Physical Chemistry
for Energy Engineering
(10ʳʰ: 2018/10/15)

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Course schedule (tentative)

Lecture #	Date	Contents
1	3-Sep	Introduction
2	5-Sep	1. Thermodynamics: Basic concepts of thermodynamics
3	10-Sep	1. Thermodynamics: The first law of thermodynamics
4	12-Sep	1. Thermodynamics: Thermodynamic process and cycle
5	17-Sep	1. Thermodynamics: The second and third laws of thermodynamics-1
6	19-Sep	1. Thermodynamics: The second and third laws of thermodynamics-2
	24-Sep	No lecture (holiday)
	26-Sep	No lecture (holiday)
7	1-Oct	1. Thermodynamics: The second and third laws of thermodynamics-3 (1. Equation of state of gas will be covered in future)
	3-Oct	No lecture (holiday)
8	8-Oct	Answer of homework-1
9	10-Oct	Exam-01 (2 hour)
10	15-Oct	2. Introduction to equilibrium theory
11	17-Oct	2. Free energy-1
12	22-Oct	2. Free energy-2
13	24-Oct	2. Calculation of thermodynamic quantities
	29-Oct	No lecture
	31-Oct	

Contents of today

\<Today's class\>

✓ In practical situation, we often want to know: "what products (material) we can obtain after mixing multiple raw materials and then waiting for a sufficiently long time", or "how system evolves and what the final state when waiting for a sufficiently long time".

   ✓ Here, "a sufficiently long time" means that the time is long enough to achieve an equilibrium state, and "the final state" is an equilibrium state.

Index

Spontaneous process

Equilibrium

time

Sufficiently long time

Insufficient
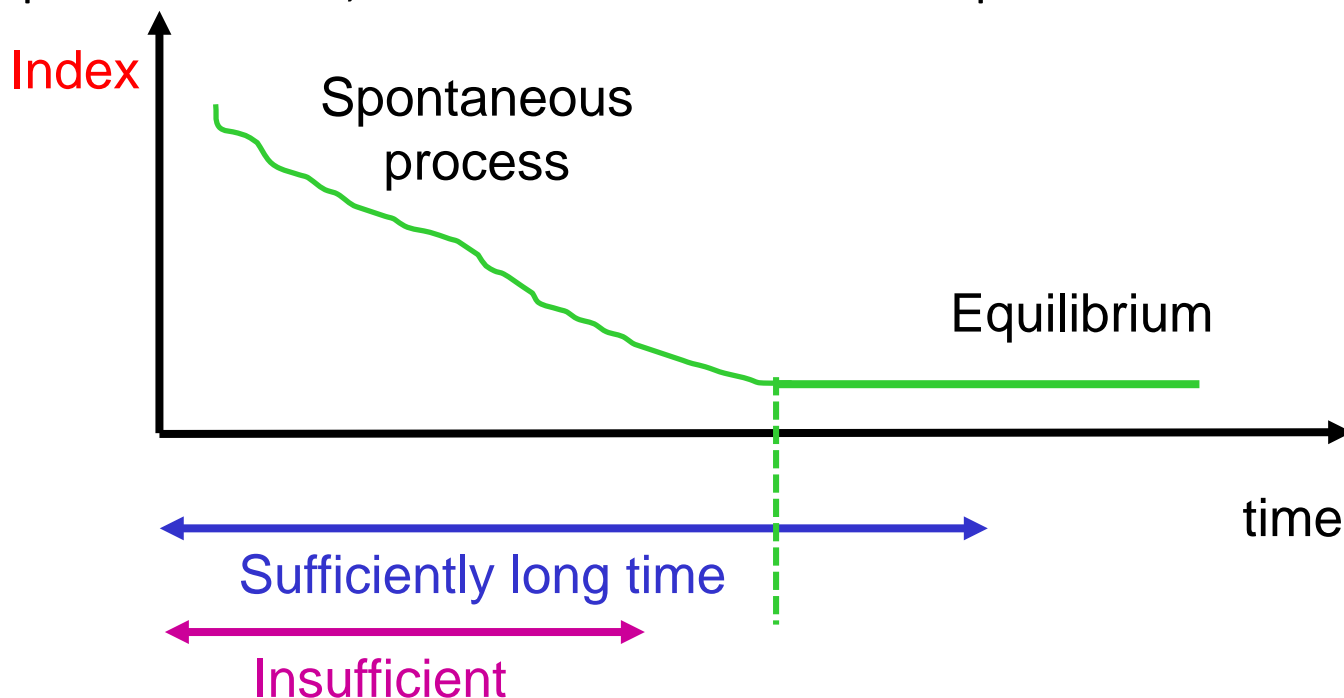
Entropy and free energy are good indexes to predict the equilibrium state and the direction of system evolution (direction of reaction).

Free energy as well as entropy is a good index to predict the equilibrium state and the direction of reaction.

- ✓ For an isolated system

    → Entropy: S

- ✓ For a system of constant T and constant V

    → Helmholtz (free) energy: A

    $$A = U - TS$$

- ✓ For a system of constant T and constant P
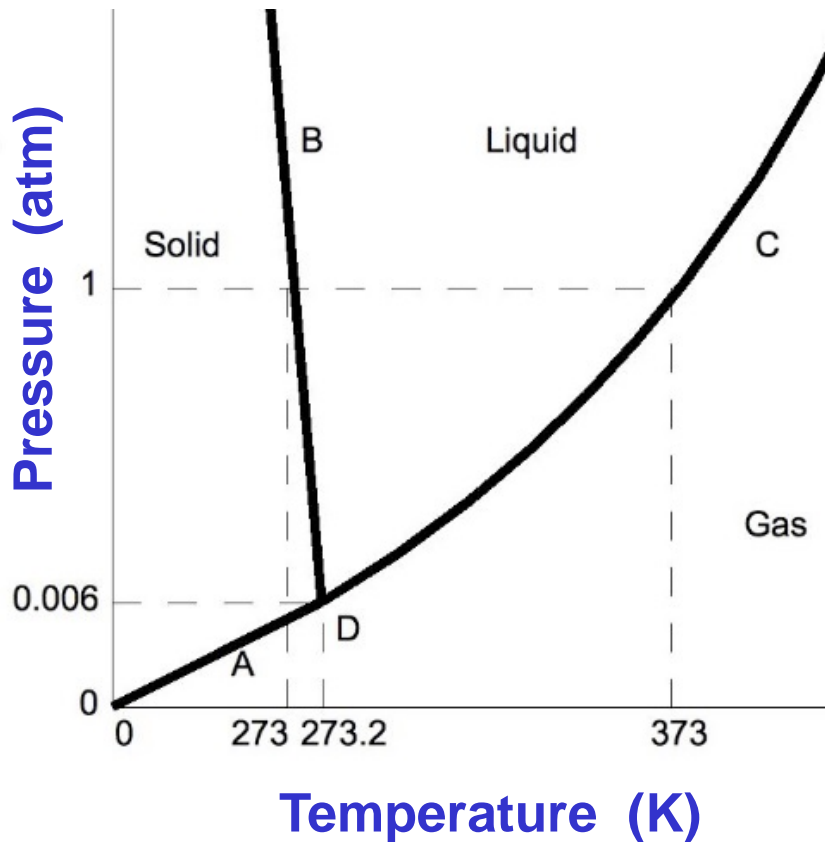
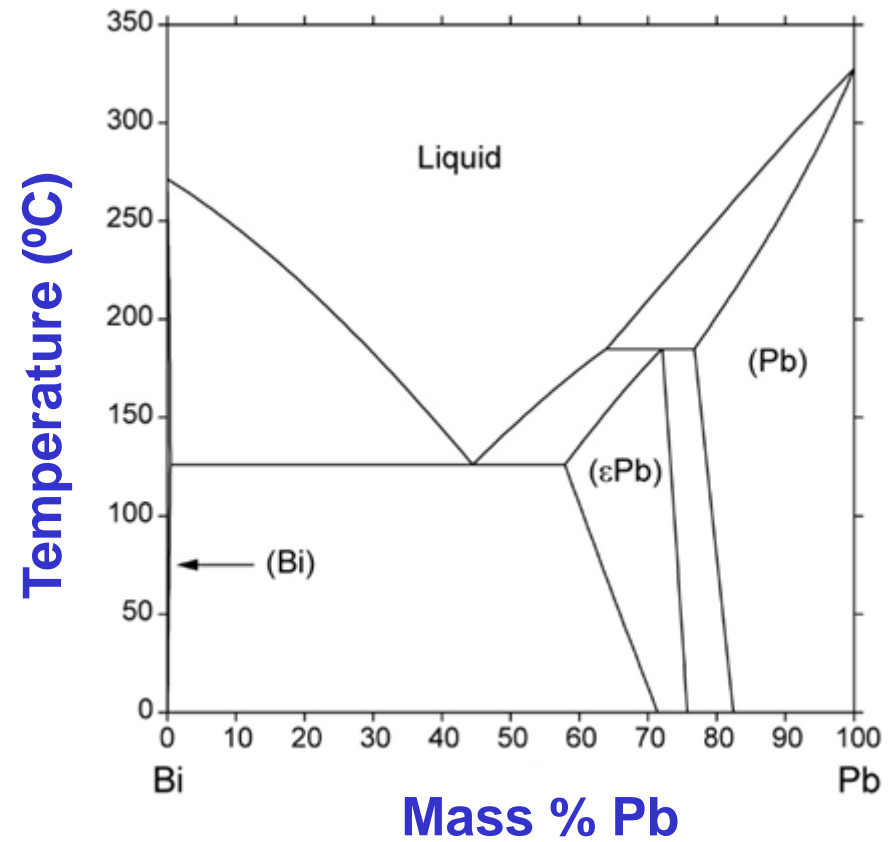   → Gibbs (free) energy: G

    $$G = H - TS = A + PV$$

We are going to apply equilibrium theory to two cases:
(1) phase equilibrium & (2) chemical equilibrium.

H$_2$O (single component)

Pb-Bi (two components, binary)

*(left) http://chemwiki.ucdavis.edu/Physical_Chemistry
*(right) http://www.metallurgy.nist.gov/phase/solder/bipb-w.jpg

In a chemical reaction, chemical equilibrium is the state in which both reactants and products are present in concentrations which have no further tendency to change with time. (*wikipedia)

- ✓ [Problem-1] We have 1 mol of $N_2O_4(g)$. If we keep the system as 298 K and 1 atm, what products do we have at the equilibrium state?
- ✓ [Problem-2] We have 2 mol of $NO_2(g)$. If we keep the system as 298 K and 1 atm, what products do we have at the equilibrium state?

$$N_2O_4(g) \rightleftarrows 2NO_2(g)$$

$$\begin{bmatrix} N_2O_4(g): 1\text{-}\xi \text{ mol} \\ NO_2(g): 2\xi \text{ mol} \end{bmatrix}$$
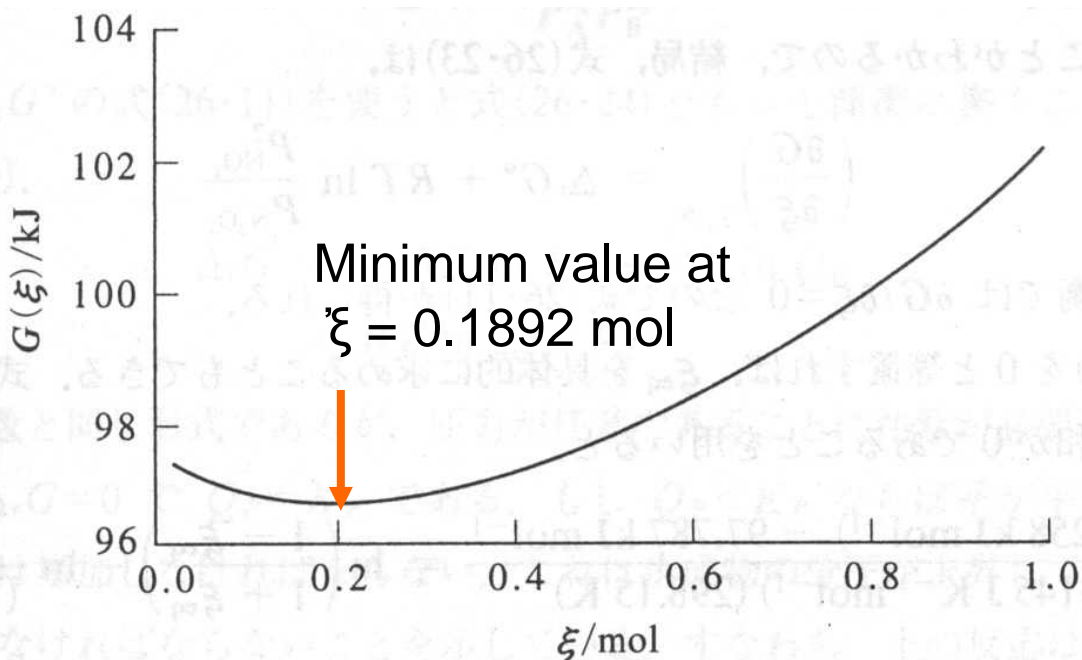
Minimum value at
$\xi = 0.1892$ mol

*D.A. McQuarrie, J.D. Simon, "Physical Chemistry: A Molecular Approach", University Science Books (1997).

Contents of today

<Today's class>

2.0. Short introduction on the contents

2.1. Equilibrium theory: Introduction

2.1.1. Direction of system evolution

2.1.2. Meaning of entropy in microscopic scale

2.1.3. Summary of processes

2.2. Equilibrium theory: free energy
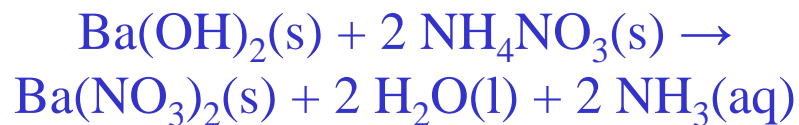
2.2.1. Helmholtz energy

✓ We are often interested in the direction of (spontaneous) system evolution. But, energy cannot necessarily indicate the direction.

➢ [Example-1] A spontaneous reaction is not necessarily exothermic. (not like "a ball always rolls downhill")

Not always
"system 1 → system 2"

Energy

System 1

System 2
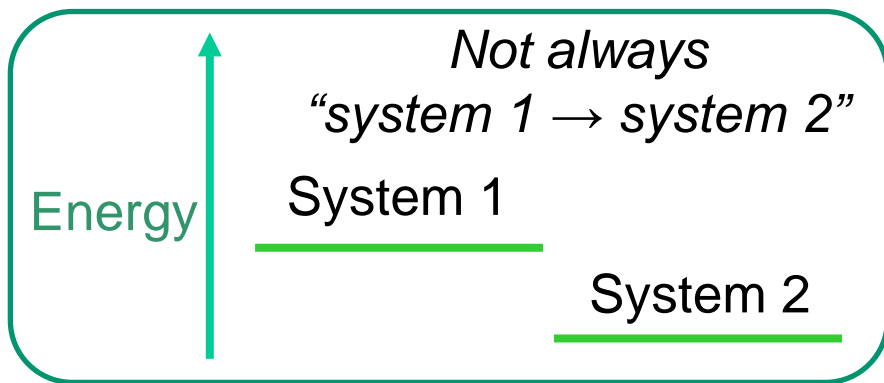
This reaction is endothermic, but spontaneously proceeds.

$$Ba(OH)_2(s) + 2\ NH_4NO_3(s) \rightarrow Ba(NO_3)_2(s) + 2\ H_2O(l) + 2\ NH_3(aq)$$

➢ [Example-2] Some process of $\Delta H = 0$ and $\Delta U = 0$ spontaneously takes place, but the reverse process cannot spontaneously occurs.

Br_2 N_2 $Br_2 + N_2$ $Br_2 + N_2$
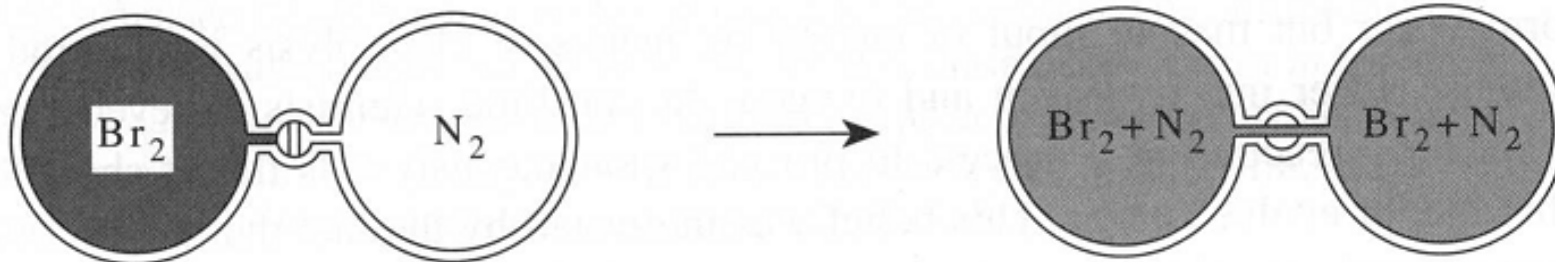
➢ [Example-3] Spontaneous heat transfer always occurs from a higher temperature object to a lower temperature object. Not a reversed way. (both are processes of $\Delta U = 0$ in total)

*D.A. McQuarrie, J.D. Simon, "Physical Chemistry: A Molecular Approach", University Science Books (1997).

- ✓ A spontaneous reaction direction which cannot be explained only by energy seems to be a direction along which disorder/randomness and uniformity of the system increases (in an atomic/molecular point of view).

- ✓ It seems that "spontaneous reaction of the system is dependent not only on energy (to decrease) but also on the disorder (to increase)".

- ✓ Indeed, isolated systems that are not in (thermodynamical) equilibrium evolve in a direction that increases their disorder.
  - ✓ A thermodynamic state function called "entropy" gives a quantitative measure of the disorder of a system.
  - ✓ Thus, "isolated systems that are not in equilibrium will evolve in a direction that increases their entropies".

<a statement of the Second Law of Thermodynamics>
There is a thermodynamic state function of a system called as entropy, S, such that for any change in the thermodynamic state of the (closed) system,

$$dS \geq \frac{\delta q}{T}$$

where the equality sign applies if the change is carried out reversibly and the inequality sign applies if the change is carried out irreversibly at any stage.

We consider a system composed by two connected sub-systems (sys-1 and sys-2):
- ✓ These systems are composed by the same sort of ideal gas having the same amount (n mol) and heat capacity.
- ✓ These two system can exchange neither mass nor energy with the surroundings.
- ✓ These two systems can exchange energy as heat with each other. Sys-1 is of higher temperature ($T_e + \alpha$) than sys-2 ($T_e - \alpha$).
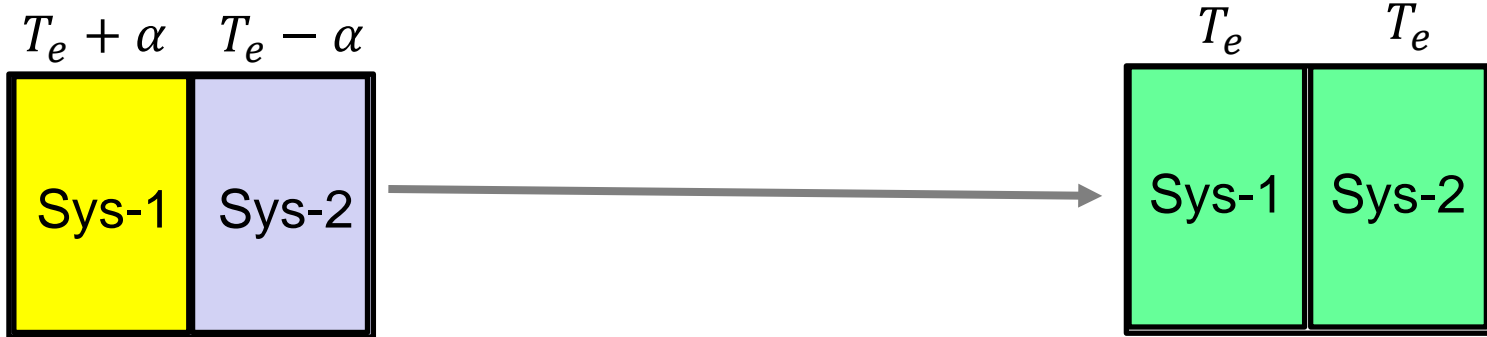- ✓ The volume are constant during the process, thus this is constant-volume cooling for Sys-1 and heating for Sys-2.

$$\Delta S = C_V \ln \frac{T_2}{T_1} + nR \ln \frac{V_2}{V_1}$$

by a process from state-1 (T_1, V_1) to state-2 (T_2, V_2) for ideal gas

$T_e + \alpha$ $T_e - \alpha$

T_e T_e

| Sys-1 | Sys-2 |

| Sys-1 | Sys-2 |

Using the entropy change expression for the ideal gas,

$$\Delta S_1 = C_V \ln \frac{T_{fin}}{T_{ini}} = C_V \ln \frac{T_e}{T_e + \alpha} \qquad \Delta S_2 = C_V \ln \frac{T_{fin}}{T_{ini}} = C_V \ln \frac{T_e}{T_e - \alpha}$$

If we consider these 2 systems as a 1 combined system, this system is regarded as an isolated system as no energy and no mass were transferred in this internal process. Then,
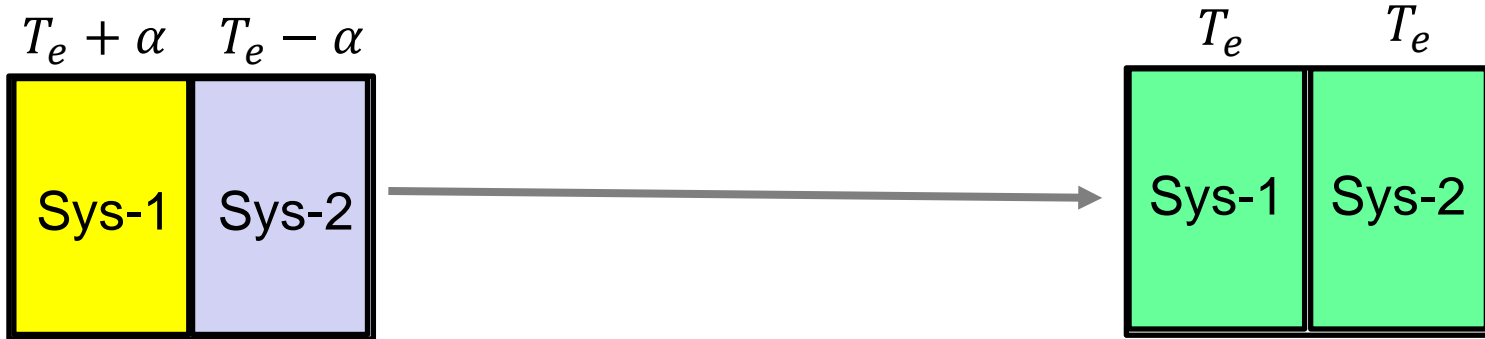
$$\Delta S_{comb-sys} = \Delta S_1 + \Delta S_2 = \cdots.$$

$$\Delta S = C_V \ln \frac{T_2}{T_1} + nR \ln \frac{V_2}{V_1}$$

by a process from state-1 (T_1, V_1) to state-2 (T_2, V_2) for ideal gas

$T_e + \alpha$ $T_e - \alpha$ T_e T_e

Sys-1 Sys-2   →   Sys-1 Sys-2

Using the entropy change expression for the ideal gas,

$$\Delta S_1 = C_V \ln \frac{T_{fin}}{T_{ini}} = C_V \ln \frac{T_e}{T_e + \alpha} \qquad \Delta S_2 = C_V \ln \frac{T_{fin}}{T_{ini}} = C_V \ln \frac{T_e}{T_e - \alpha}$$

If we consider these 2 systems as a 1 combined system, this system is regarded as an isolated system as no energy and no mass were transferred in this internal process. Then,
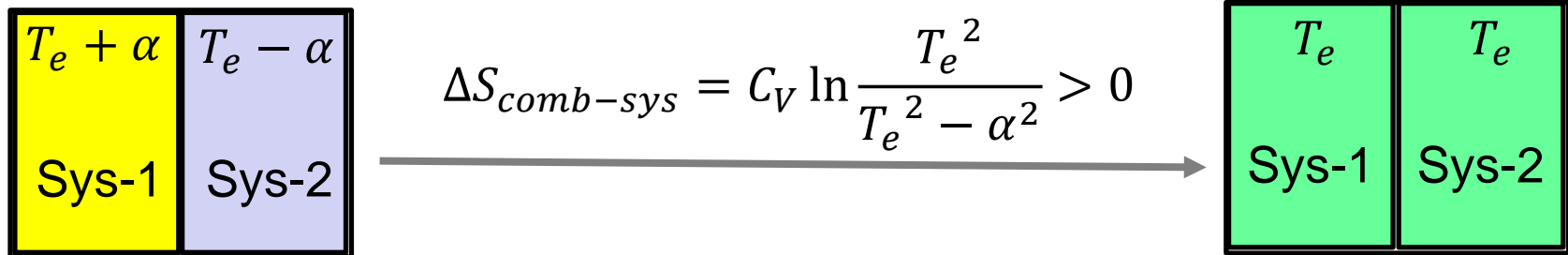
$$\Delta S_{comb-sys} = \Delta S_1 + \Delta S_2 = C_V \ln \frac{T_e}{T_e + \alpha} + C_V \ln \frac{T_e}{T_e - \alpha} = C_V \ln \frac{T_e^{\,2}}{T_e^{\,2} - \alpha^2} > 0$$

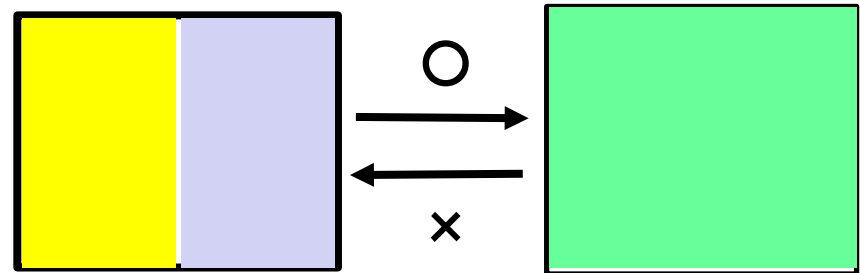As this combined system is an isolated system, the process is irreversible.

$T_e + \alpha$ | $T_e - \alpha$
Sys-1 | Sys-2

$$\Delta S_{comb-sys} = C_V \ln \frac{T_e^2}{T_e^2 - \alpha^2} > 0$$

T_e | T_e
Sys-1 | Sys-2

✓ This equation means that "energy transfer as heat between two systems of different temperatures is irreversible process".

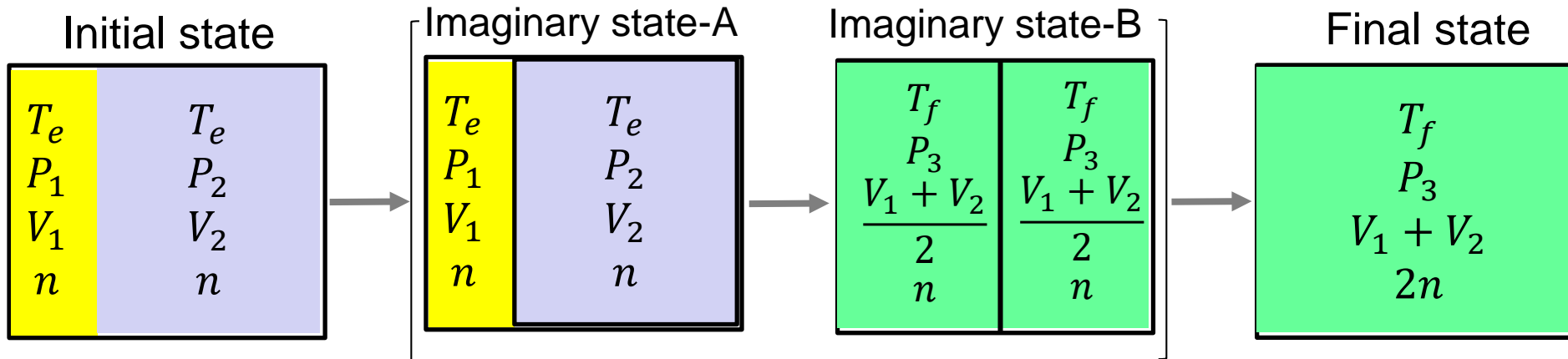Then, we consider a system where temperature is not spatially uniform in it.

✓ If this isolated system moves from uniform to non-uniform state, $\Delta S < 0$, which should require some energy transfer from the surroundings.
✓ If this isolated system moves from non-uniform to uniform state, $\Delta S > 0$, which is the same with irreversible process.
   ✓ This evolution is "natural" and should take place spontaneously.
   ✓ In nature, if the system becomes uniform (which has the highest entropy), no additional change happens and thus $\Delta S = 0$.

2.1.1. Direction of spontaneous system evolution - (example-2) due to non-uniform matter distribution-

$$\Delta S = C_V \ln\frac{T_2}{T_1} + nR \ln\frac{V_2}{V_1}$$

by a process from state-1 (T_1, V_1) to state-2 (T_2, V_2) for ideal gas

Initial state

T_e	T_e
P_1	P_2
V_1	V_2
n	n

Imaginary state-A

T_e	T_e
P_1	P_2
V_1	V_2
n	n

Imaginary state-B

T_f	T_f
P_3	P_3
$\dfrac{V_1+V_2}{2}$	$\dfrac{V_1+V_2}{2}$
n	n

Final state

T_f
P_3
V_1+V_2
$2n$

As the ideal gas, $U = \alpha nR$. Then, for energy conservation

$$\alpha nRT_e + \alpha nRT_e = 2\alpha nRT_f \text{ thus } T_e = T_f$$

Using the equation of state for ideal gas

$$P_1V_1 = nRT_e, \quad P_2V_2 = nRT_e, \quad P_3(V_1+V_2) = 2nRT_f = 2nRT_e$$
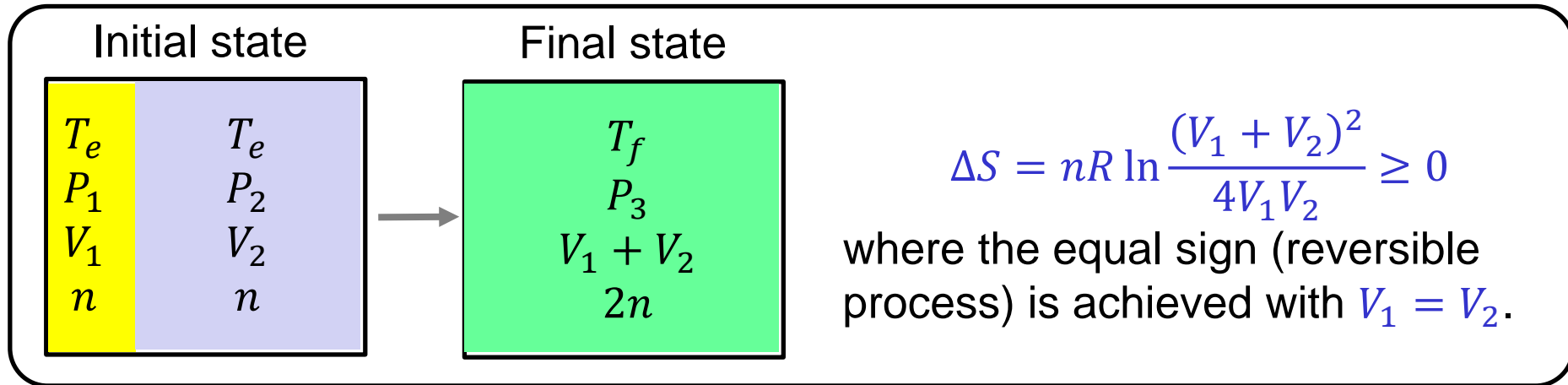
then, $\quad P_1V_1 + P_2V_2 = P_3(V_1+V_2)$

The entropy change between state-A and state-B is:

$$\Delta S = nR \ln\frac{(V_1+V_2)/2}{V_1} + nR \ln\frac{(V_1+V_2)/2}{V_2} = nR \ln\frac{(V_1+V_2)^2}{4V_1V_2}$$

where $(V_1+V_2)^2 = (V_1-V_2)^2 + 4V_1V_2 > 4V_1V_2$

Hence, $\Delta S = nR \ln\frac{(V_1+V_2)^2}{4V_1V_2} \geq 0$ where the equal sign is achieved with $V_1 = V_2$

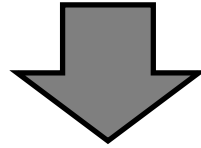| Initial state		Final state

$$\begin{array}{ll} T_e & T_e \\ P_1 & P_2 \\ V_1 & V_2 \\ n & n \end{array} \longrightarrow \begin{array}{c} T_f \\ P_3 \\ V_1 + V_2 \\ 2n \end{array}$$

$$\Delta S = nR \ln \frac{(V_1 + V_2)^2}{4 V_1 V_2} \geq 0$$

where the equal sign (reversible process) is achieved with $V_1 = V_2$.

✓ "$V_1 = V_2$" requires "$P_1 = P_2$", which means the system is spatially uniform even at the beginning. So, $V_1 = V_2$ means no change happened in the system (and $\Delta S = 0$).

✓ If this isolated system moves from uniform to non-uniform state (reverse direction), $\Delta S < 0$, which cannot be taken place spontaneously (requires some manipulation from the surroundings).

✓ If this isolated system moves from non-uniform to uniform state, $\Delta S > 0$, which is the same with irreversible process.

    ✓ This evolution is natural and should take place spontaneously.

    ✓ In nature, if the system becomes uniform (which has the maximum entropy), no additional change happens and thus $\Delta S = 0$.

Entropy seems to tell us the evolution direction of an isolated system.

- ✓ If a reaction holds "$dS > 0$" ($\Delta S > 0$), this reaction seems to take place spontaneously.
  - ✓ This condition is of irreversible processes of an isolated system.

- ✓ If a reaction holds "$dS = 0$", this reaction is indeed "no evolution of the system".
  - ✓ This condition is of reversible processes of an isolated system.
  - ✓ This is reasonable because the system is at an thermodynamical equilibrium state during any reversible process. And as "equilibrium", the system should be spatially and temporally uniform.

- ✓ If a reaction holds "$dS < 0$", this reaction requires some manipulation from the surroundings to proceed.
  - ✓ Indeed, such manipulation violates the assumption of "isolated system", this condition is never achievable for an isolated system.
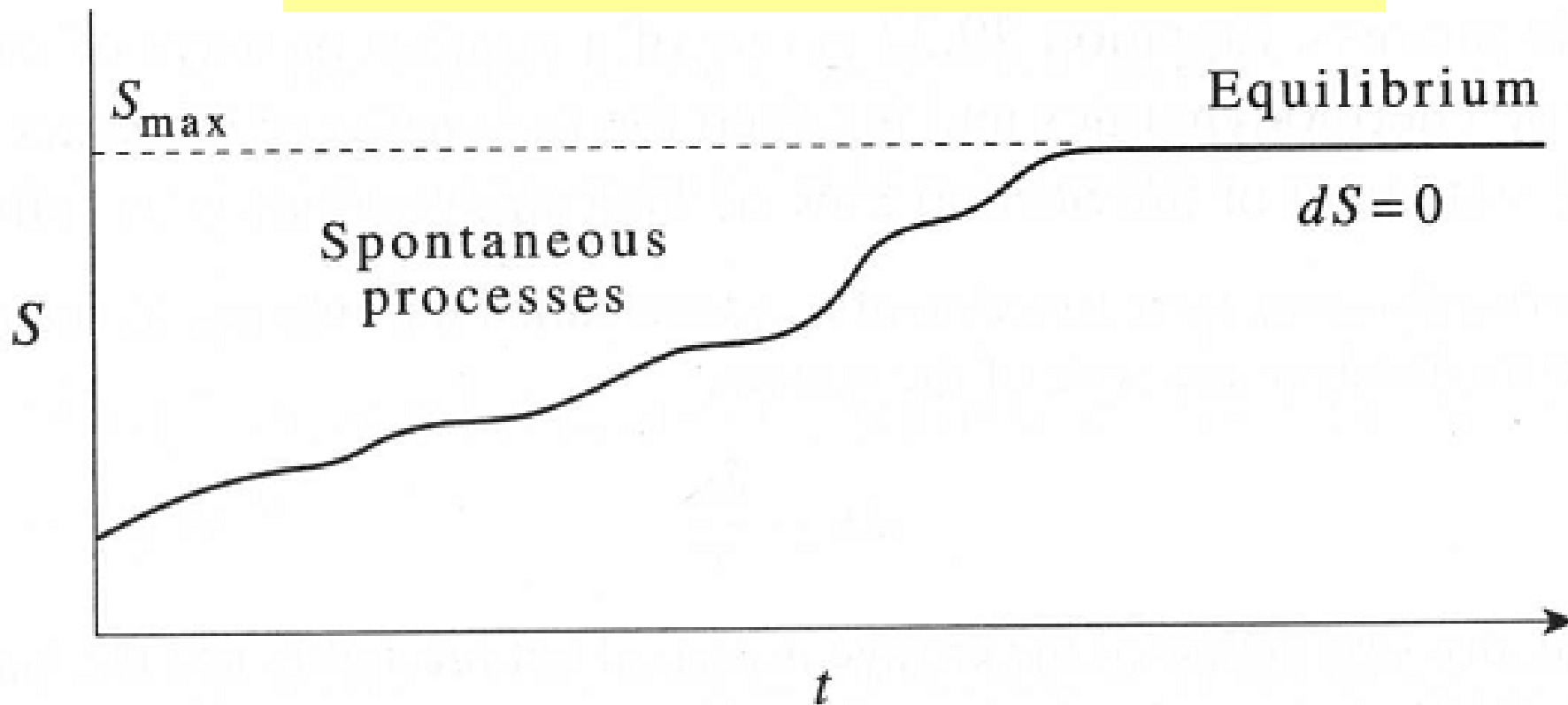
✓ "$dS > 0$", the condition for spontaneous reactions.
✓ "$dS = 0$", the condition of equilibrium state.

*We just consider an isolated system.

*This is for isolated system.

*D.A. McQuarrie, J.D. Simon, "Physical Chemistry: A Molecular Approach", University Science Books (1997).

To more generalize the idea, we consider another isolated system.

✓ To focus on the entropy only (excluding an energy-driven spontaneous process), we consider an isolated system where the energy is conserved. In isolated systems, the driving force for any spontaneous process is to increase the entropy ($dS>0$).

✓ As the system is isolated and thus no heat transfer occurs, if the entropy increases, it should be the one generated within the system itself.
   *Note that entropy is not necessarily conserved, unlike energy.

✓ The entropy keeps rising until no more spontaneous processes occurs, in which case the system will be in equilibrium. Thus, the entropy is maximized when the system Is in equilibrium. Consequently, $dS=0$ at equilibrium.

✓ Since a reversible process assumes that the system remains in equilibrium during the entire process, $dS=0$ is also achieved in a reversible process.

➢ $dS > 0$ for a spontaneous process in an isolated system
➢ $dS = 0$ for a reversible process and for a thermodynamical equilibrium state in an isolated system

<Today's class>

    2.0. Short introduction on the contents

    2.1. Equilibrium theory: Introduction

        2.1.1. Direction of system evolution

        2.1.2. Meaning of entropy in microscopic scale

        2.1.3. Summary of processes

   2.2. Equilibrium theory: free energy

        2.2.1. Helmholtz energy

In thermodynamics, entropy (usual symbol S) is a measure of the number of specific ways in which a thermodynamic system may be arranged, commonly understood as a measure of disorder. (*wikipedia)

✓ In microscopic scale, entropy is regarded as an index to represent the disorder of system. In statistical dynamics, entropy is given as:

$$S = k_B \ln W \, ,$$

where W indicates the number of possible configurations of a state of interest, k_B is Boltzmann constant ($k_B = \frac{R}{N_A} = 1.38 \times 10^{-23}$ J K^{-1}), and N_A is Avogadro constant.

✓ For example, if we put 2 <u>indistinguishable balls</u> into 3 boxes, the number of possible configurations is $W = {}_3C_2 = 3$.
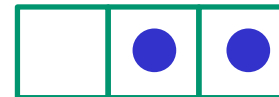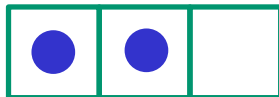
✓ The entropy (specifically, "configurational entropy") of this state is obtained as
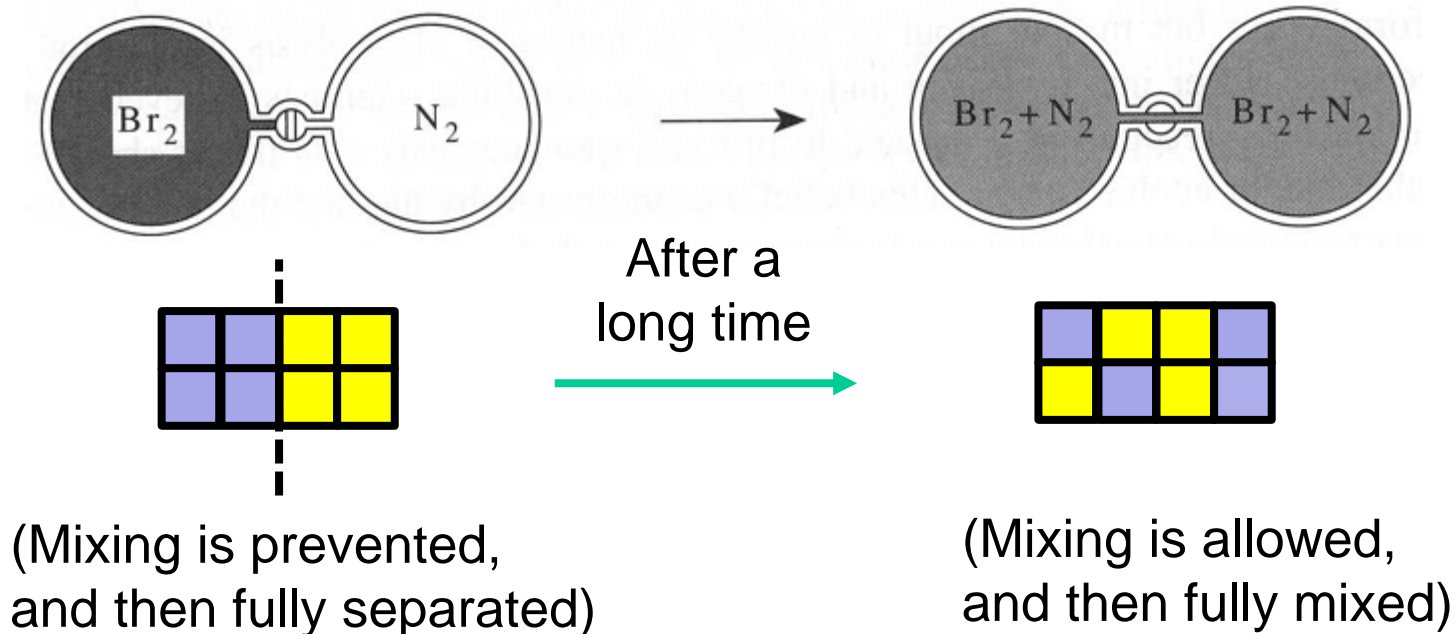
$$S = k_B \ln W = k_B \ln 3$$
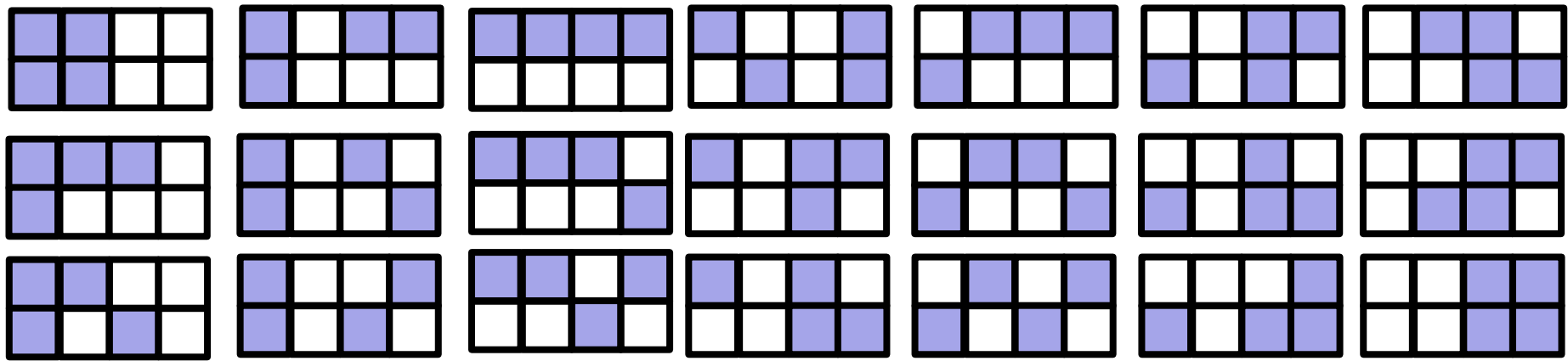
$$S = k_B \ln W$$

Entropy definition in microscopic scale based on statistical dynamics

* W indicates *"the number of possible configurations that corresponds to a concerned thermodynamic state"*.

[Example-2] Even a process of $\Delta H=0$ and $\Delta U=0$ spontaneously takes place, although a reverse process cannot spontaneously occur.
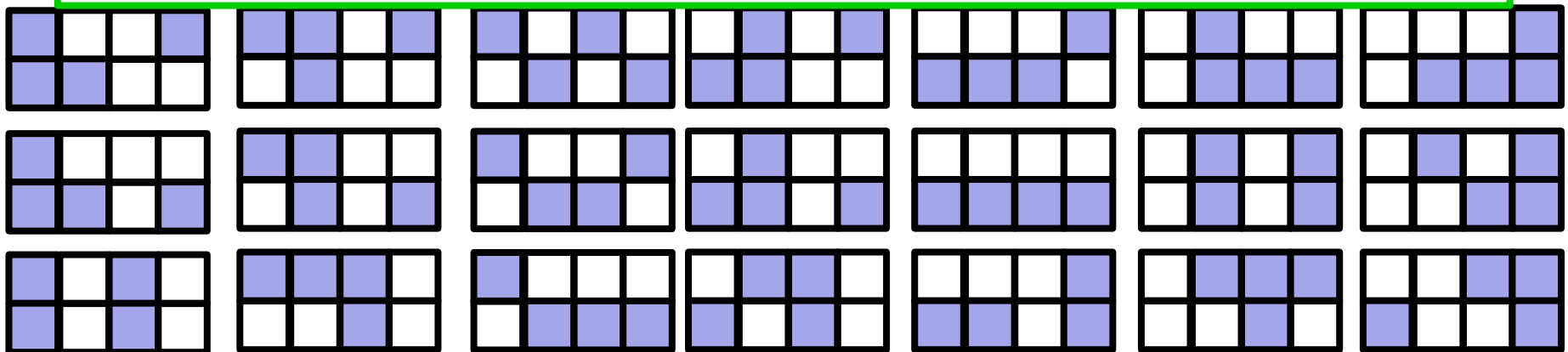

After a long time

(Mixing is prevented, and then fully separated)

(Mixing is allowed, and then fully mixed)

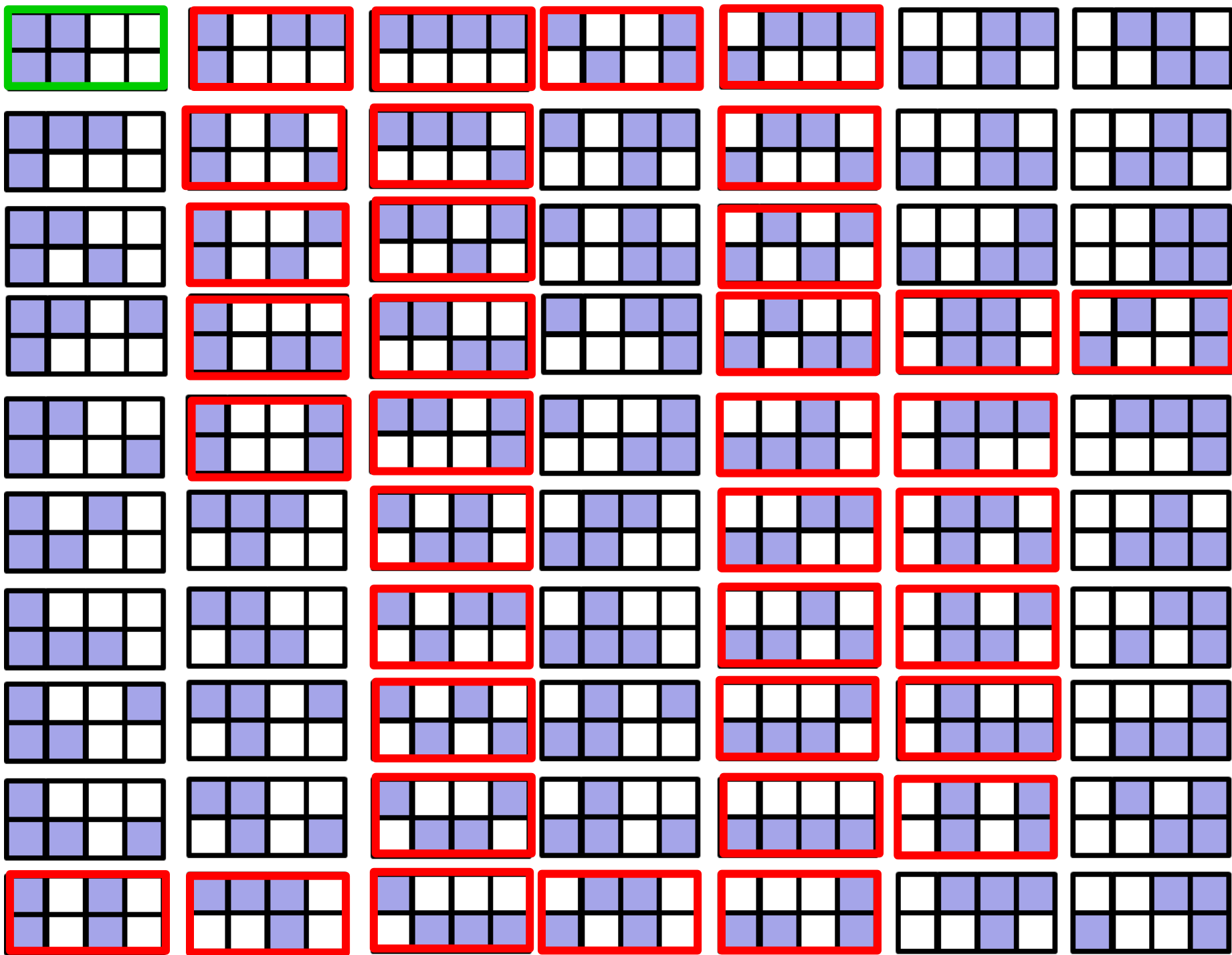In which case "the number of possible configurations" is larger?

<Quiz>

[Q-1] How many configurations are available for a state "where all Br atoms (blue blocks) are located at the left chamber".
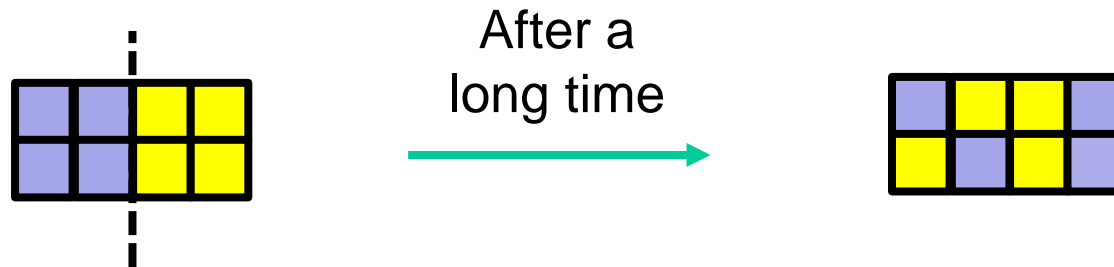
[Q-2] How many configurations are available for a sate "where Br atoms are equally located at each chamber. (2 for the left and 2 for the right)".

After a
long time

$\checkmark$ All combinations: $_8C_4 = 70$

$\checkmark$ (1) The number of configurations for state-(1) where all Br atoms stay at the left chamber: $_4C_4=1$.

$\checkmark$ (2) The number of configurations for state-(2) where Br atoms equally stay at each chamber: $_4C_2 \times _4C_2 = 36$

   $\checkmark$ If there is no "preference" between state-(1) and state-(2), state-(2) should be more natural.

   $\checkmark$ "Preference" is expressed by energy. Lower energy is more preferred in nature.

      $\checkmark$ In nature, transition from a higher-energy state to a lower-energy state takes place more easily (frequently). When the energy difference gets larger, the frequency difference gets larger.

$\checkmark$ Hence, in nature, the reaction (=system evolution) is derived by entropy and energy. (if isolated system, only entropy.)
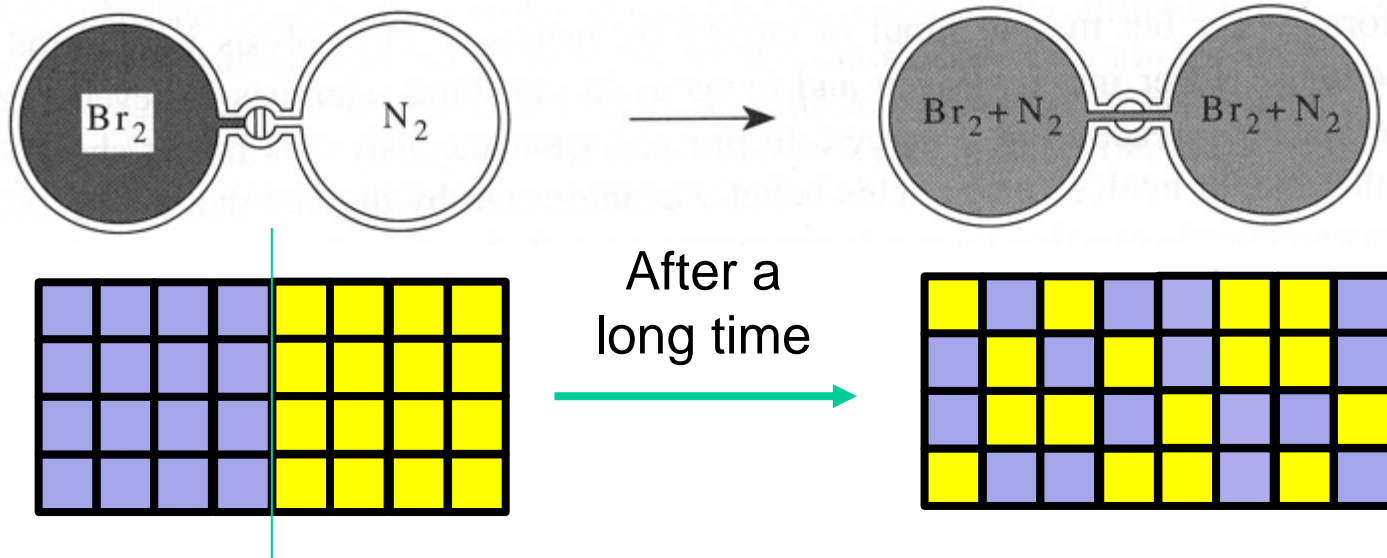
[Example-2] Even a process of $\Delta H=0$ and $\Delta U=0$ spontaneously takes place, although a reverse process cannot spontaneously occur.

After a
long time
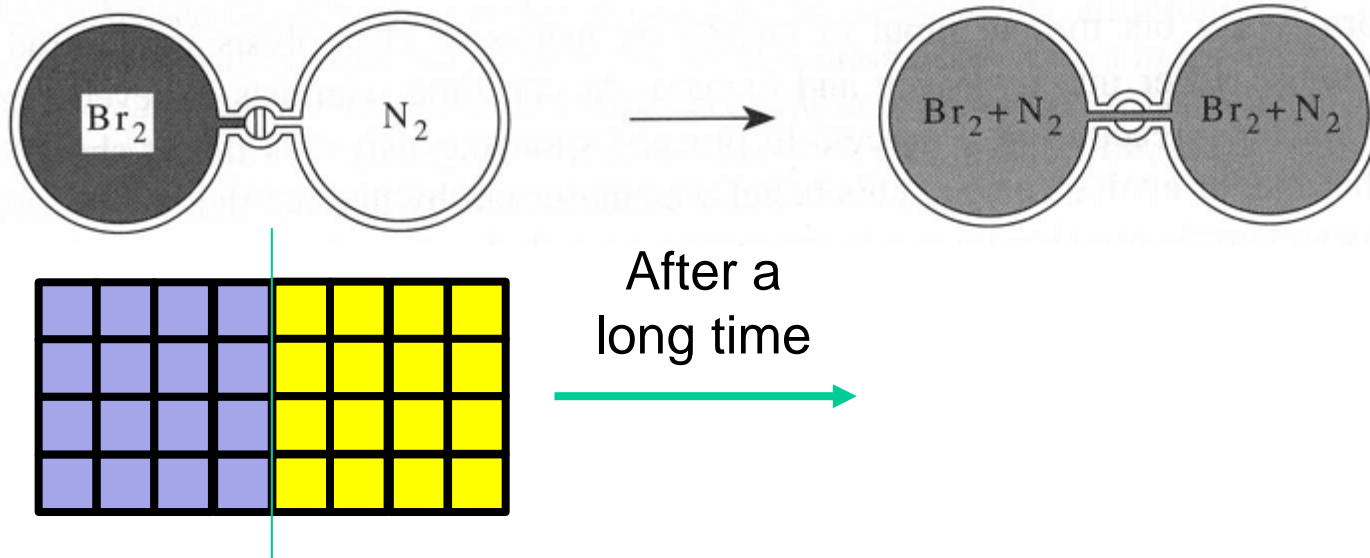
[Example-2] Even a process of $\Delta H=0$ and $\Delta U=0$ spontaneously takes place, although a reverse process cannot spontaneously occur.
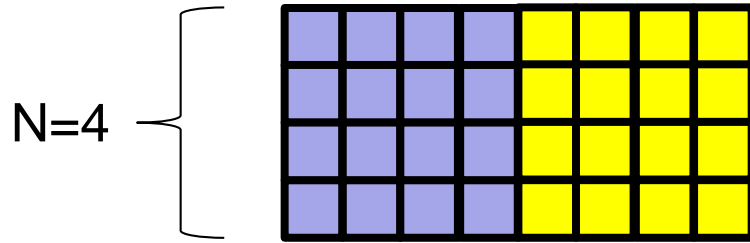

After a long time

The occupation of the blue atoms in the left side is $P_{occ}=1.0$ for this case.

$P_{occ}=0.75$ for this case.

N=4

N=4
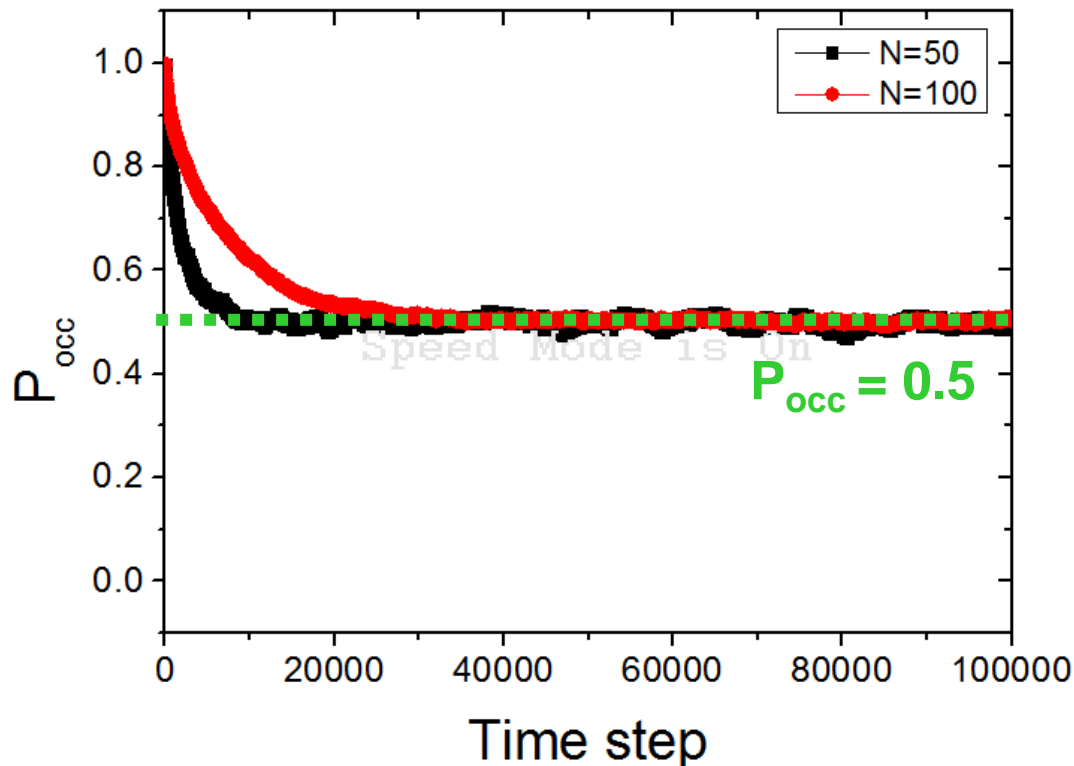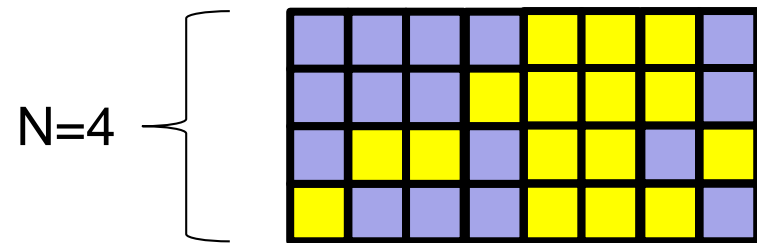
$P_{occ} = 0.5$

➢ As the number of molecules increase, full-mixing state ($P_{occ}=0.5$) dominantly appears.

➢ Never returns to the total separation ($P_{occ}=0$ or 1)

- ✓ By simulation of molecules motions (random movement), if no interaction between molecules (like ideal gas and $\Delta U = 0$), the mixing state dominantly appears due to that full-mixing has the largest number of available states.
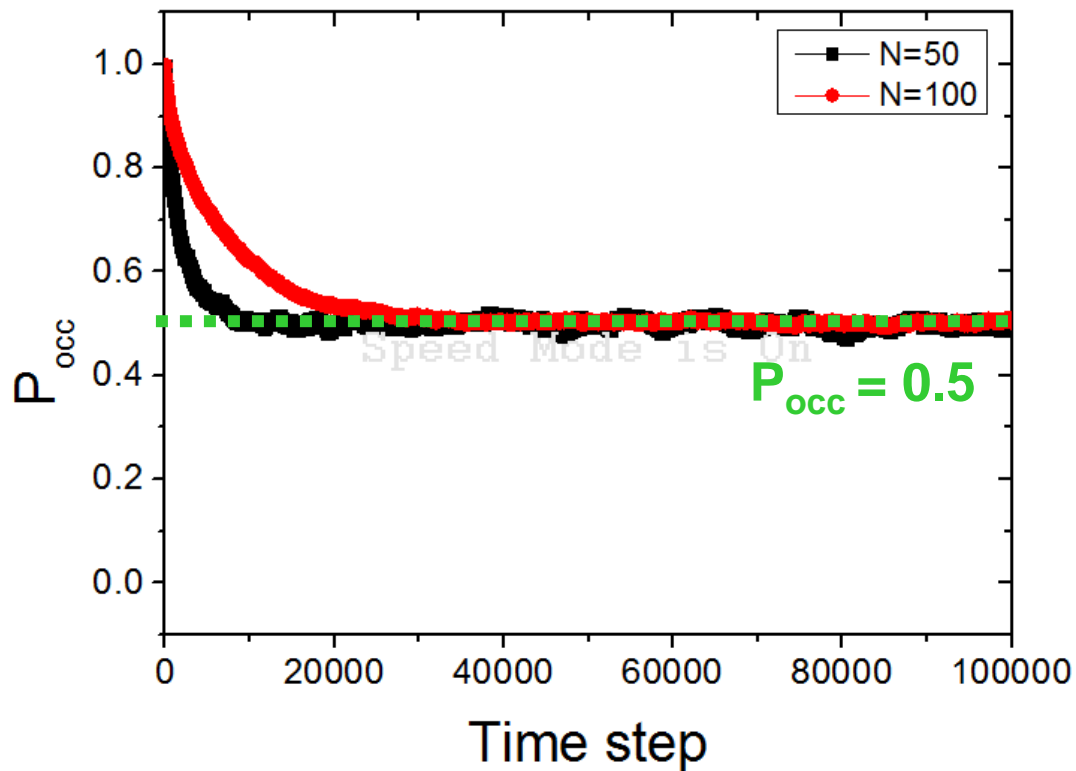
- ✓ Entropy of classical thermodynamics accounts for this character (namely disorder). In statistical dynamics, we can also define and calculate entropy based on statistics, which is indeed equivalent with thermodynamical one.

$$\Delta S = C_V \ln \frac{T_2}{T_1} + nR \ln \frac{V_2}{V_1}$$

by a process from state-1 (T_1, V_1) to state-2 (T_2, V_2) for ideal gas

State-1   State-2

He   Vacuum   ⟶   He   He

✓ The same amounts of He gas exist in both states (n mol).
✓ Temperatures are the same between the two states ($T_1 = T_2$)
✓ The volume for He (ideal gas) in state-2 is twice as large as that in state-1 ($V_2 = 2 V_1$).

$$\Delta S = S_2 - S_1 = ...$$

*D.A. McQuarrie, J.D. Simon, "Physical Chemistry: A Molecular Approach", University Science Books (1997).

$$\Delta S = C_V \ln \frac{T_2}{T_1} + nR \ln \frac{V_2}{V_1}$$

by a process from state-1 (T_1, V_1) to state-2 (T_2, V_2) for ideal gas

State-1   He   Vacuum   →   State-2   He   He
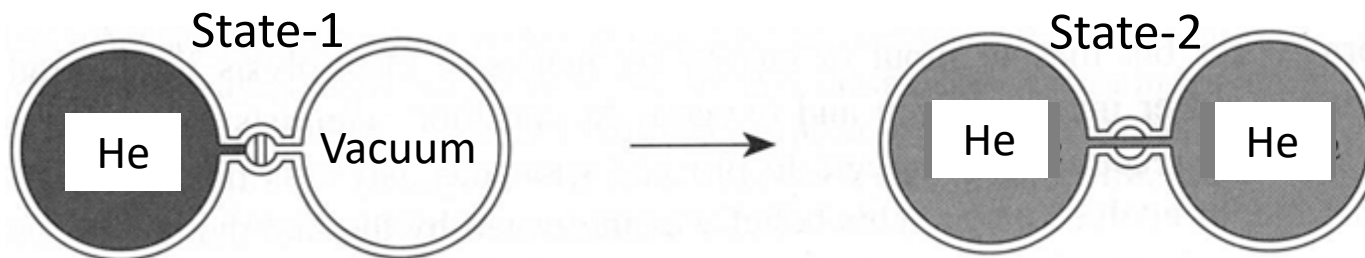
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✓ Temperatures are the same between the two states ($T_1 = T_2$)
✓ The volume for He (ideal gas) in state-2 is twice as large as that in state-1 ($V_2 = 2 V_1$).

$$\Delta S = S_2 - S_1 = nc_v \ln \frac{T_1}{T_1} + nR \ln \frac{2V_1}{V_1} = nR \ln 2$$

*D.A. McQuarrie, J.D. Simon, "Physical Chemistry: A Molecular Approach", University Science Books (1997).

$$S = k_B \ln W$$

where W indicates the number of available configurations for a state of interest, k_B is Boltzmann constant ($k_B = \frac{R}{N_A} = 1.38 \times 10^{-23}$ J K^{-1}), and N_A is Avogadro constant.

In the system, there are $N = nN_A$ atoms. We assume that there are M rooms for atoms for each sphere ($M \gg N$),

*For example, M is equal to V/v$_{He}$, where v$_{He}$ is the volume of He atom.

$$\Delta S = k_B \ln W_2 - k_B \ln W_1 = ...$$

$$W_1 = ...$$

$$W_2 = ...$$

*D.A. McQuarrie, J.D. Simon, "Physical Chemistry: A Molecular Approach", University Science Books (1997).

State-1   State-2

He   Vacuum   He   He

$S = k_B \ln W$
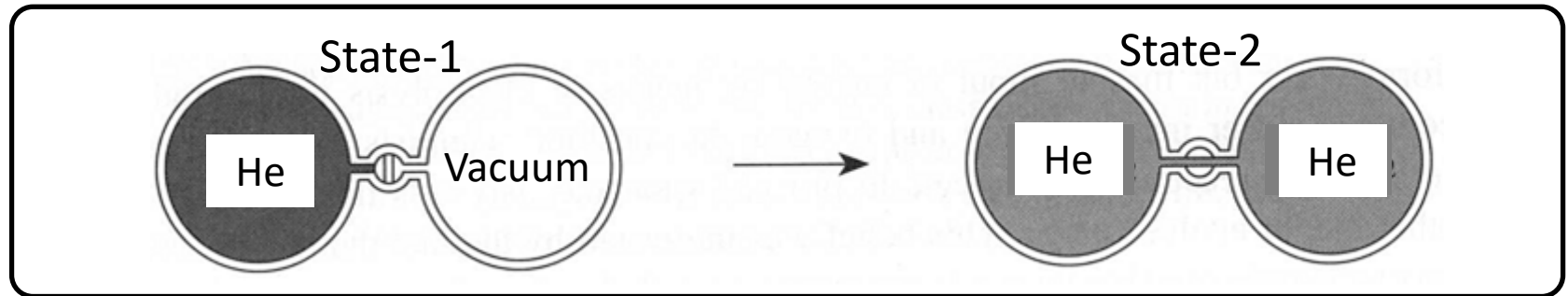
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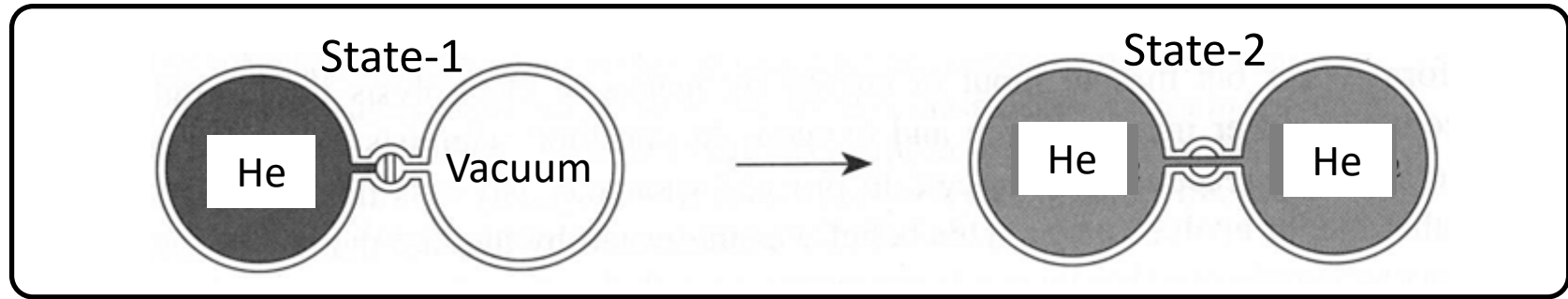
$$\Delta S = k_B \ln W_2 - k_B \ln W_1 = ...$$

$$W_1 = \,_M C_N = \frac{M!}{(M-N)!N!}$$

$$W_2 = \,_M C_{N/2} \times \,_M C_{N/2} = \left(\frac{M!}{(M-N/2)!(N/2)!} \right)^2$$

<Starling's approx.>

$$N! \sim N^N e^{-N}$$

$$\ln N! \sim N \ln N - N$$

In the system, there are $N=nN_A$ atoms.
Then we have M rooms for them for
each sphere (M>>N).

$$S = k_B \ln W$$

<Starling's approx.>
$$\ln N! \sim N \ln N - N$$

$$W_1 = {}_M C_N = \frac{M!}{(M-N)!N!} \qquad W_2 = {}_M C_{N/2} \times {}_M C_{N/2} = \left(\frac{M!}{(M-N/2)!(N/2)!} \right)^2$$

$$\Delta S / k_B = \ln W_2 - \ln W_1 \sim 2\{M \ln M - (M-N/2)\ln(M-N/2) - (N/2)\ln(N/2)\}$$

$$-\{M \ln M - (M-N)\ln(M-N) - N \ln N\}$$

$$= M \ln M - 2(M-N/2)\ln(M-N/2) + (M-N)\ln(M-N) + N \ln 2$$

$$= M \ln M - 2(M-N/2)\{\ln M + \ln(1-(N/2)/M)\} + (M-N)\{\ln M + \ln(1-N/M)\} + N \ln 2$$

$$\sim (M-2M+N+M-N)\ln M + 2(M-N/2)((N/2)/M) + (M-N)(-N/M) + N \ln 2$$

$$= N\left(\ln 2 + \frac{N}{2M} \right) \sim N \ln 2$$

$$\ln(1+x) \sim x \qquad \text{if } x << 1$$

$$\Delta S = S_2 - S_1 = k_B N \ln 2 = nR \ln 2$$

This result confirms the entropy defined in the statistical physics (for microscopic)
is exactly the same with that defined in thermodynamics (for macroscopic).

Contents of today

<Today's class>

    2.0. Short introduction on the contents

    2.1. Equilibrium theory: Introduction

        2.1.1. Direction of system evolution

        2.1.2. Meaning of entropy in microscopic scale

        2.1.3. Summary of processes

    2.2. Equilibrium theory: free energy

        2.2.1. Helmholtz energy

<Definition of quasi-static process (In this lecture, definition (1) is used) >
1) Very (infinitesimally) slow process so that we consider the system is always at some equilibrium state, where we have a specific value for each state function..
2) Very (infinitesimally) slow process and the process takes place with adhering the system to some equilibrium state and keeping concerned variables of the system and the surroundings equal.
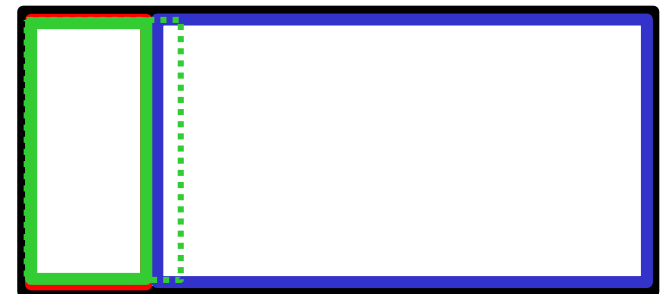>> for this definition, "quasi-static" is equivalent with "reversible".

[Definition-1]

All processes
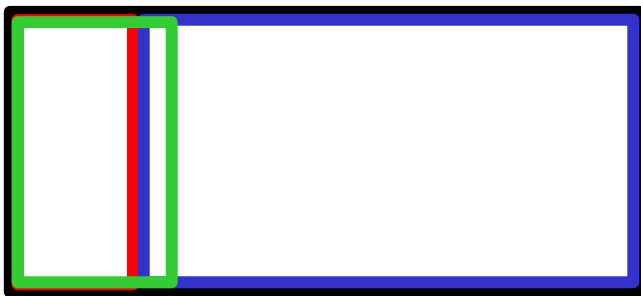
Reversible
Irreversible
Quasi-static

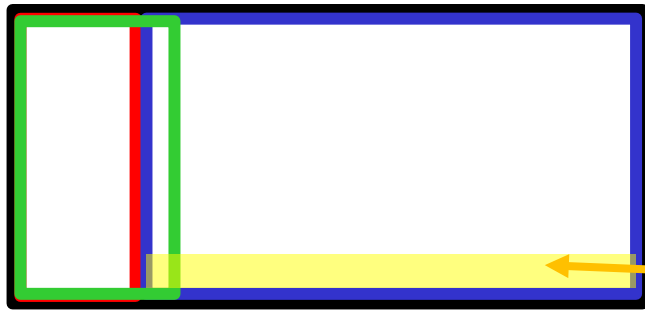[Definition-2]

All processes

✓ Any process is rev. or irrev.
✓ Any rev. process is quasi-static.
✓ Some irrev. process is quasi-static.

✓ Any process is rev. or irrev.
✓ Rev. process = quasi-static process.
✓ No irrev. process is quasi-static.

✓ For a reversible process, we need to introduce an infinitesimal change in surroundings to induce some change in state function(s) of the system.
- ✓ So, if we do nothing to the system, nothing happens in the system as it is at an equilibrium state. The system eternally stays at a stationary state, which an (thermodynamical) equilibrium state.

✓ For an irreversible process, on the other hand, some unbalance in temperature, pressure, etc (or some non-uniformity in the system) initially exist between the system and the surroundings.
- ✓ So, if we do nothing to the system or to the surroundings, the system suffers some change to mitigate/expel the unbalance. For example, heat transfer, expansion/compression, mixing, etc.

✓ For a spontaneous process, the process proceeds without any manipulations of the system and/or the surroundings.
- ✓ Thus, the initial state of the system should be an non-equilibrium state. And thus, the spontaneous process must be an irreversible process.
  - ✓ If the initial state is an equilibrium state, no reaction takes place "spontaneously".

- ✓ <Reversible process> process from one equilibrium state to another equilibrium state. During the process, the system is always at some equilibrium state.
  - ➢ For an isolated system, $dS = 0$
- ✓ <Quasi-static process> process from a state to another state. During the process, the system or all sub-systems in the system are always at some equilibrium state.
- ✓ <Spontaneous process> process from a non-equilibrium state to an equilibrium or to a non-equilibrium state. We may / may not define thermodynamic quantities during the process. (*the initial state of spontaneous process must be a non-equilibrium state.)
  - ➢ For an isolated system, if quasi-static (we can define dS), $dS > 0$.
- ✓ <Irreversible process> processes other than reversible processes. We may / may not define thermodynamic quantities during the process.
  - ➢ For an isolated system , if quasi-static (we can define dS), $dS > 0$
    - ➢ We may consider the condition as $dS \neq 0$. However, in reality, processes of $dS < 0$ violates the condition "isolated".

✓ As spontaneous process is a kind of irreversible process, the criteria for spontaneous and irreversible processes are identical.

➢ (1) For an isolated system, if quasi-static (we can define dS), $dS > 0$.

➢ (2) For an isolated system, if not quasi-static (we cannot define dS) but we know the entropies of initial and final states, $\Delta S = S_{fin} - S_{ini} > 0$.

➢ (3) For an isolated system, if not quasi-static (we cannot define dS) and the entropies of initial and final states cannot defined, we cannot use this criterion….

➢ We normally do not consider this kind of case in equilibrium theory.

Contents of today

<Today's class>

    2.0. Short introduction on the contents

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    2.2. Equilibrium theory: free energy

        2.2.1. Helmholtz energy

✓ The following criteria just work for an isolated system; hence it is not so practical. (Isolated systems are very rare, e.g. universe)

  ✓ $dS > 0$ for a spontaneous process (irreversible process)
  ✓ $dS = 0$ for an equilibrium state (reversible process

✓ To applied it to a practical case, the total entropy change, equal to the sum of entropies of system and surroundings ($\Delta S_{total} = \Delta S_{system} + \Delta S_{sur.}$), need to be checked, where we re-consider "system + surroundings" as an isolated system.

  ✓ $dS \geq \frac{\delta q}{T}$ works in any systems, but evaluating δq is often difficult as q is not a state function)

✓ In this chapter ($22), two state functions are introduced, which indicates the direction of a spontaneous process in systems that are not isolated. These state functions are Helmholtz and Gibbs (free) energies.

A new state function, called Helmholtz energy, is introduced as:
$$A = U - TS$$

Its total derivative is given as:
$$dA = d(U - TS) = dU - TdS - SdT$$

Here we consider the 1st law of a reversible constant-V process:
$$dU = TdS - PdV = TdS \quad \text{then} \quad dU - TdS = 0 \quad \textit{[rev. const-V]}$$

Further, we assume the process is constant-T as well:
$$d(U - TS) = dU - TdS - SdT = dU - TdS = 0 \quad \textit{[rev. const-V const-T]}$$

Hence, we have the following condition for reversible constant-T constant-V process.

$$dA = d(U - TS) = 0 \quad \textit{[rev. const-V const-T]}$$

*If we only assume constant-V or constant-T, Helmholtz energy can be written as follows:
- ✓ *[Rev. const-V]* $dA = dU - TdS - SdT = (TdS - PdV) - TdS - SdT = -SdT$
- ✓ *[Rev. const-T]* $dA = dU - TdS - SdT = (TdS - PdV) - TdS - SdT = -PdV$

We consider a process in a constant-volume constant-temperature system.

✓ This system often appears in a real chemistry, but the criterion "$dS \geq 0$" does not apply to this system because a "constant-temperature" system is not isolated (heat transfer can happen to keep the temperature constant).

✓ Hence, we need a criterion other than "$dS \geq 0$".

As the first law: $dU = \delta q + \delta w$, And $\delta w = -P_{external}dV$
As a constant-volume system: $dV = 0$, then $\delta w = 0$. Hence, $dU = \delta q$

Here, we apply the equation above into the second law ($dS \geq \delta q/T$).
Then, finally we obtain the following equation, where the equality holds for a reversible process and the inequality for an irreversible process.

$$dU \leq TdS \quad \text{then} \quad dU - TdS \leq 0 \quad [const.-V]$$

*Be sure that the second law ($dS \geq \delta q/T$) is true for any change in the thermodynamic state of a system.

We consider a process in a constant-volume constant-temperature system.

Helmholtz energy is defined as:
$$A = U - TS$$
$$dA = dU - TdS - SdT$$

$$dU - TdS \leq 0 \quad \text{[const.-V]}$$

where the equality holds for a reversible process and the inequality for an irreversible process.

In constant-T condition, the derivative of Helmholtz energy is written as:
$$dA = dU - TdS - SdT = dU - TdS \quad \text{[quasi-static const.-T]}$$
If we introduce this relation into the equation to judge whether the process is reversible or irreversible:
$$dU - TdS = dA \leq 0 \quad \text{[quasi-static const.-T const-V]}$$

$$dA = d(U - TS) = 0 \quad \text{[rev. const-V const-T]}$$

Consequently, we have a criterion for const-V const-T system.
- ✓ dA < 0 for a spontaneous process (irreversible process)
- ✓ dA = 0 for an equilibrium state (reversible process)

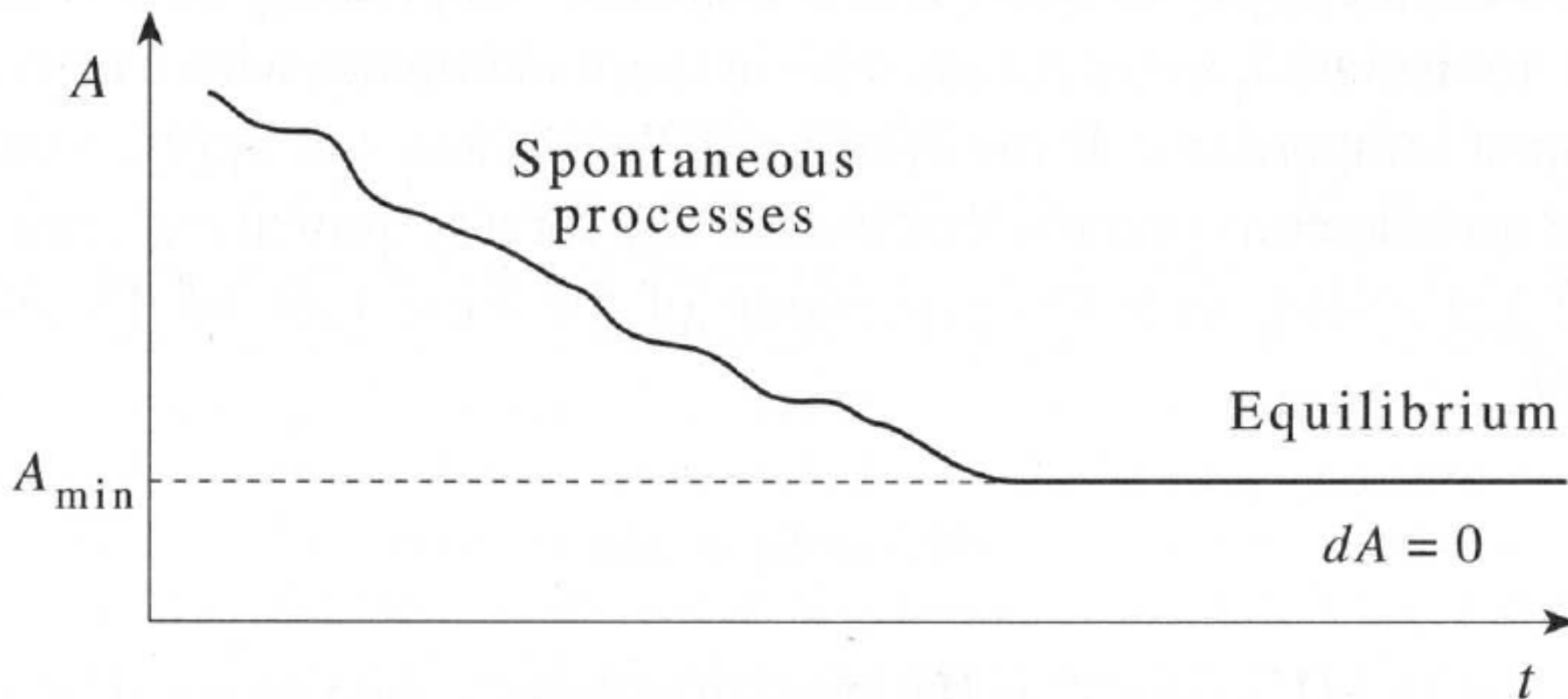Consequently, we have a criterion for const-V const-T system.
- ✓ $dA < 0$ for a spontaneous process (irreversible process)
  - ✓ (Integral form) $\Delta A = \Delta U - T\Delta S < 0$
- ✓ $dA = 0$ for an equilibrium state (reversible process)
  - ✓ (Integral form) $\Delta A = \Delta U - T\Delta S = 0$

This result means that
- ➢ "a process of "$\Delta A < 0$" takes place spontaneously in a system at constant T and V until it becomes "$\Delta A = 0$" (thus, until A will be a minimum).
  - ➢ Ex-1) when $\Delta U < 0$ (some energy will be gained) and $\Delta S > 0$ (the system will be more disordered), ΔA is clearly less than 0, and thus this process spontaneously takes place.
  - ➢ Ex-2) a process where ΔU and ΔS have the same signs, ΔA gives a quantitative measure of whether is process is spontaneous or not. Basically, because of the factor of T multiplying ΔS, the ΔU dominates at low temperatures and TΔS dominates at high temperatures.
    - ➢ We say "entropy effect is stronger at higher temperature".

*textbook, figure 22.1

*This is for const-T const-V system.