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Lecture 13 Entropy

(Sec.3.6 of Hess – 2nd Law of Thermodynamics)

- We have noted in earlier lectures that the work done in a cyclic process is not necessarily equal to 0, in general, i.e.

$$\oint p d\alpha \neq 0 . \tag{13.1}$$

In addition, the amount of work done by the system is equal to the area enclosed by the contour representing the cyclic process in an *α-p* diagram.

- Based on the 1st law of thermodynamics,

$$dq = c_v dT + p d\alpha , \tag{13.2}$$

the amount of heat change for a cyclic process can be obtained by taking a closed line integral of the above equation, Eq. (13.2), then apply (13.1) to obtain

$$\oint dq = \oint p d\alpha \neq 0.$$

- Mathematically, this means dq is not an exact differential. However, if we divide the alternative form of 1st law, $dq = c_p dT - \alpha dp$, by T and apply the equation to the last term, then it becomes

$$\frac{dq}{T} = c_p \frac{dT}{T} - R \frac{dp}{p} , \tag{13.3a}$$

or

$$\frac{dq}{T} = c_p d(\ln T) - R d(\ln p) . \tag{13.3b}$$

Taking closed line integral of (13.3b) gives

$$\oint \frac{dq}{T} = 0 . \tag{13.4}$$

Since both terms on the right-hand side are exact differential.

Therefore, even though *dq* is not an exact differential, *dq/T* is.

- Thus, we may define a new variable s to represent this new exact differential,

$$ds = \frac{dq}{T} \tag{13.5}$$

where s is called entropy, or more precisely specific entropy (i.e., entropy per unit mass).

- Note that the concept of entropy is introduced from mathematical considerations, but as we will see, and its physical meaning is found to be related to the second law of thermodynamics.

- Claim: Entropy is related to potential temperature.
[In fact, it can be stated that an isentropic process is an adiabatic process and vice versa.]

Proof: Taking *ln* (natural log) of potential temperature

$$\theta = T\left(\frac{p_o}{p}\right)^{R/c_p} , \tag{13.6}$$

and multiplying it by c_p leads to

$$c_p \ln\theta = c_p \ln T + R\ln p_o - R\ln p . \tag{13.17}$$

Differentiating the above equation gives

$$c_p d(\ln\theta) = c_p d(\ln T) - R d(\ln p)\,. \qquad (13.18)$$

Because

$$ds = \frac{dq}{T} = c_p d(\ln T) - R d(\ln p) \qquad (13.19)$$

We have

$$ds = c_p d(\ln\theta) \qquad (13.20)$$

or after integration

$$\Delta s = c_p ln\theta + C, \qquad (13.21)$$

where Δs is the change of the entropy between the initial and final states, C is the integration constant.

This means that entropy of a system is related to potential temperature. For adiabatic processes, potential temperature is conserved, therefore, so is entropy. In other words, entropy remains constant along an adiabat (constant θ lines). For this reason, an adiabatic process is also called an isentropic process.

On an α-p diagram, we may draw isotherms (constant T) and adiabats (constant θ). The isotherms are drawn according to the equation of state:

$$p\alpha = RT = const. \qquad (13.22)$$

The adiabats are drawn according to Poisson's equation, e.g.,

$$p\alpha^{\gamma} = const. \qquad (13.23)$$

The right side of (13.23) is related to θ. Note that (13.23) is the same as (3.5.8) in Ch. 10 of the lecture notes. Since $\gamma = c_p/c_v > 1$, *adiabats are steeper than isotherms*.

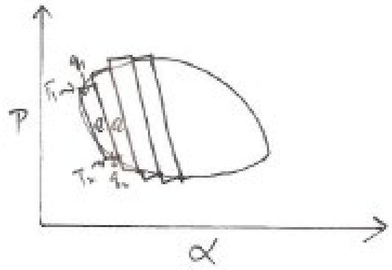
Consider the cyclic process ABCD in a Carnot cycle. In passing reversibly from one adiabat to another along an isotherm, either heat is absorbed or rejected. Since $q_2/q_1 = T_2/T_1$, we have

$$\frac{q_1}{T_1} = \frac{q_2}{T_2} = const.$$

This means that for the Carnot cycle, the ratio q/T is constant. Also, note that the entropy is conserved in the Carnot cycle since it is a cyclic process,

$$\oint ds = \oint \frac{dq}{T} = \frac{q_1}{T_1} - \frac{q_2}{T_2} = 0.$$

Any reversible processes can be considered as being made up of infinite number of Carnot cycle (see figure).



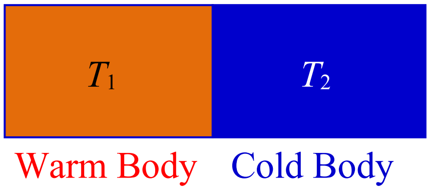
Thus, *entropy does not change for any cyclic reversible processes.*

Most of the real processes are irreversible. Thus, entropy changes.

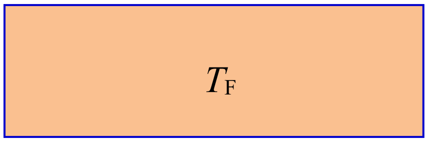
The direction of natural (real) processes is determined by the second law.

For example, let us consider two isolated ideal gases at temperatures of T_1 and T_2, separated by some conductive, expandable material (such as membrane).

Initial state (T_1, T_2)



Final State (T_F)

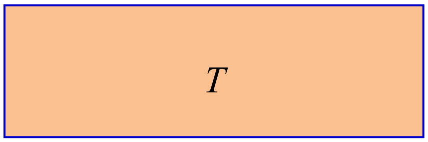


$$T_1 > T_2$$

The first law of thermodynamics, $dq=c_p dT-\alpha dp$, can be applied to individual gas, which leads to $dq=c_p dT$ since p does not change in each part.

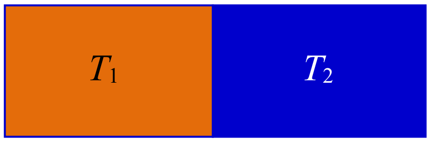
Now assume the reversible situation was tried:

Initial state



$$T = (T_1 + T_2)/2$$

Final State



The above process will not occur, yet it does not violate the first law. Thus, the first law does not tell us anything about the direction in which a natural process will take place.

Question: *Does entropy increase or decrease in a natural (irreversible) process?*

The answer is that the entropy can only be increased in a real (irreversible) processes. This can be proved more rigorously; however, we will simply use the above example to show it.

If T_1=290 K and T_2=300 K, then $\overline{T}$=295 K. Therefore,

$$ds = dq/T = c_p dT/T, \text{ since } dq=c_p dT-\alpha dp=c_p dT.$$

This leads to

$$\Delta s = c_p ln\left[\frac{T_f}{T_i}\right]$$

For the first process:

for gas 1:

$$\Delta s = c_p \ln\left(\frac{295}{290}\right)=17.163,$$

for gas 2:

$$\Delta s = c_p \ln\left(\frac{295}{300}\right)=-16.874.$$

Thus, the sum of entropy is .287 J/kg-K, which is greater than 0.

Suppose the second process did take place, then

for gas 1:

$$\Delta s = c_p \ln\left(\frac{290}{295}\right) = -17.163,$$

for gas 2:

$$\Delta s = c_p \ln\left(\frac{300}{295}\right) = 16.867.$$

The sum of is Δs=-.296, which is less than 0.

The second law of thermodynamics may also be stated as:

Process in which the entropy of an isolated system would decrease does not occur.

Thus, we have

- Reversible processes: $\Delta s = 0$ (s is constant)
- Irreversible (natural) processes: $\Delta s > 0$ (s increases)

- Impossible processes: $\Delta s < 0$ (s decreases)