Reduced heats, reversibility and entropy

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In this work a didactic approach to some fundamental thermodynamic concepts as reversibility, possible and impossible processes and entropy is proposed. The approach is obtained through the concepts of heat transfer flows and reduced heat. A broad essay with undergraduate engineering students taking their first and second formal course on classic Thermodynamics has been made. The common difficulties that they usually have to understand entropy and the second law implications may be improved with this approach. By an intuitive and historical development departing from easy examples of heat and reduced heat balances, the efficiency of thermal engines is analyzed and shown that the energy generation is bounded by the Carnot cycle efficiency and Clausius inequality. A generalization of the reduced heat concept is used to obtain the integral Clausius inequality, and the entropy and reversibility concepts. Finally, an example of entropy generation minimization is presented.

Keywords: Education; entropy; reduced heat; reversible process; thermodynamics.

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1. Introduction

Basic thermodynamic courses begin with the relations between \( p, V \), and \( T \) (pressure, volume and temperature). Then using the first law for closed systems: \( dU = dQ - dW \), the internal energy \( (U) \) is obtained as another state variable and energy balances are performed; where \( Q \) and \( W \) are heat and work. In ref. 1 some suggestions are given on how to surmount some didactic difficulties in the starting stages of thermodynamic learning process.

Afterwards the calculation of \( p, V, T, U \) and \( S \) (entropy) and energy balances for a change of phase of a pure substance are included. In Ref. 2 some basic aspects of the teaching of phase changes are reported. The work presented in the next sections deals with Clausius inequality, entropy and reversibility concepts based on the reduced heat concept. It is important to notice that in the courses the second law of thermodynamics is taught following the Clausius-Kelvin postulates [3]. These postulates, that have an historic priority, are very well taken by the students. Particularly, students are attracted by the Clausius postulate [4]: heat cannot flow from a cold body to a hotter body.

2. Reduced Heats and Clausius Inequality

The efficiency of a Carnot cycle is expressed as follows:

\[
\eta_C = 1 \frac{Q_L}{Q_H} = 1 - \frac{T_L}{T_H}
\]

(1)

where \( T_H \) and \( T_L \) represent high and low temperatures \( (T_H > T_L) \); \( Q_L \) and \( Q_H \) are the transferred and admitted heats, respectively.

These equations are equal and can be expressed as:

\[
\frac{Q_H}{T_H} + \frac{Q_L}{T_L} = 0
\]

(2)

Ratios of the form \( Q/T \) are called reduced heats. Then, the sum of the reduced heats in a Carnot cycle is zero. If we denote by \( (Q/T)_{sys} \) the reduced heat transferred to the Carnot cycle, and with \( (Q/T)_{ext} \) the one sent to the exterior by the engine, (2) is written as:

\[
\left( \frac{Q}{T} \right)_{ext} + \left( \frac{Q}{T} \right)_{sys} = 0
\]

(3)

Now, it can be shown that the concept of reduced heat is adequate to justify an inevitable result in a basic course of
thermodynamics. Consider an *isolated* system composed of two parts $A$ and $B$, with temperatures $T_A > T_B$. The second law says that the direction of heat is from the body with higher temperature towards the one with lower temperature. Therefore, body $A$ transfers flow of heat $-Q_{AB} < 0$ to $B$, while the body $B$ receives $Q_{AB}$ thermal energy units. The algebraic sum of both reduced heats is:

$$\frac{Q_{AB}}{T_B} - \frac{Q_{AB}}{T_A} = \frac{Q_{AB}}{T_AT_B}(T_A - T_B) > 0 \quad (4)$$

If the temperature difference between $T_A$ and $T_B$ is very small, $T_B = T_A + \Delta T$ (in the limit $\Delta T \to 0$), (4) reduces to:

$$\frac{Q_{AB}}{T_B} - \frac{Q_{AB}}{T_A} = 0 \quad (5)$$

and when $T_A > T_B$ (a finite temperature difference), (4) is:

$$\frac{Q_{AB}}{T_B} - \frac{Q_{AB}}{T_A} > 0 \quad (6)$$

Then the difference of the reduced heats of an isolated system cannot be negative. Thus, while there is no infinitesimal thermal imbalance between $T_A$ and the equilibrium temperature $T_B$, the algebraic sum of the reduced heats of the isolated system, $\Sigma(Q/T)$, remains greater than zero, and it is only zero when the steady state is achieved.

Another fundamental result that can be developed, with reduced heats, is the following inequality. According to the second law of thermodynamics the efficiency of any thermal engine operating in a temperature interval $[T_L, T_H]$ is less than or equal to that of a Carnot engine, *i.e.*

$$\eta = 1 - \frac{Q_L}{Q_H} \leq \eta_C = 1 - \frac{T_L}{T_H} \quad (7)$$

where $\eta_C$ is the efficiency of the Carnot engine. And the next version (in the form of reduced heats) of the Clausius inequality is obtained

$$\frac{Q_H}{T_H} + \frac{Q_L}{T_L} \leq 0 \quad (8)$$

The importance of (8) can be exemplified by the following problem:

Consider two temperature reservoirs, one at 600K and the other at 300K, among which there is a transfer of heat of 800 kJ. To take advantage of this heat flow, seven different Carnot heat engines are going to be installed between the two reservoirs. The first will supply 100 kJ of work, the second 200 kJ, and so on until the seventh with 700 kJ. Determine which engines are possible and which one provides the maximum work.

Table I shows, for each of the seven engines, the admitted heat (800 kJ), the delivered work, heat transferred to the exterior ($Q_L = W - Q_H$) and the sum of transferred heats.

Based on the seven admitted heats (all equal), and the seven heats transferred (all different from each other), Table II presents the seven couples of reduced heats and their sum.

Note that the sum of the transferred heats from the seven engines is positive (Table I, last row). In contrast the sum of reduced heats can be negative, zero or positive (Table II, last row). Only for the fourth Carnot engine the sum of reduced heats is zero.

To select the possible engines and discard the impossible ones the Clausius inequality (6) can be used, which in this problem is:

$$Q_H \leq -2 Q_L \quad (9)$$

Then only the first four engines in Table I fulfil the requirement of the Clausius inequality and are therefore possible. The last three engines do not comply and must be discarded. And the one that maximizes the work is that whose sum of reduced heats is zero.

The concept of reduced heats can also help to analyze some unique properties of the Carnot cycle, as follows. In the isothermal expansion the system receives $Q_H$ units of heat from outside and in the isothermal compression it transfers $Q_L$ units to the exterior. This two heat transfers are both different from zero in this cycle and have different magnitudes. It can be concluded that the amount of heat that flows from

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Table I. Energy flows in kJ for each of the seven heat engines.

Table II. Reduced heats (kJ/K) for each of the seven heat engines.
the high temperature reservoir to the low temperature reservoir in a Carnot cycle is not constant. Nevertheless, the reduced heats are constant since they satisfy:

\[ \frac{Q_H}{T_H} = -\frac{Q_L}{T_L} \]  

As for the energy transferred as work, its two adiabatic transfers cancel each other, and the isothermal in a cycle of ideal gas satisfy the following: \( W_{\text{ext}} = Q_H \) and \( W_{\text{int}} = Q_L \). Thus, in any Carnot cycle of an ideal gas the values of the form \( W/T \) make sense, and therefore the following is true: in a Carnot cycle of an ideal gas the energy transferred, heat and work, divided by the corresponding temperature are invariant. That is, they fulfill:

\[ \frac{Q_H}{T_H} - \frac{Q_L}{T_L} = 0; \quad \frac{W_{\text{ext}}}{T_H} - \frac{W_{\text{int}}}{T_L} = 0 \]  

### 3. Clausius Inequality

The integral form of Clausius inequality is given by,

\[ \oint \frac{dQ}{T} \leq 0 \]  

and can be early included in a Thermodynamics basic course as follows.

The reduced heat concept has no physical sense in isometric and isobaric processes. To overcome this limitation the concept of reduced heat can be generalized following the idea of Rudolph Clausius [4], approximating an arbitrary cycle (see Fig. 1) using Carnot cycles (see Fig. 2).

The eight isotherms —two per Carnot cycle— do not have any segment in common. Consequently, the sum of the eight reduced heats is equal to:

\[ \sum_{k=1}^{8} \frac{Q_k}{T_k} = 0 \]  

### 4. Reversibility

As in a Carnot cycle, a process can be required to satisfy the sum of reduced heats given in (3). But as in isobaric and isometric processes the concept of reduced heat does not make sense, two fundamental processes would be out of consideration. To be sure that they are included, as well as any other process, the entropy concept is employed in equality (3) (extending the concept of reduced heat) as follows: It is said that a process is reversible if it satisfies:

\[ \int \left( \frac{dQ}{T} \right)_{\text{ext}} + \int \left( \frac{dQ}{T} \right)_{\text{sys}} = 0 \]  

There are two more possibilities in Eq. (16): greater than zero or less than zero. Of course the possibility of being greater than zero is entirely correct and processes that satisfy it are called irreversible. In contrast, the less than zero possibility contradicts the second law of thermodynamics. And
the only two options that can be present in a process are expressed in the inequality [5]:

\[ \int \left( \frac{dQ}{T} \right)_\text{ext} + \int \left( \frac{dQ}{T} \right)_\text{sys} \geq 0 \quad (17) \]

An indispensable example of (17) to be included in the courses is as follows:

Determine if it is possible to construct a cyclic engine consisting of two reservoirs, one of heat (always with constant temperature \( T_H \)) and another one of work. That is, an engine with 100% thermal efficiency.

The selection is an isolated system of a reservoir of temperature \( T_H \), a cyclic engine and the environment surrounding it. In each cycle the temperature reservoir transfers \( Q \) units of heat (\( Q > 0 \)), and then its reduced heat is \( -\frac{Q}{T_H} \).

The reduced heat of the engine is zero. Thus:

\[ \int \left( \frac{dQ}{T} \right)_\text{ext} + \int \left( \frac{dQ}{T} \right)_\text{sys} = -\frac{Q}{T_H} < 0 \quad (18) \]

Then this isolated system satisfies the inequality opposite to (17). If the possibility that in an isolated system the inequality opposite to (17) is accepted, implies the existence of an engine with 100% efficiency, and this violates to the second law of thermodynamics, so this engine is not possible.

5. Discussion and conclusions

Most of the conceptual difficulties that undergraduates go through to understand their first formal course of Thermodynamics can be lighten using the reduced heat concept, that gives access to the analysis of power cycles, and to the distinction between possible and impossible cycles through a simple balance that distinguishes three outcomes: \( Q/T \) less than, equal to or greater than zero.

Any cycle is less efficient that Carnot cycle since it delivers less work and transfers more heat to the exterior. This condition is expressed as:

\[ \frac{Q_H}{T_H} + \frac{Q_L}{T_L} < 0 \quad (19) \]

An ideal Carnot cycle has the exclusive condition:

\[ \frac{Q_H}{T_H} + \frac{Q_L}{T_L} = 0 \quad (20) \]

which conduces to the condition of maximum work and constitutes a solid base to define the concept of reversibility. The generalization of the reduced heat concept leads to the integral \( \oint \left( \frac{dQ}{T} \right) = 0 \), and then to the concept of entropy, as will be seen, and based on the examples developed with reduced heats helps to test the certainty of the Clausius inequality \( \oint \left( \frac{dQ}{T} \right) \leq 0 \) [6].

Indeed, the integral \( \oint \left( \frac{dQ}{T} \right) = 0 \) indicates that \( \int \left( \frac{dQ}{T} \right) \) is independent of the reversible process. Assume two different states, 1 and 2, joint with three arbitrary reversible processes: \( A \), \( B \) and \( C \) (Fig. 3).

As there is one cycle through the process \( A - B \) and another one with \( B - C \), necessarily

\[ \int_1^2 \left( \frac{dQ}{T} \right)_A + \int_2^1 \left( \frac{dQ}{T} \right)_B = 0 \quad (21) \]

and

\[ \int_1^2 \left( \frac{dQ}{T} \right)_C + \int_2^1 \left( \frac{dQ}{T} \right)_B = 0 \quad (22) \]

subtraction of Eqs. (21) and (22) results,

\[ \int_1^2 \left( \frac{dQ}{T} \right)_A = \int_1^2 \left( \frac{dQ}{T} \right)_C \quad (23) \]

Then, when two states are linked by a reversible process the value

\[ \int_1^2 \left( \frac{dQ}{T} \right) \]

is the same for any path. If the value of this integral, that does not depend on the process, is expressed as the difference \( S_2 - S_1 \)

\[ \int_1^2 \left( \frac{dQ}{T} \right)_A = \int_1^2 \left( \frac{dQ}{T} \right)_C = S_2 - S_1 \quad (24) \]

and the state 2 is brought infinitely close to the state 1, at the limit, \( dS = dQ/T \). In 1865 Rudolph Clausius introduced the integrals aforementioned and named the function \( S \) as entropy.

If in Fig. 3 the process \( 1 - B - 2 \) is irreversible, Clausius inequality becomes

\[ \int_1^2 \left( \frac{dQ}{T} \right)_A + \int_2^1 \left( \frac{dQ}{T} \right)_B = \oint \frac{dQ}{T} < 0 \quad (25) \]
then:
\[
\int_1^2 \left( \frac{dQ}{T} \right)_B < S_2 - S_1 \tag{26}
\]

This inequality represents the second law. Consequently, the difference between the possible reversible or irreversible processes is described by the entropy generation \( S_{\text{gen}} \):
\[
S_{\text{gen}} = S_2 - S_1 - \int_1^2 \left( \frac{dQ}{T} \right)_{\text{irr}} \geq 0 \tag{27}
\]

In particular, for the example of the engine with 100% efficiency (Sec. 4):
\[
S_{\text{gen}} = \Delta S_{\text{Reservoir}} + \Delta S_{\text{Engine}} + \Delta S_{\text{surroundings}} \tag{28}
\]

Then the entropy production is:
\[
S_{\text{gen}} = -\frac{Q}{T_H} \tag{29}
\]

Therefore, when entropy is generated the process is irreversible. The increase direction of entropy corresponds to real processes that inevitably generate entropy [6].

Finally, various problems of thermodynamic optimization can be solved as problems of minimization of the entropy generated by irreversible processes. The importance of this can be exemplified by:

A system consisting of a body with a heat capacity \( C \) (independent of temperature), is warmed up from a temperature \( T_B \) (fixed) to a temperature \( T_A \) (fixed). A deposit of an intermediate temperature \( T_I \) is available. According to second law of thermodynamics the finite heat transfers are irreversible processes. What would it be the intermediate temperature for which the entropy generated is a minimum?

The heat transfer is given by:
\[
dQ = CdT \tag{30}
\]

Entropy generation is divided into two parts. The first is the difference between the entropy increase in the body and the entropy extracted from the deposit while it is transferring heat:
\[
S_{\text{gen1}} = \int_B^I \frac{dQ}{T} \frac{Q_I}{T_I} = c \left( \ln \frac{T_I}{T_B} - \frac{T_I - T_B}{T_I} \right) \tag{31}
\]

the second part:
\[
S_{\text{gen2}} = C \left( \ln \frac{T_A}{T_I} - \frac{T_A - T_I}{T_I} \right) \tag{32}
\]
so,
\[
S_{\text{gen}} = S_{\text{gen1}} + S_{\text{gen2}} = C \left( \ln \frac{T_A}{T_B} - 2+ \frac{T_B}{T_I} + \frac{T_I}{T_A} \right) \tag{33}
\]

Thus if the total generation of entropy is to be minimized over \( T_I \), we must have:
\[
dS_{\text{gen}} = -\frac{Q}{T_B} + \frac{1}{T_A} = 0 \tag{34}
\]

and
\[
T_I = \sqrt{T_BT_A} \tag{35}
\]

The optimum intermediate temperature is the geometric average of the fixed extreme temperatures. If the temperature difference is small, this geometric average will equal the arithmetic average. In conclusion, the minimization of entropy generation [7] is a powerful tool to optimize processes and should be included in the teaching of Thermodynamics.

**Appendix**

\[
\begin{array}{ll}
Q_H & \text{admitted heat (kJ)} \\
Q_L & \text{transferred heat (kJ)} \\
Q/T & \text{reduced heat (kJ/K)} \\
S & \text{entropy (kJ/K)} \\
S_{\text{gen}} & \text{generated entropy.} \\
T_H & \text{hot temperature reservoir (K)} \\
T_B & \text{cold temperature reservoir (K)} \\
W & \text{work (kJ)} \\
\eta & \text{thermal efficiency} \\
\eta_C & \text{Carnot efficiency}
\end{array}
\]