

**ESO201A**  
**Lecture#34**  
**(Class Lecture)**

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By  
Dr. P.S. Ghoshdastidar

## Entropy for a Control

(1)

### Mars

Up to this point in our consideration of the second law of thermodynamics, we have dealt only with thermodynamic cycles. Although this is a very important and useful approach, we are often concerned with processes rather than cycles. Thus, we might be interested in the second-law analysis of processes we encounter daily, such as combustion processes in an automobile engine, the cooling of a cup of coffee, or the chemical processes that take place in our bodies.

In our consideration of the first law, we initially stated the law in terms of a cycle, but we then defined a property, the internal energy, that enables us to use the first law quantitatively for processes. Similarly, we have stated the second law for a cycle, and we now find that the second law leads to a property called entropy, that enables us to treat the second law quantitatively for processes.

## The Inequality of Clausius

The first step in our consideration of the property we call entropy is to establish the inequality of Clausius, which is

$$\oint \frac{dQ}{T} \leq 0$$

The inequality of Clausius is a corollary or a consequence of the second law of thermodynamics. It will be demonstrated to be valid for all possible cycles, including both reversible and irreversible heat engines and refrigerators.

Heat Engines (Reversible)  
 Consider first a reversible (Carnot) heat engine cycle operating between reservoirs  $T_H$  and  $T_L$ , as shown in Fig. 1. For this cycle, the cyclic integral of the heat transfer,  $\oint dQ$ , is greater than zero.

$$\oint dQ = Q_H - Q_L > 0$$

(3)

Since  $T_H$  and  $T_L$  are constant, from the definition of the absolute temperature scale and from the fact that this is a reversible cycle, it follows that

$$\oint \frac{\delta Q}{T} = \frac{Q_H}{T_H} - \frac{Q_L}{T_L} = 0$$

$$(\text{Note: } \frac{Q_H}{Q_L} = \frac{T_H}{T_L})$$

from the definition  
of thermodynamic  
temp. scale based  
on reversible engines)

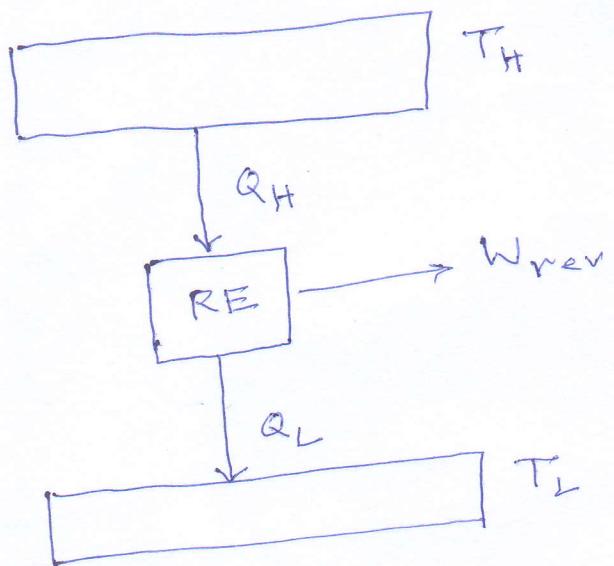


Fig. 1 Reversible heat engine cycle for the demonstration of the inequality of clausius

(A)

If  $\oint \delta Q$ , the cyclic integral of  $\delta Q$  approaches zero (by making  $T_H$  approach  $T_L$ ) and the cycle remains reversible, the cyclic integral of  $\delta Q/T$  remains zero. Thus, we conclude that for all reversible heat engine cycles

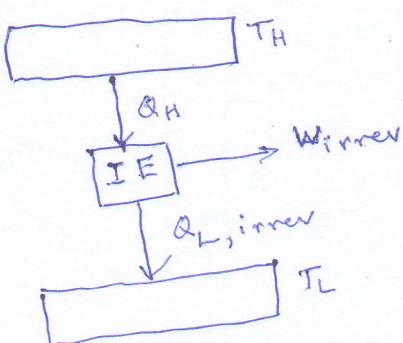
$$\oint \frac{\delta Q}{T} \geq 0$$

and

$$\oint \frac{\delta Q}{T} = 0$$

Heat Engines (Irreversible)  
Now, consider an irreversible cyclic heat engine operating between the same  $T_H$  and  $T_L$  as the reversible engine in Fig. 1 and receiving the same quantity of heat  $Q_H$ . Comparing the irreversible cycle with the reversible one, we conclude from the second law that

$$W_{irrev} < W_{rev}$$



(5)

Since  $Q_H - Q_L = W$  for both the reversible and irreversible cycles, we conclude that

$$Q_H - Q_L, \text{irrev} < Q_H - Q_L, \text{rev}$$

and therefore,

$$Q_L, \text{irrev} > Q_L, \text{rev}$$

Consequently, for the irreversible cyclic engine,

$$\oint \delta Q = Q_H - Q_L, \text{irrev} > 0$$

$$\oint \frac{\delta Q}{T} = \frac{Q_H}{T_H} - \frac{Q_L, \text{irrev}}{T_L}$$

$$= \frac{Q_H}{T_H} - \frac{m Q_L}{T_L} \quad (m > 1)$$

$$= \frac{Q_L}{T_L} - \frac{m Q_L}{T_L}$$

$$= \frac{Q_L}{T_L} (1 - m) < 0$$

(Note:  $\frac{Q_H}{T_H} = \frac{Q_L}{T_L}$  also used here  
since in the irreversible engine  $Q_H, T_H$  are same as in the reversible engine.)

(6)

Suppose that we cause the engine to become more and more irreversible but keep  $Q_H$ ,  $T_H$  and  $T_L$  fixed. Then cyclic integral  $\delta Q$  then approaches zero, and that for  $\delta Q/T$  becomes a progressively large negative value. In the limit, as the work output goes to zero,

$$\oint \delta Q = 0$$

$$\oint \frac{\delta Q}{T} < 0$$

As  $Q_L, \text{irrev}$   
tends to  $Q_H, \text{Wmax}$   
 $m \gg 1$

Thus, we conclude that for all irreversible heat engine cycles

$$\oint \delta Q \neq 0$$

$$\oint \frac{\delta Q}{T} < 0$$

(7)

## Refrigerators

To complete the demonstration of the inequality of Clausius, we must perform similar analyses for both reversible and irreversible refrigeration cycles. For the reversible refrigeration cycle shown in Fig. 2,

$$\oint \delta Q = -Q_H + Q_L < 0$$

$$\text{and } \oint \frac{\delta Q}{T} = -\frac{Q_H}{T_H} + \frac{Q_L}{T_L} = 0$$

$$(\text{Note: } \frac{Q_H}{Q_L} = \frac{T_H}{T_L})$$

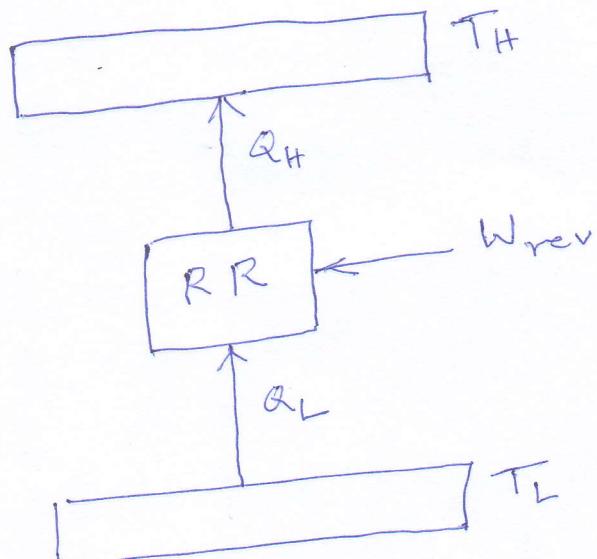


Fig. 2

Reversible refrigeration cycle for demonstration of the inequality of Clausius

As the cyclic integral of  $\delta Q$  approaches zero reversibly ( $T_H$  approaches  $T_L$ ), the cyclic integral of  $\delta Q/T$  remains at zero. In the limit,

$$\oint \delta Q = 0$$

$$\oint \frac{\delta Q}{T} = 0$$

Thus, for all reversible refrigeration cycles,

$$\oint \delta Q \leq 0$$

$$\oint \frac{\delta Q}{T} = 0$$

Finally, let an irreversible cyclic refrigerator operate between temperatures  $T_H$  and  $T_L$  and receive the same amount of heat  $Q_L$  as the reversible refrigerator in Fig. 2.

(9)

From the second law, we conclude that the work input required will be greater for the irreversible refrigerator, or

$$W_{\text{irrev}} > W_{\text{rev}}$$

Since  $Q_H - Q_L = W$  for each cycle, it follows that

$$Q_{H,\text{irrev}} - Q_L > Q_{H,\text{rev}} - Q_L$$

and therefore,

$$Q_{H,\text{irrev}} > Q_{H,\text{rev}}$$

That is, the heat rejected by the irreversible refrigerator to the high-temperature reservoir is greater than the heat rejected by the reversible refrigerator.

(10)

Therefore, for the irreversible refrigerator

$$\oint \delta Q = -Q_{H, \text{irrev}} + Q_L < 0$$

$$\oint \frac{\delta Q}{T} = -\frac{Q_{H, \text{irrev}}}{T_H} + \frac{Q_L}{T_L} < 0$$

As we make this machine progressively more irreversible but keep  $Q_L$ ,  $T_H$  and  $T_L$  constant, the cyclic integrals of  $\delta Q$  and  $\delta Q/T$  both become larger in negative direction. Consequently, a limiting case as the cyclic integral of  $\delta Q$  approaches zero does not exist for the irreversible refrigerator.

for all irreversible refrigeration cycles,  $\oint \delta Q < 0$

$$\oint \frac{\delta Q}{T} < 0$$

Summarizing, we note that in regard to the sign of  $\oint \delta Q$ , we have considered all possible reversible cycles (i.e.  $\oint \delta Q \geq 0$ ), and for each of these reversible cycles,

$$\oint \frac{\delta Q}{T} = 0$$

We have also considered all possible irreversible cycles for the sign of  $\oint \delta Q$  (i.e.  $\oint \delta Q > 0$ ), and for all these irreversible cycles,

$$\oint \frac{\delta Q}{T} < 0$$

Thus, for all cycles we can write

$$\oint \frac{\delta Q}{T} \leq 0$$

where equality holds for reversible cycles and the inequality holds for irreversible cycles. Equation (1) is called the inequality of Clausius.

## Entropy - A Property of a System

Figure 3 shows a system (control mass) undergoing a reversible process from state 1 to state 2 along a path A, and let the cycle be completed along path B, which is also reversible.

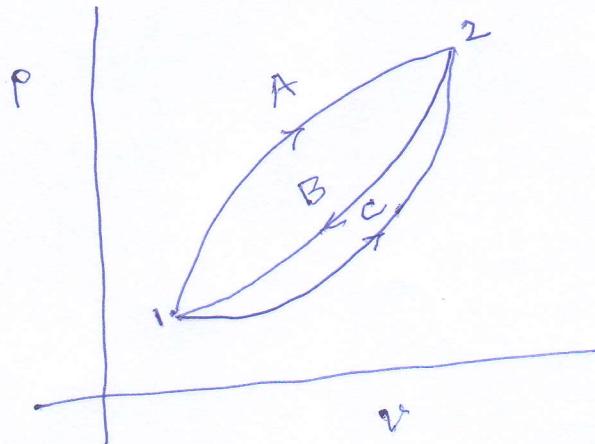


Fig. 3 Two reversible cycles demonstrating that entropy is a property of a substance

Because this is a reversible cycle, we can write

$$\oint \frac{\delta Q}{T} = 0 = \int_1^2 \left( \frac{\delta Q}{T} \right)_A + \int_2^1 \left( \frac{\delta Q}{T} \right)_B \quad (1)$$

Now consider another reversible cycle, which proceeds first along path C and is then completed along path B. For this cycle we can write

$$\oint \frac{\delta Q}{T} = 0 = \int_1^2 \left( \frac{\delta Q}{T} \right)_C + \int_2^1 \left( \frac{\delta Q}{T} \right)_B \quad (2)$$

Subtracting eq. (2) from eq. (1), we have

$$\int_1^2 \left( \frac{\delta Q}{T} \right)_A = \int_1^2 \left( \frac{\delta Q}{T} \right)_C$$

Since  $\oint \frac{\delta Q}{T}$  is the same for all reversible paths between states 1 and 2, we conclude that this quantity is independent of the path and is a function of the end states only. It is therefore called entropy. This property is designated as

S.

(14)

It follows that entropy may be defined as a property of a substance in accordance with the relation

$$dS = \left( \frac{\delta Q}{T} \right)_{rev} \quad (3)$$

Entropy is an extensive property, and the entropy per unit mass is designated as  $s$ . It is important to note that entropy is defined here in terms of a reversible process.

The change in entropy of a system as it undergoes a change of state may be found by integrating

eq. (3). Thus,

$$S_2 - S_1 = \int_1^2 \left( \frac{\delta Q}{T} \right)_{rev} \quad (4)$$

To integrate eq. (4) we must know the relation between  $T$  and  $Q$ .

The important point is that since entropy is a property, the change in the entropy of a substance in going from one state to another is the same for all processes, both reversible and irreversible, between these two states. Equation (4) enables us to find the change in entropy only along a reversible path. However, once the change has been evaluated, this value is the magnitude of all processes between these states.

Also, note that although  $\delta Q$  is an inexact differential,  $(\delta Q/T)_{rev}$  is a thermodynamic property and hence, it is an exact differential. Hence, entropy is a point function.

## The Entropy of a Pure Substance

Entropy is an extensive property. Values of specific entropy (entropy per unit mass) are given in tables of thermodynamic properties in the same manner as specific volume and specific enthalpy. The unit of specific entropy is  $\text{kJ/kg K}$ , and the values are given relative to an arbitrary reference state. In the steam tables the entropy of saturated liquid at  $0.01^\circ\text{C}$  is given the value of zero. For many refrigerants, the entropy of saturated liquid at  $-40^\circ\text{C}$  is assigned the value of zero.

In the saturation region, the entropy may be calculated using the quality. The relations are similar to those for specific volume, internal energy and enthalpy.

$$S = (1-x)S_f + xS_g \quad (5)$$

$$\text{or } S = S_f + xS_{fg}$$

The entropy of a compressed liquid is tabulated in the same manner as the other properties. The properties of a compressed liquid are primarily a function of the temperature and are not greatly different from those for saturated liquid at the same temperature.

The thermodynamic properties of a substance are often shown on a temperature-entropy diagram. The general features of such diagrams are the same for all pure substances. See Fig. 4 showing T-S diagram for a pure substance undergoing phase change.

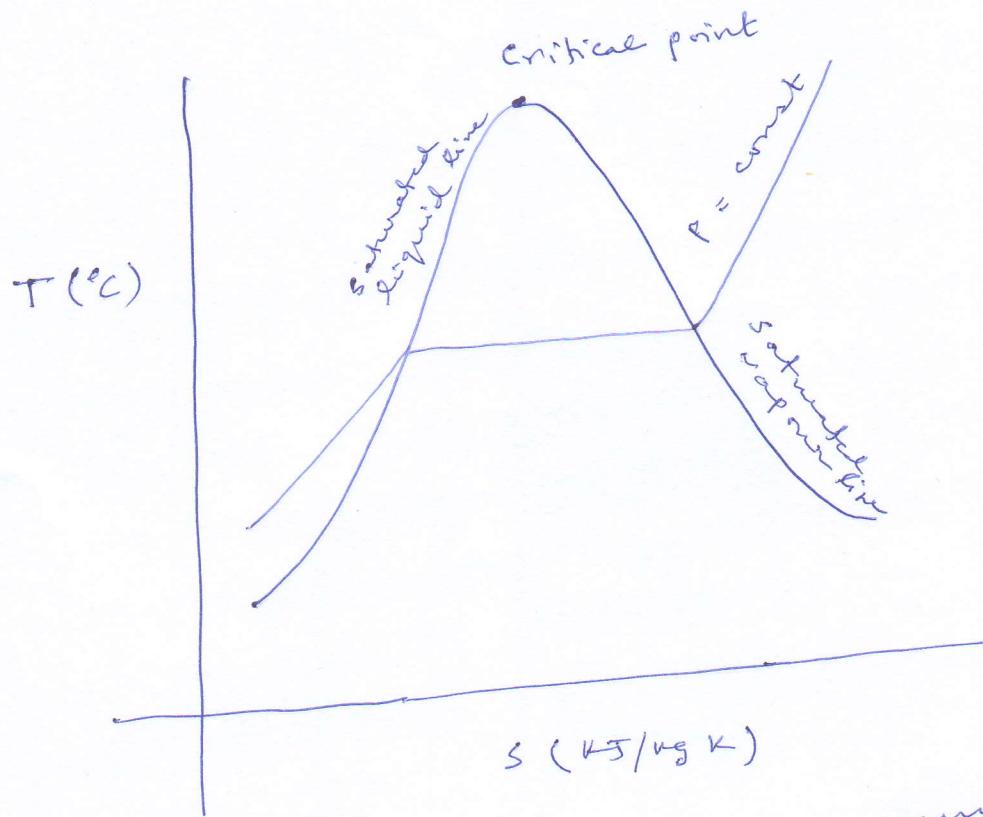


Fig. 4 General T-S diagram  
for a pure substance  
undergoing phase change