Lecture 13 Entropy
(Ref.: Sec.3.6 of Hess – 2nd Law of Thermodynamics)

➢ We have noted in earlier lectures that

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

in general. Also note that the amount of work done by the system is equal to the area enclosed by the contour representing the cyclic process in a α-p diagram.

➢ From the 1st law of thermodynamics,

$$dq = c_v dT + p d\alpha ,$$

The amount of heat change for a cyclic process is

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

➢ 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, then

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

or

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

This implies that

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

Therefore although dq is not an exact differential, dq/T is.

➤ Since ds is an exact differential, we may define a new variable s as

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

where s is called entropy, or more precisely specific entropy.

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

➤ Claim: An isentropic process is adiabatic and reversible.

Proof: From the definition of potential temperature

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

Taking *ln* and multiplying c_p of the above equation leads to

$$c_p \ln \theta = c_p \ln T + R \ln p_o - R \ln p$$

Differentiating the above equation gives

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

Because

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

we have

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

Or after integration

$$\Delta s = c_p \ln\theta + C,$$

where C is a constant resulted from integration of the equation above.

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:

$$p\alpha = RT = const.$$

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

$$p\alpha^{\gamma} = const.$$

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, heat is absorbed or rejected. Since $q_2/q_1 = T_2/T_1$,

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

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,

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

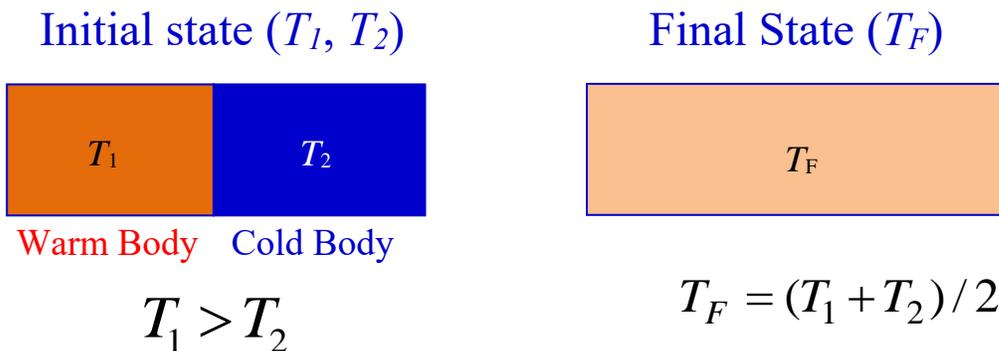Any reversible processes can be considered as being made up of infinite number of Carnot cycle (see figure).
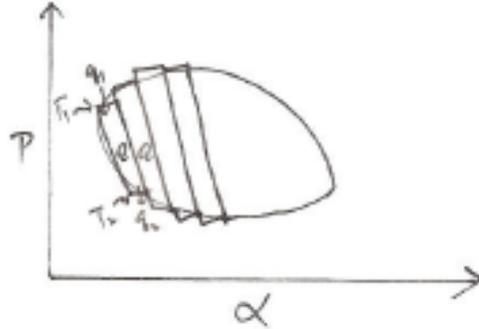
Thus, *entropy does not change for any cyclic reversible processes*.

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

T_F

Warm Body   Cold Body

$$T_1 > T_2$$

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

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The thermodynamic equation $dq = c_p dT - \alpha dp$ 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 in the 2nd process:

Initial state

Final State

T

T_1 T_2

$T = (T_1 + T_2)/2$
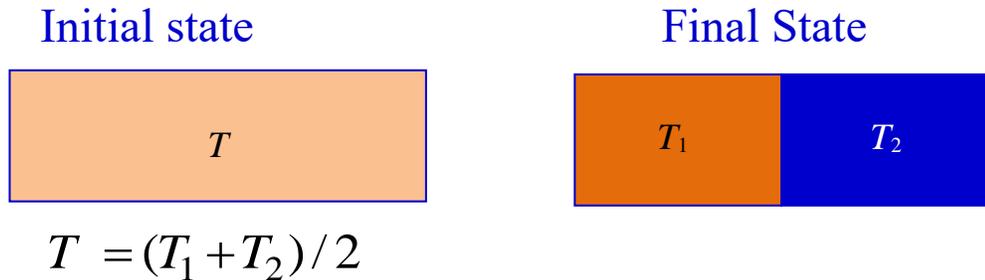
The above process will not occur, yet it does not violate the first law. Thus, the first law does not tell us anything about the direction in which a natural process will take place.

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

Answer: 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,

$ds = dq/T = c_p dT/T$, 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:

$$\Delta s_1 = c_p ln \left(\frac{295}{290} \right) = 17.163$$

For gas 2:

$$\Delta s_2 = c_p ln \left(\frac{295}{300} \right) = -16.874$$

Thus, the sum of entropy is 0.287 J/kg-K > 0.

Suppose the second process did take place, then

For gas 1:

$$\Delta s_1 = c_p ln \left(\frac{290}{295} \right) = -17.163$$

For gas 2:

$$\Delta s_2 = c_p ln \left(\frac{300}{295} \right) = 16.874$$

The sum of is Δs = -.289 J/kg-K < 0.

The second law of thermodynamics may also be stated as:

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

Thus, we have

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

Mathematically, we may express the second law of thermodynamics as that for an isolated system,

$$ds = \frac{dq}{T} \text{ for a reversible process}$$

$$ds > \frac{dq}{T} \text{ for an irreversible process.}$$

Or, for any processes in an isolated system, we have

$$ds \geq \frac{dq}{T}.$$

Since $ds=dq/T$, we may also write the second law as

$$ds \geq du + pd\alpha.$$