

ESO201A
Lecture#35
(Class Lecture)

Date: 4.11.22

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Entropy change in Reversible Processes

Having established that entropy is a thermodynamic property of a system, we now consider its significance in various processes. The Carnot cycle, reversible heat-transfer processes, and reversible adiabatic processes will be considered.

Carnot cycle

Let the working fluid of a heat engine operating on the Carnot cycle make up the system. The first process is the isothermal transfer of heat to the working fluid (Fig. 1) from the high-temperature reservoir. For this process we can write

$$S_2 - S_1 = \int_1^2 \left(\frac{\delta Q}{T} \right)_{rev}$$

Since this is a reversible process in which the temperature of the working fluid remains constant, the equation can be integrated to give

$$S_2 - S_1 = \frac{1}{T_H} \int_1^2 \delta Q = \frac{Q_{1-2}}{T_H}$$

(20)

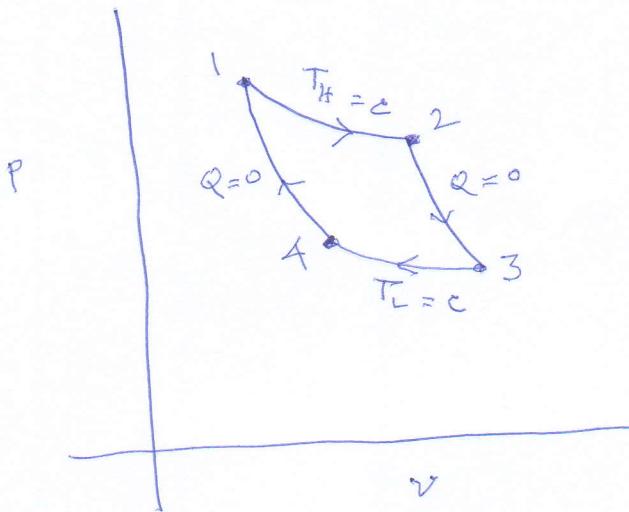


Fig. 1 Carnot heat engine cycle (P-v diagram)

The Carnot cycle for heat engine is shown in Fig. 2(a) on T-S coordinates.

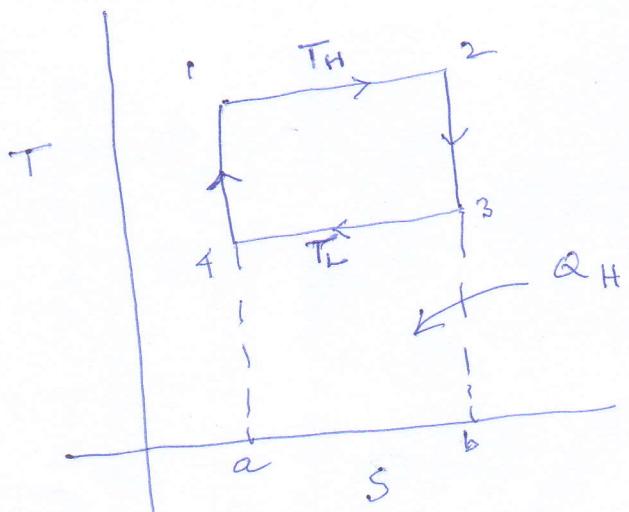


Fig. 2 (a) The Carnot cycle for heat engine on the T-S diagram.

The area under line 1-2, area 1-2-b-a-1, represents the heat transferred to the working fluid during the process.

The second process of a Carnot cycle is a reversible adiabatic one. From the definition of entropy,

$$dS = \left(\frac{\delta Q}{T} \right)_{rev}$$

The entropy remains constant in a reversible adiabatic process since $\delta Q = 0$ and hence, $dS = 0$. A constant-entropy process is called an isentropic process. Line 2-3 represents this process, and this process is concluded at state 3 when the temperature of the working fluid reaches T_L .

The third process is the reversible isothermal process in which heat is transferred from the working fluid to the low-temperature reservoir. For this process we can write

$$S_4 - S_3 = \left(\frac{\delta Q}{T} \right)_{rev} = \frac{Q_{3-4}}{T_L}$$

Because during this process the heat transfer is negative (in regard of the working fluid), the entropy of the working fluid decreases. Moreover, because the final process 4-1, which completes the cycle, is a reversible adiabatic process (and therefore isentropic), it is evident that the entropy decrease in process 3-4 must exactly equal the entropy increase in process 1-2. The area under line 3-4, area 3-4-a-b-3, represents the heat transferred from the working fluid to the low-temperature reservoir.

Since the net work of the cycle is equal to the net heat transfer, area 1-2-3-4-1 must represent the net work of the cycle. The efficiency of the cycle may also be expressed in terms of areas:

$$\eta_{th} = \frac{W_{net}}{Q_H} = \frac{\text{area } 1-2-3-4-1}{\text{area } 1-2-b-a-1}$$

Some statements made earlier about efficiencies may now be understood graphically. For example, increasing T_H while T_L remains constant increases the efficiency. It is also evident that decreasing T_L while T_H remains constant increases the efficiency. The efficiency approaches 100% as the absolute temperature at which heat is rejected approaches zero.

If the cycle is reversed, we have a refrigerator or heat pump. The Carnot cycle for a refrigerator is shown in Fig. 2(b). Notice that the entropy of the working fluid increases at T_L , since heat is transferred to the working fluid at T_L . The entropy decreases at T_H because of heat transfer from the working fluid.

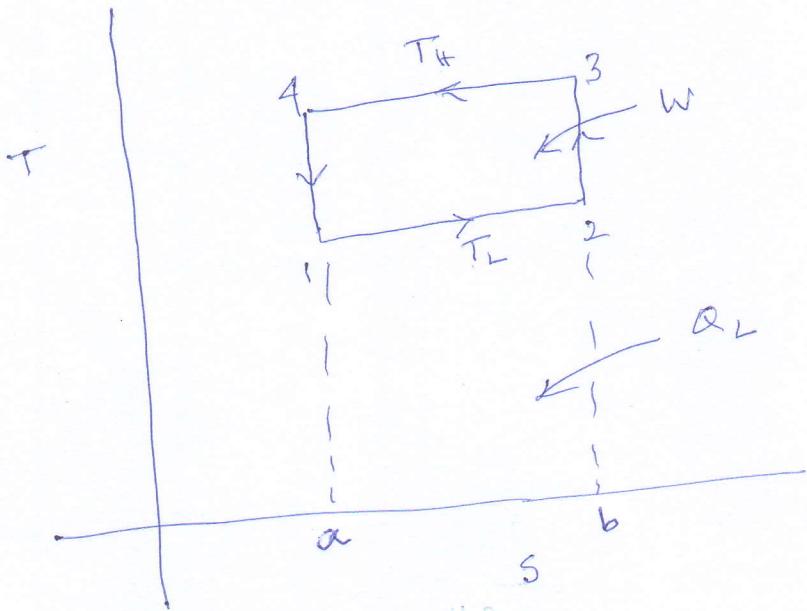


Fig. 2 (b) cannot cycle on
T-S diagram for
a refrigerator

Reversible Heat Transfer Processes
Let us next consider reversible
heat transfer processes. Actually,
we are concerned here with processes
that are internally reversible, that is,
processes that have no irreversibilities
within the boundary of the system.
For such processes, the heat transfer

to or from a system can be shown as an area on a temperature-entropy diagram. For example, consider the phase change from liquid to saturated vapour at constant pressure. This process would correspond to process 1-2 on the T-S diagram of Fig. 3 (note that absolute temperature is required here), and area 1-2-b-a-1 represents the heat transfer.

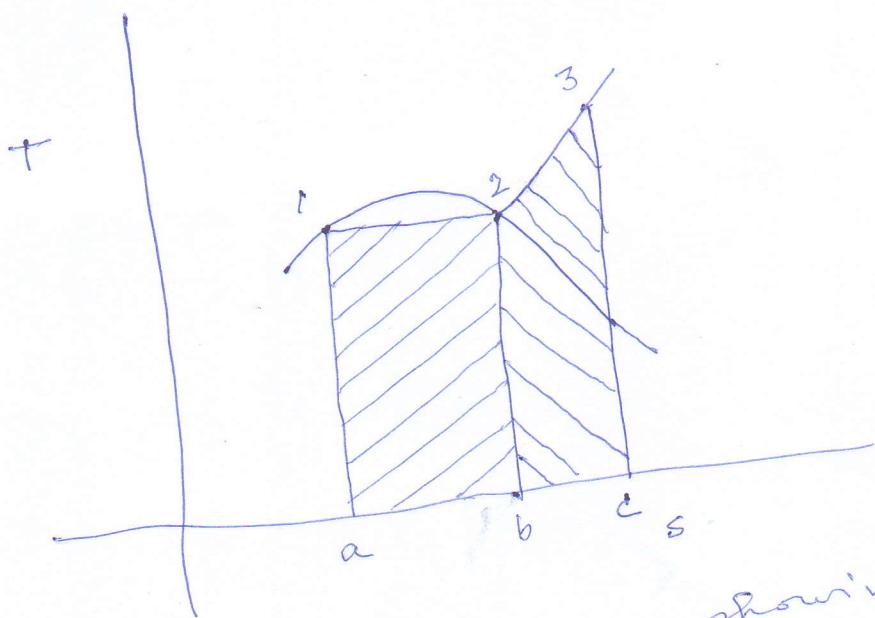


Fig. 3 A T-S diagram showing areas that represent heat transfer for an internally reversible process.

Since this is a constant-pressure process, the heat transfer per unit mass is equal to h_{fg} . Thus,

$$s_2 - s_1 = s_{fg} = \frac{1}{m} \int_1^2 \left(\frac{\delta Q}{T} \right)_{rev}$$

$$= \frac{1}{mT} \int_1^2 \delta Q = \frac{q_{1-2}}{T}$$

$$= \frac{h_{fg}}{T}$$

This relation gives a clue about how s_{fg} is calculated for tabulation in tables of thermodynamic properties.

If heat is transferred to the saturated vapour at constant pressure, the steam is superheated along line 2-3. For this process we can write

$$q_{2-3} = \frac{1}{m} \int_2^3 \delta Q = \int_2^3 T ds$$

Since T is not constant, this equation cannot be integrated unless we know a relation between temperature and entropy. However, we do realize that the area under line 2-3, area $2-3-c-b-2$, represents $\int_2^3 T ds$ and therefore represents the heat transferred during this reversible process.

The important conclusion to draw here is that for processes that are internally reversible, the area underneath the process line on a $T-s$ diagram represents the quantity of heat transferred. This is not true for irreversible processes, as will be demonstrated later.

The Thermodynamic Property Relation

At this point we derive two important thermodynamic relations for a simple compressible substance. These relations are

$$\boxed{\begin{aligned} T dS &= dU + P dV \\ T dS &= dH - V dP \end{aligned}}$$

The first of the above relations can be derived by considering a simple compressible substance in the absence of motion or gravitational effects. The first law for a change of state under these conditions can be written

$$\delta Q = dU + \delta W$$

For a reversible process of a simple compressible substance, we can write

$$\delta Q = T dS$$

$$\text{and } \delta W = P dV$$

Substituting these relations into the first-law equation, we have

$$T dS = dU + P dV \quad (17)$$

which is the equation we set out to derive.

Note that eq. (1) is derived by assuming a reversible process. This equation can therefore be integrated for any reversible process, for during such a process the state of the substance can be identified at any point during the process.

We also note that eq. (1) deals only with properties. Suppose we have an irreversible process taking place between the given initial and final states. The properties of a substance depends only on the state, and therefore the changes in the properties during a given change of state are the same for an irreversible process as for a reversible process. Therefore, eq. (1) is often applied to an irreversible process between two given states, but the integration of eq. (1) is performed along a reversible path between the same two states.

Since enthalpy is defined as

$$H = U + PV$$

it follows that

$$\begin{aligned} dH &= dU + PdV + VdP \\ \Rightarrow dU &= dH - PdV - VdP \end{aligned}$$

Substituting this relation into eq. (1),

we have

$$\begin{aligned} TdS &= dH - \cancel{PdV} - \cancel{VdP} \\ &\quad + \cancel{PdV} \\ &= dH - VdP \end{aligned} \quad (2)$$

$$\Rightarrow TdS = dH - VdP$$

which is the second relation we set out to derive.

Equations (1) and (2) are two forms of the thermodynamic property relation and are frequently called Gibbs equations.

These equations can also be written for a unit mass:

$$TdS = du + PdV \quad (3)$$

$$TdS = dh - VdP \quad (4)$$

Entropy Change of a Solid or Liquid

Earlier we considered the calculation of the internal energy and enthalpy changes with temperature for solids and liquids and found that, in general, it is possible to express both in terms of the specific heat, such as

(1)

$$dh \approx du \approx c dT$$

where c is either the constant-volume or the constant-pressure specific heat, as the two would be nearly the same.

In many processes involving a solid or a liquid, we might further assume that the specific heat in eq. (1) is constant (unless the process occurs at low temperature or over a wide range of temperatures). Equation (1) can then be integrated

$$h_2 - h_1 \approx u_2 - u_1 \approx c (T_2 - T_1)$$

$$\text{to } h_2 - h_1 \approx u_2 - u_1 \approx c (T_2 - T_1) \quad (2)$$

We can now use eq. (1) and the thermodynamic property relation $T dS = du + P dV$, to calculate the entropy change for a solid or liquid. Note that for such a phase the specific volume term in the relation $T dS = du + P dV$ is very small. So, we get

$$dS = \frac{du}{T} \approx \frac{c dT}{T} \quad (3)$$

Considering $c = \text{constant}$,

$$\int_1^2 dS = c \int_1^2 \frac{dT}{T} \quad (4)$$

$$\Rightarrow S_2 - S_1 = c \ln \frac{T_2}{T_1}$$

If the specific heat is not constant, then commonly c is known as a function of T , in which case eq. (3) can also be integrated to find the entropy change. Equation (4) illustrates what happens in a reversible adiabatic ($dq = 0$) process, which therefore is isentropic. In this process, the approximation of constant V leads to constant temperature, which explains why pumping liquid does not change the temperature.

Entropy Change of an Ideal Gas

Gibbs equations can be used to develop two very useful equations for computing the entropy change of an ideal gas.

$$TdS = dH + PdV \quad (1)$$

$$\Rightarrow dS = dH/T + \frac{P}{T}dV \quad (1a)$$

For an ideal gas

$$dH = C_V dT \quad (2)$$

$$\text{and } \frac{P}{T} = \frac{R}{V} \quad (3)$$

Therefore, from eqs. (2) and (3), and eq. (1a),

$$dS = C_V \frac{dT}{T} + \frac{RdV}{V} \quad (4)$$

$$\Rightarrow S_2 - S_1 = \int_1^2 C_V \frac{dT}{T} + R \ln \frac{V_2}{V_1} \quad (4)$$

Similarly,

$$TdS = dH - VdP \quad (5)$$

$$\Rightarrow dS = dH/T - \frac{V}{T}dP \quad (5a)$$

For an ideal gas

$$dH = C_P dT \quad (6)$$

$$\text{and } \frac{V}{T} = \frac{R}{P} \quad (7)$$

Therefore, substituting eqs. (6) and (7) into eq. (5a),

$$dS = C_P \frac{dT}{T} - R \frac{dP}{P} \quad (8)$$

$$\Rightarrow S_2 - S_1 = \int_1^2 c_p \frac{dT}{T} - R \ln \frac{P_2}{P_1} \quad (8)$$

To integrate eqs. (4) and (8), we must know the temperature dependence of the specific heats. Since $c_p - c_v = R$, which is a constant, we realize that we need to examine the temperature dependence of only one of the specific heats.

For constant c_p ,

$$S_2 - S_1 = c_p \ln \frac{T_2}{T_1} - R \ln \frac{P_2}{P_1} \quad (9)$$

For constant c_v ,

$$S_2 - S_1 = c_v \ln \frac{T_2}{T_1} + R \ln \frac{V_2}{V_1} \quad (10)$$

Ideal gas Undergoing Isentropic Process

Let us now consider the case of an ideal gas undergoing an isentropic process, a situation that is analyzed frequently.

From eq. (9), for constant specific heat at constant pressure, C_{P_0} ,

$$S_2 - S_1 = 0 = C_{P_0} \ln \frac{T_2}{T_1} - R \ln \frac{P_2}{P_1}$$

$$\Rightarrow \ln \left(\frac{T_2}{T_1} \right) = \frac{R}{C_{P_0}} \ln \left(\frac{P_2}{P_1} \right) \quad (12)$$

or $\frac{T_2}{T_1} = \left(\frac{P_2}{P_1} \right)^{\frac{R}{C_{P_0}}}$

However,

$$\frac{R}{C_{P_0}} = \frac{C_{P_0} - C_{V_0}}{C_{P_0}} \quad \gamma = 1 - \frac{C_{V_0}}{C_{P_0}}$$

$$\Rightarrow \frac{R}{C_{P_0}} = 1 - \frac{1}{\kappa} = \frac{\kappa - 1}{\kappa} \quad (\text{since } \kappa = \frac{C_{P_0}}{C_{V_0}})$$

Equation (12) is now conveniently written as

$$\frac{T_2}{T_1} = \left(\frac{P_2}{P_1} \right)^{\frac{\kappa - 1}{\kappa}} \quad (12)$$

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From the ideal-gas equation
of state,

$$Pv = RT$$

$$P_1 v_1 = RT_1$$

$$P_2 v_2 = RT_2$$

$$\text{or } \frac{P_2}{P_1} \cdot \frac{v_2}{v_1} = \frac{T_2}{T_1} \Rightarrow \frac{P_2}{P_1} = \frac{T_2}{T_1} \frac{v_1}{v_2} \quad (13)$$

From eq. (12), or (13),

$$\frac{T_2}{T_1} = \left(\frac{T_2}{T_1} \frac{v_1}{v_2} \right)$$

$$\Rightarrow \frac{T_2}{T_1} = \left(\frac{T_2}{T_1} \right)^{\frac{k-1}{k}} \cdot \left(\frac{v_1}{v_2} \right)^{\frac{k-1}{k}}$$

$$\Rightarrow \left(\frac{T_2}{T_1} \right)^{\frac{k-k+1}{k}} = \left(\frac{v_1}{v_2} \right)^{\frac{k-1}{k}}$$

$$\Rightarrow \left(\frac{T_2}{T_1} \right)^{\frac{1}{k}} = \left(\frac{v_1}{v_2} \right)^{\frac{k-1}{k}}$$

$$\Rightarrow \left(\frac{T_2}{T_1} \right)^{\frac{1}{k}} = \left(\frac{v_1}{v_2} \right)^{\frac{k-1}{k}}$$

$$\Rightarrow \frac{T_2}{T_1} = \left(\frac{v_1}{v_2} \right)^{\frac{k-1}{k}}$$

(13a)

From eq. (13),

$$\frac{P_2}{P_1} = \frac{T_2}{T_1} \frac{v_1}{v_2}$$

From eq. (13a),

$$\frac{P_2}{P_1} = \left(\frac{v_1}{v_2} \right)^{k-1} \frac{v_1}{v_2}$$

$$= \frac{v_1}{v_2}^{\frac{k-1+1}{k-1+1}}$$

$$= \left(\frac{v_1}{v_2} \right)^k$$

$$\Rightarrow \boxed{\frac{P_2}{P_1} = \left(\frac{v_1}{v_2} \right)^k} \quad (14)$$

From eq. (14), we note that for this process

$$P v^k = \text{const}$$

This is a special case of a polytropic process in which the polytropic exponent n is equal to the specific heat ratio κ .

For monatomic gases, $\kappa = 1.667$

For diatomic gases, $\kappa = 1.4$