial engine operating at $M_0 = 0.8$, $\pi_n$ is on the order of 0.97 or better.
On the other hand military engines almost always employ some sort of variable area nozzle and in several modern systems the nozzle is also designed to be vectored. The most well known example is the planar nozzle of the F22. After-burning engines especially require a variable area nozzle. When the afterburner is turned on, and the exit gas temperature is increased according to (4.125), the nozzle throat area must be increased in a coordinated way to preserve the mass flow through the engine without putting an undue load on the turbine. Remember the exhaust nozzle is choked. With the augmentor on, the turbine temperature ratio is

$$\tau_t = \left( \frac{A_4^*}{A_8} \sqrt{\tau_a} \right)^{\frac{2(\gamma - 1)}{\gamma + 1}}.$$  \hspace{1cm} (4.126)

In order to keep the turbine temperature ratio unchanged and the rest of the engine at the same operating point when the augmentor is turned on, it is necessary to program the nozzle area so that $\sqrt{\tau_a}/A_8$ remains constant. If this is not done the dimensionless mass flow through the engine will decrease, the actual mass flow may decrease and the desired thrust increment will not occur, or worse, the compressor might stall.

4.13 Problems

Problem 1 - Consider the turbojet engine shown in Figure 4.22.

The engine operates at a free stream Mach number $M_0 = 0.8$. The ambient temperature is $T_0 = 216 K$. The turbine inlet temperature is $T_{t4} = 1944 K$ and $\pi_c = 20$. Relevant area ratios are $A_2/A_4^* = 10$ and $A_2/A_{1\text{thrott}} = 1.2$. Assume the compressor, burner and turbine all operate ideally. The nozzle is of a simple converging type and stagnation pressure losses due to wall friction in the inlet and nozzle are negligible. Determine $f (M_2)$. Sketch the compressor operating line. Suppose $T_{t4}$ is increased. What value of $T_{t4}$ would cause the inlet to choke? Assume $f << 1$. 

Figure 4.22: Turbojet in subsonic flow.
Problem 2 - A turbojet engine operates at a Mach number of 2.0 with a normal shock ahead of the inlet as shown in the sketch in Figure 4.23. The flow between the shock and station 2 is all subsonic. Assume $f << 1$ where appropriate and assume the static pressure outside the nozzle exit has recovered to the free stream value as indicated in the sketch. The ambient temperature and pressure are $T_0 = 216 \, K$ and $P_0 = 2 \times 10^4 \, N/m^2$.

![Figure 4.23: Turbojet with upstream normal shock.](image)

The turbine inlet temperature is $T_{t4} = 1512 \, K$, the compressor pressure ratio is $\pi_c = 20$ and $A_2/A_4^* = 18$. Assume the compressor, burner and turbine all operate ideally and stagnation pressure losses due to wall friction in the inlet and nozzle are negligible. Assume $f << 1$. Determine $A_2/A_0$, the pressure ratio $P_e/P_0$, temperature ratio $T_e/T_0$ and dimensionless thrust $T/P_0A_0$.

Problem 3 - Consider the turbojet engine shown in Figure 4.24.

![Figure 4.24: Operating turbojet at rest.](image)

The engine operates at zero free stream Mach number $M_0 = 0$. The ambient temperature and pressure are $T_0 = 273 \, K$ and $P_0 = 1.01 \times 10^5 \, N/m^2$. The turbine inlet temperature is $T_{t4} = 1638 \, K$ and $\pi_c = 20$. Relevant area ratios are $A_2/A_4^* = 10$ and $A_2/A_{throat} = 1.2$. Assume the compressor, burner and turbine all operate ideally. The nozzle is fully expanded $P_e = P_0$ and stagnation pressure losses due to wall friction in the inlet and nozzle are negligible. Assume $f << 1$. Determine the overall pressure ratio $P_e/P_0$ and dimensionless thrust $T/P_0A_2$.

Problem 4 - Figure 4.25 shows a typical turbojet engine flying supersonically. In Figure 4.26 are typical stagnation pressure and stagnation temperature ratios at various points inside the engine (the figures are not drawn to scale).
Figure 4.25: Turbojet in supersonic flow.

Figure 4.26: Stagnation pressure and stagnation temperature through a turbojet engine with inlet shock.
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The turbine inlet and nozzle exit are choked, and the compressor, burner and turbine operate ideally. Supersonic flow is established in the inlet and a normal shock is positioned downstream of the inlet throat. The inlet and nozzle are adiabatic. Neglect wall friction and assume \( f << 1 \).

Suppose \( \tau_\lambda \) is increased while the flight Mach number and engine areas including the nozzle throat area are constant.

1) Show whether \( P_{t3}/P_{t0} \) increases, decreases or remains the same.

2) At each of the stations indicated above explain how the stagnation pressure and stagnation temperature change in response to the increase in \( \tau_\lambda \).

Problem 5 - A turbojet operates supersonically at \( M_0 = 2 \) with \( f(M_2) = 0.5 \), \( \pi_c = 20 \) and \( T_{t4} = 2160 \, \text{K} \). The compressor and turbine polytropic efficiencies are \( \eta_{pc} = \eta_{pt} = 1 \). At the condition shown in Figure 4.27, the engine operates semi-ideally with \( \pi_d = \pi_b = \pi_n = 1 \) but with a simple convergent nozzle. The relevant inlet areas are \( A_1/A_{1.5} = 1.688 \) and \( A_2/A_{1.5} = 2 \). Assume \( \gamma = 1.4, R = 287 \, \text{m}^2/\text{(sec}^2 \cdot \text{K}) , \, C_p = 1005 \, \text{m}^2/\text{(sec}^2 \cdot \text{K}) \). The fuel heating value is \( h_f = 4.28 \times 10^7 \, \text{J/kg} \). The ambient temperature and pressure are \( T_0 = 216 \, \text{K} \) and \( P_0 = 2 \times 10^4 \, \text{N/m}^2 \). These are typical values in the atmosphere at an altitude of about 12,000 meters.

![Figure 4.27: Turbojet at Mach 2.0.](image)

Assume throughout that the fuel/air ratio is much less than one and that all areas of the engine structure remain fixed.

1) Determine \( A_2/A_4^* \) and \( A_4^*/A_e \).

2) For each of the following three cases determine \( f(M_2), f(M_{1.5}), f(M_1), A_0/A_1 \) and \( T/P_0 A_1 \).

Case I - First \( T_{t4} \) is slowly raised to 2376 K.

Case II - Then \( T_{t4} \) is reduced to 1944 K.

Case III - Finally \( T_{t4} \) is increased back to 2160 K.

Problem 6 - Consider the turbojet engine shown in Figure 4.28.
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Figure 4.28: Generic turbojet engine.

The engine has a converging-diverging nozzle and operates at a free stream Mach number $M_0 = 0.8$. The turbine inlet temperature is $T_{t4} = 1800 K$. Instead of me giving you a lot of information from which you can determine engine thrust, I would like to turn the question around and have you supply me with the information necessary to design the engine. Since this is a very preliminary design you may assume ideal behavior where appropriate. Note however that the polytropic efficiency of the compressor is $\eta_{pc} = 0.85$ and that of the turbine is $\eta_{pt} = 0.90$. Note also that my crude engine drawing is not to scale! After you finish the design, make a sketch for yourself that is more to scale.

The goal of the design is to produce as much thrust per unit area as possible for the given operating conditions. You are asked to supply the following.

1) The compressor pressure ratio, $\pi_c$.

2) The fuel/air ratio.

3) The compressor face mass flow parameter, $f(M_2)$.

4) All relevant area ratios, $A_{4throat}/A_{5throat}, A_{5throat}/A_{e}, A_{2}/A_{4throat}, A_{0}/A_{4throat}, A_{1throat}/A_{2}, A_{1throat}/A_{1}$.

5) The engine thrust, $T/P_0A_0$.

You may find that not every quantity that you are asked to supply is fixed by specifying the engine operating point. Where this is the case, you will need to use your experience to choose reasonable values. Be sure to explain your choices.

Assume $\gamma = 1.4$, $R = 287 \text{ m}^2/(\text{sec}^2 - \text{K})$, $C_p = 1005 \text{ m}^2/(\text{sec}^2 - \text{K})$. The fuel heating value is $h_f = 4.28 \times 10^7 \text{ J/kg}$. The ambient temperature and pressure are $T_0 = 216 \text{ K}$ and $P_0 = 2 \times 10^4 \text{ N/m}^2$. These are typical values in the atmosphere at an altitude of about 12,000 meters.

Problem 7 - A test facility designed to measure the mass flow and pressure characteristics of a jet engine compressor is shown in Figure 4.29. An electric motor is used to power the compressor. The facility draws air in from the surroundings which is at a pressure of one atmosphere and a temperature of 300 $K$. The air passes through the inlet throat at station
1, is compressed from 2 to 3 and then exhausted through a simple convergent nozzle at station e. Assume the compressor (2-3) has a polytropic efficiency of $\eta_{pc} = 0.95$.

Figure 4.29: A compressor test facility.

Relevant area ratios of the rig are $A_1/A_e = 8$ and $A_1/A_2 = 0.5$. Suppose the power to the compressor is slowly increased from zero.

1) Determine the compressor pressure ratio $P_{t3}/P_{t2}$ at which the nozzle chokes.

2) Determine the compressor pressure ratio $P_{t3}/P_{t2}$ at which the inlet throat chokes.

3) Plot the overall pressure ratio $P_{te}/P_0$ versus the temperature ratio $T_{te}/T_0$ over the full range from less than sonic flow at e to beyond the point where a normal shock forms in the inlet.

Problem 8 - Because of their incredible reliability, surplus jet engines are sometimes used for power generation in remote locations. By de-rating the engine a bit and operating at lower than normal temperatures, the system can run twenty four hours a day for many years with little or no servicing. Figure 4.30 shows such an engine supplying shaft power $P$ to an electric generator. Assume that there are no mechanical losses in the shaft.

Figure 4.30: A gas-turbine based power plant.

The ambient temperature and pressure are $T_0 = 273 \, K$ and $P_0 = 1.01 \times 10^5 \, N/m^2$. The turbine inlet temperature is $T_{t4} = 1638 \, K$ and $\pi_e = 20$. Relevant area ratios are $A_2/A_e = 15$ and $A_2/A_{1\text{throttle}} = 1.5$. Assume the compressor, burner and turbine all operate ideally. The nozzle is a simple convergent design and stagnation pressure losses due to wall friction in the inlet and nozzle are negligible. Assume $f << 1$. Let the nozzle area be set so that $P_{t5}/P_0 = 2$.

1) Is there a shock in the inlet?
2) How much dimensionless shaft power $P/\left(\dot{m}_a C_p T_0\right)$ is generated at this operating condition?

**Problem 9** - Consider the afterburning turbojet shown in Figure 4.31. The inlet operates with a normal shock in the diverging section. The nozzle is of simple convergent type.

![Figure 4.31: Turbojet with afterburner.](image)

Initially the afterburner is off so that $P_{te} = P_{t5}$ and $T_{te} = T_{t5}$. At the condition shown the overall engine pressure ratio is $P_{te}/P_{t1} = 5.6$ and the temperature ratio is $T_{te}/T_{t1} = 3.1$.

1) Determine $A_e/A_1$.
2) Determine the thrust $T/P_0 A_0$.
3) Suppose the afterburner is turned on increasing the exit temperature to $T_{te}/T_{t5} = 1.5$. Assume that, as the afterburner is turned on, the nozzle area is increased so that $P_{t5}$ remains constant thus avoiding any disturbance to the rest of the engine. Determine the new value of $T/P_0 A_0$. State any assumptions used to solve the problem.

**Problem 10** - For this problem assume the properties of air are $\gamma = 1.4$, $R = 287 \text{ m}^2/\left(\text{sec}^2 - K\right)$, $C_p = 1005 \text{ m}^2/\left(\text{sec}^2 - K\right)$. Where appropriate assume $f << 1$. Figure 4.32 shows a flow facility used to test a small turbojet engine. The facility is designed to simulate various flight Mach numbers by setting the value of $P_0/P_0 > 1$.

![Figure 4.32: A turbojet test facility.](image)

The relevant areas are $A_{1.5}/A_e = 1/2$, $A_{1.5}/A_{4t} = 5$, $A_2/A_{1.5} = 2$. Assume that the compressor, burner and turbine operate ideally and that there is no stagnation pressure or
stagnation temperature loss in the nozzle.

1) Let $T_{t4}/T_{t0} = 6$. Determine, $\pi_c$, $\pi_d$, $f(M_2)$ and the engine stagnation pressure ratio, $\pi_d \pi_c \pi_t$. Assuming $P_{t0}/P_0 > 1$ can you be certain that $A_e$ is choked?

2) Let $P_{t0}/P_0 = 7.82$ and $T_{t4}/T_{t0} = 6$. What flight Mach number is being simulated at this facility pressure ratio? Determine $P_e/P_0$.

3) On the compressor map, $(\pi_c$ versus $f(M_2)$ indicate the operating point for part 1. Sketch the change in engine operating point when $A_e$ is increased with $T_{t4}/T_{t0}$ fixed.

**Problem 11** - Consider an ideal turbojet with after-burning. Show that for a given total fuel flow, part to the main burner and part to the afterburner, the compressor temperature ratio for maximum thrust is

$$\pi_c|_{\text{max thrust turbojet with afterburning}} = \frac{1}{2} \left(1 + \frac{T_\lambda}{T_r}\right). \tag{4.127}$$

Recall that for a non-afterburning turbojet $\pi_c|_{\text{max thrust turbojet}} = \sqrt{T_\lambda/T_r}$. For typical values of $T_\lambda$ and $T_r$ the compressor pressure ratio with after-burning will be somewhat larger than that without after-burning.

**Problem 12** - In the movie Top Gun there is depicted a fairly realistic sequence where two F-14s are engaged in a dogfight at subsonic Mach numbers with another aircraft. During a maneuver, one F-14 inadvertently flies through the hot wake of the other. This causes both engines of the trailing F-14 to experience compressor stall and subsequently flame-out leading to loss of the aircraft and crew. Can you explain what happened? Why might the sudden ingestion of hot air cause the compressor to stall?

**Problem 13** - Figure 4.33 below depicts the flow across a compressor rotor. The axial speed is $c_z = 200 \text{ m/sec}$ and the blade speed is $U_{blade} = 300 \text{ m/sec}$. Relevant angles are $\alpha_{2a} = 30^\circ$ and $\beta_{2b} = 30^\circ$. Determine $T_{t2a}/T_{t2a}$ where $T_{t2a} = 260 \text{ K}$.

**Problem 14** - Figure 4.34 depicts the flow across a compressor stage composed of two counter-rotating rotors.

The axial speed is $c_z = 150 \text{ m/sec}$ and the blade speed is $U_{blade} = 250 \text{ m/sec}$. Tangential velocities are $c_{2a} = 50 \text{ m/sec}$, $c_{2b} = -50 \text{ m/sec}$ and $c_{3b} = 50 \text{ m/sec}$.

1) Determine $T_{t3b}/T_{t2a}$ where $T_{t2a} = 300 \text{ K}$.

2) Let the polytropic efficiency of compression be $\eta_{pc} = 0.85$. Determine $P_{t3b}/P_{t2a}$.

3) What benefits can you see in this design, what disadvantages?

**Problem 15** - Figure 4.35 depicts the flow across a compressor rotor. The axial speed is $c_z = 150 \text{ m/sec}$ and the blade speed is $U_{blade} = 250 \text{ m/sec}$.
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Figure 4.33: Compressor rotor flow diagram.

Figure 4.34: Compressor stage flow diagram.

Figure 4.35: Compressor rotor.
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Relevant angles are $\alpha_2 = 30^\circ$ and $\beta_2 = 30^\circ$.

1) Determine $T_{t2a}/T_{t2b}$, where $T_{t2a} = 350 \text{ K}$.

2) Let the polytopic efficiency of compression be $\eta_{pc} = 0.9$. Determine $P_{t2a}/P_{t2b}$.

**Problem 16** - Consider the turbojet engine shown in Figure 4.36.

![Figure 4.36: Turbojet schematic.](image)

The engine operates at a free stream Mach number $M_0 = 0.8$. The turbine inlet temperature is $T_{t4} = 1296 \text{ K}$ and $\pi_c = 15$. The compressor face to turbine inlet area ratio is $A_2/A_4^* = 10$. Assume the compressor, and turbine operate ideally and there is no stagnation pressure loss across the burner. The nozzle is of a simple converging type and stagnation pressure losses due to wall friction in the inlet and nozzle are negligible. The nozzle throat area $A_e$ can be varied. The ambient temperature and pressure are $T_0 = 216 \text{ K}$ and $P_0 = 2 \times 10^4 \text{ N/m}^2$.

1) Determine $\tau_t$, $A_4^*/A_e$, and $f(M_2)$.

2) Now suppose that the compressor operates non-ideally with $\eta_{pc} = 0.8$. The turbine inlet temperature is kept at $T_{t4} = 1296 \text{ K}$. What value of $A_4^*/A_e$ is required to maintain the same value of $\pi_c = 15$?

**Problem 17** - An aircraft powered by a turbojet engine shown in Figure 4.37 is ready for take-off. The ambient temperature and pressure are $T_0 = 300 \text{ K}$ and $P_0 = 10^5 \text{ N/m}^2$. The turbine inlet temperature is $T_{t4} = 1500 \text{ K}$. The compressor pressure ratio is $\pi_c = 25$ and $A_2/A_4^* = 15$. The compressor polytropic efficiency is $\eta_{pc} = 0.85$ and the turbine polytropic efficiency is $\eta_{pe} = 0.9$. Assume that stagnation pressure losses in the inlet, burner and nozzle are negligible. Determine the pressure ratio $P_e/P_0$, temperature ratio $T_e/T_0$ and dimensionless thrust $T/P_0A_2$. The fuel heating value is $h_f = 4.28 \times 10^7 \text{ J/kg}$. The nozzle is of simple converging type as shown.

**Problem 18** - Consider the turbojet engine shown in Figure 4.38.

The engine operates at a free stream Mach number $M_0 = 0.6$. The turbine inlet temperature is $T_{t4} = 1296 \text{ K}$ and $\pi_c = 15$. The compressor face to turbine inlet area ratio is $A_2/A_4^* = 10$ and $A_{1.5}/A_2 = 0.8$. Assume the compressor, burner and turbine operate
ideally. The nozzle is of a simple converging type and stagnation pressure losses due to wall friction in the inlet and nozzle are negligible.

1) Determine $\tau_t$, $A^*_t/A_e$, and $f(M_2)$.

2) Suppose $T_{t4}$ is increased. What value of $T_{t4}$ would cause the inlet to choke?

**Problem 19** - In the 1950s engine designers sought to decrease engine weight by increasing the compression achieved per stage of a jet engine compressor. In their endeavors theytoyed with the idea of greatly increasing the relative Mach number of the flow entering the compressor to values exceeding Mach one. Thus was born the concept of a supersonically operating compressor and today the fans of most turbofan engines do in fact operate with blade tip Mach numbers that are greater than one. Axial Mach numbers still remain well below one. One of the most innovative design ideas during this period came from Arthur Kantrowitz of Cornell University. He conceived the idea of a *shock in rotor* compressor that could operate at Mach numbers considerably greater than one. The idea is illustrated in Figure 4.39.

Let $T_{2a} = 354 \, K$, $U_{blade} = 800 \, m/\sec$ and $C_{2a_z} = 800 \, m/\sec$. The velocity vector entering the compressor is exactly aligned with the leading edge of the rotor blade as seen by an observer attached to the rotor. This is shown in the figure above. The tangential (swirl) velocity entering the stage is zero. The flow through the rotor passes through a $M = 2.0$ shock wave and then exits the rotor at the same angle it entered. In other words there is no turning of the flow by the blade in the frame of reference of the blade.

a) In a frame of reference attached to the rotor determine

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**Figure 4.37:** Turbojet schematic.

**Figure 4.38:** Turbojet schematic.
1) $M_{2a}$, $P_{t2b}/P_{t2a}$ and $M_{2b}$
2) $T_{t2b}/T_{t2a}$ and $P_{t2b}/P_{t2a}$.

b) In the frame of a non-moving observer determine
1) $T_{t2b_{rest\,frame}}/T_{t2a_{rest\,frame}}$
2) $P_{t2b_{rest\,frame}}/P_{t2a_{rest\,frame}}$

c) Determine the polytropic efficiency of the compression process in the non-moving frame.
Chapter 5

The Turbofan cycle

5.1 Turbofan thrust

Figure 5.1 illustrates two generic turbofan engine designs. The upper figure shows a modern high bypass ratio engine designed for long distance cruise at subsonic Mach numbers around 0.83 typical of a commercial aircraft. The fan utilizes a single stage composed of a large diameter fan (rotor) with wide chord blades followed by a single nozzle stage (stator). The bypass ratio is 5.8 and the fan pressure ratio is 1.9. The lower figure shows a military turbofan designed for high performance at supersonic Mach numbers in the range of 1.1 to 1.5. The fan on this engine has three stages with an overall pressure ratio of about 6 and a bypass ratio of only about 0.6. One of the goals of this chapter is to understand why these engines look so different in terms the differences in flight condition for which they are designed. In this context we will begin to appreciate that the thermodynamic and gas dynamic analysis of these engines defines a continuum of cycles as a function of Mach number. We had a glimpse of this when we determined that the maximum thrust turbojet is characterized by

\[ \tau_{c_{\text{max thrust}}} = \frac{\sqrt{\tau_\Lambda}}{\tau_T}. \]  

(5.1)

For fixed turbine inlet temperature and altitude, as the Mach number increases the optimum compression decreases and at some point it becomes desirable to convert the turbojet to a ramjet. We will see a similar kind of trend emerge for the turbofan where it replaces the turbojet as the optimum cycle for lower Mach numbers. Superimposed on all this is a historical technology trend where, with better materials and cooling schemes, the allowable turbine inlet temperature has increased with time. This tends to lead to an optimum cycle with higher compression and higher bypass ratio at a given Mach number.
Figure 5.1: Turbofan engine numbering and component notation.
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The thrust equation for the turbofan is similar to the usual relation except that it includes the thrust produced by the fan.

\[ T = \dot{m}_{a_{\text{core}}} (U_e - U_0) + \dot{m}_{a_{\text{fan}}} (U_{e1} - U_0) + \dot{m}_f U_e + (P_e - P_0) A_e + (P_{e1} - P_0) A_{1e} \]  

(5.2)

The total air mass flow is

\[ \dot{m}_a = \dot{m}_{a_{\text{core}}} + \dot{m}_{a_{\text{fan}}} \]  

(5.3)

The fuel/air ratio is defined in terms of the total air mass flow.

\[ f = \frac{\dot{m}_f}{\dot{m}_a} \]  

(5.4)

The bypass fraction is defined as

\[ B = \frac{\dot{m}_{a_{\text{fan}}}}{\dot{m}_{a_{\text{fan}}} + \dot{m}_{a_{\text{core}}}} \]  

(5.5)

and the bypass ratio is

\[ \beta = \frac{\dot{m}_{a_{\text{fan}}}}{\dot{m}_{a_{\text{core}}}} \]  

(5.6)

Note that

\[ \beta = \frac{B}{1 - B} \]  

(5.7)

\[ B = \frac{\beta}{1 + \beta} \]

5.2 The ideal turbofan cycle

The ideal turbofan cycle is characterized by the following assumptions
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\[ P_e = P_0 \]  
\[ P_{e1} = P_0 \] (5.8)

and

\[ \pi_d = 1 \]  
\[ \pi_b = 1 \]  
\[ \pi_n = 1 \]  
\[ \pi_{n1} = 1 \] (5.9)

and

\[ \pi_e = \tau_c \gamma^{-1} \]  
\[ \pi_{e1} = \tau_c \gamma^{-1} \] (5.10)

\[ \pi_t = \tau_c \gamma^{-1}. \]

For a fully expanded exhaust the normalized thrust is

\[ \frac{T}{\dot{m}_a a_0} = M_0 \left( (1 - B + f) \left( \frac{U_e}{U_0} - 1 \right) + B \left( \frac{U_{e1}}{U_0} - 1 \right) + f \right) \] (5.11)

or, in terms of the bypass ratio with \( f << 1 \),

\[ \frac{T}{\dot{m}_a a_0} = M_0 \left( \left( \frac{1}{1 + \beta} \right) \left( \frac{U_e}{U_0} - 1 \right) + \left( \frac{\beta}{1 + \beta} \right) \left( \frac{U_{e1}}{U_0} - 1 \right) \right) . \] (5.12)

5.2.1 The fan bypass stream

First work out the velocity ratio for the fan stream.

\[ \frac{U_{e1}}{U_0} = \frac{M_{e1}}{M_0} \sqrt{\frac{T_{e1}}{T_0}} \] (5.13)
CHAPTER 5. THE TURBOFAN CYCLE

The exit Mach number is determined from the stagnation pressure.

\[ P_{te1} = P_0 \tau_r \tau_{c1} = P_{e1} \left( 1 + \frac{\gamma - 1}{2} M_{e1}^2 \right)^{\frac{\gamma}{\gamma-1}} \] (5.14)

Since the nozzle is fully expanded and the fan is assumed to behave isentropically, we can write

\[ \tau_r \tau_{c1} = \left( 1 + \frac{\gamma - 1}{2} M_{e1}^2 \right) \] (5.15)

therefore

\[ \frac{M_{e1}^2}{M_0^2} = \frac{\tau_r \tau_{c1} - 1}{\tau_r - 1}. \] (5.16)

The exit temperature is determined from the stagnation temperature.

\[ T_{te1} = T_0 \tau_r \tau_{c1} = T_{e1} \left( 1 + \frac{\gamma - 1}{2} M_{e1}^2 \right) \] (5.17)

Noting (5.15) we can conclude that for the ideal fan

\[ T_{e1} = T_0. \] (5.18)

The exit static temperature is equal to the ambient static temperature. The velocity ratio of the fan stream is

\[ \left( \frac{U_{e1}}{U_0} \right)^2 = \frac{\tau_r \tau_{c1} - 1}{\tau_r - 1}. \] (5.19)

5.2.2 The core stream

The velocity ratio across the core is

\[ \frac{U_e}{U_0} = \frac{M_e}{M_0} \sqrt{\frac{T_e}{T_0}}. \] (5.20)
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The analysis of the stagnation pressure and temperature is exactly the same as for the ideal turbojet.

\[ P_{te} = P_0 \pi_r \pi_c \pi_t = P_c \left( 1 + \frac{\gamma - 1}{2} M_e^2 \right)^{\frac{\gamma}{\gamma - 1}} \quad (5.21) \]

Since the nozzle is fully expanded and the compressor and turbine operate ideally the Mach number ratio is

\[ \frac{M_e^2}{M_0^2} = \frac{\tau_r \tau_c \tau_t - 1}{\tau_r - 1}. \quad (5.22) \]

The temperature ratio is also determined in the same way in terms of component temperature parameters.

\[ T_{te} = T_0 \tau_r \tau_c \tau_t \tau_b \tau_n \quad (5.23) \]

In the ideal turbofan we assume that the diffuser and nozzle flows are adiabatic and so

\[ T_{te} = T_0 \tau_r \tau_c \tau_t \tau_b \tau_t = T_c \left( 1 + \frac{\gamma - 1}{2} M_e^2 \right) = T_c \tau_r \tau_c \tau_t \quad (5.24) \]

from which is determined

\[ T_e \frac{T_e}{T_0} = \tau_b = \frac{\tau_c}{\tau_r \tau_c}. \quad (5.25) \]

The velocity ratio across the core is

\[ \left( \frac{U_e}{U_0} \right)^2 = \left( \frac{\tau_r \tau_c \tau_t - 1}{\tau_r - 1} \right) \frac{\tau_c}{\tau_r \tau_c}. \quad (5.26) \]

5.2.3 Turbine-compressor-fan matching

The work taken out of the flow by the high and low pressure turbine is used to drive both the compressor and the fan.

\[ (\dot{m}_{acore} + \dot{m}_f) (h_{t4} - h_{t5}) = \dot{m}_{acore} (h_{t3} - h_{t2}) + \dot{m}_{afan} (h_{t31} - h_{t2}) \quad (5.27) \]
Divide \((5.27)\) by \(\dot{m}_a C_p T_0\) and rearrange. The work matching condition for a turbofan is

\[
\tau_t = 1 - \frac{\tau_r}{\tau_\lambda} \left( \frac{1 - B}{1 - B + f} (\tau_c - 1) + \frac{B}{1 - B + f} (\tau_{c1} - 1) \right). \tag{5.28}
\]

The approximation \(f \ll 1\) is generally pretty good for a turbofan. Using this approximation the work matching condition becomes

\[
\tau_t = 1 - \frac{\tau_r}{\tau_\lambda} (\tau_c - 1 + \beta (\tau_{c1} - 1)) \tag{5.29}
\]

where the bypass ratio \(\beta\) appears for the first time. If the bypass ratio goes to zero the matching condition reduces to the usual turbojet formula.

### 5.2.4 The fuel/air ratio

The fuel/air ratio is determined from the energy balance across the burner.

\[
\dot{m}_f (h_f - h_{t4}) = \dot{m}_{a,\text{core}} (h_{t4} - h_{t3}) \tag{5.30}
\]

Divide \((5.30)\) by \(\dot{m}_a C_p T_0\) and rearrange. The result is

\[
f = \left( \frac{1}{1 + \beta} \right) \frac{\tau_\lambda - \tau_r \tau_c}{\tau_f - \tau_\lambda}. \tag{5.31}
\]

### 5.3 Maximum specific impulse ideal turbofan

The non-dimensionalized specific impulse can be expressed in terms of thrust and fuel/air ratio as

\[
\frac{I_{sp} g}{a_0} = \left( \frac{T}{\dot{m}_f g} \right) \frac{g}{a_0} = \left( \frac{T}{\dot{m}_a a_0} \right) \left( \frac{1}{f} \right). \tag{5.32}
\]

Substitute \((5.12)\) and \((5.31)\) into \((5.32)\). The result is

\[
\frac{I_{sp} g}{a_0} = M_0 \left( \frac{\tau_f - \tau_\lambda}{\tau_\lambda - \tau_r \tau_c} \right) \left( \frac{U_c}{U_0} - 1 \right) + \beta \left( \frac{U_{c1}}{U_0} - 1 \right). \tag{5.33}
\]
The question is: what value of $\beta$ maximizes the specific impulse? Differentiate (5.33) with respect to $\beta$ and note that $\beta$ appears in (5.29).

$$
\frac{\partial}{\partial \beta} \left( \frac{I_{spg}}{a_0} \right) = M_0 \left( \frac{\tau_f - \tau_\lambda}{\tau_\lambda - \tau_r \tau_c} \right) \left( \frac{\partial}{\partial \beta} \left( \frac{U_e}{U_0} \right) + \left( \frac{U_{e1}}{U_0} - 1 \right) \right) = 0 \quad (5.34)
$$

We can write (5.34) as

$$
\frac{1}{2 \left( \frac{U_e}{U_0} \right)} \frac{\partial}{\partial \beta} \left( \frac{U_e}{U_0} \right)^2 + \left( \frac{U_{e1}}{U_0} - 1 \right) = 0 \quad (5.35)
$$

or

$$
\frac{1}{2 \left( \frac{U_e}{U_0} \right)} \left( \frac{\tau_\lambda}{\tau_r - 1} \right) \frac{\partial \tau_t}{\partial \beta} = - \left( \frac{U_{e1}}{U_0} - 1 \right). \quad (5.36)
$$

Equation (5.36) becomes

$$
\frac{1}{2 \left( \frac{U_e}{U_0} \right)} \left( \frac{\tau_r (U_{e1} - 1)}{\tau_r - 1} \right) = \left( \frac{U_{e1}}{U_0} - 1 \right). \quad (5.37)
$$

From (5.19), the expression in parentheses on the left side of (5.37) can be written

$$
\frac{1}{2 \left( \frac{U_e}{U_0} \right)} \left( \left( \frac{U_{e1}}{U_0} \right)^2 - 1 \right) = \left( \frac{U_{e1}}{U_0} - 1 \right). \quad (5.38)
$$

Factor the left side of (5.38) and cancel common factors on both sides. The velocity condition for a maximum impulse ideal turbofan is

$$
\left( \frac{U_{e1}}{U_0} - 1 \right) = 2 \left( \frac{U_e}{U_0} - 1 \right). \quad (5.39)
$$

According to this result, for an ideal turbofan one would want to design the turbine such that the velocity increment across the fan was twice that across the core in order to achieve maximum specific impulse. Recall that $U_e/U_0$ depends on $\beta$ through (5.29) (and weakly through (5.31) which we neglect). The value of $\beta$ that produces the condition (5.39) corresponding to the maximum impulse ideal turbofan is
\[ \beta_{\text{max impulse ideal turbofan}} = \frac{1}{\tau_{c1} - 1} \left( \left( \frac{\tau_{\lambda}}{\tau_{r} \tau_{c}} - 1 \right) \left( \tau_{c} - 1 \right) + \frac{\tau_{\lambda} \left( \tau_{r} - 1 \right)}{\tau_{r}^{2} \tau_{c}} - \frac{1}{4} \left( \frac{\tau_{r} - 1}{\tau_{r}} \right) \left( \frac{\tau_{r} \tau_{c1} - 1}{\tau_{r} - 1} \right)^{1/2} + 1 \right) \right). \] (5.40)

Figure 5.2 shows how the optimum bypass ratio (5.40) varies with flight Mach number for a given set of engine parameters.

Figure 5.2: Ideal turbofan bypass ratio for maximum specific impulse as a function of Mach number.

It is clear from this figure that, as the Mach number increases, the optimum bypass ratio decreases until a point is reached where one would like to get rid of the fan altogether and convert the engine to a turbojet. For the ideal cycle the turbojet limit occurs at an unrealistically high Mach number of approximately 3.9. Non-ideal component behavior greatly reduces this optimum Mach number. Figure 5.3 provides another cut on this issue. Here the optimum bypass ratio is plotted versus the fan temperature (or pressure) ratio. Several curves are shown for increasing Mach number.

It is clear that increasing the fan pressure ratio leads to an optimum at a lower bypass ratio. The curves all seem to allow for optimum systems at very low fan pressure ratios and high bypass ratios. This is an artifact of the assumptions underlying the ideal turbofan. As soon as non-ideal effects are included the low fan pressure ratio solutions reduce to much lower bypass ratios. To see this, we will shortly study the non-ideal case.

### 5.4 Turbofan thermal efficiency

Recall the definition of thermal efficiency from Chapter 2.
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5-10

Figure 5.3: Ideal turbofan bypass ratio for maximum specific impulse as a function of fan temperature ratio for several Mach numbers.

\[ \eta_{th} = \frac{\text{Power to the vehicle} + \frac{\Delta \text{kinetic energy of air}}{\text{second}} + \frac{\Delta \text{kinetic energy of fuel}}{\text{second}}}{\dot{m}_f h_f} \] (5.41)

For a turbofan with a core and bypass stream the thermal efficiency is

\[ \eta_{th} = \frac{TU_0 + \left( \frac{\dot{m}_{acore}(U_e - U_0)^2}{2} + \frac{\dot{m}_{afan}(U_{e1} - U_0)^2}{2} \right) + \left( \frac{\dot{m}_f(U_e - U_0)^2}{2} - \frac{\dot{m}_f(U_0)^2}{2} \right)}{\dot{m}_f h_f}. \] (5.42)

Remember, the frame of reference for Equation (5.42) is one where the air ahead of the engine is at rest. If both exhausts are fully expanded, so that \( P_e = P_0; \) \( P_{e1} = P_0 \) the thermal efficiency becomes

\[ \eta_{th} = \frac{\left( \dot{m}_{acore}(U_e - U_0) + \dot{m}_{afan}(U_{e1} - U_0) + \dot{m}_f U_e \right) U_0}{\dot{m}_f h_f} + \frac{\left( \frac{\dot{m}_{acore}(U_e - U_0)^2}{2} + \frac{\dot{m}_{afan}(U_{e1} - U_0)^2}{2} \right) + \left( \frac{\dot{m}_f(U_e - U_0)^2}{2} - \frac{\dot{m}_f(U_0)^2}{2} \right)}{\dot{m}_f h_f} \] (5.43)

which reduces to

\[ \eta_{th} = \frac{\left( \dot{m}_{acore} \left( \frac{U_e^2}{2} - \frac{U_0^2}{2} \right) + \dot{m}_{afan} \left( \frac{U_{e1}^2}{2} - \frac{U_0^2}{2} \right) + \dot{m}_f \frac{U_e^2}{2} \right) U_0}{\dot{m}_f h_f}. \] (5.44)
We can recast (5.44) in terms of enthalpies using the following relations

\[ \dot{m}_f (h_f - h_t4) = \dot{m}_{a_{\text{core}}} (h_t4 - h_t3) \]

\[ h_{t5} = h_e + \frac{U_e^2}{2} \] \hspace{1cm} (5.45)

\[ h_{t31} = h_{e1} + \frac{U_{e1}^2}{2} \]

where the fan and core nozzle streams are assumed to be adiabatic. Now

\[ \eta_{th} = \frac{\dot{m}_{a_{\text{core}}} ((h_{t5} - h_e) - (h_{t0} - h_0)) + \dot{m}_{a_{fan}} ((h_{t31} - h_{e1}) - (h_{t0} - h_0)) + \dot{m}_f (h_{t5} - h_e)}{(\dot{m}_f + \dot{m}_{a_{core}}) h_{t4} - \dot{m}_{a_{core}} h_{t3}}. \] \hspace{1cm} (5.46)

Rearrange (5.46) to read

\[ \eta_{th} = \frac{\dot{m}_{a_{core}} (h_{e} - h_0) + \dot{m}_{a_{fan}} (h_{e1} - h_0) + \dot{m}_f h_e}{(\dot{m}_f + \dot{m}_{a_{core}}) h_{t4} - \dot{m}_{a_{core}} h_{t3}}. \] \hspace{1cm} (5.47)

Recall the turbofan work balance (5.27). This relation can be rearranged to read

\[ (\dot{m}_f + \dot{m}_{a_{core}}) h_{t4} - \dot{m}_{a_{core}} h_{t3} = (\dot{m}_{a_{core}} + \dot{m}_f) h_{t5} + \dot{m}_{a_{fan}} h_{t31} - (\dot{m}_{a_{core}} + \dot{m}_{a_{fan}}) h_{t0} \] \hspace{1cm} (5.48)

where it has been assumed that the inlet is adiabatic \( h_{t2} = h_{t0} \). Now use (5.48) to replace the numerator or denominator in the first term of (5.47). The thermal efficiency finally reads

\[ \eta_{th} = 1 - \frac{Q_{\text{rejected during the cycle}}}{Q_{\text{input during the cycle}}} = 1 - \frac{(\dot{m}_{a_{core}} + \dot{m}_f) (h_e - h_0) + \dot{m}_{a_{fan}} (h_{e1} - h_0) + \dot{m}_f h_0}{(\dot{m}_f + \dot{m}_{a_{core}}) h_{t4} - \dot{m}_{a_{core}} h_{t3}}. \] \hspace{1cm} (5.49)

The expression in (5.49) for the heat rejected during the cycle
\[ Q_{\text{rejected during the cycle}} = (\dot{m}_{a,\text{core}} + \dot{m}_f)(h_e - h_0) + \dot{m}_{a,\text{fan}}(h_{e1} - h_0) + \dot{m}_fh_0 \quad (5.50) \]

brings to mind the discussion of thermal efficiency in Chapter 2. The heat rejected comprises heat conduction to the surrounding atmosphere from the fan and core mass flows plus physical removal from the thermally equilibrated nozzle flow of a portion equal to the added fuel mass flow. From this perspective the added fuel mass carries its fuel enthalpy into the system and the exhausted fuel mass carries its ambient enthalpy out of the system and there is no net mass increase or decrease to the system.

The main assumptions underlying (5.49) are that the engine operates adiabatically, the shaft mechanical efficiency is one, and the burner combustion efficiency is one. Engine components are not assumed to operate ideally; They are not assumed to be isentropic.

### 5.4.1 Thermal efficiency of the ideal turbofan

For the ideal cycle, assuming constant \( C_p \), equation (5.49) in terms of temperatures becomes

\[
\eta_{\text{thermal, turbofan}} = 1 - \left( \frac{1 + (1 + \beta)f}{1 + (1 + \beta)f} \right) \frac{T_e - T_0}{T_{t4} - T_{t3}} = 1 - \left( \frac{1}{\tau_r \tau_c} \right) \left( \frac{(1 + (1 + \beta)f)}{(1 + (1 + \beta)f) \frac{T_e}{T_0} - 1} \right). 
\quad (5.51)
\]

Using (5.25) Equation (5.51) becomes

\[
\eta_{\text{thermal, turbofan}} = 1 - \left( \frac{1}{\tau_r \tau_c} \right) 
\quad (5.52)
\]

which is identical to the thermal efficiency of the ideal turbojet. Notice that for the ideal turbofan with

\[
h_{e1} = h_0
\]

the heat rejected by the fan stream is zero. Therefore the thermal efficiency of the ideal turbofan is independent of the parameters of the fan stream.

### 5.5 The non-ideal turbofan

The fan, compressor and turbine polytropic relations are
\[
\pi_{c1} = \tau_{c1}^{\gamma \eta_{pc1}} \gamma - 1 \\
\pi_c = \tau_c^{\gamma \eta_{pc}} \\
\pi_t = \tau_t^{(\gamma - 1) \eta_{pe}} 
\] (5.53)

where \( \eta_{pc1} \) is the polytropic efficiency of the fan. The polytropic efficiencies \( \eta_{pc}, \eta_{pc1} \) and \( \eta_{pe} \) are all less than one. The inlet, burner and nozzles all operate with some stagnation pressure loss.

\[
\pi_d < 1 \\
\pi_{n1} < 1 \\
\pi_n < 1 \\
\pi_b < 1 
\] (5.54)

### 5.5.1 Non-ideal fan stream

The stagnation pressure ratio across the fan is

\[
P_{te1} = P_0 \tau_r \pi_d \pi_{c1} \pi_{n1} = P_{e1} \left( 1 + \frac{\gamma - 1}{2} M_{e1}^2 \right)^{\frac{\gamma}{\gamma - 1}}. 
\] (5.55)

The fan nozzle is still assumed to be fully expanded and so the Mach number ratio for the non-ideal turbofan is

\[
\left( \frac{M_{e1}}{M_0} \right)^2 = \frac{\tau_r \tau_{c1} \eta_{pc1} (\pi_d \pi_{n1})^{\gamma - 1}}{\tau_r - 1}. 
\] (5.56)

The stagnation temperature is (assuming the inlet and fan nozzle are adiabatic)

\[
T_{te1} = T_0 \tau_r \tau_{c1} = T_{e1} \left( 1 + \frac{\gamma - 1}{2} M_{e1}^2 \right) = T_{e1} \tau_r \tau_{c1} \eta_{pc1} (\pi_d \pi_{n1})^{\gamma - 1} 
\] (5.57)

and
\[
\frac{T_{e1}}{T_0} = \frac{\tau_c^{1-\eta pc}}{\left(\frac{\pi_d\pi_n}{\lambda}\right)^{\gamma-1}}.
\]  
(5.58)

Now the velocity ratio across the non-ideal fan is

\[
\left(\frac{U_{e1}}{U_0}\right)^2 = \frac{1}{\tau_r - 1} \left(\tau_r \tau_c^{1-\eta pc} - \frac{\tau_c^{1-\eta pc}}{\left(\frac{\pi_d\pi_n}{\lambda}\right)^{\gamma-1}}\right).
\]  
(5.59)

### 5.5.2 Non-ideal core stream

The stagnation pressure across the core is

\[
P_{te1} = P_0\pi_r\pi_d\pi_c\pi_b\pi_t\pi_n = P_e\left(1 + \frac{\gamma - 1}{2} M_e^2\right)^{\frac{\gamma}{\gamma-1}}.
\]  
(5.60)

The core nozzle is fully expanded and so the Mach number ratio across the non-ideal core is

\[
\left(\frac{M_e}{M_0}\right)^2 = \frac{\tau_r \tau_c^{\eta pc} \tau_l^{\frac{1}{\eta pc}} \left(\frac{\pi_d\pi_b\pi_n}{\lambda}\right)^{\frac{\gamma-1}{\gamma}} - 1}{\tau_r - 1}.
\]  
(5.61)

In the non-ideal turbofan we continue to assume that the diffuser and nozzle flows are adiabatic and so

\[
T_{te} = T_e \tau_r \tau_c^{\eta pc} \tau_l^{\frac{1}{\eta pc}} \left(\frac{\pi_d\pi_b\pi_n}{\lambda}\right)^{\frac{\gamma-1}{\gamma}}
\]  
(5.62)

from which is determined

\[
\frac{T_e}{T_0} = \frac{\tau_c^{1-\eta pc} \tau_l \left(\frac{1}{\eta pc}\right)}{\tau_r \tau_c \left(\frac{\pi_d\pi_b\pi_n}{\lambda}\right)^{\frac{\gamma-1}{\gamma}}}.
\]  
(5.63)

The velocity ratio across the non-ideal core is

\[
\left(\frac{U_e}{U_0}\right)^2 = \frac{1}{\tau_r - 1} \left(\tau_l \tau_t - \frac{\tau_c^{1-\eta pc} \tau_l \left(\frac{1}{\eta pc}\right)}{\tau_r \tau_c \left(\frac{\pi_d\pi_b\pi_n}{\lambda}\right)^{\frac{\gamma-1}{\gamma}}}\right).
\]  
(5.64)
The work balance across the engine remains essentially the same as in the ideal cycle

\[ \tau_l = 1 - \frac{\tau_r}{\eta_m \tau_c} \left( (\tau_c - 1) + \beta (\tau c_1 - 1) \right) \]  

(5.65)

where the shaft mechanical efficiency is defined as

\[ \eta_m = \frac{\dot{m}_{a_{core}} (h_{t3} - h_{t2}) + \dot{m}_{a_{fan}} (h_{t31} - h_{t2})}{\dot{m}_f + \dot{m}_{a_{core}} (h_{t4} - h_{t5})}. \]  

(5.66)

### 5.5.3 Maximum specific impulse non-ideal cycle

Equation (5.35) remains the same as for the ideal cycle.

\[ \frac{1}{2 \left( U_e / U_0 \right)} \frac{\partial}{\partial \beta} \left( \frac{U_e}{U_0} \right)^2 + \left( \frac{U_e}{U_0} - 1 \right) = 0 \]  

(5.67)

The derivative is

\[ \frac{\partial}{\partial \beta} \left( \frac{U_e}{U_0} \right)^2 = -\frac{\tau_r}{\eta_m} \left( \tau c_1 - 1 \right) \left( 1 - \frac{1}{\eta_{pe}} \right) \frac{\tau c^{1-\eta_{pe} \gamma}}{\tau_r \tau_c (\pi_d \pi_b \pi_n)^{\frac{c-1}{\gamma}}} \]  

(5.68)

Equations (5.59), (5.64), (5.65) and (5.68) are inserted into (5.67) and the optimal bypass ratio for a set of selected engine parameters is determined implicitly. A typical numerically determined result is shown in Figure 5.4 and Figure 5.5.

These figures illustrate the strong dependence of the optimum bypass ratio on the non-ideal behavior of the engine. As the losses increase, the bypass ratio optimizes at a lower value. But note that the optimum bypass ratio of the non-ideal engine is still somewhat higher than the values generally used in real engines. The reason for this is that our analysis does not include the optimization issues connected to integrating the engine onto an aircraft where there is a premium on designing to a low frontal area so as to reduce drag while maintaining a certain clearance between the engine and the runway. Nevertheless, our analysis helps us to understand the historical trend toward higher bypass engines as turbine and fan efficiencies have improved along with increases in the turbine inlet temperature.
CHAPTER 5. THE TURBOFAN CYCLE

Figure 5.4: Turbofan bypass ratio for maximum specific impulse as a function of fan temperature ratio comparing the ideal with a non-ideal cycle. Parameters of the non-ideal cycle are $\pi_d = 0.95$, $\eta_{pc1} = 0.86$, $\pi_{n1} = 0.96$, $\eta_{pc} = 0.86$, $\pi_b = 0.95$, $\eta_m = 0.98$, $\eta_{pc} = 0.86$, $\pi_n = 0.96$.

Figure 5.5: Turbofan bypass ratio for maximum specific impulse as a function of Mach numbers comparing the ideal with a non-ideal cycle. Parameters of the non-ideal cycle are $\pi_d = 0.95$, $\eta_{pc1} = 0.86$, $\pi_{n1} = 0.96$, $\eta_{pc} = 0.86$, $\pi_b = 0.95$, $\eta_m = 0.98$, $\eta_{pc} = 0.86$, $\pi_n = 0.96$. 
5.6 Problems

Problem 1 - Assume $\gamma = 1.4$, $R = 287 \text{ m}^2/(\text{sec}^2 - K)$, $C_p = 1005 \text{ m}^2/(\text{sec}^2 - K)$. The fuel heating value is $4.28 \times 10^7 \text{ J/kg}$. Where appropriate assume $f \ll 1$. The ambient temperature and pressure are $T_0 = 216 \text{ K}$ and $P_0 = 2 \times 10^4 \text{ N/m}^2$. Consider a turbofan with the following characteristics.

\[
\begin{align*}
M_0 &= 0.85 \\
\tau_\lambda &= 8.0 \\
\pi_c &= 30 \\
\pi_{c1} &= 1.6 \\
\beta &= 5
\end{align*}
\]  

The compressor, fan and turbine polytropic efficiencies are

\[
\begin{align*}
\eta_{pc} &= 0.9 \\
\eta_{pc1} &= 0.9 \\
\eta_{pt} &= 0.95
\end{align*}
\]  

Let the burner efficiency and pressure ratio be $\eta_b = 0.99$ and $\pi_b = 0.97$. Assume the shaft efficiency is one. Both the fan and core streams use ideal simple convergent nozzles. Determine the dimensionless thrust $T/P_0 A_0$, specific fuel consumption, and overall efficiency of the engine. Suppose the engine is expected to deliver 8,000 pounds of thrust at cruise conditions. What must be the area of the fan face $A_2$?

Problem 2 - Use Matlab or Mathematica to develop a program that reproduces Figure 5.4 and Figure 5.5.

Problem 3 - Figure 5.6 shows an ideal turbofan operating with a heat exchanger at its aft end.

The heat exchanger causes a certain amount of thermal energy $Q$ (Joules/sec) to be transferred from the hot core stream to the cooler fan stream. Let the subscript $x$ refer to the heat exchanger. Assume that the heat exchanger operates without any loss of stagnation pressure $\pi_x = \pi_{x1} = 1$ and that both nozzles are fully expanded. Let $\tau_x = T_{te}/T_{t5}$ and $\tau_x 1 = T_{te1}/T_{t51}$. The thrust is given by
Figure 5.6: Turbofan with an aft heat exchanger.

\[
\frac{T}{m_{a_{\text{core}}} a_0} = M_0 \left( \left( \frac{U_e}{U_0} - 1 \right) + \beta \left( \frac{U_{c1}}{U_0} - 1 \right) \right) \tag{5.71}
\]

where we have assumed \( f \ll 1 \).

1) Derive an expression for \( T / (m_{a_{\text{core}}} a_0) \) in terms of \( \tau_\lambda, \tau_r, \tau_c, \tau_{c1}, \beta \) and \( \tau_x, \tau_{x1} \).

2) Write down an energy balance between the core and fan streams. Suppose an amount of heat \( Q \) is exchanged. Let \( \tau_x = 1 - \alpha \) where \( \alpha = Q / m_{a_{\text{core}}} C_p T_{t5}, Q > 0 \). Show that

\[
\tau_{x1} = 1 + \left( \frac{\tau_\lambda \tau_{t1}}{\beta \tau_r \tau_{c1}} \right) \alpha. \tag{5.72}
\]

3) Consider an ideal turbofan with the following characteristics.

\[
T_0 = 216K
\]
\[
M_0 = 0.85
\]
\[
\tau_\lambda = 7.5
\]
\[
\pi_c = 30
\]
\[
\pi_{c1} = 1.6
\]
\[
\beta = 5 \tag{5.73}
\]
Plot $T/\dot{m}_{a,core}a_0$ versus $\alpha$ for $0 < \alpha < \alpha_{\text{max}}$ where $\alpha_{\text{max}}$ corresponds to the value of $\alpha$ such that the two streams are brought to the same stagnation temperature coming out of the heat exchanger.

**Problem 4** - Figure 5.7 shows a turbojet engine supplying shaft power to a lift fan. Assume that there are no mechanical losses in the shaft but the clutch and gear box that transfers power to the fan has an efficiency of 80%. That is, only 80% of the shaft power is used to increase the enthalpy of the air flow through the lift fan. The air mass flow rate through the lift fan is equal to twice the air mass flow rate through the engine $\dot{m}_{\text{Lift Fan}} = 2\dot{m}_a$. The polytropic efficiency of the lift fan is $\eta_{p,\text{Lift Fan}} = 0.9$ and the air flow through the lift fan is all subsonic. The flight speed is zero.

Figure 5.7: *Turbojet engine driving a lift fan.*

The ambient temperature and pressure are $T_0 = 300 K$ and $P_0 = 1.01 \times 10^5 N/m^2$. The turbine inlet temperature is $T_{t4} = 1800 K$ and $\pi_c = 25$. Relevant area ratios are $A_2/A_4^* = 15$ and $A_{\text{throat}}/A_2 = 0.5$. Assume the compressor, burner and turbine all operate ideally. The nozzle is a simple convergent design and stagnation pressure losses due to wall friction in the inlet and nozzle are negligible. Assume $f \ll 1$. Let the nozzle area be set so that $P_{t5}/P_0 = 3$.

1) Is there a shock in the inlet of the turbojet?

2) Determine the stagnation temperature and pressure ratio across the lift fan

\[
\tau_{\text{Lift Fan}} = \frac{T_{t3,\text{Lift Fan}}}{T_{t2,\text{Lift Fan}}}
\]

\[
\pi_{\text{Lift Fan}} = \frac{P_{t3,\text{Lift Fan}}}{P_{t2,\text{Lift Fan}}}.
\]
Chapter 6

The Turboprop cycle

6.1 Propellor efficiency

The turboprop cycle can be regarded as a very high bypass limit of a turbofan. Recall that the propulsive efficiency of a thruster with $P_e = P_0$ and $f \ll 1$ is

$$\eta_{pr} = \frac{2}{1 + U_e/U_0}. \quad (6.1)$$

This expression is relevant to a propeller also where $U_e$ is replaced by $U_\infty$ the velocity, shown schematically in Figure 6.1, that would occur far downstream of the propeller if there were no mixing of the propeller wake.

The achievement of high propulsive efficiency at a given thrust requires a large mass flow with a small velocity increment. The turboprop accomplishes this by using a low pressure turbine to produce shaft power to drive a propeller. Since the propeller disc is quite large the mass flow rate is large and a high propulsive efficiency can be achieved.

The power output of a turbine is proportional to the square of the blade speed and so turbines generally operate at high rotational speeds limited by compressibility effects at the blade tips. The propeller diameter is much larger than the turbine diameter and so to avoid compressibility losses over the outer portion of the propeller a gearbox is required to step the turbine rotational speed down to values that keep the propeller tip Mach numbers below one.

It should be pointed out that Figure 6.1 is purely a schematic and the relative size of the gearbox shown in this figure is quite unrealistic. The figure below shows a cross section of
a current model of the Allison T56 turboprop engine. This is a widely used engine that has been in operation since 1954.

As the figure shows, the gearbox is massive and contains a dizzyingly complex system of gears and bearings. In fact the main disadvantage of the turboprop is the weight and maintenance cost of the gearbox as well as the maintenance cost of the propeller. In terms of cycle performance, the power losses through the gearbox are also a significant factor.

In any case if an efficient gearbox and propeller system can be developed, a turboprop should be a more efficient cycle than a turbojet or a turbofan at low Mach number. Actual cycle analysis shows that at low to moderate subsonic flight Mach numbers fuel consumption is lower for the turboprop cycle. However in the transonic and supersonic flight regime propeller driven aircraft are prohibitively noisy and propeller efficiency falls off rapidly with
Mach number due to stagnation pressure losses at the blade tips.

Part of the thrust of a turboprop comes from the flow through the core engine. We can analyze the core flow using the same approach used in the turbojet. But a major portion of the thrust comes from the propeller and because the flow through the propeller is unducted there is no simple way to relate the thrust produced by the propeller to the usual flow variables that we can analyze using basic gas-dynamic tools. Such an analysis would require a means of determining the flow speed induced by the propeller infinitely far down stream of the engine. For this reason, the analysis of the turboprop begins with a definition of the propeller efficiency.

\[ \eta_{prop} = \frac{T_{prop} U_0}{W_p} \]  

(6.2)

where \( W_p \) is the power supplied to the propeller by the low pressure turbine. As long as the propeller efficiency is known then the propeller thrust is known in terms of the flow through the turbine. To understand the nature of the propeller efficiency it is useful to factor (6.2) as follows. The thrust produced by the propeller is

\[ T_{prop} = \dot{m}_{prop} (U_\infty - U_0) . \]  

(6.3)

Using (6.3) the propeller efficiency can be factored as

\[ \eta_{prop} = \left( \frac{\dot{m}_{prop} (U_\infty - U_0) U_0}{\frac{1}{2} \dot{m}_{prop} (U_\infty^2 - U_0^2)} \right) \left( \frac{\frac{1}{2} \dot{m}_{prop} (U_\infty^2 - U_0^2)}{W_p} \right) . \]  

(6.4)

The propeller efficiency factors into a product of a propulsive efficiency multiplying a term that compares the change in kinetic energy across the propeller to the shaft work.

\[ \eta_{prop} = \left( \frac{2 U_0}{U_\infty + U_0} \right) \left( \frac{\frac{1}{2} \dot{m}_{prop} (U_\infty^2 - U_0^2)}{W_p} \right) \]  

(6.5)

Let’s look at this from a thermodynamic point of view. The stagnation enthalpy rise across the propeller produced by the shaft work is

\[ W_p = \dot{m}_{prop} (h_{13} - h_{12}) . \]  

(6.6)

In the simplest model of propeller flow, the propeller is treated as an actuator disc, a uniform disc over which there is a pressure and temperature rise that is constant over the
disc area. The flow velocity increases up to and through the disc while the flow velocity is the same just ahead and just behind the disc as shown in Figure 6.3. According to Froude’s theorem the velocity change ahead of the propeller is the same as behind and so

\[ U_2 = U_{13} = \frac{U_0 + U_\infty}{2}. \]  

(6.7)

Figure 6.3: Effect of propeller actuator disc on flow velocity, pressure and temperature.

Since the velocity is the same before and after the propeller we can write

\[ W_p = \dot{m}_{prop}C_p(T_{13} - T_2). \]  

(6.8)

The stagnation pressure and stagnation temperature across the propeller are related by a polytropic efficiency of compression which accounts for the entropy rise across the propeller.

\[ \frac{P_{13}}{P_{12}} = \left( \frac{T_{13}}{T_{12}} \right)^{\frac{\gamma \eta_{pc}}{\gamma - 1}} \]  

(6.9)

Equation (6.9) can be written as
\[
\frac{P_{13}}{P_2} \left( 1 + \frac{\gamma - 1}{2} M_{13}^2 \right)^{\frac{\gamma}{\gamma - 1}} = \left( \frac{T_{13}}{T_2} \right)^{\frac{\gamma \eta_{pc}}{\gamma - 1}} \left( 1 + \frac{\gamma - 1}{2} M_{13}^2 \right)^{\frac{\gamma \eta_{pc}}{\gamma - 1}}.
\] (6.10)

The Mach number change across the propeller is small due to the small temperature change and to a good approximation (6.10) relates the static temperatures and pressures

\[
\frac{P_{13}}{P_2} = \left( \frac{T_{13}}{T_2} \right)^{\frac{\gamma \eta_{pc}}{\gamma - 1}}.
\] (6.11)

which we can write as

\[
1 + \left( \frac{P_{13} - P_2}{P_2} \right) = \left( 1 + \frac{T_{13} - T_2}{T_2} \right)^{\frac{\gamma \eta_{pc}}{\gamma - 1}}.
\] (6.12)

For a propeller that is lightly loaded, (6.12) can be approximated as

\[
\frac{P_{13} - P_2}{P_2} \approx \frac{\gamma \eta_{pc}}{\gamma - 1} \left( \frac{T_{13} - T_2}{T_2} \right)
\] (6.13)
or

\[
P_{13} - P_2 \approx \eta_{pc} \rho_2 C_p (T_{13} - T_2).
\] (6.14)

The propeller thrust is

\[
T = (P_{13} - P_2) A
\] (6.15)

where \(A\) is the effective area of the actuator disc. Now combine (6.8), (6.14) and (6.15) to form the propeller efficiency.

\[
\eta_{prop} = \frac{\eta_{pc} \rho_2 U_0 A C_p (T_{13} - T_2)}{\dot{m}_{prop} C_p (T_{13} - T_2)} = \frac{\eta_{pc} \rho_2 U_0 A}{\rho_2 U_2 A}
\] (6.16)

Using (6.7), the propeller efficiency becomes finally

\[
\eta_{prop} = \left( \frac{2 U_0}{U_0 + U_\infty} \right) \eta_{pc}
\] (6.17)
which should be compared with (6.5). We can now interpret the energy factor in (6.5) as

\[ \eta_{pc} \approx \frac{1}{2} \frac{\mu_{prop} (U_{\infty}^2 - U_0^2)}{W_p}. \]  

(6.18)

The polytropic efficiency is also related to the entropy change across the propeller. From (6.13)

\[ \frac{dP}{P} = \eta_{pc} \left( \frac{\gamma}{\gamma - 1} \right) \frac{dT}{T}. \]  

(6.19)

According to the Gibbs equation, the entropy change across a differential part of the compression process is

\[ \frac{ds}{C_p} = \frac{dT}{T} - \left( \frac{\gamma - 1}{\gamma} \right) \frac{dP}{P} = (1 - \eta_{pc}) \frac{dT}{T} \]  

(6.20)

and so the propeller efficiency can also be written as

\[ \eta_{prop} = \left( \frac{2U_0}{U_0 + U_{\infty}} \right) \left( 1 - \frac{T}{C_p} \frac{ds}{dT} \right). \]  

(6.21)

These results tell us that the propeller efficiency is determined by two distinct mechanisms. The first is the propulsive efficiency that is directly related to the propeller loading (Thrust/Area). The higher the loading, the more power is lost to increasing the kinetic energy of the flow. A very highly loaded propeller is sensitive to blade stall and one of the advantages of putting a duct around the propeller, turning it into a fan, is that a higher thrust per unit area can be achieved.

The second mechanism is the entropy rise across the propeller due to viscous friction and stagnation pressure losses due to compressibility effects. A well designed propeller should achieve as low an entropy rise per unit temperature rise, \( ds/dT \), as possible. Note that even if we could design a propeller that operated isentropically it would still have an efficiency that is less than one.

### 6.2 Work output coefficient

The thrust equation for the turboprop is
\[ T_{\text{total}} = T_{\text{core}} + T_{\text{prop}} \]

or

\[ T = \dot{m}_a (U_e - U_0) + \dot{m}_f U_e + (P_e - P_0) A_e + \dot{m}_{\text{prop}} (U_\infty - U_0). \]  

Substitute the propeller efficiency

\[ T_{\text{total}} = \dot{m}_a (U_e - U_0) + \dot{m}_f U_e + (P_e - P_0) A_e + \eta_{\text{prop}} \frac{W_p}{U_0}. \]  

The core thrust has the usual form

\[ \frac{T_{\text{core}}}{\dot{m}_a a_0} = M_0 \left( (1 + f) \frac{M_e}{M_0} \sqrt{\frac{T_e}{T_0}} - 1 \right) \]  

where the nozzle is taken to be fully expanded \( P_e = P_0 \).

The presence of \( U_0 \) in the denominator of (6.23) indicates the inadequacy of the propeller efficiency for describing propeller thrust at low speeds. As a consequence the performance of a turboprop is usually characterized in terms of power output instead of thrust. Define the work output coefficient as

\[ C_{\text{total}} = \frac{T_{\text{total}} U_0}{\dot{m}_a C_p T_0} = C_{\text{core}} + C_{\text{prop}} \]

where from (6.23)

\[ C_{\text{core}} = (\gamma - 1) M_0^2 \left( (1 + f) \frac{M_e}{M_0} \sqrt{\frac{T_e}{T_0}} - 1 \right) \]  

and

\[ C_{\text{prop}} = \eta_{\text{prop}} \frac{W_p}{\dot{m}_a C_p T_0}. \]

The work output coefficient and the dimensionless thrust are directly proportional to one another
\[ \frac{T}{P_0 A_0} = \frac{\gamma}{\gamma - 1} C_{\text{total}}. \]  \hspace{1cm} (6.28)

The fuel efficiency of the turboprop is expressed in terms of the specific horsepower

\[ SHP = \frac{\text{pounds of fuel burned per hour}}{\text{output horsepower}} = \frac{3600 \dot{m}_f g}{T_{\text{total}} U_0} \]

or

\[ SHP = \frac{2545}{C_p T_0} \left( \frac{f}{C_{\text{total}}} \right) \]  \hspace{1cm} (6.29)

where the temperature is in degrees Rankine and the heat capacity is in BTU/lbm-hr.

### 6.3 Power balance

The turbine drives both the compressor and propeller. The power to the propeller is

\[ W_p = \eta_g \left( (\dot{m}_a + \dot{m}_f) \eta_m (h_{t4} - h_{t5}) - \dot{m}_a (h_{t3} - h_{t2}) \right) \]  \hspace{1cm} (6.30)

where \( \eta_g \) is the gearbox efficiency and \( \eta_m \) is the shaft mechanical efficiency. Substitute (6.30) into (6.27) and assume the gas is calorically perfect. The work output coefficient of the propeller is expressed in terms of cycle parameters as

\[ C_{\text{prop}} = \eta_{\text{prop}} \eta_g \left( (1 + f) \eta_m \tau_\lambda (1 - \tau_1) - \tau_r (\tau_c - 1) \right). \]  \hspace{1cm} (6.31)

### 6.4 The ideal turboprop

The assumptions of the ideal turboprop are essentially the same as for the ideal turbojet, namely
along with $P_e = P_0$. Notice that the propeller efficiency is not assumed to be one. The ideal turboprop cycle begins with a propeller efficiency below one as reflected in the proportionality of the propeller efficiency to a propulsive efficiency that is inherently less than one. There is a little bit of an inconsistency here in that the compressor is assumed to be isentropic, whereas a small part of the compression of the core air is accomplished by the propeller. This portion of the compression is assumed to be isentropic even though the rest of the propeller may behave non-isentropically. In any case there is no way to distinguish between the propulsive and frictional parts of the propeller efficiency in practice and so all of the entropy change across the propeller can be assigned to the portion of the mass flow that passes outside of the core engine.

The exit Mach number is generated in the same manner as for the ideal turbojet. The Mach number ratio is

$$\left(\frac{M_e}{M_0}\right)^2 = \left(\frac{\tau_r\tau_c\tau_t - 1}{\tau_r - 1}\right). \quad (6.33)$$

The temperature ratio is also generated in the same way.

$$\frac{T_e}{T_0} = \frac{\tau_c}{\tau_r\tau_c} \quad (6.34)$$

The work output coefficient of the core is

$$C_{core} = 2(\tau_r - 1) \left(1 + f\right) \left(\frac{\tau_c}{\tau_r\tau_c}\right)^{1/2} \left(\frac{\tau_r\tau_c\tau_t - 1}{\tau_r - 1}\right)^{1/2} - 1 \right). \quad (6.35)$$
6.4.1 Optimization of the ideal turboprop cycle

The question now is: what fraction of the total thrust should be generated by the core in order to produce the maximum work output coefficient. The answer to this question is required in order to properly select the size of the turbine. Now determine an extremum in \( C_{\text{total}} \) with respect to \( \tau_t \).

\[
\frac{\partial C_{\text{total}}}{\partial \tau_t} = \frac{\partial C_{\text{core}}}{\partial \tau_t} + \frac{\partial C_{\text{prop}}}{\partial \tau_t} = 0 \quad (6.36)
\]

Substitute \( C_{\text{core}}, (6.35) \) and \( C_{\text{prop}}, (6.31) \) into (6.36) and carry out the differentiation

\[
2 \left( \tau_r - 1 \right) \left( 1 + f \right) \left( \frac{\tau \lambda}{\tau_r \tau_c} \right)^{1/2} \left( \frac{\tau_r \tau_c \tau_t - 1}{\tau_r - 1} \right)^{-1/2} - \eta_{\text{prop}} \eta_g \left( 1 + f \right) \eta_m \tau \lambda = 0
\]

which simplifies to

\[
\left( \tau \lambda \tau_r \tau_c \right)^{1/2} \left( \frac{\tau_r \tau_c \tau_t - 1}{\tau_r - 1} \right)^{-1/2} = \eta_{\text{prop}} \eta_g \eta_m \tau \lambda. \quad (6.38)
\]

Notice that the propeller, gearbox and shaft efficiencies enter the analysis as one product. Let

\[
\eta = \eta_{\text{prop}} \eta_g \eta_m. \quad (6.39)
\]

Square (6.38) and solve for \( \tau_t \).

\[
\tau_t \mid_{\text{max thrust ideal turboprop}} = \frac{1}{\tau_r \tau_c} + \frac{\left( \tau_r - 1 \right)}{\eta^2 \tau \lambda} \quad (6.40)
\]

This result essentially defines the size of the turbine needed to achieve maximum work output coefficient which is equivalent to maximum thrust. Lets see what core engine velocity ratio this corresponds to.

\[
\left( \frac{U_c}{U_0} \right)^2 \mid_{\text{max thrust ideal turboprop}} = \frac{\tau \lambda}{\tau_r \tau_c} \left( \frac{1}{\tau_r - 1} \right) \left( \tau_r \tau_c \tau_t \mid_{\text{max thrust ideal turboprop}} - 1 \right) \quad (6.41)
\]
Substitute (6.40) into (6.41). The result is the very simple relationship

\[
\frac{U_e}{U_0}_{\text{max thrust ideal turboprop}} = \frac{1}{\eta}.
\] (6.42)

As the propeller-gearbox-shaft efficiency improves, the optimum turboprop cycle takes a larger and larger fraction of the thrust out of the propeller. This is accomplished with a larger turbine and a smaller core thrust.

The result (6.42) gives us some additional insight into the nature of the propeller efficiency. An ideal turboprop with a propeller that produced isentropic compression would have a core velocity that satisfies

\[
U_e|_{\text{max thrust ideal turboprop}} = U_0 + U_\infty \frac{1}{2}.
\] (6.43)

The core exit speed would be the average of the upstream and far downstream velocities. Referring back to (6.7) we can see that in this limit the core thruster becomes an indistinguishable part of the propeller actuator disc.

### 6.4.2 Compression for maximum thrust of an ideal turboprop

Once the turbine has been sized according to the above, then the thrust due to the core engine is fixed by (6.42). It is then a matter of choosing the compressor that maximizes \( C_{\text{prop}} \). Differentiate (6.31) with respect to \( \tau_c \). Neglect \( f \).

\[
\frac{\partial C_{\text{prop}}}{\partial \tau_c} = \eta_{\text{prop}} \eta_g \left( -\eta_m \tau_\lambda \left( \frac{\partial \tau_t}{\partial \tau_c} \right) - \tau_r \right) = \eta_{\text{prop}} \eta_g \left( -\eta_m \tau_\lambda \left( \frac{-1}{\tau_r \tau_c} \right) - \tau_r \right)
\] (6.44)

Maximum \( C_{\text{prop}} \) is achieved for

\[
\tau_c = \frac{\sqrt{\eta_m \tau_\lambda}}{\tau_r}
\] (6.45)

which is essentially the same result we obtained for the turbojet (exactly the same if we had included the shaft efficiency in the turbojet analysis). At this point the required turbine temperature ratio can determined from (6.40).
6.5 Turbine sizing for the non-ideal turboprop

The optimization problem is still essentially the same; we need to select the turbine temperature ratio so as to maximize the total work output coefficient.

$$\frac{\partial C_{\text{total}}}{\partial \tau_t} = \frac{\partial C_{\text{core}}}{\partial \tau_t} + \frac{\partial C_{\text{prop}}}{\partial \tau_t} = 0 \quad (6.46)$$

Assume the core flow is fully expanded. The squared velocity ratio across the non-ideal core is

$$\left( \frac{U_e}{U_0} \right)^2 = \frac{1}{\tau_r - 1} \left( \frac{\tau_\lambda}{\tau_r \tau_c} \right) \left( \tau_r \tau_c \tau_t - \tau_c \frac{1 - \eta_{pc} \tau_t \left( 1 - \frac{1}{T_{pe}} \right)}{\left( \frac{\pi d \pi b \pi n}{\gamma} \right)^{\frac{\gamma - 1}{\gamma}}} \right) \quad (6.47)$$

and the core work output coefficient of the non-ideal turboprop is

$$C_{\text{core}} = 2(\tau_r - 1) \left( \frac{(1 + f)}{(\tau_r - 1)^{1/2}} \left( \frac{\tau_\lambda}{\tau_r \tau_c} \right)^{1/2} \left( \frac{\tau_r \tau_c \tau_t - \tau_c \frac{1 - \eta_{pc} \tau_t \left( 1 - \frac{1}{T_{pe}} \right)}{\left( \frac{\pi d \pi b \pi n}{\gamma} \right)^{\frac{\gamma - 1}{\gamma}}} \right)^{1/2} - 1 \right) \quad (6.48)$$

For the non-ideal cycle the condition (6.46) becomes

$$\left( \frac{\tau_r - 1}{\tau_r \tau_c} \right)^{1/2} \left( \frac{\tau_\lambda}{\frac{\tau_r \tau_c}{\pi d \pi b \pi n} \left( \frac{\pi d \pi b \pi n}{\gamma} \right)^{\frac{\gamma - 1}{\gamma}}} \right)^{-1/2} \times \left( \frac{\tau_r \tau_c}{\tau_t} - \frac{1}{\eta_{pc}} \left( \frac{\tau_c \tau_t - \tau_e \left( 1 - \frac{1}{T_{pe}} \right)}{\left( \frac{\pi d \pi b \pi n}{\gamma} \right)^{\frac{\gamma - 1}{\gamma}}} \right) \right) - \eta_{prop} \eta_g \eta_m \tau_\lambda = 0 \quad (6.49)$$

Various flow parameters are specified in (6.49) and the turbine temperature ratio for maximum work output coefficient is determined implicitly. Figure 6.4 shows a typical calculation.

The optimum turbine temperature ratio increases with non-ideal effects indicating that a larger fraction of the total thrust is developed across the core engine of a non-ideal turboprop.
Figure 6.4: Comparison of turbine selection for the ideal and non-ideal turboprop cycle. Parameters of the non-ideal cycle are $\pi_d = 0.97$, $\eta_{pc} = 0.93$, $\pi_b = 0.96$, $\eta_{pe} = 0.95$, $\pi_n = 0.98$.

6.6 Problems

Problem 1 - Consider the propeller shown in Figure 6.5.

Figure 6.5: Flow through an actuator disc.

Show that for small Mach number, the velocity at the propeller is approximately

$$U_2 = U_{13} = \frac{U_0 + U_\infty}{2}, \quad (6.50)$$

In other words one-half the velocity change induced by the propeller occurs upstream of the propeller. This is known as Froude’s theorem and is one of the cornerstones of propeller theory.
Problem 2 - Compare ducted versus unducted fans. Let the fan area be the same in both cases.

Show that, for the same power input, the ducted case produces more thrust. Note that the operating point of the ducted fan is chosen to produce a capture area equal to the area of the duct. Suppose the operating point were changed. How would your answer change?

Problem 3 - Derive equation (6.28).

Problem 4 - Use Matlab or Mathematica to develop a program that reproduces Figure 6.4.

Problem 5 - An ideal turboprop engine operates at a free stream Mach number, $M_0 = 0.7$. The propeller efficiency is, $\eta_{prop} = 0.8$ and the gearbox and shaft efficiencies are both 1.0. The turbine is chosen to maximize the total work output coefficient. The compressor is chosen according to, $\tau_c = \sqrt{\tau_\lambda}/\tau_r$ and $\tau_\lambda = 6$. Determine the dimensionless thrust, $T/P_0A_0$ where $A_0$ is the capture area corresponding to the air flow through the core engine. Assume $f \ll 1$. Is the exit nozzle choked?.

Problem 6 - A non-ideal turboprop engine operates at a free stream Mach number, $M_0 = 0.6$. The propeller efficiency is, $\eta_{prop} = 0.8$ and the gearbox and shaft efficiencies are both 1.0. The operating parameters of the engine are $\tau_\lambda = 7$, $\tau_c = 2.51$, $\pi_d = 0.97$, $\eta_{pc} = 0.93$, $\pi_b = 0.96$, $\eta_{pe} = 0.95$, $\pi_n = 0.98$. Determine the dimensionless thrust, $T/P_0A_0$ where $A_0$ is the capture area corresponding to the air flow through the core engine. Do not assume $f \ll 1$.

Problem 7 - A turboprop engine operates at a free stream Mach number, $M_0 = 0.6$. The propeller efficiency is $\eta_{prop} = 0.85$, the gearbox efficiency is $\eta_g = 0.95$, and the shaft efficiency is $\eta_m = 1$. All other components operate ideally and the exhaust is fully expanded $P_e = P_0$. The operating parameters of the engine are $\tau_\lambda = 7$ and $\tau_c = 2.51$. Assume the turbine is sized to maximize $C_{total}$ and assume $f \ll 1$. Determine the total work output coefficient $C_{total}$ and dimensionless thrust $T/P_0A_0$. The ambient temperature and pressure
are $T_0 = 216 \, K$ and $P_0 = 2 \times 10^4 \, N/m^2$.

**Problem 8** - A propulsion engineer is asked by her supervisor to determine the thrust of a turboprop engine at cruise conditions. The engine is designed to cruise at $M_0 = 0.5$. At that Mach number the engine is known to be operating close to its maximum total work output coefficient $C_{total}$. She responds by asking the supervisor to provide some data on the operation of the engine at this condition. List the minimum information she would need in order to provide a rough estimate of the thrust of the engine. What assumptions would she need to make in order to produce this estimate?
Chapter 7

Rocket performance

7.1 Thrust

Figure 7.1 shows a sketch of a rocket in a test stand. The rocket produces thrust, $T$, by expelling propellant mass from a thrust chamber with a nozzle. The test stand applies an opposite force on the rocket holding it at rest. The propellant (fuel+oxidizer) mass flow rate is $\dot{m}$ and the ambient pressure of the surrounding air is $P_0$.

![Rocket thrust schematic.](image)

Other quantities defined in Figure 7.1 are as follows.

\[
\begin{align*}
A_s &= \text{outside surface of the vehicle exposed to } P_0 \\
A_c &= \text{inside surface of the combustion chamber} \\
A_e &= \text{nozzle exit area} \\
\hat{n} &= \text{outward unit normal} \\
P_e &= \text{area averaged exit gas pressure} \\
\rho_e &= \text{area averaged exit gas density} \\
U_e &= \text{area averaged } x - \text{component of velocity at the nozzle exit}
\end{align*}
\]
The vehicle is at rest and so the total force acting on it is zero.

\[ 0 = T + \int_{A_s} \left( P\vec{T} - \vec{\tau} \right) \cdot \hat{n} dA \bigg|_x + \int_{A_c} \left( P\vec{T} - \vec{\tau} \right) \cdot \hat{n} dA \bigg|_x + \dot{m}U_{xm} \]  

(7.2)

The variable \( P \) is the gas pressure acting at any point on the surface of the rocket, \( \vec{\tau} \) is the viscous stress tensor, and \( \dot{m}U_{xm} \) is the x-momentum of the propellant injected into the thrust chamber. If the rocket were inactive so that there was no force on the restraint and the outside surface and thrust chamber were all at a pressure \( P_0 \) then

\[ 0 = \int_{A_s} P_0\vec{T} \cdot \hat{n} dA \bigg|_x + \int_{A_c} P_0\vec{T} \cdot \hat{n} dA \bigg|_x. \]  

(7.3)

In this situation the control volume contains fluid all at rest and

\[ 0 = \int_{A_c} P_0\vec{T} \cdot \hat{n} dA \bigg|_x + \int_{A_e} P_0\vec{T} \cdot \hat{n} dA \bigg|_x. \]  

(7.4)

The last relation can be written as

\[ 0 = \int_{A_c} P_0\vec{T} \cdot \hat{n} dA \bigg|_x + P_0A_e. \]  

(7.5)

Note that a unit normal vector that is consistent between the control volume and the outside surface of the vehicle points inward on \( A_e \). Thus equation (7.3) becomes

\[ 0 = \int_{A_s} P_0\vec{T} \cdot \hat{n} dA \bigg|_x - P_0A_e \]  

(7.6)

and the original force balance (7.2) can be written as

\[ 0 = T + P_0A_e + \int_{A_c} \left( P\vec{T} - \vec{\tau} \right) \cdot \hat{n} dA \bigg|_x + \dot{m}U_{xm}. \]  

(7.7)

Built into (7.7) is the assumption that when the engine is operating the external surface pressure and stress distribution is unchanged.
\[
\left( \int_{A_e} (P \vec{T} - \vec{\tau}) \cdot \hat{n} dA \right)_{\text{after engine turn on}} = \left( \int_{A_e} P_0 \vec{T} \cdot \hat{n} dA \right)_{\text{before engine turn on}}.
\] (7.8)

In fact, the jet from the rocket mixes with the surrounding air setting the air near the vehicle into motion leading to slight deviations in the pressure acting on the outside of the vehicle. For a rocket of reasonable size and thrust, this is a very small effect.

With the engine on, a balance of momentum over the control volume gives

\[
\frac{D}{Dt} \int_V (\rho \vec{U}) dV = \int_V \left( \frac{\partial \rho \vec{U}}{\partial t} \right) dV = - \int_V \nabla \cdot \left( \rho \vec{U} \vec{U} + P \vec{I} - \vec{\tau} \right) dV.
\] (7.9)

We are treating the case where the flow in the combustion chamber is stationary and the integral on the left hand side of (7.9) is zero. Our goal is to relate the thrust of the engine to flow conditions on \(A_e\) and with this in mind we convert the right hand side to an integral over the surface of the control volume.

\[
0 = \int_V \nabla \cdot \left( \rho \vec{U} \vec{U} + P \vec{T} - \vec{\tau} \right) dV = \int_{A_c} \left( \rho \vec{U} \vec{U} + P \vec{T} - \vec{\tau} \right) \cdot \hat{n} dA + \int_{A_e} \left( \rho \vec{U} \vec{U} + P \vec{T} - \vec{\tau} \right) \cdot \hat{n} dA
\] (7.10)

Note that the unit normal that appears in the surface integrals in (7.10) is an inward pointing unit normal. On the surface \(A_c\), the velocity is zero by the no-slip condition (except over the injector holes) and on the surface \(A_e\) we use area-averaged values of velocity, pressure, and density

\[
\int_{A_e} \left( P \vec{T} - \vec{\tau} \right) \cdot \hat{n} dA \bigg|_{x} + \dot{m} U_m + \rho_e U_e^2 A_e + P_e A_e = 0
\] (7.11)

where the momentum of the propellant injected into the combustion chamber has been included. Small viscous normal forces on \(A_e\) are neglected. Our force balance (7.7) now becomes

\[
0 = T + P_0 A_e - (\rho_e U_e^2 A_e + P_e A_e).
\] (7.12)

Finally our rocket thrust formula is
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\[ T = \rho_e U_e^2 A_e + (P_e - P_0) A_e. \]  \hspace{1cm} (7.13)

The propellant mass flow is

\[ \dot{m} = \rho_e U_e A_e \]  \hspace{1cm} (7.14)

and the rocket thrust formula is often written

\[ T = \dot{m} U_e + (P_e - P_0) A_e. \]  \hspace{1cm} (7.15)

7.2 Momentum balance in center-of-mass coordinates

Let’s look at the question of defining the thrust from a rather different point of view. Figure 7.2 depicts a rocket referenced to a system of center-of-mass coordinates. In the analysis to follow, gravity is taken to be zero. The effects of gravitational acceleration will be taken into account later.

Figure 7.2: Center-of-mass description of the rocket and expelled propellant mass.
For \( t < 0 \) the rocket, its propellant and the surrounding atmosphere are all at rest. Sometime after ignition the rocket has translated to the right and the exhaust gases form a cloud off to the left of the center-of-mass. Because there is no external force on the system the center of mass remains at rest at the origin for all time. Conservation of momentum for the whole system of rocket vehicle, expelled combustion gases as well as the air set into motion by the drag forces on the rocket can be stated as

\[
\frac{D}{Dt} \left( \int_{V(t)} (\rho \bar{U}) dV \right) \bigg|_x + M_r(t) V_r(t) = 0 \quad (7.16)
\]

where \( M_r(t) \) is the time-dependent rocket mass. At any given instant the rocket mass comprises all of the hardware and all of the propellant contained in the tanks, piping, pumps and combustion chamber up to the exit plane of the nozzle. The time-dependent rocket velocity is \( V_r(t) \). We shall assume that all of the propellant mass contained in the rocket is moving at this velocity although there is always a small amount moving through the piping and combustion chamber at a slightly different velocity.

The gas momentum is integrated over a control volume \( V(t) \) that completely encloses all of the moving gas outside the vehicle as shown in Figure 7.2. Since there is a continuous flow of propellant mass into the combustion chamber and out of the rocket nozzle the volume required to contain the expelled gas must grow with time. This is depicted in Figure 7.2. The control volume is cylindrical in shape. The left face \( A_1 \) moves to the left at a speed sufficient to fully contain all the moving gas as well as any unsteady pressure disturbances generated by the rocket plume. The surface \( A_3 \) moves outward for the same reason. The upstream face \( A_2 \) moves to the right at velocity \( V_r(t) \) with the rocket. Finally the surface \( A_s \) is attached to the rocket fuselage and outer nozzle surface. On the solid surface, the fluid velocity is equal to the rocket velocity \( V_r(t) \) by the no slip condition. The last surface of the control volume is \( A_e \) which coincides with the nozzle exit plane and translates to the right at the rocket velocity. The momentum equation integrated over \( V(t) \) is

\[
\frac{D}{Dt} \int_{V(t)} (\rho \bar{U}) dV \bigg|_x = - \int_{A(t)} \left( \rho \bar{U} (\bar{U} - \bar{U}_A) + P \bar{T} - \bar{F} \right) \cdot \hat{n} dA \bigg|_x . \quad (7.17)
\]

The control volume is sufficiently large so that the fluid velocity on \( A_1 , A_2 \) and \( A_3 \) is zero and the pressure is \( P_0 \). Therefore over most of the surface of the selected control volume no additional momentum is being enclosed as the surface moves outward. The pressure forces on \( A_1 \) and \( A_2 \) nearly cancel except for a small deviation in pressure near the rocket nose in subsonic flight. For now we will cancel these forces but they will be included later when we develop an expression for the vehicle drag. The pressure forces on \( A_3 \) have no component in the \( x \) direction. Thus the momentum balance (7.17) becomes
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\[
\frac{D}{Dt} \int_{V(t)} (\rho \bar{U}) \, dV \bigg|_x = \\
- \int_{A_s(t)} (\rho \bar{U} (\bar{U} - \bar{U}_A) + P I - \tau) \cdot \hat{n} \, dA \bigg|_x - \\
\int_{A_e(t)} (\rho \bar{U} (\bar{U} - \bar{U}_A) + P I - \tau) \cdot \hat{n} \, dA \bigg|_x.
\]

(7.18)

Now we can use an argument similar to that used in the previous section to relate the surface integral of the ambient pressure to an integral over the nozzle area. Recall

\[
0 = \int_{A_s} P_0 \hat{I} \cdot \hat{n} \, dA \bigg|_x + P_0 A_e.
\]

(7.19)

The sign change in (7.19) compared to (7.6) comes from the change in the direction of the outward normal on \( A_e \) compared to the control volume used in Section 7.1. Subtract (7.19) from (7.18) to get

\[
\frac{D}{Dt} \int_{V(t)} (\rho \bar{U}) \, dV \bigg|_x = \\
- \int_{A_s(t)} (\rho \bar{U} (\bar{U} - \bar{U}_A) + (P - P_0) I - \tau) \cdot \hat{n} \, dA \bigg|_x - \\
\int_{A_e(t)} (\rho \bar{U} (\bar{U} - \bar{U}_A) + (P - P_0) I - \tau) \cdot \hat{n} \, dA \bigg|_x.
\]

(7.20)

On the no-slip surface of the rocket, the fluid velocity satisfies \( \bar{U} = (V_r, 0, 0) \) and the control volume surface velocity is \( \bar{U}_A = (V_r, 0, 0) \). Therefore

\[
\int_{A_e(t)} \rho \bar{U} (\bar{U} - \bar{U}_A) \cdot \hat{n} \, dA \bigg|_x = 0.
\]

(7.21)

Now
\[
\frac{D}{Dt} \int_{V(t)} \left( \rho \vec{U} \right) dV \bigg|_x = \\
- \int_{A_s(t)} \left( (P - P_0)\vec{T} - \vec{n} \right) \cdot \hat{n} dA \bigg|_x \\
\int_{A_e(t)} \left( \rho \vec{U} (\vec{U} - \vec{U}_A) + (P - P_0)\vec{T} - \vec{f} \right) \cdot \hat{n} dA \bigg|_x .
\]

(7.22)

Near the rocket, the surrounding air is dragged along due to the no-slip condition and due to compressibility effects that may generate shock waves as sketched in Figure 7.2. Note that it is the deviation of the surface pressure from ambient, \( P - P_0 \), that contributes to the change in air momentum due to the drag of the rocket. The combination of viscous skin friction drag, base pressure drag and wave drag are all accounted for by the integral over \( A_s \) on the right-hand-side of (7.22). Thus let

\[
D = - \int_{A_s(t)} \left( (P - P_0)\vec{T} - \vec{f} \right) \cdot \hat{n} dA \bigg|_x .
\]

(7.23)

Equation (7.22) becomes

\[
\frac{D}{Dt} \int_{V(t)} \left( \rho \vec{U} \right) dV \bigg|_x = D - \int_{A_e(t)} \left( \rho \vec{U} (\vec{U} - \vec{U}_A) + (P - P_0)\vec{T} - \vec{f} \right) \cdot \hat{n} dA \bigg|_x .
\]

(7.24)

Now consider the integral over \( A_e \) on the right side of (7.24). All variables are area-averaged over \( A_e \). The \( x \)-component of velocity of the gas passing through \( A_e \) in the center-of-mass frame of reference is

\[
U = V_r + U_e .
\]

(7.25)

The nozzle exhaust velocity is the same velocity defined in section 7.1 (the velocity relative to the rocket) except that in this system of coordinates \( U_e \) is negative. In this frame the speed of the surface \( A_e \) is \( V_r(t) \).
\[
\int_{A_e(t)} \left( \rho \bar{U} (\bar{U} - \bar{U}_A) + (P - P_0) \bar{T} - \bar{p} \right) \cdot \hat{n} dA \bigg|_x =
\]
\[
\rho e A_e (U_e + V_r) (U_e + V_r - V_r) + (P_e - P_0) A_e.
\]

Now the momentum change of the expelled gas is
\[
\frac{D}{Dt} \int_{V(t)} (\rho \bar{U}) dV \bigg|_x = D - (\rho e A_e (U_e + V_r) (U_e + V_r - V_r) + (P_e - P_0) A_e).
\]

Substitute (7.27) into (7.16)
\[
\frac{D}{Dt} (M_r(t) V_r(t)) + D - (\rho e A_e U_e U_r + (P_e - P_0) A_e) = 0
\]

or
\[
M_r(t) \frac{dV_r(t)}{dt} + V_r(t) \frac{dM_r(t)}{dt} + D - (\rho e A_e U_e U_r + (P_e - P_0) A_e) = 0.
\]

Note that
\[
\frac{dM_r(t)}{dt} = \rho e U_e A_e
\]
and the second and fifth terms in (7.29) cancel. Remember that in the chosen set of coordinates, \( U_e \) is negative and (7.30) is consistent with the fact that \( dM_r/dt < 0 \). Finally our momentum balance in the center-of-mass system boils down to
\[
M_r(t) \frac{dV_r(t)}{dt} = (\rho e U_e^2 A_e + (P_e - P_0) A_e) - D.
\]

In words, Equation (7.31) simply states
\[
Rocket mass \times Acceleration = Thrust - Drag.
\]

The first term on the right-hand-side of (7.31) is the same thrust expression derived in the previous section.
7.3 Effective exhaust velocity

The total mechanical impulse (total change of momentum) generated by an applied force, \( T \), is

\[
I = \int_0^t T \, dt. \tag{7.33}
\]

The total propellant mass expended is

\[
M_p = \int_0^t \dot{m} \, dt. \tag{7.34}
\]

The instantaneous change of momentum per unit expenditure of propellant mass defines the effective exhaust velocity.

\[
C = \frac{dI}{dM_p} = \frac{T}{\dot{m}} = U_e + \frac{A_e}{m} (P_e - P_0) \tag{7.35}
\]

This can be expressed in terms of the exit Mach number as follows

\[
C = U_e \left(1 + \frac{P_e A_e}{\rho_e U_e^2 A_e} \left(1 - \frac{P_0}{P_e}\right)\right) \tag{7.36}
\]

or

\[
C = U_e \left(1 + \frac{1}{\gamma M_e^2} \left(1 - \frac{P_0}{P_e}\right)\right). \tag{7.37}
\]

For a large area ratio exhaust with a large exit Mach number the pressure part of the thrust becomes a small fraction of the overall thrust.

Let’s estimate the theoretical maximum exhaust velocity that can be generated by a given set of propellants characterized by the heating value per unit propellant mass, \( q \). Consider the simple model of a rocket thrust chamber shown in Figure 7.3.

Between stations 1 and 2 combustion takes place leading to a change in stagnation enthalpy of the propellant mass.

\[
h_{t2} = h_{t1} + q = h_e + \frac{1}{2} U_e^2 \tag{7.38}
\]
Figure 7.3: Thrust chamber propellant injection, heat release and nozzle expulsion.

The last equality assumes adiabatic conditions between station 2 and the nozzle exit. The quantity, \( h_{t1} \), is the stagnation enthalpy of the gases entering the combustion chamber and, in general, is much smaller than the heat added \( h_{t1} \ll q \). If the nozzle pressure ratio is very large \( P_{t2}/P_0 \gg 1 \), and the area ratio is large \( A_e/A^* \gg 1 \), then \( U_e^2/2 \gg h_e \) and so we can define the theoretical maximum exhaust velocity as

\[
C_{\text{max}} \equiv \sqrt{2q}.
\] (7.39)

The exit velocity is directly proportional to the amount of heat added through the combustion process. Making the approximation of constant specific heat and introducing the stagnation temperature, \( h_{t2} = C_p T_{t2} \), the maximum velocity becomes,

\[
C_{\text{max}} \equiv \sqrt{2C_p T_{t2}} = \sqrt{\frac{2\gamma}{\gamma - 1} RT_{t2}}.
\] (7.40)

The gas constant in (7.40) is related to the universal gas constant by

\[
R = \frac{R_u}{M_w}
\] (7.41)

where \( M_w \) is the mean molecular weight of the combustion gas. For this highly expanded rocket engine, the exhaust velocity is approximated by

\[
C_{\text{max}} \approx \sqrt{\frac{2\gamma}{\gamma - 1} \left( \frac{R_u}{M_w} \right) T_{t2}}.
\] (7.42)

This last relation shows the key role of the molecular weight of the combustion gases on the exhaust velocity of the nozzle. The highest performing engines generally have the lightest
weight exhaust gases. The most outstanding example of this is the Space Shuttle Main Engine (SSME) which uses hydrogen and oxygen, with water vapor as the main exhaust constituent.

### 7.4 \( C^* \) efficiency

A very important characteristic velocity that is widely used in rocket motor testing is \( C^* \) defined by the mass balance

\[
\dot{m} = \frac{P_2 A^*}{C^*}.
\]

(7.43)

The reason (7.43) is so useful is that it can be used to express the combustion efficiency in the rocket chamber in terms of quantities that are relatively easy to measure: chamber pressure, propellant mass flow rate and nozzle throat area. These variables are much easier and less expensive to measure than the combustion chamber temperature and chemical composition. The \( C^* \) efficiency of a motor is defined as

\[
\eta_{C^*} = \left( \frac{P_2 A^*}{\dot{m}} \right)_{\text{measured}} \left( \frac{P_2 A^*}{\dot{m}} \right)_{\text{ideal}}^{-1}.
\]

(7.44)

The ideal value of \( C^* \) is determined using a thermochemical calculator such as CEA discussed in Chapter 9. Since the ideal calculation is assumed to take place at the same propellant mass flow rate and nozzle throat area, \( A^* \), the \( C^* \) efficiency reduces to a simple comparison between the achieved chamber pressure and the chamber pressure that would be reached if there was complete mixing and complete combustion under adiabatic conditions.

\[
\eta_{C^*} = \frac{P_{t2,\text{measured}}}{P_{t2,\text{ideal}}}
\]

(7.45)

### 7.5 Specific impulse

For historical reasons, the specific impulse has always been defined as the thrust per unit weight flow of propellant and so the gravitational acceleration at the surface of the Earth is always inserted. The specific impulse is defined as
even though the parameter $g_0 = 9.8 \text{m/sec}^2$ has no particular relevance to the problem. Generally one distinguishes between the sea level specific impulse of a vehicle where the ambient pressure detracts from the thrust and the ideal vacuum specific impulse where the exhaust is assumed to be expanded to the exhaust pressure $P_e$ with $P_0 = 0$. From the previous discussion of the theoretical maximum exhaust velocity, it is clear that the vacuum specific impulse at a very large area ratio effectively characterizes a given propellant combination. Typical solid propellant systems have specific $I_{sp_{vac}}$ in the range $230 - 290$ sec. Liquid propellant systems using a hydrocarbon fuel with liquid oxygen have $I_{sp_{vac}}$ around 360 seconds with hydrogen-oxygen systems reaching 455 seconds. One needs to not take these $I_{sp}$ numbers too literally. Such values are often quoted for some typical real system such as the Space Shuttle Main Engine without stating the actual chamber pressure and area ratio and in some cases without identifying the system. The question of the area ratio corresponding to the ideal specific impulse is particularly important. For example, for a hydrogen-oxygen system at an area ratio of, say, 4,000 the ideal $I_{sp}$ is over 500 seconds.

An accurate specification of the specific impulse of a working system requires a knowledge of the chamber pressure, nozzle area ratio, combustion efficiency and nozzle efficiency. The chamber pressure is needed to determine the composition of the combustion chamber gas at the chamber temperature. This will become clear when we study the thermochemistry of gases in Chapter 9.

### 7.6 Chamber pressure

The mass flow of propellant injected into the rocket engine and the amount of heat added between stations 1 and 2 through combustion determine the engine chamber pressure. We can see this by considering the relationship between the mass exiting the nozzle and the stagnation conditions of the gas at station 2. In general, at any point in a channel flow of a compressible gas, the mass flow can be expressed as

$$
\dot{m} = \rho U A = \frac{1}{\left(\frac{\gamma+1}{2}\right)^{\frac{\gamma+1}{2(\gamma-1)}}} \frac{\gamma P_t A}{\sqrt{\gamma RT_t}} f(M)
$$

where $f(M)$ is the well known area-Mach number relation
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\[ f(M) = \frac{A^*}{A} = \left( \frac{\gamma + 1}{2} \right)^{\frac{\gamma + 1}{2(\gamma - 1)}} \frac{M}{\left(1 + \frac{\gamma - 1}{2} M^2\right)^{\frac{\gamma + 1}{2(\gamma - 1)}}}. \] (7.48)

Equation (7.48) is plotted in Figure 7.4 for several values of \( \gamma = C_p/C_v \).

Figure 7.4: Area-Mach number relation.

The stagnation temperature at station 2 is determined by the heat released through combustion.

\[ T_{t2} = T_{t1} + \frac{q}{C_p} \] (7.49)

To a first approximation, \( T_{t2} \) is nearly independent of chamber pressure, \( P_{t2} \) and is approximately known once the propellants are specified. Generally the chamber pressure is much larger than the ambient pressure \( P_{t2}/P_0 \gg 1 \) and so the nozzle throat is choked, \( M^* = 1 \) and \( f(M^*) = 1 \). The chamber pressure is then determined by evaluating the mass flow at the nozzle throat

\[ P_{t2} = \left( \frac{\gamma + 1}{2} \right)^{\frac{\gamma + 1}{2(\gamma - 1)}} \frac{\sqrt{\gamma R T_{t1}}}{\gamma A^*} \dot{m} \] (7.50)

where adiabatic, isentropic conditions are assumed between station 2 and the nozzle throat.
7.7 Combustion chamber stagnation pressure drop

The stagnation pressure drop between stations 1 (near the injector) and station 2 due to the heat addition is given by the conventional Rayleigh line relations.

\[
\frac{P_{t2}}{P_{t1}} = \left\{ \frac{1 + \gamma M_{12}^2}{1 + \gamma M_{22}^2} \right\} \left( \frac{1 + \frac{\gamma - 1}{2} M_{22}^2}{1 + \frac{\gamma - 1}{2} M_{12}^2} \right)^{\frac{\gamma}{\gamma - 1}}. \quad (7.51)
\]

The static pressure is

\[
\frac{P_2}{P_1} = \left\{ \frac{1 + \gamma M_{12}^2}{1 + \gamma M_{22}^2} \right\}. \quad (7.52)
\]

At station 1, \( M_{12}^2 \ll 1 \), and we can approximate conditions at station 2 in terms of just the Mach number at 2.

\[
\frac{P_{t2}}{P_{t1}} = \left\{ \frac{1}{1 + \gamma M_{22}^2} \right\} \left( \frac{1 + \gamma - 1}{2} M_{22}^2 \right)^{\frac{\gamma}{\gamma - 1}} \quad (7.53)
\]

\[
\frac{P_2}{P_1} = \left\{ \frac{1}{1 + \gamma M_{22}^2} \right\}
\]

The Mach number at station 2 is determined by the internal nozzle area ratio from 2 to the throat. Assume isentropic, adiabatic, flow between \( A_2 \) and \( A^* \).

\[
\frac{A^*}{A_2} = \left( \frac{\gamma + 1}{2} \right)^{\frac{\gamma + 1}{2(\gamma - 1)}} \frac{M_2}{(1 + \frac{\gamma - 1}{2} M^2)^{\frac{\gamma + 1}{2(\gamma - 1)}}} \quad (7.54)
\]

The relations (7.53) and (7.54) effectively define a relationship between \( A_2/A^* \), \( P_{t2}/P_{t1} \) and \( P_2/P_1 \), plotted in Figure 7.5 for several values of \( \gamma \).

The desire to keep stagnation pressure losses relatively small, while avoiding an excessively large diameter combustion chamber, dictates the internal area ratio selected for the combustion chamber. It is clear from Figure 7.5 that an area ratio of about 3 is sufficient to keep the stagnation pressure losses across the combustion chamber negligibly small. Practically all rocket thrust chambers have an area ratio of about 3 for this reason.
7.8 The Tsiolkovsky rocket equation

Consider the force balance on a rocket in flight shown in Figure 7.6.

The variables identified in the figure are as follows.

\[ T = \text{vehicle thrust} \]
\[ D = \text{vehicle aerodynamic drag} \]
\[ V_r = \text{vehicle velocity} \]
\[ \theta = \text{angle with respect to the horizontal} \]
\[ \dot{m} = \text{nozzle mass flow} \]
\[ M_r = \text{vehicle mass} \]
\[ g = \text{gravitational acceleration} \]  

The balance of forces along the direction of flight was derived earlier. Here we add the gravitational component of the force balance

\[ M_r \frac{dV_r}{dt} = T - M_r g \sin(\theta) - D \]  

or
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Figure 7.6: Rocket free body diagram.

\[ M_r \frac{dV_r}{dt} = -C \frac{dM_r}{dt} - M_r g \sin(\theta) - D \]  

(7.57)

where \( C \) is the effective exhaust velocity. Divide (7.57) through by \( M_r \).

\[ \frac{dV_r}{dt} = -C \frac{d(\ln M_r)}{dt} - g \sin(\theta) - \frac{D}{M_r} \]  

(7.58)

Let

\[ M_{ri} = \text{initial mass at } t = 0 \]
\[ M_{rf} = \text{final mass at } t = t_b \]
\[ t_b = \text{time of burnout.} \]  

(7.59)

Integrate (7.58) assuming constant \( C \). The velocity change of the vehicle is

\[ \Delta V_r = V_{rb} - V_{r0} = \Delta V_r|_{\text{ideal}} - \Delta V_r|_{\text{gravitational}} - \Delta V_r|_{\text{drag}} \]  

(7.60)

where

\[ \Delta V_r|_{\text{gravitational}} = \int_0^{t_b} g \sin(\theta) dt \]  

(7.61)

\[ \Delta V_r|_{\text{drag}} = \int_0^{t_b} \left( \frac{D}{M_r} \right) dt. \]
For a typical launch vehicle headed to orbit, aerodynamic drag losses are generally quite small on the order of 100 to 500 m/sec. Gravitational losses are larger, generally ranging from 700 to 1500 m/sec depending on the shape of the trajectory to orbit. By far the largest term is the equation for the ideal velocity increment

\[ \Delta V_r |_{\text{ideal}} = C \ln \left( \frac{M_{ri}}{M_{rf}} \right) \]  

(7.62)

first derived in 1903 by the Soviet rocket pioneer Konstantin Tsiolkovsky who is credited with developing much of the early theory of rocket flight. Equation (7.62) shows the dependence of the velocity achieved by a rocket on the effective exhaust velocity (determined by the choice of propellants) and the initial to final mass ratio which is determined by what might be termed the structural efficiency of the vehicle and the density of the propellants. Notice the similarity of (7.62) to the Bruguet range equation discussed in chapter 2. In general, one seeks a very lightweight vehicle to carry high density propellants which after combustion produce very lightweight products. In practice these requirements conflict. Generally solid rockets use relatively dense, low energy propellants which do not produce very lightweight products of combustion. Whereas liquid rockets use more energetic propellants that produce light products but are not particularly dense.

### 7.9 Reaching orbit

Orbital velocity at an altitude of 115 miles, which is about the lowest altitude where a stable orbit can be maintained, is approximately 7777 m/sec. To reach this velocity from the Kennedy Space Center where the velocity due to the rotation of the Earth is approximately 427 m/sec, assuming gravitational plus drag losses of 1700 m/sec, requires an ideal velocity increment of 9050 m/sec. A hydrogen-oxygen system with an effective average exhaust velocity (from sea-level to vacuum) of 4000 m/sec would require \( \frac{M_i}{M_f} = 9.7 \). This represents a very high level of structural efficiency and is the fundamental challenge being addressed by single-stage-to-orbit concepts. At the present time existing launch vehicles require multiple stages to achieve orbit with a reasonable payload size.

Strategies for reducing gravitational losses are mainly limited to optimizing the trajectory to orbit and expending the maximum amount of propellant as possible near the earth’s surface (to avoid the work required to lift it to altitude). The latter strategy suggests that the most efficient way to orbit would be an artillery shell, however practical limitations prevent large acceleration loads on the payload. Most large launch vehicles are relatively delicate and require throttling back on thrust at low altitude to avoid large dynamic pressure loads on the vehicle.
The drag losses can be minimized by designing a slender vehicle. This can be seen as follows

\[
\Delta V_{\text{drag}} = \int_0^{t_b} \left( \frac{D}{M_r} \right) dt = \int_0^{t_b} \frac{1}{2} \rho V_r^2 A_C D M_{ri} \left( \frac{M_{ri}}{M_r} \right) dt = \frac{A}{2M_{ri}} \int_0^{t_b} \left( \rho V_r^2 C_D \right) \left( \frac{M_{ri}}{M_r} \right) dt
\]

(7.63)

where \(A\) is the cross-sectional area of the vehicle. The integral on the right-hand-side is approximately independent of vehicle size and the initial mass of the vehicle is approximately proportional to the vehicle volume, \(M_{ri} \approx \rho_{\text{vehicle}} V_{\text{vehicle}}\).

\[
\Delta V_{\text{rocket}} |_{\text{drag}} \approx \frac{\text{Frontal Area}_{\text{rocket}}}{2\text{density}_{\text{rocket}} \text{Volume}_{\text{rocket}}} \int_0^{t_b} \left( \rho V_{\text{rocket}}^2 C_D \right) \left( \frac{M_{\text{rocket},i}}{M_{\text{rocket}}} \right) dt \sim \frac{1}{\text{Length}_{\text{rocket}}}
\]

(7.64)

The last result suggests that the vehicle should be long and thin, roughly like a pencil. Note that the drag losses go down as the mass goes up, and so the velocity loss due to drag tends to become smaller as the vehicle absolute size goes up. The length to diameter ratio of the vehicle does not come into the analysis directly but, in general, the drag coefficient, \(C_d\), decreases as the \(L/D\) goes up.

### 7.10 The thrust coefficient

The thrust coefficient provides a useful dimensionless measure of engine thrust.

\[
C_F = \frac{T}{P_{t2} A^*} = \frac{\dot{m} U_e + (P_e - P_0) A_e}{P_{t2} A^*} = \left( \frac{P_e}{P_{t2}} \right) \left( \frac{A_e}{A^*} \right) \left( \gamma M_e^2 + 1 - \frac{P_0}{P_e} \right)
\]

(7.65)

This rather complicated looking expression can be written in terms of the nozzle exit Mach number and pressure

\[
C_F = \frac{1}{\left( \frac{\gamma + 1}{2} \right)^{\frac{\gamma+1}{2}}} \frac{\gamma M_e^2 + 1 - \frac{P_0}{P_e}}{M_e \left( 1 + \frac{\gamma - 1}{2} M_e^2 \right)^{\frac{1}{2}}}
\]

(7.66)

where the nozzle flow has been assumed to be isentropic. For a rocket operating in a vacuum, with a very large expansion ratio \(M_e \rightarrow \text{large}\), the thrust coefficient has an upper limit of
\[ C_{F_{\text{max}}} = \frac{\gamma}{\left(\frac{\gamma - 1}{2}\right)^{\frac{1}{2}} \left(\frac{\gamma + 1}{2}\right)^{\frac{\gamma + 1}{2(\gamma - 1)}}} \]  \hspace{1cm} (7.67)

The thrust coefficient is plotted in Figure 7.7 for several values of \( \gamma \) as a function of exit Mach number.

![Figure 7.7: Thrust coefficient versus Mach number.](image1)

The thrust coefficient is also plotted in Figure 7.8 for several values of \( \gamma \) as a function of nozzle exit area ratio.

![Figure 7.8: Thrust coefficient versus area ratio.](image2)

The thrust coefficient gives us a useful measure of the effect of nozzle expansion on thrust. It is clear from Figure 7.7 that, in principle, expanding a gas with low \( \gamma \) would have the greatest benefit. However Figure 7.4 indicates that a large area ratio nozzle is required to
reach the high exit Mach number required to obtain this benefit. We can see from Figure 7.7 and Figure 7.8 that fully expanding the flow, versus no expansion at all (a simple convergent nozzle), represents as much as a 50% increase in the thrust generated by the nozzle. Generally, high temperature combustion gases have values of $\gamma$ between 1.2 and 1.3 with the lower values characterizing high molecular weight products of combustion typical of solid rockets.

### 7.11 Problems

**Problem 1** - A monopropellant thruster using Argon gas at 100 $\text{psia}$ and 1500 $\text{K}$ exhausts through a large area ratio convergent-divergent nozzle to the vacuum of space. Determine the energy per unit mass of a parcel of gas at three locations: in the plenum, at the nozzle throat, and at the end of the expansion where the gas pressure approaches vacuum. What mechanism is responsible for the change of energy from one position to the next? How does your answer change if the gas is changed to Helium?

**Problem 2** - The designer of a spacecraft maneuvering system needs to choose between Argon (atomic weight 40) and Helium (atomic weight 4) as propellants for a monopropellant thruster. The gas pressure and temperature in the propellant tank are $5 \times 10^6 \text{N/m}^2$ and 300 $\text{K}$ respectively. The propellant tank volume is 1.0 $\text{m}^3$ and the empty mass of the vehicle is 10 $\text{kg}$.

1) Which propellant gas will give the largest velocity change to the vehicle? Estimate the vehicle velocity change for each gas?

2) Suppose the vehicle mass is 1000 $\text{kg}$, which propellant would deliver the largest velocity change?

**Problem 3** - Consider two different systems used for space propulsion. System A uses propellants with an average density of 2 $\text{gm/cm}^3$ and specific impulse of 200 seconds while system B uses propellants with an average density of 1 $\text{gm/cm}^3$ and specific impulse 300 seconds. The ideal velocity increment generated by either system is given by

$$\Delta V = I_{sp} g_0 \ln \left( \frac{m_{initial}}{m_{final}} \right)$$

(7.68)

where $g_0 = 9.8 \text{ m/sec}^2$. Two missions are under consideration.

1) Mission I involves maneuvering of a large satellite where the satellite empty mass ($m_{final}$) is 2000 kg and the required velocity increment is 100 m/sec.
2) Mission II involves a deep space mission where the vehicle empty mass \( (m_{final}) \) is 200 kg and the required velocity increment is 6000 m/sec.

The design requirement in both cases is to keep the tank volume required for the propellant as small as possible. Which propellant choice is best for each mission?

**Problem 4** - Recently one of the popular toys being sold was called a stomp rocket. The launcher consists of a flexible plastic bladder connected to a 1.5 cm diameter rigid plastic tube. The rocket is a slightly larger diameter rigid plastic tube, closed at the top end, about 20 cm long. The rocket weighs about 10 gm. The rocket slips over the tube as shown in Figure 7.9.

![Figure 7.9: Stomp rocket toy.](image)

Jumping on the bladder pressurizes the air inside and launches the rocket to a height which the manufacturer claims can exceed 50 m. The area of the bladder in contact with the ground is approximately 100 cm². Use basic principles of mechanics to roughly estimate how much a child would have to weigh to be able to achieve this height.

**Problem 5** - Consider a class of monopropellant thrusters based on the use of the noble gases including Helium \((M_w = 4)\), Neon \((M_w = 20)\), Argon \((M_w = 40)\), Krypton, \((M_w = 84)\) and Xenon \((M_w = 131)\). Radon \((M_w = 222)\) is excluded because of its radioactivity. The thruster is comprised of a tank that exhausts through a simple convergent nozzle to the vacuum of space. Onboard heaters are used to maintain the gas in the tank at a constant stagnation temperature \(T_{t2}\) as it is exhausted.

1) The thrust is often expressed in terms of an effective exhaust velocity \(T = \dot{m}C\). Show that the effective exhaust velocity of this system can be expressed as

\[
C = \left( \frac{2(\gamma + 1)}{\gamma} \left( \frac{R_u}{M_w} \right) T_{t2} \right)^{1/2}.
\] (7.69)
2) The mass of propellant contained in the tank is

\[ M_{\text{propellant}} = \frac{P_{t_2 \text{initial}} V_{\text{tan}} k M_w}{R_u T_{t_2}}. \]  \hspace{1cm} (7.70)

The initial tank pressure is some rated value (a do-not-exceed pressure) independent of the type of gas used. The designer would like to choose the propellant gas so that the velocity increment produced by the propulsion system \( \Delta V \) is as large as possible for fixed tank volume, initial pressure and gas temperature. The problem is to decide whether to choose a gas with low \( M_w \), thus achieving a high value of \( C \) but low propellant mass, or a gas with high \( M_w \) reducing \( C \) but increasing propellant mass. By mixing two or more gases, any mean atomic mass between 4 and 131 can be selected by the designer. Note that \( \gamma \) is the same regardless of what gas or mixture of gases is used.

Show that the maximum \( \Delta V \) occurs when the ratio \( M_{\text{propellant}} / M_{\text{structure}} \) is approximately 4 (actually 3.922). In other words, once the tank volume, pressure and temperature are determined and the vehicle empty mass is known, show that for maximum \( \Delta V \) the gas should be selected to have a mean atomic mass \( M_w \) such that

\[ \frac{P_{t_2 \text{initial}} V_{\text{tan}} k M_w}{R_u T_{t_2} M_{\text{structure}}} = 3.922. \]  \hspace{1cm} (7.71)

**Problem 6** - The space shuttle main engine has a nozzle throat diameter of 10.22 in a nozzle area ratio of 77.5 and produces 418,000 pounds of thrust at lift-off from Cape Canaveral. Determine the engine thrust when it reaches the vacuum of space.
Chapter 8

Multistage Rockets

8.1 Notation

With current technology and fuels, and without greatly increasing the effective $I_{sp}$ by air-breathing, a single stage rocket to Earth orbit is still not possible. So it is necessary to reach orbit using a multistage system where a certain fraction of the vehicle mass is dropped off after use, thus allowing the non-payload mass carried to orbit to be as small as possible. The final velocity of an $n$ stage launch system is the sum of the velocity gains from each stage.

\[ V_n = \Delta v_1 + \Delta v_2 + \Delta v_3 + \ldots + \Delta v_n \]  

(8.1)

The performance of an $n$-stage system can be optimized by proper selection of the structural mass, propellant mass and specific impulse of each of the $n$ stages.

Let the index $i$ refer to the $ith$ stage of an $n$ stage launch system. The structural and propellant parameters of the system are as follows.

$M_{0i}$ - The total initial mass of the $ith$ vehicle prior to firing including the payload mass, ie, the mass of $i, i+1, i+2, i+3, \ldots, n$ stages.

$M_{pi}$ - The mass of propellant in the $ith$ stage.

$M_{si}$ - Structural mass of the $ith$ stage alone including the mass of its engine, controllers and instrumentation as well as any residual propellant which is not expended by the end of the stage burn.

$M_L$ - The payload mass
Figure 8.1 schematically shows a three stage rocket at each regime of flight.

**Figure 8.1:** Three stage rocket notation.

Define the following variables.

**Payload ratio**

\[ \lambda_i = \frac{M_0(i+1)}{M_{0i} - M_{0(i+1)}} \]

\[ \lambda_n = \frac{M_0(n+1)}{M_{0n} - M_{0(n+1)}} = \frac{M_L}{M_{0n} - M_L} \] (8.2)

**Structural coefficient**

\[ \varepsilon_i = \frac{M_{SI}}{M_{0i} - M_{0(i+1)}} = \frac{M_{SI}}{M_{SI} + M_{PI}} \] (8.3)

**Mass ratio**
CHAPTER 8. MULTISTAGE ROCKETS

\[ R_i = \frac{M_{0i}}{M_{0i} - M_{P_i}} = \frac{1 + \lambda_i}{\epsilon_i + \lambda_i}. \]  
\hspace{1cm} (8.4)

**Ideal velocity increment**

\[ V_n = \sum_{i=1}^{n} C_i \ln \left( R_i \right) = \sum_{i=1}^{n} C_i \ln \left( \frac{1 + \lambda_i}{\epsilon_i + \lambda_i} \right). \]  
\hspace{1cm} (8.5)

**Payload fraction**

\[ \Gamma = \frac{M_L}{M_{01}} = \left( \frac{M_{02}}{M_{01}} \right) \left( \frac{M_{03}}{M_{02}} \right) \left( \frac{M_{04}}{M_{03}} \right) \cdots \left( \frac{M_{L}}{M_{0n}} \right) \]  
\hspace{1cm} (8.6)

\[ = \left( \frac{\lambda_1}{1 + \lambda_1} \right) \left( \frac{\lambda_2}{1 + \lambda_2} \right) \left( \frac{\lambda_3}{1 + \lambda_3} \right) \cdots \left( \frac{\lambda_n}{1 + \lambda_n} \right). \]

Take the logarithm of (8.6) to express the payload fraction as a sum in terms of the payload ratios

\[ \ln \left( \Gamma \right) = \sum_{i=1}^{n} \ln \left( \frac{\lambda_i}{1 + \lambda_i} \right). \]  
\hspace{1cm} (8.7)

**8.2 The variational problem**

The structural coefficients, \( \epsilon_i \) and effective exhaust velocities, \( C_i \), are known constants based on some prior choice of propellants and structural design for each stage. The question is: how should we distribute the total mass of the vehicle among the various stages? In other words, given \( V_n \), choose the distribution of stage masses so as to maximize the payload fraction, \( \Gamma \). It turns out that the alternative statement, given \( \Gamma \) maximize the final velocity \( V_n \), leads to the same distribution of stage masses.

The mathematical problem is to maximize

\[ \ln \left( \Gamma \right) = G (\lambda_1, \lambda_2, \lambda_3, \ldots, \lambda_n) \]  
\hspace{1cm} (8.8)

for fixed

\[ V_n = F (\lambda_1, \lambda_2, \lambda_3, \ldots, \lambda_n) \]  
\hspace{1cm} (8.9)
or, equivalently, maximize (8.9) for fixed (8.8). The approach is to vary the payload ratios, 
\( (\lambda_1, \lambda_2, \lambda_3, \ldots, \lambda_n) \), so as to maximize \( \Gamma \). Near a maximum, a small change in the \( \lambda_i \) will not change \( G \).

\[
\delta G = \left( \frac{\partial G}{\partial \lambda_i} \right) \delta \lambda_i = 0 \quad (8.10)
\]

The basic idea is shown in Figure 8.2.

![Figure 8.2: Variation of \( G \) near a maximum.](image)

The \( \delta \lambda_i \) are not independent, they must be chosen so that \( V_n \) is kept constant.

\[
\delta F = \left( \frac{\partial F}{\partial \lambda_i} \right) \delta \lambda_i = 0 \quad (8.11)
\]

Thus only \( n - 1 \) of the \( \lambda_i \) can be treated as independent. Without loss of generality let’s choose \( \lambda_n \) to be determined in terms of the other payload ratios. The sums (8.10) and (8.11) are

\[
\begin{align*}
\sum_{i=1}^{n-1} \left( \frac{\partial G}{\partial \lambda_i} \right) \delta \lambda_i + \left( \frac{\partial G}{\partial \lambda_n} \right) \delta \lambda_n &= 0 \\
\sum_{i=1}^{n-1} \left( \frac{\partial F}{\partial \lambda_i} \right) \delta \lambda_i + \left( \frac{\partial F}{\partial \lambda_n} \right) \delta \lambda_n &= 0
\end{align*}
\]

(8.12)

Use the second sum in (8.12) to replace \( \lambda_n \) in the first
\[ \sum_{i=1}^{n-1} \left\{ \left( \frac{\partial G}{\partial \lambda_i} \right) + \frac{1}{\alpha} \left( \frac{\partial F}{\partial \lambda_i} \right) \right\} \delta \lambda_i = 0 \quad (8.13) \]

where

\[ \alpha = -\left( \frac{\partial F}{\partial \lambda_n} \right) / \left( \frac{\partial G}{\partial \lambda_n} \right) \quad (8.14) \]

plays the role of a Lagrange multiplier. Since the equality (8.13) must hold for arbitrary \( \delta \lambda_i \), the coefficients in brackets must be individually zero.

\[ \left( \frac{\partial G}{\partial \lambda_i} \right) + \frac{1}{\alpha} \left( \frac{\partial F}{\partial \lambda_i} \right) = 0; \quad i = 1, 2, 3, \ldots, n-1 \quad (8.15) \]

From the definition of \( \alpha \) given by (8.14)

\[ \left( \frac{\partial G}{\partial \lambda_n} \right) + \frac{1}{\alpha} \left( \frac{\partial F}{\partial \lambda_n} \right) = 0. \quad (8.16) \]

We now have \( n+1 \) equations in the \( n+1 \) unknowns \((\lambda_1, \lambda_2, \lambda_3, \ldots, \lambda_n, \alpha)\).

\[ \begin{aligned} 
\left( \frac{\partial G}{\partial \lambda_i} \right) + \frac{1}{\alpha} \left( \frac{\partial F}{\partial \lambda_i} \right) &= 0; \quad i = 1, 2, 3, \ldots, n \\
V_n &= \sum_{i=1}^{n} C_i \ln \left( \frac{1 + \lambda_i}{\varepsilon_i + \lambda_i} \right) 
\end{aligned} \quad (8.17) \]

If we supply the expressions for \( F \) and \( G \) in (8.17) the result for the optimal set of payload ratios is (no sum on the index \( i \))

\[ \lambda_i = \frac{\alpha \varepsilon_i}{(C_i - C_i \varepsilon_i - \alpha)} \quad (8.18) \]

The Lagrange multiplier is determined from the expression for \( V_n \).

\[ V_n = \sum C_i \ln \left( \frac{C_i - \alpha}{\varepsilon_i C_i} \right) \quad (8.19) \]

Note that \( \alpha \) has units of velocity. Finally, the optimum overall payload fraction is
\[ \ln (\Gamma) = \sum_{i=1}^{n} \ln \left( \frac{\alpha \varepsilon_i}{(C_i - C_i \varepsilon_i - \alpha + \alpha \varepsilon_i)} \right). \] (8.20)

### 8.3 Example - exhaust velocity and structural coefficient the same for all stages

Let \( C_i = C \) and \( \varepsilon_i = \varepsilon \) be the same for all stages. In this case

\[ \alpha = C \left(1 - \varepsilon e^{\left(\frac{V_n}{\alpha C}\right)}\right). \] (8.21)

The payload ratio is

\[ \lambda = \frac{1 - \varepsilon e^{\left(\frac{V_n}{\alpha C}\right)}}{e^{\left(\frac{V_n}{\alpha C}\right)} - 1}. \] (8.22)

The payload fraction is

\[ \Gamma = \left(\frac{1 - \varepsilon e^{\left(\frac{V_n}{\alpha C}\right)}}{(1 - \varepsilon) e^{\left(\frac{V_n}{\alpha C}\right)}}\right)^n \] (8.23)

and the mass ratio is

\[ R = e^{\left(\frac{V_n}{\alpha C}\right)}. \] (8.24)

Consider a liquid oxygen, kerosene system. Take the specific impulse to be 360 sec implying \( C = 3528 \text{ m/sec} \); a very high performance system. Let \( V_n = 9077 \text{ m/sec} \) needed to reach orbital speed. The structural coefficient is \( \varepsilon = 0.1 \) and let the number of stages be \( n = 3 \). The stage design results are \( \alpha = 2696 \text{ m/sec} \), \( \lambda = 0.563 \), \( R = 2.3575 \) and the payload fraction is

\[ \Gamma = 0.047. \] (8.25)

Less than 5% of the overall mass of the vehicle is payload. It is of interest to see how much better we can do by increasing the number of stages in this problem. Equation (8.23) is plotted in Figure 8.3 using the parameters of the problem.
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8-7

Figure 8.3: Payload fraction as a function of number of stages for a constant parameter high performance launch vehicle.

It is clear that beyond three stages, there is very little increase in payload. Note also that one stage cannot make orbit even with zero payload for the assumed value of $\varepsilon$.

8.4 Problems

Problem 1 - A two stage rocket is to be used to put a payload of 1000 $kg$ into low earth orbit. The vehicle will be launched from Kennedy Space Center where the speed of rotation of the Earth is 427 $m/sec$. Assume gravitational velocity losses of about 1200 $m/sec$ and aerodynamic velocity losses of 500 $m/sec$. The first stage burns kerosene and oxygen producing a mean specific impulse of 320 sec averaged over the flight, while the upper stage burns hydrogen and oxygen with an average specific impulse of 450 sec. The structural coefficient of the first stage is 0.05 and that of the second is 0.07. Determine the payload ratios and the total mass of the vehicle. Suppose the same vehicle is to be used to launch a satellite into a north-south orbit from a launch complex on Kodiak island in Alaska. How does the mass of the payload change?

Problem 2 - A group of universities join together to launch a four stage rocket with a small payload to the Moon. The fourth stage needs to reach the earth escape velocity of 11,176 $m/sec$. The vehicle will be launched from Kennedy Space Center where the speed of rotation of the Earth is 427 $m/sec$. Assume gravitational velocity losses of about 1500 $m/sec$ and aerodynamic velocity losses of 600 $m/sec$. To keep cost down, four stages with the same effective exhaust velocity $C$ and structural coefficient $\varepsilon$ are used. Each stage burns kerosene and oxygen producing a mean specific impulse of 330 sec averaged over each segment of the flight. The structural coefficient of each stage is $\varepsilon = 0.1$. Is the payload
Problem 3 - A low-cost four stage rocket is to be used to launch small payloads to orbit. The concept proposed for the system utilizes propellants that are safe and cheap but provide a specific impulse of only $200\,\text{sec}$. All four stages are identical. What structural efficiency is required to reach orbit with a finite payload?
Chapter 9

Thermodynamics of reacting mixtures

9.1 Introduction

For an open system containing several reacting chemical species that can exchange mass and work with its surroundings the fundamental Gibbs equation relating equilibrium states is

$$TdS = dE + PdV - \sum_{i=1}^{I} \mu_i dn_i + \sum_{k=1}^{K} F_k dl_k.$$  \hspace{0.5cm} (9.1)

The $F_k$ are forces that can act on the system through differential displacements. Ordinarily, lower case letters will be used to denote intensive (per unit mole) quantities ($h,s,e,etc$) and upper case will designate extensive quantities ($H,S,E,etc$). Heat capacities, pressure and temperature are symbolized in capital letters. One mole is an Avagadro’s number of molecules, $6.0221415 \times 10^{23}$.

The chemical potential energy per unit mole $\mu_i$ is the amount by which the extensive energy of the system is changed when a differential number of moles $dn_i$ of species $i$ is added or removed from the system. If the system is closed so no mass can enter or leave and if it is isolated from external forces, the Gibbs equation becomes

$$TdS = dE + PdV - \sum_{i=1}^{I} \mu_i dn_i$$  \hspace{0.5cm} (9.2)
where the differential changes in the number of moles of species \( i \) occur through chemical reactions that may take place within the closed volume. The main difference between (9.1) and (9.2) is that, in the closed system, changes in mole numbers are subject to the constraint that the number of atoms of each element in the system is strictly constant. The precise expression of the chemical potential in terms of conventional thermodynamic variables of state will be established shortly. For the present it can be regarded as a new, intensive state variable for the species \( i \). Mathematically, equation (9.2) implies that

\[
\mu_i (E, V, n_1, \ldots, n_I) = -T \left( \frac{\partial S}{\partial n_i} \right)_{E, V, n_j \neq i}.
\]  

(9.3)

If no reactions occur then (9.2) reduces to the familiar form

\[
TdS = dE + PdV.
\]  

(9.4)

According to the second law of thermodynamics, for any process of a closed, isolated system

\[
TdS \geq dE + PdV.
\]  

(9.5)

Spatial gradients in any variable of the system can lead to an increase in the entropy. Smoothing out of velocity gradients (kinetic energy dissipation) and temperature gradients (temperature dissipation) constitute the two most important physical mechanisms that contribute to the increase in entropy experienced by a non-reacting system during a non-equilibrium process. If the system contains a set of chemical species that can mix, then changes in entropy can also occur through the smoothing out of concentration gradients for the various species. If the species can react, then entropy changes will occur through changes in the chemical binding energy of the various species undergoing reactions.

The inequality (9.5) can be used to establish the direction of a thermodynamic system as it evolves toward a state of equilibrium.

### 9.2 Ideal mixtures

Consider a mixture of species with mole numbers \( n_1, n_2, \ldots, n_I \). The extensive internal energy of the system is \( E \) and the volume is \( V \). The extensive entropy of the system is the function, \( S (E, V, n_1, n_2, \ldots, n_I) \). An ideal mixture is one where all molecules experience the same intermolecular forces. In an ideal mixture surface effects, (surface energy and surface tension) can be neglected and the enthalpy change when the constituents are mixed is
zero. Ideal mixtures obey Raoult’s law that states that the vapor pressure of a component of an ideal mixture is equal to the vapor pressure of the pure component times the mole fraction of that component in the mixture. In the ideal approximation the volume of the system is the sum of the volumes occupied by the pure species alone. Similarly the internal energy is the sum of internal energies of the pure species. Most real mixtures approximate ideal behavior to one degree or another. A mixture of ideal gases is perhaps the best example of an ideal mixture. Liquid mixtures where the component molecules are chemically similar, such as a mixture of benzene and toluene, behave nearly ideally. Mixtures of strongly different molecules such as water and alcohol deviate considerably from ideal behavior.

Let the mole numbers of the mixture be scaled by a common factor \( \alpha \).

\[
\begin{align*}
n_1 &= \alpha \tilde{n}_1, \quad n_2 = \alpha \tilde{n}_2, \quad n_3 = \alpha \tilde{n}_3, \ldots, \quad n_I = \alpha \tilde{n}_I
\end{align*}
\]  
(9.6)

According to the ideal assumption, the extensive properties of the system will scale by the same factor.

\[
E = \alpha \tilde{E}, \quad V = \alpha \tilde{V}
\]  
(9.7)

Similarly the extensive entropy of the system scales as

\[
S(E,V,n_1,\ldots,n_I) = \alpha \tilde{S}(\tilde{E},\tilde{V},\tilde{n}_1,\ldots,\tilde{n}_I).
\]  
(9.8)

Functions that follow this scaling are said to be homogeneous functions of order one. Differentiate (9.8) with respect to \( \alpha \).

\[
\begin{align*}
\tilde{E} \frac{\partial S}{\partial \tilde{E}} + \tilde{V} \frac{\partial S}{\partial \tilde{V}} + \sum_{i=1}^{I} \tilde{n}_i \frac{\partial S}{\partial \tilde{n}_i} &= \tilde{S}(\tilde{E},\tilde{V},\tilde{n}_1,\ldots,\tilde{n}_I)
\end{align*}
\]  
(9.9)

Multiply (9.9) by \( \alpha \) and substitute (9.8).

\[
\begin{align*}
\tilde{E} \frac{\partial S}{\partial \tilde{E}} + \tilde{V} \frac{\partial S}{\partial \tilde{V}} + \sum_{i=1}^{I} n_i \frac{\partial S}{\partial n_i} &= S(E,V,n_1,\ldots,n_I)
\end{align*}
\]  
(9.10)

The Gibbs equation is
\[
\frac{dS}{T} = \frac{dE}{T} + \frac{P}{T} dV - \sum_{i=1}^{I} \frac{\mu_i}{T} dn_i. \tag{9.11}
\]

According to (9.11) the partial derivatives of the entropy are

\[
\frac{\partial S}{\partial E} = \frac{1}{T} \quad \frac{\partial S}{\partial V} = \frac{P}{T} \quad \frac{\partial S}{\partial n_i} = -\frac{\mu_i}{T}. \tag{9.12}
\]

Inserting (9.12) into (9.10) leads to a remarkable result for an ideal mixture.

\[
E + PV - TS = \sum_{i=1}^{I} n_i \mu_i \tag{9.13}
\]

Equation (9.13) is called the Duhem-Gibbs relation. The combination of state variables that appears in (9.13) is called the Gibbs free energy.

\[
G = E + PV - TS = H - TS \tag{9.14}
\]

Equation (9.13) expresses the extensive Gibbs free energy of an ideal mixture in terms of the mole numbers and chemical potentials.

\[
G = \sum_{i=1}^{I} n_i \mu_i \tag{9.15}
\]

This important result shows that the chemical potential of species \(i\) is not really a new state variable but is defined in terms of the familiar state variables, enthalpy, temperature and entropy. The chemical potential of species \(i\) is its molar Gibbs free energy.

\[
\mu_i = g_i = h_i - Ts_i \tag{9.16}
\]

The enthalpy in (9.16) includes the chemical enthalpy associated with the formation of the species from its constituent elements.
9.3 Criterion for equilibrium

The Gibbs free energy is sometimes described as the "escaping tendency" of a substance. At low temperatures the enthalpy dominates. A chemical species with a positive enthalpy would like to break apart releasing some of its chemical enthalpy as heat and producing products with lower enthalpy. A few examples are ozone ($O_3$), hydrogen peroxide ($H_2O_2$), and nitrous oxide ($N_2O$). These are stable chemicals at room temperature but will decompose readily if their activation energy is exceeded in the presence of a heat source or a catalyst. The entropy of any substance is positive and at high temperatures the entropy term dominates the Gibbs free energy. In a chemical reaction the Gibbs free energy of any species or mixture will increasingly tend toward a state of higher entropy and lower Gibbs free energy as the temperature is increased. Take the differential of the Gibbs free energy.

$$dG = dE + PdV + VdP - TdS - SdT$$  \hspace{1cm} (9.17)

For a process that takes place at constant temperature and pressure $dT = dP = 0$. The Second Law (9.5) leads to the result that for such a process

$$dG = dE + PdV - TdS \leq 0.$$ \hspace{1cm} (9.18)

A spontaneous change of a system at constant temperature and pressure leads to a decrease of the Gibbs free energy. Equilibrium of the system is established when the Gibbs free energy reaches a minimum. This result leads to a complete theory for the equilibrium of a reacting system.

9.4 The entropy of mixing

Consider the adiabatic system shown in Figure 9.1 consisting of a set of $(n_1, n_2, \ldots, n_i, \ldots, n_I)$ moles of gas species segregated into volumes of various sizes such that the volumes are all at the same temperature and pressure.

\begin{center}
\begin{tabular}{|c|c|c|}
\hline
\multicolumn{3}{|c|}{\text{P,T}} \\
\hline
\text{n_1} & \text{n_2} & \text{n_i} \\
\text{n_j} & \text{\ldots} & \text{n_I} \\
\hline
\end{tabular}
\end{center}

Figure 9.1: A system of gases separated by partitions.
The total number of moles in the system is

$$N = \sum_{i=1}^{l} n_i.$$  \hspace{1cm} (9.19)

The entropy per unit mole of an ideal gas is determined using the Gibbs equation

$$ds = C_p \frac{dT}{T} - R_a \frac{dP}{P}$$  \hspace{1cm} (9.20)

where the units of $C_p$ are Joules/(mole−Kelvin). Tabulations of gas properties are always defined with respect to a reference temperature and standard pressure. The reference temperature is universally agreed to be $T_{ref} = 298.15$ K and the standard pressure is

$$P^o = 10^5 \, N/m^2 = 10^5 \, Pascals = 10^2 \, kPa = 1 \, bar.$$  \hspace{1cm} (9.21)

All pressures are referred to $P^o$ and the superscript "$^o$" denotes a species property evaluated at standard pressure. A cautionary note: In 1999 the International Union of Pure and Applied Chemistry (IUPAC) recommended that for evaluating the properties of all substances, the standard pressure should be taken to be precisely 100 kPa. Prior to this date, the standard pressure was taken to be one atmosphere at sea level, which is 101.325 kPa. Tabulations prior to 1999 are standardized to this value. The main effect is a small change in the standard entropy of a substance at a given temperature tabulated before and after 1999. There are also small differences in heat capacity and enthalpy as well. The IUPAC continues to provide standards for chemistry calculations and chemical nomenclature.

The pressure has no effect on the heat capacity of ideal gases, and for many condensed species the effect of pressure on heat capacity is relatively small. For this reason, tabulations of thermodynamic properties at standard pressure can be used to analyze a wide variety of chemical phenomena involving condensed and gas phase mixtures. Inaccuracies occur when evaluations of thermodynamic properties involve phase changes or critical phenomena where wide deviations from the ideal gas law occur, or condensed phases exhibit significant compressibility.

Integrating (9.20) from the reference temperature at standard pressure, the entropy per unit mole of the $ith$ gas species is

$$s_i(T, P) - s_i(T_{ref}) = \int_{T_{ref}}^{T} C_p^i (T) \frac{dT}{T} - R_a \ln \left( \frac{P}{P^o} \right).$$  \hspace{1cm} (9.22)
where the molar heat capacity \( C_{\pi i}^0 \) is tabulated as a function of temperature at standard pressure. The standard entropy of a gas species at the reference temperature is

\[
s_i^0(T_{\text{ref}}) = \int_0^{T_{\text{ref}}} C_{\pi i}^0(T) \frac{dT}{T} + s_i^0(0) \tag{9.23}
\]

where the integration is carried out at \( P = P^o \). To evaluate the standard entropy, heat capacity data is required down to absolute zero. For virtually all substances, with the exception of superfluid helium (II), the heat capacity falls off rapidly as \( T \to 0 \) so that the integral in (9.23) converges despite the apparent singularity at \( T = 0 \). From the third law, the entropy constant at absolute zero, \( s_i^0(0) \), is generally taken to be zero for a pure substance in its simplest crystalline state. For alloys and pure substances such as CO where more than one crystalline structure is possible, the entropy at absolute zero may be nonzero and tabulated entropy data for a substance may be revised from time to time as new research results become available. Generally the entropy constant is very small.

The entropy per unit mole of the \( i \)th gas species is

\[
s_i(T, P) = s_i^0(T) - R_u \ln \left( \frac{P_i}{P^o} \right). \tag{9.24}
\]

The entire effect of pressure on the system is in the logarithmic term of the entropy. The extensive entropy of the whole system before mixing is

\[
S_{\text{before}} = \sum_{i=1}^{I} n_is_i(T, P) = \sum_{i=1}^{I} n_is_i^0(T) - \sum_{i=1}^{I} n_iR_u \ln \left( \frac{P_i}{P^o} \right). \tag{9.25}
\]

Figure 9.2: System of gases with the partitions removed at the same pressure, temperature and total volume as in Figure 9.1.

If the partitions are removed as shown in Figure 9.2 then, after complete mixing, each gas takes up the entire volume and the entropy of the \( i \)th species is

\[
s_i(T, P_i) = s_i^0(T) - R_u \ln \left( \frac{P_i}{P^o} \right). \tag{9.26}
\]
where \( P_i \) is the partial pressure of the \( i \)th species. The mixture is ideal so there is no enthalpy change during the mixing. If the pressure was so high that the potential energy associated with inter-molecular forces was significant then the enthalpy of mixing would be non-zero.

The entropy of the system after mixing is

\[
S_{\text{after}} = \sum_{i=1}^{l} n_i s_i^\circ (T) = \sum_{i=1}^{l} n_i s_i^\circ (T) - \sum_{i=1}^{l} n_i R_u \ln \left( \frac{P_i}{P_0^i} \right). \quad (9.27)
\]

The change of entropy due to mixing is

\[
S_{\text{after}} - S_{\text{before}} = \left( \sum_{i=1}^{l} n_i s_i^\circ (T) - \sum_{i=1}^{l} n_i R_u \ln \left( \frac{P_i}{P_0^i} \right) \right) - \left( \sum_{i=1}^{l} n_i s_i^\circ (T) - \sum_{i=1}^{l} n_i R_u \ln \left( \frac{P}{P_0} \right) \right). \quad (9.28)
\]

Cancel common terms in (9.28).

\[
S_{\text{after}} - S_{\text{before}} = R_u \sum_{i=1}^{l} n_i \ln \left( \frac{P_i}{P_i^0} \right) > 0 \quad (9.29)
\]

Mixing clearly leads to an increase in entropy. To determine the law that governs the partial pressure let’s use the method of Lagrange multipliers to seek a maximum in the entropy after mixing subject to the constraint that

\[
P = \sum_{i=1}^{l} P_i. \quad (9.30)
\]

That is, we seek a maximum in the function

\[
W (T, n_1, n_2, ..., n_l, P_1, P_2, ..., P_l, \lambda) = \sum_{i=1}^{l} n_i s_i^\circ (T) - \sum_{i=1}^{l} n_i R_u \ln \left( \frac{P_i}{P_0^i} \right) + \lambda \left( \sum_{i=1}^{l} P_i - P \right) \quad (9.31)
\]

where \( \lambda \) is an, as yet unknown, Lagrange multiplier. The temperature of the system and number of moles of each species in the mixture are constant. Differentiate (9.31) and set the differential to zero for an extremum.
\[ dW = \frac{\partial W}{\partial P_1} dP_1 + \frac{\partial W}{\partial P_2} dP_2 + \ldots + \frac{\partial W}{\partial P_I} dP_I + \frac{\partial W}{\partial \lambda} d\lambda = 0 \] (9.32)

Now

\[ dW = -\sum_{i=1}^{I} n_i R_u \left( \frac{dP_i}{P_i} \right) + \lambda \left( \sum_{i=1}^{I} dP_i \right) + d\lambda \left( \sum_{i=1}^{I} P_i - P \right) = 0. \] (9.33)

The last term in (9.33) is zero by the constraint and the maximum entropy condition becomes.

\[ \sum_{i=1}^{I} \left( -\frac{n_i R_u}{P_i} + \lambda \right) dP_i = 0 \] (9.34)

Since the \(dP_i\) are completely independent, the only way (9.34) can be satisfied is if the Lagrange multiplier satisfies

\[ \lambda = \frac{n_i R_u}{P_i} \] (9.35)

for all \(i\). In the original, unmixed, system each species satisfies the ideal gas law.

\[ P V_i = n_i R_u T \] (9.36)

Using (9.35) and (9.36) we can form the sum

\[ \lambda \sum_{i=1}^{I} P_i = \sum_{i=1}^{I} \frac{P V_i}{T}. \] (9.37)

Finally the Lagrange multiplier is

\[ \lambda = \frac{V}{T} \] (9.38)

where, \(V = \sum_{i=1}^{I} V_i\). Using (9.35) and (9.38) the partial pressure satisfies

\[ P_i V = n_i R_u T \] (9.39)
which is Dalton’s law of partial pressures. What we learn from this exercise is, not only
that the entropy increases when the gases mix, but that the equilibrium state is one where
the entropy is a maximum. Using Dalton’s law, the mole fraction of the \( i \)th gas species is
related to the partial pressure as follows

\[
x_i = \frac{n_i}{N} = \frac{P_i}{P}
\]

(9.40)

The entropy of a mixture of ideal gases expressed in terms of mole fractions is

\[
S_{\text{gas}} = \sum_{i=1}^{l} n_i \left( s_{\text{gas}}^o (T) - R_u \ln (x_i) \right) - NR_u \ln \left( \frac{P}{P^o} \right)
\]

(9.41)

and the entropy change due to mixing, (9.29), is expressed as

\[
S_{\text{after}} - S_{\text{before}} = -NR_u \sum_{i=1}^{l} x_i \ln (x_i) > 0.
\]

(9.42)

### 9.5 Entropy of an ideal mixture of condensed species

The extensive entropy of an ideal mixture of condensed species (liquid or solid) with mole
numbers \( n_1, \ldots, n_l \) is \( S (T, P, n_1, \ldots, n_l) \). If \( s_{\text{pure}}^o (T, P) \) is the entropy of the pure form of
the \( i \)th component, then in a system where the mole numbers are fixed, the differential of
the entropy is

\[
dS (T, P, n_1, \ldots, n_l) = \sum_{i=1}^{l} n_i ds_{\text{pure}}^o (T, P)
\]

(9.43)

since \( dn_1 = 0, \ldots, dn_l = 0 \). If we integrate (9.43) the result is

\[
S (T, P, n_1, \ldots, n_l) = \sum_{i=1}^{l} n_i s_{\text{pure}}^o (T, P) + C (n_1, \ldots, n_l)
\]

(9.44)

with a constant of integration that is at most a function of the mole numbers.

In order to determine this constant we will use an argument first put forth by Max Planck
in 1932 and also described by Enrico Fermi in his 1956 book *Thermodynamics* (page 114).
Since the temperature and pressure in (9.44) are arbitrary let the pressure be reduced and the temperature be increased until all of the condensed species in the system are fully vaporized and behave as ideal gases as shown in Figure 9.3.

Figure 9.3: System of condensed species with the temperature increased and pressure decreased to fully vaporize the mixture.

Since the number of moles of each constituent has not changed, the constant of integration must be the same. The entropy of a system of ideal gases was discussed in the previous section and is given by equation (9.41).

\[
S_{gas} = \sum_{i=1}^{I} n_i \left( s_{i_{\text{gas}}}^\circ (T) - R_u \ln \left( \frac{P}{P^\circ} \right) \right) - \sum_{i=1}^{I} n_i R_u \ln \left( \frac{n_i}{N} \right) \tag{9.45}
\]

Comparing (9.44) with (9.45) we can conclude that the constant of integration must be

\[
C(n_1, \ldots, n_I) = -R_u \sum_{i=1}^{I} n_i \ln \left( \frac{n_i}{N} \right). \tag{9.46}
\]

Therefore, the entropy of a mixture of condensed species is

\[
S(T, P, n_1, \ldots, n_I) = \sum_{i=1}^{I} n_i \left( s_{i_{\text{pure}}}^\circ (T, P) - R_u \ln (x_i) \right) \tag{9.47}
\]

where the mole fraction, \( x_i = n_i / N \), is used. Finally, the contribution of each component to the extensive entropy of the mixture of condensed species is

\[
s_i(T, P) = s_{i_{\text{pure}}}^\circ (T, P) - R_u \ln (x_i). \tag{9.48}
\]
The form of this equation is very similar to that for gases and comes as something of a surprise since it involves the ideal gas constant which would seem to have no particular relevance to a liquid or a solid. According to Kestin (A Course in Thermodynamics, Ginn Blaisdell 1966) when (9.48) was first introduced it was "met with general incredulity, but its validity has since been confirmed experimentally beyond any reasonable doubt whatever."

It can be noted that if the gases in the mixing problem described in the last section were replaced by ideal liquids, and those liquids were allowed to evolve from the unmixed to the mixed state, the entropy change would be given by an expression identical to (9.29).

\[
(S_{\text{after}} - S_{\text{before}})_{\text{ideal liquids}} = -NR_u \sum_{i=1}^{I} x_i \ln (x_i) \tag{9.49}
\]

### 9.6 Thermodynamics of incompressible liquids and solids

For a single homogeneous substance the Gibbs equation is

\[
dS = \frac{dE}{T} + P \frac{dV}{T} \tag{9.50}
\]

If the substance is an incompressible solid or liquid the Gibbs equation reduces to

\[
dS = C_v(T) \frac{dT}{T} \tag{9.51}
\]

and the entropy is

\[
S - S_{\text{ref}} = \int_{T_{\text{ref}}}^{T} C_v(T) \frac{dT}{T}. \tag{9.52}
\]

The entropy and internal energy of an incompressible substance depend only on its temperature. The constant volume and constant pressure heat capacities are essentially equivalent \(C_p(T) = C_v(T) = C(T)\).

Since liquids and solids tend to be nearly incompressible, the entropy \(s_{\text{pure}}(T, P)\) tends to be independent of pressure and in most circumstances one can use

\[
s_{\text{pure}}(T, P) = s^0_i(T). \tag{9.53}
\]
Now the entropy of a condensed species in a mixture really does resemble that of an ideal gas, but without the dependence on mixture pressure.

\[ s_i(T, P) = s_{i}^{\circ}(T) - R_u \ln(x_i) \]  

(9.54)

For a general substance, the differential of the Gibbs function is

\[ dG = dE + PdV + VdP - TdS - SdT = -SdT + VdP \]  

(9.55)

where the Gibbs equation (9.4) has been used. The cross derivative test applied to the right side of (9.55) produces the Maxwell relation

\[ \left( \frac{\partial S}{\partial P} \right)_T = -\left( \frac{\partial V}{\partial T} \right)_P. \]  

(9.56)

For an incompressible material, the entropy is independent of the pressure and (9.56) implies that the coefficient of thermal expansion of the material is also zero. Therefore, for an incompressible substance

\[
\begin{align*}
\left( \frac{\partial V}{\partial P} \right)_T &= 0 \\
\left( \frac{\partial V}{\partial T} \right)_P &= 0 \\
V &= \text{constant} \\
C_P = C_V &= C \\
dE &= CdT \\
dS &= C_VdT \\
dH &= C_PdT + VdP.
\end{align*}
\]  

(9.57)

On a per unit mole basis, the enthalpy of an incompressible material referenced to the standard state is

\[ h(T, P) = h_{o}^{\circ}(T) + (P - P_{o}) v^{\circ} \]  

(9.58)

where \( v^{\circ} = \text{constant} \) is the molar volume of the material. The superscript on \( v^{\circ} \) is not really necessary since it assumed to be a constant at all pressures and temperatures but as a practical matter, when using (9.58) as an approximation for a real condensed solid or liquid, the value of the molar density will be taken to be at the standard pressure 10^5 Pa.
and the reference temperature 298.15 K. Often the pressure term in (9.58) is neglected when dealing with reacting systems of gases and condensed materials. The reason is that, while the molar enthalpy of the condensed and gaseous form of a species are of the same order, the molar volume of a solid or liquid is generally two to three orders of magnitude smaller than the gaseous molar volume.

### 9.7 Enthalpy

The enthalpy per unit mole of a gas is determined from

$$dh = C_p(T)dT.$$  

(9.59)

The enthalpy of a gas species is

$$h_i(T) - h_i(T_{ref}) = h_i^o(T) - h_i^o(T_{ref}) = \int_{T_{ref}}^{T} C_{pi}^o(T) dT.$$  

(9.60)

In principle the standard enthalpy of the $i$th gas species at the reference temperature could be taken as

$$h_i^o(T_{ref}) = \int_{0}^{T_{ref}} C_{pi}^o(T) dT + h_i^o(0).$$  

(9.61)

In this approach the enthalpy constant is the enthalpy change associated with chemical bond breaking and making that occurs when the atoms composing the species are brought together from infinity to form the molecule at absolute zero. Note that even for an atomic species, the enthalpy constant is not exactly zero. A quantum mechanical system contains energy or enthalpy arising from ground state motions that cannot be removed completely even at absolute zero temperature. In practice, enthalpies for most substances are tabulated as differences from the enthalpy at the reference temperature of 298.15 K which is much more easily accessible than absolute zero so the question of the zero point enthalpy rarely comes up. Thus the standard enthalpy of a species is

$$h_i^o(T) = \int_{T_{ref}}^{T} C_{pi}^o(T) dT + \Delta h_{f_i}^o(T_{ref})$$  

(9.62)

where $\Delta h_{f_i}^o(T)$ is the enthalpy change that occurs when the atoms of the species are brought together from at infinity at the finite temperature $T$. The enthalpy including the
heat of formation (9.62) is sometimes called the complete enthalpy. In practice certain con-
ventions are used to facilitate the tabulation of the heat of formation of a substance.

9.7.1 Enthalpy of formation and the reference reaction

The enthalpy of formation of a substance, denoted $\Delta h_f^{\circ} (T_{ref})$, is defined as the enthalpy
change that occurs when one mole of the substance is formed from its elements in their
reference state at the given temperature $T$ and standard pressure $P^\circ$. The reference state
for an element is generally taken to be its most stable state at the given temperature and
standard pressure. The reference reaction for a substance is one where the substance is the
single product of a chemical reaction between its elements in their most stable state.

This convention for defining the heat of formation of a substance is useful even if the
reference reaction is physically unlikely to ever actually occur. A consequence of this
definition is that the heat of formation of a pure element in its reference state at any
temperature is always zero. For example, the enthalpy of formation of any of the diatomic
gases is zero at all temperatures. This is clear when we write the trivial reaction to form,
for example hydrogen, from its elements in their reference state.

$$H_2 \rightarrow H_2$$  \hspace{1cm} (9.63)

The enthalpy change is clearly zero. In fact the change in any thermodynamic variable
for any element in its reference state is zero at all temperatures. A similar reference
reaction applies to any of the other diatomic species $O_2, N_2, F_2, Cl_2, Br_2, I_2$, and the heat
of formation of these substances is zero at all temperatures. The most stable form of carbon
is solid carbon or graphite and the reference reaction is

$$C_{(s)} \rightarrow C_{(s)}$$  \hspace{1cm} (9.64)

with zero heat of formation at all temperatures.

The reference reaction for carbon dioxide at 298.15K is

$$C_{(s)} + O_2 \rightarrow CO_2 \hspace{1cm} \Delta h_{fCO_2}^{\circ} (298.15) = -393.522 \text{kJ/mole.}$$  \hspace{1cm} (9.65)

Here the carbon is taken to be in the solid (graphite) form and the oxygen is taken to be
the diatomic form. Both are the most stable forms over a wide range of temperatures.
Even if the temperature is well above the point where carbon sublimes to a gas (3915K)
and significant oxygen is dissociated, the heats of formation of $C_{(s)}$ and $O_2$ remain zero
even though the most stable form of carbon at this temperature is carbon gas.
The heats of formation of metal elements are treated a little differently. The heat of formation of crystalline aluminum is zero at temperatures below the melting point and the heat of formation of liquid aluminum is zero at temperatures above the melting point. The same applies to boron, magnesium, sulfur, titanium and other metals.

The enthalpy (9.62) is usually expressed in terms of tabulated data as

$$h_i(T) = h_i^{\circ}(T) = \Delta h_i^{\circ}(T_{\text{ref}}) + \{h_i^{\circ}(T) - h_i^{\circ}(T_{\text{ref}})\}. \quad (9.66)$$

For a general reaction the enthalpy balance is

$$\Delta h^{\circ}(T_{\text{final}}) = \sum_{i_{\text{product}}} n_{i_{\text{product}}} h_{i_{\text{product}}}^{\circ}(T_{\text{final}}) - \sum_{i_{\text{reactant}}} n_{i_{\text{reactant}}} h_{i_{\text{reactant}}}^{\circ}(T_{\text{initial}_{\text{reactant}}}). \quad (9.67)$$

So for example, to determine the heat of formation of CO$_2$ at 1000 $K$ where the initial reactants are also at 1000 $K$, the calculation would be

$$\Delta h^{\circ}_{f\text{CO}_2}(1000) =$$

$$\left(\Delta h^{\circ}_{f\text{CO}_2}(298.15) + \{h^{\circ}_{f\text{CO}_2}(1000) - h^{\circ}_{f\text{CO}_2}(298.15)\}\right) -$$

$$\left(\Delta h^{\circ}_{f\text{C}^{(a)}}(298.15) + \{h^{\circ}_{f\text{C}^{(a)}}(1000) - h^{\circ}_{f\text{C}^{(a)}}(298.15)\}\right) -$$

$$\left(\Delta h^{\circ}_{f\text{O}_2}(298.15) + \{h^{\circ}_{f\text{O}_2}(1000) - h^{\circ}_{f\text{O}_2}(298.15)\}\right). \quad (9.68)$$

Putting in the numbers from tabulated data (See Appendix 2) gives

$$\Delta h^{\circ}_{f\text{CO}_2}(1000) =$$

$$[-393.522 + 33.397] - [0 + 11.795] - [0 + 22.703] = -394.623 \quad (9.69)$$

which is the tabulated value of the heat of formation of carbon dioxide at 1000 $K$. Note that the enthalpy of the reference reactants at the reaction temperature must be included in the calculation of the heat of formation calculation. Further discussion of heats of formation can be found in Appendix 1 and tables of thermo-chemical data for selected species can be found in Appendix 2.
9.8 Condensed phase equilibrium

The pressure and temperature of the system may be such that one or more or all of the species may be evolving with their condensed phase. In this case it may be necessary to vary the volume to keep the temperature and pressure constant until the system reaches equilibrium.

Figure 9.4 depicts the various species of the system in several phases all of which are in contact with each other. Let the total number of moles in each phase be \( N_1, N_2, \ldots, N_p, \ldots, N_P \). Generally only a subset of the species will be evolving with their condensed phase and so there is a different maximal index \( I_p \) for each phase. Effects of surface tensions between phases are ignored.

![Figure 9.4: System of molecular species with several phases.](image)

Note the total numbers of moles in each phase are related to the species mole numbers by

\[
N_1 = \sum_{i=1}^{I_1} n_{1i} \quad N_2 = \sum_{i=1}^{I_2} n_{2i} \quad \cdots \quad N_p = \sum_{i=1}^{I_P} n_{pi}.
\]

(9.70)

The mole fractions in each phase are

\[
x_{pi} = \frac{n_{pi}}{N_p}.
\]

(9.71)

In the gas phase, the partial pressures of the gas species add up to the mixture pressure

\[
P = \sum_{i=1}^{I_1} P_i.
\]

(9.72)
The mole fractions of the species in the gas phase are related to the partial pressures by

\[ x_{1i} = \frac{P_i}{P}. \]  

\[ (9.73) \]

Finally the mole fractions in each phase add to one.

\[ \sum_{i=1}^{I_p} x_{pi} = 1 \]

\[ (9.74) \]

The extensive Gibbs free energies in each phase are

\[ G_1 (T, P, n_{11}, n_{12}, n_{13}, ..., n_{1I_1}) = N_1 \left\{ \sum_{i=1}^{I_1} x_{1i} \left( g_{1i}^0(T) + R_u T \ln (x_{1i}) \right) + R_u T \ln \left( \frac{P}{P^0} \right) \right\} \]

\[ G_2 (T, P, n_{21}, n_{22}, n_{23}, ..., n_{2I_2}) = N_2 \sum_{i_2=1}^{I_2} x_{2i} \left( g_{2i}(T, P) + R_u T \ln (x_{2i}) \right) \]

\[ \vdots \]

\[ G_P (T, P, n_{P1}, n_{P2}, n_{P3}, ..., n_{PI_P}) = N_P \sum_{i_P=1}^{I_P} x_{pi} \left( g_{pi}(T, P) + R_u T \ln (x_{pi}) \right) \]

\[ (9.75) \]

where phase 1 is assumed to be the gas phase. In (9.75) we have assumed that all condensed phases are ideal mixtures and the entropy per mole of the condensed phase of species \( i \) does not depend on the pressure. This is a reasonable assumption for a condensed phase that is approximately incompressible as was argued earlier in conjunction with equation (9.58). There are a few examples of liquids such as liquid helium and liquid nitrous oxide that are quite compressible and the assumption would break down. This treatment of the condensed phases is similar to that used by Bill Reynolds in the development of STANJAN. The NASA Glenn code CEA is a little different. In CEA, each condensed phase is treated as a pure substance. For example, if there are two species that condense out as liquids, each is treated as a separate, distinct phase. In the approach used by CEA the mole fractions of each condensed species are one by definition. In CEA the pressure term in (9.58) is neglected. See equation 2.11 in NASA Reference Publication 1311 (1994) by Gordon and McBride.

In the case of a gas, the Gibbs free energy does depend on pressure through the dependence of entropy on pressure. This is connected to the fact that, as quantum mechanics tells us,
the number of energy states that a gas can occupy (and therefore the entropy of the gas) increases with the volume containing the gas (see Appendix 1 of the AA210a notes).

The Gibbs free energy of the whole system is

\[ G(T, P, n_{11}, n_{12}, \ldots, n_{1i}, n_{21}, n_{22}, \ldots, n_{2l}, \ldots, n_P, n_{PI}, \ldots) = \sum_{p=1}^{P} \sum_{i=1}^{I_P} n_{pi} g_{pi}(T, P, n_{pi}). \] (9.76)

With the gas phase written separately Equation (9.76) is

\[ G(T, P, n_{11}, n_{12}, \ldots, n_{1i}, n_{21}, n_{22}, \ldots, n_{2l}, \ldots, n_P, n_{PI}, \ldots) = \]

\[ \sum_{p=1}^{P} \sum_{i=1}^{I_P} n_{1i} \left( g_{1i}^o(T) + R_u T \ln(n_{1i}) - R_u T \ln \left( \sum_{i=1}^{I_1} n_{1i} \right) \right) + \]

\[ \sum_{p=2}^{P} \sum_{i=1}^{I_P} n_{pi} \left( g_{pi}(T, P) + R_u T \ln(n_{pi}) - R_u T \ln \left( \sum_{i=1}^{I_P} n_{pi} \right) \right). \] (9.77)

Differentiate (9.77).

\[ dG = \frac{\partial G}{\partial T} dT + \frac{\partial G}{\partial P} dP + \]

\[ \frac{\partial G}{\partial n_{11}} d n_{11} + \frac{\partial G}{\partial n_{12}} d n_{12} + \cdots + \frac{\partial G}{\partial n_{1I_1}} d n_{1I_1} + \]

\[ \frac{\partial G}{\partial n_{21}} d n_{21} + \frac{\partial G}{\partial n_{22}} d n_{22} + \cdots + \frac{\partial G}{\partial n_{2l}} d n_{2l} + \cdots + \]

\[ \frac{\partial G}{\partial n_{P1}} d n_{P1} + \frac{\partial G}{\partial n_{P2}} d n_{P2} + \cdots + \frac{\partial G}{\partial n_{PI}} d n_{PI}. \] (9.78)

Written out fully (9.78) is
\[ dG = \sum_{i=1}^{l_1} dn_{1i} \left( g_{1i}^o(T) + R_u T \ln(n_{1i}) - R_u T \ln \left( \sum_{i=1}^{l_1} n_{1i} \right) \right) + \]

\[ \sum_{i=1}^{l_1} n_{1i} \left( R_u T \left( \frac{dn_{1i}}{n_{1i}} \right) - R_u T \left( \frac{\sum_{i=1}^{l_1} n_{1i}}{l_1} \right) \right) + R_u T \ln \left( \frac{P}{P^o} \right) \sum_{i=1}^{l_1} dn_{1i} + \]

\[ \sum_{i=1}^{l_1} n_{1i} \left( \frac{\partial g_{1i}^o(T)}{\partial T} + R_u \ln(n_{1i}) - R_u \ln \left( \sum_{i=1}^{l_1} n_{1i} \right) \right) dT + \]

\[ \left( \sum_{i=1}^{l_1} n_{1i} \right) R_u T \left( \frac{dP}{P} \right) + \left( \sum_{i=1}^{l_1} n_{1i} \right) R_u \ln \left( \frac{P}{P^o} \right) dT + \]

\[ \sum_{p=2}^{l_p} \sum_{i=1}^{l_p} dn_{pi} \left( g_{pi}(T,P) + R_u T \ln(n_{pi}) - R_u T \ln \left( \sum_{i=1}^{l_p} n_{pi} \right) \right) + \]

\[ \sum_{p=2}^{l_p} \sum_{i=1}^{l_p} n_{pi} \left( R_u T \left( \frac{dn_{pi}}{n_{pi}} \right) - R_u T \left( \frac{\sum_{i=1}^{l_p} n_{pi}}{l_p} \right) \right) + \]

\[ \sum_{p=2}^{l_p} \sum_{i=1}^{l_p} n_{pi} \left( \frac{\partial g_{pi}(T,P)}{\partial T} \right) + R_u \ln(n_{1i}) - R_u \ln \left( \sum_{i=1}^{l_1} n_{1i} \right) \right) dT + \sum_{p=2}^{l_p} \sum_{i=1}^{l_p} n_{pi} \left( \frac{\partial g_{pi}(T,P)}{\partial T} \right) dP. \]

(9.79)

Note that

\[ \sum_{i=1}^{l_p} n_{pi} \left( \frac{dn_{pi}}{n_{pi}} - \frac{\sum_{i=1}^{l_p} n_{pi}}{\sum_{i=1}^{l_p} n_{pi}} \right) = dN_p - dN_p = 0. \]

(9.80)

At constant temperature and pressure \(dT = dP = 0\) and(9.79) becomes
\[
dG = \sum_{i=1}^{I_1} dn_{1i} \left( g_{1i}^o(T) + R_u T \ln (n_{1i}) - R_u T \ln \left( \sum_{i=1}^{I_1} n_{1i} \right) \right) + R_u T \ln \left( \frac{P}{P^o} \right) + \\
\sum_{p=2}^{P} \sum_{i=1}^{I_p} dn_{pi} \left( g_{pi}(T,P) + R_u T \ln (n_{pi}) - R_u T \ln \left( \sum_{i=1}^{I_p} n_{pi} \right) \right).
\]

(9.81)

In terms of mole fractions (9.81) reads

\[
dG = \sum_{i=1}^{I_1} dn_{1i} \left( g_{1i}^o(T) + R_u T \ln (x_{1i}) + R_u T \ln \left( \frac{P}{P^o} \right) \right) + \\
\sum_{p=2}^{P} \sum_{i=1}^{I_p} dn_{pi} \left( g_{pi}(T,P) + R_u T \ln (x_{pi}) \right).
\]

(9.82)

At equilibrium \(dG = 0\). For species that are only present in one phase, \(dn_{pi} = 0\) at equilibrium. For those species that are in equilibrium with another phase, \(dn_{\text{phase} pi} = -dn_{\text{phase}1i}\) and equation \(dG = 0\) can only be satisfied if

\[
g_{\text{phase}1i} = g_{\text{phase} pi}.
\]

(9.83)

If phase 1 is a gas species (9.83) is

\[
g_{\text{phase}1i}^o(T) + R_u T \ln (x_{\text{phase}1i}) + R_u T \ln \left( \frac{P}{P^o} \right) = g_{\text{phase} pi}^o(T,P) + R_u T \ln (x_{\text{phase} pi}).
\]

(9.84)

At equilibrium, the Gibbs free energy (or chemical potential) of species \(i\) is the same regardless of its phase. For example if gas species 1 is in equilibrium with its liquid phase, then \(g_{\text{gas}1}(T,P) = g_{\text{liquid}1}(T,P)\). There can also be more than one solid phase and so the total number of phases can exceed three. For example, in helium at very low temperature there can be multiple liquid phases.

Suppose phase \(p\) in is a pure liquid so the mole fraction is one. Also assume the liquid is incompressible so that the Gibbs function of the liquid is given by

\[
g_{\text{gas}i}^o(T) + R_u T \ln (x_{\text{gas}i}) + R_u T \ln \left( \frac{P}{P^o} \right) = g_{\text{liquid}i}^o(T) + (P - P^o) v_i^o.
\]

(9.85)
Solve for the partial pressure of the species in the gas phase.

\[ \frac{P_i}{P^\circ} = e^{\frac{(P - P^\circ) \varphi_{liq}^i}{R_u T}} \left( e^{\frac{\varphi_{liq}^i(T) - \varphi_{gas}^i(T)}{R_u T}} \right) \] (9.86)

The term in brackets is the classical form of the Clausius-Clapeyron equation that relates the vapor pressure of a gas in equilibrium with its condensed phase to the temperature of the system.

### 9.9 Chemical equilibrium, the method of element potentials

If the species are allowed to react at constant temperature and pressure, the mole fractions will evolve toward values that minimize the extensive Gibbs free energy of the system subject to the constraint that the number of moles of each element in the mixture remains fixed. The number of moles of each atom in the system is given by

\[ a_j = \sum_{p=1}^{P} \sum_{i=1}^{I_p} n_{pi} A_{pij} \] (9.87)

where \( A_{pij} \) is the number of atoms of the \( j \)th element in the \( i \)th molecular species of the \( p \)th phase. The appropriate picture of our system is shown in Figure 9.5.

Figure 9.5: System of reacting molecular species in several phases at constant temperature and pressure with fixed number of moles of each element.

Generally the number of species in each phase will be different. This may be the case even in a situation where, at a given temperature and pressure, there is phase equilibrium for a given species. Consider graphite in equilibrium with its vapor at low temperature, the mole fraction in the vapor phase may be so small as to be essentially zero and the species
may be rightly excluded from the vapor mixture. The volume required to maintain the system at constant pressure and temperature must be allowed to vary.

The Gibbs free energy of the system is

\[ G(T, P, n_{11}, n_{12}, ..., n_{p1}, ..., n_{PI}) = \sum_{p=1}^{P} N_p \sum_{i=1}^{I_p} x_{pi} g_{pi}(T, P, x_{pi}). \] (9.88)

With the gas phase written separately

\[ G(T, P, n_{11}, n_{12}, ..., n_{21}, ..., n_{PI}) = N_1 \sum_{i=1}^{I_1} x_{1i} (g_{1i}^\circ (T) + R_u T \ln (x_{1i})) + N_1 R_u T \ln \left( \frac{P}{P_\circ} \right) + \sum_{p=2}^{P} N_p \sum_{i=1}^{I_p} x_{pi} (g_{pi}(T, P) + R_u T \ln (x_{pi})). \] (9.89)

We will use the method of Lagrange multipliers to minimize the Gibbs free energy subject to the atom constraints. Minimize the function

\[ W(T, P, n_{11}, n_{12}, ..., n_{1I_1}, n_{21}, ..., n_{2I_2}, ..., n_{p1}, n_{p2}, ..., n_{pI_p}, \lambda_1, ..., \lambda_J) = G(T, P, n_{11}, n_{12}, ..., n_{1I_1}, n_{21}, ..., n_{2I_2}, ..., n_{p1}, n_{p2}, ..., n_{pI_p}) - R_u T \sum_{j=1}^{J} \lambda_j \left( \sum_{p=1}^{P} \sum_{i=1}^{I_p} n_{pi} A_{pij} - a_j \right). \] (9.90)

where the \( J \) unknown Lagrange multipliers, \( \lambda_j \), are dimensionless. Our modified equilibrium condition is

\[ dW = \frac{\partial W}{\partial T} dT + \frac{\partial W}{\partial P} dP + \frac{\partial W}{\partial n_{11}} dn_{11} + ... + \frac{\partial W}{\partial n_{pi}} dn_{pi} + \frac{\partial W}{\partial \lambda_1} d\lambda_1 + ... + \frac{\partial W}{\partial \lambda_J} d\lambda_J = 0. \] (9.91)

Substitute (9.76) into (9.91) and impose \( dP = dT = 0 \).

\[ dW = \sum_{p=1}^{P} \sum_{i=1}^{I_p} n_{pi} g_{pi}(T, P, x_{pi}) g_{pi}(T, P, x_{pi}) + g_{pi}(T, P, x_{pi}) + R_u T \sum_{j=1}^{J} \lambda_j \sum_{p=1}^{P} \sum_{i=1}^{I_p} d\lambda_j A_{pij}. \] (9.92)
The order of the sums can be rearranged so (9.92) can be written as

\[ dW = \sum_{p=1}^{P} \sum_{i=1}^{I_p} n_{pi} dg_{pi} (T, P, x_{pi}) + \sum_{p=1}^{P} \sum_{i=1}^{I_p} \left( g_{pi} (T, P, x_{pi}) - R_u T \sum_{j=1}^{J} \lambda_j A_{pij} \right) dn_{pi} = 0. \]  

(9.93)

The differential of the molar Gibbs free energy is

\[ dg_{pi} = \frac{\partial g_{pi}}{\partial T} dT + \frac{\partial g_{pi}}{\partial P} dP + R_u T \frac{dx_{pi}}{x_{pi}}. \]  

(9.94)

For a process that takes place at constant temperature and pressure

\[ dW = R_u T \sum_{p=1}^{P} \sum_{i=1}^{I_p} n_{pi} \frac{dx_{pi}}{x_{pi}} + \sum_{p=1}^{P} \sum_{i=1}^{I_p} \left( g_{pi} (T, P, x_{pi}) - R_u T \sum_{j=1}^{J} \lambda_j A_{pij} \right) dn_{pi} = 0. \]  

(9.95)

The first sum in (9.95) can be re-written as follows

\[ dW = R_u T \sum_{p=1}^{P} N_p \sum_{i=1}^{I_p} dx_{pi} + \sum_{p=1}^{P} \sum_{i=1}^{I_p} \left( g_{pi} (T, P, x_{pi}) - R_u T \sum_{j=1}^{J} \lambda_j A_{pij} \right) dn_{pi} = 0 \]  

(9.96)

or

\[ dW = R_u T \sum_{p=1}^{P} N_p \sum_{i=1}^{I_p} dx_{pi} - \sum_{p=1}^{P} \sum_{i=1}^{I_p} \left( g_{pi} (T, P, x_{pi}) - R_u T \sum_{j=1}^{J} \lambda_j A_{pij} \right) dn_{pi} = 0. \]  

(9.97)

But the normalization conditions for the mole fractions of each phase imply that

\[ \sum_{i=1}^{I_p} dx_{pi} = d \left( \sum_{i=1}^{I_p} x_{pi} \right) = d (1) = 0. \]  

(9.98)
\[ dW = \sum_{p=1}^{P} \sum_{i=1}^{I_p} \left( g_{pi} (T, P, x_{pi}) - R_u T \sum_{j=1}^{J} \lambda_j A_{pij} \right) \, dn_{pi} = 0. \] (9.99)

Since the \( dn_{pi} \) are completely free, the condition (9.99) can only be satisfied if

\[ g_{pi} (T, P, x_{pi}) = R_u T \sum_{j=1}^{J} \lambda_j A_{pij}. \] (9.100)

The Gibbs free energy of the system is

\[ G (T, P, n_{11}, n_{12}, ..., n_{p1}, ..., n_{PI_P}) = R_u T \sum_{p=1}^{P} \sum_{i=1}^{I_p} \sum_{j=1}^{J} n_{pi} \lambda_j A_{pij}. \] (9.101)

Each atom in the mixture contributes equally to the extensive Gibbs free energy regardless of which molecule it is in or which phase it is in. The molar Gibbs free energy of the \( ith \) gas phase species is

\[ g_{1i}(T, P) = g_{1i}^\circ(T) + R_u T \ln (x_{1i}) + R_u T \ln \left( \frac{P}{P_{1i}} \right). \] (9.102)

Insert into (9.100). For the gas phase species

\[ \frac{g_{1i}^\circ(T)}{R_u T} + \ln (x_{1i}) + \ln \left( \frac{P}{P_{1i}} \right) = \sum_{j=1}^{J} \lambda_j A_{1ij}. \] (9.103)

For the condensed phase species

\[ \frac{g_{pi}(T, P)}{R_u T} + \ln (x_{pi}) = \sum_{j=1}^{J} \lambda_j A_{pij} \quad p = 2, \ldots, P. \] (9.104)

Solve for the mole fraction of the \( ith \) species in the \( pth \) phase.
\[ x_{1i} = \exp \left\{ \frac{g_{1i}(T)}{R_u T} - \ln \left( \frac{P}{P^\circ} \right) + \sum_{j=1}^{J} \lambda_{ji} A_{1ij} \right\} \]
\[ x_{pi} = \exp \left\{ -\frac{g_{pi}(T, P)}{R_u T} + \sum_{j=1}^{J} \lambda_{pj} A_{pij} \right\} \quad p = 2, \ldots, P \]

The constraints on the atoms are

\[ a_j = \sum_{p=1}^{P} N_p \sum_{i=1}^{I_p} x_{pi} A_{pij}. \]  

Substitute (9.105) into (9.106).

\[ a_j = N_1 \sum_{i=1}^{I_1} A_{1ij} \exp \left\{ -\frac{g_{1i}(T)}{R_u T} - \ln \left( \frac{P}{P^\circ} \right) + \sum_{j=1}^{J} \lambda_{ji} A_{1ij} \right\} + \]
\[ \sum_{p=2}^{P} N_p \sum_{i=1}^{I_p} A_{pij} \exp \left\{ -\frac{g_{pi}(T, P)}{R_u T} + \sum_{j=1}^{J} \lambda_{pj} A_{pij} \right\} \quad j = 1, \ldots, J. \]  

Note that we have to introduce the dummy index \( j_1 \) in the formula for \( x_{pi} \) when we make the substitution. The normalization conditions on the mole fractions give

\[ \left\{ -\frac{g_{1i}(T)}{R_u T} - \ln \left( \frac{P}{P^\circ} \right) + \sum_{j=1}^{J} \lambda_{ji} A_{1ij} \right\} = 1 \]  

and

\[ \sum_{i=1}^{I_p} \exp \left\{ -\frac{g_{pi}(T, P)}{R_u T} + \sum_{j=1}^{J} \lambda_{pj} A_{pij} \right\} = 1 \quad p = 2, \ldots, P. \]  

The total number of moles in the mixture is

\[ \sum_{p=1}^{P} N_p = N. \]
Equations, (9.107), (9.108), (9.109) and (9.110) are \( J + P + 1 \) equations in the unknowns \( \lambda_1, ..., \lambda_J, N_1, ..., N_P \) and \( N \).

As a practical matter, it is easier to compute the solution to equations (9.107), (9.108), (9.109) and (9.110) by reformulating the equations to get rid of the exponentials. Define

\[
B_{1i}(T) \equiv \exp \left\{ -\frac{g^{\circ}_{1i}(T)}{R_uT} \right\} 
\]

(9.111)

and for the condensed species, \( p > 1 \)

\[
B_{pi}(T, P) \equiv \exp \left\{ -\frac{g_{pi}(T, P)}{R_uT} \right\} .
\]

(9.112)

In addition, define

\[
y_j = \exp (\lambda_j).
\]

(9.113)

The mole fractions become

\[
x_{1i} = \left( \frac{P^o}{P} \right) B_{1i} \prod_{j=1}^{J} (y_j)^{A_{1ij}}
\]

\[
x_{pi} = B_{pi} \prod_{j=1}^{J} (y_j)^{A_{pij}} \quad p = 2, \ldots, P.
\]

(9.114)

The system of equations that needs to be solved now becomes
\[
\left( \frac{P^\circ}{P} \right) N_1 \sum_{i=1}^{I_1} A_{1ij} B_{1i} \prod_{j_1=1}^{J} (y_{j_1})^{A_{1jj1}} + \sum_{p=2}^{P} N_p \sum_{i=1}^{I_p} A_{piz} B_{pi} \prod_{j_1=1}^{J} (y_{j_1})^{A_{piz1}} = a_j, \quad j = 1, \ldots, J
\]
\[
\left( \frac{P^\circ}{P} \right) \sum_{i=1}^{I_1} B_{1i} \prod_{j=1}^{J} (y_j)^{A_{1ij}} = 1
\]
\[
\sum_{i=1}^{I_p} B_{pi} \prod_{j=1}^{J} (y_j)^{A_{piz}} = 1, \quad p = 2, \ldots, P
\]
\[
\sum_{p=1}^{P} N_p = N.
\]

(9.115)

Note that in this formulation only the always positive \( y_j \) are needed to determine the mole fractions. The element potentials \( \lambda_j \), which are the logarithm of the \( y_j \), never actually need to be calculated.

A key advantage of this formulation of the problem is that the equations that need to be solved for the unknown \( y_i \) and \( N_p \) are multivariate polynomials, and algorithms are available that enable the roots to be determined without requiring an initial guess of the solution. Typically a number of real and complex roots are returned. The correct root is the one with all positive real values of the \( y_i \) and \( N_p \). In general, there is only one such root.

### 9.9.1 Rescaled equations

The equations (9.115) admit an interesting scaling invariance where any constants, say \( \alpha_j \), \( j = 1, \ldots, J \) can be added to the normalized Gibbs free energies as long as the coefficients and unknowns are transformed as

\[
B_{pi} = \tilde{B}_{pi} \prod_{j=1}^{J} (\alpha_j)^{A_{piz}}
\]

\[
y_j = \tilde{y}_j / \alpha_j.
\]

(9.116)

If the transformations (9.116) are substituted into (9.115) the system of equations remains the same but expressed in tildaed variables. This leads to the following reformulation of the problem.
Rewrite (9.111) and (9.112) by adding and subtracting the standard Gibbs free energies of the elements that make up the given species.

\[
B_{1i} = \exp\left\{-\frac{g_{1i}(T)}{R_u T} + \sum_{j=1}^{J} \frac{A_{1ij} g_j^o(T)}{R_u T} - \sum_{j=1}^{J} \frac{A_{1ij} g_j^o(T)}{R_u T}\right\}
\]

\[
B_{pi} = \exp\left\{-\frac{g_{pi}(T,P)}{R_u T} + \sum_{j=1}^{J} \frac{A_{pij} g_j(T,P)}{R_u T} - \sum_{j=1}^{J} \frac{A_{pij} g_j(T,P)}{R_u T}\right\} \quad p > 1
\]  

(9.117)

The first two terms in the bracket in equation (9.117) constitute the Gibbs free energy of formation of the given species from its individual elements.

\[
B_{1i} = \exp\left\{-\frac{\Delta g_{1i}^o(T)}{R_u T} - \sum_{j=1}^{J} \frac{A_{1ij} g_j^o(T)}{R_u T}\right\}
\]

\[
B_{pi} = \exp\left\{-\frac{\Delta g_{pi}^o(T,P)}{R_u T} - \sum_{j=1}^{J} \frac{A_{pij} g_j(T,P)}{R_u T}\right\} \quad p > 1
\]  

(9.118)

where

\[
\Delta g_{1i}^o(T) = g_{1i}^o(T) - \sum_{j=1}^{J} A_{1ij} g_j^o(T)
\]

\[
\Delta g_{pi}^o(T,P) = g_{pi}^o(T,P) - \sum_{j=1}^{J} A_{pij} g_j(T,P) \quad p > 1.
\]  

(9.119)

We can write (9.118) as

\[
B_{1i} = \tilde{B}_{1i} \prod_{j=1}^{J} \exp\left(-\frac{A_{1ij} g_j^o(T)}{R_u T}\right)
\]

\[
B_{pi} = \tilde{B}_{pi} \prod_{j=1}^{J} \exp\left(-\frac{A_{pij} g_j(T,P)}{R_u T}\right) \quad p > 1
\]  

(9.120)

where
\[ \tilde{B}_{1i} = \exp \left\{ -\frac{\Delta g_{1i}^\circ(T)}{R_uT} \right\} \]
\[ \tilde{B}_{pi} = \exp \left\{ -\frac{\Delta g_{pi}(T,P)}{R_uT} \right\} \quad p > 1. \quad (9.121) \]

The system of equations (9.115) can now be written as

\[
\left( \frac{P^o}{P} \right)^{\frac{N_1}{I_1}} \sum_{i=1}^{I_1} A_{1ij} \tilde{B}_{1i} \prod_{j=1}^{J} (\tilde{y}_j)^{A_{1ij}} + \sum_{p=2}^{P} \frac{N_p}{I_p} \sum_{i=1}^{I_p} A_{pij} \tilde{B}_{pi} \prod_{j=1}^{J} (\tilde{y}_j)^{A_{pij}} = a_j, \quad j = 1, \ldots, J
\]

\[
\left( \frac{P^o}{P} \right)^{\frac{I_p}{I_p}} \sum_{i=1}^{I_p} \tilde{B}_{pi} \prod_{j=1}^{J} (\tilde{y}_j)^{A_{pij}} = 1
\]

\[
\sum_{i=1}^{I_p} \tilde{B}_{pi} \prod_{j=1}^{J} (\tilde{y}_j)^{A_{pij}} = 1 \quad p = 2, \ldots, P
\]

\[
\sum_{p=1}^{P} N_p = N \quad (9.122)
\]

where

\[
\tilde{y}_j = y_j \exp \left( -\frac{g_j^\circ(T)}{R_uT} \right) \quad j = 1, \ldots, J. \quad (9.123)
\]

The mole fractions in scaled variables are

\[
x_{1i} = \left( \frac{P^o}{P} \right)^{\frac{I_p}{I_p}} \tilde{B}_{1i} \prod_{j=1}^{J} (\tilde{y}_j)^{A_{1ij}}
\]

\[
x_{pi} = \tilde{B}_{pi} \prod_{j=1}^{J} (\tilde{y}_j)^{A_{pij}} \quad p = 2, \ldots, P. \quad (9.124)
\]

Note that the governing equations (9.115) and (9.122) have exactly the same form and the \( \tilde{y}_j \) determine the mole fractions. The implication of this result is that the calculation of mole fractions can be carried out either in terms of the standard Gibbs free energy of a species or the Gibbs free energy of formation of the species.
Generally the Gibbs free energy of formation of a substance is less than the Gibbs free energy itself and so usually $\bar{B}_{pi} < B_{pi}$ making the numerical solution of (9.122) simpler than (9.115). This is especially important for gas calculations at low temperature where $g_{j}^{0}/R_{u}T$ can be quite large producing values of the $B_{pi}$ that can range over many orders of magnitude. For many calculations, the Gibbs free energy of formation of a substance is the only data tabulated. This is especially true for reactions in aqueous solution.

### 9.10 Example - combustion of carbon monoxide

If we mix carbon monoxide (CO) and oxygen (O\textsubscript{2}) at $10^{5} Pa$ and 298.15 K then ignite the mixture, the result is a strongly exothermic reaction. The simplest model of such a reaction takes one mole of CO plus half a mole of O\textsubscript{2} to produce one mole of carbon dioxide.

$$CO + \frac{1}{2}O_{2} \rightarrow CO_{2}$$ \hspace{1cm} (9.125)

But this model is not very meaningful without some information about the temperature of the process. If the reaction occurs in an adiabatic system at constant pressure, the final temperature is very high and at that temperature the hot gas consists of a mixture of a number of species beside CO\textsubscript{2}. A more realistic model assumes that the composition includes virtually all of the combinations of carbon and oxygen that one can think of including

$$C, CO, CO_{2}, O, O_{2}.$$ \hspace{1cm} (9.126)

Other more complex molecules are possible such as C\textsubscript{2} and O\textsubscript{3} but are only present in extraordinarily low concentrations. For the composition (9.125) the temperature of the mixture at one atmosphere turns out to be 2975.34 K. This is called the adiabatic flame temperature.

Let’s use the minimization of the Gibbs free energy to determine the relative concentrations of each molecular species for the mixture (9.126) at the equilibrium temperature 2975.34 K. We will order the species as in (9.126). In this case all the species are in the gas phase and the matrix of element coefficients $A_{ij}$ is shown in Figure 9.6.

For this system of molecular species, (9.107) and (9.108) lead to the following equations governing the mole fractions and the total number of moles. Note that $P = P^{0}$ in this case.
Figure 9.6: Matrix of element coefficients for the CO, O\textsubscript{2} system.

\[ a_1 = N \left( A_{11} \exp \left( -\frac{g^0_1}{R_u T} + \lambda_1 A_{11} + \lambda_2 A_{12} \right) + A_{21} \exp \left( -\frac{g^0_2}{R_u T} + \lambda_1 A_{21} + \lambda_2 A_{22} \right) + A_{31} \exp \left( -\frac{g^0_3}{R_u T} + \lambda_1 A_{31} + \lambda_2 A_{32} \right) + A_{41} \exp \left( -\frac{g^0_4}{R_u T} + \lambda_1 A_{41} + \lambda_2 A_{42} \right) + A_{51} \exp \left( -\frac{g^0_5}{R_u T} + \lambda_1 A_{51} + \lambda_2 A_{52} \right) \right) \]  
\[ (9.127) \]

\[ a_2 = N \left( A_{12} \exp \left( -\frac{g^0_1}{R_u T} + \lambda_1 A_{11} + \lambda_2 A_{12} \right) + A_{22} \exp \left( -\frac{g^0_2}{R_u T} + \lambda_1 A_{21} + \lambda_2 A_{22} \right) + A_{32} \exp \left( -\frac{g^0_3}{R_u T} + \lambda_1 A_{31} + \lambda_2 A_{32} \right) + A_{42} \exp \left( -\frac{g^0_4}{R_u T} + \lambda_1 A_{41} + \lambda_2 A_{42} \right) + A_{52} \exp \left( -\frac{g^0_5}{R_u T} + \lambda_1 A_{51} + \lambda_2 A_{52} \right) \right) \]  
\[ (9.128) \]

\[ 1 = \exp \left( -\frac{g^0_1}{R_u T} + \lambda_1 A_{11} + \lambda_2 A_{12} \right) + \exp \left( -\frac{g^0_2}{R_u T} + \lambda_1 A_{21} + \lambda_2 A_{22} \right) + \exp \left( -\frac{g^0_3}{R_u T} + \lambda_1 A_{31} + \lambda_2 A_{32} \right) + \exp \left( -\frac{g^0_4}{R_u T} + \lambda_1 A_{41} + \lambda_2 A_{42} \right) + \exp \left( -\frac{g^0_5}{R_u T} + \lambda_1 A_{51} + \lambda_2 A_{52} \right) \]  
\[ (9.129) \]

The unknowns in this system are the two Lagrange multipliers \( \lambda_1 \) and \( \lambda_2 \) corresponding to each element in the mixture and the total number of moles. The number of moles of carbon atoms is \( a_1 = 1 \) and the number of moles of oxygen atoms is \( a_2 = 2 \). The great advantage of this method is that the number of unknowns is limited to the number of elements in the mixture not the number of molecular species. Use (9.111) and (9.113) to rewrite (9.127), (9.128) and (9.129) in the form of (9.115).
According to (9.116) these equations can be rescaled as follows. Let

\begin{align*}
B_1 &= \tilde{B}_1 \alpha_1 A_{11} \alpha_2 A_{12} \\
B_2 &= \tilde{B}_2 \alpha_1 A_{21} \alpha_2 A_{22} \\
B_3 &= \tilde{B}_3 \alpha_1 A_{31} \alpha_2 A_{32} \\
B_4 &= \tilde{B}_4 \alpha_1 A_{41} \alpha_2 A_{42} \\
B_5 &= \tilde{B}_5 \alpha_1 A_{51} \alpha_2 A_{52} \quad (9.133)
\end{align*}

and

\begin{align*}
y_1 &= \frac{\tilde{y}_1}{\alpha_1} \\
y_2 &= \frac{\tilde{y}_2}{\alpha_2} \quad (9.134)
\end{align*}

If (9.133) and (9.134) are substituted into (9.130), (9.131) and (9.132) the resulting equations read exactly the same except in terms of tildaed variables. This invariance can be exploited to reduce the range of magnitudes of the coefficients in the equation if needed. Now

\begin{align*}
1 &= N \left( B_1 y_1 + B_2 y_1 y_2 + B_3 y_1 y_2^2 \right) \\
2 &= N \left( B_2 y_1 y_2 + 2B_3 y_1 y_2^2 + B_4 y_2 + 2B_5 y_2^2 \right) \\
1 &= B_1 y_1 + B_2 y_1 y_2 + B_3 y_1 y_2^2 + B_4 y_2 + B_5 y_2^2 \quad (9.137)
\end{align*}

where the coefficients are
\[ B_1 = e^{-\frac{g_C^o}{R_uT}} \]
\[ B_2 = e^{-\frac{g_{CO}^o}{R_uT}} \]
\[ B_3 = e^{-\frac{g_{CO_2}^o}{R_uT}} \]
\[ B_4 = e^{-\frac{g_O^o}{R_uT}} \]
\[ B_5 = e^{-\frac{g_{O_2}^o}{R_uT}}. \]

(9.138)

At this point we need to use tabulated thermodynamic data to evaluate the coefficients. The Gibbs free energy of the \( i \)th molecular species is

\[ g_i^o (T) = \Delta h_{fi}^o (T_{ref}) + \{ h_i^o (T) - h_i^o (T_{ref}) \} - T s_i^o (T). \]

(9.139)

Data for each species is as follows (See appendix 2). In the same order as (9.126)

\[ g_C^o (2975.34) = 715.004 + 56.208 - 2975.34 (0.206054) = 158.131 kJ/mole \]
\[ g_{CO}^o (2975.34) = -110.541 + 92.705 - 2975.34 (0.273228) = -830.782 kJ/mole \]
\[ g_{CO_2}^o (2975.34) = -393.522 + 151.465 - 2975.34 (0.333615) = -1234.68 kJ/mole \]
\[ g_O^o (2975.34) = 249.195 + 56.1033 - 2975.34 (0.209443) = -317.866 kJ/mole \]
\[ g_{O_2}^o (2975.34) = 0.00 + 97.1985 - 2975.34 (0.284098) = -748.09 kJ/mole. \]

(9.140)

The universal gas constant in appropriate units is

\[ R_u = 8.314472 \times 10^{-3} kJ/mole - K \]

(9.141)

and \( R_uT = 24.7384 kJ/mole \). Now the coefficients are

\[ B_1 = Exp \left( -\frac{g_C^o}{R_uT} \right) = Exp \left( -\frac{158.131}{24.7382} \right) = 1.67346 \times 10^{-3} \]
\[ B_2 = Exp \left( -\frac{g_{CO}^o}{R_uT} \right) = Exp \left( \frac{830.782}{24.7382} \right) = 3.84498 \times 10^{14} \]
\[ B_3 = Exp \left( -\frac{g_{CO_2}^o}{R_uT} \right) = Exp \left( \frac{1234.68}{24.7382} \right) = 4.73778 \times 10^{21} \]
\[ B_4 = Exp \left( -\frac{g_O^o}{R_uT} \right) = Exp \left( \frac{317.866}{24.7382} \right) = 3.80483 \times 10^{5} \]
\[ B_5 = Exp \left( -\frac{g_{O_2}^o}{R_uT} \right) = Exp \left( \frac{748.090}{24.7382} \right) = 1.35889 \times 10^{13}. \]

(9.142)
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9-35

Notice the ill conditioned nature of this problem. The constants in (9.142) vary over many orders of magnitude requiring high accuracy and very careful numerical analysis. The scaling (9.133) is

\[ \begin{align*}
B_1 &= \tilde{B}_1 \alpha_1 \\
B_2 &= \tilde{B}_2 \alpha_1 \alpha_2 \\
B_3 &= \tilde{B}_3 \alpha_1 \alpha_2^2 \\
B_4 &= \tilde{B}_4 \alpha_2 \\
B_5 &= \tilde{B}_5 \alpha_2^2.
\end{align*} \tag{9.143} \]

Choose \( \alpha_2 = \sqrt{1.35889 \times 10^{13}} \) so that \( \tilde{B}_5 = 1 \) and \( \alpha_1 = 1.67346 \times 10^{-3} \) so that \( \tilde{B}_1 = 1 \). The scaled coefficients are

\[ \begin{align*}
\tilde{B}_1 &= B_1 / \alpha_1 = 1.67346 \times 10^{-3} / 1.67346 \times 10^{-3} = 1 \\
\tilde{B}_2 &= B_2 / \alpha_1 \alpha_2 = 3.84498 \times 10^{14} / \left( 1.67346 \times 10^{-3} \sqrt{1.35889 \times 10^{13}} \right) = 6.23285 \times 10^{10} \\
\tilde{B}_3 &= B_3 / \alpha_1 \alpha_2^2 = 4.73778 \times 10^{21} / \left( 1.67346 \times 10^{-3} \left( 1.35889 \times 10^{13} \right) \right) = 2.08341 \times 10^{11} \\
\tilde{B}_4 &= B_4 / \alpha_2 = 3.80483 \times 10^{5} / \sqrt{1.35889 \times 10^{13}} = 0.103215 \\
\tilde{B}_5 &= B_5 / \alpha_2^2 = 1.35889 \times 10^{13} / 1.35889 \times 10^{13} = 1.
\end{align*} \tag{9.144} \]

Using this procedure we have reduced the range of the coefficients from 24 down to 11 orders of magnitude, a very significant reduction. The equations we need to solve are as follows.

\[ 1 = N \left( \tilde{B}_1 \tilde{y}_1 + \tilde{B}_2 \tilde{y}_1 \tilde{y}_2 + \tilde{B}_3 \tilde{y}_1 \tilde{y}_2^2 \right) \tag{9.145} \]

\[ 2 = N \left( \tilde{B}_2 \tilde{y}_1 \tilde{y}_2 + 2 \tilde{B}_3 \tilde{y}_1 \tilde{y}_2^2 + \tilde{B}_4 \tilde{y}_2 + 2 \tilde{B}_5 \tilde{y}_2^2 \right) \tag{9.146} \]

\[ 1 = \tilde{B}_1 \tilde{y}_1 + \tilde{B}_2 \tilde{y}_1 \tilde{y}_2 + \tilde{B}_3 \tilde{y}_1 \tilde{y}_2^2 + \tilde{B}_4 \tilde{y}_2 + \tilde{B}_5 \tilde{y}_2^2 \tag{9.147} \]

I used Mathematica to solve the system, (9.145), (9.146), and (9.147). The result is

\[ \begin{align*}
\tilde{y}_1 &= 1.42474 \times 10^{-11} \\
\tilde{y}_2 &= 0.392402 \\
n &= 1.24144
\end{align*} \tag{9.148} \]
At the mixture temperature $T = 2975.34 \, K$, the mole fractions of the various species are

\[ x_C = \tilde{B}_1 \tilde{y}_1 = 1.42474 \times 10^{-11} \]
\[ x_{CO} = \tilde{B}_2 \tilde{y}_1 \tilde{y}_2 = 6.23285 \times 10^{10} \times 1.42474 \times 10^{-11} \times 0.392402 = 0.34846 \]
\[ x_{CO_2} = \tilde{B}_3 \tilde{y}_1 \tilde{y}_2^2 = 2.08341 \times 10^{11} \times 1.42474 \times 10^{-11} \times 0.392402^2 = 0.45706 \quad (9.149) \]
\[ x_O = \tilde{B}_4 \tilde{y}_2 = 0.103215 \times 0.392402 = 0.0405018 \]
\[ x_{O_2} = \tilde{B}_5 \tilde{y}_2^2 = 0.392402^2 = 0.153979. \]

Note that there is almost no free carbon at this temperature. We could have dropped $C$ from the mixture (9.126) and still gotten practically the same result.

### 9.10.1 CO Combustion at 2975.34K using Gibbs free energy of formation.

The Gibbs free energies of formation of the various species are

\[ \Delta g_C^\circ (2975.34) = 250.012 \, kJ/mole \]
\[ \Delta g_{CO}^\circ (2975.34) = -365.761 \, kJ/mole \]
\[ \Delta g_{CO_2}^\circ (2975.34) = -395.141 \, kJ/mole \]
\[ \Delta g_O^\circ (2975.34) = 55.8281 \, kJ/mole \]
\[ \Delta g_{O_2}^\circ (2975.34) = 0.0 \, kJ/mole. \]  

(9.150)

These values can be found in the JANAF tables in Appendix 2. Using the Gibbs free energies of formation, the coefficients of the element potential equations are

\[ B_1 = \exp \left[ -\frac{\Delta g_C^\circ (2975.34)}{R_uT} \right] = \exp \left[ -\frac{250.012}{24.7382} \right] = 4.0821 \times 10^{-5} \]
\[ B_2 = \exp \left[ -\frac{\Delta g_{CO}^\circ (2975.34)}{R_uT} \right] = \exp \left[ -\frac{365.761}{24.7382} \right] = 2.63731 \times 10^6 \]
\[ B_3 = \exp \left[ -\frac{\Delta g_{CO_2}^\circ (2975.34)}{R_uT} \right] = \exp \left[ -\frac{395.141}{24.7382} \right] = 8.6486 \times 10^6 \quad (9.151) \]
\[ B_4 = \exp \left[ -\frac{\Delta g_O^\circ (2975.34)}{R_uT} \right] = \exp \left[ -\frac{55.8281}{24.7382} \right] = 0.104689 \]
\[ B_5 = \exp \left[ -\frac{\Delta g_{O_2}^\circ (2975.34)}{R_uT} \right] = \exp \left[ -\frac{0.0}{24.7382} \right] = 1.00. \]

The results using Mathematica to solve this system are
\[ y_1 = 3.382049 \times 10^{-7} \]
\[ y_2 = 0.3935536 \]
\[ n = 1.24391 \]

and the mole fractions are

\[ x_C = B_1 y_1 = 1.380743 \times 10^{-11} \]
\[ x_{CO} = B_2 y_1 y_2 = 0.3509709 \]
\[ x_{CO_2} = B_3 y_1 y_2^2 = 0.4529426 \]
\[ x_O = B_4 y_2 = 0.04120202 \]
\[ x_{O_2} = B_5 y_2^2 = 0.15488445 \]

These results agree closely with the results in (9.149) and with calculations using CEA.

Now transfer heat out of the gas mixture to bring the temperature back to 298.15 K at one atmosphere. The standard Gibbs free energies of the species at this temperature are

\[ g^\circ_C(298.15) = 669.54219 \text{ kJ/mole} \]
\[ g^\circ_{CO}(298.15) = -169.46747 \text{ kJ/mole} \]
\[ g^\circ_{CO_2}(298.15) = -457.25071 \text{ kJ/mole} \]
\[ g^\circ_O(298.15) = 201.15482 \text{ kJ/mole} \]
\[ g^\circ_{O_2}(298.15) = -61.16531 \text{ kJ/mole} \]

and \( R_u T = 2.47897 \text{ kJ/mole}. \) The coefficients are

\[ B_1 = \exp\left(-\frac{g^\circ_C}{R_u T}\right) = \exp\left(-\frac{669.54219}{2.47897}\right) = 5.03442 \times 10^{-118} \]
\[ B_2 = \exp\left(-\frac{g^\circ_{CO}}{R_u T}\right) = \exp\left(-\frac{169.46747}{2.47897}\right) = 4.88930 \times 10^{29} \]
\[ B_3 = \exp\left(-\frac{g^\circ_{CO_2}}{R_u T}\right) = \exp\left(-\frac{457.25071}{2.47897}\right) = 1.277622 \times 10^{80} \]
\[ B_4 = \exp\left(-\frac{g^\circ_O}{R_u T}\right) = \exp\left(-\frac{201.15482}{2.47897}\right) = 5.74645 \times 10^{-36} \]
\[ B_5 = \exp\left(-\frac{g^\circ_{O_2}}{R_u T}\right) = \exp\left(-\frac{61.16531}{2.47897}\right) = 5.19563 \times 10^{10}. \]

At this relatively low temperature the coefficients range over 198 orders of magnitude! Despite this a good modern solver should be able to find the solution of (9.135), (9.136) and (9.137) for this difficult case even without the scaling used earlier. For example, Mathematica has a feature where the user can specify an arbitrary number of digits of precision for the calculation. The solution of (9.135), (9.136) and (9.137) at this temperature is
The resulting mole fractions at $T = 298.15\, K$ are

\[
\begin{align*}
    y_1 &= 7.07098 \times 10^{-40} \\
    \tilde{y}_2 &= 3.32704 \times 10^{-21} \\
    n &= 1.0000 
\end{align*}
\]

(9.156)

Only when the mixture is brought back to low temperature is the reaction model (9.125) valid. The enthalpy change for this last step is

\[
\left. h^\circ \right|_{\text{mixture at } 298.15\, K} - \left. h^\circ \right|_{\text{mixture at } 2975.34\, K} = -8.94 \times 10^6 + 2.51 \times 10^6 = -6.43 \times 10^6 \, J/kg. 
\]

(9.158)

This is the chemical energy released by the reaction (9.125) and is called the heat of reaction.

\subsection*{9.10.2 Adiabatic flame temperature}

In the example in the previous section the products of combustion were evaluated at the adiabatic flame temperature. This can be defined at constant volume or constant pressure. For our purposes we will use the adiabatic flame temperature at constant pressure. Imagine the reactants brought together in a piston-cylinder combination permitting the volume to be adjusted to keep the pressure constant as the reaction proceeds. A source of ignition is used to start the reaction that evolves to the equilibrium state defined by the equilibrium species concentrations at the original pressure and at an elevated temperature called the adiabatic flame temperature. In the process the Gibbs function is minimized and since the process is adiabatic, the enthalpy before and after the reaction is the same.

The general enthalpy balance for a reaction is given in (9.67). Fully written out the balance is
\[
\Delta h^\circ (T_{\text{final}}) = \sum_{i_{\text{product}}} n_{i_{\text{product}}} \left\{ \Delta h^\circ_{f_{i_{\text{product}}} (298.15)} + \left( h^\circ_{i_{\text{product}}} (T_{\text{final}}) - h^\circ_{i_{\text{product}}} (298.15) \right) \right\} - \\
\sum_{i_{\text{reactant}}} n_{i_{\text{reactant}}} \left\{ \Delta h^\circ_{f_{i_{\text{reactant}}} (298.15)} + \left( h^\circ_{i_{\text{reactant}}} (T_{i_{\text{reactant}}}) - h^\circ_{i_{\text{reactant}}} (298.15) \right) \right\}.
\]

(9.159)

If the reaction takes place adiabatically then \( \Delta h^\circ (T_{\text{final}}) = 0 \) and

\[
\sum_{i_{\text{product}}} n_{i_{\text{product}}} \left\{ \Delta h^\circ_{f_{i_{\text{product}}} (298.15)} + \left( h^\circ_{i_{\text{product}}} (T_{\text{final}}) - h^\circ_{i_{\text{product}}} (298.15) \right) \right\} = \\
\sum_{i_{\text{reactant}}} n_{i_{\text{reactant}}} \left\{ \Delta h^\circ_{f_{i_{\text{reactant}}} (298.15)} + \left( h^\circ_{i_{\text{reactant}}} (T_{i_{\text{reactant}}}) - h^\circ_{i_{\text{reactant}}} (298.15) \right) \right\}.
\]

(9.160)

Equation (9.160) can be solved along with (9.135), (9.136) and (9.137) to determine the final temperature of the mixture along with the mole fractions and total number of moles.

In the carbon monoxide combustion example of the previous section we would write

\[
n_C \left\{ \Delta h^\circ_C (298.15) + (h^\circ_C (T_{\text{final}}) - h^\circ_C (298.15)) \right\} + \\
n_{CO} \left\{ \Delta h^\circ_{CO} (298.15) + (h^\circ_{CO} (T_{\text{final}}) - h^\circ_{CO} (298.15)) \right\} + \\
n_{CO_2} \left\{ \Delta h^\circ_{CO_2} (298.15) + (h^\circ_{CO_2} (T_{\text{final}}) - h^\circ_{CO_2} (298.15)) \right\} + \\
n_O \left\{ \Delta h^\circ_O (298.15) + (h^\circ_O (T_{final}) - h^\circ_O (298.15)) \right\} + \\
n_{O_2} \left\{ \Delta h^\circ_{O_2} (298.15) + (h^\circ_{O_2} (T_{\text{final}}) - h^\circ_{O_2} (298.15)) \right\} = \\
n_{CO} \left\{ \Delta h^\circ_{fCO} (298.15) \right\} + n_{O_2} \left\{ \Delta h^\circ_{fO_2} (298.15) \right\}.
\]

(9.161)

The enthalpy of the reactants is

\[
n_{CO} \left\{ \Delta h^\circ_{fCO} (298.15) \right\} + n_{O_2} \left\{ \Delta h^\circ_{fO_2} (298.15) \right\} = \\
1.0 \text{ kmole} \left\{ -110.527 \times 10^3 \text{ kJ/kgmole} \right\} + 0.5 \text{ kmole} \left\{ 0 \text{ kJ/kgmole} \right\} = \\
-110.527 \times 10^3 \text{ kJ}.
\]

(9.162)

On a per unit mass basis the enthalpy of the reactant mixture is

\[
\frac{-110.527 \times 10^6 \text{ J}}{1 \times 28.014 + 0.5 \times 31.98} = -2.5117 \times 10^6 \text{ J/kg}.
\]

(9.163)
The enthalpy per unit mass of the product mixture at various temperatures is plotted in Figure 9.7.

![Figure 9.7: Enthalpy of the product mixture as a function of temperature.](image)

As the products of combustion are cooled from 4000 \( K \) the enthalpy decreases monotonically. The only temperature where the enthalpy of the product mixture matches that of the original reactants is the adiabatic flame temperature, 2975.34 \( K \).

### 9.10.3 Isentropic expansion

Now consider an isentropic expansion from a known initial state, \((T_{\text{initial}}, P_{\text{initial}})\) to a final state \((T_{\text{final}}, P_{\text{final}})\) with the final pressure known. The condition that determines the temperature of the final state is

\[
S(T_{\text{final}}, P_{\text{final}}, n_{1_{\text{final}}}, n_{2_{\text{final}}}, n_{3_{\text{final}}}, ..., n_{I_{\text{final}}}) = S(T_{\text{initial}}, P_{\text{initial}}, n_{1_{\text{initial}}}, n_{2_{\text{initial}}}, n_{3_{\text{initial}}}, ..., n_{I_{\text{initial}}})
\]

or

\[
\sum_{i=1}^{I} n_{i_{\text{final}}} s_{i}^{\circ} (T_{\text{final}}) - N_{\text{final}} R u \sum_{i=1}^{I} x_{i_{\text{final}}} \ln (x_{i_{\text{final}}}) - N_{\text{final}} R u \ln \left( \frac{P_{\text{final}}}{P^{\circ}} \right) = \\
\sum_{i=1}^{I} n_{i_{\text{initial}}} s_{i}^{\circ} (T_{\text{initial}}) - N_{\text{initial}} R u \sum_{i=1}^{I} x_{i_{\text{initial}}} \ln (x_{i_{\text{initial}}}) - N_{\text{initial}} R u \ln \left( \frac{P_{\text{initial}}}{P^{\circ}} \right)
\]

Equation (9.165) can be solved along with (9.135), (9.136) and (9.137) to determine the final temperature of the mixture after isentropic expansion along with the mole fractions and total number of moles.
For example, take the mixture from the previous section at the initial state, \( T_{\text{initial}} = 2975.34 \) \( K \) and \( P_{\text{initial}} = 1 \) bar. The entropy of the system on a per unit mass basis is 8.7357 \( J/kg-K \) which is essentially equivalent to the extensive entropy. Now expand the mixture to \( P_{\text{final}} = 0.1 \) bar. If we calculate the entropy of the system at this pressure and various temperatures, the result is the following plot.

Figure 9.8: Entropy of the product mixture as a function of temperature.

The temperature at which the entropy of the final state is the same as the initial state is \( T_{\text{final}} = 2566.13 \) \( K \).

9.10.4 Nozzle expansion

If we interpret the expansion just described as an adiabatic, isentropic expansion in a nozzle we can use the conservation of stagnation enthalpy to determine the speed of the gas mixture at the end of the expansion.

\[
H_{\text{initial}} = H_{\text{final}} + \frac{1}{2} U^2 \tag{9.166}
\]

The initial enthalpy is taken to be the reservoir value. For this example the numbers are

\[
U = \sqrt{2 (H_{\text{initial}} - H_{\text{final}})} = \sqrt{2 (-2.51162 + 3.94733) \times 10^6 \ J/kg} = 1694.53 \ m/\sec \ . \tag{9.167}
\]

Ordinarily we are given the geometric area ratio of the nozzle rather than the pressure ratio. Determining the exit velocity in this case is a little more involved. Here we need to carry out a series of calculations at constant entropy and varying final pressure. For each calculation we need to determine the density and velocity of the mixture and plot the
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product $\rho U$ as a function of the pressure ratio. Beginning with the mixture at the adiabatic flame temperature as the reservoir condition, the results are plotted below.

![Figure 9.9: Mass flux in a converging-diverging nozzle as a function of nozzle static pressure ratio.](image)

The maximum mass flux occurs at the nozzle throat. Equate the mass flow at the throat and the nozzle exit. For $P_{\text{initial}}/P_{\text{final}} = 10.0$ the nozzle area ratio is

$$\frac{A_e}{A_t} = \frac{\rho_t U_t}{\rho_e U_e} = \frac{73.6768}{29.8354} = 2.46944. \hspace{1cm} (9.168)$$

This completes the specification of the nozzle flow. The case we have considered here is called the shifting equilibrium case where the gas mixture is at equilibrium at every point in the nozzle. One can also consider the case of frozen flow where the composition of the gas mixture is held fixed at the reservoir condition.

### 9.10.5 Fuel-rich combustion, multiple phases

Suppose we choose a mixture of $CO$ and $O_2$ that has an excess of $CO$. In this case the overall balance of carbon and oxygen can be satisfied in more than one way when the products of the reaction are brought back to low temperature. For example, if we mix 2 moles of $CO$ with 0.5 moles of $O_2$ at a pressure of $10^5 N/m^2$ we could end up with either of the following.

$$2CO + \frac{1}{2}O_2 \rightarrow CO_2 + CO \hspace{1cm} (9.169)$$

$$2CO + \frac{1}{2}O_2 \rightarrow \frac{3}{2}CO_2 + \frac{1}{2}C_{(gr)}$$
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Which balance actually occurs is of course determined by which one minimizes the Gibbs free energy at the given temperature. The set of species in the mixture is now

\[ C, CO, CO_2, O, O_2, C_{(gr)} \]  \hspace{1cm} (9.170)

where we have allowed for the possible condensation of solid carbon. The matrices of element coefficients \( A_{pij} \) for the two phases are shown in Figure 9.10.

![Figure 9.10: Matrix of element coefficients for the CO, O_2 system with condensed species (graphite).](image)

The governing equations (9.122) become the following.

\[
2 = N_1 \left( B_{11}y_1 + B_{12}y_1y_2 + B_{13}y_1y_2^2 \right) + N_2 \left( B_{21}y_1 \right) \hspace{1cm} (9.171)
\]

\[
3 = N_1 \left( B_{12}y_1y_2 + 2B_{13}y_1y_2^2 + B_{14}y_2 + 2B_{15}y_2^2 \right) \hspace{1cm} (9.172)
\]

\[
1 = B_{11}y_1 + B_{12}y_1y_2 + B_{13}y_1y_2^2 + B_{14}y_2 + B_{15}y_2^2 \hspace{1cm} (9.173)
\]

\[
1 = B_{21}y_1 \hspace{1cm} (9.174)
\]

\[
N = N_1 + N_2 \hspace{1cm} (9.175)
\]

The coefficients are
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\[ B_{11} = e^{-\frac{\phi_C^o}{RT}} \]
\[ B_{12} = e^{-\frac{\phi_{CO}^o}{RT}} \]
\[ B_{13} = e^{-\frac{\phi_{CO_2}}{RT}} \]
\[ B_{14} = e^{-\frac{\phi_O^o}{RT}} \]
\[ B_{15} = e^{-\frac{\phi_{O_2}}{RT}} \]  

\[ B_{21} = e^{-\frac{\phi_{C(gr)^o}}{RT}} . \]  

(9.176)  

(9.177)

As an example, let’s solve for the various mole fractions at a mixture temperature of 940 K. From tables, the standard Gibbs free energies at this temperature are

\[ g_C^o (940) = 558.95895 \text{ kJ/mole} \]
\[ g_{CO}^o (940) = -309.37696 \text{ kJ/mole} \]
\[ g_{CO_2}^o (940) = -613.34861 \text{ kJ/mole} \]
\[ g_O^o (940) = 88.41203 \text{ kJ/mole} \]
\[ g_{O_2}^o (940) = -206.32876 \text{ kJ/mole} \]
\[ g_{C(gr)^o} (940) = -11.22955 \text{ kJ/mole} . \]  

(9.178)

The number of moles of each species in the mixture at \( T = 940 \text{ K} \) are

\[ n_C = N_1 B_{11} y_1 = 4.11775 \times 10^{-32} \]
\[ n_{CO} = N_1 B_{12} y_1 y_2 = 0.977065 \]
\[ n_{CO_2} = N_1 B_{13} y_1 y_2^2 = 1.011467 \]
\[ n_O = N_1 B_{14} y_2 = 3.23469 \times 10^{-22} \]
\[ n_{O_2} = N_1 B_{15} y_2^2 = 1.027845 \times 10^{-22} \]
\[ n_{C(gr)} = N_2 B_{21} y_1 = 0.011467 . \]  

(9.179)

At this temperature, the mixture is predominately \( CO \) and \( CO_2 \) with some \( C_{(gr)} \). Figure 9.11 shows the mole fraction of \( CO \) and \( C_{(gr)} \) at a pressure of \( 10^5 \text{ N/m}^2 \) based on the total number of moles in the mixture for a variety of mixture temperatures.

The excess \( CO \) begins to react and solid carbon begins to condense out at about \( T = 942.2 \text{ K} \). Below 600 K there is virtually no \( CO \) in the mixture.
9.11 Rocket performance using CEA

The equilibrium combustion package CEA (Chemical Equilibrium with Applications) from NASA Glenn can also be used to perform equilibrium chemistry calculations and has a capability similar to STANJAN but with a much wider range of chemicals with data based on the current standard pressure. Some typical performance parameters for several propellant combinations at two chamber pressures are shown in Figure 9.12. The propellants are taken to be at an equivalence ratio of one (complete consumption of fuel and oxidizer) and so the exhaust velocity is not optimized. The numbers correspond to the effective exhaust velocity for the given chamber pressure and area ratio assuming vacuum ambient pressure. The maximum effective exhaust velocity generally occurs with a somewhat fuel rich mixture that produces more low molecular weight species in the exhaust stream.

9.12 Problems

**Problem 1** - A nuclear reactor is used to heat hydrogen gas in a rocket chamber to a temperature of 4000 K. The pressure in the chamber is 100 atm. At these conditions a significant fraction of the H₂ is dissociated to form atomic H. What are the mole fractions of H, H₂ in the mixture? Relevant thermochemical data is provided in Figure 9.13. The reference temperature is 298.15 K.

Work the problem by hand and compare with CEA.

**Problem 2** - Hydrogen gas heated to 4000 K is fed at a mass flow rate of 200 kg/sec into a rocket chamber with a throat area of 0.2 m². The gas is exhausted adiabatically and
CHAPTER 9. THERMODYNAMICS OF REACTING MIXTURES

Figure 9.12: Some typical performance parameters for several propellant combinations at two chamber pressures.

<table>
<thead>
<tr>
<th>Propellant</th>
<th>P_{chamber} bar</th>
<th>T_{chamber} K</th>
<th>C* MSec</th>
<th>C_{i/A-100} MSec</th>
<th>C_{i/A-∞} MSec</th>
</tr>
</thead>
<tbody>
<tr>
<td>H_{2} + \frac{1}{2}O_{2}</td>
<td>50</td>
<td>3626</td>
<td>2186</td>
<td>4541</td>
<td>5285</td>
</tr>
<tr>
<td></td>
<td>100</td>
<td>3730</td>
<td>2203</td>
<td>4562</td>
<td>5287</td>
</tr>
<tr>
<td>N_{2}H_{4} + \frac{3}{2}N_{2}O_{4}</td>
<td>50</td>
<td>3379</td>
<td>1818</td>
<td>3637</td>
<td>4030</td>
</tr>
<tr>
<td></td>
<td>100</td>
<td>3451</td>
<td>1829</td>
<td>3643</td>
<td>4032</td>
</tr>
<tr>
<td>(1.0)RP-1 + (3.4)O_{2} by mass</td>
<td>50</td>
<td>3676</td>
<td>1733</td>
<td>3631</td>
<td>4467</td>
</tr>
<tr>
<td></td>
<td>100</td>
<td>3787</td>
<td>1749</td>
<td>3654</td>
<td>4469</td>
</tr>
<tr>
<td>(0.1)Al + (0.85)NH_{4}ClO_{4} + (0.05)C_{a}H_{6} by mass</td>
<td>50</td>
<td>3434</td>
<td>1511</td>
<td>3160</td>
<td>3726</td>
</tr>
<tr>
<td></td>
<td>100</td>
<td>3514</td>
<td>1520</td>
<td>3171</td>
<td>3728</td>
</tr>
</tbody>
</table>

Figure 9.13: Hydrogen dissociation at 4000 K.
isentropically through a nozzle with an area ratio of 40. Determine the exhaust velocity for the following cases.

i) Expansion of undissociated $H_2$.

ii) Frozen flow expansion of dissociated $H_2$ at the rocket chamber composition of $H$ and $H_2$.

(III) Shifting equilibrium expansion.

**Problem 3** - An exotic concept for chemical rocket propulsion is to try to harness the energy released when two atoms of hydrogen combine to form $H_2$. The idea is to store the hydrogen atoms in solid helium at extremely low temperatures. Suppose a space engine is designed with a very large area ratio nozzle. Let a 50-50 mixture by mass of atomic hydrogen and helium be introduced into the combustion chamber at low temperature. The propellant vaporizes and the hydrogen atoms react releasing heat. The gas exhausts through the nozzle to the vacuum of space. Estimate the exhaust velocity of this rocket.

**Problem 4** - I would like you to consider the Space Shuttle Main Engine (SSME). Use the thermochemical calculator CEA or an equivalent application to help solve the problem. The specifications of the SSME are

\[
\begin{align*}
P_{t_2} &= 3000 \text{ psia} \\
T_{t_2} &= 3250 \text{ K} \\
A_e/A_t &= 77.5
\end{align*}
\] (9.180)

and

\[
\begin{align*}
\dot{m}_{H_2} &= 69 \text{ kg/sec} \\
\dot{m}_{O_2} &= 400 \text{ kg/sec}
\end{align*}
\] (9.181)

i) Determine the adiabatic flame temperature and equilibrium mass fractions of the system $(H, H_2, H_2O, O, O_2)$ at the given chamber pressure.

ii) You will find that the temperature in (1) is higher than the specified chamber temperature. Bring your mixture to the specified chamber pressure and temperature (in effect accounting for some heat loss from the engine).

Determine the exhaust velocity and sea level thrust assuming that the mixture remains at equilibrium during the expansion process. Suppose the mass flow rates are changed to the stoichiometric ratio.
\[
\dot{m}_{H_2} = 52.5 \text{ kg/sec} \\
\dot{m}_{O_2} = 416.5 \text{ kg/sec}.
\] (9.182)

How much does the exhaust velocity change?

**Problem 5** - A monopropellant thruster for space applications uses nitrous oxide \(N_2O\) at a low initial temperature as a monopropellant. The gas is passed through a catalyst bed where it is decomposed releasing heat. The hot gas is expelled through a large area ratio nozzle to the vacuum of space. The exhaust gas is composed of \(O_2\) and \(N_2\). The enthalpy of formation of \(N_2O\) at the initial temperature is \(1.86 \times 10^6 \text{ J/kg}\). Estimate the exhaust velocity of this rocket.

**Problem 6** - Element number three in the periodic table is Lithium which is a soft, silvery white, highly reactive metal at room temperature. Because of its low atomic weight it has been considered as a propellant for propulsion applications. Above \(1615 \text{ K}\) it is a monatomic gas. At high temperatures and pressures the diatomic gas begins to form. At the super extreme conditions of \(7000 \text{ K}\) and \(10^5 \text{ bar}\) almost 92% of the mixture is \(Li_2\) and only 8% is \(Li\). By the way, at these conditions the density of the mixture is \(2.3 \times 10^3 \text{ kg/m}^3\), greater than Uranium. Perhaps this is the di-Lithium crystal propellant that, according to Gene Roddenberry, will in the future power generations of starships. Suppose this mixture at an enthalpy \(h_{\text{initial}} = 38.4 \times 10^6 \text{ J/kg}\) expands isentropically from a rocket chamber to a nozzle exit where the enthalpy is \(h_{\text{final}} = 9.3 \times 10^6 \text{ J/kg}\). What is the nozzle exit velocity? What is the composition of the mixture at the nozzle exit?

**Problem 7** - One mole per second of methane \(CH_4\) reacts with 2 moles per second of \(O_2\) in a rocket chamber. The reaction produces products at \(3000 \text{ K}\) and \(100 \text{ bar}\). Assume the mixture contains \((CO, CO_2, H, H_2, H_2O, O, OH, O_2)\). Set up the system of equations (9.115) for this problem. Use data from Appendix 2 to evaluate the coefficients in these equations and solve for the mole fractions. Compare your results with CEA. The gas exhausts isentropically to the vacuum of space through a nozzle with an area ratio of 80. Determine the thrust.

**Problem 8** - Ozone \((O_3)\) releases energy when it decomposes and can be used as a monopropellant for a space thruster. Let ozone be decomposed across a manganese oxide catalyst bed and introduced into a thrust chamber. The pressure and temperature in the chamber are \(10^5 \text{ N/m}^2\) and \(2688 \text{ K}\). At these conditions the mixture is composed of only two constituents, \(O_2\) and \(O\). Relevant thermo-chemical data is given in Figure 9.14.

In the units used in this table the ideal gas constant is \(R_u = 0.00831451 \text{ kJ/(mole} - \text{ K})\).

a) Determine the mole fractions of \(O_2\) and \(O\) in the mixture.

b) Determine the total number of moles in the mixture.
c) Determine the enthalpy per unit mass of the mixture.

d) If the gas is exhausted to the vacuum of space what is the maximum gas speed that could be reached.

<table>
<thead>
<tr>
<th>Species</th>
<th>Molar mass (grams/mole)</th>
<th>( \Delta \tilde{h}(298.15) ) (kl/mole)</th>
<th>( \tilde{h}(2688) - \tilde{h}(298.15) ) (kl/mole)</th>
<th>( s(2688) ) (kl/(mole-K))</th>
</tr>
</thead>
<tbody>
<tr>
<td>( O_2 )</td>
<td>31.9988</td>
<td>0.0</td>
<td>85.7423</td>
<td>0.28017</td>
</tr>
<tr>
<td>( O )</td>
<td>15.9994</td>
<td>249.175</td>
<td>50.0515</td>
<td>0.20741</td>
</tr>
</tbody>
</table>

Figure 9.14: Ozone decomposition at 2688 K.
Chapter 10

Solid Rockets

10.1 Introduction

Figure 10.1 shows a section view of a typical solid propellant rocket.

There are basically two types of propellant grains.

1) Homogeneous or double base propellants - Here fuel and oxidizer are contained within the same molecule which decomposes during combustion. Typical examples are Nitroglycerine and Nitrocellulose.

2) Composite propellants - heterogeneous mixtures of oxidizing crystals in an organic plastic- like fuel binder typically synthetic rubber.

Sometimes metal powders such as Aluminum are added to the propellant to increase the energy of the combustion process as well as fuel density. Typically these may be 12 to 22 % of propellant mass although in the space shuttle booster Aluminum is the primary fuel.
10.2 Combustion chamber pressure

The combustion proceeds from the surface of the propellant grain. The rate at which combustion gases are generated is expressed in terms of the regression speed of the grain as indicated in Figure 10.2.

\[ \dot{m}_g = \rho_p A_b \dot{r} \]  

(10.1)

where

\[ \rho_p = \text{solid propellant density} \]
\[ A_b = \text{area of the burning surface} \]
\[ \dot{r} = \text{surface regression speed} \]
\[ \dot{m}_g = \text{rate of gas generation at the propellant surface}. \]

The phase transition and combustion physics underlying the surface regression speed is extremely complex. In general, \( \dot{r} \) depends on the propellant initial temperature and the chamber pressure.

\[ \dot{r} = \frac{K}{T_1 - T_p} (P_{t2})^n \]  

(10.3)

The variables in (10.3) are as follows.

\[ P_{t2} = \text{combustion chamber pressure} \]
\[ K = \text{imprirical constant for a given propellant} \]
\[ T_1 = \text{imprirical detonation temperature} \]
\[ T_p = \text{propellant temperature} \]
\[ n = \text{imprirical exponent, approximately independent of temperature} \]
In general $0.4 < n < 0.7$ and $T_1$ is considerably larger than $T_p$ by several hundred degrees.

Let $M_g$ be the mass of gas in the combustion chamber at a given instant, $\rho_g$ is the gas density and $V$ is the chamber volume.

\[
\frac{dM_g}{dt} = \frac{d}{dt}(\rho_g V) = \rho_g \frac{dV}{dt} + V \frac{d\rho_g}{dt} \tag{10.5}
\]

The chamber volume changes as the propellant is converted from solid to gas.

\[
\frac{dV}{dt} = \dot{r} A_b \tag{10.6}
\]

To a good approximation, the chamber stagnation temperature, $T_{t2}$, is determined by the propellant energy density and tends to be independent of $P_{t2}$. From the ideal gas law, $P_{t2} = \rho_g R T_{t2}$ and

\[
\frac{d\rho_g}{dt} = \frac{1}{RT_{t2}} \frac{dP_{t2}}{dt}. \tag{10.7}
\]

The mass flow out of the nozzle is

\[
\dot{m}_n = \frac{\gamma}{\left(\frac{\gamma+1}{2}\right)^{\frac{\gamma+1}{\gamma-1}}} \frac{P_{t2} A^*}{\sqrt{\gamma R T_{t2}}}. \tag{10.8}
\]

The mass generated at the propellant surface is divided between the mass flow exiting the nozzle and the time dependent mass accumulation in the combustion chamber volume.

\[
\dot{m}_g = \frac{dM_g}{dt} + \dot{m}_n \tag{10.9}
\]

Fill in the various terms in (10.9)

\[
\rho_g \dot{r} A_b = \rho_g \dot{r} A_b + V \frac{d\rho_g}{dt} + \frac{\gamma}{\left(\frac{\gamma+1}{2}\right)^{\frac{\gamma+1}{\gamma-1}}} \frac{P_{t2} A^*}{\sqrt{\gamma R T_{t2}}} \tag{10.10}
\]

or
\[
K \frac{(\rho_p - \rho_g) A_b}{T_1 - T_p} (P_{t2})^n = \frac{V}{RT_{t2}} \frac{dP_{t2}}{dt} + \frac{\gamma}{\left(\frac{\gamma+1}{2}\right)^\frac{\gamma+1}{2(\gamma-1)} \sqrt{\gamma R T_{t2}}} P_{t2} A^*.
\] (10.11)

Rearrange (10.11) to read
\[
\frac{V}{RT_{t2}} \frac{dP_{t2}}{dt} + \frac{\gamma}{\left(\frac{\gamma+1}{2}\right)^\frac{\gamma+1}{2(\gamma-1)} \sqrt{\gamma R T_{t2}}} P_{t2} A^* - \frac{K (\rho_p - \rho_g) A_b}{T_1 - T_p} (P_{t2})^n = 0.
\] (10.12)

After a startup transient, during which \(P_{t2}\) changes rapidly with time, the pressure reaches a quasi-steady state where the time derivative term in (10.12) can be regarded as small compared to the other terms. To a good approximation
\[
\frac{\gamma}{\left(\frac{\gamma+1}{2}\right)^\frac{\gamma+1}{2(\gamma-1)} \sqrt{\gamma R T_{t2}}} P_{t2} A^* = \frac{K (\rho_p - \rho_g) A_b}{T_1 - T_p} (P_{t2})^n.
\] (10.13)

Solve for the chamber pressure
\[
P_{t2} = \left(\frac{\gamma+1}{2}\right)^\frac{\gamma+1}{2(\gamma-1)} \frac{K (\rho_p - \rho_g) A_b}{\gamma (T_1 - T_p)} \left(\frac{A^*}{A^*}\right) \left(\frac{\sqrt{\gamma R T_{t2}}}{V}\right)^{1-n}.
\] (10.14)

This formula can be used as long as \(A_b(t)\) is a slow function of time. All the quantities in (10.14) are apriori data with the exception of \(T_{t2}\) which must be estimated or calculated from a propellant chemistry model. Note that there is a tendency for the chamber pressure to increase as the burning area increases.

### 10.3 Dynamic analysis

Rearrange (10.12) to read
\[
\frac{dP_{t2}}{dt} + \left(\frac{(\gamma R T_{t2})^{1/2}}{\left(\frac{\gamma+1}{2}\right)^\frac{\gamma+1}{2(\gamma-1)} \left(\frac{A^*}{V}\right)}\right) P_{t2} - \left(\frac{K (\rho_p - \rho_g) A_b}{T_1 - T_p} \left(\frac{RT_{t2}}{V}\right)\right) (P_{t2})^n = 0.
\] (10.15)
This is a nonlinear first order ordinary differential equation for the chamber pressure of the form

\[
\frac{dP_{t2}}{dt} + \left(\frac{1}{\tau}\right) P_{t2} - \beta(P_{t2})^n = 0 \tag{10.16}
\]

where the characteristic time is

\[
\tau = \left(\frac{\gamma+1}{2}\right)^{\frac{\gamma+1}{2(\gamma-1)}} \left(\frac{V}{A^*}\right). \tag{10.17}
\]

This time is proportional to the time required for an acoustic wave to travel the length of the combustion chamber multiplied by the internal area ratio of the nozzle. The system has the character of a Helmholtz resonator and the inverse of (10.17) is the natural "Coke bottle" frequency of the rocket motor.

The constant in the nonlinear term is

\[
\beta = \left(\frac{K(\rho_p - \rho_g)}{T_1 - T_p}\right) \left(\frac{RT_{t2}}{V}\right). \tag{10.18}
\]

Let’s look at the linearized behavior of (10.16) near a steady state operating point. Let

\[
P_{t2}(t) = \overline{P}_{t2} + p_{t2}(t) \tag{10.19}
\]

where \(p_{t2}\) is a small deviation in the pressure from the steady state. Substitute into (10.16) and expand the nonlinear term in a binomial series. With higher order terms in the series neglected, the result is

\[
\frac{dp_{t2}}{dt} + \left(\frac{1}{\tau}\right) \overline{P}_{t2} + \left(\frac{1}{\tau}\right) p_{t2} - \beta(\overline{P}_{t2})^n - \beta n(\overline{P}_{t2})^{n-1} p_{t2} = 0. \tag{10.20}
\]

The steady state terms satisfy

\[
\left(\frac{1}{\tau}\right) \overline{P}_{t2} - \beta(\overline{P}_{t2})^n = 0 \tag{10.21}
\]

and the dynamical equation becomes
\[ \frac{dp_{t2}}{dt} + \left( \frac{1}{\tau} - \beta n(P_{t2})^{n-1} \right) p_{t2} = 0. \]  
\[ (10.22) \]

Note that from (10.21)

\[ \frac{1}{\tau} = \beta n (P_{t2})^{n-1} \]  
\[ (10.23) \]

and so

\[ \frac{dp_{t2}}{dt} + \left( \frac{1 - n}{\tau} \right) p_{t2} = 0. \]  
\[ (10.24) \]

The solution of (10.24) is

\[ \frac{p_{t2}}{p_{t2}(0)} = e^{\left(\frac{1-n}{\tau}\right)t}. \]  
\[ (10.25) \]

If \( n < 1 \) a small deviation in pressure will be restored to the equilibrium value (the extra nozzle flow exceeds the extra gas generation from the propellant surface). But if \( n > 1 \) the gas generation rate exceeds the nozzle exhaust mass flow and the chamber pressure will increase exponentially; The vehicle will explode!

If the fluid velocity over the surface becomes very large, enhanced heat transfer can lead to a situation called erosive burning. In this case the burning rate can vary considerably along the port and excessive gas generation can lead to a failure.

In the case of very low chamber pressure, the combustion process can become unsteady or cease altogether this defines the combustion limit of a particular propellant. There is also an upper pressure limit above which combustion again becomes erratic or unpredictable. For most propellants this is above 5000 psi.

10.3.1 Exact solution

The chamber pressure is governed by the equation

\[ \frac{dP_{t2}}{dt} + \left( \frac{1}{\tau} \right) P_{t2} - \beta (P_{t2})^n = 0. \]  
\[ (10.26) \]

Let’s determine the exact integral of this equation and compare the behavior of the system with the linearized solution for both \( n < 1 \) and \( n > 1 \). It is virtually always best to work in
terms of dimensionless variables. The steady state solution of (10.26) for which the time
derivative term is zero is

\[ P_{t2} = (\tau \beta)^{\frac{1}{1-n}}. \]  
(10.27)

Let

\[ H = \frac{P_{t2}}{P_{t2}} \]
\[ \eta = \frac{t - t_0}{\tau}. \]  
(10.28)

In terms of new variables (10.26) becomes

\[ \frac{dH}{d\eta} = H^n - H. \]  
(10.29)

Equation (10.29) is rearranged as

\[ \frac{dH}{H^n - H} = d\eta \]  
(10.30)

which integrates to

\[ \frac{1 - H^{1-n}}{1 - H_0^{1-n}} = e^{-(1-n)\eta} \]  
(10.31)

where \( H_0 \) is the initial value of \( P_{t2}/P_{t2} \) and the initial value of \( \eta \) is taken to be zero. Now solve for \( H \).

\[ H = \left( 1 - \left( 1 - H_0^{1-n} \right) e^{-(1-n)\eta} \right)^{\frac{1}{1-n}} \]  
(10.32)

Several cases are shown in Figure 10.3.

The exact solution is consistent with the linear analysis and shows that if \( n > 1 \) there
is no actual steady state, the chamber pressure either decays to zero or blows up. If
\( n < 1 \) then the chamber pressure will return to the steady state value even in the face
of a large deviation away from steady state. The motor is stable in the face of finite
disturbances.
10.3.2 Chamber pressure history

The analysis in the last section is useful for determining the behavior of the motor during transients such as start-up and shut down where the chamber pressure responds on a very short time scale measured by $\tau$. As the burning area of a circular port increases over the course of the burn the chamber pressure changes on a much longer time scale and we can use the steady state balance (10.14) together with the regression rate law (10.3) to determine the port radius as a function of time. Rewrite (10.14) as

$$P_{t2} = \left( \alpha \left( \frac{r}{r_i} \right) \right)^{\frac{1}{1-n}}$$

(10.33)

where

$$\alpha = \left( \frac{\gamma + 1}{2} \right)^{\frac{\gamma+1}{2(\gamma-1)}} K \frac{(\rho_p - \rho_g)}{\gamma (T_1 - T_p)} \sqrt{\gamma RT_{t2}} \left( \frac{2\pi r_i L}{A^*} \right)$$

(10.34)

and $L$ is the length of the port assumed to be constant. Now solve

$$\frac{dr}{dt} = \frac{K}{T_1 - T_p} \left( \alpha \left( \frac{r}{r_i} \right) \right)^{\frac{n}{1-n}}$$

(10.35)

for the radius of the port as a function of time.
Integrating (10.36) leads to

\[
\frac{r}{r_i} = \left(1 + \frac{1 - 2n}{1 - n} \frac{K\alpha(\frac{n}{1-n})t}{(T_1 - T_p) r_i} \right)^{\frac{1}{1-2n}} \quad n \neq 0.5
\]

\[
\frac{r}{r_i} = e^{\frac{K\alpha(\frac{n}{1-n})t}{(T_1 - T_p) r_i}} \quad n = 0.5.
\]

This defines a much longer time scale

\[
\tau_{burn} = \frac{(T_1 - T_p) r_i}{K\alpha(\frac{n}{1-n})}
\]

This time scale characterizes the change in chamber pressure during the burn. The burn time is determined by the outer radius of the motor.

\[
t_{burnout} = \left(\left(\frac{r_f}{r_i}\right)^{\frac{1}{1-2n}} - 1\right) \left(\frac{1 - n}{1 - 2n}\right) \tau_{burn} \quad n \neq 0.5
\]

\[
t_{burnout} = Ln\left(\frac{r_f}{r_i}\right) \tau_{burn} \quad n = 0.5
\]

### 10.4 Problems

**Problem 1** - It is a beautiful summer day at the Cape and a space shuttle astronaut on her second mission finds that the g forces during launch are noticeably larger than during her first mission that previous December. Can you offer a plausible explanation for this?

**Problem 2** - A solid propellant rocket operates in a vacuum with a 10 cm diameter nozzle throat and a nozzle area ratio of 100. The motor has a cylindrical port 300 cm long. At the beginning of the burn the port is 20 cm in diameter and the propellant recession velocity is 1 cm/sec. The port diameter at the end of the burn is 80 cm. The regression rate law is
\[ \dot{r} = aP_{t2}^{0.5}. \] (10.40)

The solid propellant density is 2 grams/cm\(^3\) and the combustion gas has \(\gamma = 1.2\) and molecular weight equal to 20. The combustion chamber temperature is 2500 \(K\). Determine the thrust versus time history of the motor.

**Problem 3** - One of the simplest types of solid rocket designs utilizes an end burning propellant grain as shown in Figure 10.4.

![Figure 10.4: Solid rocket with end burning grain.](image)

The motor diameter is 100 \(cm\) and the grain length at the beginning of the burn is 200 \(cm\). The solid propellant density is 2 grams/cm\(^3\). The combustion gas has \(\gamma = 1.2\) and molecular weight equal to 20. The combustion chamber temperature is 2500 \(K\) and, at the beginning of the burn, the pressure is \(P_{t2} = 5 \times 10^5 N/m^2\). The motor exhausts to vacuum through a 30 \(cm\) diameter nozzle throat and a nozzle area ratio of 10. Sketch the thrust-time history of the motor and determine the total impulse

\[ I = \int_0^{t_b} (\text{Thrust})dt \] (10.41)

in units of \(kg \cdot m/sec\).

**Problem 4** - The thrust versus time history of a solid rocket with a circular port is shown in Figure 10.5.

![Figure 10.5: Typical thrust time history of a solid rocket with a circular port.](image)
The regression rate of the propellant surface follows a law of the form

\[ \dot{r} = \alpha P t^n \]  \hspace{1cm} (10.42)

where the exponent \( n \) is in the range of 0.4 to 0.7. Briefly show why the thrust tends to increase over the course of the burn.

**Problem 5** - A solid propellant upper stage rocket operates in space. The motor has a 0.2 m diameter nozzle throat and a cylindrical port 4.2 m long. At the end of the burn the port is 0.8 m in diameter. The regression rate law is

\[ \dot{r} = 3.8 \times 10^{-6} P t^{0.5} \]  \hspace{1cm} (10.43)

where the pressure is expressed in \( N/m^2 \). The solid propellant density is 2000 \( kg/m^3 \) and the combustion gas has \( \gamma = 1.2 \) and molecular weight equal to 32. The combustion chamber temperature is 3000 \( K \). The quasi-equilibrium chamber pressure at the end of the startup transient is \( P_t = 3.0 \times 10^6 N/m^2 \).

1) Determine the characteristic time \( \tau \) for the start-up transient.

2) Determine the propellant mass expended during the startup transient. Take the start-up time to be 8\( \tau \).

3) Determine the mass flow and quasi-equilibrium chamber pressure \( P_t \) at the end of the burn.

4) Once the propellant is all burned the remaining gas in the chamber is expelled through the nozzle and the pressure in the chamber drops to zero. Calculate the time required for the pressure to drop to 10\% of its value at the end of the burn.

5) Sketch the pressure-time history of the motor.
Chapter 11

Hybrid Rockets

11.1 Conventional bi-propellant systems

A liquid bi-propellant chemical rocket system is shown schematically in Figure 11.1. Oxidizer and fuel from separate tanks are pressure-fed or pump-fed into a combustion chamber where atomization, mixing, ignition and combustion takes place. Despite the apparent simplicity of the diagram, liquid rockets are extremely complex. The complexity comes from the fact that the chamber pressure is usually quite high and one or both of the propellants may be cryogenic. In addition, the liquids are usually fed into the combustion chamber at very high mass flow rates requiring high performance turbo-pumps usually powered by a small flow of the propellants through a separate burner and turbine. Many of the most spectacular rocket failures have involved liquid bi-propellant systems.

![Figure 11.1: Schematic of a liquid bi-propellant rocket system.](image)

Perhaps the most widely recognizable liquid engines are the space shuttle main engines that burn hydrogen and oxygen. These engines also make use of a pre-burner where most of the oxygen is burned with a small amount of hydrogen to raise the temperature of the gases that are injected into the main combustion chamber along with the rest of the hydrogen. The hydrogen is also used to regeneratively cool the rocket chamber and nozzle prior to mixing
CHAPTER 11. HYBRID ROCKETS

with the oxygen. Many different oxidizers are used in bi-propellant systems. The two most popular are LOx (liquid oxygen) and $N_2O_4$. These are both very energetic oxidizers and burn readily with hydrocarbon fuels such as kerosene and alcohol as well as hydrazine ($N_2H_4$). The ideal specific impulse of kerosene burning with LOx is approximately 360 seconds depending on the chamber pressure and nozzle area ratio.

Liquid rockets can be throttled by controlling the flow of fuel and oxidizer while keeping the ratio of oxidizer to fuel flow the same. Wide throttle ratios are somewhat difficult to achieve because of the reduced mixing that can occur at low liquid flow rates. Liquid rockets are subject to a variety of instabilities and the design and development of a new injector and combustion chamber is an expensive multi-year process.

Figure 11.2 depicts a solid rocket system. Though mechanically much simpler than liquids, the solid rocket is complicated by the use of an explosive mixture of fuel and oxidizer that involves a very complex and expensive manufacturing process. In addition solid rockets require stringent safety precautions in manufacture, handling and launch.

![Figure 11.2: Schematic of a solid rocket motor.](image)

The propellant regression rate for a solid rocket is proportional to the chamber pressure according to a relation of the form

$$\dot{r} = \alpha P_t^{2n}$$  (11.1)

where $n < 1$. Probably the most well known solids are the large re-usable space shuttle boosters. Each uses approximately a million pounds of propellant and produces roughly three million pounds of thrust at launch. The fuel is mainly aluminum in a polymer binder (Hydroxyl Terminated Poly-butadiene, HTPB) and the oxidizer is ammonium perchlorate (AP) which is the most widely used solid oxidizer. In general solid rockets use somewhat less energetic oxidizers than liquids and the specific impulse of solids is generally lower. The ideal specific impulse of the shuttle booster propellant is approximately 280 seconds depending on the nozzle area ratio. Recently ammonium perchlorate has been found in the groundwater near many of the rocket propellant processing plants across the US and concerns have been raised about the possible environmental impact of this chlorinated compound.
The hazardous operation of the two basic types of chemical rocket propulsion comes mainly from the oxidizer and fuel that must be mixed to release energy in the rocket combustion chamber. In liquid bi-propellant rockets, a pump leak or tank rupture that brings these chemicals together in an uncontrolled way can result in a large explosion. In solid propellant rockets, the fuel and oxidizer are pre-mixed and held together in a polymer binder. Cracks or imperfections in the propellant can cause uncontrolled combustion and explosion.

11.2 The hybrid rocket idea

Figure 11.3 shows a hybrid rocket. The hybrid is inherently safer than other rocket designs. The idea is to store the oxidizer as a liquid and the fuel as a solid, producing a design that is less susceptible to chemical explosion than conventional solid and bi-propellant liquid designs. The fuel is contained within the rocket combustion chamber in the form of a cylinder with a circular channel called a port hollowed out along its axis. Upon ignition, a diffusion flame forms over the fuel surface along the length of the port. The combustion is sustained by heat transfer from the flame to the solid fuel causing continuous fuel vaporization until the oxidizer flow is turned off. In the event of a structural failure, oxidizer and fuel cannot mix intimately leading to a catastrophic explosion that might endanger personnel or destroy a launch pad.

The idea of the hybrid rocket has been known since the first flight in 1933 by Soviet researchers, but wasn’t given serious attention until the 1960’s. The primary motivation was the non-explosive character of the fuel, which led to safety in both operation and manufacture. The fuel could be fabricated at any conventional commercial site and even at the launch complex with no danger of explosion. Thus a large cost saving could be realized both in manufacture and launch operation. Additional advantages over the solid rocket are: greatly reduced sensitivity to cracks and de-bonds in the propellant, better specific impulse, throttle-ability to optimize the trajectory during atmospheric launch and orbit injection and the ability to thrust terminate on demand. The products of combustion are environmentally benign unlike conventional solids that produce acid forming gases such as hydrogen chloride.

The hybrid rocket requires one rather than two liquid containment and delivery systems. The complexity is further reduced by omission of a regenerative cooling system for both the chamber and nozzle. Throttling control in a hybrid is simpler because it alleviates the requirement to match the momenta of the dual propellant streams during the mixing process. Throttle ratios up to 10 have been common in hybrid motors. The fact that the fuel is in the solid phase makes it very easy to add performance enhancing materials to the fuel such as aluminum powder. In principle, this could enable the hybrid to gain an $I_{sp}$ advantage over a comparable hydrocarbon fueled liquid system.
Boundary layer combustion is the primary mechanism of hot gas generation in hybrid rockets. The idealized sketch in Figure 11.4 illustrates the flow configuration. The hybrid normally uses a liquid oxidizer that burns with a solid fuel although reverse hybrids such as liquid hydrogen burning with solid oxygen have been studied. The flame thickness and location in the boundary layer are shown roughly to scale. The flame zone is relatively deep in the boundary layer and the flame tends to be fuel rich based on the observed flame position and relatively low flame temperatures measured in the boundary layer. The hybrid enjoys many safety and environmental advantages over conventional systems, however large hybrids have not been commercially successful. The reason is that traditional systems use polymeric fuels that evaporate too slowly making it difficult to produce the high thrust needed for most applications.

11.2.1 The fuel regression rate law

Theory shows that the fuel mass transfer rate is proportional to the mass flux averaged
across the port. The mass flow rate increases with axial distance along the port leading to coupling between the local fuel regression rate and the local mass flux. For proper design, accurate expressions are needed for both the time dependent oxidizer-to-fuel ratio at the end of the port, and the time at which all the fuel is consumed. As the fuel is depleted the flame approaches the motor case at which point the burn must be terminated. The coupling between the local regression rate and the local mass flow rate means that both variables depend on time and space. This complicates the analysis of the thrust time behavior of the hybrid compared to a solid rocket. The problem is governed by two coupled first-order partial differential equations, the regression rate equation

\[ \frac{\partial r(x,t)}{\partial t} = \frac{a}{x^m} \left( \frac{\dot{m}_{\text{port}}}{\pi r^2} \right)^n \]  

(11.2)

and the mass flow growth equation

\[ \frac{\partial \dot{m}_{\text{port}}(x,t)}{\partial x} = \rho_f (2\pi r) a \frac{\dot{m}_{\text{port}}}{\pi r^2} \left( \frac{\dot{m}_{\text{port}}}{\pi r^2} \right)^n. \]  

(11.3)

The local mass flux in the port is generally denoted \( G \) where

\[ G = \frac{\dot{m}_{\text{port}}}{\pi r^2} = \frac{\dot{m}_{\text{ox}} + \dot{m}_f}{\pi r^2}. \]  

(11.4)

The local port mass flow rate, \( \dot{m}_{\text{port}} \), is the sum of the oxidizer mass flow rate, \( \dot{m}_{\text{ox}} \), injected at the entrance to the port and the accumulated fuel mass flow rate, \( \dot{m}_f \), transferred from the fuel grain upstream of a location \( x \). The coefficient \( a \) is an empirical constant determined by the choice of fuel and oxidizer. The units of the regression rate constant are

\[ [a] = \frac{\text{Length}^{2n+m+1}}{\text{Mass}^n \text{Time}^{1-n}}. \]  

(11.5)

The dependence of regression rate on mass flux \( G \) and stream-wise coordinate \( x \) arises from the dependence of the skin friction and heat transfer rate on Reynolds number based on distance along the port. Values of the exponents suggested by theory are \( m = 0.2 \) and \( n = 0.8 \). Measured values of \( n \) tend to be in the range 0.3 to 0.8 depending on the choice of fuel and oxidizer. Values of \( n \) greater than 0.8 or less than about 0.3 are generally not observed. The length exponent turns out to be very difficult to measure since it is relatively small and would require a large number of motor tests at a wide range of scales to be determined accurately. As nearly as one can tell at this point \( m \) is considerably smaller than the prediction of classical theory.
A widely used approximation to (11.2) and (11.3) is the single equation

\[
\frac{dr}{dt} = a_o G_{ox}^n.
\]

(11.6)

where the port length effect is neglected and the fuel regression rate is assumed to only depend on the oxidizer mass flux, which is constant along the port. In general, equation (11.6) underestimates the fuel mass generation rate. However, (11.6) can be a reasonably accurate approximation in situations where the design \( O/F \) ratio is relatively large, more than 5 or so.

A greater problem is that the vast majority of values of the regression rate constant reported in the literature correspond to \( a_o \) based on data measured against (11.6). The problem with this is that every change in the value of \( O/F \) for a given test motor requires the determination of a new value of \( a_o \). In point of fact the \( O/F \) generally varies during the course of a burn and so the reported value of \( a_o \) also depends on how the mean \( O/F \) is determined. Consider

\[
\frac{\partial r (x,t)}{\partial t} = \frac{a}{x^m} \left( \frac{\dot{m}_{\text{port}}}{\pi r^2} \right)^n = \frac{a}{x^m} \left( \frac{\dot{m}_{\text{ox}} (1 + 1/ (\dot{m}_{\text{ox}}/\dot{m}_f (x,t)))}{\pi r^2} \right)^n = a(1 + 1/(OF (x,t)))^n \left( \frac{\dot{m}_{\text{ox}}}{\pi r^2} \right)^n.
\]

(11.7)

If the basic regression rate equations (11.3) and (11.4) are to be believed then

\[
a_o = a(1 + 1/(OF (x,t)))^n.
\]

(11.8)

In principle \( a_o \) is a function of space and time. It can only be treated as a constant if some scheme of space time averaging of the \( O/F \) ratio is used for a given run and, even then, \( a_o \) will have a new value every time the \( O/F \) is changed. Unfortunately, when \( a_o \) is reported in the literature, the corresponding \( O/F \) is often not reported. A consequence is that today we often do not have good, solid empirical values of the regression rate constants for many propellant combinations.

In marked contrast to solid rockets, the regression rate of a hybrid is insensitive to the chamber pressure except at very low fluxes where radiation effects become important and at very high fluxes where chemical kinetics effects are important. This important characteristic enables the chamber pressure to be a free variable in the motor design enabling the designer to optimize the chamber pressure for a given mission. Although the hybrid seems to lie somewhere between a liquid and a solid system it has advantages that are unique and not enjoyed by liquids or solids.
11.2.2 Specific impulse

The theoretical specific impulse of a hybrid rocket is more appropriately compared to a bi-propellant liquid than a solid. The oxidizer can be any of the oxidizers used with liquid bi-propellant engines. Typically, the solid fuel is a polymeric hydrocarbon such as hydroxyl-terminated-poly-butadiene (HTPB), a common solid propellant binder with an energy density comparable to kerosene. But, hybrid solid fuel mass densities are typically 15-20% greater than the density of liquid kerosene. Figure 11.5 (left) depicts the theoretical specific impulse versus oxidizer to fuel \( O/F \) ratio of liquid oxygen (LOx) burning with paraffin and HTPB. A plot of LOx burning with liquid kerosene would look very similar.

Figure 11.5: Left figure, ideal specific impulse for paraffin and HTPB burning with LOx. Right figure paraffin-aluminum mixtures burning with nitrogen tetroxide. The IUS (Inertial Upper Stage) motor was a solid rocket built by the Chemical Systems Division of United Technologies and used as an upper stage in Boeing satellite launches for many years.

The plot on the right of Figure 11.5 shows the specific impulse of paraffin burning with \( N_2O_4 \) with varying percentages of aluminum added to the fuel by mass. Aluminum addition tends to increase the specific impulse slightly while reducing the optimal \( O/F \) allowing the designer to use a smaller liquid storage and feed system. These figures give a pretty good illustration of the range of \( O/F \) ratios used in typical systems. Generally, the oxidizer mass flow rate tends to be two or more times the fuel mass flow rate at the end of the port.

11.2.3 The problem of low regression rate

The main drawback of the hybrid is that the combustion process relies on a relatively slow mechanism of fuel melting, evaporation and diffusive mixing as depicted in Figure 11.4. In a solid rocket, the flame is much closer to the fuel surface and the regression rate is typically an order of magnitude larger. As a rough comparison, the regression rate in a solid rocket
at a typical rocket combustion chamber pressure may be on the order of $1.0 \text{ cm/sec}$ whereas a typical hybrid using a classical polymeric fuel such as HTPB may have a regression rate on the order of $0.1 \text{ cm/sec}$. To compensate for the low regression rate, the surface area for burning must be increased. This is accomplished through the use of a multi-port fuel grain such as that depicted in Figure 11.6. Most attempts to increase the regression rate involve some method for increasing the heat transfer rate to the fuel surface. This can be done, for example, by increasing turbulence levels in the port or by adding roughness to the fuel grain. The problem is that as the heat transfer rate is increased, the radial velocity of the evaporating fuel toward the center of the port increases. This so-called "blocking effect" tends to decrease the temperature gradient at the fuel surface leading to a reduction in the amount of heat transfer increase that can be achieved. A regression rate increase on the order of 25-30 % or so can be obtained using this approach - not the factor of 2 or 3 that is needed for a single port design.

![Figure 11.6: Single versus multi-port (wagon wheel) grain design.](image)

The most obvious problem with the multi-port design is that the amount of fuel that can be loaded into a given volume is reduced, leading to an increase in the vehicle diameter for a given total fuel mass. There are other problems. The grain may need to be produced in segments and each segment must be supported structurally, adding weight and complexity. In addition it is very difficult to get each port to burn at the same rate. If one burns slightly faster than another, then the oxidizer will tend to follow the path of least resistance leading to further disparity in the oxidizer flow rate variation from port to port. Toward the end of burning, the port that reaches the liner first forces the motor to be shut down prematurely leading to an inordinately large sliver fraction of unburned fuel. Small pressure differences from port to port can lead to grain structural failure and loss of fuel fragments through the nozzle. Aside from possible damage to the nozzle, the resulting increase in the overall $O/F$ ratio leads to a reduction of the specific impulse and an increase in the nozzle throat erosion rate. Due to the high erosion, the nozzle area ratio decreases excessively leading to an additional loss of specific impulse.
11.3 Historical perspective

Early hybrid rocket development and flight test programs were initiated both in Europe and the U.S. in the 1960’s. The European programs in France and Sweden involved small sounding rockets, whereas the American flight programs were target drones (Sandpiper, HAST, and Firebolt) which required supersonic flight in the upper atmosphere for up to 5 minutes. These latter applications were suitable for the conventional hybrid because its very low burning rate was ideal for a long duration sustainer operation.

Despite the very low regression rate of the fuel, in the late 1960’s Chemical Systems Division of United Technologies (CSD/UTC) investigated motor designs of larger diameters that could produce high thrust suitable for space launch vehicles. They experimented with a 38 inch diameter motor delivering 40,000 lbs of thrust. In order to achieve a high mass flow rate, a motor with 12 ports in the fuel grain was required. Although the motor was successfully fired several times, it was recognized that the poor volumetric fuel loading efficiency would lead to a deficit in vehicle performance.

Interest in the hybrid was revived again in the late 1970’s when concern was expressed for the storage and handling of the large solid propellant segments of the Shuttle booster. The storage of potentially explosive grains is costly in terms of requirements for reinforced structures and interline distance separation. The same safety concern arose again after the Space Shuttle Challenger disaster, where it was recognized that a thrust termination option might have avoided the failure. This concern was heightened when, a few months later, there was a Titan failure, caused by an explosion of one of the solid boosters.

Several hybrid propulsion programs were initiated in the late 80’s and early 90’s. The Joint Government/Industry Research and Development (JIRAD) program involved the testing of 11 and 24 inch diameter hybrid motors at the Marshall Space Flight Center. Another hybrid program initiated during the early 90s was DARPA’s Hybrid Technology Options Project (HyTOP). The goal of this program was to develop the HyFlyer launch vehicle and demonstrate the feasibility of hybrid boosters for space applications. The members of the HyTOP team were AMROC, Martin Marietta and CSD/UTC.

In the 1990s, two significant hybrid efforts occurred. One was the formation of the American Rocket Company (AMROC), an entrepreneurial industrial company devoted entirely to the development of large hybrid boosters. The second, with encouragement from NASA, was the formation of the Hybrid Propulsion Industry Action Group (HPIAG) composed of both system and propulsion companies devoted to exploring the possible use of hybrids for the Shuttle booster and other launch booster applications. Both efforts ran into technical stumbling blocks, basically caused by the low regression rate fuels, which resulted in large diameter motors with many ports to satisfy thrust requirements. The resulting configuration not only compromised potential retrofit for the Shuttle and Titan boosters
but also raised questions about the internal ballistic performance of a thin web multi-port motor, especially toward the end of burning when the web approaches structural failure. Although AMROC had many successful tests in 51 inch diameter motors, they ran into difficulties when the motor was scaled to 6 foot diameter and 250,000 pounds of thrust. The low regression rate of the fuel dictated a 15 port grain design and problems of poor grain integrity were the result. In 1995 AMROC filed for bankruptcy.

The Hybrid Propulsion Demonstration Program (HPDP) began in March 1995. The goal of the HPDP was to enhance and demonstrate several critical technologies that are essential for the full scale development of hybrid rocket boosters for space launch applications. The government and industry participants in the program were NASA, DARPA, Lockheed Martin, CSD/UTC, Thiokol, Rocketdyne, Allied Signal and Environmental Aeroscience Corporation. Even though the tasks of the HPDP program included systems studies and sub-scale testing, the main objective of the program was the design and fabrication of a 250,000 pound thrust test-bed. The design of the motor was guided by the sub-scale motor tests performed under the JIRAD program. The wagon wheel 7+1 multi-port fuel grain was made of conventional hydroxyl-terminated-polybutadiene (HTPB)/ Escorez fuel. The motor was fired for short times in July 1999. The motor exhibited large pressure oscillations and unequal burning rates in the various ports. Later the motor was stabilized by substantially increasing the heat input at the fore end of the motor. Problems related to low regression rate inherent in conventional hybrids fuels were not solved.

The most recent advance in hybrid rockets occurred in the Fall of 2004 when SpaceShipOne carried a pilot to over 328,000 feet to win the Ansari X-prize. This privately funded, sub-orbital flight seemed to usher in a new era in space tourism although the follow-on SpaceShipTwo has experienced lengthy delays in development.

![Space Ship One carried aloft by the White Knight carrier aircraft.](image)

The propulsion system for Space Ship One used a four port motor fueled by HTPB with nitrous oxide ($N_2O$) as the oxidizer. Although the flight of Space Ship One was a great success, it was not exactly a walk in the park for the pilot. The description in Figure 11.9
reveals a pretty sobering picture of the flight.

The conclusion from this history is that if a significantly higher burning rate fuel can be developed for the hybrid motor, the multi-port difficulties just described can be alleviated and a smaller, safer more efficient motor can be designed. Although this deficiency of conventional hybrid fuels was recognized more than forty years ago, attempts to increase the burning rate by more than 50-100 %, without compromising the safety and low-cost features of the hybrid design, have been largely unsuccessful until recently.
11.4 High regression rate fuels

In the late 1990s, the U.S. Air Force studied some exotic cryogenic designs for hybrid rockets. One scheme would have swapped the roles of the fuel and oxidizer. The fuel was liquid hydrogen and the oxidizer was solid oxygen. While investigating this unusual configuration, the Air Force also studied a different combination of cryogenic propellants: liquid oxygen and pentane, a hydrocarbon that is liquid at room temperature, but in this application was frozen solid using a bath of liquid nitrogen. The Air Force researchers found that solid pentane burns 3 to 4 times faster than normal fuels. The Air Force researchers kindly shared their data with us and after some careful analysis it appeared that mass transfer from the surface of this fuel involved more than simple evaporation.

Pentane produces a very thin, low viscosity, low surface tension, liquid layer on the fuel surface when it burns. The instability of this layer driven by the shearing effect of the oxidizer gas flow in the port leads to the lift-off and entrainment of droplets into the gas stream greatly increasing the overall fuel mass transfer rate. The multitude of entrained droplets offers an enormous amount of surface area for evaporation and burning without the usual reduction caused by the blocking effect. The basic mechanism is sketched in Figure 11.10.

![Liquid layer entrainment mechanism.](image)

In effect, this mechanism acts like a continuous spray injection system distributed along the port with most of the fuel vaporization occurring around droplets convecting between the melt layer and the flame front. Since droplet entrainment is not limited by diffusive heat transfer to the fuel from the combustion zone, this mechanism can lead to much higher surface regression rates than can be achieved with conventional polymeric fuels that rely solely on evaporation. Equation (11.9) shows how the entrainment mass transfer component of the regression rate illustrated in Figure 11.10 depends on the parameters of the flow: the chamber pressure, $P$, liquid layer thickness, $h$, surface tension, $\sigma$ and viscosity, $\mu$. The exponents in (11.9) are determined empirically and are of order one.
The key fuel properties are in the denominator of (11.9) - low surface tension and low viscosity of the melt layer, evaluated at the characteristic temperature of the layer. This forms the basis of a fundamental criterion that can be used to identify high regression rate fuels. Not all fuels that form a melt layer at the fuel surface will entrain. For example, high-density-polyethelene (HDPE), which is a conventional hybrid fuel, does form a melt layer but the viscosity of the liquid is four orders of magnitude larger than pentane - too viscous to permit significant droplet entrainment. But frozen pentane itself is not a particularly promising fuel. It is not practical to have to soak the rocket motor in a liquid nitrogen bath before launch. This led to a search for a fuel that would be solid at room temperature, that would produce a low-viscosity liquid when it melted, and would be strong enough to withstand the high-temperature, high-pressure, high-vibration environment of a rocket motor’s combustion chamber. To achieve this goal it was necessary to solve a puzzle.

Figure 11.11 shows the effect of molecular weight on the melt temperature and boiling temperature for the normal alkanes. The middle curve is an estimate of the mean melt layer temperature. The normal alkanes are linear, fully saturated hydrocarbons with the formula \( C_nH_{2n+2}\). Familiar examples include methane (one carbon atom per molecule), ethane (two carbons), and propane (three carbons). As the number of carbon atoms in the molecule increases, the normal alkanes become room-temperature liquids, such as pentane (five carbons), and eventually solids such as waxes and polyethylene.
to decrease exponentially fast with temperature. These facts can be applied to the melt layer of the normal alkanes. At high molecular weight, where the melt layer temperature increases only slowly, the viscosity increases through the dominance of the molecular weight effect. But at lower molecular weight, where the melt layer temperature increases rapidly, the tendency for the viscosity to increase with molecular weight is strongly offset by the tendency for viscosity to decrease with temperature.

The design goal is to find a hydrocarbon with the right molecular weight. At high molecular weights, the viscosity of the liquid form of the alkane is too large for droplets to form readily. At low molecular weights, the alkanes are either gaseous or liquid or soft solids, much too weak to withstand the rigors of a rocket combustion chamber. In between is a sweet spot; Fuels with roughly 25 to 50 carbon atoms per molecule that are structurally robust and produce low-viscosity liquids when they melt. Figure 11.12 indicates schematically the range of carbon numbers that are likely to produce significant entrainment mass transfer.

Figure 11.12: Schematic diagram indicating the normal alkanes that are expected to exhibit high regression rate.

These fuels, which include the paraffin waxes and polyethylene waxes, are predicted to have high regression rates at oxidizer mass fluxes covering a wide range of hybrid rocket applications. In fact, the viscosity of the melt layer in paraffin is comparable to pentane and so the regression rate is also similar despite the disparity in molecular weight. The kind of paraffin wax we use is a relatively high carbon number, fully refined, wax sometimes called sculptor’s wax or hurricane wax. Fabricating, handling, and transporting traditional solid-rocket propellants is usually very costly, but a paraffin-based fuel is easy to deal with in all those regards. It is nontoxic, and indeed not hazardous at all. What’s more, the complete combustion of this fuel with oxygen produces no hazardous gases. The products are simply
carbon dioxide and water. In contrast, the by-products of burning conventional solid rocket propellant often include carbon monoxide as well as acid forming gases such as hydrogen chloride. A more benign, easier to use, rocket fuel could hardly be imagined!

Regression rates 3 to 4 times the predicted classical rate have been observed in a laboratory scale motor using gaseous oxygen and an industrial grade paraffin wax. The specific impulse of a paraffin-based hybrid motor is slightly higher than that of a kerosene-based liquid motor and solid paraffin is approximately 20% more dense than liquid kerosene. Figure 11.4 shows the ideal specific impulse of paraffin wax and HTPB burning with liquid oxygen. The waxes comprise a wide range of molecular weight, surface tension and viscosity and therefore can be used to create mixtures whose regression rate characteristics are tailored for a given mission.

11.5 The $O/F$ shift

Over the course of a burn at a fixed oxidizer mass flow rate there is a tendency for the oxidizer to fuel ($O/F$) ratio to shift to higher values as the port opens up. This can be seen from the following. For a single circular port a rough estimate of the $O/F$ ratio at the end of the port is, using (11.6)

$$O/F = \frac{\dot{m}_o}{\dot{m}_f} = \frac{\dot{m}_o}{\rho_f \pi D \alpha (\frac{m_o}{\pi r})^n} = \frac{\dot{m}_o^{1-n} D^{2n-1}}{4^n \pi^{1-n} \alpha \rho_f L}$$

(11.10)

where $L$ is the port length and $r$ is the port radius. Recall that the exponent is generally in the range $0.6 < n < 0.8$. As the port diameter increases the burning area increases and the oxidizer mass flux goes down. For $n > 0.5$ the decrease in mass flux dominates the increase in burning area and the overall generation rate of fuel mass goes down. The net effect is to cause the chamber pressure and hence the thrust to decrease naturally over the course of the burn as the vehicle mass decreases. This feature is desirable for a launch system where the payload is subject to a maximum acceleration constraint. Compare this to a solid rocket where the thrust tends to increase during the burn and a throttling option is not available.

Note the relatively strong sensitivity in Figure 11.4 of the specific impulse to the $O/F$ ratio. The change of $O/F$ implies a change in specific impulse and a possible reduction in vehicle performance. This is a factor that must be taken into account by the designer seeking to get maximum total delivered impulse from the motor. In practice the maximum payload acceleration limit leads to a requirement that the oxidizer mass flow be throttled back while the port opens up and the two effects tend to offset one another. A typical case might be a factor of two decrease in the oxidizer mass flow rate and a factor of three
increase in the port diameter. For \( n = 0.62 \) the net effect is less than a one percent change in \( O/F \).

### 11.6 Scale-up tests

To demonstrate the feasibility of high regression rate fuels, a series of tests were carried out on intermediate scale motors at pressures and mass fluxes representative of commercial applications. A hybrid test facility designed to study these fuels was developed by NASA and Stanford researchers at NASA Ames Research Center. An image from one of these tests is shown in Figure 11.13.

![Image of hybrid rocket motor tests](image)

**Figure 11.13:** Hybrid motor tests at Stanford and NASA Ames showing a typical pressure time history of the Ames tests. Thrust in the image shown is approximately 10000 Newtons with a simple convergent nozzle.

Figure 11.14 shows the main results of these tests as well as earlier results of testing on a laboratory scale motor at Stanford. The results are compared with HTPB.

The main conclusions from these tests are the following.

1) The regression rate behavior observed in the small scale tests at Stanford prevails when the motor is scaled up to chamber pressures and mass fluxes characteristic of operational systems. Moreover the regression rate data from large and small motors matches quite well indicating that small scale tests can be used to infer the behavior of larger motors.
This is extremely useful when it comes to developing the right fuel formulation for a given mission.

2) Paraffin-based fuels provide reliable ignition and stable combustion over the entire range of mass fluxes encountered ($50 - 600 \text{ kg/m}^2 - \text{sec}$).

3) The fuel exhibited excellent structural integrity over the range of chamber pressures used ($10 - 65 \text{ bar}$).

### 11.7 Regression rate analysis

#### 11.7.1 Regression rate with the effect of fuel mass flow neglected.

The simplest approach to determining how the port radius varies with time is to neglect the effect of accumulated fuel mass flow on the regression rate and assume the length exponent $m = 0$ so the port radius is independent of $x$. This utilizes the fact that $m$ is known to be small allowing the singularity at $x = 0$ to be removed. Moreover the optimal $O/F$ is often three or more so the oxidizer usually comprises most of the mass flow. Recall (11.6) and express the mass flux in terms of the radius and oxidizer mass flow.

$$\frac{dr(t)}{dt} = a_o \left( \frac{\dot{m}_{\text{ox}}(t)}{\pi r^2} \right)^n$$  \hspace{1cm} (11.11)
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Integrate (11.11) with respect to time.

\[
r(t) = \left( r(0)^{2n+1} + (2n + 1) \frac{a_o}{\pi^n} \int_0^t \dot{m}_{ox}(t')^n dt' \right)^{\frac{1}{2n+1}}
\]  

(11.12)

Under the assumed regression rate (11.11) law the mass flow increases linearly along the port.

\[
\frac{\dot{m}_{port}}{\dot{m}_{ox}} = \frac{\dot{m}_f + \dot{m}_{ox}}{\dot{m}_{ox}} = 1 + \left( \frac{2\pi^{-n}a_o\rho_f}{\dot{m}_{ox}^{1-n}\left(r(0)^{2n+1} + (2n + 1) \frac{a_o}{\pi^n} \int_0^t \dot{m}_{ox}(t')^n dt' \right)^{\frac{2n-1}{2n+1}}} \right) x
\]  

(11.13)

11.7.2 Exact solution of the coupled space-time problem for \( n = 1/2 \).

In reality the regression rate is dependent on the local total mass flux including the fuel mass accumulated along the port and, in turn, the local mass flux depends on the local radius. The problem is governed by two coupled first-order partial differential equations, (11.2) and (11.3). For \( n = 1/2 \) the equations simplify to

\[
\frac{\partial}{\partial t} \left( r^2 \right) = 2\pi^{-1/2}a \frac{\dot{m}_{port}^{1/2}}{x^m}
\]  

(11.14)

and

\[
\frac{\partial \dot{m}_{port}}{\partial x} = 2\pi^{1/2}a\rho_f \frac{\dot{m}_{port}^{1/2}}{x^m}
\]  

(11.15)

The solution of (11.14) and (11.15) is

\[
r(x, t) = \left( r(x, 0)^2 + \frac{2a}{x^m \pi^{1/2}} \left( \int_0^t \dot{m}_{ox}(t')^{1/2} dt' + \frac{\pi^{1/2}a\rho_f x^{1-m} t}{1-m} \right) \right)^{1/2}
\]  

(11.16)

and

\[
\dot{m}_{port}(x, t) = \left( \dot{m}_{ox}(t)^{1/2} + \frac{\pi^{1/2}a\rho_f x^{1-m}}{1-m} \right)^2
\]  

(11.17)
For \( n = 1/2 \), the increased fuel mass generation due to the increase in port surface area is exactly compensated by the decrease in mass flux due to the growth in port cross-sectional area. As a result the total mass flow rate (11.17) at any point in the port is independent of time if \( \dot{m}_{\text{ox}} \) is constant. For \( n > 1/2 \) the effect of decreasing mass flux dominates the increase in port surface area and the mass flow rate at a given coordinate along the port decreases with time as the port opens up. If \( n < 1/2 \) the mass flow rate increases with time. Note that according to (11.16), shortly after the oxidizer flow is initiated the radius of the fore end of the port is infinite if the length exponent, \( m > 0 \). Figure 11.15 shows a typical shape of the port after some period of time has elapsed after ignition. There is typically a minimum radius point near the fore end of the port downstream of which the port opens up slightly.

![Figure 11.15: Typical port shape at the end of a burn for \( m > 0 \).](image)

### 11.7.3 Similarity solution of the coupled space-time problem for general \( n \) and \( m \).

For general values of \( n \) and \( m \) the coupled equations (11.2) and (11.3) can be solved numerically given the initial port geometry and oxidizer mass flow rate, \( \dot{m}_{\text{ox}} (t) \). Reference [1] discusses the coupled problem and includes an example of a numerical solution. As it turns out, (11.2) and (11.3) admit a similarity solution for constant \( \dot{m}_{\text{ox}} \). This allows the equations to be reduced to a pair of ODEs in the similarity variable

\[
\theta = \left( \frac{(\pi - n_a)^2 (2\pi \rho f)^{(2n+1)}}{\dot{m}_{\text{ox}}} \right)^{\frac{1}{2n-2m+1}} \frac{x}{t^{\frac{2n-1}{2n-2m+1}}}.
\]

The similarity solution is derived in reference [2]. It can be used to generate accurate solutions for the port radius and \( O/F \) ratio. The similarity solution can even be applied
to the case where $\dot{m}_{\text{ox}}$ does change with time by using a staircase function to approximate $\dot{m}_{\text{ox}}$.

### 11.7.4 Numerical solution for the coupled space-time problem, for general $n$ and $m$ and variable oxidizer flow rate.

The coupled equations (11.2) and (11.3) can be solved for a general initial port radius distribution and variable oxidizer mass flow rate using a first order forward difference scheme. First, the equations are non-dimensionalized using the initial oxidizer mass flow rate, $\dot{m}_{\text{ox}}(0)$, the initial port radius at the fore end, $r(0,0)$ and the burn time, $t_{\text{burntime}}$. Dimensionless variables as follows.

\[
\begin{align*}
\chi &= \frac{x}{r(0,0)} \\
\tau &= \frac{t}{t_{\text{burntime}}} \\
R &= \frac{r(x,t)}{r(0,0)} \\
\end{align*}
\]

\[
\begin{align*}
\dot{J}(x,t) &= \frac{\dot{m}_{\text{port}}}{\dot{m}_{\text{ox}}(0)} = \frac{\dot{m}_{\text{ox}}(t) + \dot{m}_{f}(x,t)}{\dot{m}_{\text{ox}}(0)} = \\
&= \frac{\dot{m}_{\text{ox}}(0) + \dot{m}_{f}(x,t)}{\dot{m}_{\text{ox}}(0)} + \left( \frac{\dot{m}_{\text{ox}}(t) - \dot{m}_{\text{ox}}(0)}{\dot{m}_{\text{ox}}(0)} \right) \\
J(x,t) &= \frac{\dot{m}_{\text{ox}}(0) + \dot{m}_{f}(x,t)}{\dot{m}_{\text{ox}}(0)} \\
\lambda(t) &= \frac{\dot{m}_{\text{ox}}(t) - \dot{m}_{\text{ox}}(0)}{\dot{m}_{\text{ox}}(0)} \\
\end{align*}
\]

In dimensionless form, the coupled equations are

\[
\frac{\partial R}{\partial \tau} = C_R \frac{1}{\chi^m} \left( \frac{J + \lambda}{\pi R^2} \right)^n
\]

and
\[ \frac{\partial J}{\partial \tau} = C_J \left( \frac{J + \lambda}{\pi R^2} \right)^n \]  

(11.21)

where

\[ C_R = \frac{a t_{burntime} \dot{m}_{ox}(0)^n}{r(0,0)^{2n+m+1}} \]  

(11.22)

and

\[ C_J = \frac{a \rho_f \dot{m}_{ox}(0)^{n-1}}{r(0,0)^{2n+m-2}} \]  

(11.23)

are dimensionless constants. The variable ranges are

\[ 0 < \chi < \frac{L_{port}}{r(0,0)} \]  

(11.24)

\[ 0 < \tau < 1 \]

where \( L_{port} \) is the port length.

Equations (11.20) and (11.21) can be integrated using a simple first order forward difference scheme.

Step 1 - Specify \( r(0,0) \), \( L_{port} \), \( t_{burntime} \), and the regression rate constants, \( a \), \( n \), and \( m \). Calculate \( C_R \) and \( C_J \). If the initial port radius is not constant along the port, specify \( R(\chi,0) \). If the oxidizer mass flow rate varies with time, specify \( \lambda(\tau) \).

Step 2 - Choose a grid of \( \chi \) and \( \tau \) coordinates.

\[ \chi_i = \left( i/i_{\text{max}} \right) \left( L_{port}/r(0,0) \right), \quad i = 1, \ldots, i_{\text{max}} \]

\[ \tau_j = \left( j/j_{\text{max}} \right), \quad j = 1, \ldots, j_{\text{max}} \]  

(11.25)

Step 3 - Create tables defining the initial port geometry, \( R(\chi_i,0), \quad i = 1, \ldots, i_{\text{max}} \), and oxidizer mass flow rate values, \( \lambda(\tau_j), \quad j = 1, \ldots, j_{\text{max}} \).

Step 4 - Create tables defining the initial values of the radius and mass flow functions.
\[ R(\chi_i, \tau_j) = R(\chi_i, 0), \quad i = 1, \ldots, i_{\text{max}}, \quad j = 1, \ldots, j_{\text{max}} \]  
\[ J(\chi_i, \tau_j) = 1, \quad i = 1, \ldots, i_{\text{max}}, \quad j = 1, \ldots, j_{\text{max}} \]  
\hline

Step 5 - Update the \( R \) and \( J \) tables over the length of the port and for the length of the burn using the following first-order iterative scheme.

\[ R(\chi_i, \tau_{j+1}) = R(\chi_i, \tau_j) + \Delta \tau \frac{CR}{\chi_i^m} \left( \frac{J(\chi_i, \tau_j) + \lambda(\tau_j)}{\pi R(\chi_i, \tau_j)^2} \right)^n \]  
\[ J(\chi_{i+1}, \tau_j) = J(\chi_i, \tau_j) + \Delta \chi \frac{C_J}{\chi_i^m} \left( \frac{J(\chi_i, \tau_j) + \lambda(\tau_j)}{\pi R(\chi_i, \tau_j)^2} \right)^n \]  
\hline

where the differences in time and space are

\[ \Delta \tau = 1/j_{\text{max}} \]  
\[ \Delta \chi = (1/i_{\text{max}}) \left( \frac{L_{\text{port}}}{r(0,0)} \right) \]  
\hline

The resulting tables of \( R(\chi_i, \tau_j) \) and \( J(\chi_i, \tau_j) \) can be used to generate all of the information needed to characterize the burn.

11.7.5 Example - Numerical solution of the coupled problem for a long burning, midsize motor as presented in reference [1].

Regression rate data in Figure 11.14 from the tests described above of a 10,000 Newton class hybrid rocket motor at NASA Ames led to the following exponents for Liquid Oxygen burning with Paraffin, \( n = 0.62, m = 0.015 \). The multiplier was found to be \( a = 9.27 \times 10^{-5} \) kg \( m^{2n+m+1} \) kg^{-n} sec^{-1} \( m^{2.39} \) kg^{-0.62} sec^{-0.38}. Generally the motor ran for about 8 seconds during which time the port radius increased by a factor of a little less than 2. The port length is \( L_{\text{port}} = 1.143 \) m. Initially, the port radius is \( r(0,0) = 0.0508 \) m and is constant along the port. The fuel density is \( \rho_f = 920.0 \) kg/m^3. In the numerical results shown in Figures 11.16 and 11.17, the burn is continued for up to 100 seconds.
Figure 11.16: Port functions during a 100 sec burn; (a) Port radius as a function of $x$ at several times during the burn; (b) Fuel mass flow as a function of time at the downstream end of the port; (c) Oxidizer to fuel ratio as a function of time at the downstream end of the port; (d) Mass flux as a function of time at the downstream end of the port.

Figure 11.17: Port functions during a 100 sec burn; (a) Close-up of the port radius function of $x$ at the end of the burn; (b) Unburned fuel sliver at the end of the burn.
The computations in Figures 11.16 and 11.17 were carried out on an \( i_{\text{max}} = 2000 \) by \( j_{\text{max}} = 2000 \) grid with uniform increments in the \( x \) and \( t \) directions. I used \textit{Mathematica} for the computation which took 62 seconds on my 3.4 GHz Intel Core i7 imac. In the 2007 JPP paper, reference [1], a higher order scheme was used on a much coarser grid.

A couple of features in Figure 11.16 (a) should be mentioned. Due to the singularity in \( x \) in the denominator of the coupled equations, the radius and regression rate are infinite at \( x = 0 \). To avoid the singularity, the first numerical evaluation in \( x \) is at \( x = L_{\text{port}}/i_{\text{max}} \). The similarity solution described in the previous section can accurately resolve the solution near \( x = 0 \). There is a minimum in the port radius near the fore end of the port, the location of which depends on \( m \). Beyond the minimum the port opens up slightly with the maximum radius occurring at the end of the port, a feature called "coning". Another important aspect of Figure 11.16 (a) is the slowing rate of increase in port radius with time as the burn progresses. This is reflected in Figure 11.16 (b) which depicts the decreasing rate of fuel generation as the port opens up, and in Figure 11.16 (c) which shows the corresponding increase in \( O/F \) ratio. For \( n > 0.5 \) the decrease in mass flux depicted in Figure 11.16 (d) dominates the increase in port surface area leading to a decrease in the fuel mass flow rate with time. A consequence of the increase in port radius with \( x \) is that when the burn ends, there is a sliver of fuel that remains unburned. This is shown in Figure 11.17 (a) and (b). One way to alleviate this in practice is to fabricate the initial port with a slight decrease in radius with \( x \) and a computation of this case is included in reference [1]. The required amount of decrease depends on the planned burn time.

### 11.7.6 Sensitivity of the coupled space-time problem to small changes in \( a, n, \) and \( m \).

There is quite a bit of scatter in the data reported in the literature for the values of the regression rate parameters even for the same propellant combinations. It is of interest therefore to see how sensitive the regression rate is to small changes in the parameters \( a, n, \) and \( m \). Let the parameters be changed by small amounts.

\[
\begin{align*}
    a & \rightarrow aa' \\
    n & \rightarrow n + n' \\
    m & \rightarrow m + m'
\end{align*}
\]  

(11.29)

The regression rate equations become
\[
\frac{\partial r(x,t)}{\partial t} = \frac{aa'}{x^{m+m'}} \left( \frac{\dot{m}_{\text{port}}(x,t) + \Delta \dot{m}_{\text{ox}}(t)}{\pi r^2} \right)^{n+n'}
\]

\[
\frac{\partial \dot{m}_{\text{port}}(x,t)}{\partial x} = \rho_f (2\pi r) \frac{(aa')}{x^{m+m'}} \left( \frac{\dot{m}_{\text{port}}(x,t) + \Delta \dot{m}_{\text{ox}}(t)}{\pi r^2} \right)^{n+n'}.
\]

The ratio of the disturbed to undisturbed regression rate and mass flow rate is

\[
\left. \frac{\partial R}{\partial \tau} \right|_{(n',m')=(0,0)} = \left. \frac{\partial J}{\partial \chi} \right|_{(n',m')=(0,0)} = \frac{a' \pi^{n'} \left( \frac{\dot{m}_{\text{ox}}(0)}{\pi r(0,0)^2} \right)^{n'}}{r(0,0)^{m'}} \frac{1}{\lambda} \left( J + \frac{\lambda}{\pi R^2} \right)^{n'}
\]

The relative error in both rates is the same. Notice that \(a\) and \(a'\) do not have the same units and that \(a'\) is a number close to one.

\[
[a] = \frac{L^{2n+m+1}T^{n-1}}{M^n}
\]

\[
[a'] = \frac{L^{2n'+m'}T^{n'}}{M^{n'}}
\]

For small changes in \(n\) and \(m\), and values of \(a'\) very close to one we can approximate Equation (11.31) as

\[
\left. \frac{\partial R}{\partial \tau} \right|_{(n',m')=(0,0)} = \left. \frac{\partial J}{\partial \chi} \right|_{(n',m')=(0,0)} \cong 1 + n' \left\{ \ln \left( \frac{(a')^{1/n'} \pi}{r(0,0)^{m'/n'}} \left( \frac{\dot{m}_{\text{ox}}(0)}{\pi r(0,0)^2} \right) \right) + \ln \left( \frac{J + \lambda}{\lambda \pi R^2} \right) \right\}
\]

The first term in (11.33) in brackets is a fixed number and, to a good approximation, is the logarithm of \(\pi\) times the initial flux in the port, typically a number in the range 5 to 8. The second term in brackets is approximately the logarithm of the dimensionless flux in the port and depends on space and time. The dimensionless flux is generally less than one so this factor tends to be negative except near the port entrance. For \(m = 0\) the second factor is approximately \(\ln (1/\pi) = -1.14\). In general, small changes in \(n\) change the rates.
substantially more than comparable changes in $a$ or $m$. Figure 11.18 shows the sensitivity to small changes in $n$ for the 100 second run considered in the last section.

References


11.8 Problems

Problem 1 - The thrust versus time history of a hybrid rocket with a circular port is shown in Figure 11.19. The oxidizer mass flow rate is constant during the burn. The regression rate of the fuel surface follows a law of the form
\[ \dot{r} = \alpha G^n \]  \hspace{1cm} (11.34)

where the exponent \( n \) is in the range of 0.6 to 0.8 and \( G \) is the mass flux in the port. Briefly discuss why the thrust tends to decrease over the course of the burn. How would the thrust vary if the exponent was less than 0.5?

**Problem 2** - A research project at NASA Ames called Peregrine has the goal of launching a fairly large sounding rocket to an altitude of 100 km from NASA Wallops. The current design uses a paraffin - \( \text{N}_2\text{O} \) hybrid rocket motor that operates with a nozzle throat diameter of 10 cm and a nozzle exit diameter of 30 cm. The motor has a cylindrical port and the fuel grain is 143 cm long. At the beginning of the burn the \( \text{N}_2\text{O} \) mass flow is 24.0 kg/sec, and the port diameter is 23.3 cm. The diameter at the end of the port and the end of the burn is 38 cm. Assume that the mass flow rate of the \( \text{N}_2\text{O} \) is constant over the burn. The regression rate law in mks units is

\[ \dot{r} = 14.84 \times 10^{-5} G^{0.5} \text{ m/sec}. \]  \hspace{1cm} (11.35)

The paraffin density is 924.5 kg/m\(^3\). The chemical formula of the paraffin used is \( C_{32}H_{66} \) and the heat of formation is 698.52 kJ/mole.

1) Determine port diameter as a function of \( x \) at the end of the burn. How long is the burn? Assume the outer diameter of the fuel grain is constant and matches the port diameter at the end of the port at the end of the burn. What is the mass of unburned fuel?

2) Determine the mass flow rate and \( O/F \) ratio at the end of the port.

3) Determine the chamber pressure.

4) Plot the sea level thrust-time history of the motor and estimate the total delivered impulse (the integral of the thrust time curve). Use CEA to determine the specific impulse, \( C^* \) and the nozzle exit pressure.
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Problem 3 - A paraffin-oxygen hybrid rocket operates in a vacuum with a 10 cm diameter nozzle throat and a nozzle area ratio of 70. The motor has a cylindrical port 300 cm long. At the beginning of the burn the port is 20 cm in diameter and $O/F = 2.3$. The port diameter at the end of the burn is 60 cm. The regression rate law is

$$\dot{r} = 9.27 \times 10^{-5} \Gamma^{0.62} \text{ m/sec}.$$  (11.36)

The fuel density is 924.5 $kg/m^3$ and the combustion gas has $\gamma = 1.15$ and average molecular weight equal to 30. Assume the oxidizer flow rate is constant and the combustion chamber temperature remains constant over the course of the burn. Approximate the specific impulse by a mean value of 360 sec over the course of the burn.

1) Estimate the chamber pressure at the beginning of the burn.
2) Plot the diameter of the port as a function of time.
3) Plot the thrust-time history of the burn and estimate the total delivered impulse (the integral of the thrust time curve).
4) Use Figure 11.4 to estimate the specific impulse at the end of the burn.

Problem 4 - A hybrid rocket with an initial mass of $m_{\text{initial}} = 900 \, kg$ operates in space. The fuel is paraffin with a density 0.93 $gm/cm^3$ and the oxidizer is nitrous oxide. The oxidizer mass flow rate is held fixed at $2.4 \times 10^4 \, gm/sec$. The motor has a 10 cm diameter nozzle throat, 30 cm diameter exit, and a cylindrical port 143 cm long. The initial port radius is 8.75 cm. At the end of the burn the port radius is 15.5 cm. The regression rate law is $\dot{r} = 0.035 \Gamma^{0.6} \text{ cm/sec}$. A calculation using CEA shows that $c^* = 1.64 \times 10^5 \text{ cm/sec}$ where $C^*$ is defined by $\dot{m} = P t_2 A^*/C^*$ and the effective nozzle exit velocity is $C = 2.8 \times 10^5 \text{ cm/sec}$.

1) When the fuel is all burned the oxidizer flow is turned off. Determine the time when this occurs.
2) Determine the total mass flow rate and motor thrust at the beginning and end of the burn.
3) Determine the chamber pressure at the beginning and end of the burn.
4) Determine the velocity change of the vehicle.
Appendix A

Thermochemistry

A.1 Thermochemical tables

In Chapter 9 we developed the theory for determining the equilibrium composition of a mixture of reacting gases. The procedure requires knowledge of the standard Gibbs free energy for each molecule in the mixture

\[ g_i^\circ (T) = \Delta h_i^\circ (T_{\text{ref}}) + \{ h_i^\circ (T) - h_i^\circ (T_{\text{ref}}) \} - T s_i^\circ (T) \]  (A.1)

where \( \Delta h_i^\circ (T_{\text{ref}}) \) is the standard heat of formation of the \( i \)th chemical species at some reference temperature, \( \{ h_i^\circ (T) - h_i^\circ (T_{\text{ref}}) \} \) is the change in the standard enthalpy from the reference temperature and \( s_i^\circ (T) \) is the standard entropy. Data for these variables for a given chemical species can be found in tabulations of thermochemical properties that have been developed from experimental measurements of heat capacity over many decades.

The purpose of this appendix is to describe the tables, explain the data and connect thermodynamic properties of gases to the chemical bonds between the atoms that make up the gas. Perhaps the most widely used thermochemical data is from the compilation produced by the JANAF (Joint Army, Navy, Air Force) Committee. Parts of the JANAF tables for monatomic and diatomic hydrogen are shown in Figure A.1.

All quantities are quoted on a per mole basis and in units of Joules and degrees Kelvin. One mole is an Avagadros number, \( \text{6.0221415} \times 10^{23} \), of molecules. In the table headings in Figure A.1 properties are symbolized using capital letters, whereas, we have adopted the convention that all intensive (per unit mass or per unit mole) variables are denoted with lower case letters as in (A.1) and we will stick to that convention. Full tables for a variety of chemical species are provided in Appendix B.
A.2 Standard pressure

Conservation of energy for a system containing some substance is expressed as the First Law of thermodynamics.

\[ \delta q = de + PdV \]  \hspace{1cm} (A.2)

The enthalpy is defined as

\[ h = e + PV. \]  \hspace{1cm} (A.3)

If we use (A.3) to replace the internal energy in (A.2) the result is an equivalent form of the first law expressed in terms of the enthalpy

\[ \delta q = dh - VdP. \]  \hspace{1cm} (A.4)

The internal energy \( e \) and enthalpy \( h \) are related to the temperature, pressure and volume of the system through the definitions of the specific heats.

\[
C_V = \frac{\partial e}{\partial T} |_{Volume} \\
C_P = \frac{\partial e}{\partial T} |_{Pressure}
\]

(A.5)

For a process that takes place at constant pressure, the heat added or removed from the system is given by the change of enthalpy.
\[ \delta q|_{P=\text{constant}} = dh|_{P=\text{constant}} = C_P dT \]  

(A.6)

It is probably fair to say that the use of the tables of thermochemical properties is dominated by applications to mixtures of reacting gases typical of combustion at elevated temperatures. As long as the pressure is not extreme, and the system is not near a phase boundary, the equation of state for each gas in the mixture is the ideal gas law

\[ P_i V = n_i R_u T \]  

(A.7)

where \( n_i \) is the number of moles of the \( i \)th component of the mixture, \( P_i \) is the partial pressure and \( V \) is the volume of the mixture. The universal gas constant is

\[ R_u = 8.314510 \text{ J/mole} - \text{K}. \]  

(A.8)

For a general substance the heat capacity, enthalpy, entropy and Gibbs potential are functions of temperature and pressure.

\[ C_P(T, P) \]  
\[ h(T, P) \]  
\[ s(T, P) \]  
\[ g(T, P) \]  

(A.9)

For any substance that follows the ideal gas law equation of state, the heat capacities, internal energy and enthalpy are independent of pressure and the entropy and Gibbs free energy depend in a known way on the logarithm of the pressure. It therefore makes sense to standardize all thermochemical data at a standard pressure rather than, say, at standard volume.

The thermodynamic properties of a substance, whether it is an ideal gas or not, are always tabulated as a function of temperature at standard pressure. That the data is tabulated this way is indicated by the \( ^\circ \) superscript that appears with each symbol in the tables. In various units, the standard pressure we will use in this course is

\[ P^\circ = 10^5 \text{ N/m}^2 = 10^5 \text{ Pascals} = 100 \text{ kPa} = 1 \text{ bar}. \]  

(A.10)

The various thermodynamic variables for any species at standard pressure are denoted by
\[ C_P(T, 100) = C_P^o(T) \]
\[ h(T, P) = h^o(T) \]
\[ s(T, P) = s^o(T) \]
\[ g(T, P) = g^o(T). \]  \hspace{1cm} (A.11)

The standard pressure is very close to one atmosphere \(1 \text{ atm} = 1.01325 \times 10^5 \text{ Pa}\) and indeed before 1982 the standard was atmospheric pressure at sea level. In 1982 the International Union of Pure and Applied Chemistry (IUPAC) recommended that for the purposes of specifying the physical properties of substances the standard pressure should be defined as precisely \(100 \text{ kPa}\). This had the immediate effect of simplifying thermochemical calculations and the practical effect of specifying the standard pressure to be closer to the actual average altitude above sea level where most people around the world live.

### A.2.1 What about pressures other than standard?

For substances in their gaseous state at elevated temperatures where the ideal gas law applies and the heat capacities, energy and enthalpy are independent of pressure the enthalpy is simply

\[ h(T, P) = h^o(T) = \Delta h_f(298.15) + \int_{T_{ref}}^{T} C_P^o(T) \, dT. \]  \hspace{1cm} (A.12)

The entropy is

\[ s(T, P) = \int_{T_{ref}}^{T} C_P^o(T) \, \frac{dT}{T} - R_u \ln \left( \frac{P}{100} \right) = s^o(T) - R_u \ln \left( \frac{P}{100} \right) \]  \hspace{1cm} (A.13)

and the Gibbs free energy is determined from the definition

\[ g(T, P) = h - Ts = h^o(T) - Ts^o(T) + (R_u T) \ln \left( \frac{P}{100} \right) = g^o(T) + (R_u T) \ln \left( \frac{P}{100} \right). \]  \hspace{1cm} (A.14)

In principle, the standard entropy requires an integration of the heat capacity from absolute zero.
A.2.2 Equilibrium between phases

For a liquid in equilibrium with its vapor the Gibbs free energy of the liquid is equal to the Gibbs free energy of the vapor.

\[ g_{\text{liquid}} (T, P) = g_{\text{gas}} (T, P) \]  

(A.15)

In terms of the definition of the Gibbs free energy

\[ h_{\text{liquid}} (T, P) - T s_{\text{liquid}} (T, P) = h_{\text{gas}} (T, P) - T s_{\text{gas}} (T, P). \]  

(A.16)

Differentiate (A.16).

\[ dh_{\text{liquid}} (T, P) - T ds_{\text{liquid}} (T, P) - s_{\text{liquid}} (T, P) \, dT = dh_{\text{gas}} (T, P) - T ds_{\text{gas}} (T, P) - s_{\text{gas}} (T, P) \, dT \]  

(A.17)

The Gibbs equation is

\[ T ds_{\text{liquid}} (T, P) = dh_{\text{liquid}} (T, P) - v_{\text{liquid}} dP \]
\[ T ds_{\text{gas}} (T, P) = dh_{\text{gas}} (T, P) - v_{\text{gas}} dP \]  

(A.18)

where \( v = V/n \) is the molar density of the substance. Substitute (A.18) into (A.17). The result is

\[ v_{\text{liquid}} dP - s_{\text{liquid}} dT = v_{\text{gas}} dP - s_{\text{gas}} dT. \]  

(A.19)

With a little bit of rearrangement (A.19) becomes

\[ \frac{dP}{dT} = \frac{s_{\text{gas}} - s_{\text{liquid}}}{v_{\text{gas}} - v_{\text{liquid}}}. \]  

(A.20)

The heat required to convert a mole of liquid to gas at constant temperature is called the latent heat of vaporization. From (A.16)

\[ \Delta h_{\text{vap}} = h_{\text{gas}} - h_{\text{liquid}} = T (s_{\text{gas}} - s_{\text{liquid}}). \]  

(A.21)

If we substitute (A.21) into (A.20) the result is the famous Clausius-Clapeyron equation
\[ \frac{dP}{dT} = \frac{\Delta h_{\text{vap}}}{T (v_{\text{gas}} - v_{\text{liquid}})} \] (A.22)

that relates the vapor pressure of a gas-liquid system to the temperature. Generally the temperature of the system is specified and the vapor pressure is to be determined. In some cases the condensed phase is a solid such as the graphite form of carbon or solid iodine sublimating directly from the solid to the vapor phase.

In the case of a solid in equilibrium with its liquid such as water and ice, the Gibbs free energies of the solid and liquid phases are equal and a similar relation governs the transition between phases. The enthalpy change is called the latent heat of fusion. In a solid-liquid system, usually the pressure is the specified condition and the temperature of melting is the property to be determined.

The heat of vaporization depends on the temperature according to

\[
\begin{align*}
    h_{\text{gas}}(T) &= h_{\text{gas}}(T_{\text{ref}}) + C_{P_{\text{gas}}}(T - T_{\text{ref}}) \\
    h_{\text{liquid}}(T) &= h_{\text{liquid}}(T_{\text{ref}}) + C_{P_{\text{liquid}}}(T - T_{\text{ref}}) \\
    \Delta h_{\text{vap}}(T) &= \Delta h_{\text{vap}}(T_{\text{ref}}) + (C_{P_{\text{gas}}} - C_{P_{\text{liquid}}})(T - T_{\text{ref}}).
\end{align*}
\] (A.23)

Generally speaking the heat capacity term is relatively small for modest changes in temperature. For example, for water between its freezing and boiling point

\[
\begin{align*}
    \Delta h_{\text{vap}}(273.15K) &= \Delta h_{\text{vap}}(373.15K) + (33 - 75)(-100) \\
    &= 40.65 \text{kJ/mole} + 4.20 \text{kJ/mole} = 44.85 \text{kJ/mole}. \quad (A.24)
\end{align*}
\]

If the effect of heat capacity differences on the latent heat of vaporization is neglected, and the liquid molar volume is much smaller than the gas, and the gas follows the ideal gas law, then (A.22) can be integrated to give

\[
\frac{P}{P_{\text{ref}}} = e^{\frac{\Delta h_{\text{vap}}(T_{\text{ref}})}{R_T}} \left( \frac{1}{T} - \frac{1}{T_{\text{ref}}} \right). \quad (A.25)
\]

The reference temperature and pressure are generally taken at the boiling point where the vapor pressure equals the gas pressure.

The Clausius-Clapeyron equation provides a direct connection between the temperature of a mixture of gases and the partial pressure of any constituent that is in equilibrium with its condensed phase.

In order to determine the heat capacity and enthalpy of a substance at conditions where pressure effects do apply, either in its condensed state or in a gaseous state close to the
vaporization temperature at some given pressure, an equation of state is needed in order to evaluate \( h(T, P) = e(T, P) + PV \). The heat capacities are determined using the definitions in (A.5). Generally the effect of pressure on the heat capacities of most liquids and solids is well understood and relatively small.

### A.2.3 Reference temperature

The standard enthalpy of a species is usually tabulated as the difference between the standard enthalpy at a given temperature and the standard enthalpy at a reference temperature. In this course, and in most combustion applications, the reference temperature is taken to be 298.15 K and this temperature is indicated in the headings of the tables shown in Figure A.1. The enthalpy of a species is expressed as

\[
h^\circ(T) = h^\circ(298.15) + \{h^\circ(T) - h^\circ(298.15)\}. \tag{A.26}
\]

This seemingly trivial representation of the enthalpy in (A.26) is explained in the next two sections.

### A.3 Reference reaction and reference state for elements

The thermochemical tables are designed to enable one to analyze systems of reacting gases and condensed materials. To facilitate this, the enthalpy of a substance is defined to include the energy contained in the chemical bonds that hold together the various atoms that compose the substance. This leads to the concept of a reference reaction for a substance, the corresponding reference state for the elements that make up the substance, and the heat of formation for the substance.

The reference reaction for a given substance is the reaction in which the substance is created from its elements when those elements are in their reference state. The reference state for elements is always taken to be the thermodynamically stable state of the element at the standard temperature 298.15 K. For elements that are gases at 298.15 K and 100 kPa the reference state is taken by convention to be gaseous over the entire range of temperatures from 0 K up to the highest temperature tabulated (typically 6000 K). For elements that are condensed at 298.15 K such as metals like aluminum or titanium, the reference state is taken to be the element in its condensed state over the entire temperature range.

The great advantage of using a reference temperature of 25 C close to room temperature is that, for applications at elevated temperature the enthalpy can be determined by integrating the heat capacity from the reference temperature without having to address the
complexities of a given substance at low temperature. A choice of, say, 0 K for the refer-
ence temperature would not offer this same convenience. For the analysis of systems at
low temperature such as the cryogenic liquids used in rocket propulsion applications the
tables are not very useful since the heat capacity data and enthalpy are often not provided
below 100 K. Often the best source of data in this range is from the commercial suppliers
of the liquid.

A.4 The heat of formation

The enthalpy (heat) of formation of a substance is defined as the enthalpy change that oc-
curs when the substance is formed from its elements in their reference state at temperature
T and standard pressure $P^\circ$ and is denoted

$$\Delta h_f^\circ(T)$$ (A.27)

A consequence of this definition is that the heat of formation of a pure element in its
reference state at any temperature is always zero. For example, the enthalpy of formation
of any of the diatomic gases is zero at all temperatures. This is clear when we write the
(trivial) reaction to form $H_2$ from its elements in their reference state as

$$H_2 \rightarrow H_2.$$ (A.28)

The enthalpy change is clearly zero. In fact the change in any thermodynamic variable
for any element in its reference state is zero at all temperatures. This is the reason for all
the zeros in the last three columns in the left data set in Figure A.1. A similar reference
reaction applies to any of the other diatomic species $O_2, N_2, F_2, Cl_2, Br_2, I_2,$ etc and the
heat of formation of these elements is zero at all temperatures.

The most stable form of carbon is solid carbon or graphite and the reference reaction
is

$$C_{solid} \rightarrow C_{solid}$$ (A.29)

with zero heat of formation at all temperatures. The heat of formation of crystalline
aluminum is zero at temperatures below the melting point, and the heat of formation of
liquid aluminum is zero at temperatures above the melting point. The same applies to
Boron, Magnesium, Sulfur, Titanium, and other metals.

The enthalpy of a substance is tied to its heat of formation by the equality
\[ h^\circ (298.15) = \Delta h_f^\circ (298.15). \] (A.30)

Using (A.30) in (A.26), the standard enthalpy of a substance is expressed as

\[ h^\circ (T) = \Delta h_f^\circ (298.15) + \{h^\circ (T) - h^\circ (298.15)\}. \] (A.31)

The two terms in (A.31) are the quantities that are tabulated.

**A.4.1 Example - heat of formation of monatomic hydrogen at 298.15 K and at 1000 K.**

The heat of formation of atomic hydrogen at 298.15 K is by definition the enthalpy change of the reference reaction.

\[ \frac{1}{2}H_2 \rvert_{gas \atop 298.15 K} \rightarrow H \rvert_{gas \atop 298.15 K} \] (A.32)

Using the data in Figure A.1, the enthalpy change for (A.32) is

\[
\begin{align*}
\Delta h_f^\circ (298.15)\rvert_H &= \\
\Delta h_f^\circ (298.15)\rvert_H - \frac{1}{2} \Delta h_f^\circ (298.15)\rvert_{H_2 \text{ in its reference state}} &= \\
217.999 - \frac{1}{2} (0) &= \\
217.999 \text{ kJ/mole of H formed}.
\end{align*}
\] (A.33)

The positive heat of formation of (A.33) indicates that the heat is absorbed in the process and the reaction is said to be endothermic. The conceptual physical process that is envisioned by these calculations is illustrated in Figure A.2. The emphasis here is on the word conceptual. This is not an experiment that actually could be performed since the reactivity of monatomic hydrogen is so strong that it would be impossible to stabilize the gas depicted in state 2 at room temperature. However that does not stop us from analyzing the energetics of such a reaction.

The appearance of the term \( \Delta h_f^\circ_{H_2} (298.15) \) on both sides of (A.33) should not cause too much concern. It is just a reminder of the fact that for any reference reaction the heats of formation of the reactants are always zero by definition.

Now lets use the heat capacity data in Figure A.1 to determine the heat of formation of atomic hydrogen at 1000 K. We need the data from the tables in Figure A.1 for the
Figure A.2: Dissociation of diatomic hydrogen to produce monatomic hydrogen by the addition of heat.

The somewhat higher value than that calculated in (A.33) comes from the larger volume change that occurs when the number of moles is doubled at 1000 K versus doubling the number of moles at 298.15 K.

A.4.2 Example - heat of formation of gaseous and liquid water

In this case the reference reaction is


\[
H_2 + \frac{1}{2}O_2 \rightarrow H_2O_{\text{gas}}, \quad (A.36)
\]

Using the data for gaseous water in Appendix B, the enthalpy balance is

\[
\Delta h^o_f (298.15)|_{H_2O} = \Delta h^o_f (298.15)|_{H_2O} - \left( \frac{1}{2} \Delta h^o_f (298.15)|_{O_2 \text{in its reference state}} + \Delta h^o_f (298.15)|_{H_2 \text{in its reference state}} \right) = -241.826 - \frac{1}{2} (0) - (0) = -241.826 \text{ kJ/moles of } H_2O \text{ formed.} \quad (A.37)
\]

Figure A.3 below depicts one possible experiment that would be used to measure this heat of formation.

![Figure A.3: Reference reaction for (gaseous) water.](image)

Half a mole of diatomic oxygen and one mole of diatomic hydrogen are placed in an adiabatic piston-cylinder combination. The two will not react spontaneously and so a small source of ignition is needed to exceed the threshold energy to start the reaction. Once the reaction proceeds, the chemical energy contained in the chemical bonds of the reactants is released and a mixture of gases at a temperature of 3078 K results. The piston is withdrawn to keep the pressure constant during the reaction. The mixture contains atoms and molecules that essentially represent all the reasonable combinations of \(H\) and \(O\) that one could conceive although more complex molecules such as \(H_2O_2\) and \(O_3\) would only be present in extremely low concentrations. More complex molecules, though possible in principle, are too unlikely to be worth considering.
Sufficient heat is removed and the piston is compressed to bring the mixture back to the original temperature and pressure. In the process the various molecules and atoms in the mixture combine to form gaseous water which is the most stable molecule with the lowest Gibbs free energy. State 3 in Figure A.3 is assumed to be pure water vapor. The water vapor in state 3 is not stable but will tend to condense to form liquid water in equilibrium with its vapor. This is really the lowest Gibbs free energy state of the system.

The last step in the process is illustrated in Figure A.4. The water vapor condenses to liquid water. At a temperature of 298.15 K the vapor pressure of the liquid is much lower than the pressure of the system and since the system is closed with no possible mixing of outside gas with the vapor virtually all the water vapor must condense to form liquid.

\[
H_2 + \frac{1}{2}O_2 \rightarrow H_2O_{\text{liquid}} \quad \Delta h_f^\circ (298.15) = -283.666 \text{ kJ/mole.} \quad (A.38)
\]

Subtraction of (A.36) and (A.38) gives the heat released when steam condenses to form liquid water at the reference temperature.

\[
\begin{align*}
H_2 + \frac{1}{2}O_2 & \rightarrow H_2O_{\text{liquid}} \quad \Delta h_f^\circ (298.15) = -283.666 \text{ kJ/mole} \\
\text{minus} & \\
H_2 + \frac{1}{2}O_2 & \rightarrow H_2O_{\text{gas}} \quad \Delta h_f^\circ (298.15) = -241.826 \text{ kJ/mole} \\
\text{equals} & \\
H_2O_{\text{gas}} & \rightarrow H_2O_{\text{liquid}} \quad \Delta h_f^\circ (298.15) = -41.840 \text{ kJ/mole} \quad (A.39)
\end{align*}
\]

In practice the experimental measurement of the heat of formation would probably not be carried out in such a complex apparatus as a piston and cylinder but would be carried out at constant volume in a device called a bomb calorimeter. The amount of heat removed in
the experiment would then be used to work out the heat that would have been released if the process were at constant pressure.

A.4.3 Example - combustion of hydrogen and oxygen diluted by nitrogen

Now let's look at an example where liquid water is produced in equilibrium with its vapor. We start with a mixture in state 1 of diatomic hydrogen, oxygen and nitrogen. A source of ignition is used to initiate the reaction and the mixture comes to state 2 at equilibrium at 2709 K. A fair amount of the nitrogen reacts to form NO and NO₂. As the mixture temperature is lowered these gases react leaving only trace amounts in the final mixture which is composed of approximately one mole of N₂ and one mole of water. The partial pressure of water vapor in the gas mixture is determined by the vapor pressure equation (A.40) repeated here for convenience.

\[
\frac{P}{P_{ref}} = e^{-\frac{\Delta h_{vap}^\circ(T_{ref})}{R_u} \left(\frac{1}{T} - \frac{1}{T_{ref}}\right)}
\]  

(A.40)

![Figure A.5: Hydrogen-oxygen combustion in the presence of nitrogen diluent.](image)

The heat of vaporization at the pressure and temperature of interest is, from (A.39), \( \Delta h_{vap}^\circ(T_{ref}) = 41.84 \text{kJ/mole} \). The reference temperature is the boiling temperature \( T_{ref} = 373.15 \text{K} \) at the reference pressure of one atmosphere, \( P^o = 1.0132 \times 10^5 \text{ Pa} \). The simplified solution of the Clausius-Clapeyron, Equation (A.40) gives the vapor pressure as
corresponding to \( n_{H_2O|_{gas}} = 0.035 \) moles which is reasonably close to the more precise value of 0.032 moles shown in Figure A.5 derived from the tables.

### A.4.4 Example - combustion of methane

The heats of formation of various species can be used to evaluate the enthalpy released or absorbed during a reaction involving those species. From the data in Appendix B, the reference reactions to produce carbon dioxide and methane are

\[
C|_{solid} + O_2 \rightarrow CO_2 \quad \Delta h_f^o (298.15) = -393.510 \text{ kJ/mole} \quad (A.42)
\]

and

\[
C|_{solid} + 2H_2 \rightarrow CH_4 \quad \Delta h_f^o (298.15) = -74.600 \text{ kJ/mole} \quad (A.43)
\]

This data together with (A.36) and (A.38) can be used to evaluate the heat released by the combustion of methane with oxygen to form carbon dioxide and liquid water at 298.15 K. The reaction is

\[
CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O|_{liquid} \quad (A.44)
\]

To produce (A.44) the algebra for the various reactions can be viewed as

\[
\begin{align*}
C|_{solid} + O_2 & \rightarrow CO_2 \\
plus & \quad 2 \times \left( H_2 + \frac{1}{2}O_2 \rightarrow H_2O|_{liquid} \right) \\
minus & \quad C|_{solid} + 2H_2 \rightarrow CH_4 \\
minus & \quad 2 \times (O_2 \rightarrow O_2) \\
equals & \quad CH_4 + 2O_2 \rightarrow CO_2 + H_2O|_{liquid}
\end{align*}
\]

and the algebra for the heats of formation is
\[
\Delta h^\circ (298.15)|_{reaction} = \\
\left( \Delta h_j^\circ (298.15)|_{CO_2} + 2 \times \Delta h_j^\circ (298.15)|_{H_2O_{liquid}} \right) - \\
\left( \Delta h_j^\circ (298.15)|_{CH_4} + 2 \times \Delta h_j^\circ (298.15)|_{O_2} \right) = \\
-393.510 + 2 (-283.666) - (-74.600) - 2 (0) = \\
-886.242 \text{ kJ/mole of CH}_4 \text{ burned.} \\
\] (A.46)

In general the reactants can be at different temperatures. Note that the reaction (A.45) is somewhat artificial in that, at equilibrium, there would actually be a small amount of water vapor mixed with the carbon dioxide and in equilibrium with the liquid water.

The general enthalpy balance for a reaction at standard pressure is

\[
\Delta h^\circ (T_{final}) = \left( \sum_{i=1}^{I} n_i h_i^\circ (T_{final}) \right)_{products} - \left( \sum_{j=1}^{J} n_j h_j^\circ (T_j) \right)_{reactants} \\
\] (A.47)

where it is recognized that the products are mixed at the final temperature of the reaction.

Equation (A.47) fully written out is

\[
\Delta h^\circ (T_{final}) = \\
\sum_{i=1}^{I} n_i \left( \Delta h_i^\circ (298.15) + \left\{ h_i^\circ (T_{final}) - h_i^\circ (298.15) \right\} \right) - \\
\sum_{j=1}^{J} n_j \left( \Delta h_j^\circ (298.15) + \left\{ h_j^\circ (T_j) - h_j^\circ (298.15) \right\} \right). \\
\] (A.48)

For example, suppose in the methane-oxygen combustion problem above, the methane is initially at 600 K and the oxygen is at 800 K while the products are assumed to be at 1500 K. The heat of reaction is determined from

\[
\Delta h^\circ (1500) = \\
\left( \Delta h_{fCO_2}^\circ (298.15) + \left\{ h_{CO_2}^\circ (1500) - h_{CO_2}^\circ (298.15) \right\} \right) + \\
2 \left( \Delta h_{fH_2O_{gas}}^\circ (298.15) + \left\{ h_{H_2O_{gas}}^\circ (1500) - h_{H_2O_{gas}}^\circ (298.15) \right\} \right) - \\
\left( \Delta h_{fCH_4}^\circ (298.15) + \left\{ h_{CH_4}^\circ (600) - h_{CH_4}^\circ (298.15) \right\} \right) - \\
2 \left( \Delta h_{fO_2}^\circ (298.15) + \left\{ h_{O_2}^\circ (800) - h_{O_2}^\circ (298.15) \right\} \right). \\
\] (A.49)

The data is
\[ \Delta h^\circ (1500) = (-393.510 + 61.705) + 2 (-241.826 + 48.151) - (-74.600 + 13.130) - 2 (0 + 15.835) = -689.355 \text{ kJ/mole of CH}_4 \text{ burned.} \]  

Somewhat less enthalpy is evolved compared to the enthalpy change at the reference temperature.

**A.4.5 Example - the heating value of JP-4**

In Chapter 2 a typical value of the fuel enthalpy for JP-4 jet fuel was given as

\[ h_f|_{J P-4 @ 298.15 K} = 4.28 \times 10^7 \text{ J/kg} \]  

although we never stated explicitly that this refers to the fuel and its products of combustion at a temperature of 298.15 \( K \). Where does this number come from and how does it relate to the heat of formation of JP-4? According to CEA the effective molecular formula and heat of formation of JP-4 are

\[ CH_{1.94} \Delta h_f^\circ (298.15) = -22.723 \text{ kJ/mole.} \]  

The reaction of this fuel with oxygen is

\[ CH_{1.94} + 1.485O_2 \rightarrow CO_2 + 0.97H_2O \]  

and the enthalpy released by the reaction is

\[ \Delta h^\circ (298.15) = \left( \Delta h_f^\circ (298.15)|_{CO_2} + 0.97 \times \Delta h_f^\circ (298.15)|_{H_2O_{gas}} \right) - \left( \Delta h_f^\circ (298.15)|_{CH_{1.94}} + 1.485 \times \Delta h_f^\circ (298.15)|_{O_2} \right) = -393.510 + 0.97 (-241.826) - (-22.723) - 1.485 (0) = -605.358 \text{ kJ/mole of CH}_1.94 \text{ burned.} \]

On a per mass basis the heating value is

\[ h_f|_{J P-4 @ 298.15 K} = \frac{-605.358 \text{ kJ/mole}}{13.9664 \times 10^{-3} \text{ kg/mole}} = -4.33 \times 10^7 \text{ J/kg} \]
which agrees closely with the accepted value (A.51). Notice the relatively small contribution of the actual enthalpy of formation of JP-4 to the calculation of the heat of reaction (A.54). Note also that the water formed in the reaction is taken to be in the gas phase and the values given in (A.51) and (A.55) are what would be called the lower heating value of JP-4. If the water is assumed to condense to its liquid phase in equilibrium with its vapor at 298.15K (see Figure A.5), which of course it does, the enthalpy change is

\[
\frac{h_f^{\text{JP-4}}_{298.15K}}{13.9664 \times 10^{-3} \text{kJ/mole}} = \frac{-605.358 - 0.97 \times 0.968 \times 41.85}{13.9664 \times 10^{-3}} = -644.653 \text{kJ/mole}
\]

which would be called the higher heating value.

### A.5 Heat capacity

The key piece of data needed for any species is its heat capacity. One of the most complete collections of such data can be found in the well known reference NASA/TP - 2002-211556 - NASA Glenn Coefficients for Calculating Thermodynamic Properties of Individual Species by Bonnie J. McBride, Michael J. Zehe, and Sanford Gordon, Glenn Research Center, Cleveland, Ohio. These authors provide accurate curve fits for the standard heat capacities, enthalpies and entropies of a vast range of species over the temperature range 200 K to 6000 K.

The enthalpy change terms in (A.35) are

\[
\begin{align*}
\int_{298.15}^{1000} C_P^O_H (T) dT & = h_f^O_H (1000) - h_f^O_H (298.15) \\
\int_{298.15}^{1000} C_P^O_H (T) dT & = h_f^O_{H_2} (1000) - h_f^O_{H_2} (298.15)
\end{align*}
\]

The molar heat gas capacities of both monatomic hydrogen and gaseous diatomic hydrogen are consistent with the classic formula from kinetic theory

\[
C_P = \left( \frac{\beta + 2}{2} \right) R_u
\]

where \(\beta\) is the number of degrees of freedom of the gas molecular model. Atomic hydrogen is a gas at all temperatures with three translational degrees of freedom, \(\beta = 3\) and one can
expect that

\[
C^0_{PH} = \frac{5}{2} R_u = 20.786 J/(\text{mole} - K)
\] (A.59)

over a wide temperature range. That this is the case is clear from the right-hand table in Figure A.1. In fact, by convention, this value of the heat capacity of monatomic hydrogen is assumed valid up to 6000 K which is the temperature at which the tables stop. Somewhat below this temperature the actual heat capacity of a gas of hydrogen atoms would begin to increase slightly as electronic degrees of freedom begin to be excited. The enthalpy change for monatomic hydrogen is

\[
h^0_H (T) - h^0_H (298.15) = \frac{5}{2} R_u (T - 298.15)
\] (A.60)

which reproduces the tabulated data very well.

The number of degrees of freedom for diatomic hydrogen at room temperature is nominally \(\beta = 5\) with three translational degrees of freedom and two rotational degrees. Kinetic theory (A.58) predicts

\[
C^0_{PH_2} = \frac{7}{2} R_u = 29.101 J/(\text{mole} - K).
\] (A.61)

Actually the tabulated heat capacity is slightly less than this since the rotational degrees are not absolutely fully excited at room temperature.

As the gas is heated, vibrational degrees of freedom begin to come into play and the number increases to \(\beta = 7\) at high combustion temperatures. Quantum statistical mechanics can be used to develop a theory for the onset of vibrational excitation. According to this theory, the specific heat of a diatomic gas from room temperature up to high combustion temperatures is accurately predicted by

\[
\frac{C^0_P}{R_u} = \frac{7}{2} + \left\{ \frac{\theta_v / 2T}{\sinh (\theta_v / 2T)} \right\}^2
\] (A.62)

where \(\theta_v\) is the vibrational transition temperature for a given gas. Values of the vibrational transition temperature for several common diatomic species are presented in Figure A.6.

The vibrational transition temperatures for common diatomic molecules are all at high combustion temperatures. Using the results of this theory, the standard enthalpy change of a diatomic gas heated to temperatures above room temperature can be expressed as
Figure A.6: Vibrational transition temperature for several gases.

\[ h^\circ(T) - h^\circ_H(298.15) = \int_{298.15}^{T} C^p_{v}(T) \, dT = \]
\[ R_u \int_{298.15}^{T} \left( \frac{7}{2} + \left\{ \frac{\theta_v}{2T} \left\{ \frac{\theta_v}{2T} \right\} \right\}^2 \right) \, dT \]  
\[ (A.63) \]
which integrates to

\[ \frac{h^\circ(T) - h^\circ_H(298.15)}{R_u(T - 298.15)} = \]
\[ \frac{7}{2} + \frac{\theta_v}{2(T - 298.15)} \left\{ \text{Coth} \left( \frac{\theta_v}{2T} \right) - \text{Coth} \left( \frac{\theta_v}{2(298.15)} \right) \right\}^2 \]  
\[ (A.64) \]

plotted in Figure A.7 for diatomic hydrogen. This equation produces good approximate results for the enthalpy changes in hydrogen and other diatomic molecules. For hydrogen (A.64) gives \( h^\circ_{H_2}(2000) - h^\circ_{H_2}(298.15) = 51872.5 \, J/mole \) which compares well with the value \( 52951 \, J/mole \) given in the left table in Figure A.1.

Figure A.7: Enthalpy change for diatomic hydrogen at elevated temperature.
A.6 Chemical bonds and the heat of formation

A.6.1 Potential energy of two hydrogen atoms

Figure A.8 below depicts the variation in potential energy as two hydrogen atoms at zero energy are brought together from infinity.

![Potential energy of two hydrogen atoms as a function of bond distance.](image)

The molecule is stable at a bond length of 74 \( \text{picometers} \). Noting the existence of minimum energy quantum vibrations, this distance can be viewed as an approximate measure of the bond length between the two nuclei.

The potential energy of the system at this spacing is \(-4.476 \text{ electron-volts}\) where \(1 \text{ ev} = 1.60217646 \times 10^{19} \text{ Joules}\). This is the bond energy that is radiated away when the two atoms are allowed to approach each other through mutual attraction and react to form the chemical bond that holds them together in a stable molecule. It is also the energy that would have to be added to the molecule in order to dissociate the two atoms and return them to their zero energy state at infinity. The hydrogen molecule is a classic example of a covalent bond where the mutual attraction of the two nuclei arises from the attraction of each nucleus to the electron pair that is concentrated in the space between them. Some other bond lengths and zero Kelvin bond energies are given in Figure A.9.

Covalent bonds are the strongest chemical bonds found in nature and are always formed from the sharing of one or more pairs of electrons. Typical covalent bond energies range from \(-1.5417 \text{ ev}\) for the single bond in diatomic iodine to \(-6.364 \text{ ev}\) for the double bond between two carbon atoms to \(-9.756 \text{ ev}\) for the triple bond that occurs between two atoms.
Figure A.9: Bond lengths and bond energies for several diatomic molecules at 0K. Reference: Moelwyn-Hughes, Physical Chemistry, page 427.

<table>
<thead>
<tr>
<th>Molecule</th>
<th>Bond length ($\times 10^{\delta}$ cm)</th>
<th>Bond energy at 0K (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$H_2$</td>
<td>0.7415</td>
<td>4.476</td>
</tr>
<tr>
<td>$O_2$</td>
<td>1.20739</td>
<td>5.080</td>
</tr>
<tr>
<td>$N_2$</td>
<td>1.0976</td>
<td>9.756</td>
</tr>
<tr>
<td>$F_2$</td>
<td>1.442</td>
<td>1.59</td>
</tr>
<tr>
<td>$Cl_2$</td>
<td>1.988</td>
<td>2.475</td>
</tr>
<tr>
<td>$Br_2$</td>
<td>2.283</td>
<td>1.971</td>
</tr>
<tr>
<td>$I_2$</td>
<td>2.666</td>
<td>1.5417</td>
</tr>
<tr>
<td>$OH$</td>
<td>0.9706</td>
<td>4.35</td>
</tr>
<tr>
<td>$CH$</td>
<td>1.1198</td>
<td>3.47</td>
</tr>
<tr>
<td>$CO$</td>
<td>1.1281</td>
<td>11.11</td>
</tr>
</tbody>
</table>
of nitrogen. For comparison the thermal energy per molecule of air at 298.15 K is only about 0.064 eV. This is the reason why covalently bonded molecules tend be so difficult to break by heating.

Although, in principle, it is possible to analyze the energetics of all chemical reactions as a process of breaking down reactants and assembling products to and from their constituent atoms at zero Kelvin it is not particularly convenient to do so. The reason is that virtually all chemical reactions of interest take place in a surrounding gas at some pressure above vacuum and, in accounting for all the energy changes, it is necessary to include the work associated with the changes in volume that occur during the reaction. Consider the reaction depicted in Figure A.10 which is the opposite of the reaction shown in Figure A.2.

![Diagram of the reaction process](image)

**Figure A.10:** Reaction of atomic hydrogen to form diatomic hydrogen at standard pressure and temperature.

Two moles of hydrogen atoms are placed in an adiabatic piston-cylinder combination at a temperature $T = 298.15 \text{ K}$ and pressure $P = 10^5 \text{ N/m}^2$. The atoms in state 1 are allowed to react and the piston is withdrawn to produce a mixture of $H$ and $H_2$ in state 2 at very high temperature and at the original pressure. Heat is removed and the piston is compressed to bring the gas back to the original temperature and pressure at state 3. At the relatively low final temperature of 298.15 K virtually all of the atomic hydrogen has reacted to produce one mole of diatomic hydrogen.

### A.6.2 Atomic hydrogen

Taking the reference energy of the hydrogen atoms to be zero at absolute zero, the atomic hydrogen is brought to state 1 through the addition of heat and the production of work as the collection of atoms expands from essentially zero volume against the surrounding
constant pressure.

Any phase changes that may occur in atomic hydrogen are ignored and it seems that little is known about the nature or even the existence of a stable solid or liquid state of atomic hydrogen in the neighborhood of absolute zero. There are papers on the subject that describe theoretical models of atomic hydrogen in a face-centered cubic crystal but there is no definitive experimental evidence of solid hydrogen near absolute zero. If such a condensed state does exist, the temperature of any phase change would be extremely low and would make only a very small contribution to the enthalpy.

The total enthalpy change needed to bring the two moles of atomic hydrogen from zero energy at \( 0 \) \( K \) to state 1 at \( 298.15 \) \( K \) is therefore determined from the gas phase heat capacity.

\[
n (h^e_H (298.15) - h^e_H (0)) = \int_0^{298.15} C_{P_H} (T) \, dT = 2 \times 20.785 \times 298.15 = 12394 \, J
\]  

(A.65)

The enthalpy required per mole of \( H \) is

\[
h^e_H (298.15) - h^e_H (0) = \frac{12394}{2} = 6197 \, J/mole \, of \, H
\]  

(A.66)

This is the enthalpy change given in the tables in Figure A.1 but with the opposite sign.

**A.6.3 Diatomic hydrogen**

An accurate determination of the enthalpy of state 3 requires a knowledge of the heat capacity of diatomic hydrogen at very low temperatures as well as data for the heat of fusion and vaporization. The number of degrees of freedom for diatomic hydrogen is \( \beta = 5 \) at room temperature and drops to \( \beta = 3 \) near the vaporization point as rotational degrees of freedom freeze out. Hydrogen is somewhat unusual in this respect. Because of the strong bond reflected in the short bond length between the two hydrogen atoms and the correspondingly low vaporization point, the freezing out of the rotational degrees of freedom is evident in the gas heat capacity with a transition temperature at about 87 \( K \). For other diatomic gases the theoretical transition temperature tends to be far below the vaporization point and is therefore less evident in the heat capacity function.

The heats of fusion and vaporization of diatomic hydrogen are well known. Equation (A.67) shows some data at \( P = P^o = 10^5 \) \( kPa \).
Heat capacity, $C_P @ 0.0 K = 0.0 J/(mole - K)$

Heat capacity, $C_P @ 13.15 K = 5.729 J/(mole - K)$

Enthalpy of fusion = 117.25 J/mole @ 13.15 K

Heat capacity, $C_P @ 20.0 K = 19.4895 J/(mole - K)$

Enthalpy of vaporization = 912.0 J/mole @ 20.28 K

Heat capacity, $C_P @ 175.0 K = 26.4499 J/(mole - K)$

Heat capacity, $C_P @ 250.0 K = 28.3248 J/(mole - K)$

Heat capacity, $C_P @ 298.15 K = 28.836 J/(mole - K)$.

The heat capacity of all materials is zero at absolute zero. An approximation to the heat capacity of gaseous $H_2$ that works reasonably well between the temperatures of 20.28 K and 298.15 K is

$$C_{P_{H_2}}(T) = 18.834 + 1.30487 \times 10^3 T^2 - 1.14829 \times 10^5 T^3 + 3.98205 \times 10^{-8} T^4 - 4.9369 \times 10^{-11} T^5. \quad (A.67)$$

This model for the heat capacity is plotted in Figure A.11. For simplicity we assume the heat capacities of the solid and liquid states vary linearly between the values given in (A.67). Actually this model of the heat capacity of diatomic hydrogen is over simplified. Any sample of hydrogen contains both the ortho and para forms of hydrogen and each has a somewhat different heat capacity. As a result there is a range of temperatures around 100 K where the heat capacity of the mixture actually decreases with increasing temperature.

Figure A.11: Approximation to the heat capacity of gaseous $H_2$ at low temperatures and $P = 100kPa$.

The enthalpy of a species including the absolute zero energy of the chemical bond is
\[ h(T, P) = \]
\[ E_{\text{chemical bond energy/mole}}(0, P) + \]
\[ \int_0^{T_{\text{melting}(P)}} C_P(T, P) \, dT + \Delta h_{\text{fusion}}(T_{\text{melting}}(P), P) + \]
\[ \int_{T_{\text{melting}(P)}}^{T_{\text{vaporization}(P)}} C_P(T, P) \, dT + \Delta h_{\text{vaporization}}(T_{\text{vaporization}}(P), P) + \]
\[ \int_{T_{\text{vaporization}(P)}}^{T} C_P(T, P) \, dT. \]
\[ (A.69) \]

The pressure dependence comes primarily from the effect of pressure on the heat of vaporization and to a lesser extent on the heat of fusion as well as the possible pressure dependence of the heat capacities of the condensed phases particularly near phase transition points. The gas phase heat capacity becomes independent of pressure as the gas approaches ideal gas behavior at increasing temperatures above the vaporization temperature.

On a per unit mole basis the chemical bond energy of \( H_2 \) at zero Kelvin is

\[ E_{\text{chemical bond energy/mole}}(0, P^\circ) = \]
\[ -4.476 \, \text{electron volts/molecule} \times 6.0221415 \times 10^{23} \, \text{molecules/mole} \times 1.60217646 \times 10^{-19} \, \text{J/electron volts} = \]
\[ -431.87 \times 10^3 \, \text{J/mole} \]
\[ (A.70) \]

Using the data in (A.67), the enthalpy at \( T = 298.15 \, K \) and \( P = 100 \, kPa \) including the chemical bond energy is

\[ h_{H_2}^\circ(298.15, 100) = -431.87 \times 10^3 + \int_0^{13.95} \left( \frac{5.729}{13.95} \right) T \, dT + 117.25 + \]
\[ \int_{13.95}^{20.28} \left( 5.729 + \left( \frac{19.49 - 5.729}{20.28 - 13.95} \right) (T - 13.95) \right) dT + 912 + \int_{20.28}^{298.15} C_P^\circ(T) \, dT \]
\[ (A.71) \]

Use (A.68) to carry out the last integral in (A.71) giving
The heat released by the reaction to form diatomic hydrogen from its atoms at 298.15 K and 1 atmosphere is

$$
\Delta h^\circ = h^\circ_{\text{H}_2} (298.15, 100) - 2h^\circ_{\text{H}} (298.15, 100) = $$
$$
(-431.87 \times 10^3 + 8206) - 2 \times 6197.35 =$$
$$-436.059 \times 10^3 \text{ J/moles of H}_2 \text{ formed}
$$

The result (A.73) is the enthalpy released during the reaction of atomic hydrogen to form diatomic hydrogen at a temperature of 298.15 K and pressure $10^5 \text{ N/m}^2$. This result can be found in the right table in Figure A.1 as twice the heat of formation of one mole of monatomic hydrogen. We worked this out in equation (A.33).

Note that, because the heat input and work needed to bring two moles of atomic hydrogen to the initial temperature of 298.15 K is greater than that needed to bring one mole of diatomic hydrogen to the same temperature, the reaction releases four more kilo-Joules of enthalpy than it would if the reaction was carried out at zero Kelvin.

### A.7 Heats of formation computed from bond energies

We began this appendix by discussing tabulations of the heats of formation of various species from their elements in their reference state. In this last section we will describe how heats of formation can be determined from bond energies. The enthalpy changes involved in chemical reactions come from the breaking and making of chemical bonds to decompose the reactants and then compose the products.

Figure A.12 gives average bond energies for a variety of diatomic molecules.

Consider the reference reaction for water

$$
H_2 + \frac{1}{2}O_2 \rightarrow H_2O_{|\text{gas}} \quad \Delta h^\circ_{H_2O_{|\text{gas}}} (298.15) = -241.826 \text{kJ/mole}
$$

To break down the reactants we have to break the 0.5 mole of $O_2$ double bonds as well as one mole of $H_2$ single bonds. When we compose the products we will make two $OH$ single bonds. All the bond changes are evaluated at 298.15 $K$. The heat of the reaction is
APPENDIX A. THERMOCHEMISTRY

Figure A.12: Average single, and multiple bond energies for several diatomic molecules at 298.15K.

\[ \Delta h^\circ \approx \sum \Delta h^\circ_{\text{bonds broken}} - \sum \Delta h^\circ_{\text{bonds made}}. \]  

(A.75)

Using the data in Figure A.12 we get

\[ \Delta h^\circ = 436 + \frac{1}{2} (498) - 2 (463) = -241 \text{ kJ/moles of H}_2\text{O formed}. \]  

(A.76)

which is very close to the tabulated heat of formation.

A certain amount of caution is always required when computing heats of formation from bond energies. The energy of a chemical bond always depends on the particular atomic configuration of the molecule where the bond appears. For example to remove one of the hydrogens from a molecule of water requires 502 kJ/mole whereas the energy required to break the remaining OH bond is only 424 kJ/mole. Therefore the average bond energy is 463 kJ/mole.

For methane 435 kJ/mole is required to break a single CH whereas it takes 1662 kJ/mole to break all four bonds therefore the average bond energy is 416 kJ/mole not 435 kJ/mole.
A.8 References


In addition to providing curve fits for the heat capacity, enthalpy and entropy for a wide range of species, a number of variables are also tabulated in this reference including $\Delta h_f^o (298.15)$, $h^o (0)$ and $\Delta h_f^o (0)$. 
Appendix B

Selected JANAF data
## Appendix B. Selected JANAF Data

### Figure B.1: JANAF data for monatomic carbon gas.

<table>
<thead>
<tr>
<th>Temperature (°K)</th>
<th>Enthalpy of Formation (kJ mol⁻¹)</th>
<th>Formation Temperature (°K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>300</td>
<td>20.836</td>
<td>158.100</td>
</tr>
<tr>
<td>350</td>
<td>20.846</td>
<td>158.100</td>
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<tr>
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<td>20.856</td>
<td>158.100</td>
</tr>
<tr>
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<td>20.866</td>
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<td>158.100</td>
</tr>
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<td>800</td>
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<tr>
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<tr>
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<td>158.100</td>
</tr>
</tbody>
</table>

**Note:** JANAF data for monatomic carbon gas.
Figure B.2: JANAF data for solid carbon in the form of graphite.
Figure B.3: JANAF data for acetylene gas.
Figure B.4: JANAF data for ethene gas.
### APPENDIX B. SELECTED JANAF DATA

#### Enthalpy Reference Temperature $T_0 = 298.15$ K

<table>
<thead>
<tr>
<th>$T/K$</th>
<th>$C_p^o$</th>
<th>$\Delta H^o$</th>
<th>$\Delta G^o$</th>
<th>$\Delta S^o$</th>
<th>$\log K_T$</th>
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<tbody>
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<td>0.000</td>
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<td>0.000</td>
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<td>0.000</td>
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<td>0.000</td>
</tr>
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<td>0.000</td>
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<td>0.000</td>
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<td>-177.159</td>
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</tr>
</tbody>
</table>

---

**Figure B.5:** JANAF data for methane gas.
**APPENDIX B. SELECTED JANAF DATA**

### Carbon Monoxide (CO), ideal gas, mol. wt. = 28.0104

<table>
<thead>
<tr>
<th>T/K</th>
<th>( C_v^P )</th>
<th>( S^P )</th>
<th>( -\Delta^o G^P(T)/T )</th>
<th>( H^P(T)/T )</th>
<th>( \Delta^P(T) )</th>
<th>( \Delta^o C_v^P )</th>
<th>Log ( K_f )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
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<tr>
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<td>62.987</td>
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<tr>
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<td>29.108</td>
<td>166.025</td>
<td>209.317</td>
<td>-112.092</td>
<td>118.987</td>
<td>62.987</td>
<td></td>
</tr>
</tbody>
</table>

**Figure B.6: JANAF data for carbon monoxide gas.**
Carbon Dioxide (CO₂), ideal gas, mol. wt. = 44.0098

<table>
<thead>
<tr>
<th>T/K</th>
<th>C₆</th>
<th>S/μmol⁻¹</th>
<th>ΔH/μmol⁻¹</th>
<th>ΔS/μmol⁻¹</th>
<th>ΔG/μmol⁻¹</th>
<th>kJ mol⁻¹</th>
<th>J mol⁻¹ K⁻¹</th>
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</tr>
</tbody>
</table>

Figure B.7: JANAF data for carbon dioxide gas.
# APPENDIX B. SELECTED JANAF DATA

## Appendix B. Selected JANAF Data

### Hydrogen (H₂), ideal gas-reference state, mol. wt. = 2.01588

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>( C_p )</th>
<th>( S^\circ )</th>
<th>( (\Delta H^\circ - R T) / T )</th>
<th>( (\Delta H^\circ - R T) / T )</th>
<th>( \Delta H^\circ )</th>
<th>( \Delta G^\circ )</th>
<th>( \log K_r )</th>
</tr>
</thead>
<tbody>
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Figure B.8: JANAF data for diatomic hydrogen gas.
**APPENDIX B. SELECTED JANAF DATA**

**Figure B.9:** JANAF data for monatomic hydrogen gas.

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<th>Standard State Pressure $p_s = 0.1$ MPa</th>
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</thead>
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Figure B.9: JANAF data for monatomic hydrogen gas.
APPENDIX B. SELECTED JANAF DATA

Hydroperoxyl (H\textsubscript{2}O\textsubscript{2}), ideal gas, mol. wt. = 33.00674

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<th>\Delta G\textsubscript{f}</th>
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Figure B.10: JANAF data for hydroperoxide gas.
## APPENDIX B. SELECTED JANAF DATA

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Figure B.11: JANAF data for hydroxyl gas.
Figure B.12: JANAF data for water vapor.
Figure B.13: JANAF data for diatomic nitrogen gas.
Figure B.14: JANAF data for monatomic nitrogen gas.
**APPENDIX B. SELECTED JANAF DATA**

**Figure B.15:** JANAF data for ammonia gas.

### Table: JANAF data for ammonia gas

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Ammonia (NH$_3$), ideal gas, mol. wt. = 17.0352
## Nitrogen Dioxide (NO₂), Ideal Gas, mol. wt. = 46.0055

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<th>Standard State Pressure (p₀ = 81 MPa)</th>
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<td>ΔG° kJ mol⁻¹</td>
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Figure B.16: JANAF data for nitrogen dioxide gas.
Figure B.17: JANAF data for nitric oxide gas.
Figure B.18: JANAF data for diatomic oxygen gas.
### APPENDIX B. SELECTED JANAF DATA

#### Figure B.19: JANAF data for monatomic oxygen gas.

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<th>$C_p$ (J mol(^{-1})K(^{-1}))</th>
<th>$S$ (J mol(^{-1})K(^{-1}))</th>
<th>$H$ (kJ mol(^{-1}))</th>
<th>$A$ (kJ mol(^{-1}))</th>
<th>$\log K$</th>
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</table>

The data represents the thermodynamic properties of monatomic oxygen gas at various temperatures, with values for specific heat capacity, entropy, enthalpy, and other thermodynamic quantities.
APPENDIX B. SELECTED JANAF DATA

Figure B.20: JANAF data for ozone gas.