Applications of the Second Law

(Lecture 7)

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Advanced Thermodynamics (M2794.007900)

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Entropy Changes in Reversible Processes

- To evaluate the entropy changes in reversible processes, we combine the first and the second laws.

$$du = \delta q_r - \delta w_r \;\rightarrow\; \delta q_r = du + \delta w_r = du + Pdv$$

$$\rightarrow \frac{\delta q_r}{T} = \frac{du}{T} + \frac{P}{T}dv = ds \text{ (by Clausius' definition)}$$

- For some special cases,

  1. Adiabatic process: $\delta q_r = 0, ds = 0$, $s = \text{const}$

     (reversible adiabatic process = isentropic process)

  2. Isothermal process:

$$s_2 - s_1 = \int_1^2 \frac{\delta q_r}{T} = \frac{q_r}{T}$$

Entropy Changes in Reversible Processes

- Continue on.

3. Isothermal and isobaric change of phase:

$$s_2 - s_1 = \int_1^2 \frac{\delta q_r}{T} = \frac{q_r}{T} = \frac{l}{T}$$

$$\text{where } \delta q_r = du + Pdv = dh - vdP = dh$$

$$q_r = h_2 - h_1 = l \text{ (latent heat)}$$

4. Isochoric process:

$$s_2 - s_1 = \int_1^2 \left(\frac{du}{T} + \frac{P}{T} dv \right) = \int_1^2 \frac{du}{T} = \int_1^2 c_v \frac{dT}{T}$$

$$\text{if } c_v = \text{const}, \; s_2 - s_1 = c_v \ln \frac{T_2}{T_1}$$

$$\boxed{du = \left(\frac{\partial u}{\partial v} \right)_T \cancel{dv} + \left(\frac{\partial u}{\partial T} \right)_v dT = c_v dT}$$

Entropy Changes in Reversible Processes

➔ Continue on.

5. Isobaric process:

$$\delta q_r = du + Pdv = dh - vdP$$

$$\frac{\delta q_r}{T} = \frac{dh}{T} - \frac{v}{T}dP = ds$$

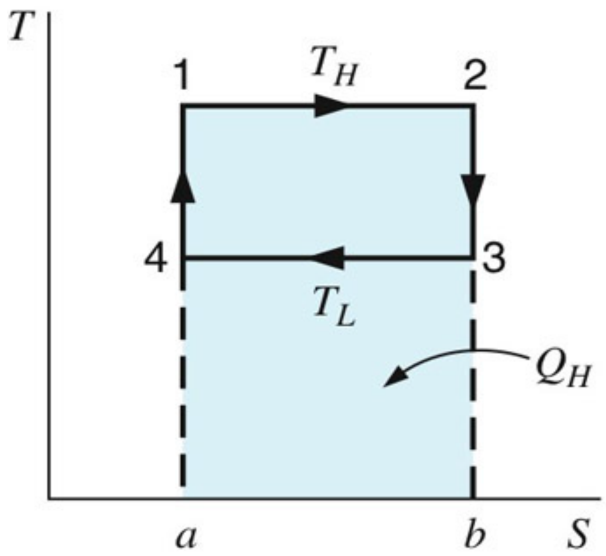
$$s_2 - s_1 = \int_1^2 \left(\frac{dh}{T} - \frac{v}{T}dP \right) = \int_1^2 \frac{dh}{T} = \int_1^2 c_P \frac{dT}{T}$$

$$\boxed{dh = \left(\frac{\partial h}{\partial P}\right)_T \cancel{dP} + \left(\frac{\partial h}{\partial T}\right)_P dT = c_P dT}$$

$$\text{if} \ \ c_P = \text{const}, \ \ s_2 - s_1 = c_P \ln \frac{T_2}{T_1}$$

Temperature-Entropy (T-S) Diagrams

- For a Carnot cycle, we can draw T-S diagram for the processes.
  - 1 -> 2: rev. isothermal Q_H (heat addition)
  - 2 -> 3: rev. adiabatic Working Fluid : $T_H \rightarrow T_L$
  - 3 -> 4: rev. isothermal Q_L (heat rejection)
  - 4 -> 1: rev. adiabatic Working Fluid : $T_L \rightarrow T_H$



$$S_2 - S_1 = \int_1^2 \left(\frac{\delta Q_{in}}{T} \right)_{rev} = \frac{Q_{in,1\to 2}}{T_H} = \frac{Q_H}{T_H} \quad (Q_H > 0)$$

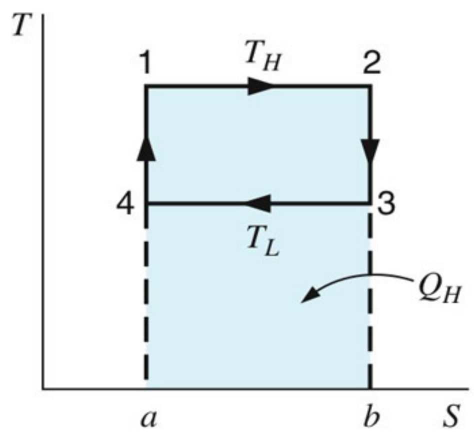
$$S_3 - S_2 = 0$$

$$S_4 - S_3 = \int_3^4 \left(\frac{\delta Q_{in}}{T} \right)_{rev} = \frac{Q_{in,3\to 4}}{T_L} = -\frac{Q_L}{T_L} \quad (Q_L > 0)$$

$$S_1 - S_4 = 0$$

Temperature-Entropy (T-S) Diagrams

- The area under the REVERSIBLE process in T-s diagram represents the heat transfer during the process.



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

$$\delta Q_{rev} = TdS$$

$$\int \delta Q_{rev} = \int TdS$$

$$Q_H = T_H(S_2 - S_1): \text{ area } 1\text{-}2\text{-b-a-}1$$

$$Q_L = -T_L(S_4 - S_3): \text{ area } 3\text{-}4\text{-a-b-}3$$

$$W_{net} = Q_H - Q_L: \text{ area } 1\text{-}2\text{-}3\text{-}4\text{-}1$$

$$\Rightarrow \boxed{\eta_{th} = \frac{W_{net}}{Q_H} = \frac{\text{area } 1\text{-}2\text{-}3\text{-}4\text{-}1}{\text{area } 1\text{-}2\text{-b-a-}1}}$$

Entropy Generation associated with Heat Transfer

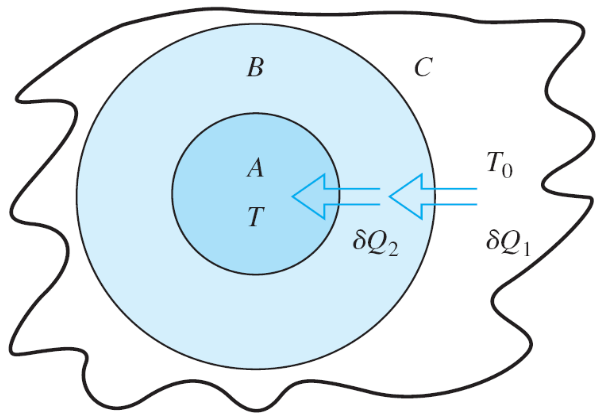
Consider a heat transfer process between a finite temperature difference.

For the boundary B with no change of state in time,

Energy Eq.: $$dE = 0 = \delta Q_1 - \delta Q_2 \Rightarrow \delta Q_1 = \delta Q_2 = \delta Q$$

Entropy Eq.: $$dS = 0 = \frac{\delta Q}{T_0} - \frac{\delta Q}{T} + \delta S_{\text{gen } B}$$

$$\boxed{\delta S_{\text{gen } B} = \frac{\delta Q}{T} - \frac{\delta Q}{T_0} = \delta Q\left(\frac{1}{T} - \frac{1}{T_0}\right) \geq 0}$$



A: system at T
B: boundary at steady state
C: surrounding at T_0

The second law tells $\delta S_{gen} > 0$ for an irreversible process:

If $T_0 > T$, $\delta Q > 0$.

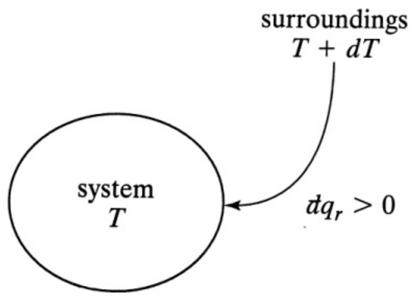
If $T_0 < T$, $\delta Q < 0$.

The second law tells $\delta S_{gen} = 0$ for a reversible process:

If $\delta Q \neq 0$, $T_0 = T$.

Entropy Changes of the Surroundings for a Reversible Process

➔ In a reversible process in which there is a reversible flow of heat between a system and its surroundings, temperatures of both are essentially equal, differing only by *dT* (→ 0).



$$ds_{universe} = ds_{system} + ds_{surroundings}$$

Here,

$$ds_{surroundings} = \left(\frac{-dq_r}{T+dT}\right) \approx \left(\frac{-dq_r}{T}\right) = -\left(\frac{dq_r}{T}\right) = -ds_{system}$$

$$\rightarrow ds_{universe} = 0$$

"In any reversible process, the entropy change of the universe is always zero. Any change in entropy of the system will be accompanied by an entropy change in the surroundings equal in magnitude but opposite in sign."

Entropy Change for an Ideal Gas

- For the same initial and final equilibrium states, you can use Gibbs equation for entropy change in both reversible and irreversible processes.

$$ds = \frac{du}{T} + \frac{P}{T}dv$$

For ideal gas, $du = c_v dT$ and $\frac{P}{T} = \frac{R}{v}$

Then, $ds = c_v \frac{dT}{T} + R\frac{dv}{v}$

$$s_2 - s_1 = \int_{T_1}^{T_2} c_v \frac{dT}{T} + \int_{v_1}^{v_2} R\frac{dv}{v} = c_v \ln\frac{T_2}{T_1} + R\ln\frac{v_2}{v_1}$$

If c_v is constant

Entropy Change for an Ideal Gas

- The final equation implies the followings (which holds for all solids, liquids, and gases, in general):

$$s_2 - s_1 = c_v \ln \frac{T_2}{T_1} + R \ln \frac{v_2}{v_1}$$

1. The higher the temperature rise, the greater the increase in entropy
2. The larger the volume expansion, the greater the increase in entropy

- For example, for isentropic expansion of a gas (*ds*=0),

gas expansion → temperature decrease → entropy decrease

gas expansion → volume increase → entropy increase

cancel each other

TdS Equations

➔ Gibbs equation can be expressed as a function of different variables:

$$\beta \equiv \frac{1}{v}\left(\frac{\partial v}{\partial T}\right)_P \quad \text{(expansivity)}$$

$$\kappa \equiv -\frac{1}{v}\left(\frac{\partial v}{\partial P}\right)_T \quad \text{(isothermal compressibility)}$$

$$Tds = du + Pdv = dh - vdP$$

$$Tds = c_v dT + T\left(\frac{\partial P}{\partial T}\right)_v dv = c_v dT + \frac{T\beta}{\kappa}dv, \quad s = s(T,v)$$

$$Tds = c_P dT - T\left(\frac{\partial v}{\partial T}\right)_P dP = c_P dT - Tv\beta dP, \quad s = s(T,P)$$

$$Tds = c_P\left(\frac{\partial T}{\partial v}\right)_P dv + c_v\left(\frac{\partial T}{\partial P}\right)_v dP = \frac{c_P}{\beta v}dv + \frac{c_v\kappa}{\beta}dP, \quad s = s(v,P)$$

1. It can be used to calculate the heat transfer during a reversible process.
2. Entropy can be obtained by dividing by T and integrating. (EOS for entropy!)
3. Reversible heat flow or entropy is expressed in terms of measurable properties.
4. The equations provide relations between pairs of coordinates in an isentropic process.

TdS Equations

➔ Continue on. Let's derive the following *TdS* equation.

$$\boxed{Tds = c_P dT - T\left(\frac{\partial v}{\partial T}\right)_P dP = c_P dT - Tv\beta dP, \quad s = s(T, P)}$$

Gibbs equation becomes,

$$Tds = dh - vdP = \overset{c_P}{\left(\frac{\partial h}{\partial T}\right)_P} dT + \left(\frac{\partial h}{\partial P}\right)_T dP - vdP$$

$$\rightarrow \quad ds = \frac{1}{T}\left(\frac{\partial h}{\partial T}\right)_P dT + \frac{1}{T}\left[\left(\frac{\partial h}{\partial P}\right)_T - v\right] dP$$

Since *dS* is exact different,

$$\frac{\partial}{\partial P}\left[\frac{1}{T}\left(\frac{\partial h}{\partial T}\right)_P\right]_T = \frac{\partial}{\partial T}\left\{\frac{1}{T}\left[\left(\frac{\partial h}{\partial P}\right)_T - v\right]\right\}_P$$

After carrying out the differentiation, the equation becomes,

$$\left(\frac{\partial h}{\partial P}\right)_T = -T\left(\frac{\partial v}{\partial T}\right)_P + v = -Tv\beta + v$$

Entropy Change in Irreversible Processes

- To calculate the entropy change in irreversible process, we choose any convenient reversible process having the same initial and final states, and evaluate the associated entropy change. (entropy is state variable!)

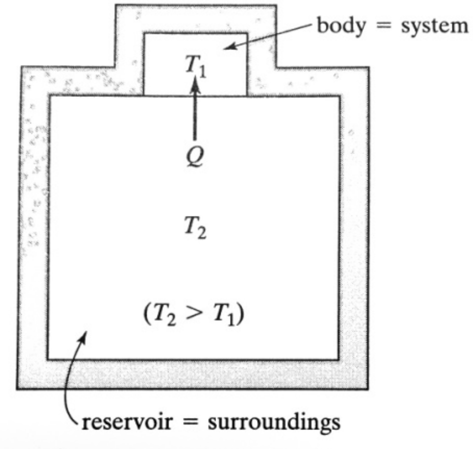
- (First example) Thermal equilibrium with a heat reservoir at constant *P*

  irreversibility – finite temperature difference between the body and the reservoir

  initial state – body at T_1, reservoir at T_2

  final state – body at T_2, reservoir at T_2

  choice of reversible path – there are series of thermal reservoir between T_1 and T_2, which conduct the heat to the body reversibly.



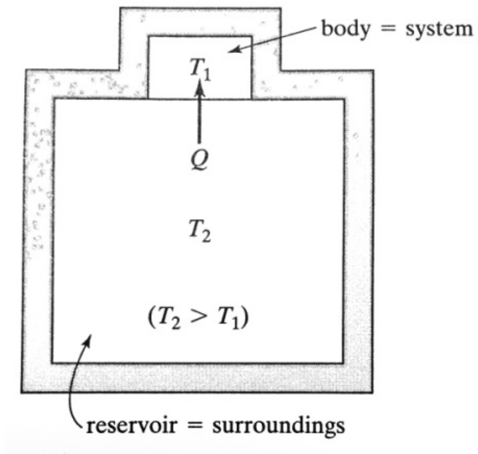
Entropy Change in Irreversible Processes

- Continue on.

The first and second laws for the body in a reversible process become,

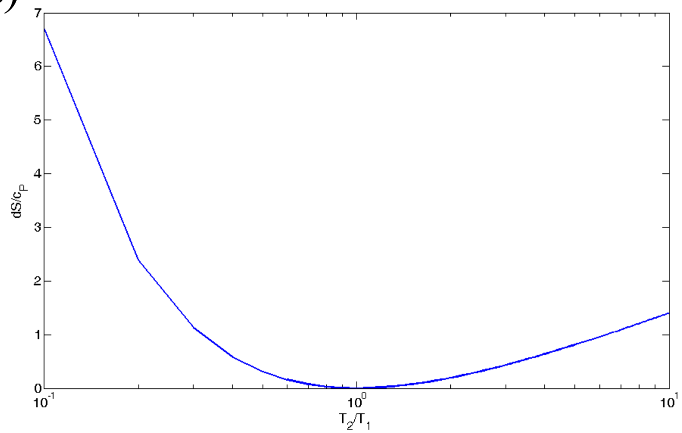
$$\delta q_r = Tds = c_P dT - vdP = c_P dT \quad (\because \text{ isobaric})$$

$$ds = \frac{\delta q_r}{T} = c_P \frac{dT}{T}$$



Then, $$(\Delta s)_{body} = c_P \ln\left(\frac{T_2}{T_1}\right) \quad (\text{when } c_P : \text{const})$$

$$(\Delta s)_{reservoir} = -\frac{|q_r|}{T_2} = -c_P \frac{T_2 - T_1}{T_2} \quad (\text{when } c_P : \text{const})$$



Finally, $$(\Delta s)_{universe} = (\Delta s)_{body} + (\Delta s)_{reservoir}$$

$$= c_P \left[\ln\left(\frac{T_2}{T_1}\right) - \frac{T_2 - T_1}{T_2} \right]$$

Entropy Change in Irreversible Processes

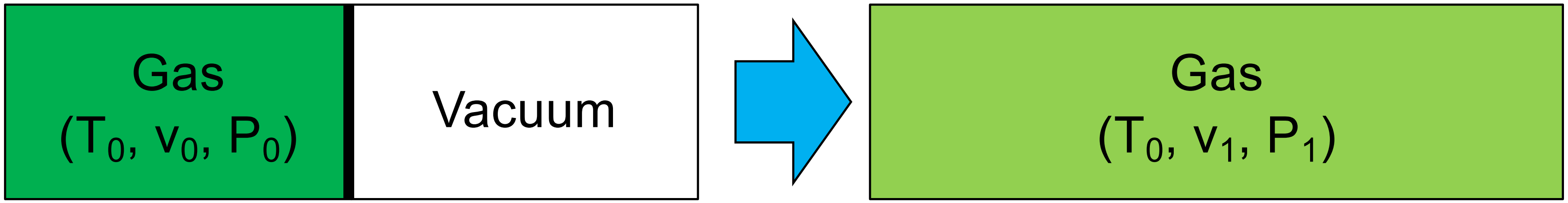
- (Second example) Free expansion of an ideal gas

irreversibility – rapid expansion of a gas

initial state – gas at T_0, v_0, P_0

final state – gas at T_0, v_1, P_1

choice of reversible path – reversible, isothermal expansion from v_0 to v_1



Applying the Gibbs equation to a reversible path of an ideal gas,

$$ds = c_v \frac{dT}{T} + R\frac{dv}{v} = R\frac{dv}{v} \quad (\because \text{isothermal})$$

$$(\Delta s)_{system} = R \ln\left(\frac{v_1}{v_0}\right) = (\Delta s)_{universe} \quad (> 0)$$

Entropy Change in Irreversible Processes

- Continue on.

In a free expansion, we know that

$$\delta w = 0,\ \delta u = 0,\ \text{and}\ \delta q = 0$$

In a reversible, isothermal expansion,

$$w_r = RT_0 \ln\left(\frac{v_1}{v_0}\right),\ \Delta u = 0,\ \text{and}\ q_r = w_r$$

$$\Delta s = \frac{q_r}{T_0} = R\ln\left(\frac{v_1}{v_0}\right)$$

In a free expansion, the entropy change is as if work were done in a reversible, isothermal process between the same initial and final thermodynamic states.

Entropy Change for a Liquid or Solid

➔ Let's calculate entropy change for a liquid or solid. We assume

$$v \approx v_0 \text{ (const.) and } \beta, c_P \sim \text{const.}$$

$$\beta \equiv \frac{1}{v}\left(\frac{\partial v}{\partial T}\right)_P \text{ (expansivity)}$$

By using Gibbs equation in terms of T, P (from previous slide),

$$Tds = c_P dT - Tv\beta dP \approx c_P dT - Tv_0 \beta dP$$

$$\rightarrow \quad ds = c_P \frac{dT}{T} - v_0 \beta dP$$

Integrating,

$$s - s_0 = c_P \, ln\left(\frac{T}{T_0}\right) - v_0 \beta \left(P - P_0\right)$$

1. Entropy increases with temperature
2. Entropy decreases with pressure