

Chapter 2

Heat, Work, Internal Energy, Enthalpy
and the First Law of Thermodynamics

Physical Chemistry, 3rd Edition

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Objectives

- Introduction of internal energy (내부에너지), U .
- Introduction of the first law of thermodynamics.
- Discussion of the concepts of the heat capacity, the difference between state and path functions, and reversible versus irreversible processes.
- Introduction of enthalpy, H , as a form of energy.
- Calculation of ΔU , ΔH , q , and w for processes involving ideal gases.

Chapter Outline (pp.17-44)

1. The ΔU and the First Law of Thermodynamics (열역학1법칙)
2. Work (일)
3. Heat (열)
4. Doing Work on the System and Changing the System Energy from a Molecular Level Perspective (new addition in 3rd edition)
5. Heat Capacity (열용량)
6. State Functions and Path Functions (상태/경로함수)
7. Equilibrium, Change, and Reversibility (가역성)
8. Comparing Work for Reversible and Irreversible Processes
9. Determining ΔU and Introducing ΔH , a New State Function
10. Calculating q , w , ΔU , and ΔH for Processes Involving Id. Gases
11. The Reversible Adiabatic Expansion and Compression of an Ideal Gas

2.1 The Internal Energy and the First Law of TD

- **Internal energy** is total energy of the system of interest.
- **The first law of thermodynamics** states that energy can be neither created nor destroyed, if both system and the surroundings are taken into account.
- **The internal energy, U , of an isolated system is constant.** 즉 우주의 에너지는 일정하다. ← 1st law of TD

$$U_{universe} = constant \rightarrow \Delta U_{universe} = 0$$

$$\Delta U_{universe} = \Delta U_{system} + \Delta U_{surroundings} = 0 \quad (2.1)$$

$$\Delta U_{system} = -\Delta U_{surroundings} \quad (2.2)$$

2.1 The Internal Energy and the First Law of TD

- For any decrease of U_{system} , $U_{surroundings}$ must increase by exactly the same amount. * 하첨자 없으면 system
- This leads to a more useful formulation of the first law:
Experience has shown that all changes in a closed system in which no chemical reactions or phase changes occur can be classified only as
- heat, work, or a combination of both

$$\Delta U = q + w \quad \text{where } \Delta = \text{final value} - \text{initial value} \quad (2.3)$$

$q = \text{heat} ; w = \text{work}$

- Isothermal process(등온과정) : constant T
 - Isobaric process(등압과정) : constant P
 - Isochoric (isometric) process(등적과정) : constant V
-
- Isotropic process(등엔트로피과정) : constant S
 - Isenthalpic process(등엔탈피과정) : constant H

2.2 Work

- **Heat is Work and Work is Heat !!**

both=energy in transit during a change in state of the system and surroundings.

- Sign convention (부호에 관한 약속)

- $q > 0$ if heat is added to the system
 < 0 " surroundings
- $w > 0$ if work is done on the system
 < 0 " surroundings

* ex: compression $w > 0$; expansion $w < 0$

- In case of $\Delta U \equiv q - w$, then $w < 0$ for compression and $w > 0$ for expansion since $w \equiv \int P_{\text{external}} dV$. In Fig.2.1, the surr^s does the work on the system by lowering the mass, m . Thus, the energy of the sys increases. $\Delta U_{\text{system}} = q - w = -mg\Delta h > 0 \because \Delta h < 0$

2.2 Work

* $\Delta E_{\text{potential}} = -mg\Delta h$

- Work** is defined as any quantity of energy that “flows” across the boundary to overcome an external force.

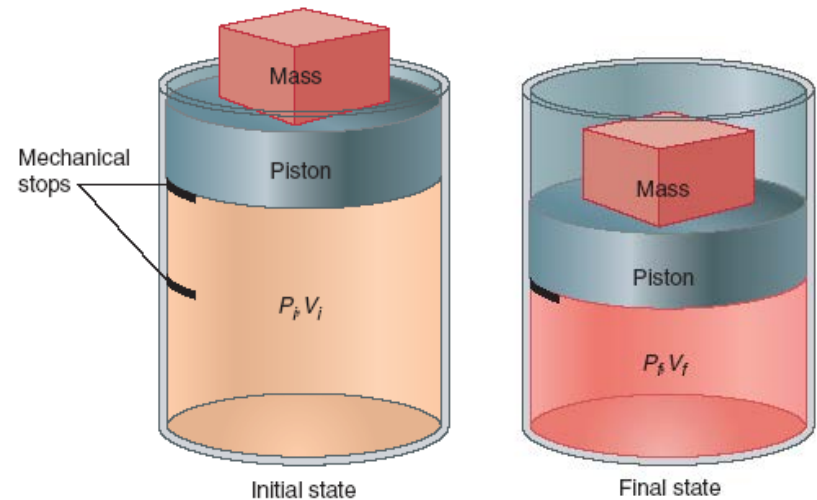
expansion work

- When a gas in an adiabatic piston and cylinder assembly is being compressed, the work done in moving the mass is given by

$$w \equiv \int_{x_i}^{x_f} F \cdot dx \quad (2.4)$$

$$w = \int_{x_i}^{x_f} F \cdot dx = - \int_{x_i}^{x_f} P_{\text{external}} A dx \quad (2.5)$$

$$= - \int_{x_i}^{x_f} P_{\text{external}} dV$$



$$P_{\text{external}} = P_{\text{opposing}} \quad (\text{외부압력} = \text{대항압력})$$

Fig.2.1 System with compression work.

(2.5)에서 w_{exp} (팽창일, $dV > 0$) < 0 로 하기 위해 음(-) 부호 필요

P_{external} needs not equal the system pressure, P_{gas} .

2.2 Work

electrical work

- From electrostatics, the work done in transporting a charge $Q (= It)$ through an electrical potential ϕ is

$$w_{\text{electrical}} = Q\phi = I\phi t \quad (2.6, 2.7)$$

- The system also does work on the surroundings through the increase in the volume of the gas phase at the constant external pressure P_i , as shown by the raised mass on the piston. The total work done is.

$$\begin{aligned} w &= w_{\text{electrical}} + w_{P-V} = I\phi t - \int P_{\text{ext}} dV \\ &= I\phi t - P_{\text{ext}}(V_f - V_i) \end{aligned} \quad (2.8)$$

I : current, A
 ϕ : electrical potential, V
 Q : electrical charge, C
 t : time

system=content of cylinder

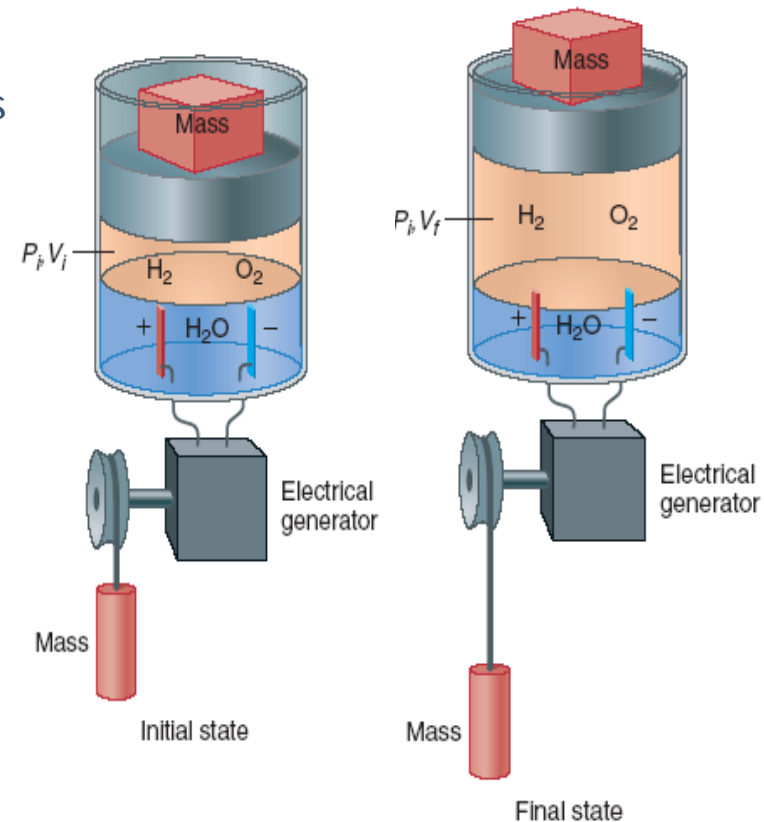




Fig.2.2 Electrical work.

2.2 Work

- Table 2.1 shows the expressions for work for four different cases.

TABLE 2.1 Types of Work

Types of Work	Variables	Equation for Work	Conventional Units
Volume expansion (3D)	Pressure (P), volume (V)	$w = - \int_{V_i}^{V_f} P_{external} dV$	$\text{Pa m}^3 = \text{J}$
Stretching (1D)	Force (F), length (l)	$w = \int_{x_i}^{x_f} \mathbf{F} \cdot d\mathbf{l}$	$\text{N m} = \text{J}$
Surface expansion (2D)	Surface tension (γ), area (σ)	$w = \int_{\sigma_i}^{\sigma_f} \gamma \cdot d\sigma$	$(\text{N m}^{-1})(\text{m}^2) = \text{J}$  Ch.8
Electrical (0D)	Electrical potential (ϕ), electrical charge (Q)	$w = \int_0^Q \phi dQ'$	$\text{V C} = \text{J}$  Ch.11

보강

Example Problem 2.1

- a. Calculate the work involved in expanding 20.0 L of an ideal gas to a final volume of 85.0 L against a constant external pressure of 2.50 bar .
- b. A water bubble is expanded from a radius of 1.00 cm to a radius of 3.25 cm . The surface tension of water is 71.99 N/m . How much work is done in the process?
- c. A current of 3.20 A is passed through a heating coil (전열선) for 30.0 s . The electrical potential across the resistor is 14.5 V . Calculate the work done on the coil.

Solution

$$\begin{aligned} \text{a. } w &= -\int P_{\text{external}} dV = -P_{\text{external}} (V_f - V_i) \\ &= -2.50 \text{ bar} \times \frac{10^5 \text{ Pa}}{\text{bar}} \times (85.0 \text{ L} - 20.0 \text{ L}) \times \frac{10^{-3} \text{ m}^3}{\text{L}} = -16,300 \text{ J} = -16.3 \text{ kJ} \end{aligned}$$

b. A factor of 2 should be included as a bubble has an inner and an outer surface: See [8.8] for more detail.

$$\begin{aligned} w &= -\int \gamma d\sigma = 2\gamma 4\pi (r_f^2 - r_i^2) \\ &= -8\pi \times 71.99 \left(3.25^2 - 1.00^2 \right) \times \frac{10^{-4} \text{ m}^2}{\text{cm}^2} = -1.73 \text{ J} \end{aligned}$$

$$\text{c. } w = \int \phi dQ = \phi Q = I \phi t = 3.20 \text{ A} \times 14.5 \text{ V} \times 30.0 \text{ s} = 1.39 \text{ kJ}$$

- d. We must distinguish between \mathbf{F} , the restoring force on the fiber, and \mathbf{F}' , the force exerted by the person stretching the fiber. They are related by $\mathbf{F} = -\mathbf{F}'$. If we calculate the work done on the fiber, $\mathbf{F}' \cdot d\mathbf{l} = F' dl$ because the vectors \mathbf{F}' and $d\mathbf{l}$ point in the same direction

$$w = \int \mathbf{F}' \cdot d\mathbf{l} = \int_{x_0}^{x_f} kx dx = \left[\frac{kx^2}{2} \right]_{x_0}^{x_f} = \left[\frac{100. \text{ N m}^{-1} \times x^2}{2} \right]_0^{0.15} = 1.1 \text{ J}$$

If we calculate the work done by the fiber, the sign of w is reversed because \mathbf{F} and $d\mathbf{l}$ point in opposite directions.

2.3 Heat

- Heat is defined in thermodynamics as the quantity of energy that flows across the boundary between the system and surroundings because of a temperature difference between the system and the surroundings.
- Heat always flows spontaneously from regions of high temperature to regions of low temperature

Characteristics of Heat:

- Heat is transitory, in that it only appears during a change in state of the system and surroundings. Heat is not associated with the initial and final states of the system and the surroundings.
- The net effect of heat is to change the internal energy of the system and surroundings in accordance with the first law. The quantity of heat that has flowed is directly proportional to the change in temperature of the reservoir.
- The sign convention for heat is as follows. If the temperature of the system is raised, q is positive; if it is lowered, q is negative.
- Generally, we say that if q is positive, i.e., heat is withdrawn from the surroundings and deposited in the system. If q is negative, heat is withdrawn from the system and deposited in the surroundings.

2.3 Heat

* In Fig. 2.3, $\Delta U_{original} = q + w = q < 0$ and $\Delta U_{composite} = 0 + 0 = 0$.

※ Misusage of the terms such as heat & heat capacity. Note the transitory nature of heat.

- **Heat** is the quantity of energy that 'flows' across the boundary between the system and surroundings because of a temperature difference. Exothermic rx. (발열반응), $q < 0$, $\Delta T_{inner} > 0$; system = P&R mixture in rx vessel
- In Fig. 2.3, an exothermic chemical reaction that is carried out in a rigid sealed container with diathermal walls. During the reaction, heat flows out of the system, and the temperature of the inner water bath increases to T_f . Using an electrical heater, the temperature of the outer water bath is increased so that at all times, at this point $\Delta T = 0$, $w = 0$, $\Delta U = 0$ thus, $T_{outer} = T_{inner}$
- Using Fig. 2.4 to establish the relationship between q , w , ΔU . For this, using an isolated system, divided into two subsystems, I and II. In both cases, system I consists solely of the liquid in the beaker, and everything else including the rigid adiabatic walls is in system II. Consider, system I as the system and system II as the surroundings.
 - (a)에서 계1을 분젠버너로 가열 $\Delta T_1 > 0$ 따라서 $\Delta U_1 > 0$, $w_1 = 0$; 계2 $\Delta U_2 < 0$ (\because TD1 법칙), $w_2 = 0$ 따라서 $\Delta U_1 > 0$, $w_1 = 0$ 이므로 $q_1 > 0$ 이고, 계2의 경우 $\Delta U_2 < 0$, $w_2 = 0$ 이므로 $q_2 < 0$ 즉 $-q_1 = q_2$
 - (b)에서 추가 하강하여 발전된 전기가 계1을 가열 $\Delta T_1 > 0$ 따라서 $\Delta U_1 > 0$, $w_1 = 0$; 계2 $\Delta U_2 < 0$ (1법칙), $w_2 < 0$ 따라서 $\Delta U_1 > 0$, $w_1 = 0$ 이므로 $q_1 > 0$ 이고, 계2의 경우 $\Delta U_2 < 0$, $w_2 = -q_1 = -I\phi t < 0$ 이고 $q_2 = 0$

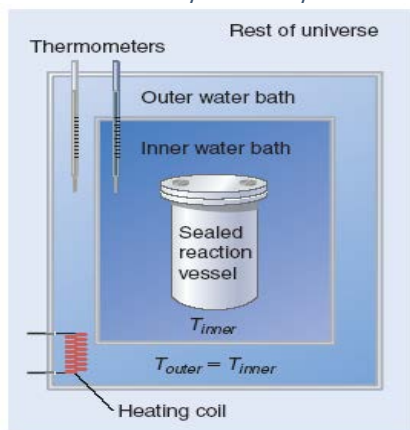


Fig. 2.3 An isolated composite system.

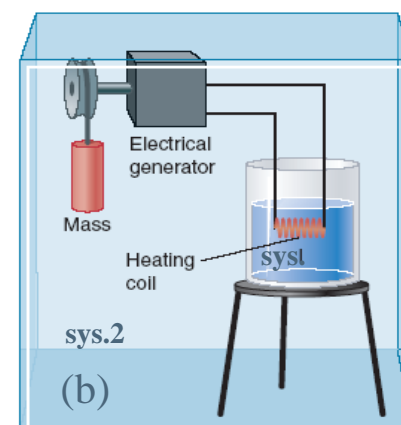
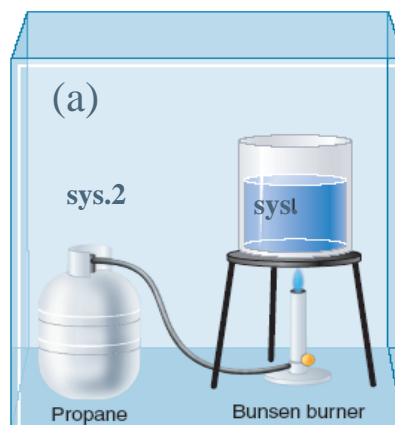


Fig. 2.4 Two other isolated composite systems.

Example Problem 2.2

A heating coil is completely immersed in a 100-*g* sample of H_2O liquid which boils at $99.61^\circ C$ in an open insulated beaker on a laboratory bench at 1 *bar* pressure. In this process, 10 *wt%* of the liquid is converted to the gaseous form at a pressure of 1 *bar*.

A current of 2.00 *A* flows through the heater from a 12.0-*V* battery for 1.00×10^3 *s* to effect the transformation. The densities of liquid and gaseous water under these conditions are 997 and 0.590 *kg / m³*, respectively.

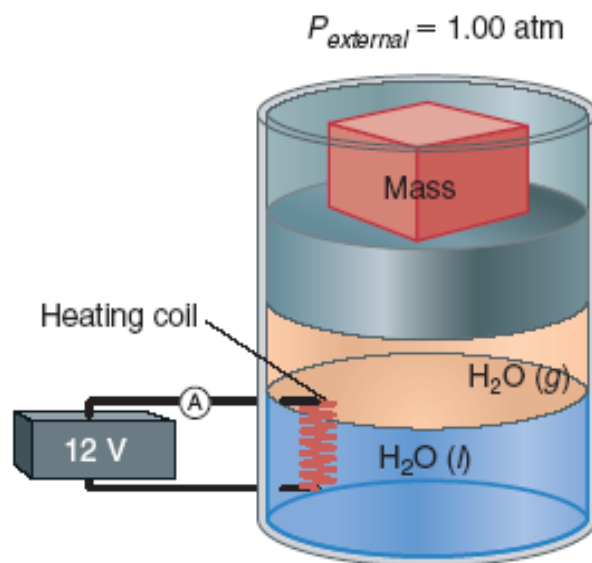
Example Problem 2.2

- a. It is often useful to replace a real process by a model that exhibits the important features of the process. Design a system and surroundings model, like those shown in Figs. 2.1-2.2, that would allow you to measure the heat and work associated with this transformation. For the model, define the system and surroundings as well as the boundary between them.
- b. How can you define the system for the open insulated beaker on the laboratory bench such that the work is properly described?
- c. Calculate q and w for the process.

Solution

- a. The system model is shown in the following figure. The cylinder walls and the piston form adiabatic walls. The external pressure is held constant by a suitable weight.

System=contents inside the cylinder



Proposed model system .

Solution

b. Define the system as the liquid in the beaker and the volume containing only molecules of H_2O in the gas phase. This volume will consist of disconnected volume elements dispersed in the air above the laboratory bench.

c. The heat input to the liquid water can be equated with the work done on the heating coil. Therefore,

$$q = I\phi t = 2.00A \times 12.0V \times 1.00 \times 10^3 s = 24.0 kJ$$

As the liquid is vaporized, the volume of the system increases at a constant external pressure. Therefore, the work done by the system on the surroundings is

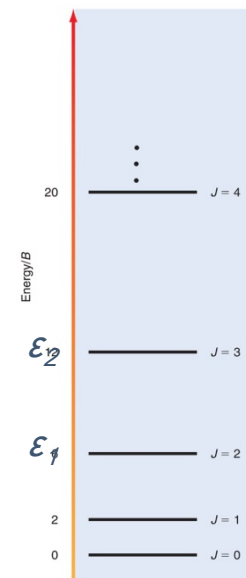
$$w = -P_{external}(V_f - V_i) = -10^5 Pa \left(\frac{10.0 \times 10^{-3} kg}{0.590 kg / m^3} + \frac{90.0 \times 10^{-3} kg}{997 kg / m^3} - \frac{100.0 \times 10^{-3} kg}{997 kg / m^3} \right) = -1.70 kJ$$

2.4 Doing Work on the System and Changing the System Energy from a Molecular Level Perspective (new)

- From Statistical Thermodynamics, Ch.15:
 - * Classical Mechanics: The energy is a continuous vble.
 - * Quantum Mechanics: The energy levels are discrete and molecules can only possess amounts of energy that correspond to these values.
 - * Statistical Mechanics: The relative probability of a molecule being in a state corresponding to the allowed energy values ϵ_1 and ϵ_2 at T is given by

$$\exp[-(\epsilon_2 - \epsilon_1)/k_B T] = \frac{\exp[-\epsilon_2/k_B T]}{\exp[-\epsilon_1/k_B T]}$$

← from Boltzmann distrib', Ch.13.



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Discrete energy levels.

보강

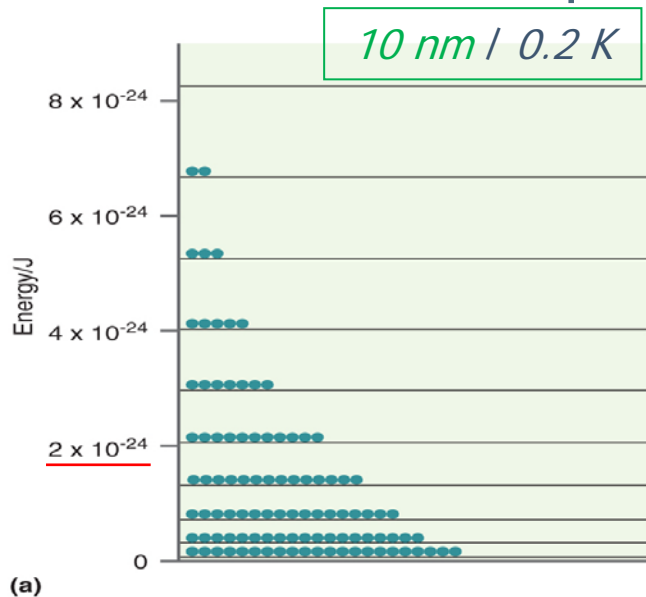
Note : $k_B T = 4.1 \times 10^{-21} \text{ J} = 0.026 \text{ eV}$ at 300 K

$1 \text{ eV} = 96484 \text{ J/mol} = 23 \text{ kcal/mol}$ & $k_B = 1.38 \times 10^{-23} \text{ J}$

- ★ Heat capacity is a capacity of a substance to take up heat and store it in the form of energy.



Particle-in-a-box problem



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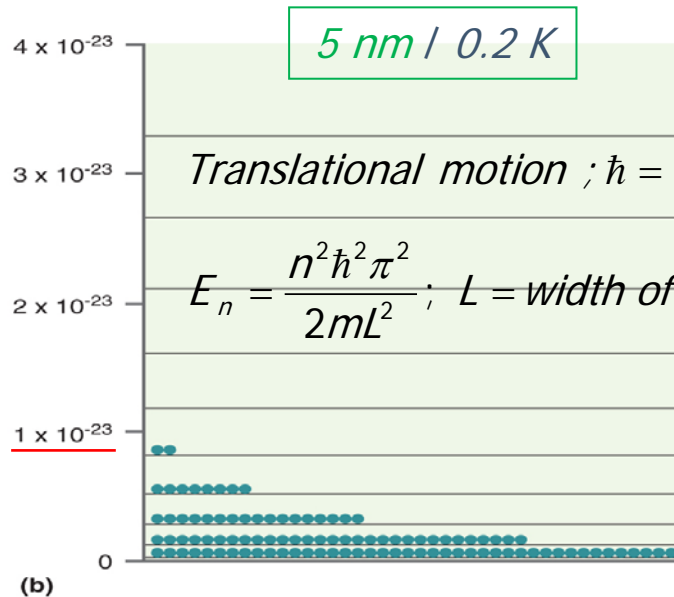
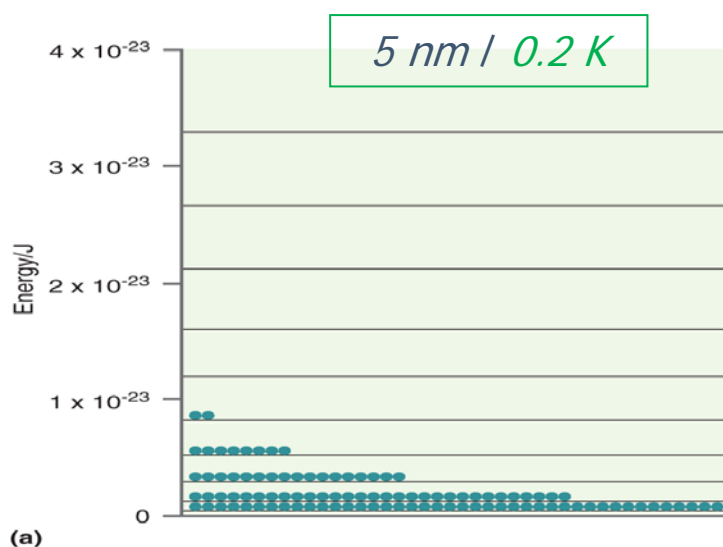
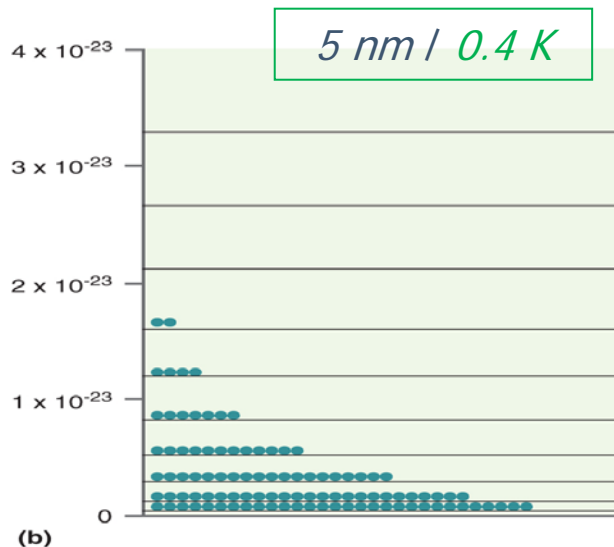


Fig.2.5 One He atom in 1-D box of width 10 nm. Energy levels are shifted to higher values.



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$E = f(T)$

Fig.2.6 Energy levels are unchanged, but the energy of the system increases.

2.5 Heat Capacity

※ C depends on the T measurement conditions: $C_{V,m}$ and $C_{P,m}$.

- The heat capacity(열용량) is a material-dependent property defined by the relation: ~thermal response to heat flow can be well described by

$$C \equiv \lim_{\Delta T \rightarrow 0} \frac{q}{T_f - T_i} = \frac{dq}{dT}$$

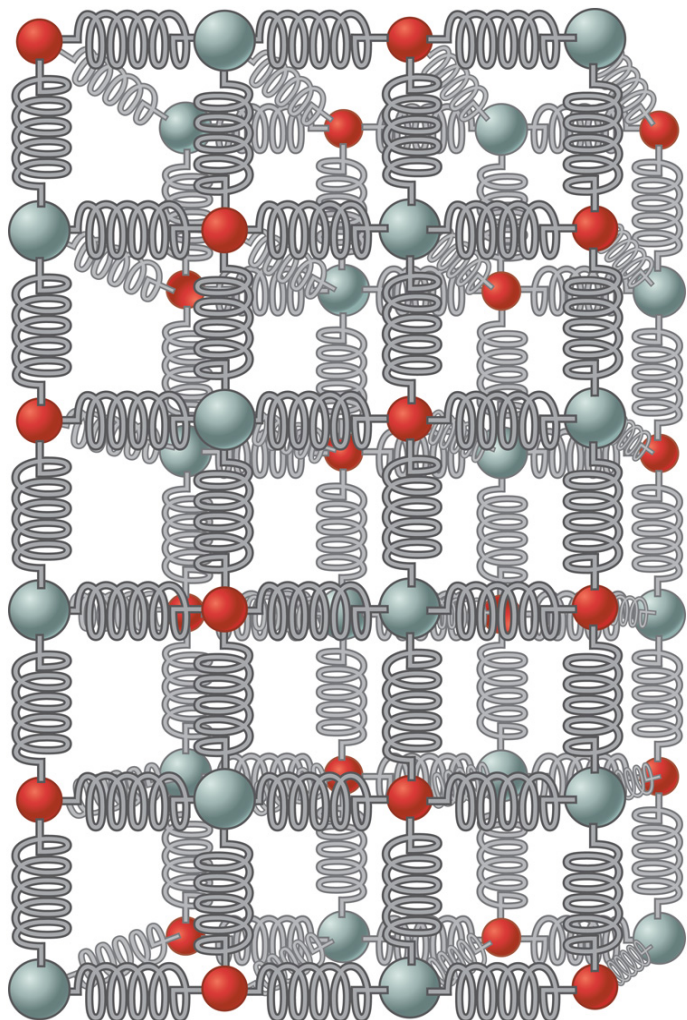
~amt of heat needed to increase the temperature of a substance

(2.9)

where C has the SI unit of $J K^{-1}$, extensive property.

- Most common are **const volume heat capacity**, C_V (정적열용량) and **constant pressure heat capacity**, C_P (정압열용량) : details for C_V in [3.2] and C_P in [3.4].
- 본디 크기성질이지만 그램열용량, C_g (gram heat capacity, $J/K/g$)
Excess heat capacity, C_m (molar heat capacity, $J/K/mol$)은 세기성질.
 C_m is most used in calculations : 물질 1 g몰을 1 °C(1K) 올리는 데 필요한 열량.
- See Table 2.3-2.6 and Table 4.1-4.2 (App. A, Data Table, pp.555-563) for $C_{P,m}$ values.

Typo, p.25: Table 2.2→Table 2.3; Table 2.4 and 2.5→ Table 2.5 and 2.6



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Fig.5.11 A useful model of a solid.

- The solid is a connecting body of harmonic oscillators (Fig.5.11, p.103).
- At cryogenic temperatures, the E-spacing of the vibration mode is too large. Since it is not absorbed,
- C_m is very low and increases in proportion to T^3 . (Debye law).
- In the case of liquid, the vibration mode of the solid state C_m is relatively increased because some are in rotation mode.
- When it becomes a gas, all local vibration modes in the liquid state are converted to a translational mode, which it absorbs less energy than the vibration mode, so C_m decreases. In general, liquify up to C_m !

$$\begin{aligned}
 \text{cf : gas} &= (T:3) + (R:2 \text{ or } 3) + (V:3N-5 \text{ or } 6) \\
 \text{liquid} &= (R:2 \text{ or } 3) + (V:3N-2 \text{ or } 3) \\
 \text{solid} &= (V: \text{all } 3N)
 \end{aligned}$$

Solids=Harmonic Oscillators (조화 진동자)

Note : $k_B T$ at $300K = 4.1 \times 10^{-21} J = 0.026 eV$

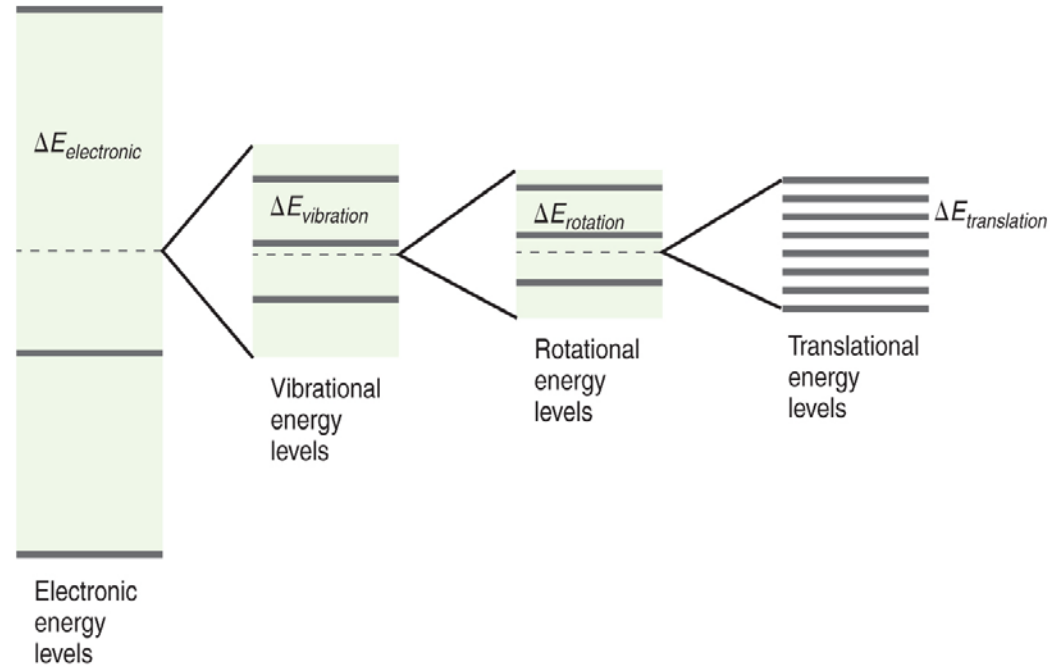


TABLE 2.2 Energy Level Spacings for Different Degrees of Freedom

Degree of Freedom	Energy Level Spacing
Electronic	$5 \times 10^{-19} \text{ J}$
Vibration	$2 \times 10^{-20} \text{ J}$
Rotation	$2 \times 10^{-23} \text{ J}$
Translation	$2 \times 10^{-41} \text{ J}$

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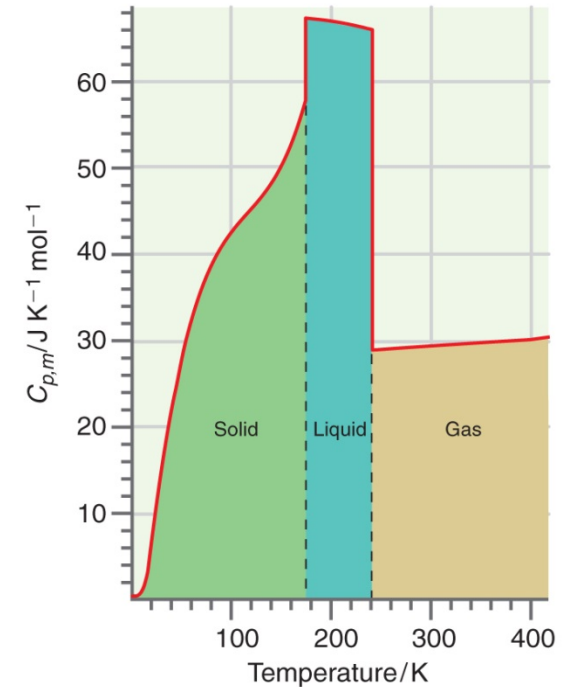
Fig.2.7 Energy levels are shown schematically.

$$\Delta E_{\text{electronic}} \gg \Delta E_{\text{vibration}} \gg \Delta E_{\text{rotation}} \gg \Delta E_{\text{translation}}$$

2.5 Heat Capacity

👉 LN 2-??

Note : $k_B T$ at $300\text{K} = 4.1 \times 10^{-21}\text{J} = 0.026\text{eV}$



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Fig.2.9 $C_{p,m}$ as a function of T for Cl_2 .

- At constant pressure, heat flow btn the sys and surrs can be written as

$$q_P = \int_{T_{sys,i}}^{T_{sys,f}} C_P^{\text{system}}(T) dT = - \int_{T_{surr,i}}^{T_{surr,f}} C_P^{\text{surroundings}}(T) dT$$

(2.10)

~ in case of const V, C_V for C_P

2.5 Heat Capacity

- Atoms with only translational degrees of freedom have low $C_{V,m}$, indep of temp. (*He* gas) $\rightarrow 3R/2$
- Gases with vibrational degrees of freedom have higher $C_{V,m}$. (*CO* & *CO₂*)

$$3T+2R+V \uparrow \uparrow$$

$$=5R/2+R=7R/2=29 \text{ J/K/mol}$$

$$3T+2R+4V$$

$$=5R/2+4R=13R/2=54 \text{ J/K/mol}$$
- $C_{V,m}$ always positive.
 ~ thermal stability criterion

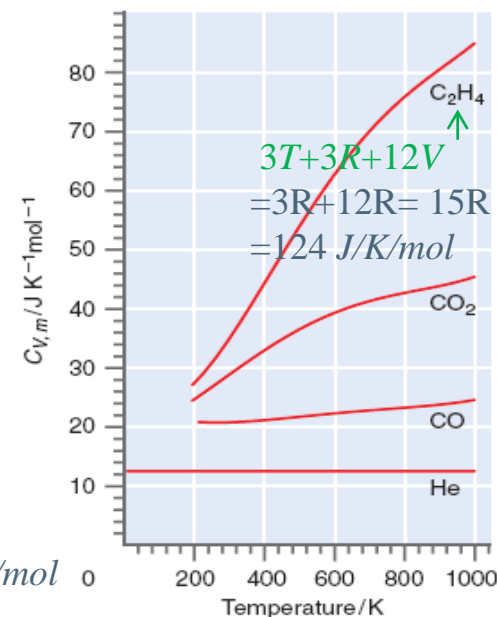


Fig.2.8 $C_{V,m}$ for some gases.

The heat capacity $C_{V,m}$ for a gas at temperature T not much lower than 300 K is $R/2$ for each translation and rotational degree of freedom, where R is the ideal gas constant. Each vibrational degree of freedom for which the relation $\Delta E/kT < 0.1$ is obeyed contributes R to $C_{V,m}$. If $\Delta E/k_B T > 10$, the degree of freedom does not contribute to $C_{V,m}$. For $10 > \Delta E/k_B T > 0.1$, the degree of freedom contributes partially to $C_{V,m}$.
 $10\Delta E > kT > 0.1\Delta E$

Example Problem 2.3

The volume of a system consisting of an ideal gas decreases at constant pressure. As a result, the temperature of a 1.50-kg water bath in the surrs increases by 14.2 °C. Calculate q_p for the system.

Solution:

$$\begin{aligned}
 q_p &= - \int_{T_{surr,i}}^{T_{surr,f}} C_P^{surroundings}(T) dT = -C_P^{surroundings} \Delta T \\
 &= -m \times C_{P,g} \times \Delta T \\
 &= -1.50 \text{ kg} \times \frac{10^3 \text{ g}}{1 \text{ kg}} \times 4.18 \frac{\text{J}}{\text{g} \cdot \text{K}} \times 14.2 \text{ K} = -89.1 \text{ kJ}
 \end{aligned}$$

When $v_1 \xrightarrow{1} v_2 \xrightarrow{2} v_3 \xrightarrow{3} v_4$ for a molecule of mass m

$$\begin{aligned}
 \Delta E_k &= \left(\frac{1}{2} m v_2^2 - \frac{1}{2} m v_1^2 \right) + \left(\frac{1}{2} m v_3^2 - \frac{1}{2} m v_2^2 \right) + \left(\frac{1}{2} m v_4^2 - \frac{1}{2} m v_3^2 \right) \\
 &= \left(\frac{1}{2} m v_4^2 - \frac{1}{2} m v_1^2 \right)
 \end{aligned}$$

~ 중간속도의 수나 값에 무관,
즉 경로에 무관 like 승강기

(2.12)

2.5 Heat Capacity

- For an ideal gas:

$$C_P - C_V = nR \quad \text{or} \quad C_{P,m} - C_{V,m} = R \quad (2.11)$$

(Cf) [3.5], LN p.3-36

- Not all the heat flow into the system can be used to increase ΔU in a constant pressure process since the system expands as heat flows in doing work on the surrs.

(즉 자체팽창으로 주위에 일, 덜 승온)

Therefore, always $C_p > C_v$.

- The same argument applies to liq & sol as long as $V \propto T$, but not much difference due to a small change in V and $C_p \approx C_v$.

예외: H_2O at $0 \sim 4^\circ\text{C}$

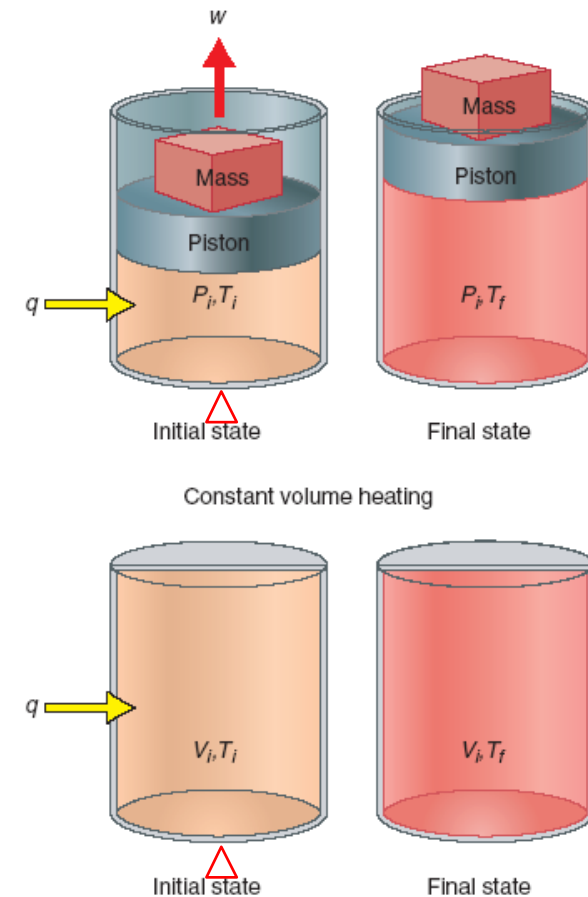


Fig. 2.10 The difference in C_p and C_v .

2.6 State Functions and Path Functions

- Any function whose change is independent of the path and depends only on the initial and final states is a **state function**, just like ΔU . $\Delta E_k \rightarrow (2.12)$ LN p.2.23
- Any **State Function**(상태함수), for example, U must satisfy the (2.13) and has an exact differential(완전미분), dU .

$$\Delta U = \int_i^f dU = U_f - U_i \quad \sim \text{in more detail in Ch.3} \quad (2.13)$$

- A **cyclic path** (순환경로) is such that the initial and final states are identical,

$$\oint dU = U_f - U_f = 0 \quad : \oint = \text{cyclic integral(순환적분)} \quad \text{For cyclic, initial and final states are same} \quad (2.14)$$

- For a single phase system at fixed composition, the degree of freedom (자유도, dof , F) = 2 $\leftarrow F = 2 + C - P$. Therefore, U can be written in any of the three forms $U(T, V)$, $U(P, T)$, or $U(P, V)$. (cf) [8.3], LN p.8.18,19

예: 물의 삼중점 : 611 Pa, 0.01 °C $\rightarrow doF = 2 + 1 - 3 = 0$ 즉 불변수 (invariant) 계

2.6 State Functions and Path Functions

What is **Path Function** (경로함수)?

- If the height of the mass in the surroundings is lower after **via** the compression, w is positive and U is increased.
- Step1 = const P_{ext} comp, T_1 increases to T_2 ; Step2 = const $V(V_2)$ heating to T_3
Repeat this two-step process w/ various masses keeping the initial (P_1, V_1, T_1) & final (P_3, V_2, T_3) states identical, then from the 1st law of TD:

$$\Delta U = U(T_3, V_2) - U(T_1, V_1) = q + w \quad (2.16)$$

Typo in p.28: $T_3 < T_1 \rightarrow T_3 \gg T_1$

$U=q+w$ - work is done by the surrounding on the system, then W is +ve
 $U=q-w$ -work is done by the system to the surrounding

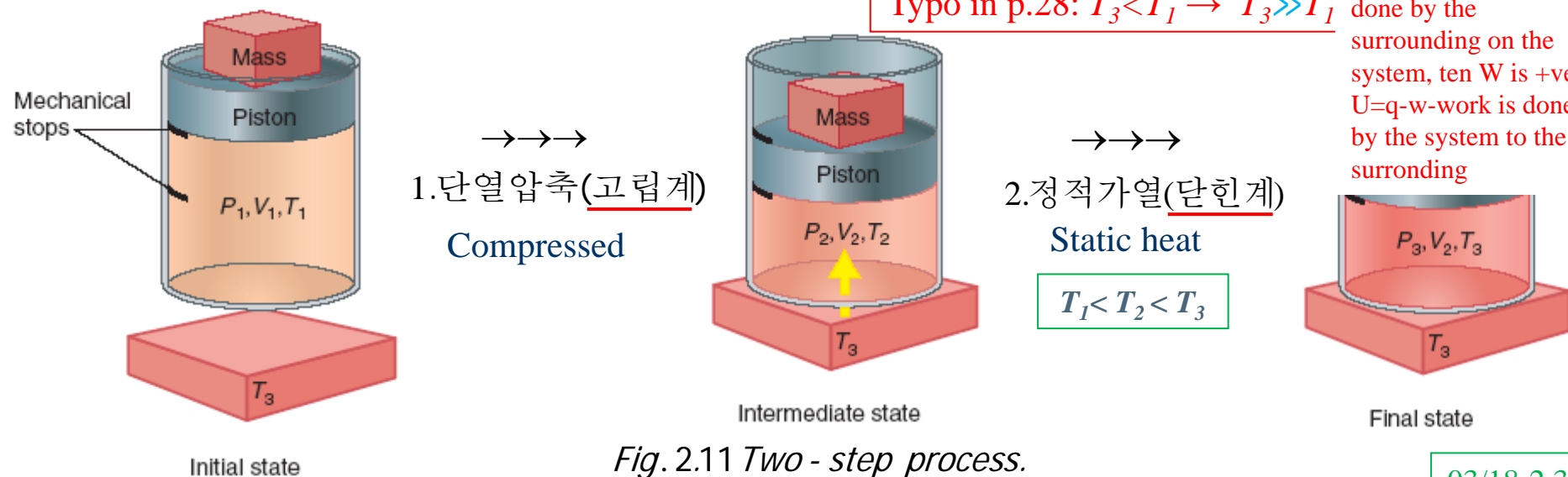


Fig. 2.11 Two - step process.

2.6 State Functions and Path Functions

P1 is
same

$Q2 : V_2, T_3 \rightarrow V_1, T_1$ w/ different mass 때 P_1 은 같을까?

- What values will the q & w have according to each path?
 - $w = -P_{ext} \Delta V$ (2.17). The w changes since P_{ext} changes even if ΔV is const. Going back to initial state w/ different mass, the cyclic integral of w is not '0'.
 - $q = \Delta U - w = \Delta U + P_{ext} \Delta V$ (2.18). ΔU is constant but since w varies due to different P_{ext} , therefore, the cyclic integral of q is not also '0'.
- As above, when a function has a different value for each path it takes, it is a path function!! A path function doesn't have exact differential and its cyclic integral is not always zero.
- Since both q and w are path functions, exact differentials are not allowed and dw and dq mean infinitesimal amount of work and heat, respectively.

A2 : Yes from id gas law.

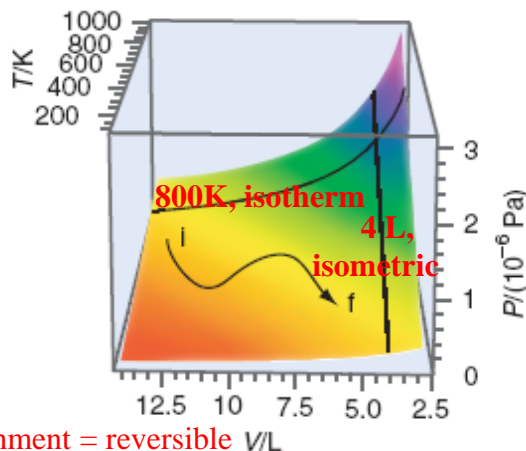
$dw, dq, q_i, w_f, \Delta w, \Delta q$ are nonsense!!!

$$\Delta q \neq \int_i^f dq \neq q_f - q_i \quad \text{and} \quad \Delta w \neq \int_i^f dw \neq w_f - w_i \quad (\beta)$$

2.7 Equilibrium, Change, and Reversibility

Q3: How can we calculate q and w for a macroscopic change of the system? Reconciliation!

- All the TD eqns can only apply to systems in internal eqm(내적평형상태) and all the chem. eqm are dynamic eqm(동적평형): forward rx rate = reverse rx rate (정반응속도=역반응속도)
- A **quasi-static process** (준정적準靜的 공정) is the process where rate of change of the macroscopic variables is negligibly small, and the sys (surrs) passes thru a succession of internal eqm as it goes from the initial to the final state. i.e. system and surr. change while maintaining the internal eqm.
- When a sys in an internal eqm changes in state keeping an eqm with surroundings, it is rev change, otherwise irrev change.



※ macroscopic state vbles = P, V, T

※ isometric (equal dimension) or
isochoric (**constant volume**),
정적定積) process

Dynamic:-The ratio of reactants/products changes, but substances move between the chemicals at an equal rate, meaning there is no net change

Fig. 2.12 Isotherm and isometric of ideal gas on PVT space.

- Internal and external equilibrium
- Equilibrium between system and environment = reversible

2.7 Equilibrium, Change, and Reversibility

- If an infinitesimal opposing change in the driving force (a grain of sand in the figure) can reverse the direction of the process, the process is **reversible** and visa versa.
- Figure 2.13 explains reversible and irreversible processes. As the two masses have the same value the net force acting on each end of the wire is zero, and the masses will not move. If an additional mass is placed on either of the two masses, the system is no longer in mechanical equilibrium, and the masses will move.
- In the limit in which the incremental mass approaches zero, the velocity at which the initial masses move approaches zero. In this case, one refers to the process as being **reversible**, meaning that the direction of the process can be reversed by placing the infinitesimal mass on the other side of the pulley
- Three characteristics of reversible process
 - takes forever
 - infinitesimal drive force
 - hypothetical(supposed) process

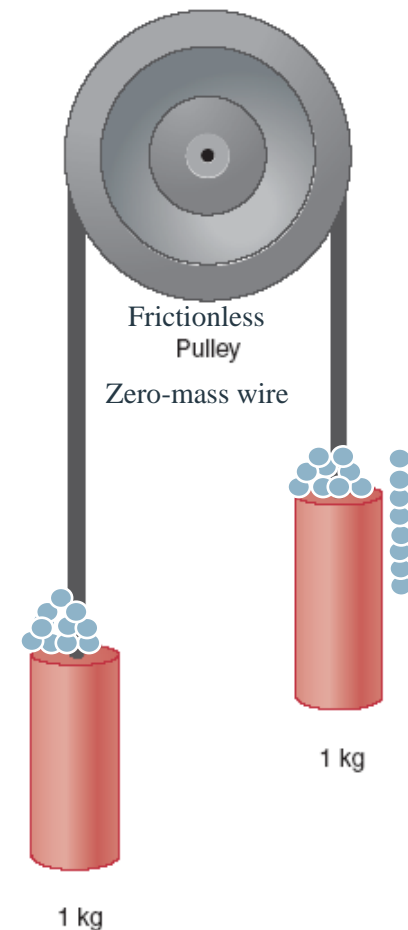


Fig. 2.13 *Illustration of reversible process.*

* Purpose : $w_{max/min}$, ΔS , state functions, etc.

2.8 Comparing Work for Reversible and Irreversible Processes

irrev cycle

Isothermal (등온) process ← diathermal wall

* No mech. stops used

$P_1, V_1, T \rightarrow (\text{expansion}) \rightarrow P_2, V_2, T (P_1 > P_2) : w = P_2 \times \Delta V = \text{red}$ ← wt removed

$P_1, V_1, T \leftarrow (\text{contraction}) \leftarrow P_2, V_2, T (V_1 < V_2) : w = P_1 \times \Delta V = \text{red} + \text{yellow}$ ← wt restored

- Indicator diagram** shows the relationship between P and V for the process graphically.
Expansion work is red area.
Compression work is red+yellow area.
The total(net) work is yellow area.

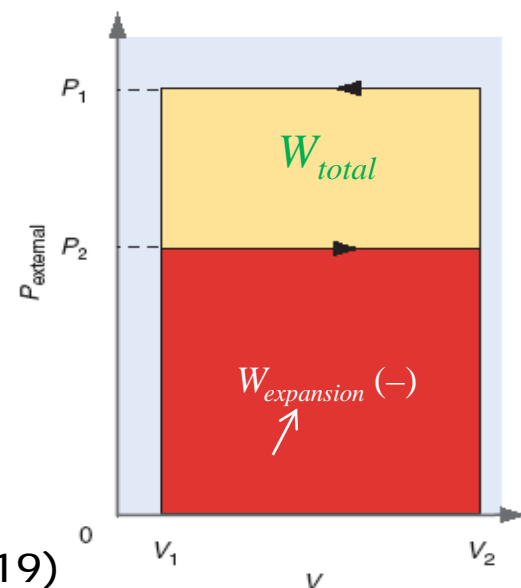


Fig. 2.14 Indicator diagram.

- * Expansion and compression w/o mechanical stops

$$\begin{aligned} w_{total} &= w_{expansion}^{(-)} + w_{compression}^{(+)} \\ &= -P_2(V_2 - V_1) - P_1(V_1 - V_2) = -(P_2 - P_1)(V_2 - V_1) > 0 \quad (2.19) \end{aligned}$$

- Since $\Delta U_{sys} = w_{total} + q_{total} = 0$, $q_{total} < 0 \rightarrow q_{surr} > 0$.

- * The sys restored the original state, but surr^s lost some energy doing some work on the sys ($w_{surr} < 0$) and gained some thermal energy ($q_{surr} > 0$). However, due to abrupt expansion and contraction that must have caused inevitable agitation of air, etc., the surr^s have not been restored.

2.8 Comparing Work for Rev and Irrev Processes

rev cycle For rev process, $P_{ext} = P$ at every step of the cycle.

$$w_{expansion} = - \int P_{ext} dV = - \int P dV = - nRT \int \frac{dV}{V} = - nRT \ln \frac{V_2}{V_1}$$

~ by pulverizing the mass into pieces
(2.20)

- When the process is reversed and the compression work is calculated, the following result is obtained:

$$w_{compression} = - nRT \ln \frac{V_1}{V_2} \quad (2.21)$$

- Expansion work is red area and comp work is also red area, thus the total(net) work is **zero**, that is

- $$w_{total} = w_{exp} + w_{comp}$$

$$= - nRT \ln \frac{V_2}{V_1} - nRT \ln \frac{V_1}{V_2} = 0 \quad (2.22)$$

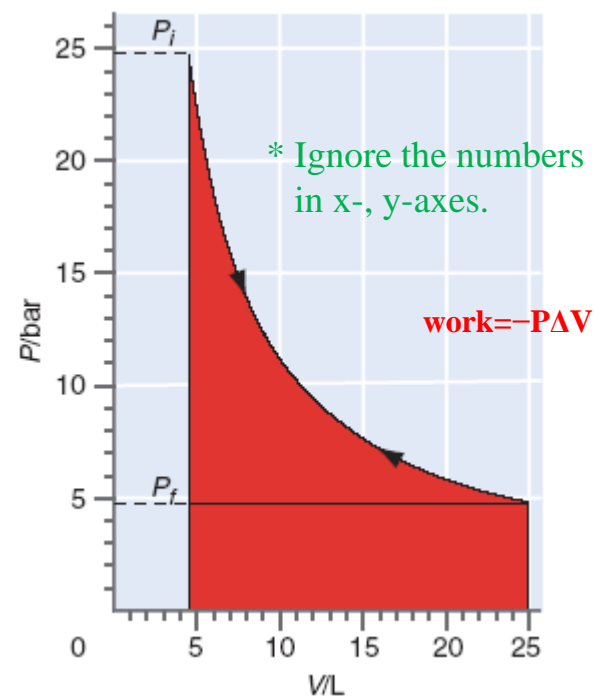


Fig. 2.15 Reversible process.

Example Problem 2.4

Advice : To visualize the question, draw the corresponding PV diagram.

In this example, 2.00 *mol* of an id gas undergoes isothermal expansion along three different paths:

- (1) rev expansion from $P_i = 25.0 \text{ bar}$ and $V_i = 4.50 \text{ L}$ to $P_f = 4.50 \text{ bar}$;
- (2) a single-step expansion against a constant external pressure of 4.50 *bar*, and
- (3) a two-step expansion consisting initially of an expansion against a constant external pressure of 11.0 *bar* until $P = P_{\text{external}}$, followed by an expansion against a constant external pressure of 4.50 *bar* until $P = P_{\text{external}}$.

Calculate the work for each of these processes. For which of the two irrev processes is the magnitude of the work greater?

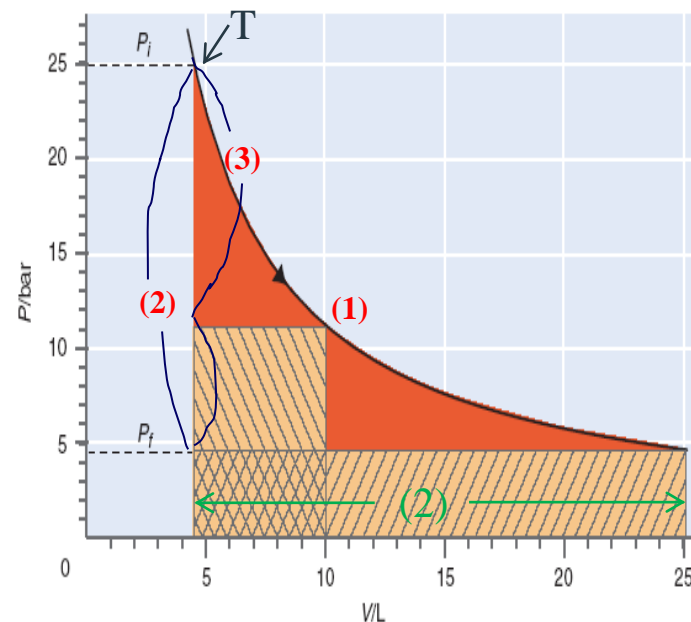
Solution

We first calculate the constant temperature at which the process is carried out, the final volume, and the intermediate volume in the two-step expansion:

$$T = \frac{P_i V_i}{nR} = \frac{(25.0 \text{ bar})(4.50 \text{ L})}{(2.00 \text{ mol}) \left(8.314 \times 10^{-2} \frac{\text{L} \cdot \text{bar}}{\text{mol} \cdot \text{K}} \right)} = 677 \text{ K}$$

$$V_f = \frac{nRT}{P_f} = \frac{(2.00 \text{ mol})(8.314 \times 10^{-2})(677 \text{ K})}{4.50 \text{ bar}} = 25.0 \text{ L}$$

$$V_{\text{int}} = \frac{nRT}{P_{\text{int}}} = \frac{(2.00 \text{ mol})(8.314 \times 10^{-2})(677 \text{ K})}{11.0 \text{ bar}} = 10.2 \text{ L}$$



Visualization of Example Problem 2.4, ttbk p. 32.

Solution

The work of the rev process from (2.20) is given by

$$w = -nRT_1 \ln \frac{V_f}{V_i} = -(2.00 \text{ mol}) \times 8.314 \frac{\text{J}}{\text{K} \cdot \text{mol}} \times (677 \text{ K}) \times \ln \frac{25.0}{4.50} = -19.3 \times 10^3 \text{ J}$$

For irrev processes:

$$w_{\text{one-step}} = -P_{\text{ext}} \Delta V = -(4.50 \times 10^5 \text{ Pa})(25.00 \text{ L} - 4.50 \text{ L}) \frac{10^{-3} \text{ m}^3}{\text{L}} = -9.23 \times 10^3 \text{ J}$$

$$\begin{aligned} w_{\text{two-step}} &= -P_{\text{ext}} \Delta V = -(11.0 \times 10^5 \text{ Pa})(10.2 - 4.50) \frac{10^{-3} \text{ m}^3}{\text{L}} - (4.50 \times 10^5 \text{ Pa})(25.0 - 10.2) \frac{10^{-3} \text{ m}^3}{\text{L}} \\ &= -12.9 \times 10^3 \text{ J} \end{aligned}$$

* Comparison of absolute exp work : rev > 2-step > 1-step expansion

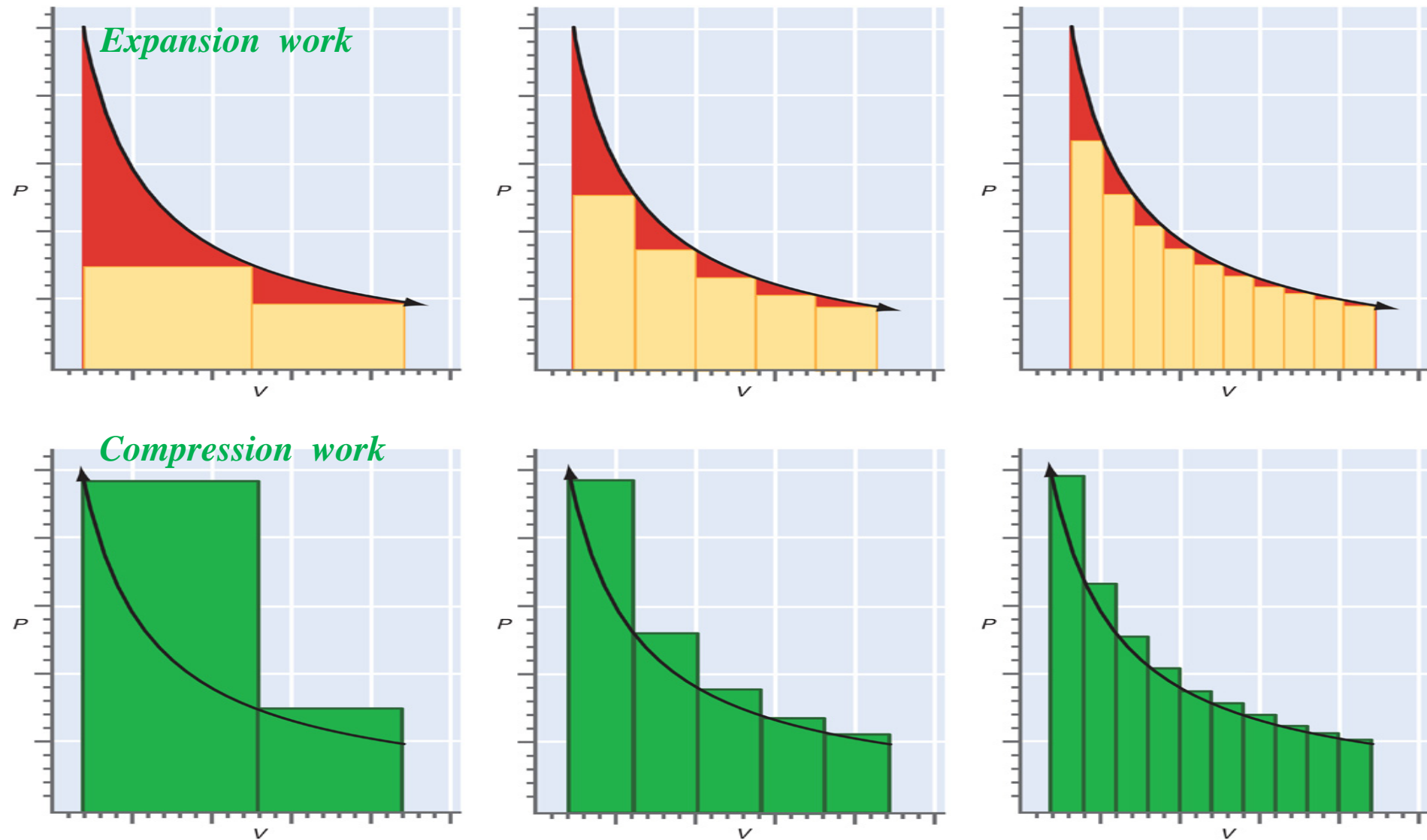
* Comparison of absolute comp work : rev < 2-step < 1-step compression

As a conclusion, reversible process gives (cf. Fig.2.16, LN 2-35)

In expansion : $|w_{\text{irrev}}| \leq |w_{\text{rev}}|$ (2.23) → maximum work (최대일)

In compression : $|w_{\text{irrev}}| \geq |w_{\text{rev}}|$ (2.24) → minimum work (최소일)

Fig.2.16 Limiting multi-stage irrev proc. vs. rev proc.



2.9 Determining ΔU and Introducing Enthalpy, a New State Function

- If a process is carried out under const volume conditions and non-expansion work is not possible, then we have

$$\Rightarrow \Delta U = q_V \sim \text{to be measured via calorimeter (열량계), Fig. 4.3} \quad (2.25)$$

- For reversible & isobaric processes, $P_{ext} \approx P_g = \text{constant}$

Gas rx w/o
mech. stop

$$dU = \delta q - P_{ext}dV = \delta q_p - PdV \text{ and integration gives} \quad (2.26)$$

$$\int_i^f dU = \int_i^f \delta q_p - \int_{V_i}^{V_f} PdV$$

$$U_f - U_i = q_p - P(V_f - V_i) \text{ and rearranging gives} \quad (2.27)$$

$$(U_f + PV_f) - (U_i + PV_i) = q_p \quad (2.28)$$

- If we define $H \equiv U + PV$, (2.28) becomes $H_f - H_i = q_p$

$$\Rightarrow \Delta H = q_p \sim \text{to be measured ; more common practice, Fig. 4.4} \quad (2.30)$$

→ If $\Delta H > 0$: endothermic R. if $\Delta H < 0$: exothermic R.

2.9 Determining ΔU and Introducing Enthalpy, a New State Function

- Because P , V , and U are all state functions, $U+PV$ is also a state function and is called **enthalpy**, H , extensive property just like U .

$$H \equiv U + PV \quad (2.29)$$

- At constant pressure,

$$\Delta H = q_P \sim \text{compare with } \Delta U = q_V \text{ (2.25)} \quad (2.30)$$

- ΔU for a temperature range over which C_V is constant,

$$\Delta U = q_V = C_V (T_f - T_i) \sim \text{id gas / 실제기체는 isochoric process (정적)} \quad (2.31)$$

$$\text{즉 } \Delta U = \Delta U(T)$$

$$\text{cf. } C \equiv \dot{dq}/dT \text{ (2.9)} \rightarrow \dot{dq} = C dT$$

- For **id gas**,

$$\Delta H = \Delta U + \Delta(PV) = \Delta U(T) + \Delta(nRT) = \Delta H(T) \quad (2.32)$$

- Thus, $\Delta H = q_P = C_P (T_f - T_i) \sim \text{id gas / 실제기체는 isobaric process (정압)} \quad (2.33)$

2.10 Calculating q , w , ΔU , and ΔH for Processes Involving Ideal Gases

- From $w = -\int P_{ext} dV$ (2.34)

- For isobaric processes, (2.35) becomes

$$w = -P_{ext}(V_f - V_i) \quad (2.35)$$

- For rev process, $P \approx P_{ext}$ and then (2.35) becomes for an id gas

$$w = -\int P dV = -\int \frac{nRT}{V} dV \quad (2.36)$$

- For rev isothermal compression/expansion of an id gas,

$$w = -nRT \int \frac{dV}{V} = -nRT \ln \frac{V_f}{V_i} \quad (2.37)$$

- Isochoric heating or cooling of an id gas

<ER, EP2.5, p.37>

- Rev cyclic processes

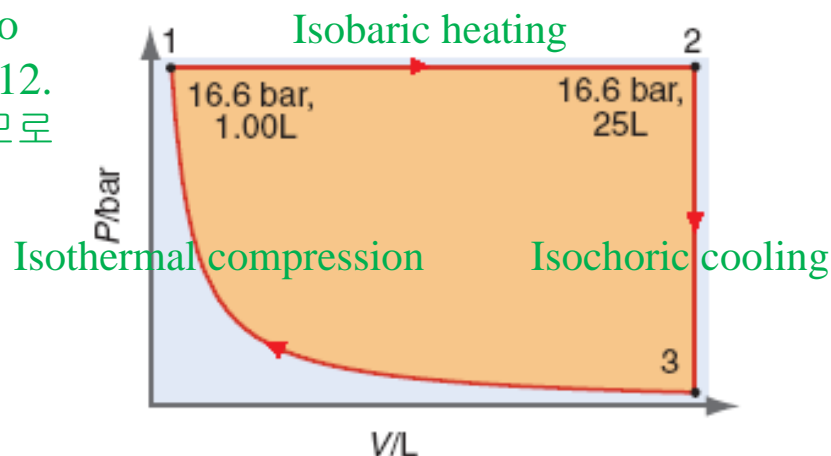
<ER, EP2.5, p.37>

Example Problem 2.5

Advice: Try to understand the question. → effortless gift

A system containing 2.50 mol of an **ideal gas** for which $C_{V,m} = 20.79 \text{ J/mol/K}$ is taken through the cycle in the following diagram in the direction indicated by the arrows. The curved path corresponds to $PV = nRT$, where $T = T_1 = T_3$.

↑ meaning rev compression due to quasi-static process as in Fig.2.12.
압축시 압력이 기체압력을 따르므로



- Calculate q , w , ΔU and ΔH for each segment and for the cycle.
- Calculate q , w , ΔU and ΔH for each segment and for the cycle in which the direction of each process is reversed.

Solution

Because the path b/n states 3 and 1 is isothermal, $\Delta U_{3 \rightarrow 1} = \Delta H_{3 \rightarrow 1} = 0$ for this segment. Therefore, from the TD 1st law $q_{3 \rightarrow 1} = -w_{3 \rightarrow 1}$. Because $\Delta V = 0$ along the path b/n states 2 and 3, $w_{2 \rightarrow 3} = 0$ and $\Delta U_{2 \rightarrow 3} = q_{2 \rightarrow 3}$. Since the total process is cyclic, $\Delta U = \Delta H = 0$ for the cycle.

a) **Segment 1→2** (isobaric heating-horizontal)

$$\begin{aligned}\Delta U_{1 \rightarrow 2} &= nC_{V,m}(T_2 - T_1) = nC_{V,m} \left(\frac{P_2 V_2}{nR} - \frac{P_1 V_1}{nR} \right) = \frac{nC_{V,m}}{nR} (P_2 V_2 - P_1 V_1) \\ &= \left(\frac{20.79 \text{ J / mol / K}}{0.08314 \text{ L} \cdot \text{bar / mol / K}} \right) (16.6 \text{ bar} \times 25 \text{ L} - 16.6 \text{ bar} \times 1.00 \text{ L}) \\ &= 99,600 \text{ J} = 99.6 \text{ kJ}\end{aligned}$$

The process takes place at constant pressure, so

$$w = -P_{\text{external}}(V_2 - V_1) = -(16.6 \times 10^5 \text{ Pa}) (25 \times 10^{-3} \text{ m}^3 - 1.00 \times 10^{-3} \text{ m}^3) = -39.8 \text{ kJ}$$

Solution

Using the first law

$$q = \Delta U - w = 99.6 \text{ kJ} + 39.8 \text{ kJ} = 139.4 \text{ kJ}$$

We next calculate T_2 , and then $\Delta H_{1 \rightarrow 2}$:

$$T_2 = \frac{P_2 V_2}{nR} = \frac{16.6 \text{ bar} \times 25 \text{ L}}{2.5 \text{ mol} \times 0.08314 \text{ L} \cdot \text{bar} / \text{mol} / \text{K}} = 2.00 \times 10^3 \text{ K}$$

We next calculate $T_3 = T_1$,

$$T_1 = \frac{P_1 V_1}{nR} = \frac{16.6 \text{ bar} \times 1.00 \text{ L}}{2.5 \text{ mol} \times 0.08314 \text{ L} \cdot \text{bar} / \text{mol} / \text{K}} = 79.9 \text{ K}$$

$$\begin{aligned} \Delta H_{1 \rightarrow 2} &= \Delta U_{1 \rightarrow 2} + \Delta(PV) = \Delta U_{1 \rightarrow 2} + nR(T_2 - T_1) \\ &= 99.6 \times 10^3 + 2.5 \times 8.314 \times (2000 - 79.9) = 139.4 \text{ kJ} \end{aligned}$$

Or, $\Delta H_{1 \rightarrow 2} = nC_{P,m} \Delta T = n(C_{V,m} + R)(T_2 - T_1)$

$$= (2.5 \text{ mol}) \left(20.79 \frac{\text{J}}{\text{K} \cdot \text{mol}} + 8.314 \frac{\text{J}}{\text{K} \cdot \text{mol}} \right) (2000 \text{ K} - 79.9 \text{ K}) = 139.4 \text{ kJ}$$

Solution

Segment 2→3 (isochoric cooling-vertical)

As noted above, $w=0$ for isochoric change, and

$$\begin{aligned}\Delta U_{2\rightarrow 3} &= q_{2\rightarrow 3} = nC_{V,m}(T_3 - T_2) \\ &= (2.50 \text{ mol})(20.79 \text{ J / mol / K})(79.9 \text{ K} - 2000 \text{ K}) \\ &= -99.6 \text{ kJ}\end{aligned}$$

Or, the numerical result should be equal in magnitude, but opposite in sign to $\Delta U_{1\rightarrow 2}$ because $T_3 = T_1$. $\leftarrow U \& H = f(T), \Delta U_{2\rightarrow 3} = -\Delta U_{1\rightarrow 2}$

For the same reason, $\Delta H_{2\rightarrow 3} = -\Delta H_{1\rightarrow 2}$ since H is also a function of T only for an id gas.

$$\Delta H_{2\rightarrow 3} = -\Delta H_{1\rightarrow 2} = -139.4 \text{ kJ}$$

Solution

Segment 3→1 (isothermal compression-curved)

For this segment, $\Delta U_{3 \rightarrow 1} = 0$ and $\Delta H_{3 \rightarrow 1} = 0$ since it is an isothermal change and therefore $w_{3 \rightarrow 1} = -q_{3 \rightarrow 1}$.

Because this is a reversible isothermal compression, from (2.21), LN 2-30:

$$w_{3 \rightarrow 1} = -nRT \ln \frac{V_1}{V_3} = -2.50 \times 8.314 \times 79.9 \times \ln \frac{1.0 \times 10^{-3}}{25.0 \times 10^{-3}} = 5.35 \text{ kJ}$$

Path	q (kJ)	w (kJ)	ΔU (kJ)	ΔH (kJ)
1 → 2	139.4	-39.8	99.6	139.4
2 → 3	-99.6	0	-99.6	-139.4
3 → 1	-5.35	5.35	0	0
Cycle	34.5	-34.5	0	0

b) If the cycle is traversed in the reverse direction, the magnitudes of all quantities remain same, but all signs change.

2.11 The Reversible Adiabatic Expansion and Compression of an Ideal Gas

- For the adiabatic expansion of an id gas, the 1st law of TD is

$$\Delta U = w \text{ or } C_V dT = -P_{ext} dV \quad (2.38)$$

- Moreover for rev proc, $P = P_{ext}$, and

$$C_V dT = -nRT \frac{dV}{V} \text{ or, equivalently, } C_V \frac{dT}{T} = -nR \frac{dV}{V} \quad (2.39)$$

- When we integrate (2.39) if C_V is constant over the temperature interval $T_f - T_i$, then

$$\overset{\text{red arrow}}{C_{V,m}} \ln \frac{T_f}{T_i} = -R \ln \frac{V_f}{V_i} \quad \sim \text{id gas \& adiabatic and rev proc} \quad (2.40)$$

- As $C_{p,m} - C_{V,m} = R$ for an id gas, $\gamma - 1 = R/C_{V,m}$

$$\ln \left(\frac{T_f}{T_i} \right) = -(\gamma - 1) \ln \left(\frac{V_f}{V_i} \right) \text{ or, equivalently, } \frac{T_f}{T_i} = \left(\frac{V_f}{V_i} \right)^{1-\gamma} \quad (2.42)$$

where $\gamma = C_{p,m}/C_{V,m} > 1$ (heat capacity ratio, 열용량비).

2.11 The Reversible Adiabatic Expansion and Compression of an Ideal Gas

- Substituting $T_f/T_i = P_f V_f / P_i V_i$ into (2.42), we obtain

$$P_i V_i^\gamma = P_f V_f^\gamma \quad \sim \text{id gas \& adiabatic and rev proc} \quad (2.43)$$

- From (2.42) rev adiabatic compression leads to heating, and rev adiabatic expansion leads to cooling since $\gamma > 1$.
- Under isothermal condition, heat flows out of the system when compressed and heat flows into the system when expanded to keep T constant.

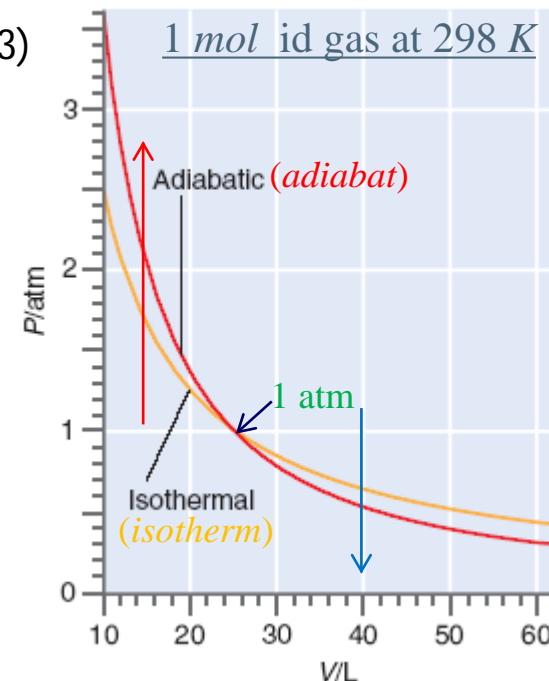


Fig. 2.17 *Adiabatic and isothermal proc.*

Fig.2.17에서 1기압에서 같은 부피를 가지지만 압축시 단열의 경우 열이 빠져나가지 못하므로 온도가 등온공정보다 상승하여, 같은 부피라 하더라도 단열공정이 보다 높은 압력을 갖게 됨 and vice versa.

- Rev Adiabatic Heating or Cooling of an Ideal Gas

<ER, EP2.7, p.40>

Example Problem 2.7

A cloud mass moving across the ocean at an altitude of 2000 m encounters a coastal mountain range. As it rises to a height of 3500 m to pass over the mountains, it undergoes an adiabatic expansion. The pressure at 2000 and 3500 m is 0.802 and 0.602 atm , respectively. If the initial temperature of the cloud mass is 288 K , what is the cloud temperature as it passes over the mountains? Assume $C_{p,m}$ for air is 28.86 $J/mol/K$ and that air obeys the ideal gas law. If you are on the mountain, should you expect rain or snow?

* We need $T=f(P)$.

Solution

As the process is adiabatic, $q = 0$, and $\Delta U = w$.

$$\ln\left(\frac{T_f}{T_i}\right) \stackrel{(2.42), \text{ p.44}}{=} -(\gamma - 1) \ln\left(\frac{V_f}{V_i}\right) = -(\gamma - 1) \ln\left(\frac{T_f}{T_i} \frac{P_i}{P_f}\right) = -(\gamma - 1) \ln\left(\frac{T_f}{T_i}\right) - (\gamma - 1) \ln\left(\frac{P_i}{P_f}\right)$$

$$\ln\left(\frac{T_f}{T_i}\right) + (\gamma - 1) \ln\left(\frac{T_f}{T_i}\right) = -(\gamma - 1) \ln\left(\frac{P_i}{P_f}\right) \rightarrow \gamma \ln\left(\frac{T_f}{T_i}\right) = -(\gamma - 1) \ln\left(\frac{P_i}{P_f}\right)$$

$$\ln\left(\frac{T_f}{T_i}\right) = -\frac{(\gamma - 1)}{\gamma} \ln\left(\frac{P_i}{P_f}\right) = -\frac{\left(\frac{C_{P,m}}{C_{P,m} - R} - 1\right)}{\frac{C_{P,m}}{C_{P,m} - R}} \ln\left(\frac{P_i}{P_f}\right), \quad \text{cf : } \left(\frac{T_f}{T_i}\right)^\gamma = \left(\frac{P_i}{P_f}\right)^{1-\gamma} \leftarrow GWC (7.58)$$

$$= -\frac{\left(\frac{28.86}{28.86 - 8.314} - 1\right)}{\left(\frac{28.86}{28.86 - 8.314}\right)} \times \ln\left(\frac{0.802 \text{ atm}}{0.602 \text{ atm}}\right) = -0.0826 \rightarrow \frac{T_f}{T_i} = e^{-0.0826} = 0.9207$$

$T_f = 0.9207 T_i = 0.9207 \times 288 = 265 \text{ K}$. *Since it is below 0° C , we expect snow!*

Homework

1. An ideal gas is expanded adiabatically into a vacuum. Decide which of q , w , ΔU , and ΔH are positive, negative, or zero.
2. For 1.25 mol of an ideal gas, $P_{\text{external}} = P = 350 \times 10^3 \text{ pa}$. The temperature is changed from 135°C to 21.2°C , and $C_{v,m} = 3R/2$. Calculate q , w , ΔU , and ΔH .

Thank you