Physical Chemistry for Energy Engineering (3rd: 2018/09/10)

Takuji Oda

Assistant Professor, Department of Nuclear Engineering Seoul National University

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

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. 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

<Last class>

- 1.1.1. Basics of thermodynamics
- 1.1.2. The first law of thermodynamics

<Today's class>

- **1.1.2.** The first law of thermodynamics
- 1.2.1. Thermodynamic process
- 1.2.2. Thermodynamic cycle

Review of the last class -quasi-static/reversible/irreversible process>

- < Definition of quasi-static process (in this course, we use definition (1)!) >
 - Very (infinitesimally) slow process so that we consider the system is always at 1) some equilibrium state.
 - Very (infinitesimally) slow process and the process takes place with adhering 2) 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"
 - >> In this course, this is the definition of reversible process.



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

Review

- two energy transfer ways: heat & work -

- ✓ Heat (q) is a way of energy transfer that occurs due to a difference in temperature b/w two systems (or b/w the system and the surroundings).
- Work (w) is a way of energy transfer that occurs due to an un-balance in force/pressure b/w two systems (or b/w the system and the surroundings).
 *The unit of g and w is the same with the unit of energy (a.g. [1])

*The unit of q and w is the same with the unit of energy (e.g. [J]).

<How energy transfer as "heat" occurs ?>



- ✓ If the temperature of a system is different from that of the surroundings, some energy can be transferred b/w the system and the surroundings.
- Energy is always transferred from a higher-temperature side to a lower-temperature side.
 - ▶ If $T_{external} > T_{system}$, q > 0. It means system energy is increased.
 - > If $T_{system} > T_{external}$, q < 0. It means system energy is decreased.
 - > If $T_{system} = T_{external}$, q = 0. It means no energy transfer as heat.

1.1.2. The First Law of Thermodynamics (\$19.1)

- A typical work in thermodynamics: Pressure-Volume work-

<How energy transfer as "work" occurs?>





M: the mass of the weight [kg] *g*: the gravitational acceleration (9.8 [m/s^s]) *h*: the change in the height [m] *A*: the area of the bottom plane of piston [m²] $P_{external}$: the pressure of the surroundings *the surroundings is "piston + weight"

w = -Fs = -(Mg)h as in classical mechanics (s is displacement) = $-\frac{Mg}{A} \times Ah$ = $-P_{external}\Delta V$ as "Ah" corresponds to volume change (ΔV)

as "Ah" corresponds to volume change (ΔV) *Regarding the unit: [N/m²] [m² m] = [Pa] [m³]

(exercise)



M: the mass of the weight [kg] g: the gravitational acceleration (9.8 [m/s^s]) *h*: the change in the height [m] A: the area of the bottom plane of piston [m²] $P_{external}$: the pressure of the surroundings

Let's apply : M = 10 kg, h = 0.10 m, $A = 1.0 \text{ m}^2$

(1) How much work did the system make to the surroundings?

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

$$P_{external} = \frac{Mg}{A} = \frac{10 \times 9.8}{1.0} = 98 \text{ [Pa]}$$

$$\Delta V = Ah = 1.0 \times 0.10 = 0.10 \text{ [m^3]}$$

$$-w = -(-P_{external}\Delta V) = 98 \times 0.10 = 9.8 \text{ [J]}$$

(2) How much energy did the surroundings obtain by lifting up the weigh?

 \checkmark By this, the potential energy of surroundings (piston + weight) is increased as: $\Delta U_{surroundings} = Mgh = 10 \times 9.8 \times 0.10 = 9.8 \text{ [J]}$

So, in this process, the energy loss of the system is equal to the energy gain of the surroundings, as energy conservation in classical mechanics.

1.1.2. The First Law of Thermodynamics

- (Appendix) kinds of "work"-

✓ In thermodynamics, the most common work is "pressure-volume work".

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



- \checkmark In addition to it, we have several other forms of work.
 - ✓ Mechanical forms
 - ► P-V work: $w = -Fs = -(Mg)h = -\frac{Mg}{A} \times Ah = -P_{external}\Delta V$
 - Shaft work: $w = -Fs = 2\pi nT$
 - * *T* is the torque and *n* is the number of revolutions.

• Spring work:
$$w = -Fs = \frac{1}{2}kx^2 - \frac{1}{2}kx_0^2$$

* k is the spring constant.

- ✓ Non-mechanical forms
 - \blacktriangleright Electrical work: e.g. $w = \frac{q_1 q_2}{4\pi\varepsilon_0} \frac{1}{r}$
 - Magnetic work
 - Gravitational work

1.1.2. The First Law of Thermodynamics (\$19.1) - how to calculate Pressure-Volume work-



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

M: the mass of the weight [kg] *g*: the gravitational acceleration (9.8 [m/s^s]) *h*: the change in the height [m] *A*: the area of the bottom plane of piston [m²] $P_{external}$: the pressure of the surroundings

- ✓ If we only consider "a piston with a weight", the pressure $(P_{external} = \frac{Mg}{A})$ is always constant.
- ✓ If we consider some gasses or mechanical devices as the surroundings, the pressure can be changed ($P_{external}(V)$). Then, we need an integral as:

$$w = -\int_{V_{system-initial}}^{V_{system-final}} P_{external} \, dV = -\int_{V_{ini}}^{V_{fin}} P_{ext} \, dV$$

* This integral form is more general because if $P_{ext} = const.$, this equation gives: $w = -\int P_{ext} dV = -P_{ext} \int dV = -P_{ext} \Delta V.$

1.1.2. The First Law of Thermodynamics (\$19.1)

- how to calculate P-V work-



$$w = -\int_{V_{ini}}^{V_{fin}} P_{ext} \, dV$$

✓ To make this integral, P_{ext} should be expressed as a function of *V*, like $P_{ext} = P_{ext}(V)$.

*Note this *V* is the system volume, not the volume of the surroundings.



We use external pressure (not system pressure) for work calculation !

1.1.2. The First Law of Thermodynamics (\$19.1) - how to calculate P-V work: compression case -

Here, we consider compression case.



✓ At state-1, due to the pin, $P_{sys} = P_{ext}(<\frac{Mg}{A})$.

 ✓ [Process 1→2] Taking out the pin. Because no change in system volume, no work is brought.

✓ At state-2, because the pin is out, $P_{sys} < P_{ext}$ (= $\frac{Mg}{A}$).

✓ [Process 2 → 3] Compressing the system.

✓ At state-3,
$$P_{sys} = P_{ext}(=\frac{Mg}{A})$$
.

1.1.2. The First Law of Thermodynamics

- how to calculate P-V work: comp. b/w expansion & compression-

<<u>Expansion></u>
 <pr

P-V work is defined as:

$$w = -\int_{V_{ini}}^{V_{fin}} P_{ext} \, dV$$
f $P_{ext} = const$. like the left figures,

 $w = -P_{ext} \,\Delta V$

<<u> Compression></u>



Because pressure cannot take a negative value ($P_{ext} \ge 0$)

- ✓ for expansion ($\Delta V > 0$), " $w \le 0$ " is always achieved, which mean the system energy is decreased.
- ✓ for compression ($\Delta V < 0$), " $w \ge 0$ " is always achieved, which mean the system energy is increased.

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

1.1.2. The First Law of Thermodynamics (\$19.1)

- compression with different external pressures-



✓ w_A < w_B, as the work depends on P_{ext}, not on P_{sys}. (P_{ext-A} < P_{ext-B})
 ✓ To induce compression, P_{ext} > P_{sys} is needed. However, if ΔP = P_{ext} - P_{sys} is too large, more energy (as work) is needed for the compression. Case-A is more effective.

1.1.2. The First Law of Thermodynamics (\$19.1)

- how to make expansion in an effective way?-

<How to make compression effectively?>

- ✓ To make a compression process, it is needed to keep the external pressure larger than the system pressure ($P_{ext} > P_{sys}$).
- ✓ If P_{ext} is decreased close to P_{sys} , we can imaginarily consider "compression with keeping $P_{ext} = P_{sys}$ ".
 - ✓ In this condition, this process is quasi-static and reversible.
 - ✓ In this condition, the work needed to give to the system for compression is minimized, thus most effective.



1.1.2. The First Law of Thermodynamics (\$19.1) - how to make expansion in an effective way?-

<How to make expansion effectively?>

- ✓ To make an expansion process, it is needed to keep the external pressure smaller than the system pressure ($P_{ext} < P_{sys}$).
- ✓ If P_{ext} is increased close to P_{sys} , we can imaginarily consider "expression with keeping $P_{ext} = P_{sys}$ ".
 - ✓ In this condition, this process is quasi-static and reversible.
 - ✓ In this condition, the work extracted from the system by expansion is maximized, thus most effective.





1.1.2. The First Law of Thermodynamics (\$19.1) - how to calculate P-V work in reversible process (quasi-static) -



✓ P-V work is determined as:

$$w = -\int_{V_{ini}}^{V_{fin}} P_{ext} \, dV$$
✓ If the process is reversible, $P_{ext} = P_{sys}$. Then,

$$w = -\int_{V_{ini}}^{V_{fin}} P_{ext} \, dV = -\int_{V_{ini}}^{V_{fin}} P dV$$
*we usually write *P* to mean P_{sys} .

Review of the last class -quasi-static/reversible/irreversible process>

- < Definition of quasi-static process (in this course, we use definition (1)!) >
 - Very (infinitesimally) slow process so that we consider the system is always at 1) some equilibrium state.
 - Very (infinitesimally) slow process and the process takes place with adhering 2) 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"
 - >> In this course, this is the definition of reversible process.



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

Quiz



✓ If the process is reversible, $P_{ext} = P$ is achieved. (*P* means P_{sys}). Then, the P-V work is defined as:

$$w = -\int_{V_{ini}}^{V_{fin}} PdV$$
(for reference)

(for reversible processes)

[Q01] If *P* behaves as $P = 2.0 \times V^{-2}$ in SI units, how much is the minimum work required to compress the system from 3.0 m³ to 2.0 m³.

Quiz



✓ If the process is reversible, $P_{ext} = P$ is achieved. (*P* means P_{sys}). Then, the P-V work is defined as:

$$w = -\int_{V_{ini}}^{V_{fin}} PdV$$
(for re

(for reversible processes)

[Q01] If *P* behaves as $P = 2.0 \times V^{-2}$ in SI units, how much is the minimum work required to compress the system from 3.0 m³ to 2.0 m³.

The minimum work is achieved for reversible process. Thus $P_{ext} = P$ and then,

$$w = -\int_{V_{ini}}^{V_{fin}} PdV = -\int_{3.0}^{2.0} (2.0 \times V^{-2})dV = 2.0[V^{-1}]_{3.0}^{2.0} = 0.33 [J]$$

This value corresponds to the energy transferred from the surroundings to the system as work.

1.1.2. The First Law of Thermodynamics (\$19.2) - energy is a state function, but work is not a state functions -

- Energy is a state function. Thus, it depends only on the current state, not on the history of the state of the system.
 - ✓ In a process, the energy change depends only on energy difference between the initial state and the final state, not on the path.



 $\Delta U = \int_{state-1}^{state-2} dU = U_2 - U_1$

$$\Delta U_{path-1} = \Delta U_{path-2}$$

- ✓ On the other hand, work is not a state function. It means the amount of work depends on the path/process, which is called "path function".
 - ✓ For example, if the external pressure is increased, the work is increased, as we learned.
 - ✓ So, even if the initial and the final state are identical between 2 paths, the work may be different each other. ($w_{path-1} \neq w_{path-2}$)

1.1.2. The First Law of Thermodynamics (\$19.2) - energy is a state function, but work is not a state functions -



(Appendix)

- ✓ If dU = 0 throughout the process, always $\Delta U = \int dU = 0$. ✓ However, $\Delta U = 0$ does not guarantee dU = 0.
- ✓ If $\delta w = 0$ throughout the process, always $w = \int \delta w = 0$. ✓ However, w = 0 does not guarantee $\delta w = 0$.

1.1.2. The First Law of Thermodynamics (\$19.2) - heat is also a path function, like work -

 Heat (q), which is a way of energy transfer that occurs due to a difference in temperature between two systems (or the system and its surroundings), is not a state function but a path function, as the same with work.



Is there any constraint in dU, δw and δq ?? >> YES !!

1.1.2. The First Law of Thermodynamics (\$19.3) - the 1st law as energy conservation law for thermodynamics -

<The first law of thermodynamics (energy conservation)> $dU = \delta q + \delta w (+\delta z) \qquad \Delta U = q + w (+z)$

- ✓ The term δz accounts for energy transfer due to matter transfer, which is needed for open system. If the concerned system is isolated or closed, this term is 0 ($\delta z = 0$). (we usually omit this term it in this course).
- ✓ Due to this constraint in heat and work (energy transfers), the energy is conserved, although each can take an arbitrary value.
 - ✓ For example, let's consider three paths having identical initial and final states, and thus $\Delta U = U_{fin} U_{ini} = 10$ [J]
 - ▶ If $q_{path-1} = 5 [J]$, it must be $w_{path-1} = 5 [J]$.
 - ▶ If $q_{path-2} = 10 [J]$, it must be $w_{path-2} = 0 [J]$.
 - ▶ If $q_{path-3} = -20 [J]$, it must be $w_{path-3} = 30 [J]$.
- ✓ In classical mechanics, the energy conservation is considered only for work. In thermodynamics, heat is additionally involved.

1.1.2. The First Law of Thermodynamics (\$19.3) - description of the 1st law -

"The first law of thermodynamics is a version of the law of conservation of energy, adapted for thermodynamic systems. The law of conservation of energy states that the total energy of an isolated system is constant; energy can be transformed from one form to another, but cannot be created or destroyed."

(*wikipedia)

- \checkmark There exists for every system a property called energy (E).
 - E = internal energy (arising from molecular motion primarily a function of temperature) + kinetic energy (**macroscopic)+ potential energy (**macroscopic) + chemical energy (**which usually contained in internal energy).

The change in energy of a system is equal to the difference between the heat added to the system and the work done by the system. (** "done to the system" in our definition)

(*http://web.mit.edu/16.unified/www/FALL/thermodynamics/thermo_4.htm)

> dU = $\delta q + \delta w$ (in this course)
> dU = $\delta q - \delta w$ (in some textbooks)

Quiz

- ✓ [Q02] " δq and δw does not depend on a pathway of the process, but just depend on the initial and the final states of the process." Is this statement correct?
- ✓ [Q03] "dU does not depend on a pathway of the process, but just depend on the initial and the final states of the process." Is this statement correct?

Quiz

- ✓ [Q02] δq and δw does not depend on a pathway of the process, but just depend on the initial and the final states of the process.
 > No.
- ✓ [Q03] dU does not depend on a pathway of the process, but just depend on the initial and the final states of the process.

>> No. dU depend on a process (path). What does not depend on the pathway is $\Delta U = U_{fin} - U_{ini}$, which only depends on the initial and final states.

Contents of today

<Last class>

- 1.1.1. Basics of thermodynamics
- 1.1.2. The first law of thermodynamics

<Today's class>

- 1.1.2. The first law of thermodynamics
- **1.2.1. Thermodynamic process**
- 1.2.2. Thermodynamic cycle

1.2.1. Thermodynamic process - basics -

- ✓ "process" is an operation to cause a change of the system from one state (initial state) to another state (final state)".
- ✓ A process often accompanies an energy transfer as heat or/and work.
- ✓ During the process, the 1st law (and other 2nd and 3rd laws) should be preserved.

1st law: $dU = \delta q + \delta w$



1.2.1. Thermodynamic process - some widely-applied simplifications -

✓ In thermodynamics, we normally consider only P-V work.

$$\delta w = -P_{ext}dV$$
$$w = \int \delta w = -\int P_{ext}dV$$



- ✓ If we consider non P-V work, " $\delta w = -P_{ext}dV + \delta w_{non-PV}$ " *Hereafter, if not specified, work is only P-V work ($\delta w_{non-PV} = 0$)
- ✓ If we consider enter/escape of some matter (e.g. molecules) to/from the system, the 1st law should be "d*U* = $\delta q + \delta w + \delta z$ " where δz represents the energy gain/loss by enter/escape of some matter. **Hereafter, if not specified, we assume* $\delta z = 0$

(assuming closed or isolated system)

1.2.1. Thermodynamic process - expansion and compression to make energy transfer as work -

Here we focus on P-V work: $\delta w = -P_{ext}dV$ and $P_{ext} \ge 0$.





dV < 0 thus $\int \delta w = w \ge 0$

*The equal sign is achieved when $P = P_{ext} = 0$, namely both system and surroundings are vacuums.

1.2.1. Thermodynamic process - heating and cooling to make energy transfer as heat -

Here we focus on heat.



Expansion & Compression: energy transfer by work

✓ Heat & Cooling: energy transfer by heat



✓ If we also consider non-PV work: $dU = \delta q + \delta w_{PV} + \delta w_{non-PV} = \delta q + \delta w_{non-PV}$.

1.2.1. Thermodynamic process - constant-pressure heating/cooling (dP = 0)-

1st law: $dU = \delta q + \delta w$

(2) Constant-pressure heating/cooling: dP = 0 (P = const.)



*In the right graph, if the system is an ideal gas, the volume is linearly change with the temperature, as PV = nRT.

✓ If we further assume the process is reversible, where $P = P_{ext}$, $T = T_{ext}$, etc, then:

 $\delta w = -PdV$ thus $\Delta U = q - P\Delta V$

Quiz

✓ [Q04] A system goes through a reversible constant-volume heating process at 0.020 m³ from 300 K to 500 K. The system is composed by 1 mole of ideal gas whose energy is defined as $U = \frac{3}{2}nRT$. Please determine (1) ΔU , (2) w and (3) q in this process.

Quiz

- ✓ [Q04] A system goes through a reversible constant-volume heating process at 0.020 m³ from 300 K to 500 K. The system is composed by 1 mole of ideal gas whose energy is defined as $U = \frac{3}{2}nRT$. Please determine (1) ΔU , (2) w and (3) q in this process.
 - Because constant-volume process (dV = 0), $\delta w = -PdV = 0$. Hence, $w = \int \delta w = 0$.
 - Using the energy expression of ideal gas, $\Delta U = \frac{3}{2}nR\Delta T = \frac{3}{2} \times 1 \times 8.31 \times (300 - 500) = 2.5 \times 10^3 \text{ [J]}$ According to 1st law, dU = $\delta q + \delta w = \delta q$. Thus, $\Delta U = q$. Hence, $\Delta U = q = 2.5 \times 10^3 \text{ [J]}$, w = 0 [J].