1 Technical aspects of energy

1.1 Conservation of energy (the 1st law of thermodynamics)

Energy is discussed and brought up at length in everyday life, but it is seldom accurately defined. Given the title of the course, we should probably rigorously define it: **Energy is simply a certain quantity that has been observed as remaining constant during physical, chemical and/or biological changes**.

Based on this observation (or I should say, observations made over the course of centuries), a postulate was made that energy is conserved. From this and one other postulate (which has to do with entropy and that we shall bring up shortly), an entire mathematical construct was built, which we know as thermodynamics. For this reason, the conservation of energy is often referred to as the *first law of thermodynamics*.

If energy is conserved, that means that the universe's energy is constant. For practical purposes and for studying a specific "closed" system (i.e. no exit/entry of matter from/to the system), the universe can be defined as a *closed system* + *surroundings*. In such a case, the first law of thermodynamics can be stated as:

$$\Delta E = Q + W \text{ [closed system]} \qquad (1.1)$$

With:

ΔE= Change in energy content of the system.

Q: heat transferred to the system *from* its surroundings.

W: amount of work done on the system *by* its surroundings[1].

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[1] In many textbooks work is defined as the amount of work done on the surroundings by the systems. Then 1.1 would become $\Delta E = Q - W$. Both are correct provided that work is defined consistently throughout.

For practical reasons let's rewrite Equation 1.1 by subdividing E and W into different components:

$$\Delta E = \Delta U + \Delta E_p + \Delta E_k = Q + W_{sh} - W_{PV} \quad \text{[closed system]} \tag{1.2}$$

Where:

ΔU= Change in internal energy (this is changed by modifying the temperature, changing the phase, modifying the molecular architectures, changing the atomic structures, etc. of the system)

ΔE_p: Change in potential energy (this is changed by shifting the system location in a force field)

ΔE_k: Change in kinetic energy (this is changed by changing the system's velocity)

W_{PV}: Pressure-Volume work or PV work. This type of work arises that any system has at least some volume, and to achieve that volume it has to move the surroundings out of the way. Similarly, if the system's volume changes, it either gives its surroundings volume by shrinking (i.e. receives work) or shoves the surroundings out of the way (performs work). Since for a positive dV the system performs work, it is convenient to add a negative sign in front of W_{PV} (see eq. 1.4).

W_{sh}: Shaft work, which we define as any work that is not PV work (this could include rotating a shaft but also electrical work, etc.)

In most cases, it is not practical to take into account E_p and E_k so let's forget about them for now (but remember that in some cases they intervene!!). This leads 1.2 to become the closed system shown in Fig. 1.1:

$$\Delta U = Q + W_{sh} - W_{PV} \quad \text{[closed system]} \tag{1.3}$$

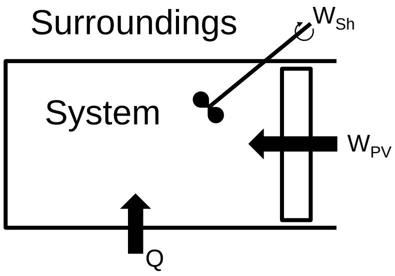

Fig. 1.1 Closed system

1.2 PV work and enthalpy

Let's expand on our definition of *PV work* (W_{PV}), which is the work done by shoving back a volume $V=V_1-V_2$ at a pressure P:

$$W_{PV} = \int_{V_1}^{V_2} PdV \tag{1.4}$$

To solve this integral for non-constant pressures, one needs an equation that relates the pressure *P* to the system's temperature *T* and volume *V*. Such an equation is called an equation of state (EOS). The most well known equation of state is of course the ideal gas law:

$$PV = nRT \text{ or } P = (\frac{n}{V})RT \tag{1.5}$$

Other EOSs include the *Van der Waals* EOS, which performs markedly better than the ideal gas law for real systems. We also commonly use more complex EOSs such as *Peng Robinson* or *Soave-Redlich-Kwong*.

It is sometimes useful to consider that the total energy of a system is not only its internal energy (U) but also the energy it is credited with for having a volume V (i.e., some energy had to be provided for our system to shove the surroundings out of the way). At constant pressure, this energy is:

$$W_{PV} = \int_0^V PdV = PV \tag{1.6}$$

To account for this energy, it is useful to define enthalpy (H), which includes PV:

$$H = U + PV \tag{1.7}$$

In systems at constant pressure[2], it is often useful to use enthalpy because you don't have to worry about remembering to account for the work done to push back the atmosphere. Therefore, taking equations 1.3 and 1.6, we have **for a closed system at constant pressure**:

$$\Delta U + W_{PV} = \Delta U + P\Delta V = \Delta H = Q + W_{sh} \tag{1.8}$$

Whereas **for a closed system at constant volume** ($W_{PV} = \int PdV = 0$), we have:

$$\Delta U = Q + W_{sh} \tag{1.9}$$

Therefore, for closed systems at constant volume it will be easier to track internal energy, whereas for closed systems at constant pressure, we will prefer enthalpy.

1.3 Entropy and the second law of thermodynamics

The first law of thermodynamics establishes the fact that you cannot create energy, which already places some limits on several important energetic processes. However, there are other limits that exist within practical systems that do not arise from the first law. An example of such a limit is the fact that heat flows from a hot to a cold source and not the other way around. These concepts are governed by entropy (S), which is often visualized as a measure of a systems disorder or inventory of random information. The second law states that disorder increases with time or at the very least remains constant. For an isolated system, the second law can be formulated as:

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[2] This could include open systems such as boiling water or burning wood in a fireplace as well as continuous systems like a flow reactor.

$\Delta S_{system} \geq 0$ [isolated system] (1.10)

For a non-isolated system, the second law only requires that the total entropy of the system and its surroundings be equal to or greater than zero:

$\Delta S_{system} + \Delta S_{surroundings} \geq 0$ [non-isolated system] (1.11)

Above, we presented ways to measure changes in internal energy (eq. 1.3) or changes in enthalpy (eq. 1.6). A similar calculation must be defined to measure entropy. Entropy is defined by the exchange in reversible heat Q_{rev} during a state change:

$$\Delta S_{system} = S_2 - S_1 = \int_{S_1}^{S_2} \frac{dQ_{rev}}{T_{System}} \tag{1.12}$$

Reversible heat (Q_{rev}) is the heat received during a *reversible* process: a process where all mechanical energy changes occur reversibly (e.g. without any friction or energy dissipation) and where all heat is exchanged reversibly (eg. while maintaining equilibrium with the surroundings and keeping the system at a uniform temperature at all times). Because of the presence of reversible heat and temperature in equation 1.12, entropy has units of energy over temperature (e.g. J/K). Of course, reversible heat is a difficult quantity to measure because no real process occurs reversibly. However, entropy is a *state* function. Therefore, a change in entropy between state 1 and 2 is completely independent of the path taken (Fig 1.2).

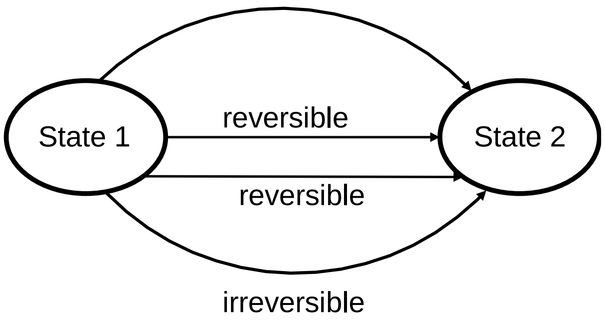

Fig. 1.2 Different paths may require different heat and work.

Therefore, for every change from state 1 to state 2, there are an infinite number of paths both reversible and irreversible. Therefore, one can always find a reversible path to go from state 1 to 2, and the Q_{rev} added during this path will allow us to calculate ΔS.

To understand this distinction, consider the following example. We have 1 kg of perfectly isolated water with a stirrer. We start the stirrer and stir until we have produced 4184 J of shaft work. After we stop stirring, the water will no longer be moving, but the stirring energy will have dissipated irreversibly as heat into the water, heating it to 21°C. This is a completely irreversible process where no heat was added ($Q_{irrev}=0$). However, we can get from state 1 (water at 20°C) to state 2 (water at 21°C) by reversibly heating the water with the same amount of energy as that used in the irreversible process. Therefore, Q_{rev}=4184 J.

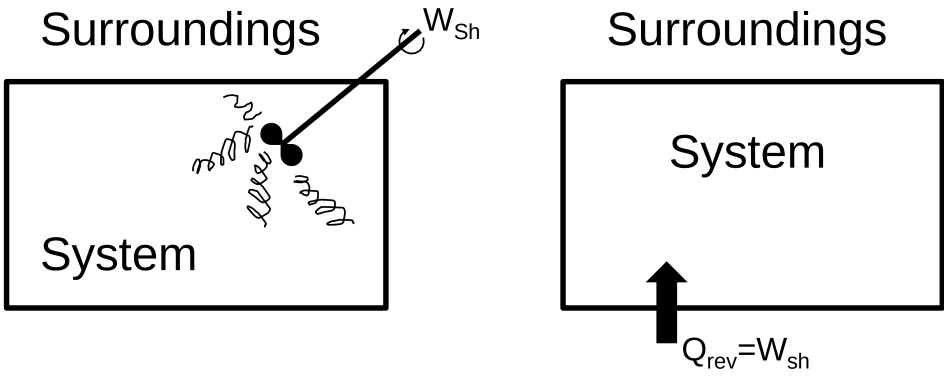

Fig. 1.3 An irreversible and reversible path to the same state.

Because Q_{rev} is dependent on the path taken (a path function) and is used to calculate □S (a state function), it is usually necessary to calculate the evolution of the system and of its properties (i.e. V, P, T, etc.). How can we know such properties? Equations of state (EOSs) can help us define one of these variables as a function of the other two. For this reason, EOSs such as those mentioned above (e.g. the ideal gas law in eq. 1.5) are sometimes necessary to calculate Q_{rev} and ΔS.

1.4 How generating work from heat can be described by entropy

Why have we spent so much time talking about obscure state functions such as internal energy U or entropy S? As it turns out, these functions are essential for understanding how we obtain, transport and convert energy. An important example of such a conversion is the transformation of heat to work. This is the most important work-generating process, and is the basis for most transportation processes.

The vast majority of work-generating processes are continuous, meaning that they stay or return frequently to the same state in a cyclical manner. The internal combustion engine is physically cyclical (i.e., its function involves distinct steps), whereas a plane reactor or gas turbine is mechanically continuous. However, from the standpoint of the fluid (i.e., the entity providing the work!), all these work-generating processes are cyclical.

Again, cyclical indicates that you return to the same state. For this reason, we can use a *state variable* to describe our system. Since a state variable (let's call it X) is independent of paths taken to and from that state, in a cyclical process, this state variable will always return to its original value (X_0). For reasons that we will see in a second, it's best to describe such a path using entropy. Recall our definition for entropy (below is a slightly modified version of Equation 1.12).

$$dS = \frac{dQ_{rev}}{T} \tag{1.13}$$

Equation 1.13 is useful to determine the greatest amount of heat that we can extract from a given cyclic path.

$$dQ_{rev} = TdS \rightarrow Q_{rev} = \int T\,dS \tag{1.14}$$

The integral on the right represents the area formed by T(S) on a *T-S diagram*, which for a cyclical process is represented on Fig. 1.4.

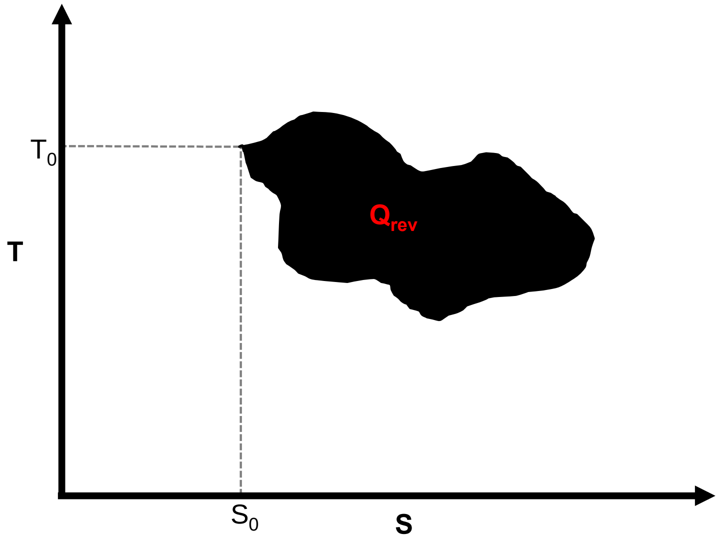

Fig. 1.4 A thermodynamic cycle on a T-S diagram

Now remember, this holds only for a *reversible* process (the best possible scenario). In an actual process, we will not recover all of this entropy as heat, but will lose it in some other way (loss of heat to the surroundings, temperature inhomogeneity in the system, etc.). Because of this:

$$dS > \frac{dQ_{actual}}{T} \rightarrow Q_{actual} < \int T\,dS \tag{1.14}$$

Therefore, the actual amount of heat we can recover will always be smaller than the hashed area shown above.

However, the first law always holds no matter what the process is, and for a cyclic process the first law becomes:

$$\Delta U = Q + W = 0 \rightarrow Q = -W \quad \text{[cyclic process]} \tag{1.15}$$

Remember, since internal energy U is a state function, it too (just like entropy) must come back to its initial value ($\Delta U = 0$!).

Therefore, for a cyclic reversible process, we have:

$$W_{rev} = -\,Q_{rev} = -\int T\,dS \tag{1.16}$$

Since Q_{rev} is equal the maximum amount of work that can be produced during a cyclic process (Eq. 1.14 and 1.15), the **area on the T-S diagram** also represents the **maximum amount of work obtainable during a cycle**.

To calculate the actual work, recall that 1.15 is always true for a cyclic process. Therefore:

$$W_{actual} = -\,Q_{actual} < -\int T\,dS \tag{1.17}$$

1.5 The Carnot engine

Above, we have discussed how a cyclical process can produce work and be represented on *T-S diagram*. In addition, we saw that the area covered on this T-S diagram corresponded to the reversible work (i.e. maximum work) that can be produced during a cycle. Let's think more precisely about what such a cycle would look like. In systems that convert heat to work, we have a heat source at a high temperature (T_H). Generally, we also need to cool our system to close the cycle and recover our initial state (think of exhaust gases being cooled in the atmosphere, or the cooling water in a Rankine cycle). In other words, we can represent any heat-to-work conversion system as shown in Fig. 1.5 A.

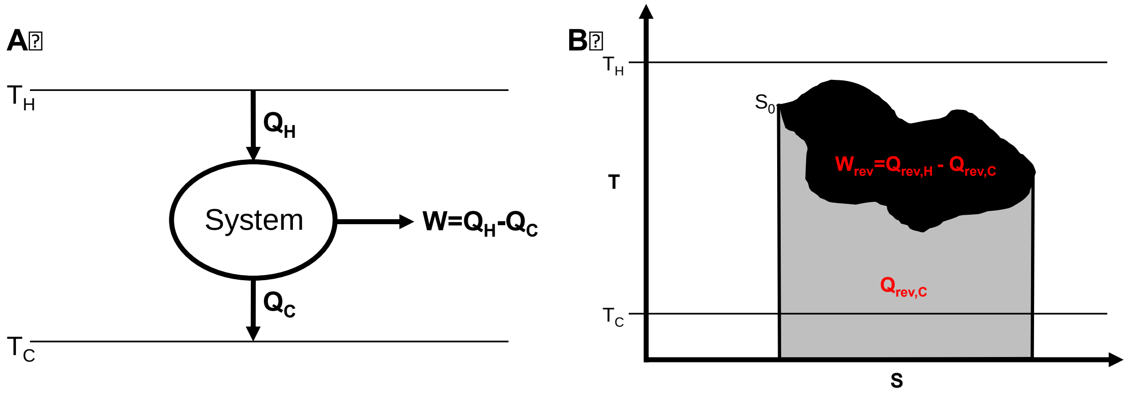

Fig. 1.5 (A) a simplified heat engine and (B) a random *T*-*S* cycle for this engine

Such a system can exchange temperature with the hot and the cold source only if it finds itself in between the two. Knowing this, we can draw a random path cycle on the *T*-*S diagram* (Fig. 1.5 B).

Now, the obvious question is the following: what is the maximum efficiency that could be obtained by a perfect heat engine operating between T_H and T_C? This is the question answered by Sadi Carnot when he developed the Carnot heat engine (the ideal heat engine). Efficiency (η) is usually defined as the work obtained divided by the heat put in at high temperature:

$$\eta = \frac{W}{Q_H} \tag{1.18}$$

The maximum amount of work will be obtained for the path that maximizes the hashed area shown in Fig. 1.5 B. Geometrically, we can see this corresponds to a square (Fig. 1.6 A). This path describes the Carnot heat engine!

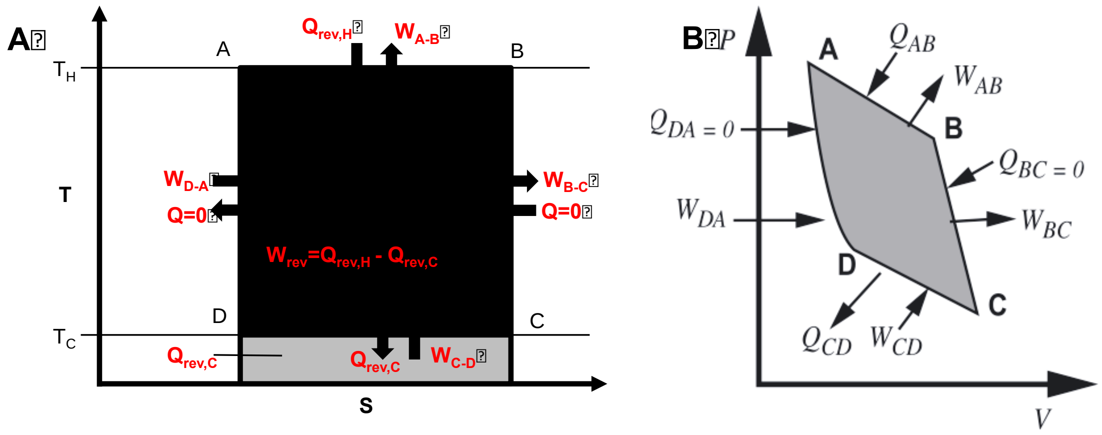

Fig. 1.6 The Carnot heat engine cycle. (A) T-S diagram and (B) P-V diagram. Note that the shaded area on the PV diagram represents the total work done by the system as well.

The steps in this cycle are:

Step AB: Add heat to expand the gas isothermally at T_H, while doing work.

Step BC: Expand the gas adiabatically until the gas reaches T_C, while doing more work.

Step CD: Remove heat to compress the gas isothermally at T_C, while providing work.

Step DA: Compress the gas adiabatically until the gas temperature rises to T_H, while providing the necessary work.

To calculate the work and heat that is given/produced at each stage, we need to use the properties of the ideal gas law.

Reminder: Thermodynamics of ideal gases

For ideal gases

$$U = f(T) \neq f(P, V) \tag{1.19}$$

This was demonstrated by the famous joule experiment, and by definition all ideal gases follow Joule's law:

$$dU = C_V dT \ \rightarrow \Delta U = C_V \Delta T \tag{1.20}$$

where C_V is the volumetric heat capacity (heat capacity at constant volume), which is constant for ideal gases. Similarly, and by definition, we have:

$$\Delta H = C_P \Delta T \tag{1.21}$$

From equation 1.7, we have (for one mole of gas):

$$\Delta U = C_V \Delta T = \Delta H - \Delta(PV) = C_P \Delta T - \Delta(RT) \tag{1.22}$$

Which leads to:

$$C_P - C_V = R \tag{1.23}$$

For ideal gases, it is also useful to define k:

$$C_P / C_V = k = 1 + R / C_V \tag{1.24}$$

For an adiabatic process, we have:

$$dU = C_V dT = dW = -pdV \tag{1.25}$$

If we separate and integrate we get:

$$\ln\left(\frac{T_2}{T_1}\right) = -\frac{R}{C_V} \ln\left(\frac{V_2}{V_1}\right) = -(k-1)\ln\left(\frac{V_2}{V_1}\right) \tag{1.26}$$

Therefore, for an adiabatic step, using 1.26 and 1.5, we can quite easily derive:

$$\left(\frac{T_2}{T_1}\right) = \left(\frac{V_1}{V_2}\right)^{k-1} \tag{1.27}$$

$$\left(\frac{T_2}{T_1}\right) = \left(\frac{P_2}{P_1}\right)^{\frac{k-1}{k}} \tag{1.28}$$

$$\left(\frac{P_2}{P_1}\right) = \left(\frac{V_1}{V_2}\right)^{k} \tag{1.29}$$

With these relations we can pursue our discussion of the Carnot Engine and calculate the heat and work that occurs at each step:

Step AB: Isothermal, closed system → $Q_{AB} = -W_{AB} = RT_H\ ln(\frac{P_A}{P_B})$

Step BC: Adiabatic expansion: $U = W = C_V(T_C - T_H)$

Step CD: Isothermal, closed system → $Q_{CD} = -W_{CD} = RT_C\ ln(\frac{P_C}{P_D})$

Step DA: Adiabatic compression: $U = W = C_V(T_H - T_C)$

To calculate efficiency (η), we need to determine the total amount of work obtained and the heat from the hot source added to the system:

$$\eta = \frac{-W_{tot}}{Q_H} = \frac{-(W_{AB}+W_{BC}+W_{CD}+W_{DA})}{Q_H} = \frac{-W_{AB}-W_{CD}}{Q_{AB}} = \frac{RT_H\ ln\left(\frac{P_A}{P_B}\right)-RT_C\ ln(\frac{P_D}{P_C})}{RT_H\ ln(\frac{P_A}{P_B})} \tag{1.30}$$

As a side note, you will notice that the sum of all the work terms corresponds to the integral of the path on the cycle's PV diagram (Fig. 1.6B). We add a minus sign in front of the total work done by the system (W_{tot}) to correct for the fact that from the system's reference, this work will be "lost" and therefore be negative. From eq. 1.28, we know that for an adiabatic reversible process between the same temperatures, the ratios of the initial and final pressures are constant ($P_A/P_B= P_D/P_C$):

$$\eta = \frac{T_H-T_C}{T_H} \tag{1.31}$$

This is an important result, because it means that for most practical engines, the theoretical efficiency is not 100%! To approach 100%, we have to maximize the difference between T_H and T_C. However, for real systems T_C is never lower than 240 K, and is usually around 290 K, which limits any possibilities that are available.

From the Carnot cycle, we can quite easily deduce the ideal behavior of a heat pump. Heat pumps consume work and bring heat to a hot source. Heat pumps are being used more and more to heat houses, but their most common occurrences are in cooling systems such as refrigerators and air conditioners. If you think about it, an ideal heat pump is simply a Carnot cycle run in reverse (Fig. 1.7).

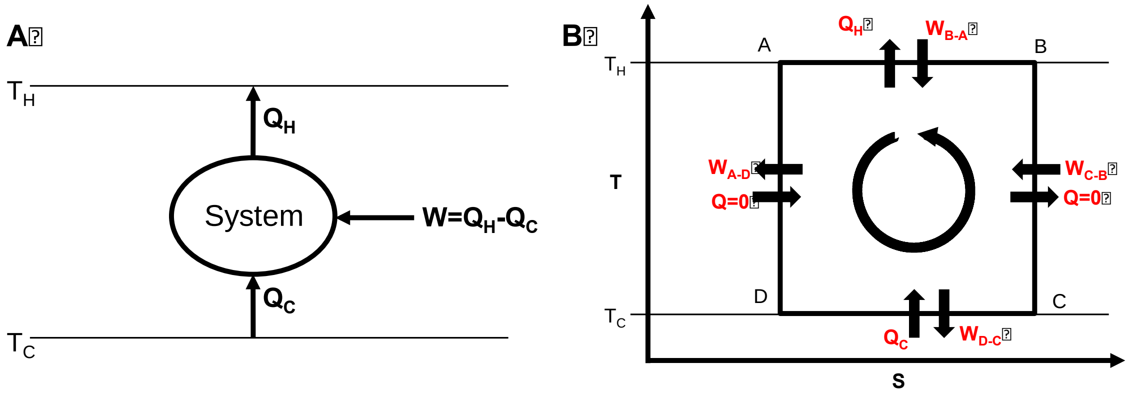

Fig. 1.7 (A) Representation of an ideal heat pump. (B) As a *T*-*S* cycle.

We can calculate the efficiency, which is usually referred to as the coefficient of performance or *COP*, of a heat pump by analogy to the regular Carnot cycle.

$$COP_W = \frac{-Q_H}{W} = \frac{-Q_{BA}}{W_{BA}+W_{CB}+W_{DC}+W_{AD}} = \frac{-RT_H\, ln(\frac{P_B}{P_A})}{-RT_H\, ln\left(\frac{P_B}{P_A}\right)-RT_C\, ln(\frac{P_D}{P_C})} = \frac{T_H}{T_H-T_C} \qquad (1.32)$$

The subscript (*W*) indicates *winter* as a heat pump is usually run as such in the winter. In the summer, the pump is generally reversed and becomes an air conditioner. In this case, COP_S is based on Q_C:

$$COP_S = \frac{Q_{DC}}{W_{BA}+W_{CB}+W_{DC}+W_{AD}} = \frac{RT_H\, ln(\frac{P_D}{P_C})}{-RT_H\, ln\left(\frac{P_A}{P_B}\right)-RT_C\, ln(\frac{P_D}{P_C})} = \frac{T_C}{T_H-T_C} \qquad (1.33)$$

1.6 Real work heat engines

The Rankine cycle

At this point we have explored the efficiency of an idealized heat-to-work or work-to-heat system. What about real systems? Well we could try to operate this with water and steam (a common and cheap fluid). If we try to closely replicate what is seen in Fig. 1.6 (A), then we must operate in the two-phase region, as it is the only way to provide heat to the system at constant temperature. Such a system, along with the phase boundary, is shown in Fig. 1.8.

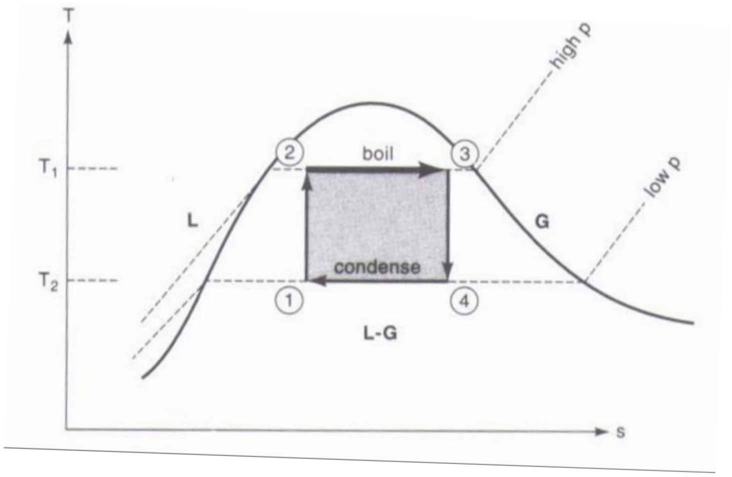

Fig. 1.8 Carnot Cycle in a 2-phase system.

However, in practice, this type of system would imply pumping and expanding a two-phase system as they further change phases. However, mechanical problems that include cavitation in pumps and erosion of turbine blades make it impractical to operate these two-unit operations in the two-phase zone. Therefore, we are forced to extend the system to make sure the pumping and expansion are done outside the two-phase boundary. Therefore, water is completely condensed before pumping and steam is superheated (to much higher than the boiling temperature) to ensure that it will not condense during expansion (Fig. 1.9). The resulting system is called a Rankine cycle.

Path 1-2-3-4-5-6-1 represents the ideal Rankine cycle. For safety reasons, a real turbine is often run with a path closer to 1-2-3-4-5’-6’-1. This is to assure that the turbine operates well outside of the two-phase region. We can use enthalpy (assuming negligible kinetic and potential energy contributions) to calculate the efficiency of a Rankine steam cycle. For the ideal case, we have:

$$\eta = \frac{Q_H - Q_C}{Q_H} = \frac{(H_5 - H_2) - (H_6 - H_1)}{(H_5 - H_2)} \qquad (1.34)$$

We can neglect the energy it takes to compress a liquid, which is very small ($H_1 \approx H_2$), which leads to:

$$\eta = \frac{H_5 - H_6}{H_5 - H_1} \quad \text{or} \quad \eta = \frac{H_{5\prime} - H_{6\prime}}{H_{5\prime} - H_1} \text{ (a more realistic system)} \qquad (1.35)$$

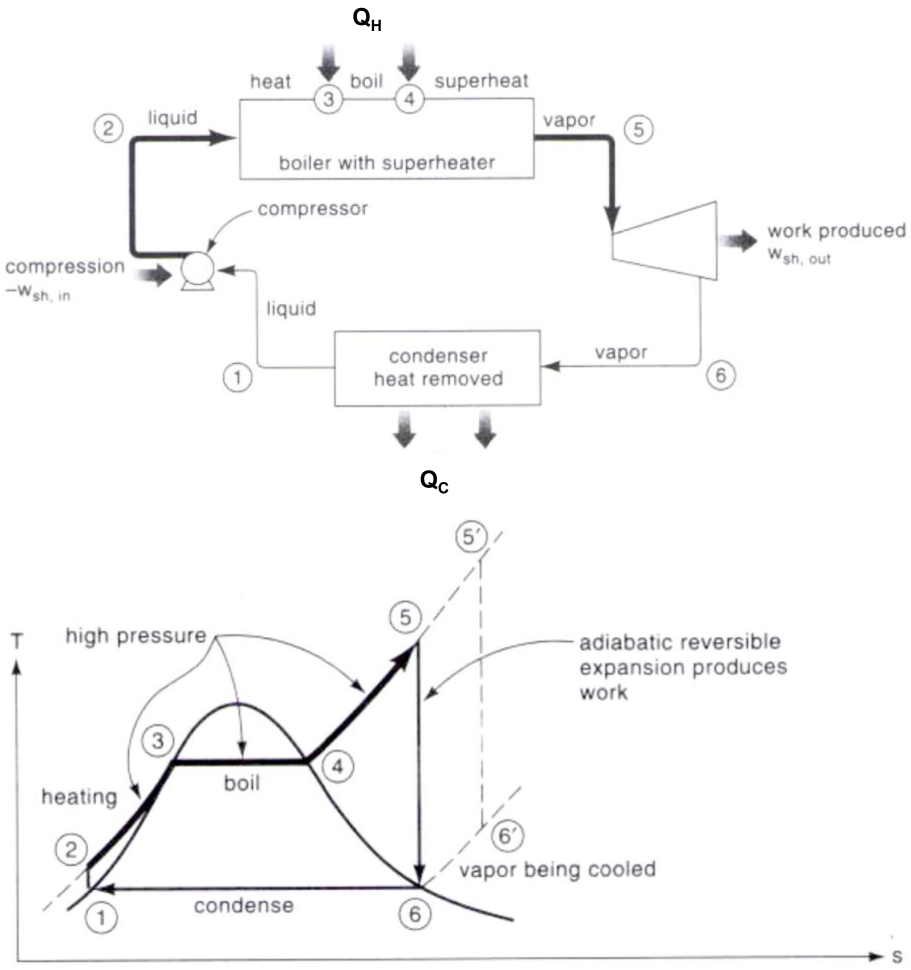

Fig. 1.10 A Rankine cycle and its corresponding TS cycle

We can see that a Rankine cycle, even an ideal one, has an efficiency that is quite a bit lower than that of a Carnot engine. This can be improved on a little bit by using one or more reheat cycles (Fig. 1.11). This is especially helpful when one does not have access to a stream at a temperature at which to superheat the steam.

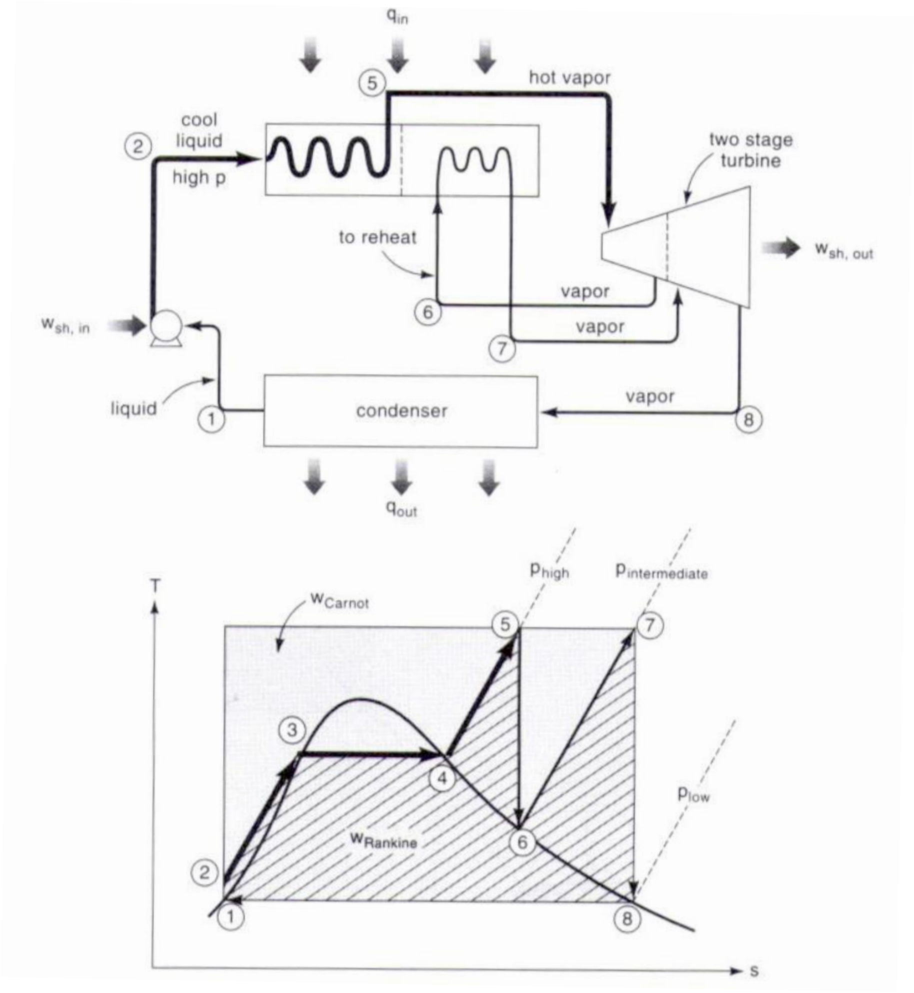

Fig. 1.11 A Rankine cycle with a single reheat cycle and its corresponding TS cycle

The Rankine refrigeration cycle

Like the Carnot cycle, the Rankine cycle can be run in reverse to form a refrigeration cycle or a heat pump. In this case, the physical constraints are slightly different. Let’s again begin by imagining the ideal Carnot case within a real fluid (path 1’-2’-3-4’). In practice, it is preferable to compress a pure gas than a gas liquid mixture, so we shift from 1’ to 1. Additionally, an adiabatic reversible expansion is not possible to replicate, so in practice this is replaced by a simple expansion valve, which is not reversible and therefore leads to an increase in entropy (see pathway 3-4).

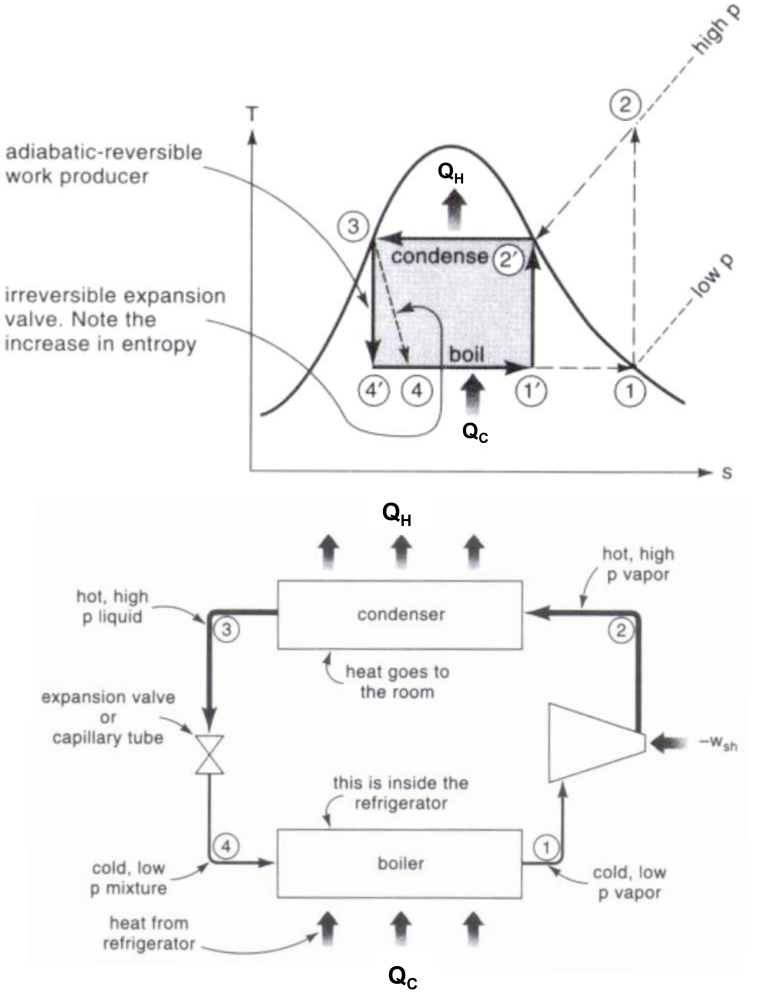

Fig. 1.12 T-S diagram of a reversed Rankine Cycle and its representation for refrigerator.

A more realistic overall pathway is therefore 1-2-3-4 with a COP$_{\text{Refrigeration}}$ efficiency of:

$$COP_{Refrigeration} = \frac{|q_C|}{|W|} = \frac{h_1 - h_4}{h_2 - h_1} \tag{1.36}$$

For the analogous Rankine heat pump, we have:

$$COP_{heat\ pump} = \frac{|q_h|}{|W|} = \frac{h_2 - h_3}{h_2 - h_1} \tag{1.37}$$

The Otto cycle: gasoline engines

Rankine cycles are very useful to understand and calculate the efficiencies of generating electrical power from heat (e.g. processes in various power plants) as well as heat pumps and refrigeration cycles. However, they are not very well suited for describing combustion engines. There are several cycles that are each used to represent different engine types (e.g. the Otto cycle that describes a gasoline engine, the diesel cycle for a diesel engine, the Brayton cycle for a combustion gas turbine or turbojet engine), all of which are very relevant to our current energy use. Let's briefly go over them, starting with the Otto cycle.

This cycle is used to describe a typical gasoline engine and is generally described as a six-step cycle between 6 states (Fig. 1.13):

- State 0-1: The gasoline is pulled in and expanded by mixing with air.
- State 1-2: The mixture is adiabatically compressed (causing it to heat up).
- State 2-3: The spark plug ignites the gas, releasing the combustion heat and causing a large increase in T and P.
- State 3-4: The pressure pushes the piston down, causing an adiabatic expansion and work creation (reducing T).
- State 4-6: The hot exhaust is removed from the engine. Thermodynamically this is represented as two steps. First heat removal (to stage 5) and then return of the cylinder to its original volume (from stage 5 to 6).

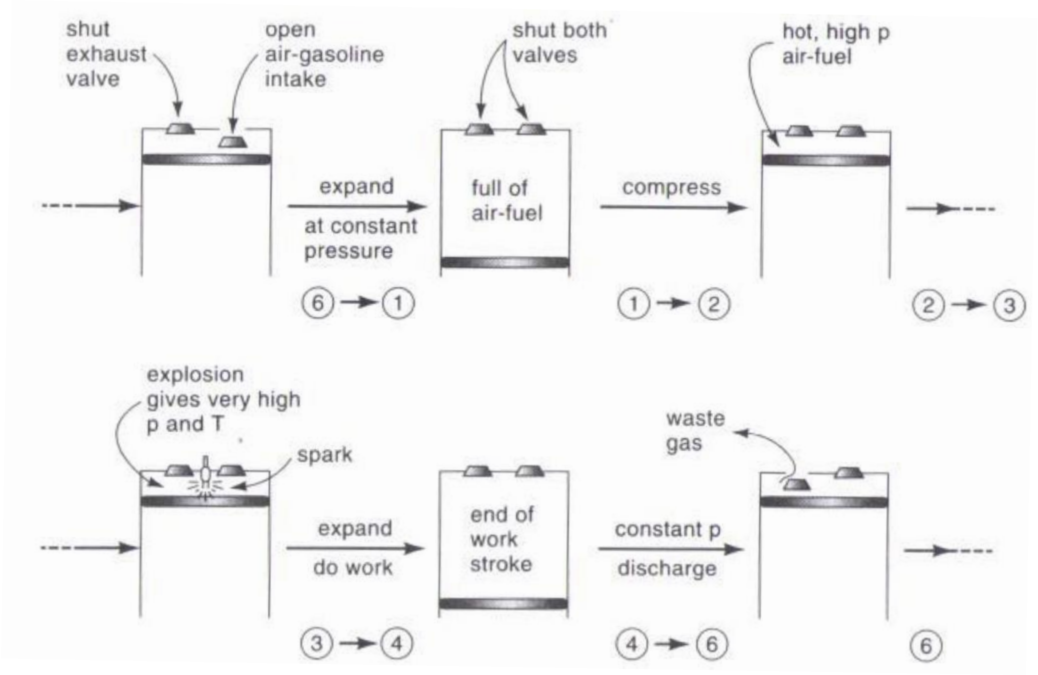

Fig. 1.13 Illustration of the 6 steps of the Otto cycle in a 4 stroke gasoline engine.

Thermodynamically, first (0-1) and last (5-6) steps are trivial and the cycle itself occurs between stages 1 and 5 (Fig. 1.14).

The steps comprising the thermodynamic cycle are:

A. The adiabatic compression of the fuel mixture, which takes work

B. Heating at constant volume by release of the heat of combustion

C. Adiabatic expansion of the combustion chamber along with the production of work

D. Residual heat is removed when exhaust gas is discarded (at constant volume because no compression is applied)

Note that the exhaust and intake are volume changes at constant pressure because no compression or expansion is applied to the gas as it enters and exits the chamber.

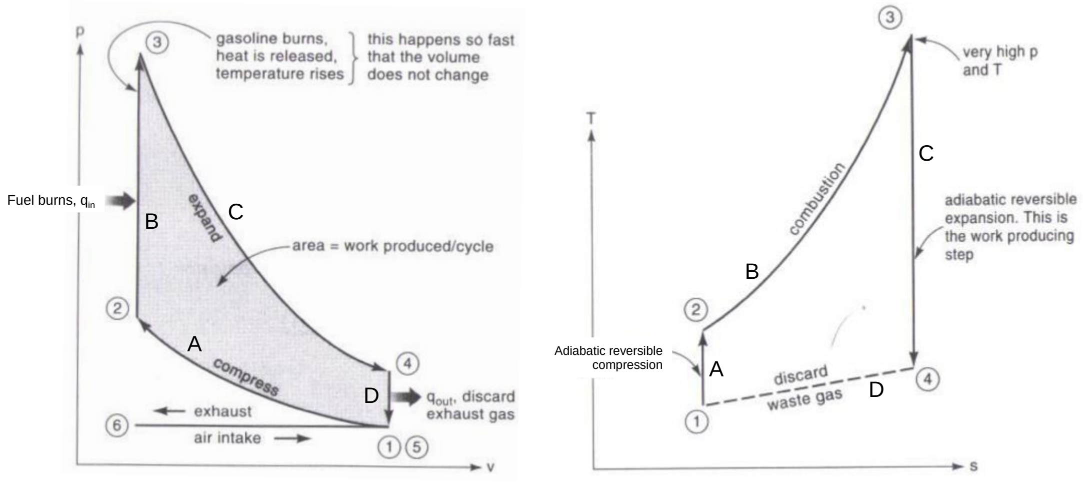

Fig. 1.14 PV (left) and TS diagrams (right) for the Otto cycle.

We want to calculate the efficiency of the engine, which is defined as the work produced over the heat of combustion:

$$\eta = \frac{W}{\Delta H_{comb}} = \frac{W}{Q_{in}} = \frac{Q_{in} - Q_{out}}{Q_{in}} \tag{1.38}$$

We can calculate the heat or work produced at each step:

A. For an adiabatic compression:

$$Q = 0 \;\rightarrow\; \Delta U_{1\to 2} = Q + W_{in} = W_{in} = C_V(T_2 - T_1) \tag{1.39}$$

B. Heating at constant volume

$$W = pdV = 0 \;\rightarrow\; Q_{in} = C_V(T_3 - T_2) \tag{1.40}$$

C. Adiabatic expansion:

$$Q = 0 \;\rightarrow\; \Delta U_{3\to 4} = Q + W_{out} = W_{out} = C_V(T_3 - T_4) \tag{1.41}$$

D. Cooling at constant volume:

$$W = 0 \;\rightarrow\; Q_{out} = C_V(T_4 - T_1)$$

The efficiency can then be calculated as:

$$\eta = \frac{C_V(T_3-T_2)-C_V(T_4-T_1)}{C_V(T_3-T_2)} = \frac{(T_3-T_2)-(T_4-T_1)}{(T_3-T_2)} \tag{1.42}$$

Assuming that the gases involved act ideally and because $V_1=V_4$ and $V_2=V_3$ (see Fig. 1.14):

$$\frac{T_2}{T_1} = \left(\frac{V_1}{V_2}\right)^{k-1} = \left(\frac{V_4}{V_3}\right)^{k-1} = \frac{T_3}{T_4} \tag{1.43}$$

Dividing equation 1.42 in the numerator and denominator by T_3, we get:

$$\eta = \frac{(1-T_2/T_3)-(T_4/T_3-T_1/T_3)}{(1-T_2/T_3)} = \frac{(1-T_2/T_3)-(T_1/T_2-T_1/T_3)}{(1-T_2/T_3)} = 1 - \frac{(T_1/T_2-T_1/T_3)}{(1-T_2/T_3)} \quad = 1 - \frac{T_1}{T_2}\frac{\left(1-\frac{T_2}{T_3}\right)}{\left(1-\frac{T_2}{T_3}\right)} =$$

$$\eta = 1 - \frac{T_1}{T_2} \tag{1.44}$$

We can introduce the compression ratio ($r_c = V_1/V_2$) and rewrite the efficiency as:

$$\eta = 1 - \frac{T_1}{T_2} = 1 - r_C^{1-k} \text{ with } r_c = \frac{V_1}{V_2} = \frac{V_4}{V_3} \tag{1.45}$$

For modern engines, the compression ratio (r_c) is around 8-9 for modern engines and k~1.3, the maximum efficiencies are around 45% for an *ideal* engine, which is much lower than an ideal Carnot cycle. Because of additional inefficiencies in a real system the efficiency is actually closer to 20%.

The Diesel cycle: Diesel engines

The Diesel cycle (unsurprisingly) describes Diesel engines which function in a slightly different way compared to gasoline engines. In gasoline engines, the spark leads to an explosion of a mixture of compressed fuel and air. This leads to an isochoric (constant volume) rapid combustion; i.e. a rapid rise in pressure and temperature at constant volume. In the Diesel engine the diesel fuel is injected after compression of air. The high temperature of the compressed air ignites the fuel, which combusts more slowly than an injection allowing for a simultaneous expansion during combustion (i.e. not isochoric as was the case as was the case for the gasoline engine).

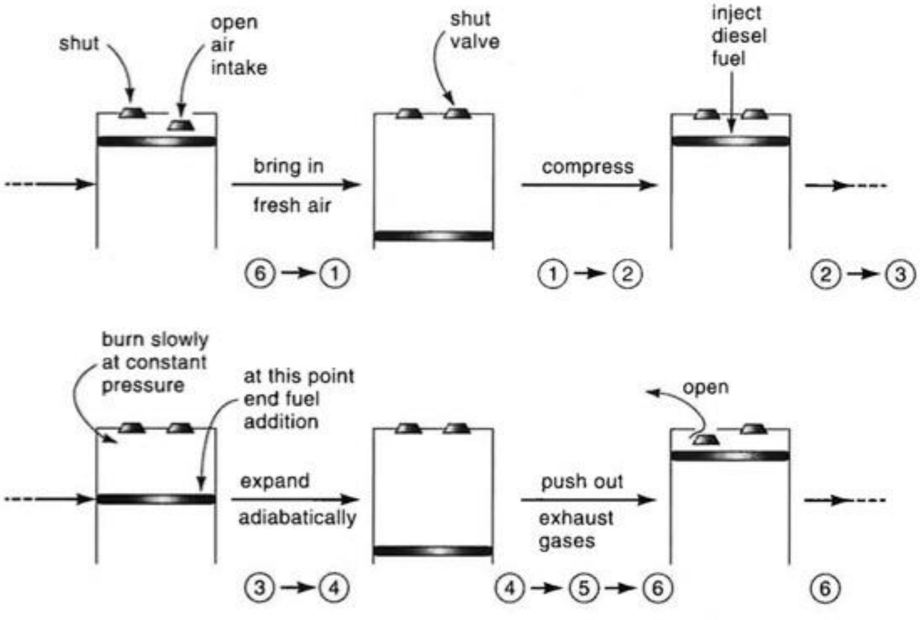

Fig. 1.15 Illustration of the 6 steps of the ideal Diesel cycle in a typical Diesel engine.

Specifically, can be described as going through 6 states (Fig. 1.15):

- State 6-1: The fuel is pulled into the engine cylinder expanding the volume at constant pressure.
- State 1-2: The air is adiabatically compressed (causing it to heat up, same as the Otto cycle except it's pure air).
- State 2-3: The diesel enters the chamber and starts burning. This increases the temperature slowly enough that the piston is pushed back (i.e. a volume increase) without causing an increase in pressure.
- State 3-4: After the combustion is over, the excess pressure compared to atmospheric leads the expansion to continue (this time adiabatically), this time leading to a drop in pressure until fully expanded.

- State 4-6: The hot exhaust is removed from the engine. Similarly to the gasoline engine, thermodynamically this is represented as two steps. First heat removal (to stage 5) and then return of the cylinder to its original volume (from stage 5 to 6).

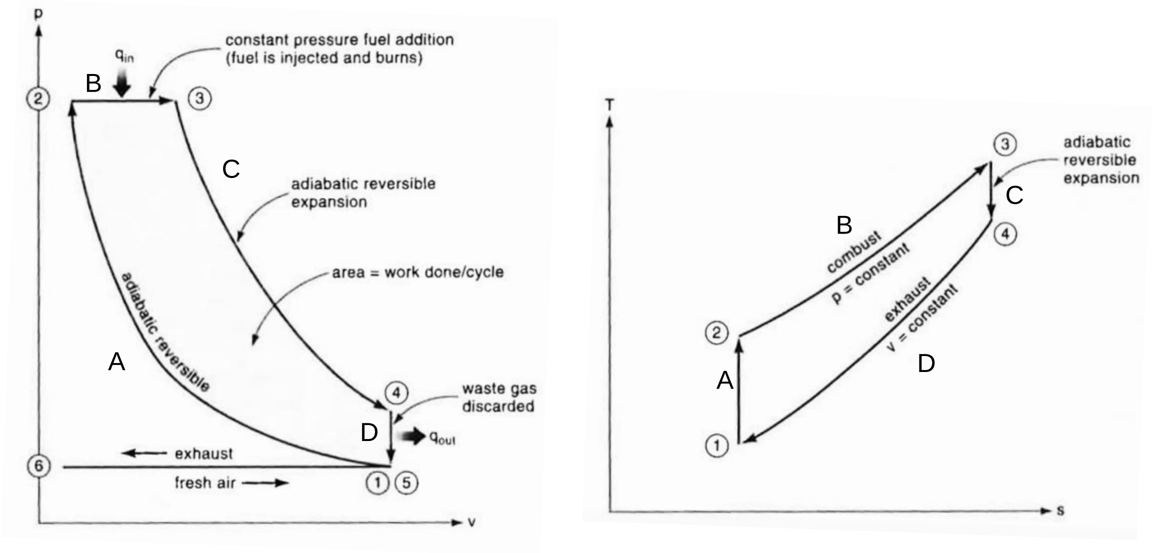

Fig. 1.16 PV (left) and TS diagrams (right) for the Diesel cycle.

Let's again calculate the efficiency of the system, which is defined in the same way as the Otto cycle:

$$\eta = \frac{W}{\Delta H_{comb}} = \frac{W}{Q_{in}} = \frac{Q_{in} - Q_{out}}{Q_{in}} = \frac{|Q_{2-3}| - |Q_{4-5}|}{|Q_{2-3}|} \tag{1.46}$$

We need to calculate the heat exchanged in steps 2-3 (step B) and 4-5 (step D):

B. For a system with heat exchange doing only PV work at constant pressure we have (see Eq. 1.8 and 1.21):

$$Q_{in} = \Delta U + P\Delta V = \Delta H = C_P(T_3 - T_2) \tag{1.47}$$

D. For a system at constant volume, we have:

$$W = pdV = 0 \ \rightarrow \ |Q_{out}| = C_V(T_4 - T_1) \tag{1.48}$$

This leads to the following efficiency:

$$\eta = \frac{C_P(T_3 - T_2) - C_V(T_4 - T_1)}{C_P(T_3 - T_2)} = 1 - \frac{1}{k}\frac{(T_4 - T_1)}{(T_3 - T_2)} \tag{1.49}$$

To make this dependent on physical parameters of the engine, we can define two parameters:

- The compression ratio (same definition as the gasoline engine), which describes the ratio of volumes between the fully compressed and fully expanded engine cylinder: $r_c = \frac{V_1}{V_2}$ (1.50)
- The expansion ratio, which defines the further expansion after the injection of fuel has stopped: $r_e = \frac{V_4}{V_3}$ (1.51)

For ideal gases, we can use properties of adiabatic transformations (Eq. 1.27):

$$r_c = \left(\frac{V_1}{V_2}\right) = \left(\frac{T_2}{T_1}\right)^{1/(k-1)} \rightarrow\ T_2 = T_1(r_c)^{k-1} \rightarrow\ T_1 = T_2\left(\frac{1}{r_c}\right)^{k-1} \tag{1.52}$$

$$r_e = \left(\frac{V_4}{V_3}\right) = \left(\frac{T_3}{T_4}\right)^{1/(k-1)} \rightarrow\ \ T_3 = T_4(r_e)^{k-1} \rightarrow T_4 = T_3\left(\frac{1}{r_e}\right)^{k-1} \tag{1.53}$$

Therefore, the efficiency becomes:

$$\eta = 1 - \frac{1}{k}\frac{(T_4-T_1)}{(T_3-T_2)} \tag{1.54}$$

With:

$$\frac{(T_4-T_1)}{(T_3-T_2)} = \frac{T_3\left(\frac{1}{r_e}\right)^{k-1} - T_2\left(\frac{1}{r_c}\right)^{k-1}}{(T_3-T_2)} = \frac{\frac{T_3(T_3-T_2)}{T_3-T_2}\left(\frac{1}{r_e}\right)^{k-1} - \frac{T_2(T_3-T_2)}{T_3-T_2}\left(\frac{1}{r_c}\right)^{k-1}}{(T_3-T_2)} = \frac{\frac{(T_3-T_2)}{1-\frac{T_2}{T_3}}\left(\frac{1}{r_e}\right)^{k-1} - \frac{(T_3-T_2)}{\frac{T_3}{T_2}-1}\left(\frac{1}{r_c}\right)^{k-1}}{(T_3-T_2)} =$$

$$\frac{(T_3-T_2)\left(\frac{\left(\frac{1}{r_e}\right)^{k-1}}{1-T_2/T_3} - \frac{\left(\frac{1}{r_c}\right)^{k-1}}{T_3/T_2-1}\right)}{(T_3-T_2)} = \left(\frac{\left(\frac{1}{r_e}\right)^{k-1}}{1-T_2/T_3} - \frac{\left(\frac{1}{r_c}\right)^{k-1}}{T_3/T_2-1}\right) \tag{1.55}$$

Stage 2→ 3 is an isobaric transformation ($P_2 = P_3$) and we can also use that Stage 4→1 is an isochoric transformation ($V_4 = V_1$):

$$\frac{T_3}{T_2} = \frac{P_3V_3}{P_2V_2} = \frac{V_3}{V_2} = \frac{V_3/V_4}{V_2/V_1} = \frac{r_c}{r_e} \tag{1.56}$$

Leading to:

$$\frac{(T_4-T_1)}{(T_3-T_2)} = \frac{\left(\frac{1}{r_e}\right)^{k-1}}{1-\frac{r_e}{r_c}} - \frac{\left(\frac{1}{r_c}\right)^{k-1}}{\frac{r_c}{r_e}-1} = \frac{\left(\frac{1}{r_e}\right)^{k}}{\frac{1}{r_e}-\frac{1}{r_c}} - \frac{\left(\frac{1}{r_c}\right)^{k}}{\frac{1}{r_e}-\frac{1}{r_c}} \tag{1.57}$$

And an efficiency of:

$$\eta = 1 - \frac{1}{k}\frac{\left(\frac{1}{r_e}\right)^k - \left(\frac{1}{r_c}\right)^k}{\frac{1}{r_e} - \frac{1}{r_c}} \tag{1.58}$$

This equation is slightly more complicated than for the Otto cycle. In addition, it leads to the efficiency being lower for the Diesel cycle if the same compression ratio is used. This is fairly obvious when comparing P-V diagrams with the same V_1 and V_2 used for both cycles (Fig. 1.17, *left*), where the work produced (represented by the area within the cycle of the P-V diagram) during the Otto cycle is clearly greater. However, in practice Diesel cycles can operate at much higher compression ratios (20 vs. 8-9 for gasoline engines), which actually leads to a higher amount of work produced and a higher efficiency (Fig. 1.17, *right*). This difference is because a fuel air mixture is compressed in the gasoline engine and this mixture would self-ignite (before the spark) if compressed too hard. This is not an issue for the diesel cycle. This leads an ideal Diesel cycle to efficiencies approaching 60% and in real engines can be a little above 40% (in trucks), which makes diesel engines the most efficient combustion engines available. However, the injection process of the fuel leads to local concentration gradients in the cylinder that can lead to inefficient combustion and the formation of particulates. Gradients are much less of a problem in the gasoline engine where the fuel is homogenized during expansion.

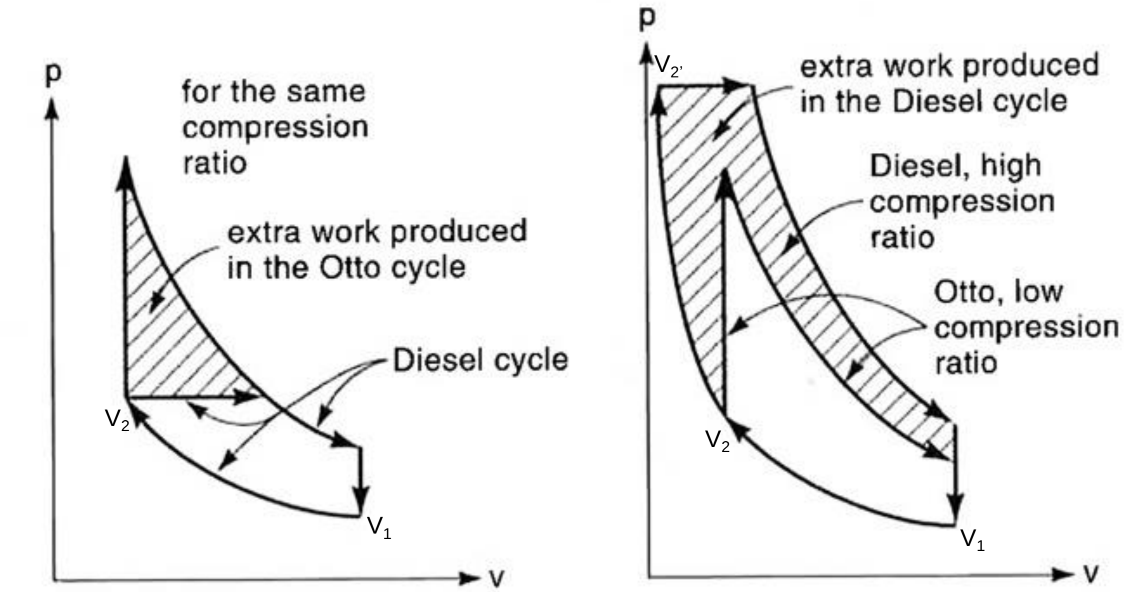

Fig. 1.17 Comparison of the Diesel and Otto cycles using P-V diagrams for cycles with the same (*left*) and different (*right*) compression ratios.

The Brayton or Joule cycle: gas turbines and jet engines

Though a Rankine cycle will have the highest efficiency, especially due to the possibilities of using reheat cycles, its use of an external heat source makes it more complicated than a cycle that integrates the combustion (internal combustion). Internal combustion systems notably avoid the use of a heat exchanger network. For this reason, combustion gas turbines are still frequently built to generate power and can be modeled using the Brayton (also called the Joule) cycle. The functioning of a gas turbine is almost identical to that of an airplane's jet engine and so they can be understood using the same cycle. The only difference is the way the efficiency is calculated because the output of a gas turbine will be mechanical work, whereas the output of a jet engine will be the thrust generated by the additional kinetic energy imparted to the exiting gases. Let's start by discussing the gas turbine.

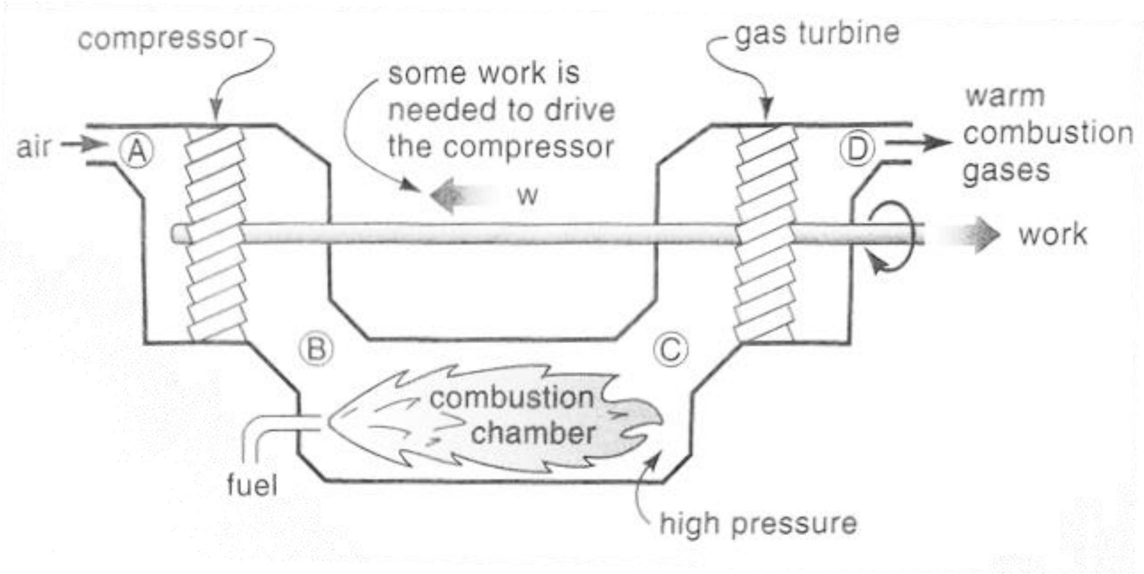

Fig. 1.18 Diagram of a gas turbine.

The Brayton cycle and by extension the gas turbine are arguably much simpler than a piston engine. Here the cycle goes through 4 states (Fig. 1.18):

- State A-B: air enters the turbine and is compressed by a compressor to a higher pressure. This can be idealized as an adiabatic compression (Fig. 1.19) where both P and T rise but there is no increase in entropy because no heat is exchanged.
- State B-C: the compressed air is mixed with fuel and burned. The idealized version of this step assumes that it is a constant pressure heating step, which expands the volume (Fig 1.19). As a result, P stays constant but V, T and S increase. The additional volume of the fuel is ignored because it is much smaller than the air going through the turbine (this is also assumed—and even closer to reality—in a jet engine that uses kerosene as fuel).
- State C-D: The high temperature gas is then expanded back to atmospheric pressure to produce work. As a mirror of step A-B this is considered to be an adiabatic (no change in S) expansion (Fig. 1.19).
- Step A-D: Since the exhaust gas will be hotter than air, its release into the atmosphere is considered as a release of heat to the surroundings at constant pressure, which brings the gas back to the same conditions as the entering gas (state A).

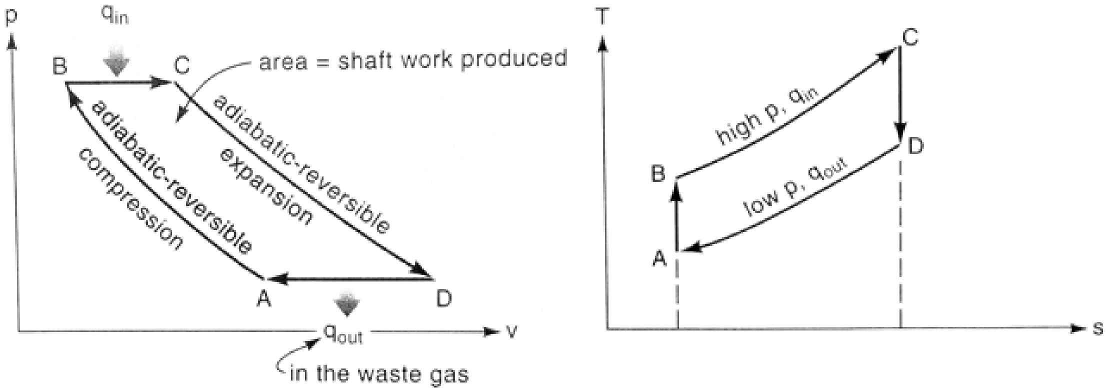

Fig. 1.19 The ideal Brayton cycle's PV (*left*) and TS diagrams (*right*) that can be used to represent a gas turbine or a turbojet engine.

The efficiency of this cycle will be the excess work generated during expansion compared to compression over the heat released by the fuel:

$$\eta = \frac{|W_{CD}|-|W_{AB}|}{|Q_{BC}|} \tag{1.59}$$

A simple energy balance shows us that this excess work has to be equal to the difference between the heat given to (Q_{in}) and the heat released by (Q_{out}) the system:

$$\eta = \frac{|Q_{BC}|-|Q_{AD}|}{|Q_{BC}|} \tag{1.60}$$

For both BC and AD steps, we have a system at constant pressure doing only PV work. Therefore:

$$Q = \Delta U + P\Delta V = \Delta H = C_P(T_F - T_I) \tag{1.61}$$

$$\eta = \frac{C_p(T_C-T_B)-C_p(T_D-T_A)}{C_p(T_C-T_B)} \tag{1.62}$$

Recall that for adiabatic steps (like A-B and C-D) we can use relations like Eq. 1.28. We can also use the fact that $P_B = P_C$ and $P_A = P_D$ (Fig. 1.19, *left*):

$$\left(\frac{T_B}{T_A}\right) = \left(\frac{P_B}{P_A}\right)^{\frac{k-1}{k}} = \left(\frac{P_C}{P_D}\right)^{\frac{k-1}{k}} = \left(\frac{T_C}{T_D}\right) \quad (1.63)$$

The efficiency becomes:

$$\eta = 1 - \frac{(T_D - T_A)}{(T_C - T_B)} = 1 - \frac{T_A}{T_B}\frac{\left(\frac{T_D}{T_A} - 1\right)}{\left(\frac{T_C}{T_B} - 1\right)} = 1 - \frac{T_A}{T_B}\frac{\left(\frac{T_C}{T_B} - 1\right)}{\left(\frac{T_C}{T_B} - 1\right)} = 1 - \frac{T_A}{T_B} = 1 - \left(\frac{P_A}{P_B}\right)^{\frac{k-1}{k}} \quad (1.64)$$

This equation tells us that the more you compress the fluid at the first stage, the higher the efficiency. The limitation is that this also increases the pre-combustion and thus post-combustion temperature. In practice, material resistance to high temperatures limits the efficiency to pressure ratios of about 20 (and a theoretical heat to work efficiency of 55-60%). Furthermore, the initial compression step is done by a compressor which requires much more energy than a liquid pump and so the compressor efficiency really matters. As shown on the diagram (Fig. 1.18), this compressor directly employs a large fraction (about 60%) of the output work produced to compress the incoming gas. Compressor efficiencies can reach about 80%, which leads to real gas turbine heat to work efficiencies of around 40-45%.

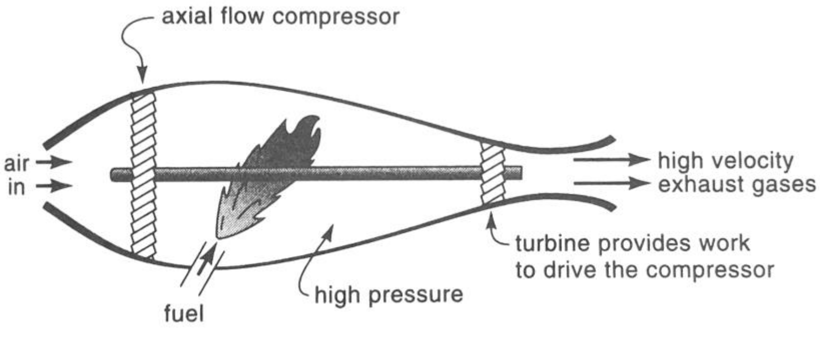

Fig 1.20 Diagram of a jet (or turbojet) engine.

The jet (or turbojet) engine works in exactly the same way. The only thing that changes is the shape of the turbine, which becomes narrower as the gases pass through it to maximize the velocity of the exiting gases to maximize propulsion. The concept of efficiency is also

also slightly different because in a jet engine, we care about how much propulsive power we generate not just work. To get to the overall efficiency of a jet engine, it is useful to break it down into the thermal efficiency, which this time describes the kinetic energy received by the fluid as opposed to the work (Eq. 1.65) and the propulsion efficiency, which is the ratio of propulsive power produced divided by the rate of production of this kinetic energy (Eq. 1.67)[3]:

$$\eta_{thermal} = \frac{(m_{air,out}v_{out}^2 - m_{air,in}v_{in}^2)/2}{Q_{in}} \tag{1.65}$$

Since all of the net work being produced is just used to accelerate the gas, this is equivalent to the Brayton cycle efficiency for the gas turbine:

$$\eta_{thermal} = 1 - \frac{T_A}{T_B} \tag{1.66}$$

$$\eta_{propulsive} = \frac{propulsive\ power}{rate\ of\ production\ of\ propulsive\ kinetic\ energy} \tag{1.67}$$

Where the rate of production of propulsive kinetic energy is simply the net kinetic energy received by a given mass of air per time ($\dot{m}_{air}$): If we neglect the amount of fuel added to the incoming air ($\dot{m}_{air,in} = \dot{m}_{air,out} = \dot{m}_{air}$), we have:

$$\eta_{propulsive} = \frac{propulsive\ power}{\dot{m}_{air}(v_{out}^2 - v_{in}^2)/2} \tag{1.68}$$

The overall efficiency is:

$$\eta_{overall} = \eta_{thermal}\eta_{propulsive} \tag{1.69}$$

Propulsive power is defined as the product of thrust and flight speed (v_{flight}), which if equivalent to the incoming airspeed is:

$$propulsive\ power = v_{flight}Thrust = v_{in}(\dot{m}_{air}(v_{out} - v_{in})) \tag{1.70}$$

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[3] This short discussion on aircraft efficiency was adapted from the notes of "Thermodynamics and Propulsion" an MIT Aerospace class by Prof. Z. S. Spakovszky

$$\eta_{propulsive} = \frac{v_{in}\left(\dot{m}_{air}(v_{out}-v_{in})\right)}{\dot{m}_{air}(v_{out}^2-v_{in}^2)/2} = \frac{2\,v_{in}}{v_{out}+v_{in}} = \frac{2}{1+\frac{v_{out}}{v_{in}}} \tag{1.71}$$

This means that the propulsive efficiency of an airplane is the highest when $v_{in} \approx v_{out}$, which is approached when the speed of the airplane is high. However, this is the point at which thrust is low (Eq. 1.70). This leads airplanes to be much more efficient at cruising altitudes rather than take-off.

Overall efficiencies of jet engines therefore combine both numbers discussed above. None of this discussion includes effects like air resistance which requires engines to maintain fairly high thrust even at high speeds. For this reasons, pure turbojet engines have efficiencies slightly above 20%. More modern engines use a so-called air bypass system, where a good deal of air that is compressed does not go through the combustion zone. This reduces $v_{out} - v_{in}$, which increases the propulsive efficiency but also increases $\dot{m}_{air}$ significantly, which increases thrust. These design improvements along with improvements in materials in engines that allow post combustion temperatures to reach 1550°C[4] has allowed modern jet engines to reach efficiencies close to 40%[5].

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[4] Peter Spittle 2003 «Gas Turbine Technology» *Phys. Educ.* **38** 504

[5] *Commercial Aircraft Propulsion and Energy Systems Research*
Reducing Global Carbon Emissions, National Academies Press (2016).

1.7 Exergy

At this point, we have been talking a lot about how to generate work. One useful concept is to know what is the maximum amount of work that can be obtained for a given process (e.g. a system going from state 1 to state 2). This is important because it will allow us to calculate a true efficiency for our work producing process. The maximum obtainable work is often referred to as "availability" in the US with a symbol of *b* or *B,* and as "exergy" in Europe. We will refer to Exergy and use the symbol W_{Ex}.

Change of exergy between two states

To calculate W_{Ex} let's take a system going from state 1 to state 2:

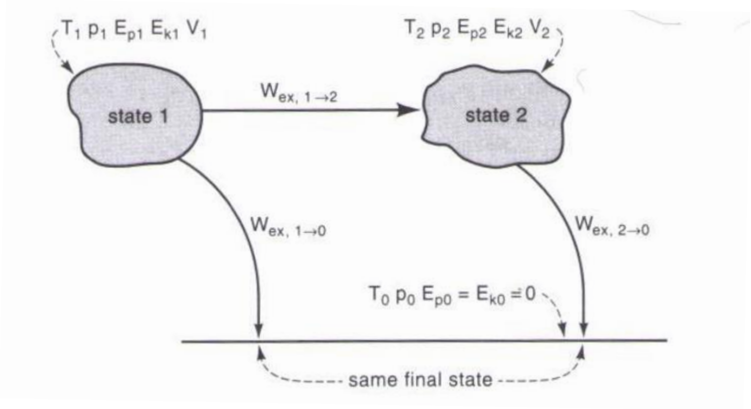

Fig. 1.21 Exergy produced from a system going from State 1 to State 2 within an environment at state 0.

The system at both State 1 and 2 can exchange with the environment, which is at the ground state (state 0). The maximum amount of work obtainable from either state 1 or 2 is obtained when they are brought down to complete equilibrium with the environment while undergoing whatever change in internal energy (U). Along the way, to obtain the maximum amount of work, you never reject any heat to the environment at a $T>T_0$. In fact, you always use a Carnot engine to bring heat to the environment at T_0. For system 1:

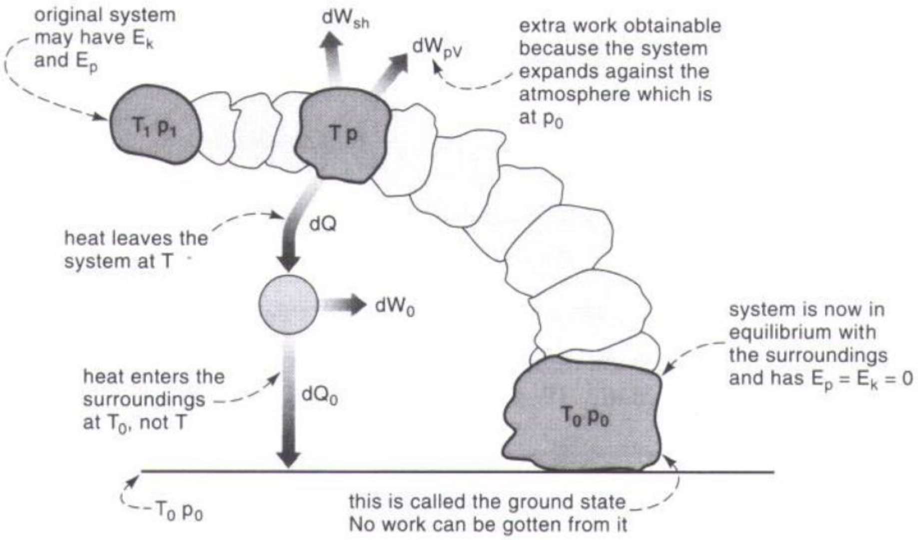

Fig. 1.22 Exergy production for system 1 brought to the ground state.

Since a Carnot engine is reversible, we know how much heat is released to the environment (eq. 1.13):

$$d|Q_0| = T_0 dS \tag{1.72}$$

From the first law, we know that (eq. 1.1):

$$dE = dQ_0 - dW = T_0 dS - dW = T_0 dS - dW_{Sh} - p_0 dV - dW_0 \tag{1.73}$$

Some of the work that is produced is needed to push back the atmosphere ($p_0 dV$) and therefore the only useful work (or exergy dW_{Ex}) is (using the previous equation):

$$dW_{Ex} = dW_{Sh} + dW_0 = -dE + T_0 dS - p_0 dV \tag{1.74}$$

Remember that $E= U+E_p+E_{ki}$. By definition, we consider the ground state has no potential or kinetic energy. Therefore:

$$W_{Ex,1\rightarrow 0} = -(U_0 - E_1) + T_0(S_0 - S_1) - p_0(V_0 - V_1) \tag{1.75}$$

For a system with no changes in kinetic or potential energy:

$$W_{Ex,1\to 0} = -(U_0 - U_1) + T_0(S_0 - S_1) - p_0(V_0 - V_1) \qquad (1.76)$$

Notice that for a system where a state change is brought back down to the same state (this is the case for most fuel conversion processes, where the fuel enters and exits more or less at T_0 and P_0, which are T_{surr} and P_{atm}), we have (remember $G=U-TS+PV$):

$$W_{Ex,1\to 0} = -\Delta G_0 \qquad (1.77)$$

Coming back to our change from State 1 to State 2, we have (using eq. 1.75):

$$W_{Ex,1\to 2} = W_{Ex,1\to 0} - W_{Ex,2\to 0} = -(E_2 - E_1) + T_0(S_2 - S_1) - p_0(V_2 - V_1) \qquad (1.78)$$

Work in a flow system

In a flow system, the principles are largely the same as in a batch (system described above). At each step, any heat released at temperature T can be extracted by use of a Carnot Engine to bring it down to T_0 (Fig. 1.23).

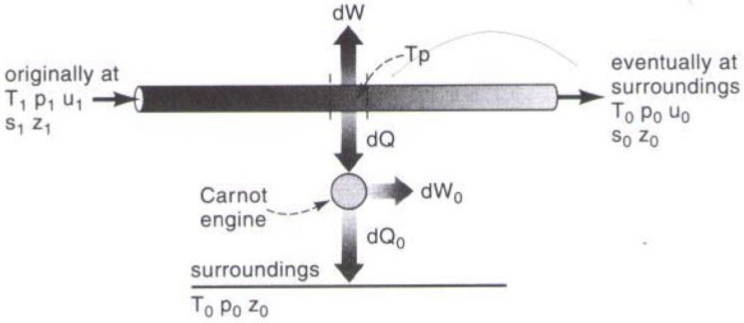

Fig. 1.23 Exergy calculation in a flow system.

The only difference is that we can use enthalpy (instead of internal energy), which, at constant pressure, already accounts for the "pushing back of the atmosphere" (see equation 1.8). By analogy with equation 1.75, we have:

$$W_{Ex,1\to 0} = -(H_0 - (H + E_p + E_k)_1) + T_0(S_0 - S_1) \qquad (1.79)$$

For a change from state 1 to 2 (and assuming the absence of kinetic and potential energy changes), we have:

$$W_{Ex,1\rightarrow2} = -(H_2 - H_1) + T_0(S_2 - S_1) \tag{1.80}$$

Given how free energy is related to enthalpy (*G*=*H*-*TS*), it is easy to see how Equation 1.78 can be found for a flow system as well.

Work lost in a real process

Exergy measures the maximum amount of work that can be produced in an ideal system, but can we measure the actual amount of lost compared to the exergy? Let's see. A change in energy from State 1 to 2 ($\Delta E_{1\rightarrow2}$, this is the same as in the ideal function because E is a state function!) will release actual work and heat:

$$\Delta E_{1\rightarrow2} = Q_{\substack{actual\ to \\ surr.}} - W_{\substack{actual\ to \\ surr.}} = T_0\Delta S_{surr.} - W_{shaft,actual} - p_0(V_2 - V_1) \tag{1.81}$$

We can then use this equation and equation 1.78 to calculate the work lost in an actual process:

$$W_{sh,lost} = W_{Ex,1\rightarrow2} - W_{shaft,actual} = T_0(S_2 - S_1) + T_0\Delta S_{surr.} = T_0\left(\Delta S_{sys.} + \Delta S_{surr.}\right) = T_0\Delta S_{tot.} \tag{1.82}$$

What does this mean? Well, in an ideal system the total entropy production is zero. We knew that already! The important point is that the $\Delta S_{sys.}$ will be the same for an ideal and real system (S is a state function!). All the work lost has to do with the surroundings! In an ideal system, the surrounding's entropy change is equal to that of the system, and the total entropy change is zero. In a non-ideal system, non-ideal events (heat transfer, friction, etc.) increase the entropy change of the surroundings, leading to an overall gain of entropy.

1.8 Electrical machines

In practice, heat to work is not the only way to generate mechanical work. In fact, in day-to-day life, you are probably more familiar with seeing mechanical work being created from electricity. For a variety of reasons—notably their efficiency, convenience and their compatibility with electricity that is produced renewably—already omnipresent electrical motors are likely to become even more frequent. Since you are chemists/chemical engineers and not electrical engineers, I will not (nor am I qualified to) give you an in-depth overview of electrical motors but will just review their basic qualitative principle.

In electric motors, electric currents are used to create a first electromagnet. This first electromagnet is combined with a second magnet that is either a permanent magnet, another electromagnet or a magnet that is created by induced current (permanent magnets or induced current magnet are both found in electric cars for example). The electromagnetic force (Lorentz force) exerted by the magnetic fields is used to create mechanical work (e.g. by turning a rotor). If you have ever used a magnet to push or rotate another magnet, you can easily visualize how magnetic fields can be used to create work. Just to give you an idea of how they work, I will describe two common types of motors, a direct current (DC) brushed motor and an alternating current (AC) induction motor.

In a brushed DC motor (Fig. 1.18), the stator is either a permanent magnet or an electromagnet. The brushes allow the current (I) to flow through a coil (or coils) in the rotor to create a magnetic field that interacts with the stator. These two magnetic fields field will create a force that pushes the rotor (Fig 1.18, A-B). If this field on the rotor was static, it's easy to see how the rotor would get stuck as it would rotate to align its south pole with the stator's north pole (Fig. 1.18, A-B). However, the break in the commutator allows the current to reverse the field on the rotor and keep the rotation going (Fig. 1.18 C).

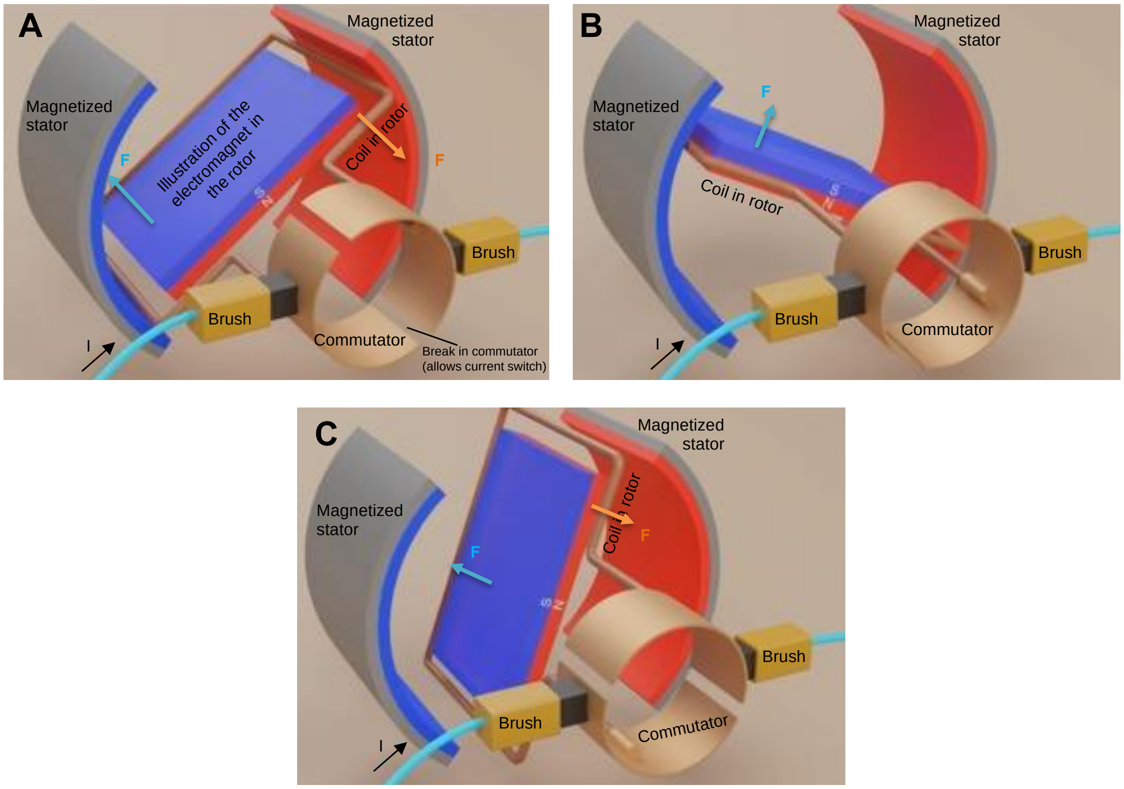

Fig. 1.18 Functioning of a brushed DC motor (modified from Jared Owen's video on youtube[6], I encourage you to watch it). Panels A-C represent different stages of the rotation. Panel C represents the state of the rotor right after passing the break in the commutator, which switches the direction of the current and reverses the magnetic field of the rotor.

In an AC induction motor, AC current (typically 3-phase) is run through the stator using a particular winding pattern that induces a rotating magnetic field (Fig. 1.19A). Any changing magnetic field, will induce a current in a conducting material within that field.

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[6] https://www.youtube.com/watch?v=CWulQ1ZSE3c

As a result, the rotor will see an induced current flowing through it (Fig. 1.19B). Since any current (induced or not), will create its own magnetic field, this will result in two magnetic fields with a force exerted between them. As a result of this force, the rotor will turn (Fig. 1.19C). However, the rotor rotation speed (N_{Rotor}) will always be slower than the stator speed (N_S). This difference in speed, known as slip, is what controls the torque of the motor because the difference drives the force between the magnetic fields.

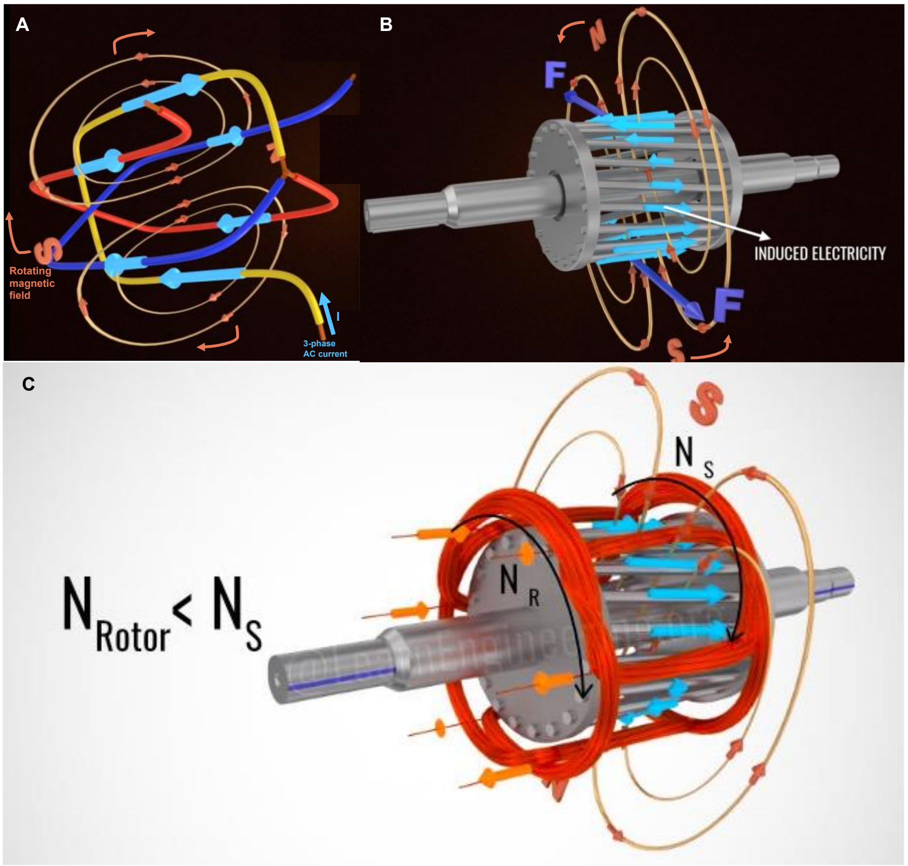

Fig. 1.19 The general concept of an AC induction motor (this figure is again adapted from a very nicely done youtube video by LearnEngineering[7], which I encourage you to watch). **A.** A particular winding pattern in the stator combined with an alternating 3 phase current (i.e. the current direction, shown by the blue arrows periodically reverses) induces a rotating magnetic field. **B.** The changing magnetic field induces a current through the rotor, which creates its own magnetic field. **C.** The force created by these two magnetic fields induces a rotation in the rotor.

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[7] https://www.youtube.com/watch?v=AQqyGNOP_3o

Beyond these exact principles, the important point is that electrical motors/generators are largely devoid of complex moving parts and suffer from minimum losses through friction or heating. **The efficiency of electrical motors is typically very high**. In ideal conditions, this efficiency is well above 90% even in practical settings. In fact, the United States Code of Regulations has even regulated minimum efficiencies for electrical motors at above around 80% for small motors (power $\leq$ 1HP, i.e. typical motors in a house such as a mixer or a fan) to around 95% for large motors (several hundred HP, typical of an electric car, at peak efficiency)[8].

These values are well above what is seen for any practical heat to power systems, especially those seen in individual or even large-scale transportation. If this is the case, why are we still using fossil fuels? The answer has to do with energy density. Electrical energy carriers (i.e. batteries) have a far, far lower energy densities than hydrocarbons and other fossil fuels (Fig. 1.20). Plainly, this means it takes far more weight and volume to carry energy stored in batteries compared to the energy stored in the chemical bonds of hydrocarbons (or renewable fuels for that matter). This has been the main challenge in the development of electric cars, which still struggle with range, and has made the development of electric planes practically impossible at this stage. The efficiency of batteries is not the problem as their charge/discharge can reach 90% or more. Their longevity and cost have been a challenge but has rapidly improved. Instead, the greatest challenge, remains to have an electric energy carrier that has a sufficient energy density and still provide electrical work efficiency.

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[8] https://www.ecfr.gov/current/title-10/chapter-II/subchapter-D/part-431

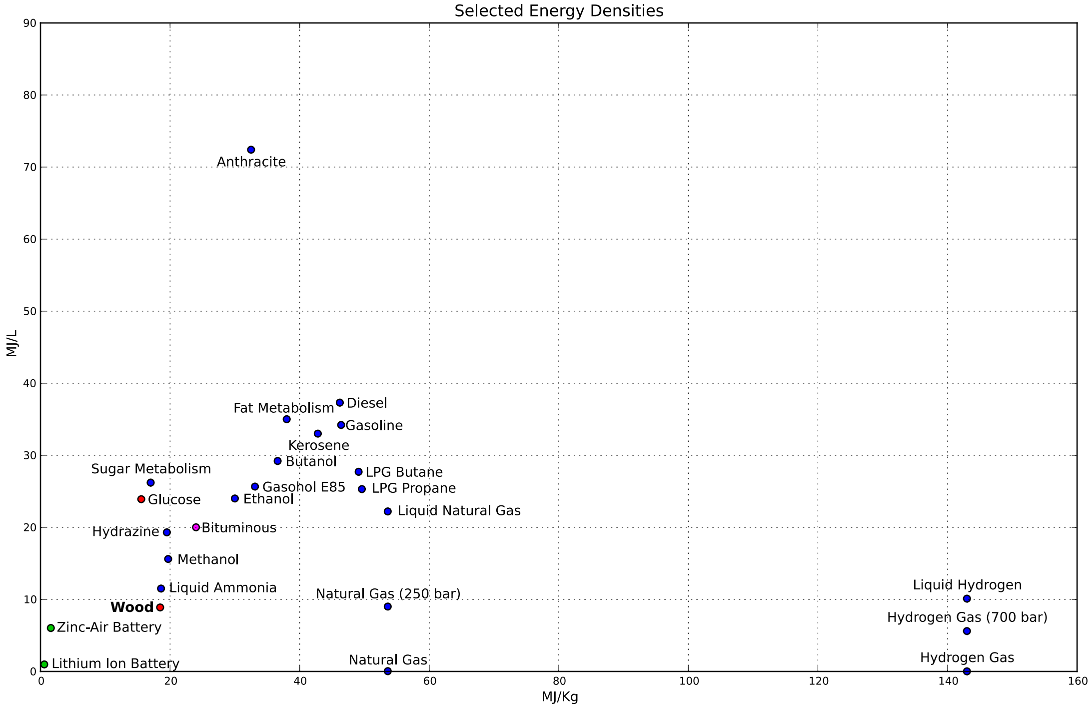

Fig. 1.20 Mass and volumetric energy densities of various energy carriers including hydrocarbons (blue), biobased (red) and batteries (green).

Given that electrical motors are so efficient and chemical fuels are so energy dense, a potential solution has been to combine the advantage as both by using these fuels to create electrical work. This idea is the working principle of a fuel cell. We will discuss their operation and especially their limits below.

1.9 Fuel cells

The goal of fuel cells is to huge high energy carriers like fuels to generate electrical power directly (i.e. without going through heat). The basic principle is that fuel combustion reactions are redox reactions and thus exchange electrons. If this exchange of electrons can be channeled instead of occurring directly between the molecules, it can be used to generate an electrical current. Let's take hydrogen combustion as an example:

$$H_2 + \frac{1}{2}O_2 \rightleftharpoons H_2O \tag{1.83}$$

In a combustion, electrons are exchanged through a series of collisions involving many elementary reactions to make this overall reaction. But in all of these elementary reactions, electrons are exchanged directly. To make the electron exchange explicit, we can split this overall reaction into two half reactions (Eq. 1.84 and 1.85). This is exactly what occurs in a hydrogen fuel cell.

$$H_2 \rightleftharpoons 2H^+ + 2e^- \tag{1.84}$$

$$\frac{1}{2}O_2 + 2H^+ + 2e^- \rightleftharpoons H_2O \tag{1.85}$$

Spatially segregating these two reactions in the right system can force the electrons to flow through an external circuit thus generating a current. This separation is done by connecting the location of these two half reactions through one medium that only allows the flow of electrons (an electrical conductor) and one that only allows the flow of ions but not electrons (an electrolyte). A simple example of this would be plunging two platinum electrodes connected by a wire into an aqueous sulfuric acid solution and bubbling hydrogen and oxygen close to each one of the electrodes (Fig. 1.21 A). The protons can flow through the sulfuric acid (as an H_2SO_4 solution is already filled with H^+) and the electrons can flow through the wire, but not vice-versa. If a load is introduced along the path of the flowing electrons (e.g. the lightbulb in Fig. 1.21 A), these electrons will power the load (making the light bulb glow).

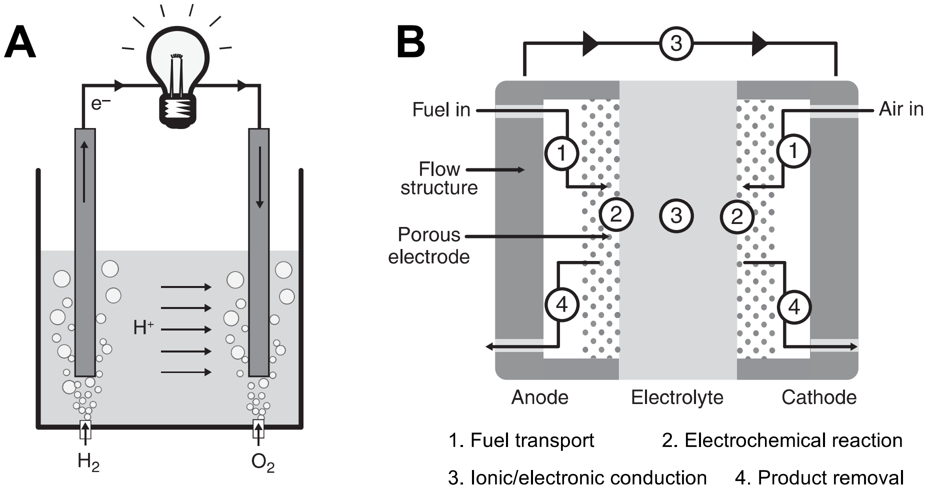

Fig. 1.21 Fuel cell representation. **A.** A basic fuel cell and **B.** A more realistic fuel cell schematic.

A more realistic cell configuration (Fig. 1.21 B) will feature porous electrodes and a controlled flow of reactants over this porous structure. The electrolyte must be designed to minimize resistance (which is much more significant than electron conduction through a metal) and maximize durability. Resistance is typically minimized by making the membrane very thin. A big challenge to durability is leakage and/or evaporation of the electrolyte. For this reason, polymer electrolytes, solid acids, solid oxides, and even molten salts have been used (the last two examples being high temperature fuel cells). However, even with all of these features, the fundamental principles remain the same as the simple fuel cells depicted in Fig. 1.21 A. Below, we will review the fundamental thermodynamic principles that control the maximum performance of fuel cells.

Thermodynamic potentials

Beyond the physical interpretation of the first law as heat and work, another (more mathematical) interpretation of the first law is that it describes the internal energy function (U) as a function of independent variables *S* and *V*. For completeness, we can also consider the case where there is a change in number of moles (*N*), which goes beyond the case of an "isolated system" that we used before.

$$dU(S,V,N) = \left(\frac{\partial U}{\partial S}\right)_{V,N} dS + \left(\frac{\partial U}{\partial V}\right)_{S,N} dV + \left(\frac{\partial U}{\partial N}\right)_{S,V} dN = TdS - PdV + \mu dN \qquad (1.86)$$

The left-hand side of the equation (with partial derivatives) arises purely from mathematics and would be true for any equation. The right-hand side is based on the definition of the first law and the thermodynamic definitions of temperature, pressure and chemical potential (μ):

$$\left(\frac{\partial U}{\partial S}\right)_{V,N} = T \qquad (1.87)$$

$$\left(\frac{\partial U}{\partial S}\right)_{S,N} = -P \qquad (1.88)$$

$$\left(\frac{\partial U}{\partial N}\right)_{S,V} = \mu \qquad (1.89)$$

The independent variables used to describe U are not very practical for two reasons. First they are extensive variables and second, concepts like entropy are fairly abstract and difficult to measure (unlike for volume, pressure or temperature, there are no entropy meters). Extensive variables are variables that depend on the size of the system and cannot be changed without modifying the system, whereas intensive variables (i.e. that don't change with the size of the system) like T and P are fairly easy to modify during an experiment.

Fortunately, there is a mathematical way of defining functions that retain all of the mathematical information of the original function but depend on alternate independent variables: Legendre Transformations. I won't go into the demonstration of why the original information is retained, but the actual transformation is fairly straightforward. If we take the basic differential of PV and apply the chain rule:

$$d(PV) = PdV + VdP \tag{1.90}$$

Rearranging and switching signs:

$$-PdV = -d(PV) + VdP \tag{1.91}$$

which if we insert into equation 1.83:

$$dU = TdS - d(PV) + VdP + \mu dN \tag{1.92}$$

Rearranging, we obtain the definition of enthalpy:

$$d(U + PV) = dH = TdS + VdP + \mu dN \tag{1.93}$$

Here, we how enthalpy emerges naturally from a mathematical transformation, which complements the physical explanation we introduced earlier.

We can do the same transformation again by taking the differential of TS:

$$d(TS) = TdS + SdT \text{ or } TdS = d(TS) - SdT \tag{1.94}$$

Doing the same transformation on equation 1.90, we get the definition of free energy (G):

$$d(U + PV - TS) = dG = -SdT + VdP + \mu dN \tag{1.95}$$

where we now have a thermodynamic potential (the name given to the properties U, H, and G), that is dependent on independent variables P and T, which are far more practical to use. As we will see, free energy is particularly important when trying to understand fuel cells.

There is fourth potential, which comes from applying Eq. 1.94 on the first law directly (Eq. 1.86), which leads to the so-called Helmholtz potential (F):

$$d(U - TS) = dF = -SdT - PdV + \mu dN \tag{1.96}$$

Physically, enthalpy could be understood as internal energy (i.e. the energy needed to create the system) plus the work (PV) needed to make room for it. Similarly, $-TS$ can be understood as also subtracting any energy provided to the system by the environment. These four potentials and their associated physical interpretations are summarized in Fig. 1.22.

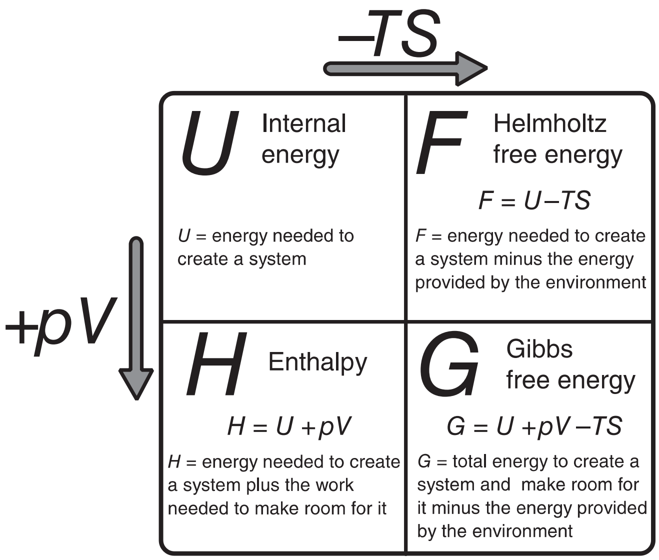

Fig. 1.22 The four thermodynamic potentials obtainable through Legendre transformation of the first law.

<u>Maximum fuel cell efficiency and voltage</u>

As we will see, Gibbs free energy will allow us to calculate the electric work potential of a fuel in a fuel cell system. Let's use the first law on a fuel cell system, where we imagine a fuel undergoing a change in internal energy, which releases heat and work (both PV and electrical). We can adapt our formulation of the first law from Eq. 1.3 for this purpose (replacing W_{shaft} with $W_{electric}$ as there are no moving parts in a fuel cell). We also use the differential form:

$$dU = dQ + dW_{electric} - dW_{PV} \tag{1.97}$$

If we imagine a reversible transformation (best case scenario). We can replace dQ with $dQ_{rev} = TdS$. We can also use PdV for volume work. Finally, we can add a negative sign in front of electric work as the fuel cell will (presumably) always be producing work, not receiving it.

$$dU = TdS - dW_{electric} - PdV \tag{1.98}$$

With the definition of free energy ($G = U + PV - TS$; Eq. 1.92):

$$dG = dU - SdT - TdS + PdV + VdP = -SdT + VdP - dW_{electric} \tag{1.99}$$

For a system at atmospheric conditions (constant T and P), we get:

$$dG = -dW_{electric} \tag{1.100}$$

In other words, for one mole of fuel operating at constant temperature and pressure (which fuel cells, typically do), the reversible work that could be obtained from a fuel cell can be calculated as:

$$W_{electric} = -\Delta G_{RXN} \tag{1.101}$$

This definition, can now allow us to calculate the efficiency of a fuel cell, which would be:

$$\eta = \frac{W_{electric}}{Total\ energy} \tag{1.102}$$

What is the total energy available in a fuel? It corresponds to the change in internal energy when you burn the fuel (which will be negative) added to the energy required to make room for the resulting products in the surroundings (which will be positive), which, if at constant pressure is equal to the enthalpy ($\Delta U + P\Delta V = \Delta H$):

$$\eta = \frac{-\Delta G_{RXN}}{-\Delta H_{RXN}} \tag{1.103}$$

At 25°C and 1 atm, hydrogen oxidation ($H_2 + 1/2O_2 \rightarrow H_2O$) has a $\Delta G_{RXN} = -237 \text{ kJ/mol}$ and $\Delta H_{RXN} = -286 \text{ kJ/mol}$, leading to a reversible efficiency of 83%.

One caveat[9] to this efficiency expression is that in certain special cases, it may not be appropriate to use. Indeed, in certain special cases, it can lead to efficiencies over 100%. Let's understand how. The definition of free energy can be rewritten as a function of enthalpy:

$$G = U + PV - TS = H - TS \tag{1.104}$$

which, at constant temperature becomes:

$$\Delta G = \Delta H - T\Delta S \tag{1.105}$$

We can use this result to rewrite the efficiency equation found in Eq. 1.103:

$$\eta = \frac{-\Delta G_{RXN}}{-\Delta H_{RXN}} = \frac{\Delta H_{RXN} - T\Delta S_{RXN}}{\Delta H_{RXN}} = 1 - \frac{T\Delta S_{RXN}}{\Delta H_{RXN}} \tag{1.106}$$

The enthalpy of any reaction that releases energy will be negative. The change in entropy, though usually negative, can be positive for some reaction. This would lead to efficiencies over 100%! Are we creating energy in such cases? Of course not, this would violate the first law. Instead, what this means is that in cases where entropy is positive, the system would be receiving heat from the surroundings to remain at constant temperature. This heat could, under these conditions, be turned into electrical work. For these special cases, this additional heat should be included in an efficiency calculation, which leads to the trivial case where the efficiency is equal to unity.

$$\eta = \frac{W_{electric}}{Total\ energy} = \frac{W_{electric}}{Energy\ from\ RX + heat\ received} = \frac{-\Delta G_{RXN}}{-\Delta H_{RXN} + T\Delta S_{RXN}} = \frac{\Delta H_{RXN} - T\Delta S_{RXN}}{\Delta H_{RXN} - T\Delta S_{RXN}} = 1 \tag{1.104}$$

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[9] This discussion is based on the article: A. E. Lutz et al. *International Journal of Hydrogen Energy* 27 (2002) 1103–1111.

In practice, these reversible efficiencies are further limited by two further effects. The first is the voltage efficiency, which captures the fact that the true voltage of a fuel cell is lower than reversible thermodynamic voltage (see below). The true voltage depends on the current drawn from the fuel cell, and the two are inversely proportional, meaning that fuel cells are <u>most efficient at low load</u>. The second is the fuel utilization efficiency. Due to kinetics not all the fuel entering the cell will be used. Some fuel might remain unconverted and exit the cell while other fuel might undergo side reactions that do not contribute to producing electricity. This is a challenge in cases when the load is not constant. For example, maximum load requires excess fuel, that might be wasted at lower load… This requires a careful control system to apply at so-called constant stoichiometry conditions. In practice this leads to efficiencies that can approach 80% at low current densities but can drop to 50-20% at higher current densities.

<u>Reversible voltage</u>

Similarly, we can use the free energy to calculate the reversible voltage that can be produced by a given reaction in a fuel cell. The electrical work done by moving a charge (q) is proportional to this voltage or electrical potential (E):

$$W_{electric} = qE \tag{1.104}$$

If this charge is carried by electrons, we have:

$$q = nF \tag{1.105}$$

where n is the number of moles of electrons transferred and $F$is Faraday's constant. With Equations, 1.104, 1.105 and 1.101, we get:

$$\Delta G_{RXN} = -nFE \quad (1.105)$$

which rearranges to (for standard temperatures and pressures):

$$E^0 = -\frac{\Delta G^0_{RXN}}{nF} \quad (1.105)$$

If we again take the standard Gibbs free energy of hydrogen oxidation (-237 kJ/mol), we get 1.23 V. In practice, the voltage will be even lower, meaning to get any kind of reasonable voltage (starting a car—much less load than powering a car!—takes 10 volts), you need to stack tens sometimes hundreds of fuel cells. For example, Toyota's Mirai car which is based on hydrogen fuel cells has 370 stacked fuel cells and an expected range of 700 km. Tesla cars typically have a range of 500-550 km with significant more battery weight. Of course, we do not yet have a hydrogen distribution network…

Literature

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