Intermediate Thermodynamics

The Second Law

Clausius postulate

"Heat cannot pass spontaneously (unaided) from a region of lower temperature to a region of higher temperature"

Kelvin-Plank postulate

"It is impossible to construct a heat engine which produces no other effect than the extraction of heat from a single source and the production of an equivalent amount of work"

Reversibility

A process is said to be ***reversible*** if at any time during the process both the system and the environment can be returned to their initial states.

Reversibility is an ideal situation. Dissipative and finite temperature difference (non-cuasistatic) effects are unavoidable. However, many processes are close to reversible and the reversible efficiency of the process is of interest because it establishes an upper limit in performance.

Cycles with Two Heat Reservoirs

The Kelvin-Plank statement implies that for a single reservoir:

$$\oint \delta W_{closed} \geq 0 \qquad (1)$$

because the system cannot develop work from a single reservoir. From conservation of energy, Eq. (1) is equivalent to:

$$\oint \delta Q_{closed} \leq 0 \qquad (2)$$

In Eqs. (1) and (2) the equality applies for the case of reversible processes.

When applying the Kelvin-Plank statement to a system in contact with two thermal reservoirs, it can be easily proved the following:

1. If the work is negative (i.e., power cycles, the system produces useful work), the heat will flow from the higher temperature to the system and from the system to the lower temperature reservoir.

2. The opposite occurs when the work is positive (refrigeration and heat pump cycles).

3. The thermal efficiency if any heat engine is defined as:

$$\eta_{th} = \frac{|W_{net}|}{Q_{in}} = 1 - \left|\frac{Q_2}{Q_1}\right| \tag{3}$$

4. In addition, the maximum attainable efficiency is the efficiency of a reversible cycle:

$$\eta_{th} \leq \eta_{th,rev} \tag{4}$$

Carnot's Principle and the Thermodynamic Temperature Scale

Three important corollaries to the Second Law statements, known as Carnot's principle, are summarized:

1. Eq. (4), which states that the thermal efficiency of any heat engine is always less than that of a reversible engine operating between the same two heat reservoirs.

2. Any two reversible engines operating between the same thermal reservoirs have the same efficiency.

3. An absolute temperature can be defined which is independent of the nature of the measuring substance.

The third corollary follows from the second. If the thermal efficiencies are the same regardless of the design of the heat engine, then the only variable is the type of heat reservoir, which is characterized only by its temperature. Accordingly, using three independent heat engines operating between the same two heat reservoirs it can be proved that:

$$\frac{Q_2}{Q_1} = \frac{f(T_2)}{f(T_1)} \tag{5}$$

where any monotonic function can be used to define the thermodynamic temperature. The **Kelvin scale** is defined using $f(T) = T$, and was adopted by the International General

Conference on Weights and Measures as the standard scale. The absolute zero then corresponds to the case in which unit efficiency can be achieved:

$$\eta_{th,rev} = \eta_{th,carnot} = 1 - \frac{T_2}{T_1} \qquad (6)$$

A reference point is necessary and was set as 273.16 K at the triple point of water, thus:

$$T = 273.16 \left| \frac{Q}{Q_{tp}} \right| \qquad (7)$$

Different fixed points have been selected to calibrate instruments along the temperature scale.

Finally, a Carnot engine can be used to transfer energy across finite temperature differences in a reversible form.

Entropy Function

Consider a system in contact with a single reservoir as shown in the Fig. 1.
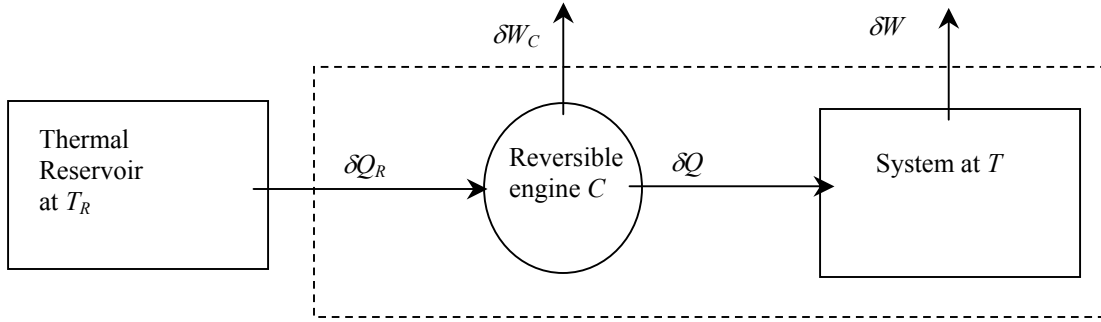

Figure 1: a thermal reservoir connected to a cyclic system through a Carnot engine.

As the system composed by the reversible engine and the cyclic system is connected to a single reservoir,

$$\oint \delta Q_R \leq 0 \qquad (8)$$

The definition of thermodynamic temperature allows us to write at the inlet and exit of the reversible engine:

$$\frac{\delta Q_R}{T_R} = -\frac{\delta Q}{T}\bigg|_C = \frac{\delta Q}{T}\bigg|_{system} \tag{9}$$

and replacing into Eq. (8) we obtain:

$$T_R \oint \frac{\delta Q_R}{T} \leq 0 \quad \Rightarrow \quad \oint \frac{\delta Q_R}{T} \leq 0 \tag{10}$$

Eq. (10) is known as the ***Clausius inequality***. In the case of a internally reversible process the equality holds, so:

$$\oint \frac{\delta Q_R}{T}\bigg|_{int\ rev} = 0 \tag{11}$$

The quantity inside the integral is a property, because its value depends only on the state of the substance. This property is denominated ***entropy*** and is denoted by S. The definition is:

$$dS \equiv \frac{\delta Q}{T}\bigg|_{int\ rev} \tag{12}$$

For general processes, we can write:

$$\Delta S \geq \int_1^2 \frac{\delta Q}{T} \tag{13}$$

Eq. (13) is usually written in compact form as an equality as:

$$dS = \frac{\delta Q}{T} + \delta \sigma \tag{14}$$

where σ is the entropy production term due to irreversibilities, which is a function of the path of the process, and can be defined using Eqs. (13) and (14) as:

$$\sigma \equiv S_2 - S_1 - \int_1^2 \frac{\delta Q}{T} \tag{15}$$

A simple extension of Eq. (14) can be made for the case of N boundaries of the system at different temperatures in a transient heat transfer case:

$$\frac{dS}{dt} = \sum_{i=1}^{N} \frac{\dot{Q}_i}{T_i} + \dot{\sigma} \tag{16}$$

Notice that the entropy change or the entropy transfer can be either positive or negative, while the entropy production will be always positive (or zero).

Work and Heat Entropy Generation

Combining Eq. (12) with the first law for a reversible process we obtain the first *TdS* equation:

$$T \, dS = dU - \delta W_{rev} \tag{17}$$

and using the first law for actual processes (reversible or irreversible) we get:

$$T \, dS = \delta Q_{act} - \delta W_{rev} + \delta W_{act} \tag{18}$$

and replacing into Eq. (14) we have:

$$\delta\sigma = \frac{\left(\delta W_{act} - \delta W_{rev}\right)}{T} \geq 0 \tag{19}$$

which represents the entropy generation due to irreversible work interactions (for instance in a friction process). That means that the actual work into a process is always larger than the reversible work, and the work out of a process is always smaller than the reversible work.

The entropy generation in a heat transfer process is related to temperature gradients. Temperature gradients mean irreversible heat transfer associated to non-equilibrium processes. Integrating Eq. (16) we can write:

$$\Delta S = \sum_{i=1}^{N} \frac{Q_i}{T_i} + \sigma \tag{20}$$

Consider now heat transfer between two heat reservoirs at temperatures $T_1 > T_2$, as shown in Fig. 2. In this case the properties are constant in the dashed system where the temperature gradient is present (a heat reservoir has constant temperature and is internally reversible). In addition, no work interactions are present, so the entropy generation is entirely due to heat transfer. Under these conditions, Eq. (20) reduces to:

$$\sigma_Q = -\sum_{i=1}^{N} \frac{Q_i}{T_i} \tag{21}$$

Applying Eq. (21) to our system, we obtain:

$$\sigma_Q = -\left(\frac{Q}{T_1} + \frac{-Q}{T_2}\right) = \frac{Q}{T_1 T_2}(T_1 - T_2) \tag{22}$$

Eq. (22) represents the entropy generation due to irreversible heat transfer between ANY two constant temperature systems. In a general system (not a heat reservoir) the heat transfer will cause a change in the system temperature, so Eq. (22) will be valid instantaneously.
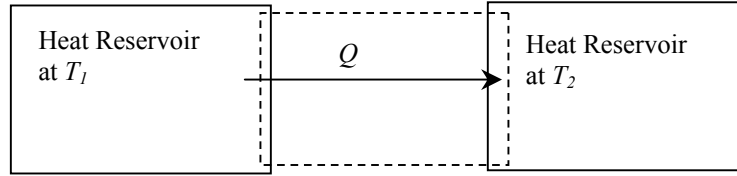

Figure 2: two heat reservoirs exchanging heat.

Entropy Balance in a Control Volume

Starting from Eq. (16), and using an analysis similar to that used for energy balance, it is possible to write an entropy balance equation for a control volume. On a time rate basis, the equation reads:

$$\frac{dS_{CV}}{dt} = \sum_{i=1}^{N} \frac{\dot{Q}_i}{T_i} + \sum_{in} \dot{m}\, s - \sum_{out} \dot{m}\, s + \dot{\sigma}_{CV} \tag{23}$$

where the entropy transfer is calculated as the sum over the different surfaces at constant temperature. In a steady-state system, with only one input (1) and one output (2), we write:

$$\dot{\sigma}_{CV} = \dot{m}(s_2 - s_1) - \sum_{i=1}^{N} \frac{\dot{Q}_i}{T_i} \geq 0 \tag{24}$$

which shows that a) the entropy change from inlet to exit can be either positive, zero or negative, b) the entropy at the device can be reduced only if the entropy transfer due to heat transfer is larger than the entropy generation inside the CV, c) an adiabatic device with

irreversibilities can only increase the entropy and d) the case with no irreversibilities and adiabatic results in isentropic flow.

The evaluation of the entropy transfer accompanying heat can be difficult, since the heat flux and the temperature might not be known at every point of the interface. We can, however, use a control volume that includes our system plus the heat reservoirs exchanging heat with the system. Recalling Eq. (22), and if we assume that we have a thermal reservoir at T_R and the environment at T_0, the entropy generation at the interface will be:

$$\sigma_Q = -\left(\frac{Q}{T}\right)_{in} + \left(\frac{Q}{T}\right)_{out} = -\sum_{i=1}^{N}\left(\frac{Q_i}{T_R} - \frac{Q_i}{T_i}\right) - \sum_{j=1}^{M}\left(\frac{Q_j}{T_0} - \frac{Q_j}{T_j}\right) \qquad (25)$$

where we have N surfaces interacting with the heat reservoir and M surfaces interacting with the environment. Now, T_R and T_0 are constants, and the total heat transfer with those constant temperature reservoirs is the sum over all the interfaces at different temperatures. Thus:

$$\sigma_Q = -\frac{Q_R}{T_R} - \frac{Q_0}{T_0} + \sum_{i=1}^{M+N}\frac{Q_i}{T_i} \qquad (26)$$

and replacing into Eq. (23) and rearranging we obtain:

$$\sigma_{tot} = \sigma_{CV} + \sigma_Q = \frac{dS_{CV}}{dt} - \sum_{in}\dot{m}\,s + \sum_{out}\dot{m}\,s - \frac{\dot{Q}_0}{T_0} - \sum_{j}\frac{\dot{Q}_j}{T_j} \geq 0 \qquad (27)$$

where we generalized for the case of j heat reservoirs plus the environment. In the simplest case of a steady-state process with only one inlet and one exit in contact with one reservoir:

$$\dot{m}(s_2 - s_1) = \frac{Q_R}{T_R} + \sigma_{tot} \qquad (28)$$

Entropy Production in Cyclic Systems

From Eq. (20), we can write for a cyclic heat engine ($\Delta S = 0$) connected to a hot reservoir at T_H and a cold reservoir at T_C:

$$\sigma_{engine} = -\left(\frac{Q_H}{T_H} + \frac{Q_C}{T_C}\right) \qquad (29)$$

where it was assumed that the engine and the reservoir are at the same temperature at the interface. If the heat engine connects with the hot reservoir at a temperature T_1 and with the colder reservoir with a surface temperature T_2, i.e. there are finite temperature differences at the interfaces, additional entropy production terms appear:

$$\sigma_{tot} = \sigma_H + \sigma_{engine} + \sigma_C = -\left(\frac{Q_H}{T_H} + \frac{Q_H}{T_1}\right) - \left(\frac{Q_H}{T_1} + \frac{Q_C}{T_2}\right) - \left(\frac{Q_C}{T_2} + \frac{Q_C}{T_C}\right) \quad (30)$$

Though several terms in Eq. (30) will cancel out, this form is useful because identifies the local terms of entropy production. The entire entropy production reduces to Eq. (29) if we draw a CV enclosing the heat transfer boundaries.

First Law Efficiencies

First law efficiencies are defined for isentropic processes. The second $T\,ds$ equation and the entropy generation equation read:

$$T\,ds = dh - v\,dP, \qquad T\,ds = \delta q_{act} + T\,\delta\sigma \quad (31)$$

Also, the energy balance for a steady-state, one inlet and one exit CV yields:

$$\delta q_{act} + \delta w_{act} = dh + d\,ke + d\,pe \quad (32)$$

Introducing dh from Eqs. (31) after canceling the $T\,ds$ terms into Eq. (32) we obtain a relationship similar to that shown in Eq. (19) for a closed system:

$$\delta w_{act} = T\,\delta\sigma + v\,dP + d\,ke + d\,pe = T\,\delta\sigma + \delta w_{rev} \quad (33)$$

For a turbine, the local efficiency is defined in terms of the delivered work as:

$$\eta_t = \frac{\delta w_{act}}{\delta w_{rev}} \quad (34)$$

that can be well approximated neglecting kinetic and potential energy changes as:

$$\eta_t = \frac{(h_1 - h_2)_{act}}{(h_1 - h_2)_{rev}} = \frac{T\,\delta\sigma_{CV} + v\,dP}{v\,dP} \quad (35)$$

which shows how internal irreversibilities reduce efficiency since dP is negative in a turbine. This can also be seen in a h-s diagram.

Application of Eq. (33) to the fully developed flow in an insulated pipe, where no external work or heat transfer exists, yields:

$$0 = T\,\delta\sigma + v\,dP + d\left(V^2/2\right) \tag{36}$$

that can be compared with the classical equation for the pressure loss equation in a pipe:

$$0 = \frac{f\,V^2 dx}{2\,D} + v\,dP + d\left(V^2/2\right) \tag{37}$$

which shows directly that the entropy generation is directly the friction loss:

$$T\,\delta\sigma_{CV} = \frac{f\,V^2 dx}{2\,D} \tag{38}$$

In the case of flow of an ideal gas, Eq. (28) reduces to $\dot{m}\left(s_2 - s_1\right) = \dot{\sigma}_{CV}$. The energy equation reduces to $h_1 = h_2$, which implies in an ideal gas that $T_1 = T_2$ and therefore $s_2 - s_1 = -R \ln P_2/P_1$. Replacing we get:

$$\dot{\sigma}_{CV} = -\dot{m}\,R \ln P_2/P_1 = -\dot{m}\,R \ln\left(1 + \frac{P_2 - P_1}{P_1}\right) \cong \dot{m}\,R\,\frac{P_1 - P_2}{P_1} \tag{39}$$

where the last approximate equality applies in the case of $\Delta P << P_1$. Similarly, in an incompressible fluid $s_2 - s_1 = c \ln T_2/T_1$ and $c\,\Delta T = -v\,\Delta P$, therefore:

$$\dot{\sigma}_{CV} = -\dot{m}\,c \ln T_2/T_1 = -\dot{m}\,c \ln\left(1 + \frac{T_2 - T_1}{T_1}\right) \cong \dot{m}\,v\,\frac{P_1 - P_2}{T_1} \tag{40}$$

where the approximation is valid if $v\,\Delta P << c\,T_1$.

Homework

Wark 2.14. Air flows isothermally at 60 °C through a constant area duct such that the entropy increase due to internal irreversibilities is 0.0544 *kJ/kg K*. Determine a) the heat added if the initial and final pressures are 400 and 320 kPa, respectively, and b) the inlet and exit velocities.