Second Law

1 Overview

Intuition tells us that some processes naturally occur in one direction only, but the First Law could not explain this physics. Based on the experiments, we find that the systems always start from organized motion to disorganized motion spontaneously, and the "quality" of energy has been degraded. This is the motivation for **entropy** and **Second Law**.

2 Entropy

We use **entropy** (S) to measure the degree of disorder of a system. Some characteristics of entropy:

1. Will increase if energy becomes more disordered.
2. Can be produced but not destroyed.
3. Its production decreases the availability of energy doing something "useful"
4. **Entropy is an extensive property**
5. Unit of entropy is J/K

3 Entropy Production

Nothing can be transferred to or from the isolated system. Therefore, recall PICO:

$$\text{Input} = \text{Output} = 0,\ \text{Production} = \text{Change} \tag{1}$$

If we define the entropy production as P_s, then:

$$\delta P_s = dS \tag{2}$$

$$P_s = S_{final} - S_{initial} = \Delta S \tag{3}$$

$$P_s \geq 0 \tag{4}$$

Which means the entropy of universe will tend to increase (assume isolated).

4 Reversibility

For an isolated system, based on the entropy production, we can categorize processes into 3 kinds:

1. $P_s < 0$: **impossible process** because the entropy can only be produced but not destroyed.
2. $P_s = 0$: **reversible process**, process does not change entropy or disorder, so the energy flow can be reversed.
3. $P_s > 0$: **irreversible process**, entropy increases. If we want to return to original state, we have to decrease entropy, which requires entropy destruction.

Notice that reversible process is an idealization. It is nearly impossible to do anything without entropy production, but still useful to imagine reversible processes.

5 Entropy Transfer

5.1 Heat Transfer

If we consider a **closed** system consisting of ice and water in a rigid container. Initially the container includes mostly ice, later it includes mostly liquid. **Liquid has more randomness in molecules**, so $S_2 > S_1$. If we assume this process is done slowly, at quasi-equilibrium, and no friction, then $P_s = 0$. So how does the entropy increase?

Now go back to the phase change process. If the ice wants to become water, it needs to absorb heat from the environment. **Heat transfer leads to entropy transfer.** In other words, heat transfer is transfer of ”randomness” and ”disorder” from one system to another system, because the increase of temperature will increase the molecular randomness.

Therefore, we define Q_{in} let entropy transfer into system, Q_{out} let entropy transfer out of system.

5.2 Work

However, **work represents transfer of organized energy/motion, but does not transfer entropy.**

Some remarks:

1. **Do work reversibly:** no entropy is produced
2. **Do work irreversibly:** entropy is produced
3. **Do heat transfer irreversibly:** which means it can both **transfer and produce entropy.**

6 Second Law Derivation

6.1 Problem Setup

By accepting the existence of entropy as a **thermodynamic property**, we can express entropy as a function of 2 independent variables:

$$S = S(U, V) \tag{5}$$

Then we imagine two systems, A and B, separated by rigid wall with constant volume, only interaction is heat transfer δQ.

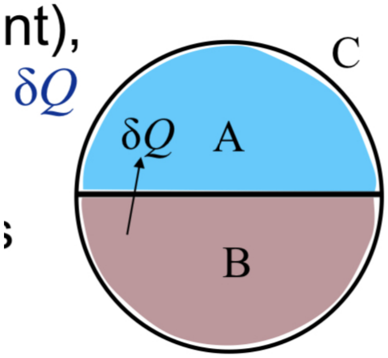

Figure 1: A, B, C System

As shown in the picture, the combined system C is isolated, so the total energy U_c is fixed. Also, because this process is spontaneous, system becomes more disorder, therefore based on second law:

$$S_{C,final} - S_{C,initial} = P_s \geq 0 \tag{6}$$

Assume A, B not in equilibrium with each other, but they are in equilibrium individually. Because entropy is extensive property, so we have:

$$S_C = S_A(U_A, V_A) + S_B(U_B, V_B) \tag{7}$$

$$U_C = U_A + U_B = \mu U_C + (1 - \mu)U_C \tag{8}$$

Where μ is the fraction of U_C that is U_A. When the system reaches the most disorder state, it will stop and stay at equilibrium. Therefore, S_C **will increase until equilibrium achieved** ($S_{C,max}$). Since V_A, V_B and U_C fixed, so the only free variable is μ. So maximizing S_C means:

$$\frac{dS_C}{d\mu} = 0 \tag{9}$$

6.2 Thermodynamic Definition of Temperature

Take derivative of S_C respect to μ:

$$\frac{dS_C}{d\mu} = (\frac{\partial S_A}{\partial U_A})|_{V_A}\frac{dU_A}{d\mu} + (\frac{\partial S_B}{\partial U_B})|_{V_B}\frac{dU_B}{d\mu} \tag{10}$$

Recall that:

$$U_A = \mu U_C \tag{11}$$

$$U_B = (1-\mu)U_C \tag{12}$$

Therefore:

$$\frac{dS_C}{d\mu} = (\frac{\partial S_A}{\partial U_A})|_{V_A}U_C + (\frac{\partial S_B}{\partial U_B})|_{V_B}(-U_C)) \tag{13}$$

We know the condition for A and B reach equilibrium is:

$$\frac{dS_C}{d\mu} = 0 \tag{14}$$

So:

$$\frac{\partial S_A}{\partial U_A}|_{V_A} = \frac{\partial S_A}{\partial U_B}|_{V_B} \tag{15}$$

So two systems are in thermal equilibrium (only heat transfer) when they have same $(\partial S/\partial U)_V$, **but same T also implies thermal equilibrium**, therefore we let:

$$T = \frac{1}{(\partial S/\partial U)_V} \tag{16}$$

The reason for 1/ is to be consistent with the energy flow direction, as shown below:

$$dS_C = (\frac{1}{T_A} - \frac{1}{T_B})U_C d\mu \tag{17}$$

If $T_B > T_A$, then we have:

$$(\frac{1}{T_A} - \frac{1}{T_B}) > 0 \tag{18}$$

Based on the second law, we know the entropy will keep increasing, so $dS_C > 0$, then we must have $d\mu > 0$.

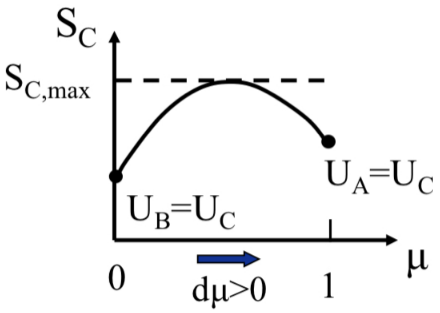

Figure 2: Energy Flow

From the graph, we can see that in this case energy flow is B to A, which is consistent with $T_B > T_A$.

6.3 Thermodynamic Definition of Pressure

The derivation process is similar with temperature. This time, we assume isolated system C composed of two closed subsystems A and B, **which can exchange energy by heat and mechanical work.**

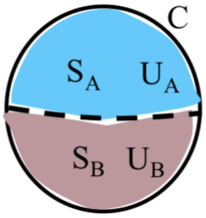

Figure 3: Thermodynamic Definition of Pressure

$$S_C = S_A(U_A, V_A) + S_B(U_B, V_B) \tag{19}$$

At this time, we could not assume the volume is constant anymore, so:

$$U_C = U_A + U_B, V_C = V_A + V_B \tag{20}$$

Because U, V are independent variables, we need to define **two progress variables** (μ_U, μ_V). At equilibrium, we need:

$$\frac{dS_C}{d\mu_U} = 0, \frac{dS_C}{d\mu_V} = 0 \tag{21}$$

μ_U derivative is the same as last section, which can show the thermodynamic definition of temperature. Now we focus on μ_V:

$$\frac{dS_C}{d\mu_V} = (\frac{\partial S_A}{\partial V_A})|_{U_A}\frac{dV_A}{d\mu_V} + (\frac{\partial S_B}{\partial V_B})|_{U_B}\frac{dV_B}{d\mu_V} = 0 \tag{22}$$

For mechanical equilibrium:

$$(\frac{\partial S_A}{\partial V_A})_{U_A} = (\frac{\partial S_B}{\partial V_B})_{U_B} \tag{23}$$

Then we have the thermodynamic definiton of pressure:

$$\frac{p}{T} = (\frac{\partial S}{\partial V})_U \tag{24}$$

Check the unit:

$$\frac{N/m^2}{K} = \frac{J/m^3}{K} = \frac{J/K}{m^3} \tag{25}$$

6.4 Derivation

To derive the complete second law, we first need to idealize the model using **Thermal Energy Reservoir (TER)**:

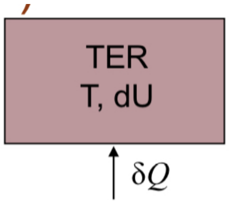

Figure 4: TER

This is control mass with **fixed volume, only exchanges energy as Q, uniform and constant T.**

Since fixed volume:

$$(\frac{\partial S}{\partial U})_V = \frac{dS}{dU} = \frac{1}{T} \tag{26}$$

Based on first law, there is no work here, so:

$$dU = \delta Q \tag{27}$$

$$\frac{dS}{dU} = \frac{dS}{\delta Q} = \frac{1}{T} \tag{28}$$

$$dS_{TER} = \frac{\delta Q}{T} \tag{29}$$

Now if we consider two interacting TERs at two Ts, isolated from surroundings:

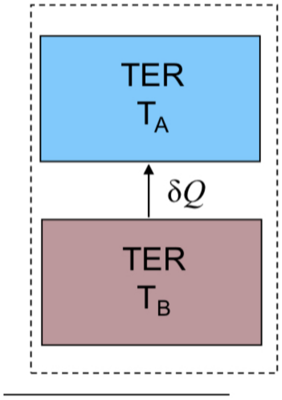

Figure 5: TER Flow

Based on the second law:

$$\delta P_S = d(S_A + S_B) = \delta Q(1/T_A - 1/T_B) > 0 \tag{30}$$

Therefore, **entropy production can result from Q across finite temperature difference.**

Now, we define **Mechanical Energy Reservoir (MER)** as a control mass with no microscopic disorder (no entropy), can only exchange energy as reversible work. Consider CM interacting with a TER and a MER, together they form isolated system:

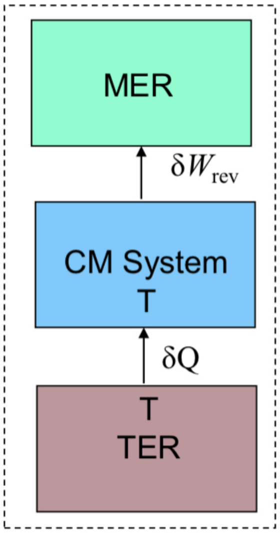

Figure 6: TER, CM, MER

Then:

$$\delta P_S = dS_{\text{isolated}} = d(S_{TER} + S_{MER} + S_{CM}) = -\frac{\delta Q}{T} + dS_{CM} \tag{31}$$

Where $S_{MER} = 0$. Finally we have:

$$dS_{CM} = \frac{\delta Q}{T} + \delta P_s \tag{32}$$

6.5 Application

From the equation above, based on PICO, we know:

$$\text{Change of Entropy} = \text{Entropy Transfer} + \text{Entropy Production} \tag{33}$$

In other form, we have:

$$S_2 - S_1 = \int_1^2 \frac{\delta Q}{T} + P_{S_{1,2}} \tag{34}$$

Some observations:

1. There are two ways to change the entropy of a fixed mass system, either by **transferring it** through heat transfer or **producing it** through irreversible process.
2. Even though the entropy production must be greater than zero, **the entropy of a CM can increase or decrease**. If we want to increase entropy, we need heat transfer in (heating) or irreversible process. If we want to decrease entropy, we need heat transfer out (cooling) **but must exceed any production**.
3. Entropy of a control mass can also remain the same during the process, **which is called isentropic process**. This could be achieved by **no production and no transfer (reversible + adiabatic)**, or **cooling perfectly balances production.**

So how can we get maximum work output? Let's assume a simple case:

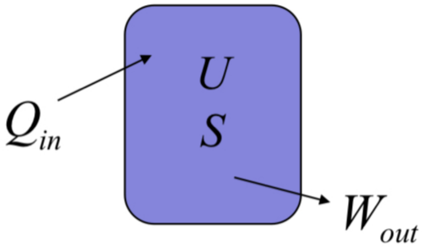

Figure 7: Maximum Work

First Law:

$$dU = \delta Q_{in} - \delta W_{out} \tag{35}$$

Second Law:

$$dS = \delta Q_{in}/T + \delta P_s \tag{36}$$

Then:

$$dU = T(dS - \delta P_s) - \delta W_{out} \tag{37}$$

$$\delta W_{out} = T(dS - \delta P_s) - dU \tag{38}$$

For a given state change, we know ΔU_{12} and ΔS_{12} will be fixed, therefore we will **get maximum work output when $P_s = 0$, which means reversible process.**

7 Open System Second Law

Recall the Reynolds Transport Theorem:

$$\frac{dB}{dt}|_{CM} = \frac{d}{dt}\int_{CV} \rho\beta dV + \int_{CS} \rho\beta(\underline{\boldsymbol{u}} \cdot \underline{\hat{\boldsymbol{n}}})dA \tag{39}$$

Now in this case:

$$B = S, \beta = s \tag{40}$$

Therefore:

$$\frac{dS}{dt}|_{CM} = \frac{d}{dt}\int_{CV} \rho s dV + \int_{CS} \rho s(\underline{\boldsymbol{u}} \cdot \underline{\hat{\boldsymbol{n}}})dA \tag{41}$$

Recall the closed system second law:

$$dS = \int_1^2 \frac{\delta Q}{T} + P_S \tag{42}$$

Rearrange:

$$\dot{P}_S + \int_{CS} \frac{\delta \dot{Q}''_{in}}{T} dA = \frac{d}{dt}\int_{CV} \rho s dV + \int_{CS} \rho s(\underline{\boldsymbol{u}} \cdot \underline{\hat{\boldsymbol{n}}})dA \tag{43}$$

In PICO:

$$P + I = C + O \tag{44}$$

If we assume the flow is steady:

$$\dot{P}_s + \sum_{\text{Surfaces}} \frac{\dot{Q}_{in}}{T_{surface}} + \sum_{inlets} \dot{m}s = \sum_{outlets} \dot{m}s \tag{45}$$

If we assume constant mass flow rate:

$$\frac{\dot{P}_s}{\dot{m}} + \frac{q}{T_o} = s_{out} - s_{in} \tag{46}$$

Recall the **First Law for Open System**:

$$q + w_u = h_{out} - h_{in} \tag{47}$$

Combine these two equations and rearrange:

$$w_u = (h_{out} - h_{in}) - T_{wall}(s_{out} - s_{in}) - \dot{P}_s/\dot{m} \tag{48}$$

Based on second law:

$$\dot{P}_s \geq 0 \tag{49}$$

Therefore, we have:

$$w_{u,min,in} = (h_{out} - h_{in}) - T_{wall}(s_{out} - s_{in}) \tag{50}$$

$$w_{u,max,out} = (h_{in} - h_{out}) - T_{wall}(s_{in} - s_{out}) \tag{51}$$

Recall the closed system result:

$$\delta W_{out} = T(dS - \delta P_s) - dU \tag{52}$$

Therefore, **enthalpy replaces internal energy for flowing system.**