

**PART 1**

**THE SECOND LAW OF THERMODYNAMICS**

## PART 1 - THE SECOND LAW OF THERMODYNAMICS

### 1.A. Background to the Second Law of Thermodynamics

[IAW 23-31 (see IAW for detailed VWB&S references); VN Chapters 2, 3, 4]

#### 1.A.1 Some Properties of Engineering Cycles; Work and Efficiency

As motivation for the development of the second law, we examine two types of processes that concern interactions between heat and work. The first of these represents the conversion of work into heat. The second, which is much more useful, concerns the conversion of heat into work. The question we will pose is how efficient can this conversion be in the two cases.

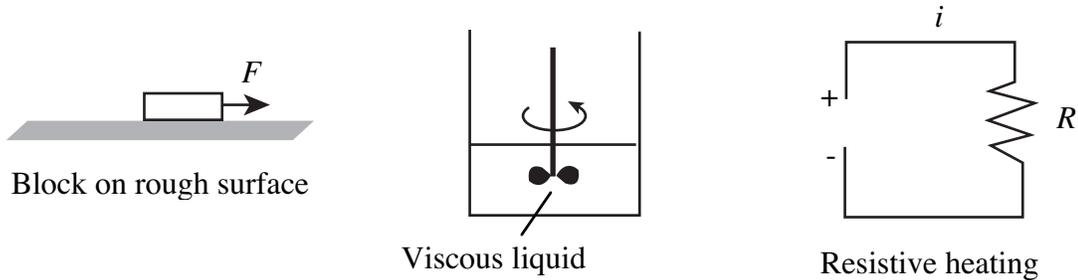


Figure A-1: Examples of the conversion of work into heat

Three examples of the first process are given above. The first is the pulling of a block on a rough horizontal surface by a force which moves through some distance. Friction resists the pulling. After the force has moved through the distance, it is removed. The block then has no kinetic energy and the same potential energy it had when the force started to act. If we measured the temperature of the block and the surface we would find that it was higher than when we started. (High temperatures can be reached if the velocities of pulling are high; this is the basis of inertia welding.) The work done to move the block has been converted totally to heat.

The second example concerns the stirring of a viscous liquid. There is work associated with the torque exerted on the shaft turning through an angle. When the stirring stops, the fluid comes to rest and there is (again) no change in kinetic or potential energy from the initial state. The fluid and the paddle wheels will be found to be hotter than when we started, however.

The final example is the passage of a current through a resistance. This is a case of electrical work being converted to heat, indeed it models operation of an electrical heater.

All the examples in Figure A-1 have 100% conversion of work into heat. This 100% conversion could go on without limit as long as work were supplied. Is this true for the conversion of heat into work?

To answer the last question, we need to have some basis for judging whether work is done in a given process. One way to do this is to ask whether we can construct a way that the process could result in the raising of a weight in a gravitational field. If so, we can say “Work has been done”. It may sometimes be difficult to make the link between a complicated thermodynamic process and the simple raising of a weight, but this is a rigorous test for the existence of work.

One example of a process in which heat is converted to work is the isothermal (constant temperature) expansion of an ideal gas, as sketched in the figure. The system is the gas inside the chamber. As the gas expands, the piston does work on some external device. For an ideal gas, the internal energy is a function of temperature only, so that if the temperature is constant for some process the internal energy change is zero. To keep the temperature constant during the expansion,

heat must be supplied. Because  $\Delta U = 0$ , the first law takes the form  $Q=W$ . This is a process that has 100% conversion of heat into work.

The work exerted by the system is given by

$$\text{Work} = \int_1^2 P dV$$

where 2 and 1 denote the two states at the beginning and end of the process. The equation of state for an ideal gas is

$$P = NRT/V,$$

with N the number of moles of the gas contained in the chamber. Using the equation of state, the expression for work can be written as

$$\text{Work during an isothermal expansion} = NRT \int_1^2 dV/V = NRT \ln\left(\frac{V_2}{V_1}\right). \quad (\text{A.1.1})$$

For an isothermal process,  $PV = \text{constant}$ , so that  $P_1/P_2 = V_2/V_1$ . The work can be written in terms of the pressures at the beginning and end as

$$\text{Work during an isothermal expansion} = NRT \ln\left(\frac{P_1}{P_2}\right). \quad (\text{A.1.2})$$

The lowest pressure to which we can expand and still receive work from the system is atmospheric pressure. Below this, we would have to do work on the system to pull the piston out further. There is thus a bound on the amount of work that can be obtained in the isothermal expansion; we cannot continue indefinitely. For a power or propulsion system, however, we would like a source of continuous power, in other words a device that would give power or propulsion as long as fuel was added to it. To do this, we need a series of processes where the system does not progress through a one-way transition from an initial state to a different final state, but rather cycles back to the initial state. What is looked for is in fact a *thermodynamic cycle* for the system.

We define several quantities for a cycle:

$Q_A$  is the heat absorbed by the system

$Q_R$  is the heat rejected by the system

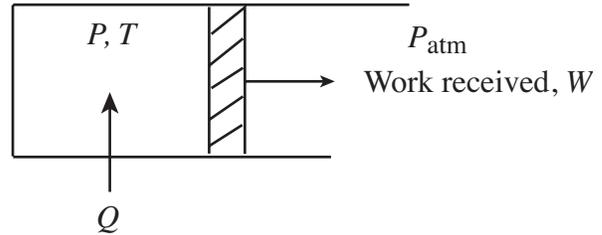
$W$  is the net work done by the system.

The cycle returns to its initial state, so the overall energy change,  $\Delta U$ , is zero. The net work done by the system is related to the magnitudes of the heat absorbed and the heat rejected by

$$W = \text{Net work} = Q_A - Q_R.$$

The thermal efficiency of the cycle is the ratio of the work done to the heat absorbed. (Efficiencies are often usefully portrayed as “What you get” versus “What you pay for”. Here what we get is work and what we pay for is heat, or rather the fuel that generates the heat.) In terms of the heat absorbed and rejected, the thermal efficiency is:

$$\begin{aligned} \eta = \text{thermal efficiency} &= \frac{\text{Work done}}{\text{Heat absorbed}} \\ &= \frac{Q_A - Q_R}{Q_A} = 1 - \frac{Q_R}{Q_A}. \end{aligned} \quad (\text{A.1.3})$$



The thermal efficiency can only be 100% (complete conversion of heat into work) if  $Q_R = 0$ , and a basic question is what is the maximum thermal efficiency for any arbitrary cycle? We examine this for two cases, the Carnot cycle and the Brayton (or Joule) cycle which is a model for the power cycle in a jet engine.

### 1.A.2 Carnot Cycles

A Carnot cycle is shown below. It has four processes. There are two adiabatic reversible legs and two isothermal reversible legs. We can construct a Carnot cycle with many different systems, but the concepts can be shown using a familiar working fluid, the ideal gas. The system can be regarded as a chamber filled with this ideal gas and with a piston.

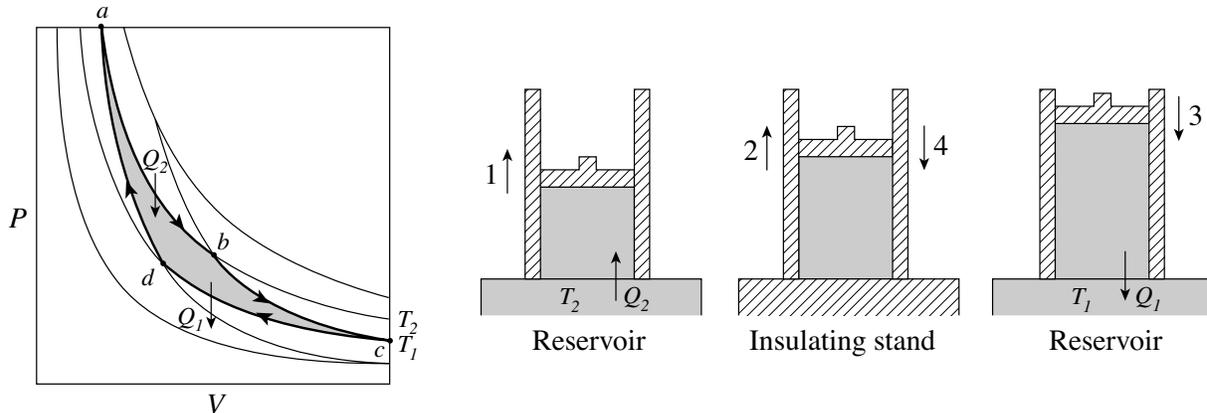


Figure A-2: Carnot cycle – thermodynamic diagram on left and schematic of the different stages in the cycle for a system composed of an ideal gas on the right

The four processes in the Carnot cycle are:

- 1) The system is at temperature  $T_2$  at state (a). It is brought in contact with a heat reservoir, which is just a liquid or solid mass of large enough extent such that its temperature does not change appreciably when some amount of heat is transferred to the system. In other words, the heat reservoir is a constant temperature source (or receiver) of heat. The system then undergoes an isothermal expansion from a to b, with heat absorbed  $Q_2$ .
- 2) At state b, the system is thermally insulated (removed from contact with the heat reservoir) and then let expand to c. During this expansion the temperature decreases to  $T_1$ . The heat exchanged during this part of the cycle,  $Q_{bc} = 0$ .
- 3) At state c the system is brought in contact with a heat reservoir at temperature  $T_1$ . It is then compressed to state d, rejecting heat  $Q_1$  in the process.
- 4) Finally, the system is compressed adiabatically back to the initial state a. The heat exchange  $Q_{da} = 0$ .

The thermal efficiency of the cycle is given by the definition

$$\eta = 1 - \frac{Q_R}{Q_A} = 1 + \frac{Q_1}{Q_2}. \quad (\text{A.2.1})$$

In this equation, there is a sign convention implied. The quantities  $Q_A, Q_R$  as defined are the magnitudes of the heat absorbed and rejected. The quantities  $Q_1, Q_2$  on the other hand are defined with reference to heat received by the system. In this example, the former is negative and the latter is positive. The heat absorbed and rejected by the system takes place during isothermal processes and we already know what their values are from Eq. (A.1.1):

$$Q_2 = W_{ab} = NRT_2 \left[ \ln(V_b/V_a) \right]$$

$$Q_1 = W_{cd} = NRT_1 \left[ \ln(V_d/V_c) \right] = - \left[ \ln(V_c/V_d) \right]. \quad (Q_1 \text{ is negative.})$$

The efficiency can now be written in terms of the volumes at the different states as:

$$\eta = 1 + \frac{T_1 [\ln(V_d/V_c)]}{T_2 [\ln(V_b/V_a)]}. \quad (\text{A.2.2})$$

The path from states  $b$  to  $c$  and from  $a$  to  $d$  are both adiabatic and reversible. For a reversible adiabatic process we know that  $PV^\gamma = \text{constant}$ . Using the ideal gas equation of state, we have  $TV^{\gamma-1} = \text{constant}$ . Along curve  $b-c$ , therefore  $T_2 V_b^{\gamma-1} = T_1 V_c^{\gamma-1}$ . Along the curve  $d-a$ ,  $T_2 V_a^{\gamma-1} = T_1 V_d^{\gamma-1}$ .

Thus,

$$\left( \frac{V_d}{V_c} \right)^{\gamma-1} = \frac{(T_2/T_1)}{(T_2/T_1)} \left( \frac{V_a}{V_b} \right)^{\gamma-1}, \text{ which means that } \frac{V_d}{V_c} = \frac{V_a}{V_b}, \text{ or } V_d/V_c = V_a/V_b.$$

Comparing the expression for thermal efficiency Eq. (A.2.1) with Eq. (A.2.2) shows two consequences. First, the heats received and rejected are related to the temperatures of the isothermal parts of the cycle by

$$\frac{Q_1}{T_1} + \frac{Q_2}{T_2} = 0. \quad (\text{A.2.3})$$

Second, the efficiency of a Carnot cycle is given compactly by

$$\eta_c = 1 - \frac{T_1}{T_2}. \quad \text{Carnot cycle efficiency} \quad (\text{A.2.4})$$

The efficiency can be 100% only if the temperature at which the heat is rejected is zero. The heat and work transfers to and from the system are shown schematically in Figure A-3.

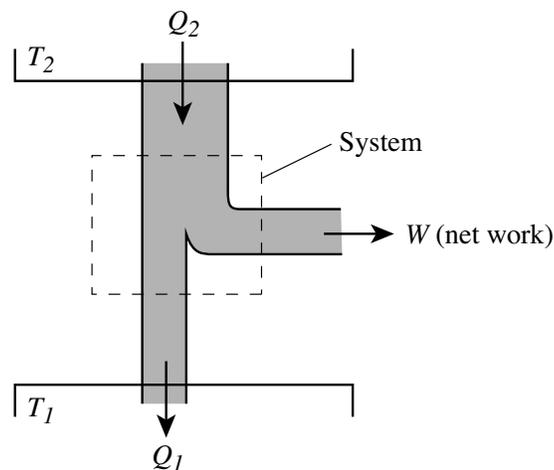


Figure A-3: Work and heat transfers in a Carnot cycle between two heat reservoirs

### Muddy points

Since  $\eta = 1 - \frac{T_1}{T_2}$ , looking at the P-V graph, does that mean the farther apart the T1, T2

isotherms are, the greater efficiency? And that if they were very close, it would be very inefficient? (MP 1A.1)

In the Carnot cycle, why are we only dealing with volume changes and not pressure changes on the adiabats and isotherms? (MP 1A.2)

Is there a physical application for the Carnot cycle? Can we design a Carnot engine for a propulsion device? (MP 1A.3)

How do we know which cycles to use as models for real processes? (MP 1A.4)

### 1A.3 Brayton Cycles (or Joule Cycles): The Power Cycle for a Gas Turbine Jet Engine

For a Brayton cycle there are two adiabatic legs and two constant pressure legs. Sketches of an engine and the corresponding cycle are given in Figure A-4.

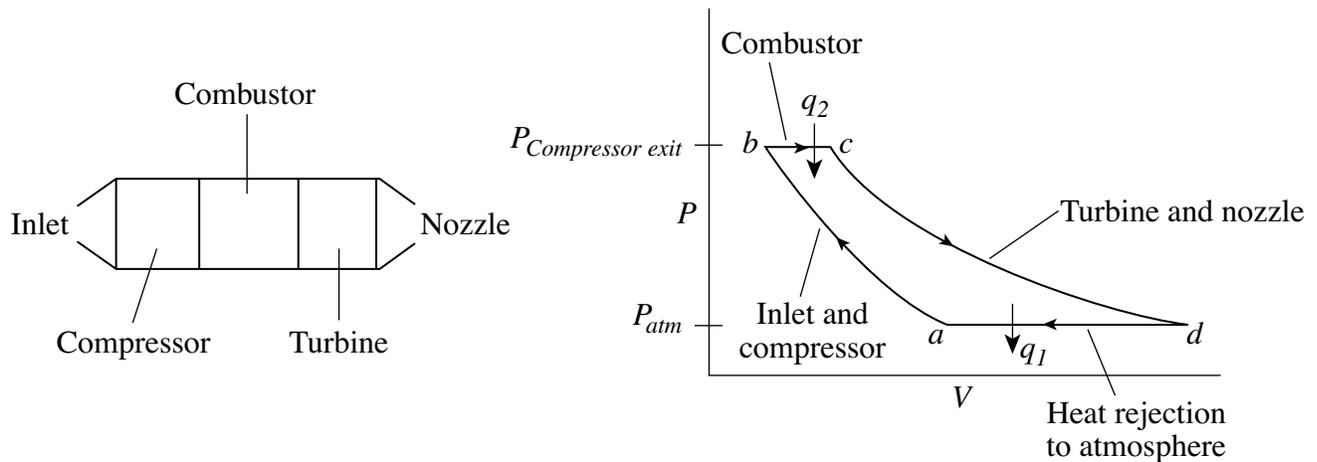


Figure A-4: Sketch of the jet engine components and corresponding thermodynamic states

Gas turbines are also used for power generation and for closed cycle operation (for example for space power generation). A depiction of the cycle in this case is shown in Figure A-5.

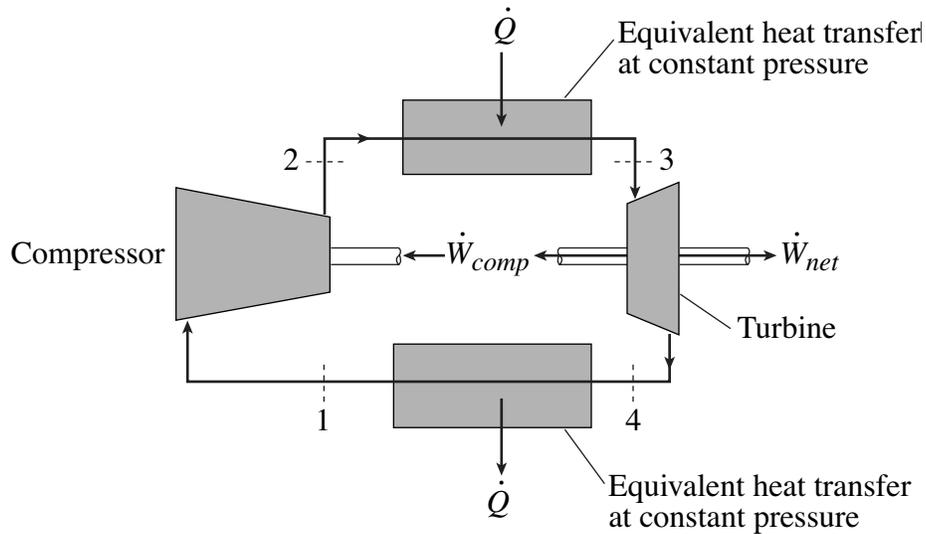


Figure A-5: Thermodynamic model of gas turbine engine cycle for power generation

The objective now is to find the work done, the heat absorbed, and the thermal efficiency of the cycle. Tracing the path shown around the cycle from a-b-c-d and back to a, the first law gives (writing the equation in terms of a unit mass),

$$\Delta u_{a-b-c-d-a} = 0 = q_2 + q_1 - w.$$

The net work done is

$$w = q_2 + q_1,$$

where  $q_1, q_2$  are defined as heat received by the system ( $q_1$  is negative). We thus need to evaluate the heat transferred in processes b-c and d-a.

For a constant pressure process the heat exchange per unit mass is

$$dh = c_p dT = dq, \text{ or } [dq]_{constant P} = dh.$$

The heat exchange can be expressed in terms of enthalpy differences between the relevant states. Treating the working fluid as an ideal gas, for the heat addition from the combustor,

$$q_2 = h_c - h_b = c_p (T_c - T_b).$$

The heat rejected is, similarly,  $q_1 = h_a - h_d = c_p (T_a - T_d)$ .

The net work per unit mass is given by

$$\text{Net work per unit mass} = q_1 + q_2 = c_p [(T_c - T_b) + (T_a - T_d)].$$

The thermal efficiency of the Brayton cycle can now be expressed in terms of the temperatures:

$$\begin{aligned}\eta &= \frac{\text{Net work}}{\text{Heat in}} = \frac{c_p[(T_c - T_b) - (T_d - T_a)]}{c_p[T_c - T_b]} \\ &= 1 - \frac{(T_d - T_a)}{(T_c - T_b)} = 1 - \frac{T_a(T_d/T_a - 1)}{T_b(T_c/T_b - 1)}.\end{aligned}\tag{A.3.1}$$

To proceed further, we need to examine the relationships between the different temperatures. We know that points *a* and *d* are on a constant pressure process as are points *b* and *c*, and  $P_a = P_d$ ;  $P_b = P_c$ . The other two legs of the cycle are adiabatic and reversible, so

$$\frac{P_d}{P_c} = \frac{P_a}{P_b} \implies \left(\frac{T_d}{T_c}\right)^{\gamma/(\gamma-1)} = \left(\frac{T_a}{T_b}\right)^{\gamma/(\gamma-1)}.$$

Therefore  $\frac{T_d}{T_c} = \frac{T_a}{T_b}$ , or, finally,  $\frac{T_d}{T_a} = \frac{T_c}{T_b}$ . Using this relation in the expression for thermal efficiency, Eq. (A.1.3) yields an expression for the thermal efficiency of a Brayton cycle:

$$\begin{aligned}\text{Ideal Brayton cycle efficiency: } \eta_B &= 1 - \frac{T_a}{T_b} \\ &= 1 - \frac{T_{\text{atmospheric}}}{T_{\text{compressor exit}}}\end{aligned}\tag{A.3.2}$$

The temperature ratio across the compressor,  $T_b/T_a = TR$ . In terms of compressor temperature ratio, and using the relation for an adiabatic reversible process we can write the efficiency in terms of the compressor (and cycle) pressure ratio, which is the parameter commonly used:

$$\eta_B = 1 - \frac{1}{TR} = 1 - \frac{1}{(PR)^{(\gamma-1)/\gamma}}.\tag{A.3.3}$$

Figure A-6 shows pressures and temperatures through a gas turbine engine (the afterburning J57, which powers the F-8 and the F-101).

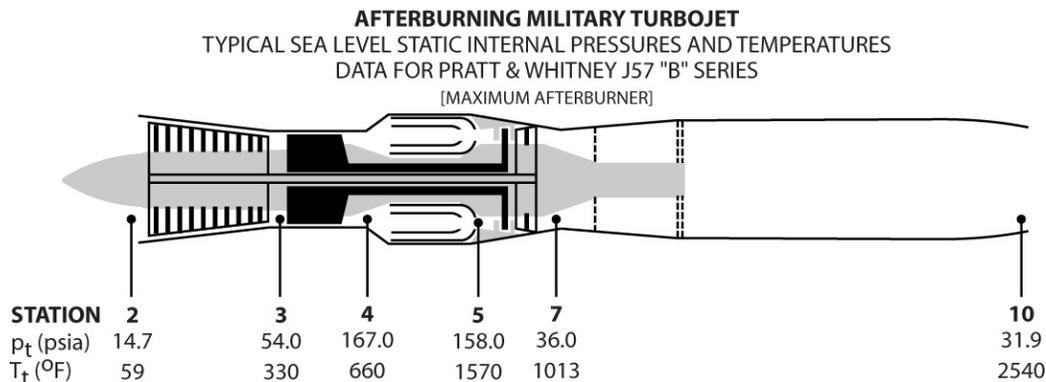


Figure A-6: Gas turbine engine pressures and temperatures

Equation (A.3.3) says that for a high cycle efficiency, the pressure ratio of the cycle should be increased. Figure A-7 shows the history of aircraft engine pressure ratio versus entry into service, and it can be seen that there has been a large increase in cycle pressure ratio. The thermodynamic concepts apply to the behavior of real aerospace devices!

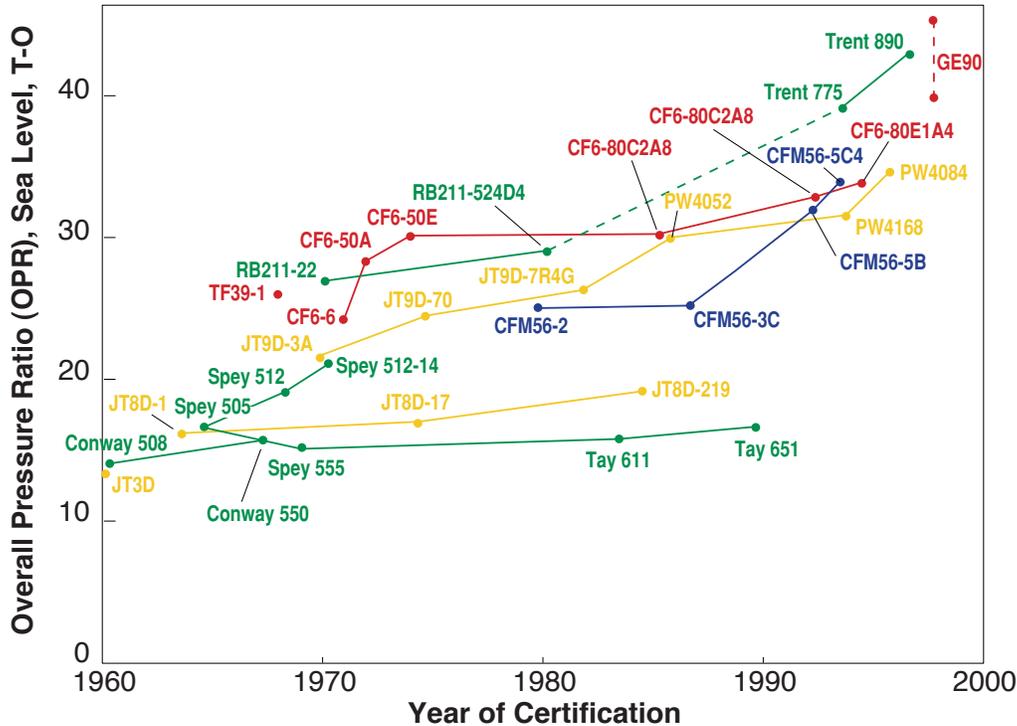


Figure A-7: Gas turbine engine pressure ratio trends (Jane's Aeroengines, 1998)

### Muddy points

When flow is accelerated in a nozzle, doesn't that reduce the internal energy of the flow and therefore the enthalpy? (MP 1A.5)

Why do we say the combustion in a gas turbine engine is constant pressure? (MP 1A.6)

Why is the Brayton cycle less efficient than the Carnot cycle? (MP 1A.7)

If the gas undergoes constant pressure cooling in the exhaust outside the engine, is that still within the system boundary? (MP 1A.8)

Does it matter what labels we put on the corners of the cycle or not? (MP 1A.9)

Is the work done in the compressor always equal to the work done in the turbine plus work out (for a Brayton cycle)? (MP 1A.10)

### 1A.4 Gas Turbine Technology and Thermodynamics

The turbine entry temperature,  $T_c$ , is fixed by materials technology and cost. (If the temperature is too high, the blades fail.) Figures A-8 and A-9 show the progression of the turbine entry temperatures in aeroengines. Figure A-8 is from Rolls Royce and Figure A-9 is from Pratt&Whitney. Note the relation between the gas temperature coming into the turbine blades and the blade melting temperature.

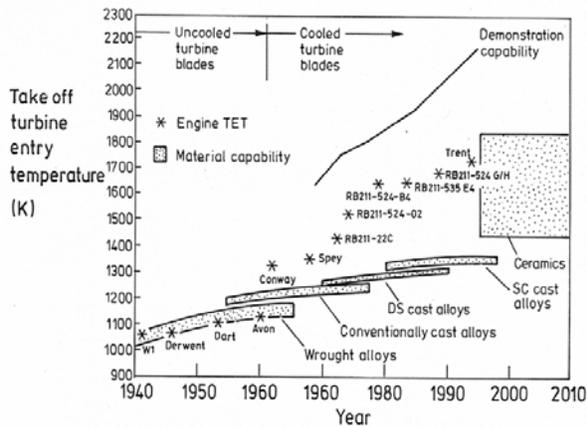


Figure A-8: Rolls-Royce high temperature technology

*Rotor inlet gas temperature vs Cooling effectiveness.*

Figure A-9: Turbine blade cooling technology [Pratt & Whitney]

For a given level of turbine technology (in other words given maximum temperature) a design question is what should the compressor TR be? What criterion should be used to decide this? Maximum thermal efficiency? Maximum work? We examine this issue below.

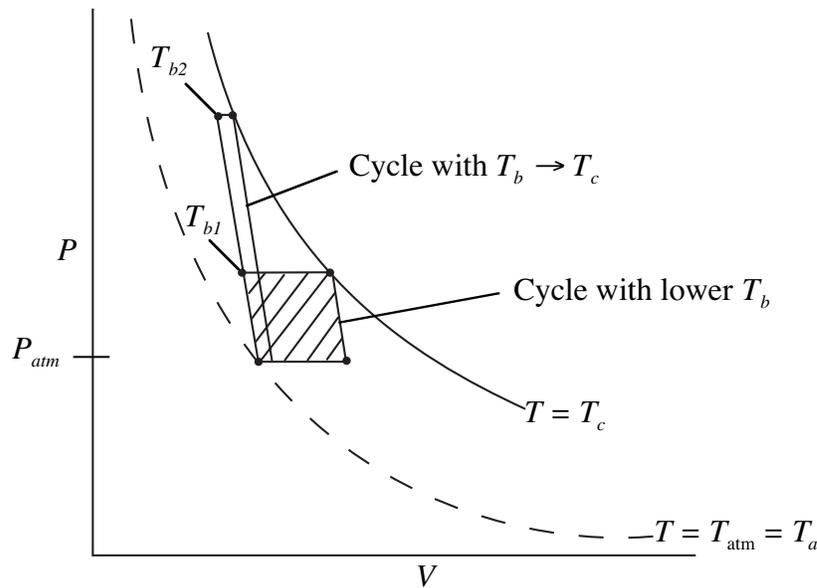


Figure A-10: Efficiency and work of two Brayton cycle engines

The problem is posed in Figure A-10, which shows two Brayton cycles. For maximum efficiency we would like  $TR$  as high as possible. This means that the compressor exit temperature approaches the turbine entry temperature. The net work will be less than the heat received; as  $T_b \rightarrow T_c$  the heat received approaches zero and so does the net work.

The net work in the cycle can also be expressed as  $\int Pdv$ , evaluated in traversing the cycle. This is the area enclosed by the curves, which is seen to approach zero as  $T_b \rightarrow T_c$ .

The conclusion from either of these arguments is that a cycle designed for maximum thermal efficiency is not very useful in that the work (power) we get out of it is zero.

A more useful criterion is that of maximum work per unit mass (maximum power per unit mass flow). This leads to compact propulsion devices. The work per unit mass is given by:

$$\text{Work/unit mass} = c_p \left[ \underbrace{(T_c - T_b)}_{\substack{\text{Max. turbine temp.} \\ \text{(Design constraint)}}} - \underbrace{(T_d - T_a)}_{\text{Atmospheric temperature}} \right]$$

The design variable is the compressor exit temperature,  $T_b$ , and to find the maximum as this is varied, we differentiate the expression for work with respect to  $T_b$ :

$$\frac{d\text{Work}}{dT_b} = c_p \left[ \frac{dT_c}{dT_b} - 1 - \frac{dT_d}{dT_b} + \frac{dT_a}{dT_b} \right].$$

The first and the fourth term on the right hand side of the above equation are both zero (the turbine entry temperature is fixed, as is the atmospheric temperature). The maximum work occurs where the derivative of work with respect to  $T_b$  is zero:

$$\frac{d\text{Work}}{dT_b} = 0 = -1 - \frac{dT_d}{dT_b}. \quad (\text{A.4.1})$$

To use Eq. (A.4.1), we need to relate  $T_d$  and  $T_b$ . We know that

$$\frac{T_d}{T_a} = \frac{T_c}{T_b} \quad \text{or} \quad T_d = \frac{T_a T_c}{T_b}.$$

Hence,

$$\frac{dT_d}{dT_b} = \frac{-T_a T_c}{T_b^2}.$$

Plugging this expression for the derivative into Eq. (A.4.1) gives the compressor exit temperature for maximum work as  $T_b = \sqrt{T_a T_c}$ . In terms of temperature ratio,

$$\text{Compressor temperature ratio for maximum work: } \frac{T_b}{T_a} = \sqrt{\frac{T_c}{T_a}}.$$

The condition for maximum work in a Brayton cycle is different than that for maximum efficiency. The role of the temperature ratio can be seen if we examine the work per unit mass which is delivered at this condition:

$$\text{Work/unit mass} = c_p \left[ T_c - \sqrt{T_a T_c} - \frac{T_a T_c}{\sqrt{T_a T_c}} + T_a \right].$$

Ratioing all temperatures to the engine inlet temperature,

$$\text{Work/unit mass} = c_p T_a \left[ \frac{T_c}{T_a} - 2 \sqrt{\frac{T_c}{T_a}} + 1 \right].$$

To find the power the engine can produce, we need to multiply the work per unit mass by the mass flow rate:

$$Power = \dot{m} c_p T_a \left[ \frac{T_c}{T_a} - 2 \sqrt{\frac{T_c}{T_a}} + 1 \right]; \text{ Maximum power for an ideal Brayton cycle} \quad (A.4.2)$$

(The units are  $\frac{\text{kg}}{\text{s}} \frac{\text{J}}{\text{kg-K}} \text{K} = \frac{\text{J}}{\text{s}} = \text{Watts}.$ )

Figures A-11a. and A-11b. available from:

B.L. Koff *Spanning the Globe with Jet Propulsion* AIAA Paper 2987, AIAA Annual Meeting and Exhibit, 1991.

C. E. Meese, *Gas Turbine Technologies of the Future*, International Symposium on Air Breathing Engines, 1995, paper 95-7006.

a) Gas turbine engine core

b) Core power vs. turbine entry temperature

Figure A-11: Aeroengine core power [Koff/Meese, 1995]

Figure A-11 shows the expression for power of an ideal cycle compared with data from actual jet engines. Figure 11a shows the gas turbine engine layout including the core (compressor, burner, and turbine). Figure 11b shows the core power for a number of different engines as a function of the turbine rotor entry temperature. The equation in the figure for horsepower (HP) is the same as that we just derived, except for the conversion factors. The analysis not only shows the qualitative trend very well but captures much of the quantitative behavior too.

A final comment (for now) on Brayton cycles concerns the value of the thermal efficiency. The Brayton cycle thermal efficiency contains the ratio of the compressor exit temperature to atmospheric temperature, so that the ratio is not based on the highest temperature in the cycle, as the Carnot efficiency is. For a given maximum cycle temperature, the Brayton cycle is therefore less efficient than a Carnot cycle.

### Muddy points

What are the units of  $w$  in  $power = \dot{m} w$ ? (MP 1A.11)

Precision about the assumptions made in the Brayton cycle for maximum efficiency and maximum work (MP 1A.12)

You said that for a gas turbine engine modeled as a Brayton cycle the work done is  $w=q_1+q_2$ , where  $q_2$  is the heat added and  $q_1$  is the heat rejected. Does this suggest that the work that you get out of the engine doesn't depend on how good your compressor and turbine are?...since the compression and expansion were modeled as adiabatic. (MP 1A.13)

### 1A.5 Refrigerators and Heat Pumps

The Carnot cycle has been used for power, but we can also run it in reverse. If so, there is now net work into the system and net heat out of the system. There will be a quantity of heat  $Q_2$  rejected at the higher temperature and a quantity of heat  $Q_1$  absorbed at the lower temperature. The former of

these is negative according to our convention and the latter is positive. The result is that work is done on the system, heat is extracted from a low temperature source and rejected to a high temperature source. The words “low” and “high” are relative and the low temperature source might be a crowded classroom on a hot day, with the heat extraction being used to cool the room. The cycle and the heat and work transfers are indicated in Figure A-12. In this mode of operation

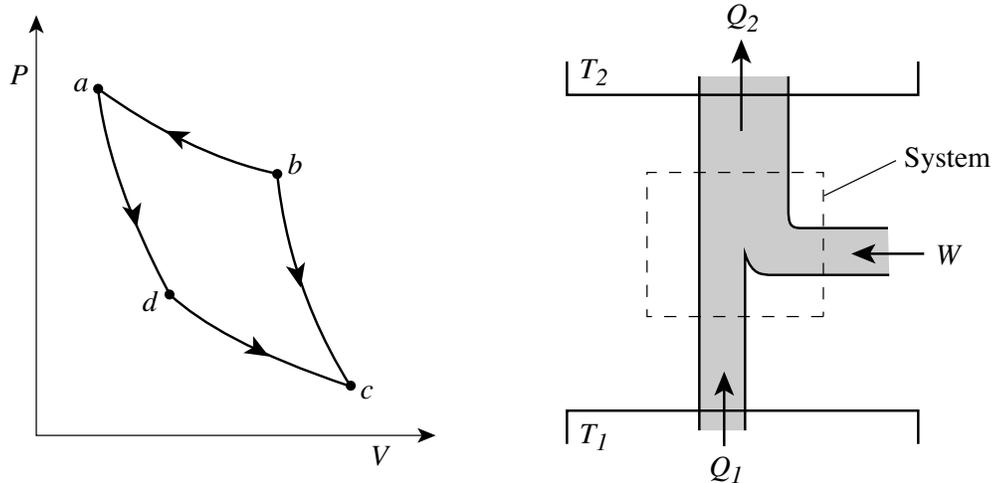


Figure A-12: Operation of a Carnot refrigerator

the cycle works as a refrigerator or heat pump. “What we pay for” is the work, and “what we get” is the amount of heat extracted. A metric for devices of this type is the coefficient of performance, defined as

$$\text{Coefficient of performance} = \frac{Q_1}{W} = \frac{Q_1}{Q_1 + Q_2}.$$

For a Carnot cycle we know the ratios of heat in to heat out when the cycle is run forward and, since the cycle is reversible, these ratios are the same when the cycle is run in reverse. The coefficient of performance is thus given in terms of the absolute temperatures as

$$\text{Coefficient of performance} = \frac{T_1}{T_2 - T_1}.$$

This can be much larger than unity.

The Carnot cycles that have been drawn are based on ideal gas behavior. For different working media, however, they will look different. We will see an example when we discuss two-phase situations. What is the same whatever the medium is the efficiency for all Carnot cycles operating between the same two temperatures.

### **Muddy points**

Would it be practical to run a Brayton cycle in reverse and use it as refrigerator? (MP 1A.14)

### **1A.6 Reversibility and Irreversibility in Natural Processes**

We wish to characterize the “direction” of natural processes; there is a basic “directionality” in nature. We start by examining a flywheel in a fluid filled insulated enclosure as shown in Figure A-13.

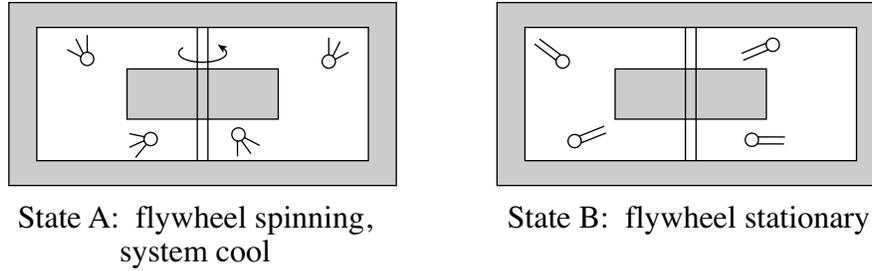


Figure A-13: Flywheel in insulated enclosure at initial and final states

A question to be asked is whether we could start with state B and then let events proceed to state A? Why or why not? The first law does not prohibit this.

The characteristics of state A are that the energy is in an organized form, the molecules in the flywheel have some circular motion, and we could extract some work by using the flywheel kinetic energy to lift a weight. In state B, in contrast, the energy is associated with disorganized motion on a molecular scale. The temperature of the fluid and flywheel are higher than in state A, so we could probably get some work out by using a Carnot cycle, but it would be much less than the work we could extract in state A. There is a qualitative difference between these states, which we need to be able to describe more precisely.

### Muddy points

Why is the ability to do work decreased in B? How do we know? (MP 1A.15)

Another example is a system composed of many bricks, half at a high temperature  $T_H$  and half at a low temperature  $T_L$  (see IAW p. 42). With the bricks separated thermally, we have the ability to obtain work by running a cycle between the two temperatures. Suppose we put two bricks together. Using the first law we can write

$$CT_H + CT_L = 2CT_M.$$

$$(T_H + T_L)/2 = T_M$$

where  $C$  is the “heat capacity” =  $\Delta Q/\Delta T$ . (For solids the heat capacities (specific heats) at constant pressure and constant volume are essentially the same.) We have lost the ability to get work out of these two bricks.

Can we restore the system to the original state without contact with the outside? The answer is no. Can we restore the system to the original state with contact with the outside? The answer is yes. We could run a refrigerator to take heat out of one brick and put it into the other, *but we would have to do work*.

We can think of the overall process involving the system (the two bricks in an insulated setting) and the surroundings (the rest of the universe) as:

- System is changed
- Surroundings are unchanged.

The composite system (system and the surroundings) is changed by putting the bricks together. *The process is not reversible—there is no way to undo the change and leave no mark on the surroundings.*

What is the measure of change in the surroundings?

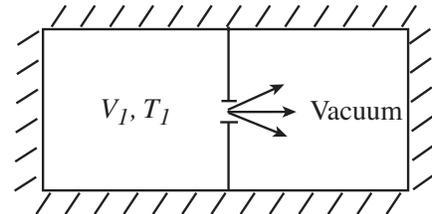
- a) Energy? This is conserved.
- b) Ability to do work? This is decreased.

The measurement and characterization of this type of changes is the subject of the second law of thermodynamics.

**1.A.7 Difference between Free Expansion of a Gas and Reversible Isothermal Expansion**

The difference between reversible and irreversible processes is brought out through examination of the isothermal expansion of an ideal gas. The question to be asked is what is the difference between the “free expansion” of a gas and the isothermal expansion against a piston? To answer this, we address the steps that we would have to take to reverse, in other words, to undo the process.

By free expansion, we mean the unrestrained expansion of a gas into a volume as shown at the right. Initially all the gas is in the volume designated as  $V_1$  with the rest of the insulated enclosure a vacuum. The total volume ( $V_1$  plus the evacuated volume) is  $V_2$ . At a given time a hole is opened in the partition and the gas rushes through to fill the rest of the enclosure.



During the expansion there is no work exchanged with the surroundings because there is no motion of the boundaries. The enclosure is insulated so there is no heat exchange. The first law tells us therefore that the internal energy is constant ( $\Delta U = 0$ ). For an ideal gas, the internal energy is a function of temperature only so that the temperature of the gas before the free expansion and after the expansion has been completed is the same. Characterizing the before and after states;

Before: State 1,  $V = V_1, T = T_1$

After: State 2,  $V = V_2, T = T_1$ .

$Q=W=0$ , so there is no change in the surroundings.

To restore the original state, i.e., to go back to the original volume at the same temperature ( $V_2 \rightarrow V_1$  at constant  $T = T_1$ ) we can compress the gas isothermally (using work from an external agency). We can do this in a quasi-equilibrium manner, with  $P_{system} \approx P_{external}$ . If so the work that

we need to do is  $W = \int_1^2 PdV$ . We have evaluated the work in a reversible isothermal expansion

(Eq. A.1.1), and we can apply the arguments to the case of a reversible isothermal compression.

The work done on the system to go from state “2” to state “1” is

$$W = \text{Work done on system} = NR T_1 \ln\left(\frac{V_2}{V_1}\right).$$

From the first law, this amount of heat must also be rejected from the gas to the surroundings if the temperature of the gas is to remain constant. A schematic of the compression process, in terms of heat and work exchanged is shown in Figure A-14.

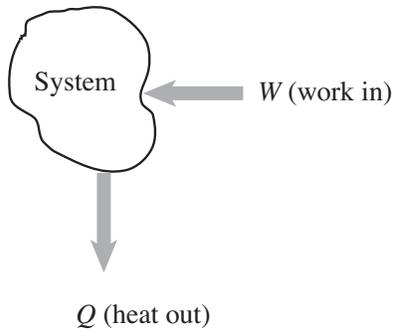
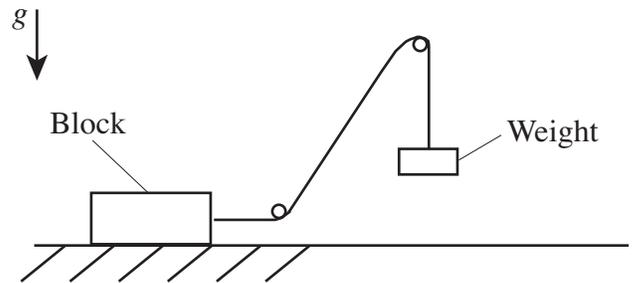


Figure A-14: Work and heat exchange in the reversible isothermal compression process

At the end of the combined process (free expansion plus reversible compression):

- The system has been returned to its initial state (no change in system state).
- The surroundings (us!) did work on the system of magnitude  $W$ .
- The surroundings received an amount of heat,  $Q$ , which is equal to  $W$ .
- The sum of all of these events is that we have converted an amount of work,  $W$ , into an amount of heat,  $Q$ , with  $W$  and  $Q$  numerically equal in Joules.

The net effect is the same as if we let a weight fall and pull a block along a rough surface, as at right. There is 100% conversion of work into heat.



The results of the free expansion can be contrasted against a process of isothermal expansion against a pressure  $dP$  which is slightly different than that of the system, as shown below.

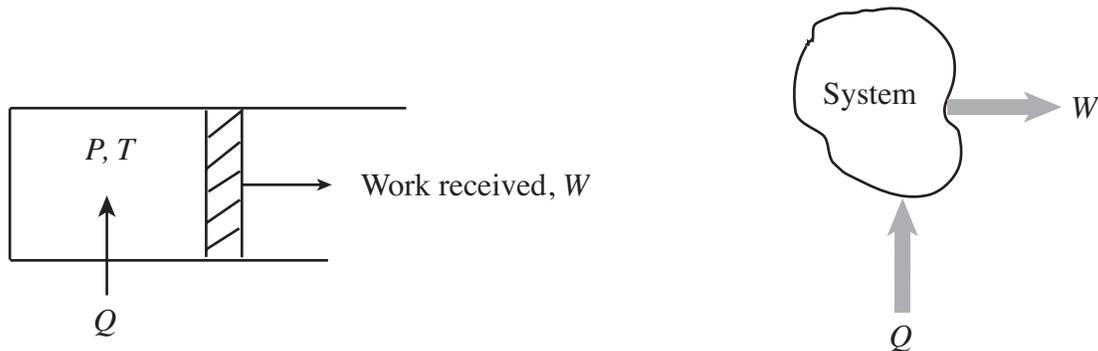


Figure A-15: Work and heat transfer in reversible isothermal expansion

During the expansion, work is done on the surroundings of magnitude  $W = \int PdV$ , where P can be taken as the system pressure. As evaluated in Eq. (A.1.1), the magnitude of the work done by the system is  $W = NR T_1 \ln\left(\frac{V_2}{V_1}\right)$ . At the end of the isothermal expansion, therefore:

- a) The surroundings have received work W
- b) The surroundings have given up heat, Q, numerically equal to W.

We now wish to restore the system to its initial state, just as we did in the free expansion. To do this we need to do work on the system and extract heat from the system, just as in the free expansion. In fact, because we are doing a transition between the same states along the same path, the work and heat exchange are the same as those for the compression process examined just above.

The overall result when we have restored the system to the initial state, however, is quite different for the reversible expansion and for the free expansion. For the reversible expansion, the work we need to do on the system to compress it has the same magnitude as the work we received during the expansion process. Indeed, we could raise a weight during the expansion and then allow it to be lowered during the compression process. Similarly the heat put into the system by us (the surroundings) during the expansion process has the same magnitude as the heat received by us during the compression process. The result is that *when the system has been restored back to its initial state, so have the surroundings*. There is no trace of the overall process on either the system or the surroundings. That is another meaning of the word “reversible”.

### Muddy points

[With the isothermal reversible expansion is  \$P\_{external}\$  constant? If so, how can we have](#)

[\$P\_{system} \cong P\_{external}\$ ? \(MP 1A.16\)](#)

[Why is the work done equal to zero in the free expansion? \(MP 1A.17\)](#)

[Is irreversibility defined by whether or not a mark is left on the outside environment? \(MP 1A.18\)](#)

### 1A.8 Features of reversible processes

Reversible processes are idealizations or models of real processes. One familiar, and widely used, example is Bernoulli’s equation, which you saw last year. They are extremely useful for defining limits to system or device behavior, for enabling identification of areas in which inefficiencies occur, and in giving targets for design.

An important feature of a reversible process is that, depending on the process, it represents the maximum work that can be extracted in going from one state to another, or the minimum work that is needed to create the state change. This is shown clearly in the discussion on page 46 of the Waitz notes. Said differently:

- The work done by a system during a reversible process is the maximum work we can get.
- The work done on a system in a reversible process is the minimum work we need to do to achieve that state change.

A process must be quasi-static (quasi-equilibrium) to be reversible. This means that the following effects must be absent or negligible.

- 1) Friction

If  $P_{external} \neq P_{system}$ , as shown in (8) of Part 0, we would have to do work to bring the system from one volume to another and return it to the initial condition. [Review (8) of Part 0]

- 2) Free (unrestrained) expansion
- 3) Heat transfer through a finite temperature difference.

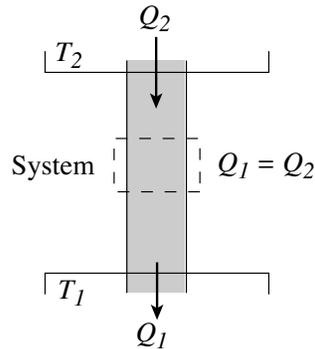


Figure A-16: Heat transfer across a finite temperature difference

Suppose we have heat transfer from a high temperature to a lower temperature as shown above. How do we restore the situation to the initial conditions? One thought would be to run a Carnot refrigerator to get an amount of heat,  $Q$ , from the lower temperature reservoir to the higher temperature reservoir. We could do this but the surroundings, again us, would need to provide some amount of work (which we could find using our analysis of the Carnot refrigerator). The net (and only) result at the end of the combined process would be a conversion of an amount of work into heat. For reversible heat transfer from a heat reservoir to a system, the temperatures of the system and the reservoir must be  $T_{heat\ reservoir} = T_{system} \pm dT$ . In other words the difference between the temperatures of the two entities involved in the heat transfer process can only differ by an infinitesimal amount,  $dT$ .

All natural processes are irreversible to some extent, and reversible processes are idealized models. In natural processes, the conditions for mechanical, thermal, and chemical equilibrium may not be satisfied. In addition, dissipative effects (viscosity, friction) exist. Reversible processes are quasi-equilibrium, with no dissipative effects. It cannot be emphasized too strongly that there are a number of engineering situations where the effect of irreversibility can be neglected and the reversible process furnishes an excellent approximation to reality.

The second law, which is the next topic we address, allows us to make a quantitative statement concerning the irreversibility of a given physical process.

*Portrait of Nicolas Sadi Carnot,  
painted by Louis Leopold Boilly,  
1813.*

Figure A-17: this is Nicolas Sadi Carnot (1796-1832), an engineer and an officer in the French army. Carnot's work is all the more remarkable because it was made without benefit of the first law, which was not discovered until 30 years later. [Atkins, *The Second Law*].

*Muddy points*

Is heat transfer across a finite temperature difference only irreversible if no device is present between the two to harvest the potential difference ? (MP 1A.19)

## Muddiest Points on Part 1A

1A.1 Since  $h = 1 - T_1/T_2$ , looking at the P-V graph, does that mean the farther apart the  $T_1, T_2$  isotherms are, the greater the efficiency? And that if they were very close, it would be very inefficient?

This is correct. However, there is a limit on the maximum achievable efficiency. We cannot convert the absorbed heat into 100% work, that is, we always must reject some amount of heat. The amount of heat we must reject is

$$Q_R = -T_1/T_2 * Q_A \quad (\text{see notes for derivation}).$$

Thus for given values of  $T_2$  and  $Q_A$ ,  $Q_R$  depends only on the temperature of the cold reservoir  $T_1$ , which is limited by the temperatures naturally available to us. These temperatures are all well above absolute zero, and there are no means to reduce  $Q_R$  to negligible values. The consequence of this is that the Carnot cycle efficiency cannot approach one ( $\eta = 1$  only if  $Q_R = 0$ , which is not possible).

1A.2 In the Carnot cycle, why are we only dealing with volume changes and not pressure changes on the adiabats and isotherms?

We are not neglecting the pressure terms and we are also dealing with pressure changes. On the adiabats we know that  $dq = 0$  (adiabatic process), so that for reversible processes we can write the first law as  $du = -Pdv$  and, using enthalpy, also as  $dh = vdP$ . With  $dh = c_p dT$  and  $du = c_v dT$  for an ideal gas, we can write the ratio of  $dh/du$  as

$$dh/du = c_p/c_v = \gamma = -(v dP) / (P dv).$$

By arranging terms we obtain

$$dP/P = -\gamma dv/v.$$

For a process we can integrate from 1 to 2 and get  $P_2 v_2^\gamma = P_1 v_1^\gamma$ , or  $Pv^\gamma = \text{const}$ . This relation shows how pressure and volume changes are related to one another during an adiabatic reversible process.

During an isothermal process, the temperature stays constant. Using the equation of state for an ideal gas  $Pv = RT$ , we find that  $Pv = \text{const}$  on an isotherm. Again, this relation tells us how pressure changes are related to volume changes during an isothermal process. Note that in the P-V diagram, adiabats ( $Pv^\gamma = \text{constant}$ ) are steeper curves than isotherms ( $Pv = \text{constant}$ ).

1A.3 Is there a physical application for the Carnot cycle? Can we design a Carnot engine for a propulsion device?

We will see that Carnot cycles are the best we can do in terms of efficiency. A constant temperature heat transfer process is, however, difficult to attain in practice for devices in which high rates of power are required. The main role of the Carnot engine is therefore as a standard against which all other cycles are compared and which shows us the direction in which design of efficient cycles should go.

1A.4 How do we know which cycles to use as models for real processes?

We have discussed this briefly for the Brayton cycle, in that we looked at the approximation that was made in saying heat addition occurred at constant pressure. You can also see that the Carnot cycle is not a good descriptor of a gas turbine engine! We will look further at this general point, not only for the Brayton cycle, but also for the Rankine cycle and for some internal combustion engine cycles. I will try to make clear what are the approximations and why the cycle under study is being used as a model.

1A.5 When flow is accelerated in a nozzle, doesn't that reduce the internal energy of the flow and therefore the enthalpy?

Indeed both enthalpy and internal energy are reduced. The *stagnation enthalpy* is the quantity that is constant.

1A.6 Why do we say that the combustion in a gas turbine engine is at constant pressure?

This is an approximation, and a key question is indeed how accurate it is and what the justification is. The pressure change in the combustor can be analyzed using the 1-dimensional compressible flow equations. The momentum equation is  $dP = -\rho c dc$ , where  $c$  is the velocity.

If we divide both sides by  $P$ , we obtain:

$$\frac{dP}{P} = -\frac{\gamma c^2}{\gamma P/\rho} \frac{dc}{c} = -\frac{\gamma c^2}{a^2} \frac{dc}{c} = -\gamma M^2 \frac{dc}{c},$$

where  $a$  is the speed of sound and  $M$  is the Mach number.

Changes in velocity are due to changes in density and in flow-through area, as given by the 1-dimensional continuity equation

$$\rho c a = \text{constant}$$

Hence

$$\ln \rho + \ln c + \ln a = \text{constant}$$

Differentiating,

$$\frac{d\rho}{\rho} + \frac{dc}{c} + \frac{da}{a} = 0, \text{ or } \frac{dc}{c} = -\frac{da}{a} - \frac{d\rho}{\rho}$$

Velocity changes are therefore related to area changes (geometry) and density changes (basically heat input). For a gas turbine combustion process the change in density is comparable with (a significant fraction of) the initial density and the area change is several times the initial area. This means that the change in velocity divided by the initial velocity is *roughly* of the order of magnitude of unity. The momentum equation thus tells us that for small Mach number (say 0.1) the ratio  $dP/P$  will be much less than one, so that the pressure can be approximated as constant. In reality the pressure does drop in the combustor, but the overall drop from inlet to exit is about 3-4%, small compared to the initial level of pressure, so that the approximation of constant pressure is a useful one.

The rapidity of the combustion process does not really have anything to do with this approximation. We could have a process, such as a nozzle, in which there was combustion at the same time that the pressure was dropping. As seen from the momentum equation, the heat addition does not "directly" affect the pressure - changes in pressure are associated with changes in velocity.

*1A.7 Why is the Brayton cycle less efficient than the Carnot cycle?*

Consider the Brayton cycle and the corresponding work done as being approximated by a number of elementary Carnot cycles, as shown by the dashed lines in Figure 1. All of these Carnot cycles have the same pressure ratio, thus the same temperature ratio, and thus the same efficiency. The temperature ratio that figures into the efficiency of the elementary Carnot cycles is the inlet temperature divided by the compressor exit temperature, not the maximum cycle temperature, which is at the combustor exit. The basic reason for the lower efficiency is that heat is absorbed at an average temperature that is lower than the maximum temperature and rejected at an average temperature higher than the minimum temperature. We will come back to this important point (which has implications for all cycles), but if you cannot wait, see Section 1-C of the notes.

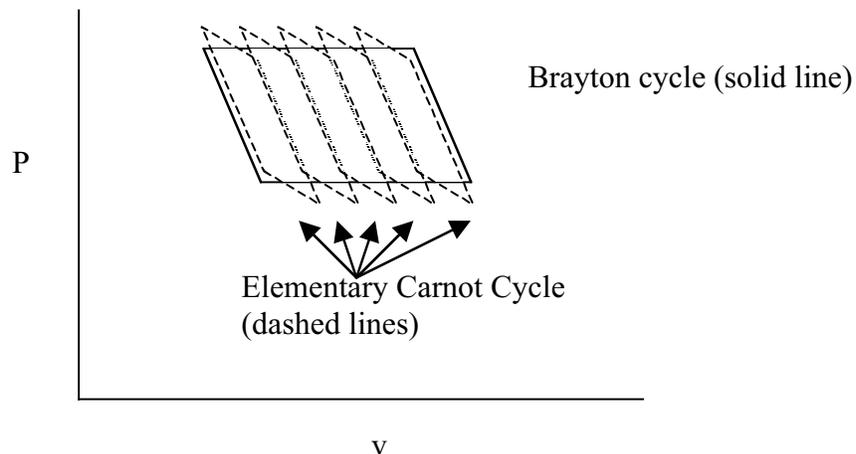


Figure 1 - Brayton cycle considered as a number of elementary Carnot cycles, all having the same pressure ratio and therefore the same temperature ratio, which is lower than the overall cycle temperature ratio,  $T_{max} / T_{min}$ .

1A.8 If the gas undergoes constant pressure cooling in the exhaust outside the engine, is that still within the system boundary?

When we analyze the state changes as we trace them around the cycle, we are viewing the changes in a system, a mass of fixed identity. Thus we follow the mass as it moves through the device and the cooling of the gas outside the engine is happening to our system.

1A.9 Does it matter what labels we put on the corners of the cycle or not?

It does not matter what labels we use on the corners of the cycle. A cycle is a series of processes. Independent of where you start in the cycle, it always brings you back to the state where you started.

1A.10 Is the work done in the compressor always equal to the work done in the turbine plus work out (for a Brayton cycle)?

NO. The work done in the compressor plus net work out equals the total turbine work. Using the 1<sup>st</sup> law, the net work we get out of the Brayton cycle is

$$w = q_2 + q_1 = c_p [(T_a - T_d) + (T_c - T_b)]$$

(see notes for details). Rearranging the temperatures we can also write

$$w = c_p [(T_c - T_d) - (T_b - T_a)] = Dh_{\text{turbine}} - Dh_{\text{compressor}}$$

Thus the net work is the difference between the enthalpy drop across the turbine (we get work from the turbine) and the enthalpy rise through the compressor (we have to supply work to the compressor).

1A.11 What are the units of  $w$  in  $\dot{m} w$ ?

The units of power are J/s (kJ/s, MJ/s) or Watts (kW, MW). The mass flow is kg/s. The units of  $w$ , work per unit mass, are thus J/kg. For the aeroengine, we can think of a given diameter (frontal area) as implying a given mass flow (think of a given Mach number and hence a given ratio of flow to choked flow). If so, for a given fan diameter power scales directly as work per unit mass.

1A.12 Precision about the assumptions made in the Brayton cycle for maximum efficiency and maximum work

We have first derived a general expression for the thermal efficiency of an **ideal** Brayton cycle (see Equation A.3.3 in your notes). The assumptions we made for the cycle were that both the compressor and turbine are **ideal**, such that they can be modeled adiabatic and reversible. We then looked at possible ideal Brayton cycles that would yield (A) maximum efficiency and (B) maximum work, keeping the assumptions of an ideal cycle

(the assumptions of adiabatic and reversible compression and expansion stem from the choice of an **ideal** cycle). One way to construct an ideal Brayton cycle in the P-V diagram is to choose the inlet temperature  $T_a$  and inlet pressure  $P_a$ , the compressor pressure ratio  $P_b/P_a$  or temperature ratio  $T_b/T_a$ , and the turbine inlet temperature  $T_c$ . Apart from setting the inlet conditions (these mainly depend on the flight altitude and Mach number and the day), we decided to fix the turbine inlet temperature (fixed by material technology or cost). So the only two "floating" cycle parameters that remain to be defined are the compressor exit temperature  $T_b$  and the turbine exit temperature  $T_d$ . Looking at equation A.3.3 we know that the higher the compressor temperature ratio  $T_b/T_a$  the higher the thermal efficiency. So, for (A) maximum efficiency we would choose the compressor exit temperature as high as possible, that is in the limit  $T_b = T_c$ . Constructing this cycle in the P-V diagram and letting  $T_b$  approach  $T_c$  shows that the area enclosed by the cycle, or in other words the net work, becomes zero. Thus a cycle constructed under the given inlet conditions and constraints on  $T_c$  is not very useful because we don't get any work out of it.

For the derivation of  $T_b$  for maximum work (keeping  $T_c$  fixed as above), see notes for details.

*1A.13 You said that for a gas turbine engine modeled as a Brayton cycle the work done is  $w=q_1+q_2$ , where  $q_2$  is the heat added and  $q_1$  is the heat rejected. Does this suggest that the work that you get out of the engine doesn't depend on how good your compressor and turbine are? ...since the compression and expansion were modeled as adiabatic.*

Using the 1<sup>st</sup> law, the net work we get out of the cycle is

$$w = q_2 + q_1 = c_p [(T_a - T_d) + (T_c - T_b)]$$

(see notes for details). Rearranging the temperatures we can also write

$$w = c_p [(T_c - T_d) - (T_b - T_a)] = \Delta h_{\text{turbine}} - \Delta h_{\text{compressor}}.$$

Thus the net work is the difference between the enthalpy drop across the turbine (we get work from the turbine) and the enthalpy rise through the compressor (we have to supply work to the compressor, this is done through the drive shaft that connects turbine and compressor).

In class we analyzed an **ideal** Brayton cycle with the assumptions of adiabatic **reversible** compression and expansion processes, meaning that the work done by the turbine is the **maximum** work we can get from the given turbine (operating between  $T_c$  and  $T_d$ ), and the work needed to drive the given compressor is the **minimum** work required. In the assumptions the emphasis is put on **reversible** rather than adiabatic. For real engines the assumption of adiabatic flow through the compressor and turbine still holds. This is an approximation – the surface inside the compressor or turbine where heat can be transferred is much smaller than the mass flow of the fluid moving through the machine

so that the heat transfer is negligible – we will discuss the different concepts of heat transfer later in class. However the compression and expansion processes in **real** engines are **irreversible** due to non-ideal behavior and loss mechanisms occurring in the turbomachinery flow. Thus the thermal efficiency and work for a **real** jet engine with losses depend on the component efficiencies of turbine and compressor and are less than for an ideal jet engine. We will discuss these component efficiencies in more detail in class.

*1A.14 Would it be practical to run a Brayton cycle in reverse and use it as refrigerator?*

Yes. In fact people in Cryogenics use reversed Brayton cycles to cool down systems where very low temperatures are required (e.g. space applications, liquefaction of propellants). One major difference between a regular Brayton cycle (such as a jet-engine or a gas-turbine) and a reversed Brayton cycle is the working fluid. In order to make a reversed Brayton cycle practical we have to choose a working fluid that is appropriate for the application.

Extremely low temperatures can be achieved when using a regenerator – a heat exchanger that preheats the fluid before it enters the compressor and cools the fluid further down before it enters the turbine. In this configuration the fluid is expanded to much lower temperatures, and more heat can be absorbed from the cooling compartment.

*1A.15 Why is the ability to do work decreased in B? How do we know?*

In state A, the energy is in organized form and the molecules move along circular paths around the spinning flywheel. We could get work out this system by using all of the kinetic energy of the flywheel and for example lift a weight with it. The energy of the system in state B (flywheel not spinning) is associated with disorganized motion (on the molecular scale). The temperature in state B is higher than in state A. We could also extract work from state B by running for example an ideal Carnot cycle between  $T_B$  and some heat reservoir at lower temperature. However the work we would get from this ideal Carnot cycle is less than the work we get from state A (all of the kinetic energy), because we must reject some heat when we convert heat into work (we cannot convert heat into 100% work). Although the energy of the system in state A is the same as in state B (we know this from 1<sup>st</sup> law) the "organization" of the energy is different, and thus the ability to do work is different.

*1A.16 With the isothermal reversible expansion, is  $P_{external}$  constant? If so, how can we have  $P_{system} \cong P_{external}$ ?*

For a reversible process, if the external pressure were constant, there would need to be a force that pushed on the piston so the process could be considered quasi-equilibrium. This force could be us, it could be a system of weights, or it could be any other work receiver. Under these conditions the system pressure would not necessarily be near the external pressure but we would have  $P_{system} \cong P_{external} + \frac{F_{work\ receiver}}{A_{piston}}$ . We can of course

think of a situation in which the external pressure was varied so it was always close to the system pressure, but that is not necessary.

*1A.17 Why is the work done equal to zero in the free expansion?*

In this problem, the system is everything inside the rigid container. There is no change in volume, no " $dV$ ", so no work done on the surroundings. Pieces of the gas might be expanding, pushing on other parts of the gas, and doing work locally inside the container (and other pieces might be compressed and thus receive work) during the free expansion process, but we are considering the system as a whole, and there is no net work done.

*1A.18 Is irreversibility defined by whether or not a mark is left on the outside environment?*

A process is irreversible when there is no way to undo the change without leaving a mark on the surroundings or "the rest of the universe". In the example with the bricks, we could undo the change by putting a Carnot refrigerator between the bricks (both at  $T_M$  after putting them together) and cooling one brick down to  $T_L$  and heating the other brick to  $T_H$  to restore the initial state. To do this we have to supply work to the refrigerator and we will also reject some heat to the surroundings. Thus we leave a mark on the environment and the process is irreversible.

*1A.19 Is heat transfer across a finite temperature difference only irreversible if no device is present between the two to harvest the potential difference?*

If we have two heat reservoirs at different temperatures, the irreversibility associated with the transfer of heat from one to the other is indeed dependent on what is between them. If there is a copper bar between them, all the heat that comes out of the high temperature reservoir goes into the low temperature reservoir, with the result given in Section 1.B.5. If there were a Carnot cycle between them, some (not all ) heat from the high temperature reservoir would be passed on to the low temperature reservoir, the process would be reversible, and work would be done. The extent to which the process is irreversible for any device can be assessed by computing the total entropy change (device plus surroundings) associated with the heat transfer.