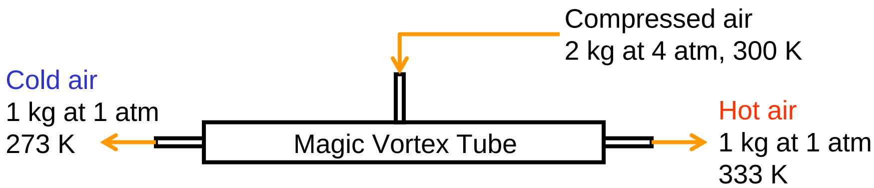
VI. Entropy

A. Introduction

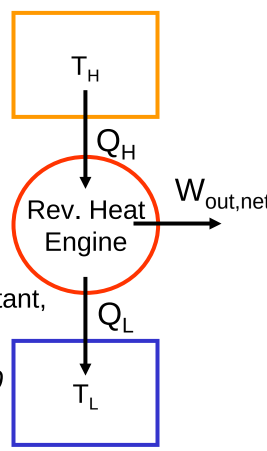
1. The first law: energy cannot be created or destroyed
2. The second law: certain processes do occur and certain processes don't
3. The magic vortex tube. Will it work or won't it?



We need a quantitative answer. This suggests that we are looking for a property (like T, P, u, or V). How can we find such a property?

VI. Entropy

B. The Clausius Inequality



For a reversible heat engine, (6-16), is

$$\frac{Q_L}{Q_H} = \frac{T_L}{T_H} \quad \text{and} \quad \frac{|Q_H|}{T_H} = \frac{|Q_L|}{T_L} \quad or \quad \oint \frac{\delta Q_{rev}}{T} = 0$$

For an irreversible heat engine, with Q_H constant,

$$Q_{L,irrev} > Q_{L,rev} \quad or \quad \frac{|Q_H|}{T_H} < \frac{|Q_L|}{T_L} \quad or \quad \oint \frac{\delta Q_{irrev}}{T} < 0$$

In general, we have the Clausius inequality,

$$\oint \frac{\delta Q}{T} \le 0 \qquad (7\text{-}1)$$

VI. Entropy

C. A New Property Called Entropy

The equality in (7-1) holds for a reversible process, the inequality for an irreversible one.

$$\oint \frac{\delta Q}{T} \le 0 \qquad (7\text{-}1)$$

We know that the cyclic integral of a property is zero. Clausius recognized that the equality in (7-1) implies the existence of a new property, entropy, which we will give the symbol S.

$$\oint \frac{\delta Q_{rev}}{T} = 0 \text{ or } \oint dS = 0 \quad \text{and} \quad \boxed{dS = \frac{\delta Q_{rev}}{T} \left(\frac{kJ}{K}\right)} \qquad (7\text{-}4)$$

Equation 7-4 can also be written as $\frac{dS}{dt} = \frac{\dot{Q}_{rev}}{T} \left(\frac{kJ}{s\,K}\right)$

lesson 16

VI. Entropy

Equation 7-4 can be used to calculate changes in entropy for an internally reversible, isothermal heat transfer process. As previously noted, isothermal heat transfer processes are internally reversible and (7-4) can be integrated to give

$$\boxed{\Delta S = S_2 - S_1 = \int_1^2 \frac{1}{T} \delta Q_{rev} = \frac{1}{T_0} \int_1^2 \delta Q_{rev} = \frac{Q}{T_0}} \qquad (7\text{-}6)$$

Example: 1 kg of sat. liquid water at 100ºC and 1 atm is heated at constant temperature and pressure until it completely vaporizes. Find the change in entropy of the water.

$$\Delta s = \frac{Q}{T_0} = \frac{2257.0 \text{ kJ/kg}}{(100 + 273.15) \text{ K}} = 6.04 \frac{\text{kJ}}{\text{kg K}}$$

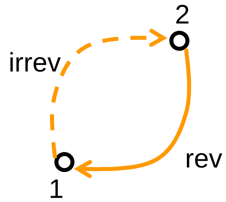
Note that ΔS is positive because heat is added to the system.

lesson 16

VI. Entropy

D. The Increase of Entropy Principle

1. We know that energy is conserved. What can we say about entropy? Consider the cycle sketched below. It consists of a reversible and an irreversible process.



We apply the Clausius inequality (7-1) to this cycle.

$$\int_2^1 \frac{\delta Q_{rev}}{T} + \int_1^2 \frac{\delta Q_{irrev}}{T} \leq 0$$

Because $\delta Q_{rev}/T$ is a perfect differential or property, the first integral is the entropy change, $S_1 - S_2$, and the inequality becomes

$$S_2 - S_1 \geq \int_1^2 \frac{\delta Q}{T}$$

VI. Entropy

D. Entropy balance for a closed system

$$S_2 - S_1 \geq \int_1^2 \frac{\delta Q}{T}$$

Reminder: T is the absolute T.

The equality only holds for a reversible process. In differential form we have

$$\frac{dS}{dt} \geq \frac{\dot{Q}}{T} \qquad \text{or} \qquad dS \geq \frac{\delta Q}{T} \qquad (7\text{-}8)$$

Conclusion: the entropy change for a closed system, undergoing an irreversible change, is always greater than the entropy transfer due to heat transfer. In other words, <u>entropy is generated during an irreversible process</u>. We will denote the amount of entropy generated by S_{gen} (kJ/K) and the rate of entropy generation by $\dot{S}_{gen}$.

VI. Entropy

D. Entropy balance for a closed system

We can use the entropy generation term, S_{gen}, to eliminate the inequality

$$S_2 - S_1 \geq \int_1^2 \frac{\delta Q}{T} \Rightarrow \boxed{\Delta S_{sys} = S_2 - S_1 = \int_1^2 \frac{\delta Q}{T} + S_{gen}} \qquad (7\text{-}9)$$

where

$$\begin{array}{l} S_{gen} > 0 \ \text{irreversible process} \\ S_{gen} = 0 \ \text{reversible process} \\ S_{gen} < 0 \ \text{impossible process} \end{array}$$

Equation 7-9 can also be written in rate form as

$$\boxed{\frac{dS_{sys}}{dt} = \sum_j \frac{\dot{Q}_j}{T_j} + \dot{S}_{gen}} \qquad \text{See (7-83)}$$

VI. Entropy

E. The Increase of Entropy Principle

If a system is isolated, $\delta Q = 0$, and

$$\Delta S = S_2 - S_1 \geq \int_1^2 \frac{\delta Q}{T} \Rightarrow \boxed{\Delta S_{isolated} \geq 0} \qquad (7\text{-}10)$$

This known as the increase of entropy principle.

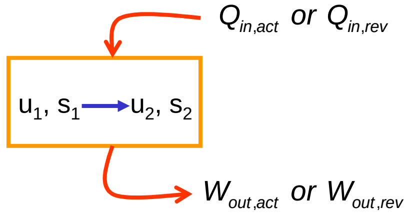
Because a system and its surroundings can be considered an isolated system, we can also write

$$\boxed{S_{gen} = \Delta S_{total} = \Delta S_{sys} + \Delta S_{surr} \geq 0} \qquad (7\text{-}11)$$

VI. Entropy

F. Reversible and Actual Work and the Generation of Entropy

Consider two closed systems, each undergoing a process, one reversible and the other irreversible (actual), with the same initial and final conditions.



Energy balances: $m(u_1 - u_2) = W_{out,act} - Q_{in,act} = W_{out,rev} - Q_{in,rev}$

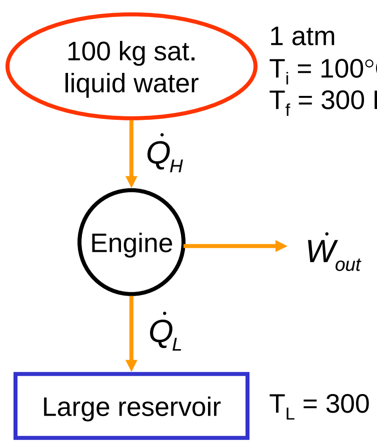
Entropy balances: $Q_{in,act} = mT(s_2 - s_1) - TS_{gen}$ and $Q_{in,rev} = mT(s_2 - s_1)$

Conclusion: $\therefore W_{out,rev} = W_{out,act} + TS_{gen}$

TS_{gen} represents the work that is "lost" due to irreversibilities.

VI. Entropy

G. Example – Maximum work obtainable from a finite, hot reservoir



1 atm
T_i = 100°C = 373 K
T_f = 300 K

T_L = 300 K

We want to find the maximum work that we can extract from the hot water. Its initial and final temperatures are T_i and T_f. The 300 K reservoir is so large that its temperature is constant.

VI. Entropy

G. Example – Maximum work obtainable from a finite, hot reservoir

The total work produced is $W_{out} = \int_0^t \dot{W}_{out} dt$ where t is time.

A Carnot or reversible heat engine will produce the maximum amount of work:

$$\eta = \frac{\dot{W}_{out}}{\dot{Q}_H} = 1 - \frac{T_L}{T} \text{ and } \dot{W}_{out} = \eta \dot{Q}_H$$

An energy balance on the hot water gives

$$\frac{dU}{dt} = -\dot{Q}_H = mc\frac{dT}{dt}$$

Our equation for maximum work produced is

$$W_{out} = \int_0^t \dot{W}_{out} dt = \int_0^t \eta \dot{Q}_H dt = -mc\int_0^t \left(1 - \frac{T_L}{T}\right)\frac{dT}{dt}dt = -mc\int_{T_i}^{T_f}\left(1 - \frac{T_L}{T}\right)dT$$

VI. Entropy

G. Example – Maximum work obtainable from a finite, hot reservoir

Performing the integration and inserting numerical values gives

$$W_{out} = mc\left[\left(T_i - T_f\right) + T_L \ln\frac{T_f}{T_i}\right]$$

$$W_{out} = 100kg\left(4.2\frac{kJ}{kgK}\right)\left[73.15 + 300\ln\frac{300}{373}\right]K = 3230\ kJ$$

VI. Entropy

H. Summary

1. Entropy is not conserved. $S_{gen} > 0$ for all real processes.
2. Isolated systems will only change in a direction that results in an increase in entropy.
3. Irreversibilities result in the generation of entropy. Highly irreversible processes have high rates of entropy generation. High rates of entropy generation usually degrade the performance of a process.
4. Is it possible or not? We need to be able to calculate the entropy changes of substances to answer this question.