Lecture 29 – What is entropy?

Purdue ME 200, Thermodynamics I

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Outline

Problem statement
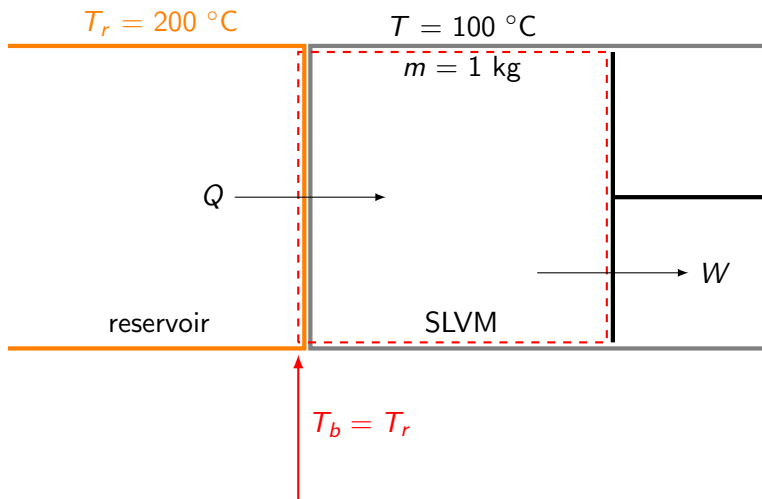
A closed insulated stationary piston-cylinder device initially contains 1 kg of saturated liquid water at 100 °C. It receives energy via heat transfer from a reservoir at 200 °C until the water is saturated vapor. Find the entropy generated over the process.

System diagram

Given and find

- **given:**
  - $m = 1$ kg
  - constant $T = 373$ K, $T_r = 473$ K
  - state 1 is saturated liquid
  - state 2 is saturated vapor
- **find:**
  - entropy generated over the process, σ

Assumptions and basic equations

- **assume:**
  - $\diamond$ closed (constant mass)
  - $\diamond$ insulated (no heat transfer other than reservoir $\rightarrow$ system)
  - $\diamond$ stationary (constant PE and KE)
  - $\diamond$ phase change (constant temperature and pressure)
  - $\diamond$ no entropy generation within reservoir
  - $\diamond$ system contains boundary layer ($T_b = T_r$)
- **basic equations:**
  - $\diamond$ 1st law for closed stationary systems: $\Delta U = Q - W$
  - $\diamond$ boundary work at constant pressure: $W = \int p \, dV = p \Delta V$
  - $\diamond$ 2nd law for closed systems: $\Delta S = \int \delta Q / T_b + \sigma$

Solution

- 2nd law for closed system in isothermal process with $T_b = T_r$:

$$\Delta S = \frac{Q}{T_r} + \sigma \implies \sigma = \Delta S - \frac{Q}{T_r}$$

- 1st law for closed stationary system at constant pressure:

$$\Delta U = Q - p\Delta V \implies Q = \Delta U + p\Delta V = \Delta H$$
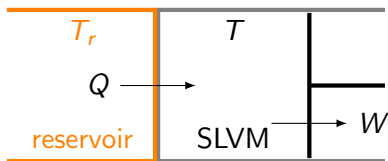
- water transitions from SL to SV, so

$$\begin{aligned}
Q &= \Delta H = m(h_v - h_\ell) \\
&= (1\text{kg})(2675.6 - 419.17)\text{kJ/kg} \\
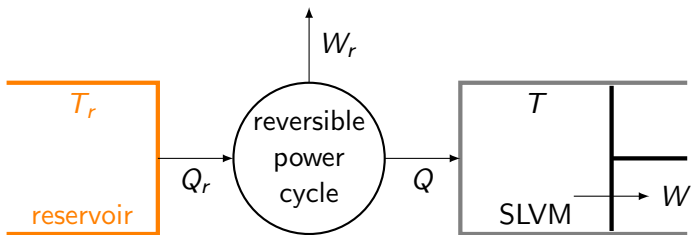&= 2256.43\text{kJ}
\end{aligned}$$

Solution (continued)

- entropy generation is

$$\sigma = \Delta S - \frac{Q}{T_r} = m(s_v - s_\ell) - \frac{Q}{T_r}$$
$$= (1\text{kg})(7.3541 - 1.3072)\frac{\text{kJ}}{\text{kg K}} - \frac{2256.43\text{kJ}}{473.15\text{K}}$$
$$= 1.2780\text{kJ/K}$$

Reversible power cycle work

- in this example, heat transfers naturally via conduction
- what if we used a reversible power cycle instead?

Reversible power cycle work (continued)

- the cycle efficiency would be $\eta = W_r/Q_r = 1 - T/T_r$, so

$$W_r = \eta Q_r = \left(1 - \frac{T}{T_r}\right) Q_r$$

- but $Q/Q_r = T/T_r$ since the cycle is reversible, so

$$\begin{aligned}
W_r &= \left(1 - \frac{T}{T_r}\right) \frac{Q T_r}{T} = \left(\frac{T_r}{T} - 1\right) Q \\
&= \left(\frac{473.15\text{K}}{373.15\text{K}} - 1\right) (2256.43\text{kJ}) \\
&= 604.7\text{kJ}
\end{aligned}$$

- curiously. . .

$$T_r \sigma = (473.15\text{K})(1.2780\text{kJ/K}) = 604.7\text{kJ} = W_r \quad ?!?$$

Heat transfer, entropy, and lost work

- more generally, suppose δQ_c transfers from T_h to T_c
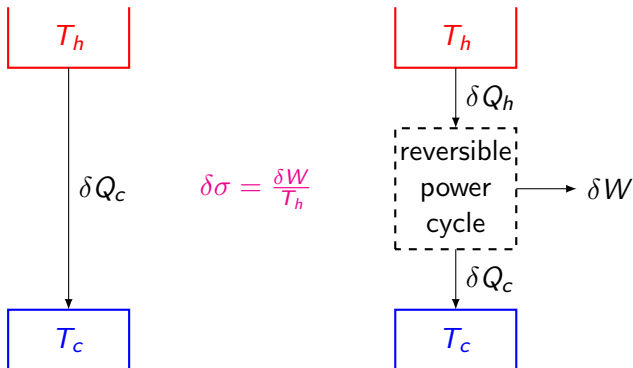- the entropy generated by this heat transfer is

$$\delta\sigma = \delta Q_c \left(\frac{1}{T_c} - \frac{1}{T_h} \right)$$

- imagine a reversible power cycle that absorbs δQ_h, emits δQ_c
- (thermodynamic temperature scale $\implies \delta Q_h/\delta Q_c = T_h/T_c$)
- the work that this imaginary, reversible cycle would do is

$$\begin{aligned}
\delta W &= \delta Q_h - \delta Q_c = \delta Q_c \left(\frac{\delta Q_h}{\delta Q_c} - 1 \right) \\
&= \delta Q_c \left(\frac{T_h}{T_c} - 1 \right) = T_h \delta Q_c \left(\frac{1}{T_c} - \frac{1}{T_h} \right) \\
&= T_h \delta\sigma
\end{aligned}$$

Summary

The entropy generated by heat transfer through a finite temperature difference can be viewed as the 'lost work' that a reversible power cycle would have produced when delivering the same amount of heat (divided by the hot reservoir temperature).

Outline
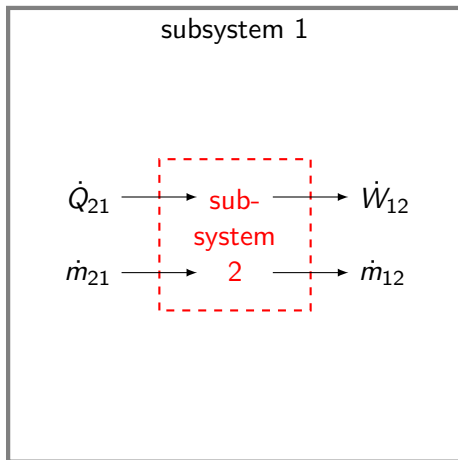
Reminder: isolated systems

- an **open system** or **control volume** is a region of space
- a **closed system** or **control mass** is a collection of matter
- an **isolated system** does not interact with the surroundings

	open	closed	isolated
energy crosses boundary?	yes	yes	no
matter crosses boundary?	yes	no	no

An isolated system

- despite internal flows, the combined system is isolated

Nondecrease of entropy for isolated systems

- for isolated systems, the entropy balance in rate form is

$$\frac{\mathrm{d}S}{\mathrm{d}t} = \sum_{j=1}^{N_{\mathrm{res}}} \frac{\dot{Q}_j}{T_j} + \sum_{i=1}^{N_{\mathrm{in}}} \dot{m}_i^{\mathrm{in}} s_i^{\mathrm{in}} - \sum_{k=1}^{N_{\mathrm{out}}} \dot{m}_k^{\mathrm{out}} s_k^{\mathrm{out}} + \dot{\sigma}$$

- internal entropy generation always satisfies $\dot{\sigma} \geq 0$
- so for isolated systems, entropy never decreases:

$$\frac{\mathrm{d}S}{\mathrm{d}t} = \dot{\sigma} \geq 0$$

Equilibrium states maximize entropy

- during any real (irreversible) process, $\dot{\sigma} > 0$
- so an isolated system's entropy
  - ◇ increases ($dS/dt > 0$) during any real process
  - ◇ only stabilizes ($dS/dt = 0$) when all processes stop
- therefore, entropy reaches a maximum in equilibrium

Outline

Microscopic arrangements and thermodynamic states

- the systems in this class are made up of many tiny things
  - ⋄ molecules
  - ⋄ atoms
  - ⋄ protons, neutrons, electrons
  - ⋄ subatomic particles, . . .
- each tiny thing can be arranged in many ways
  - ⋄ many different x, y and z positions
  - ⋄ many different x, y and z velocities
- so the overall system can be arranged in many **many** ways
- but its thermo state is just 2 independent intensive properties
- $\implies$ any thermo state has many possible microscopic arrangements

Entropy and probability

- for any given thermodynamic state, define
    - Ω, the number of its possible microscopic arrangements
    - p_i, the probability of arrangement i, for each $i = 1, \ldots, \Omega$
    - (so $p_1 \geq 0, \ldots, p_\Omega \geq 0$ and $p_1 + \cdots + p_\Omega = 1$)
- the entropy associated with the probabilities $p_1, \ldots, p_\Omega$ is

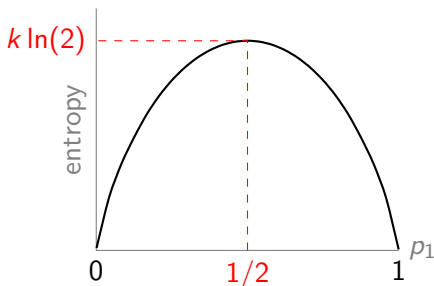$$-k \sum_{i=1}^{\Omega} p_i \ln(p_i)$$

- $k = 1.381 \times 10^{-23}$ J/K is the Boltzmann constant

The simplest example (basically a biased coin flip)

- suppose there are $\Omega = 2$ possible microscopic arrangements
- then $p_2 = 1 - p_1$, and the entropy associated with p_1 and p_2 is

$$-k \sum_{i=1}^{\Omega} p_i \ln(p_i) = -k[p_1 \ln(p_1) + p_2 \ln(p_2)]$$

$$= -k[p_1 \ln(p_1) + (1 - p_1) \ln(1 - p_1)]$$

- entropy reaches a maximum at $k \ln(2)$ when $p_1 = p_2 = 1/2$

Boltzmann's entropy formula

- recall that entropy reaches a maximum in equilibrium
- it turns out that for any Ω, entropy reaches a maximum when

$$p_1 = \cdots = p_\Omega = \frac{1}{\Omega}$$

- the entropy associated with these special $p_1, \ldots, p_\Omega$ is

$$-k \sum_{i=1}^{\Omega} \frac{1}{\Omega} \ln\left(\frac{1}{\Omega}\right) = -k\Omega\left[\frac{1}{\Omega} \ln\left(\frac{1}{\Omega}\right)\right] = -k[\ln(1) - \ln(\Omega)]$$

- this is Boltzmann's famous formula for entropy in equilibrium:

$$S = k \ln(\Omega)$$