Physical Chemistry for Energy Engineering
(2nd: 2018/09/05)

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*The class follows the text book: D.A. McQuarrie, J.D. Simon, “Physical Chemistry: A Molecular Approach", University Science Books (1997).

Course schedule (tentative) (1/3)
- lectures -

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. Equation of state of gas
	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

1. Basics of thermodynamics
2. The first law of thermodynamics

Goals of today's lecture

- ✓ Understand basic technical terms and its definitions used in thermodynamics.
- ✓ Understand the 1st law.

1. Basics of thermodynamics
- scope -

Thermodynamics

- ✓ treats macroscopic system (like one composed of 10^{23} atoms), not microscopic (e.g. atom, molecule, ….)
- ✓ treats macroscopic physical quantity (e.g. temperature, entropy, …), not microscopic (e.g. location of each atom).
  - ✓ V: volume , P: pressure, T: temperature, E: energy, S: entropy, …

    *Be careful that entropy (S) and enthalpy (H) are totally different.
  - ✓ can be extended to microscopic ones in statistical thermodynamics.
- ✓ treats only thermal equilibrium state, not non-equilibrium state.
  - ✓ For transition, focuses on change from one equilibrium state to another equilibrium state.
- ✓ is based on 3 fundamental laws. (1st/2nd/3rd law of thermodynamics)

1. Basics of thermodynamics
-$19: introduction and history -

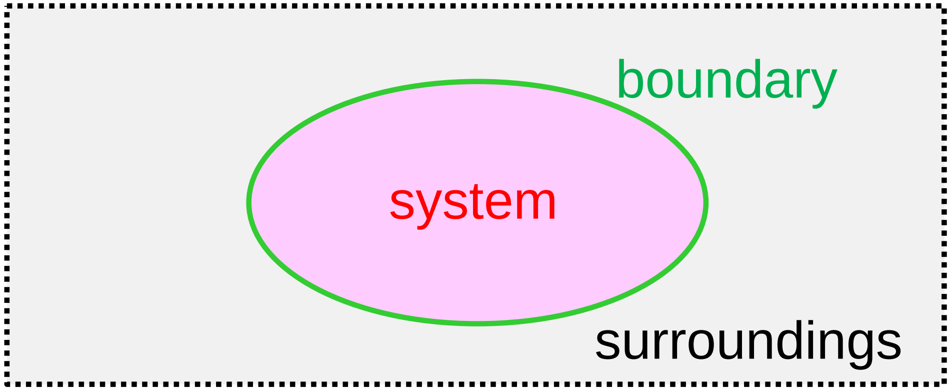
- ✓ Thermodynamics were established in 19th century.
  - ✓ Basic theories for atoms and molecules were mostly established in late 19th century and early 20th century.
  - ✓ So, (classical) thermodynamics is not based on behavior of atoms and molecules.
  - ✓ It means classical thermodynamics does not use atomic-scale information: for example, even to a molecular specie of very complex structure, we can apply thermodynamics.
  - ✓ But, it also means thermodynamics give no decisive information on atom's and molecule's nature and motion.
    - ✓ Atomic-scale bases for thermodynamics and their connection with macroscopic quantities are given by statistical mechanics/thermodynamics coupled with quantum mechanics.

- ✓ Be sure again that (classical) thermodynamics is for macroscopic quantity (not microscopic) of a system in thermal/thermodynamic equilibrium state.

1. Basics of thermodynamics
- system and surroundings -

- ✓ System: a part of space, matter, etc, that is surrounded/encompassed by a boundary.

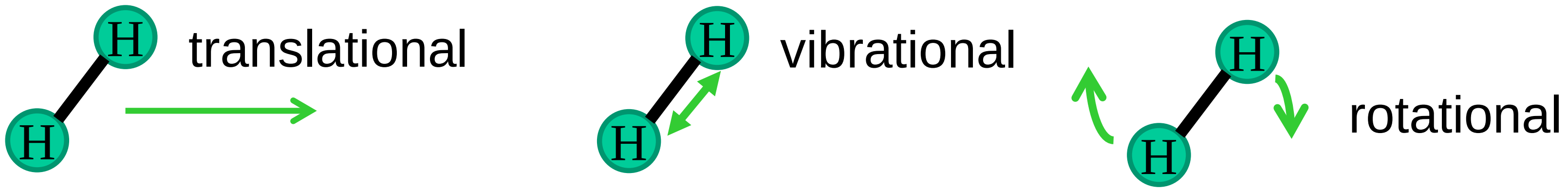
  *Everything outside the system is called surroundings (or environment)



- ✓ Closed system: a system which cannot exchange matter (e.g. molecules) with its surroundings
  - ✓ ↔ Open system: a system which can exchange matter with its surroundings
- ✓ Isolated system: s system which cannot exchange matter nor energy with its surroundings
- ✓ Therefore,
  - ✓ in a closed system, the mass of matter is conserved.
  - ✓ in an isolated system, both mass and energy are conserved.

1. Basics of thermodynamics
- internal energy -

- There are some types of energies
  : Kinetic energy, Potential energy, Nuclear energy, ….
- Macroscopic and microscopic forms of energy
  - Macroscopic form: for example, if the matter in a system moves, it holds a macroscopic form of energy.
  - Microscopic form: even if the matter in a system does not move, inside the matter, "particles" have kinetic energies and potential energies with interacting each other. These kind of energies contained in a system is the microscopic one, namely internal energy, such as
    - Translational/Vibrational/Rotational kinetic energy of atom/molecule



    - Chemical energy, related to chemical bond and interaction
    - Nuclear energy, related to nuclear fission/fusion (usually ignored in chemistry)
- The internal energy is used as a thermodynamic quantity (=macroscopic quantity), depending on temperature, pressure, etc.

Quiz

- ✓ [Q01] There is a system that can exchange energy with surroundings. This system is: (1) closed system, (2) open system, (3) isolated system.

- ✓ [Q02] There is a system that can exchange mass with surroundings, but cannot exchange energy with surroundings. This system is : (1) closed system, (2) open system, (3) isolated system.

- ✓ [Q03] (Total) energy is conserved in an isolated system, but not in a closed system. Is it right?

- ✓ [Q04] In a baseball, you hit a ball thrown by a pitcher. This ball has a “macroscopic form of energy”. Is it correct?

- ✓ [Q05] You put a ball in a shelf. This ball does not have “macroscopic form of energy”, but it should have “microscopic form of energy”, so-called “internal energy”. Is it correct?

Quiz

- ✓ [Q01] There is a system that can exchange energy with surroundings. This system is: (1) closed system, (2) open system, (3) isolated system.

  >> (1), (2)

- ✓ [Q02] There is a system that can exchange mass with surroundings, but cannot exchange energy with surroundings. This system is : (1) closed system, (2) open system, (3) isolated system.

  >> no answer

- ✓ [Q03] (Total) energy is conserved in an isolated system, but not in a closed system. Is it right?

  >> correct

- ✓ [Q04] In a baseball, you hit a ball thrown by a pitcher. This ball has a “macroscopic form of energy”. Is it correct?

  >> correct

- ✓ [Q05] You put a ball in a shelf. This ball does not have “macroscopic form of energy”, but it should have “microscopic form of energy”, so-called “internal energy”. Is it correct?

  >> correct

Quiz

[Q06] “In an isolated system composed by O_2 and H_2 gasses, if combustion takes place, some energies are released and the system temperature will increase. I think the energy is increased, and thus is not conserved in this isolated system.”

Do you agree with this statement?

Quiz

[Q07] "In an isolated system composed by O_2 and H_2 gasses, if combustion takes place, some energies are released and the system temperature will increase. I think the (total) energy is increased, and thus is not conserved in this isolated system."

Do you agree with this statement?

[Answer] In this case, the amount of internal energy is not changed, but the form of energies composing the internal energy is changed. Specifically, some chemical energies are changed mainly to kinetic energies of molecules. So, the isolated system still follows the rule "neither energy nor mass are exchanged with the surroundings" and the total energy is still conserved.

1. Basics of thermodynamics
- ideal gas (1/2)-

- ✓ An ideal gas is a theoretical gas composed of a set of randomly moving, non-interacting point particles. (*wikipedia) As 'point particle', itself has no volume.

- ✓ The ideal gas obeys a simplified equation of state (EOS).

$$pV = nRT$$

Other sophisticated EOS (more realistic for real gasses), see $16.

van der Waals equation $$\left(P + \frac{a}{\bar{V}^2}\right)(\bar{V} - b) = RT$$

Redlich-Kwong equation $$P = \frac{RT}{\bar{V} - B} - \frac{A}{T^{1/2}\bar{V}(\bar{V} + B)}$$

*here $\bar{V}$ is molar volume, defined as $\bar{V} = V/n$.

- ✓ The internal energy is simply defined as follows, and thus a sole and linear function of temperature.

$$U = U(T) = c_v n T$$

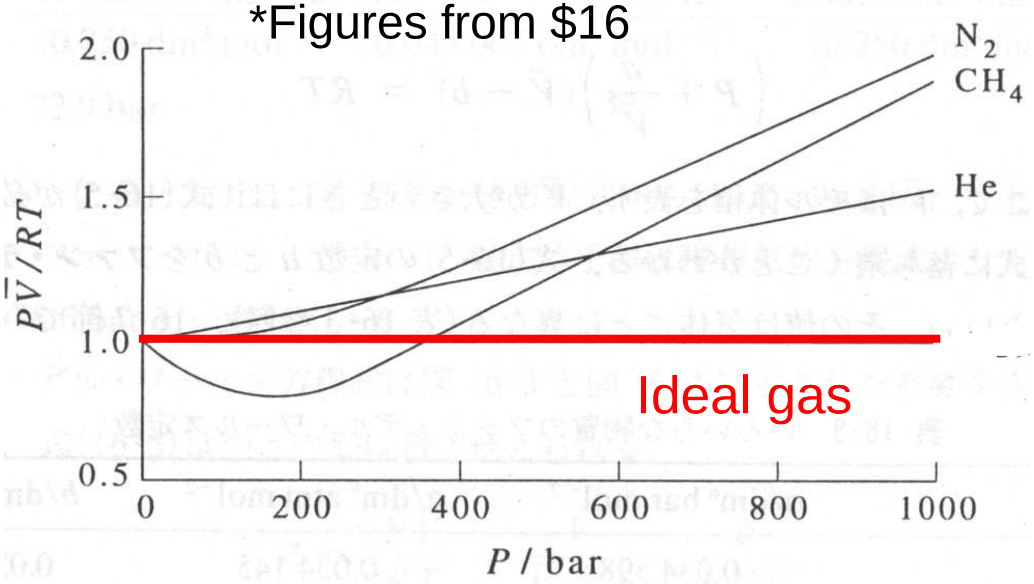
*c_v: specific heat at constant volume

Specific heat	He, O atom	O_2 molecule
c_v [J mol^{-1} K^{-1}]	*(3/2)R*	*(5/2)R*

***R** : the gas constant, 8.31 J mol^{-1} K^{-1}.

1. Basics of thermodynamics
- ideal gas (2/2) : difference from real gasses-

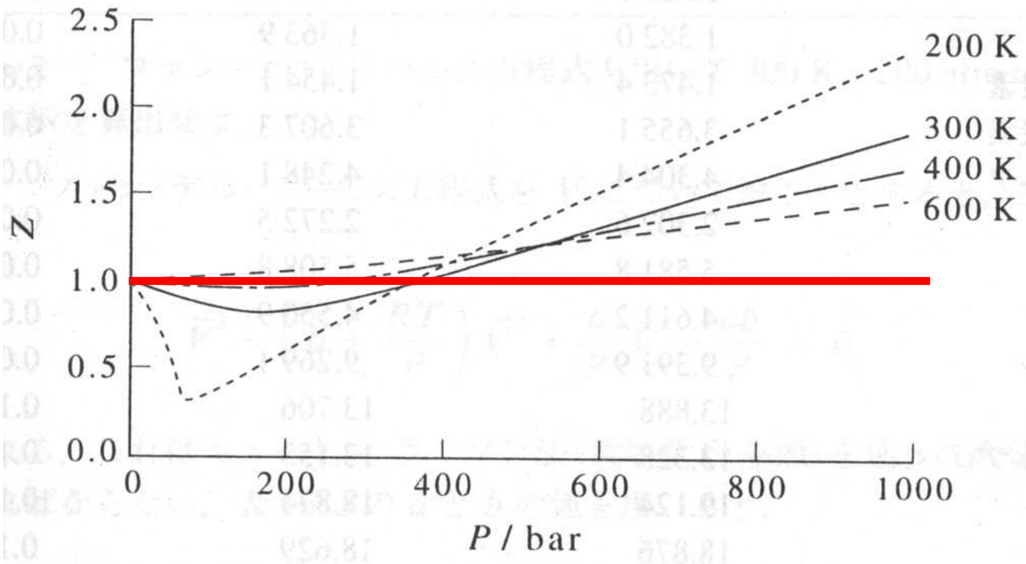
*Figures from $16



The ideal gas better describes real gasses when

the pressure is lower and.

the temperature is higher.



*1 bar = 100,000 Pa

**Z* is compressibility factor.

$$Z = \frac{RT}{P\overline{V}} = \frac{nRT}{PV}$$

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

1. Basics of thermodynamics
- state function (quantity of state) -

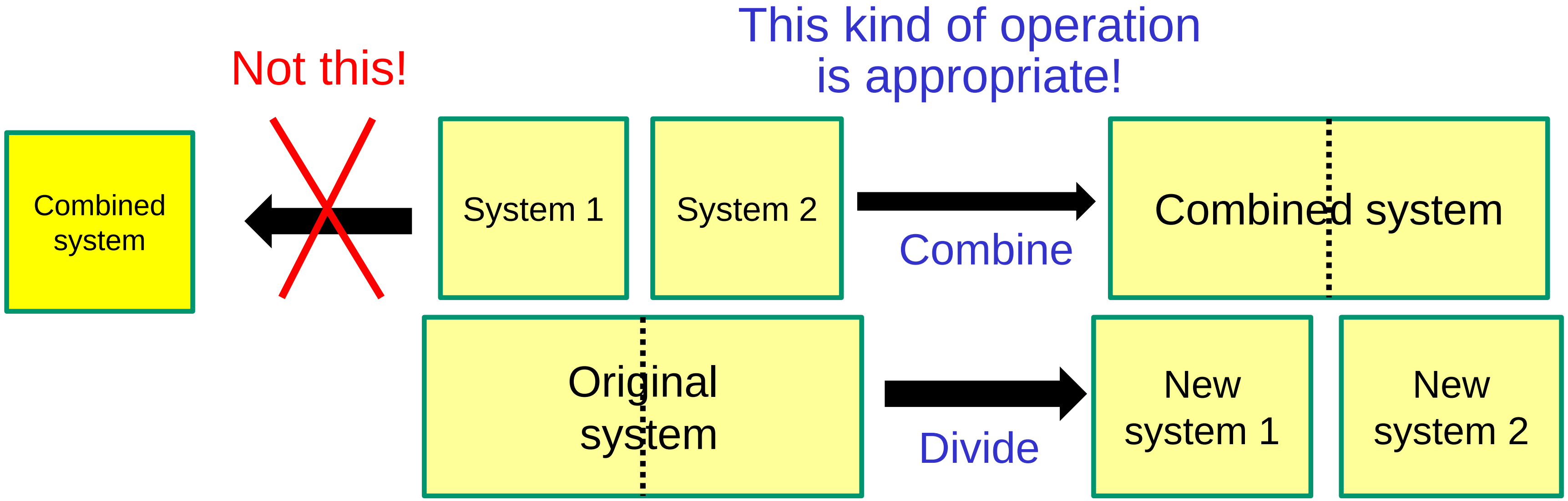
- ✓ In thermodynamic equilibrium state, some physical quantities depend only on the current state, not the history of the state. Thus, these quantities are called "state function" or "quantity of state".
  - ✓ Temperature (T), pressure (p), volume (V), internal energy (U), enthalpy (H), entropy (S), …

1. Basics of thermodynamics
- extensive and intensive quantity (1/2) -

- ✓ Extensive quantity (extensive variable, extensive property) : a quantity which is doubled when the size/extent/amount of the system is doubled.
  - ✓ This nature is called “additivity”.
- ✓ Intensive quantity (intensive variable, intensive property) : a quantity which is not changed when the size/extent/amount of the system is doubled.
    - ➢ Volume: extensive/intensive
    - ➢ Mass: extensive/intensive
    - ➢ Internal energy: extensive/intensive
    - ➢ Temperature: extensive/intensive
    - ➢ Pressure: extensive/intensive

1. Basics of thermodynamics
- extensive and intensive quantity (1/2) -

- Extensive quantity (extensive variable, extensive property) : a quantity which is doubled when the size/extent/amount of the system is doubled.
  - This nature is called “additivity”.
- Intensive quantity (intensive variable, intensive property) : a quantity which is not changed when the size/extent/amount of the system is doubled.
    - Volume: extensive/intensive
    - Mass: extensive/intensive
    - Internal energy: extensive/intensive
    - Temperature: extensive/intensive
    - Pressure: extensive/intensive



1. Basics of thermodynamics
- extensive and intensive quantity (2/2)-

- ✓ Basically,
  - ➢ [extensive] / [extensive] = [intensive]
  - ➢ [intensive] / [intensive] = [intensive]
  - ➢ [extensive] / [intensive] = [extensive]

- ✓ For an equation of thermodynamic quantities, the left-hand side and the right-hand side should have the same extensive or intensive character.
  - ✓ (example) $PV = nRT$

- ✓ For an extensive quantity, we can convert it into an intensive quantity by dividing with the mass to have "per kg" quantity:
  - ✓ e.g. specific volume (m^3/kg), specific entropy (J/K/kg), ..

- ✓ Likewise, we can consider "per mole" quantity: molar volume (m^3/mol), etc.

1. Basics of thermodynamics

- the zeroth law: definition of thermal equilibrium and temperature -

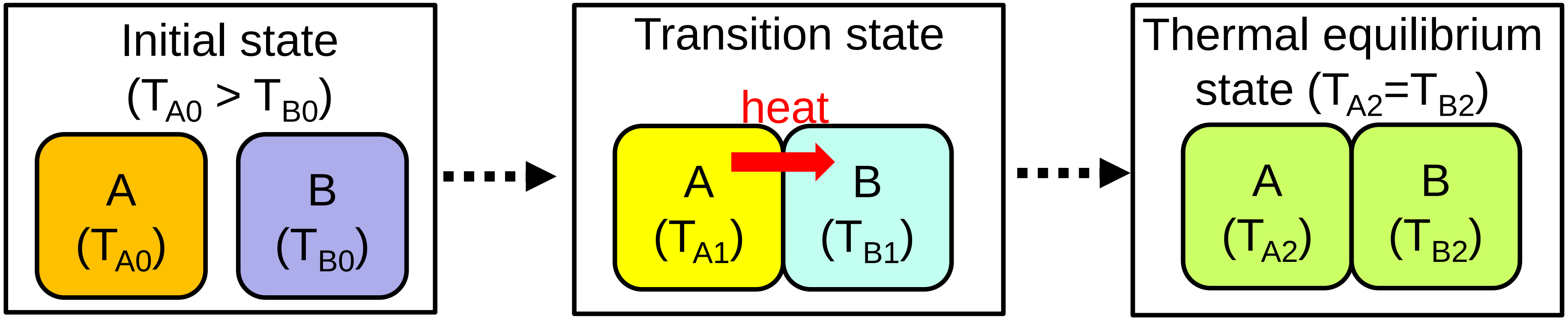
> “if two systems are each in thermal equilibrium with a third system, they are also in thermal equilibrium with each other.”

✓ If an isolated system is kept as it is for a sufficiently long time, it reaches thermal equilibrium.

  ✓ After that (equilibration), “temperature” is constant unless conditions of the surroundings change.

✓ If two (closed) systems (A and B) contact and they are regarded as an isolated system, after a sufficiently long time, they reach thermal equilibrium each other.

  ✓ After that, “temperature” of system-A is the same with that of system-B.



Initial state ($T_{A0} > T_{B0}$)

A (T_{A0}) B (T_{B0})

Transition state

heat

A (T_{A1}) B (T_{B1})

Thermal equilibrium state ($T_{A2}=T_{B2}$)

A (T_{A2}) B (T_{B2})

1. Basics of thermodynamics
- equilibrium state -

In equilibrium, the system(s) remain “unchanged” unless the conditions (e.g. condition of surroundings) are changed.

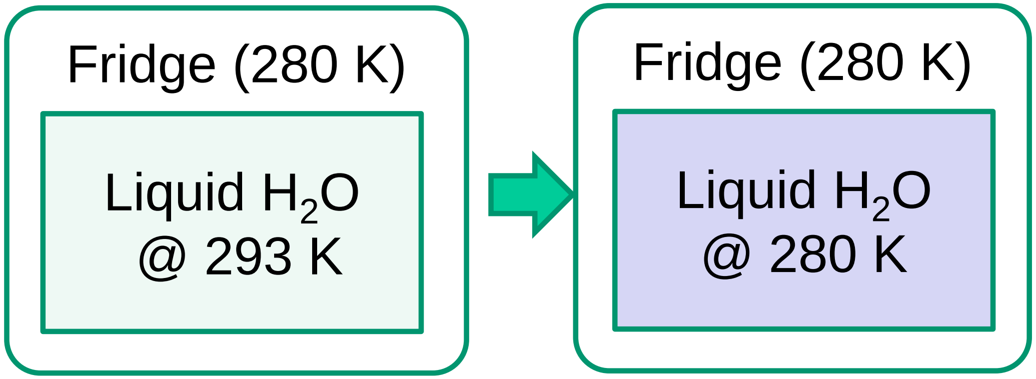
⬇

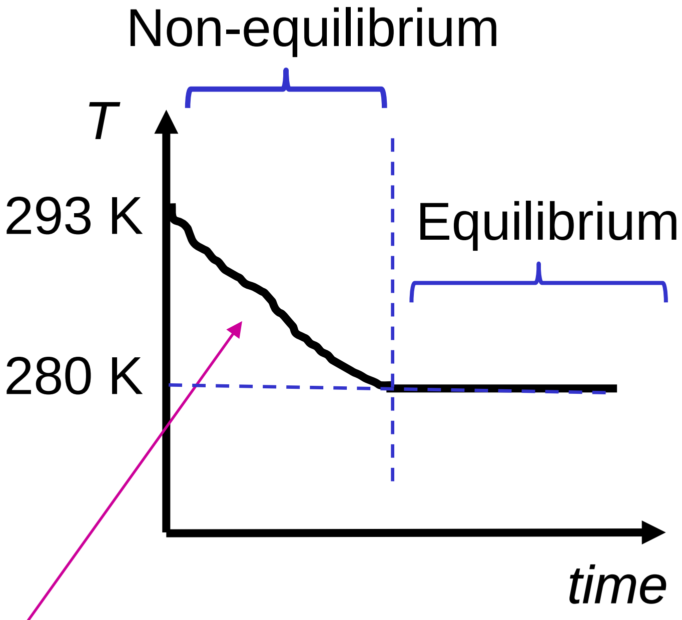
No change in some certain physical quantity(s).
Also the quantity(s) are uniform spatially and temporally.

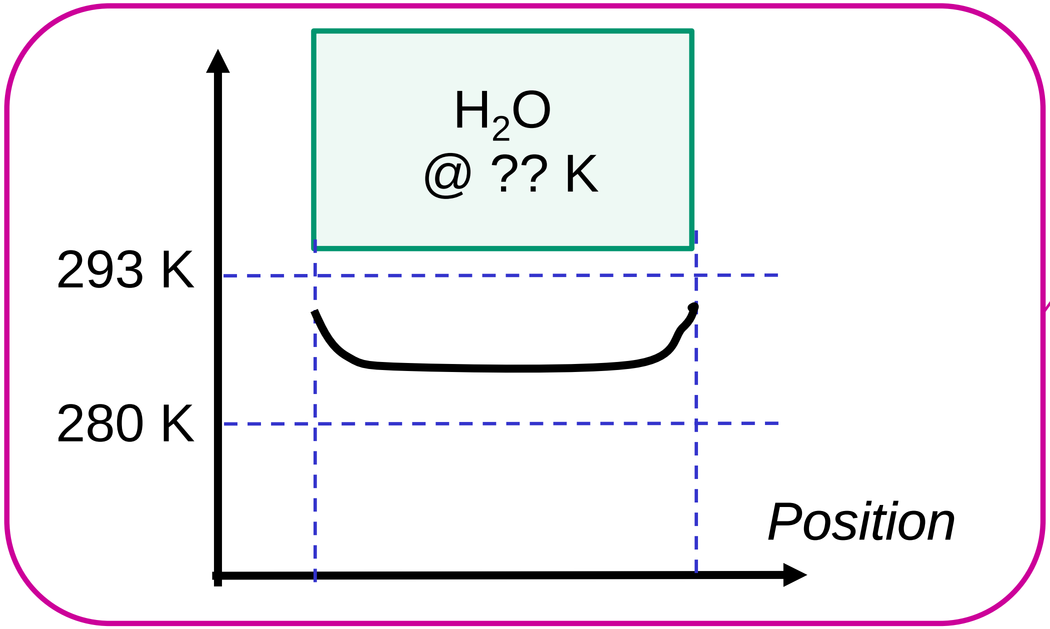
- ✓ If forces (stresses) are balanced between two connected systems, between a system and its surroundings, etc, …. >> mechanical equilibrium
  - → possible unchanged quantity: pressure
- ✓ If materials composition does not change and it is uniform in a system, …. >> chemical equilibrium
  - → possible unchanged quantity: free energy
- ✓ If multiple liquid/solid/gas phases coexist and their composition does not change,…. >> phase equilibrium
  - → possible unchanged quantity: chemical potential

If these thermal/mechanical/chemical/phase equilibriums are fully satisfied, it is called thermodynamic(al) equilibrium. (*In thermodynamics, “equilibrium” usually means “thermodynamic equilibrium”.)

1. Basics of thermodynamics
- equilibrium state: spatial and temporal uniformity -







If we look at a non-equilibrium state

At an equilibrium state, thermodynamical quantities are uniform spatially and temporally.

Quiz

- ✓ [Q07] This class room is at a thermal equilibrium state. Is it correct?
- ✓ [Q08] The water in a sealed bottle in this class room is at an equilibrium state. Is it correct?
- ✓ [Q09] I pour water in a cup and put it in a class room for 1 day. Then, is the water at an equilibrium state?
- ✓ [Q10] I put the water of Q09 into a freezer just now. Then, s the water at an equilibrium state.
- ✓ [Q11] I put the water of Q09 into a freezer 10 minutes ago. Then, is the water at an equilibrium state.
- ✓ [Q12] I put the water of Q09 into a freezer 1 day ago. Then, is the water at an equilibrium state.

Quiz

- ✓ [Q07] This class room is at a thermal equilibrium state. Is it correct?
  >> No. The temperature is not uniform spatially.
- ✓ [Q08] The water in a sealed bottle in this class room is at an equilibrium state. Is it correct?
  >> Yes.
- ✓ [Q09] I pour water in a cup and put it in a class room for 1 day. Then, is the water at an equilibrium state?
  >> No. (Yes, if we neglect evaporation)
- ✓ [Q10] I put the water of Q09 into a freezer just now. Then, s the water at an equilibrium state.
  >> No. The temperature is not uniform temporally.
- ✓ [Q11] I put the water of Q09 into a freezer 10 minutes ago. Then, is the water at an equilibrium state.
  >> No. The temperature is not uniform temporally and spatially.
- ✓ [Q12] I put the water of Q09 into a freezer 1 day ago. Then, is the water at an equilibrium state.
  >> Yes.

1. Basics of thermodynamics
- process -

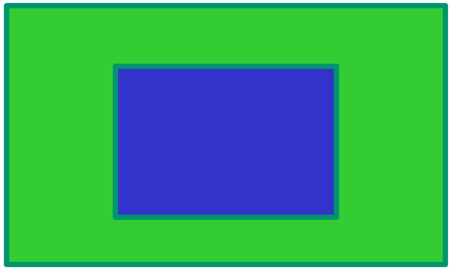
- ✓ "process" means a change of system from one state to another.


State-A
Process
State-B

- ✓ In general, thermodynamics can only "deal with" a system in an equilibrium state.
  - ✓ For example, thermodynamical quantities (*T,P,U,…*) often cannot be even defined in non-equilibrium state.

Liquid H_2O
(water) @ 293 K
[equilibrium]

Solid H_2O
(ice) @ 273 K
[equilibrium]



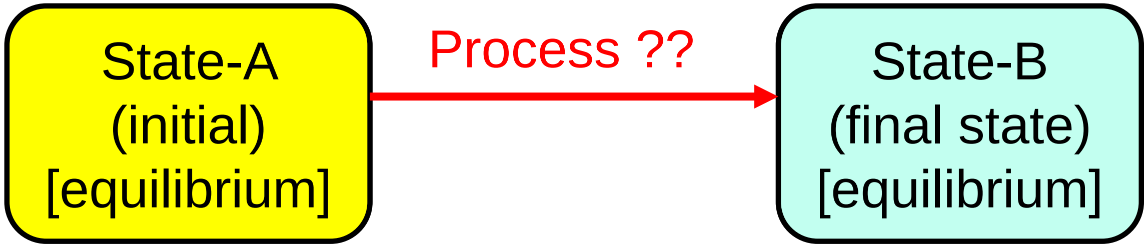
What is the temperature of this system?

After enough long time →

Liquid H_2O
(water) @ 288 K
[equilibrium]

1. Basics of thermodynamics
- process -

- ✓ So, to use thermodynamics, the system should be at an equilibrium state.
  - ✓ (1) initial state and (2) final state must be equilibrium states.
  - ✓ In addition, it is better if (3) states during the process are equilibrium states.


State-A
(initial)
[equilibrium]

Process ??

State-B
(final state)
[equilibrium]

- ✓ However, if the system is in an equilibrium state, quantities of state (state functions) should not be changed. So, no process should take place.

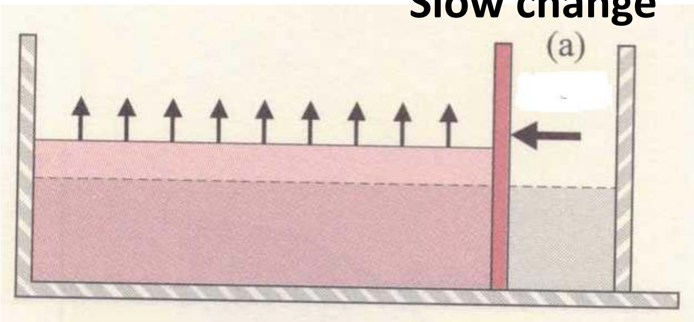
> ➢ *Thermodynamics deals with a system at an equilibrium state.*
>
> ➢ *If a system is at an equilibrium state, thermodynamical quantities (state functions) do not change.*
>
> ➢ *By process, some quantities should be changed as the system moves to a new state.*

- ✓ To simultaneously meet all requirements, we often assume an imaginary process in thermodynamics, that is "quasi-static process".

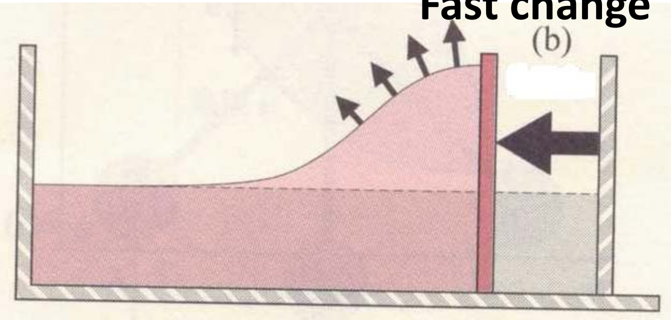
1. Basics of thermodynamics
- quasi-static process -

In a quasi-static process, the process advances infinitely slowly.
The system just suffers a minimal change from an equilibrium state to another equilibrium state, and is at a certain thermodynamic equilibrium state anytime during the process.

Slow change



Fast change



- ✓ Regarding the water level in the box (not thermodynamics though), for example, if the wall moves slowly, the water level is spatially and temporally uniform.
- ✓ In thermodynamics, concerned state functions (e.g. T, p) are spatially and temporally uniform, like the water level. This can be achieved with infinitely slow changes.

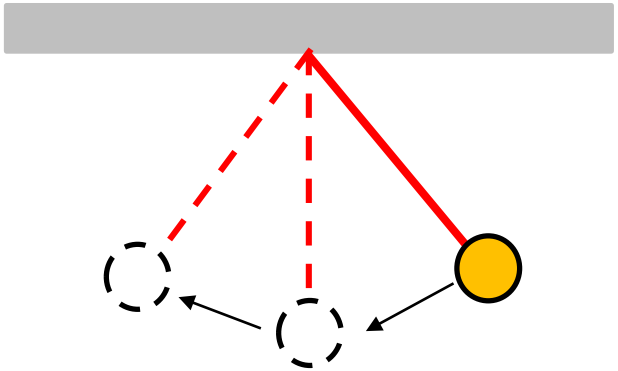
*”Thermodynamics”, JSME (2002).

Indeed, no real process is quasi-static, but some real processes can be approximately regarded as quasi-static processes when it takes very slowly.

1. Basics of thermodynamics
- reversible and irreversible process -

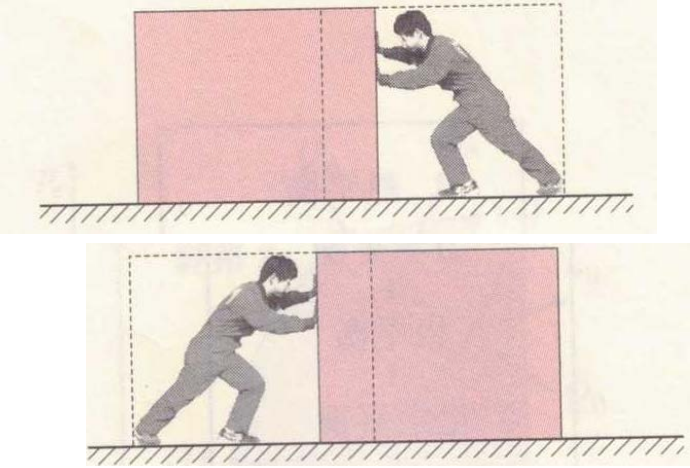
- ✓ "A reversible process is a process that, after it has taken place, can be reversed and causes no change in either the system or its surroundings." (*wikipedia)
- ✓ If some change remains, the process is an irreversible process.

Reversible
(assuming no friction)



*"Thermodynamics", JSME (2002).

Irreversible
(assuming friction)

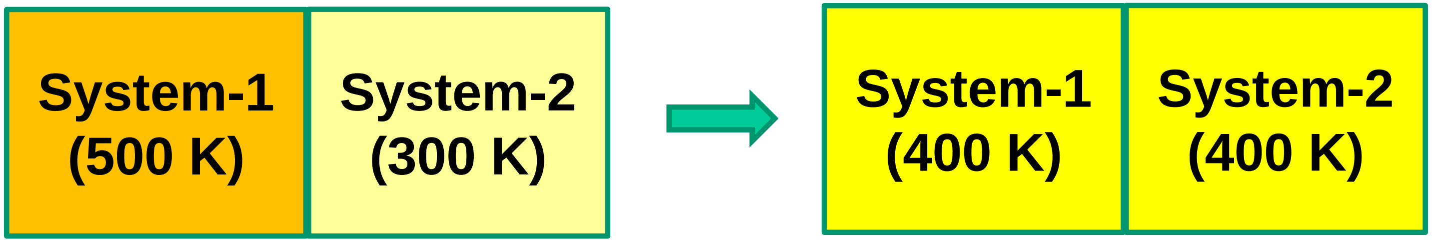


- ✓ All processes can be divided into (1) reversible process or (2) irreversible process.
  - ✓ However, in realty, (almost) no reversible process exists.

*"Thermodynamics", JSME (2002).

1. Basics of thermodynamics
- quasi-static process -

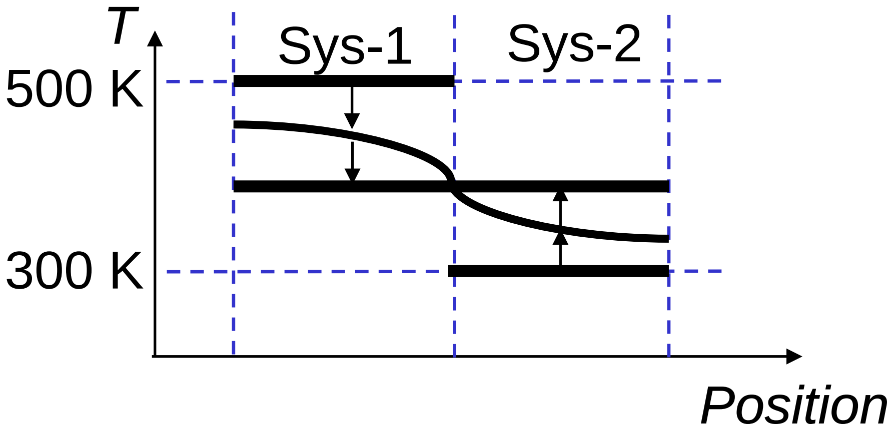
- For example, two systems having different temperatures are connected.
  - In reality, the temperature in each system is not spatially uniform during the process. In this case, we cannot define the temperature of the system.
  - in a quasi-static manner, at any moment, the temperature of each system is spatially uniform. So, each system goes through the process with always holding an equilibrium.



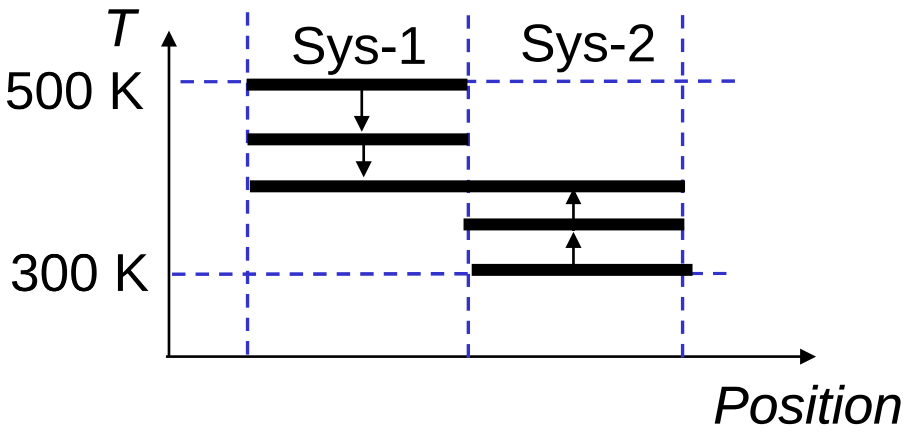
System-1 (500 K) **System-2 (300 K)**

System-1 (400 K) **System-2 (400 K)**

<Reality (not quasi-static)>



<Quasi-static>

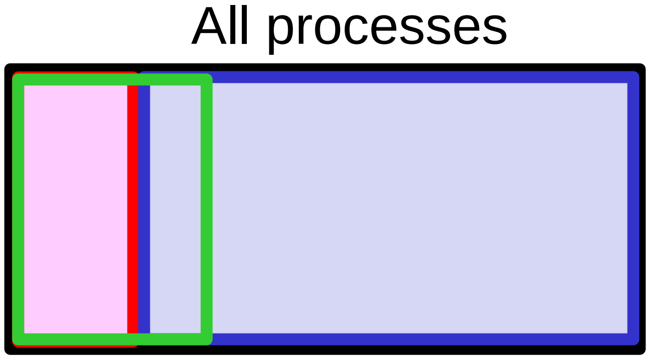


1. Basics of thermodynamics
-Relationship among reversible/irreversible and quasi-static-

< Definition of quasi-static process (in this course, we use definition (1)!) >

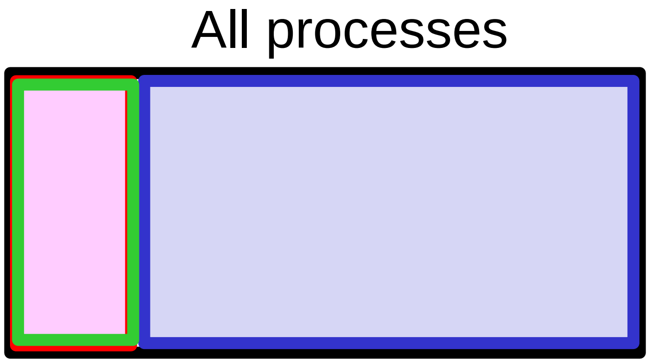
1) Very (infinitesimally) slow process so that we consider the system is always at some equilibrium state.
2) Very (infinitesimally) slow process and the process takes place with adhering the system to some equilibrium state and keeping concerned thermodynamic quantities of the system and the surroundings equal.
   >> for this definition, “quasi-static” is equivalent with “reversible”

[Definition-1]



Reversible
Irreversible
Quasi-static

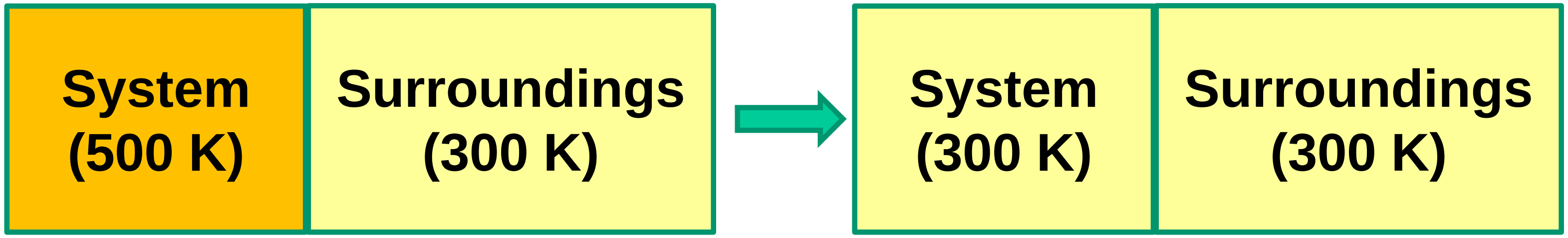
[Definition-2]



✓ 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.

1. Basics of thermodynamics
- example on the difference between definition (1) and (2) -



System
(500 K)

Surroundings
(300 K)

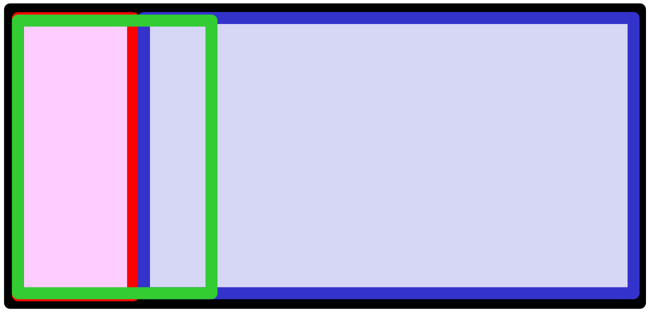
System
(300 K)

Surroundings
(300 K)

- ✓ With the definition (1), this process can be done in a quasi-static manner. This process is irreversible, as we will learn.
- ✓ With the definition (2), this process cannot be considered as a quasi-static process, because “keeping concerned thermodynamic quantities of the system and the surroundings equal” is violated. Specifically, the temperatures are different between the system and the surroundings.

1. Basics of thermodynamics
-Relationship among reversible/irreversible and quasi-static-

All processes



Reversible **Irreversible** **Quasi-static**

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

- ✓ <reversible process> process from one equilibrium state to another equilibrium state. During the process, the system is always at some equilibrium state. We can always define thermodynamic quantities.

- ✓ <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. We can always define thermodynamic quantities.

- ✓ <irreversible process> processes other than reversible processes. We may define thermodynamic quantities during the process, but normally not. (If quasi-static irreversible, we can always define).

Contents of today

1. Basics of thermodynamics
2. The first law of thermodynamics

Goals of today's lecture

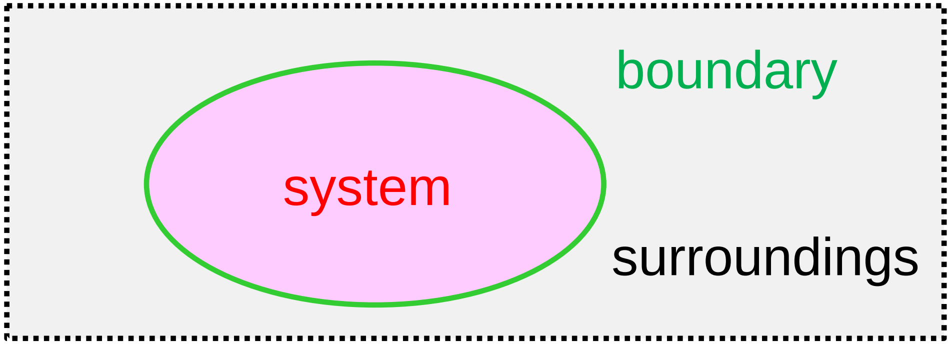
- ✓ Understand basic technical terms and its definitions used in thermodynamics.
- ✓ Understand the 1st law.

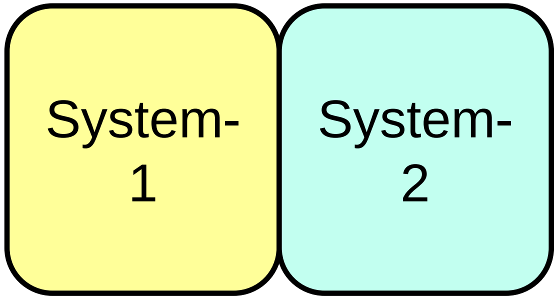
2. The First Law of Thermodynamics

- $19.1: A Common Type of Work is Pressure-Volume Work-

- ✓ Heat (*q*) is a way of energy transfer that occurs due to a difference in temperature between two systems (or between the system and its surroundings).
  - ✓ positive value: when a heat is added to the system (the energy of the system increases)
  - ✓ negative value: when a heat goes out of the system (the energy of the system decreases)
- ✓ Work (*w*) is a way of energy transfer that occurs due to an un-balance in force (in pressure, stress) between two systems or between the system and its surroundings.
  - ✓ positive: when the surroundings do a work to the system (the energy of the system increase)
  - ✓ negative: when the system does a work to the surroundings

*The sign of work may be defined in an opposite way in other textbooks.





Quiz

- ✓ [Q13] “The system has a work of 18 kJ”. Is this correct?

- ✓ [Q14] “The system has a heat of 30 J”. Is this correct?

- ✓ [Q15] “The heat of 30 J was transferred from the surroundings to the system”. Is this correct?

Quiz

- ✓ [Q13] “The system has a work of 18 kJ”. Is this correct?

  >> No. The system cannot has a work. Work is a sort of energy transfer way (and transferred amount).

- ✓ [Q14] “The system has a heat of 30 J”. Is this correct?

  >> No. The system cannot has a heat. Heat is a sort of energy transfer way (and transferred amount).

- ✓ [Q15] “The heat of 30 J was transferred from the surroundings to the system”. Is this correct?

  >> Maybe OK, but this description may not be so accurate.
  It is better to rewrite:

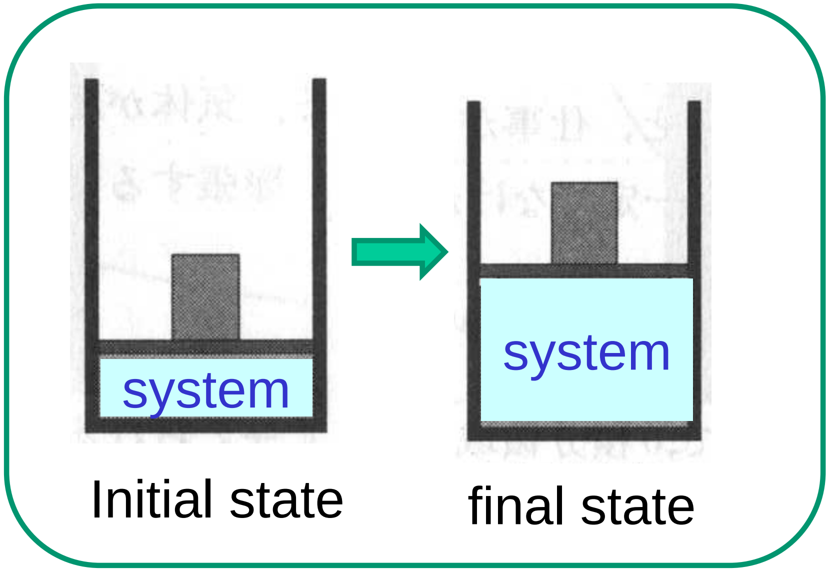
  “The energy of 30 J was transferred from the surroundings to the system as a heat.”

2. The First Law of Thermodynamics

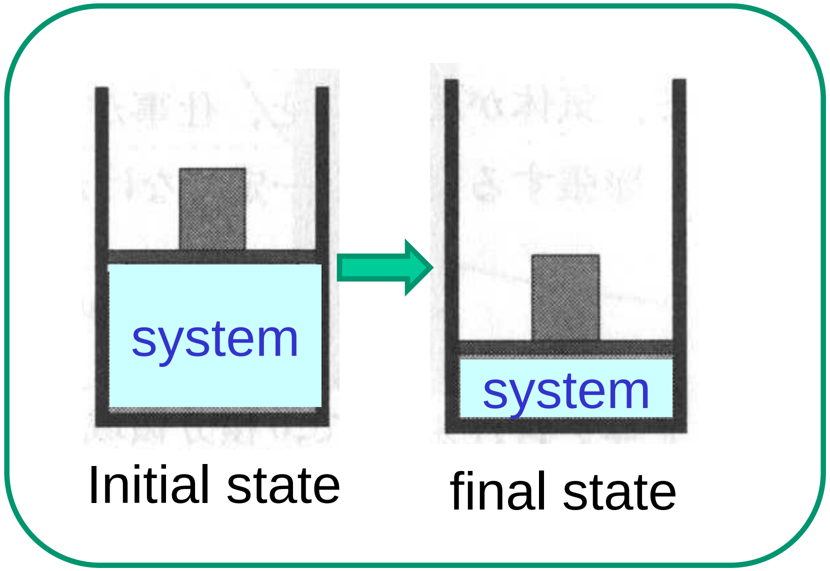
- $19.1: A Common Type of Work is Pressure-Volume Work-

- Work (w) is a way of energy transfer that occurs due to an un-balance in force (e.g. a difference in pressure) between two systems (or the system and its surroundings)
  - positive: when the surroundings do a work to the system
  - negative: when the system does a work to the surroundings

[case-a] $w < 0$



[case-b] $w > 0$

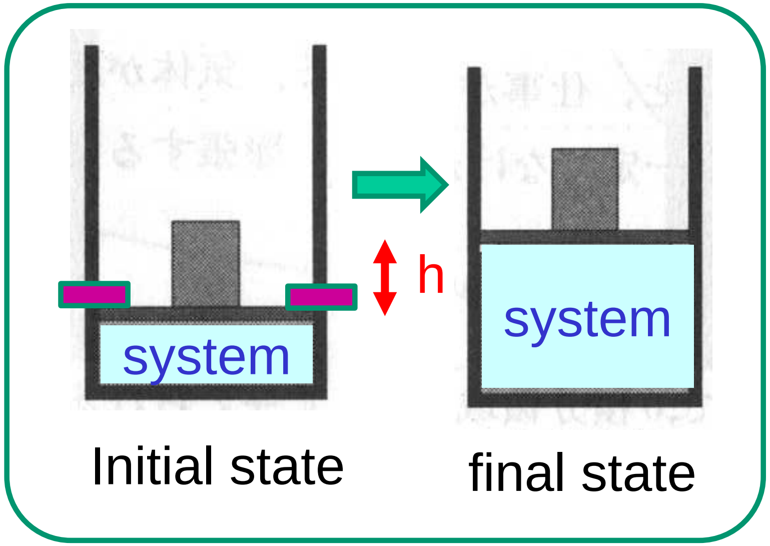


*D.A. McQuarrie, J.D. Simon, “Physical Chemistry: A Molecular Approach", University Science Books (1997).

2. The First Law of Thermodynamics

- $19.1: A Common Type of Work is Pressure-Volume Work-

[case-a] *w* < 0



M:mass of the piston [kg]
g: the gravitational acceleration (9.8 $[m/s^s]$)
h: change in the height [m]
A: area of the bottom plane of piston $[m^2]$
$P_{external}$: pressure of the surroundings

$$w = -(Mg)h$$

as "$w = F\,s$" *in classical mechanics (s is displacement)*

$$w = -\frac{Mg}{A} \times Ah$$

$$w = -P_{external}\Delta V$$

as "Ah" corresponds to volume change (ΔV)

- ✓ At the initial state, $P_{system} > P_{external}$
- ✓ At the final state, $P_{system} = P_{external}$

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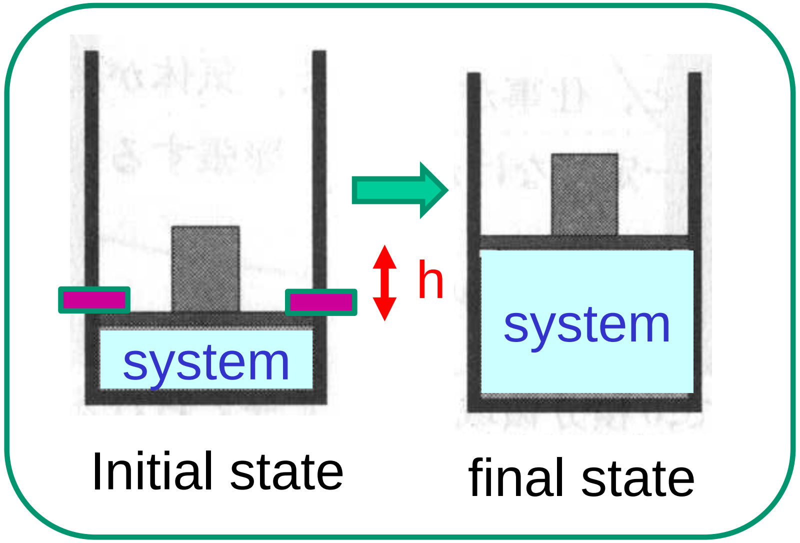
2. The First Law of Thermodynamics

- $19.1: A Common Type of Work is Pressure-Volume Work-

[case-a] $w < 0$



M:mass of the piston [kg]
g: the gravitational acceleration (9.8 $[\mathrm{m/s^s}]$)
h: change in the height [m]
A: area of the bottom plane of piston $[\mathrm{m^2}]$
$P_{external}$: pressure of the surroundings

$$w = -P_{external}\Delta V$$

If the external pressure is not constant during the expansion

$$w = -\int_{V[system-initial]}^{V[system-final]} P_{external}\, dV$$

These equations also work for compression cases.

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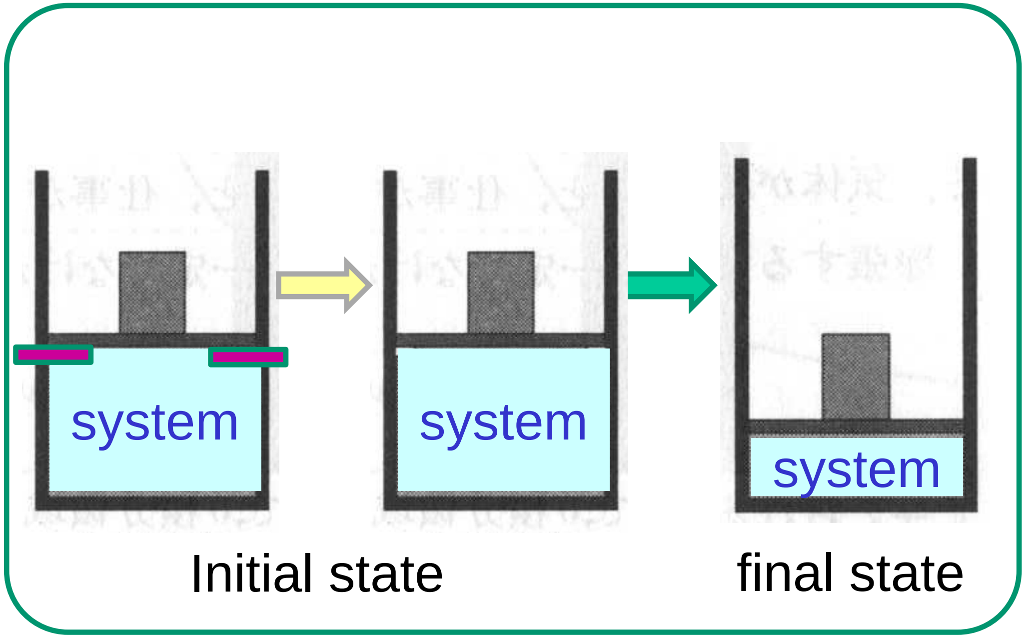
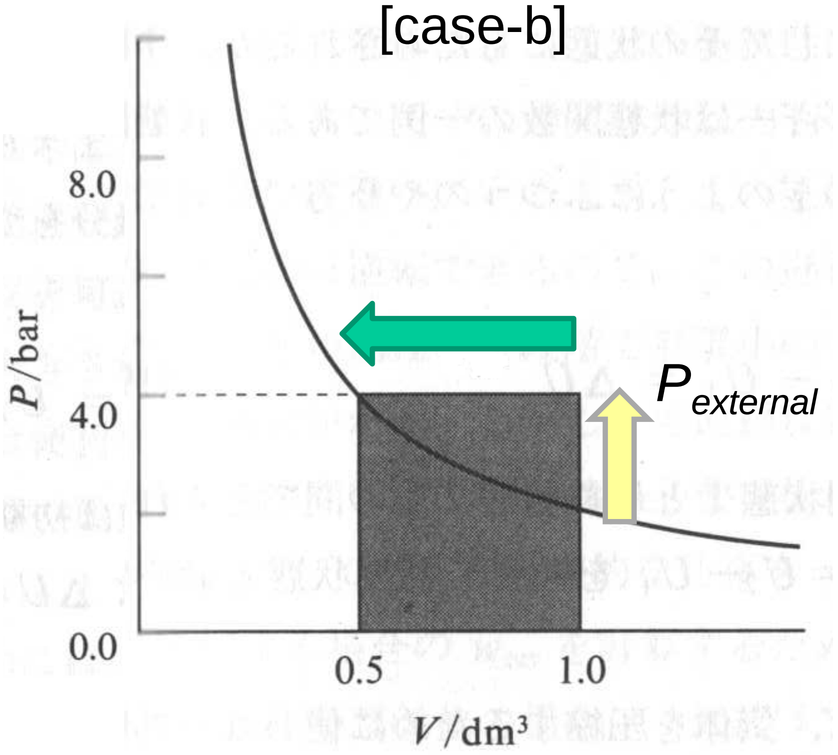
2. The First Law of Thermodynamics

- $19.1: A Common Type of Work is Pressure-Volume Work-





Here, we assume that the external pressure $P_{external}$ is fixed

- ✓ The amount of work is equal to the gray area in P-V diagram.
- ✓ The pressure is external pressure, not the system pressure.

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