Lecture TOPIC 5 (Finn: 4.7, 4.8, 4.9, 4.10)


Carnot Engine efficiency

The efficiency of a Carnot engine is independent of the nature of the working substance. Heat flows ($Q_1$ and $Q_2$) are determined solely by the temperatures ($T_1$ and $T_2$) of the heat reservoirs. It is therefore possible to define a temperature scale based on thermodynamic principles. This is in principle better than the ideal gas temperature scale which relies on the properties that real gases have in common at very low pressure. Choosing an ideal gas as a working substance we now show that the simplest definition of a thermodynamic temperature scale coincides with the ideal gas temperature scale. The ideal gas scale then provides a practical way to measure absolute thermodynamic temperature.

Heat flow and work done in an Ideal Gas Carnot cycle:

1. Isothermal expansion “ab”: For any infinitesimal part of this expansion, the First Law gives $dU = dq - PdV = 0$, since for an ideal gas $U = U(T)$. Integrate to get heat entering the gas:

\[ q_{ab} = \int_{V_a}^{V_b} PdV = nRT_1 \int_{V_a}^{V_b} \frac{dV}{V} = nRT_1 \ln\left(\frac{V_b}{V_a}\right), \]

which is positive.

(For an ideal gas $\Delta U = 0$ for an isothermal process. So heat enters the working substance to make up for the energy loss it incurs because it does mechanical work on its surroundings.)

2. Isothermal contraction or compression “cd”: For any infinitesimal part of this compression, at constant temperature $T_2$, the First Law gives $dU = dq - PdV = 0$, since for an ideal gas $U = U(T)$. Integrate as for the other isothermal stage, above, to get the heat entering the working substance:

\[ q_{cd} = \int_{V_c}^{V_d} PdV = nRT_2 \int_{V_c}^{V_d} \frac{dV}{V} = nRT_2 \ln\left(\frac{V_d}{V_c}\right), \]

which is negative.

(Heat leaves the working substance with the energy loss being balanced by the mechanical work done on it by its surroundings.)

3. In terms of the notation developed for use with heat engines, $Q_1 = q_{ab}$, but $Q_2 = -q_{cd}$. The heat rejected by the working substance is $Q_2 = nRT_2 \ln\left(\frac{V_c}{V_d}\right)$.

\[ \frac{Q_2}{Q_1} = \frac{nRT_2 \ln\left(\frac{V_c}{V_d}\right)}{nRT_1 \ln\left(\frac{V_b}{V_a}\right)} = \frac{T_2 \ln\left(\frac{V_c}{V_d}\right)}{T_1 \ln\left(\frac{V_b}{V_a}\right)} \]

We can simplify this further by using properties of the adiabats:
4. We can take the ratio of \( T_1 V_{\gamma}^{-1} = T_2 V_{\gamma}^{-1} \) and \( T_1 V_{\gamma}^{-1} = T_2 V_{\gamma}^{-1} \) to eliminate temperatures and get: 
\[
\frac{V_b}{V_a} = \frac{V_c}{V_d} \Rightarrow \ln(V_b/V_a) = \ln(V_c/V_d).
\]
so the term involving volumes is the equation for \( Q_2/Q_1 \) is just unity, and
\[
\frac{Q_2}{Q_1} = \frac{T_2}{T_1}
\]

Defining thermodynamic temperature \( T_{th} \) via
\[
\frac{T_{th2}}{T_{th1}} = \frac{Q_2}{Q_1}
\]

makes the thermodynamic temperature scale the same as the ideal gas temperature scale. Henceforth we denote temperatures on both scales by \( T \), measured in kelvin.

**Engineering definitions of efficiency including for refrigerators and heat pumps**

Specify Carnot (ideal) efficiencies in terms of the temperatures of the reservoirs. Efficiency is always defined by (what you want out)/(what you put in). So for an Engine you put heat in and get work out. For a Refrigerator, you put work in, and take heat out (from the cold region). For a Heat Pump you put work in, and get heat out (into the warm region).

![Diagram of Heat Engine and Refrigerator with Efficiency Equations]

**Heat Engine**

Efficiency \( \eta \):
\[
\eta = 1 - \frac{Q_2}{Q_1}
\]
Carnot only

**Refrigerator**

Coefficient of performance \( \eta^R \):
\[
\eta^R = \frac{Q_2}{W} = \frac{Q_2}{Q_1 - Q_2}
\]

Heat pump, efficiency \( \eta^{HP} \):
\[
\eta^{HP} = \frac{Q_1}{W} = \frac{Q_1}{Q_1 - Q_2}
\]

For a non-ideal engine losses always reduce the efficiency. e.g. Friction in the bearings \( Q_F \) reduces useful work output \( (W \rightarrow W - Q_F) \), and losses from the boiler transfer heat direct to the cold reservoir \( (Q_1 \rightarrow Q_1 + Q_L; Q_2 \rightarrow Q_2 + Q_L) \). We can write
\[
\eta_{real} = \frac{W - Q_F}{Q_1 + Q_L}
\]

\( Q_F \) must be positive from Kelvin-Planck, \( Q_L \) must be positive from Clausius.
The air standard Otto cycle: a “nearly real” engine

This is a simplified version of the two-stroke petrol engine. A single working substance is assumed – an ideal gas, rather than an air plus petrol mix. No chemical changes are considered, and the source of heat is assumed to be “external” rather than internal from the combustion of fuel. The simplified cycle that remains (the air standard Otto cycle) is a four stage process comprises two adiabatic and two constant volume (isochoric) processes. Heat exchange takes place in the irreversible isochoric process, which can be done much faster than an isothermal, meaning the power output is higher, even though efficiency is worse than for a Carnot engine.

Analysis (details in Tutorial), begin with the compression stage.

1. a – b: reversible adiabatic compression $dQ = 0$ (Piston moves in) $dU = dW$
   \[ T_a V_1^{\gamma - 1} = T_b V_2^{\gamma - 1}; \quad dW = C_V (T_a - T_b); \]

2. b – c: heat added from some external source and the working substance pressure increases at constant volume: $dW = 0$ (actually, combustion).
   \[ Q_1 = dU = C_V (T_c - T_b) \]

3. c – d: reversible adiabatic expansion $dQ = 0$; $dW = dU$ (the “power stroke”: piston moves out).
   \[ T_d V_1^{\gamma - 1} = T_c V_2^{\gamma - 1}; \quad dW = C_V (T_c - T_d); \]

4. d – a: heat rejected and the working substance cools to its original pressure, at constant volume $dW = 0; dQ = dU$ (actually, exhaust and fuel/air input)
   \[ Q_2 = C_V (T_d - T_a) \]

The efficiency $\eta$ for the engine can be specified in terms of $Q_1$ and $Q_2$. From (4) and (2):

\[ \eta = 1 - \frac{Q_2}{Q_1} = 1 - \frac{T_d - T_a}{T_c - T_b} \]

To get more insight into the factors controlling efficiency use (1) and (3) to give:

\[ \eta = 1 - \left( \frac{V_2}{V_1} \right)^{\gamma - 1} = 1 - \frac{1}{r_c^{\gamma - 1}} \]

where $r_c = V_1/V_2$, relating volume of the cylinder with the piston in or out, is called the compression ratio. If $r_c$ is $\sim 5$, $\eta \sim 50\%$. Notice that if you write efficiency in terms of volume rather than temperature, then it does depend on the working substance, through $\gamma$.

Most real engines are four-stroke. They have exhaust and intake stages between $da$ and $ab$. Other considerations limit the efficiency of real engines yielding values below the ideal Otto cycle: 50% is pretty good.
Commentary - how to tackle thermodynamics problems

Deciding how to define the system

Generally, you want to pick a system which contains a constant amount of material. In a steady flow problem, it may have constant mass, well define P, T, V etc, but not always be the same set of atoms. You also want to pick something where the boundaries have well defined pressure, temperature etc. The boundary need not be a physical object.

Defining an equivalent process

Most processes we are interested in are irreversible. However, we are often interested in state variables whose value can be defined irrespective of process. And the First Law always holds. So, to integrate between state points, we normally analyse an equivalent reversible process.

Selecting the coordinate system

There are many state variables, and typically changes in one can be expressed in terms of any two others. A good choice makes the maths simpler, for example if integrating a process at constant X, choose X as one of the independent variables.

Pressure of work

What is the \( P \) in \( PdV \)? A piston moves because the pressure is different on opposite sides. Which side to use?

If the process is reversible (quasistatic), the pressure is essentially the same on either side. However, if the process is irreversible the system is not in equilibrium and thermodynamic variables such as the pressure cannot even be defined. But work done on and by the system is equal and opposite. So we can use the pressure of the surroundings.

If the boundary is carefully chosen then the surroundings can be regarded as in equilibrium, with well defined values of T, P, etc. In this case the work done can be calculated from \( PdV \) with \( P \) the pressure of the surroundings, even if the system undergoes a non-equilibrium process.

**CALCULATION STRATEGY - EXAMPLE**

**Question:** The state of a compressible fluid is changed reversibly and infinitesimally from \((P, T)\) to \((P + \delta P, T + \delta T)\). How much work is done on the fluid?

Write the equation of state in the form that gives the state function or differential we want, in terms of the state variables whose changes are given (or conserved).

\[
dV = \left( \frac{\partial V}{\partial P} \right)_T dP + \left( \frac{\partial V}{\partial T} \right)_P dT
\]

Now identify the partial differentials with material properties, e.g. isobaric thermal expansion and isothermal bulk modulus

\[
\beta = \frac{1}{V} \left( \frac{\partial V}{\partial T} \right)_P ; \quad K = -V \left( \frac{\partial P}{\partial V} \right)_T
\]

Express the differentials in terms of standard definitions of properties,

\[
dW = -P \delta V = \frac{PV}{K} \delta P - PV \beta \delta T
\]

To get the total work in a process, we must then integrate

\[
W = \int \frac{PV}{K} dP - \int PV \beta dT
\]

Where the integrand (e.g. \( \frac{PV}{K} \)) must be manipulated to depend only on \( P \). This can be done because the path tells us how to relate \( P \) to \( V \) (e.g. adiabatic path \( V \propto P^{-\gamma} \)).