2009 fall

Advanced Physical Metallurgy

“Phase Equilibria in Materials”

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Eun Soo Park

Office: 33-316
Telephone: 880-7221
Email: espark@snu.ac.kr
Office hours: by an appointment

Contents for today's class

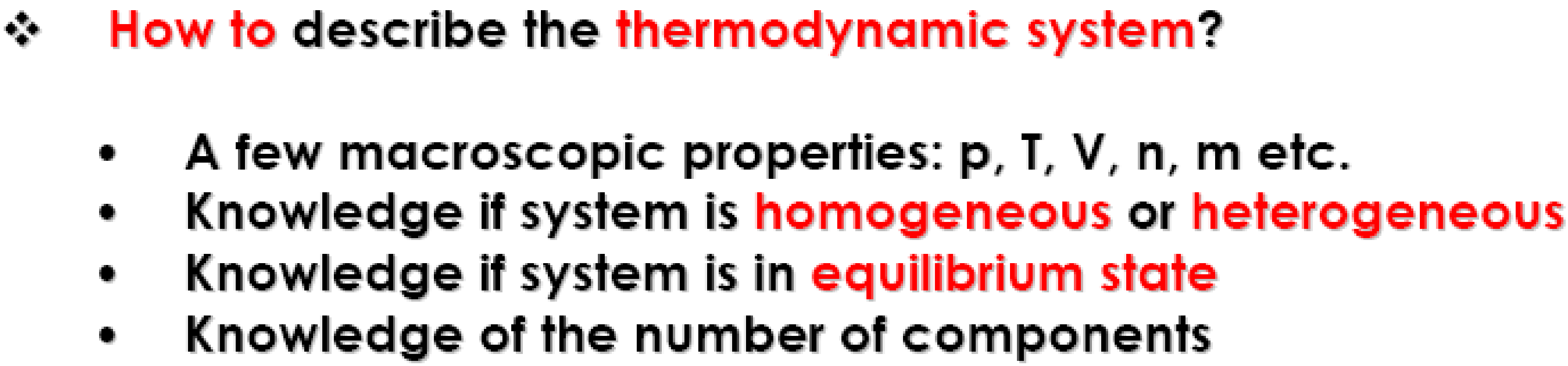
CHAPTER 1 Introductory Thermondynamics

- Thermodynamic system
- Equilibrium
- Gibbs and Helmholtz free energies
- Four laws in thermodynamics

Thermodynamics

; the investigation of energy transformations that accompany physical and chemical changes in matter

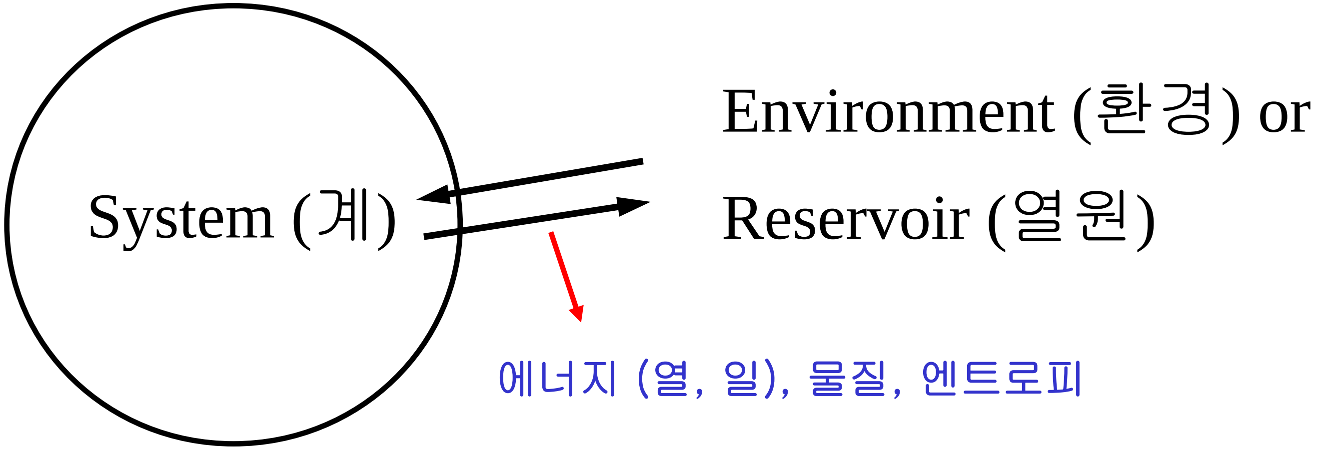
; use to evaluate the flow and interchanges of matter and energy



❖ How to describe the thermodynamic system?

- A few macroscopic properties: p, T, V, n, m etc.
- Knowledge if system is homogeneous or heterogeneous
- Knowledge if system is in equilibrium state
- Knowledge of the number of components

Thermodynamic system



System (계)

Environment (환경) or

Reservoir (열원)

에너지 (열, 일), 물질, 엔트로피

* **Isolated system** : physical system that does not interact with its surroundings.

It obeys a number of conservation laws its total energy and mass stay constant.

They cannot enter or exit, but can only move around inside.

* **Closed system** : Can interchange energy and mechanical work with other outside systems but not matter. Ex. mass conservation

* **Open system** : Can be influenced by events outside of the actual or conceptual boundaries.

Thermodynamic system

Isolated system (고립계) : 환경과 열, 물질, 일 모두 교환하지 않는 계이다.

이 말은 수학적으로 $TdS = 0, dN = 0, pdV = 0$를 의미하며, 따라서 $dE = 0$를 의미한다.

Thermodynamic system

Closed system (닫힌계) :

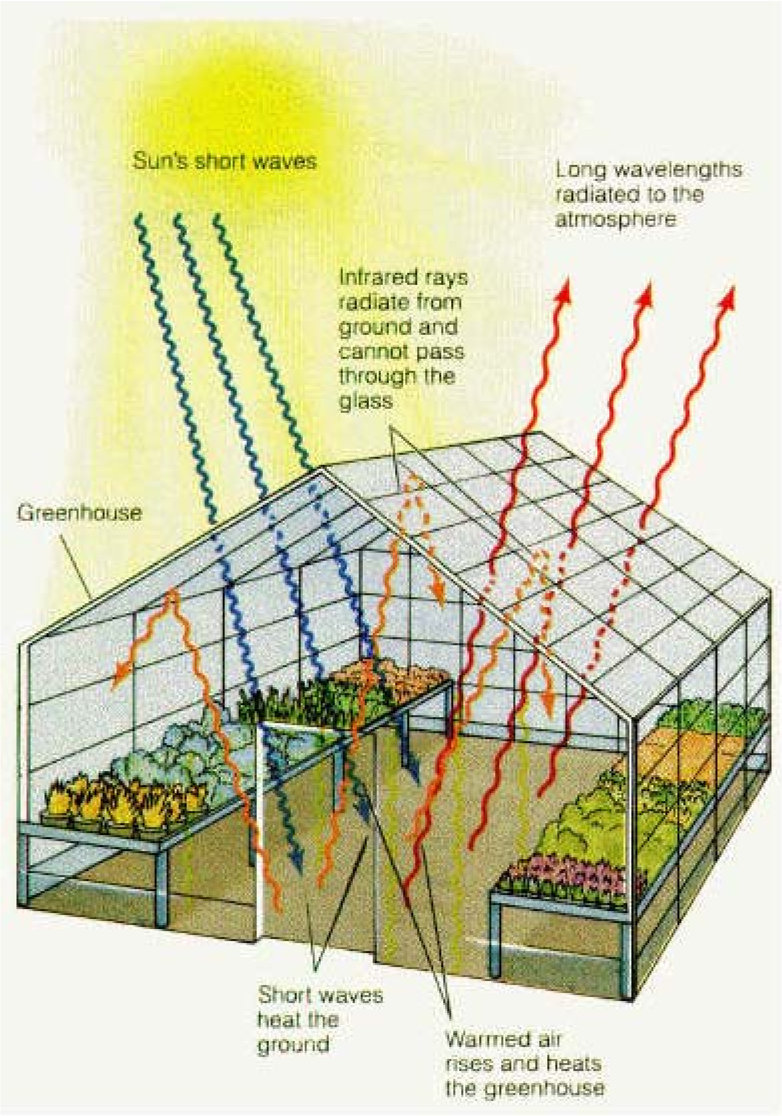
환경과 에너지(열과 일)는 교환하지만 물질은 교환하지 않는 계를 말한다.

- 단열 경계**(adiabatic boundary) :**

  열교환이 일어나지 않는다, $TdS = 0$

- 단단한 경계**(rigid boundary) :**

  일**(work)** 교환이 일어나지 않는다, $pdV = 0$



Thermodynamic system

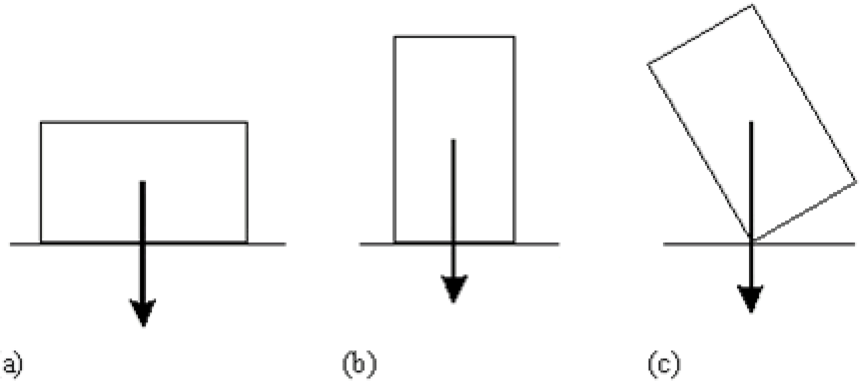
Open system (열린계) : 에너지**(**열과 일**),** 물질 모두 환경과 교환하는 계이다**.**

이런 경계는 투과성 있는**(permeable)** 경계라 한다**.**

Chapter 1.1

Equilibrium

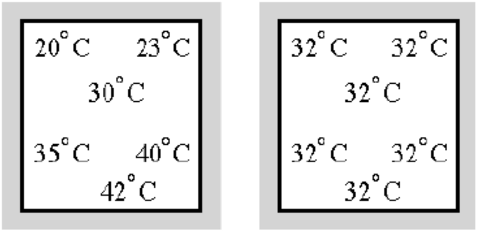
Mechanical equilibrium



: total potential energy of the system is a minimum.

Thermal equilibrium

: absence of temperature gradients in the system



(*a*) Before (*b*) After

Chemical equilibrium

: no further reaction occurs between the reacting substances
i.e. the forward and reverse rates of reaction are equal.

Thermodynamic equilibrium

: the system is under mechanical, thermal and chemical equilibrium

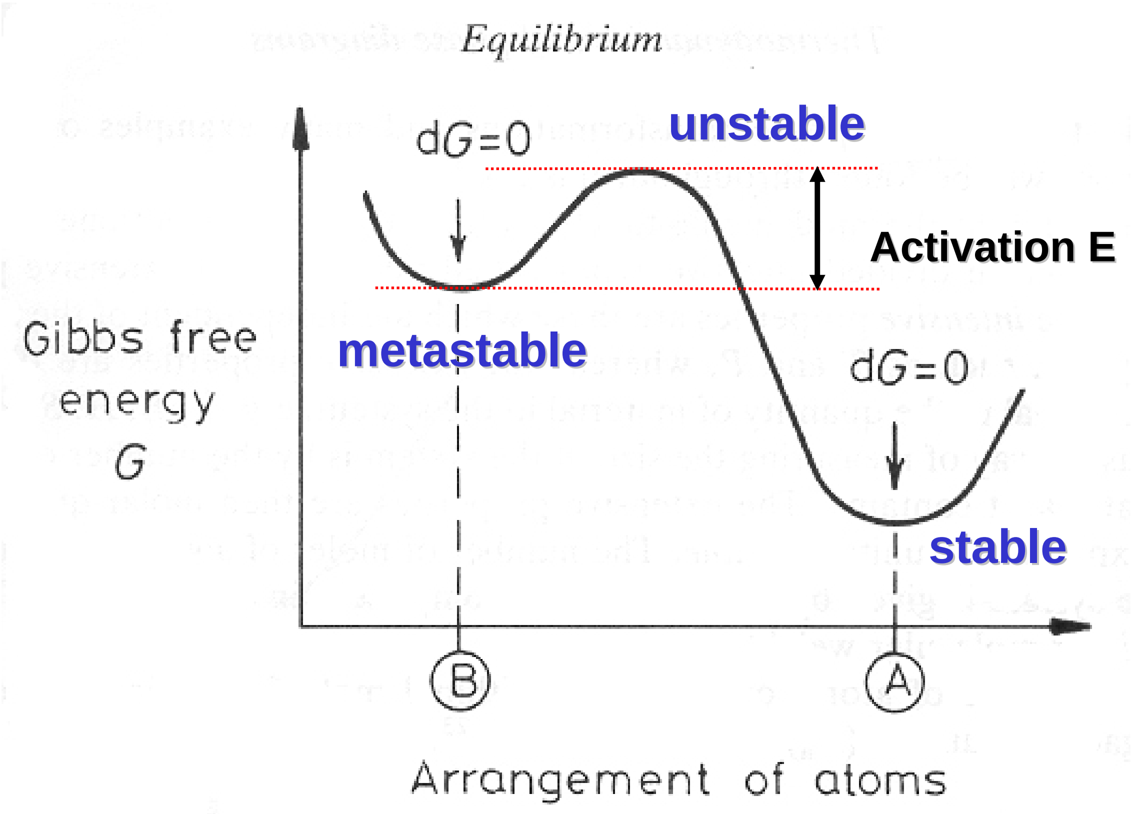
Equilibrium

$$\boxed{dG = 0}$$

The properties of the system-pressure, temperature, volume and concentrations-do not change with time.

No desire to change ad infinitum

➡ **Lowest possible value of Gibb’s Free Energy**



Phase Transformation

$$\boxed{\Delta G = G_2 - G_1 < 0}$$

Gibbs and Helmholtz free energies

When no useful work is being extracted from the sub-system, $\boxed{dX \leq 0}$

The energy X reaching a minimum at equilibrium, when $dX=0$.

If no chemical species can enter or leave the sub-system, then $\sum \mu_{iR} N_i$ can be ignored.

If furthermore the temperature of the sub-system is such that T is always equal to T_R,

then $\boxed{X = E - TS + P_R V + const}$

If the volume *V* is constrained to be constant, then $\boxed{X = E - TS + const' = A + const'}$

where F is the thermodynamic potential called Helmholtz free energy, $F=E-TS$.

Under constant volume conditions therefore, $dF < 0$ if a process is to go forward;

and $dF=0$ is the condition for equilibrium.

Helmholtz free energy **: *F=E−TS*.**

Useful when V is constrained during thermodynamic process.

Gibbs and Helmholtz free energies

If the sub-system pressure *P* is constrained to be equal to the external reservoir pressure P_R,

$$\boxed{X = E - TS + PV + const = G + const}$$

,where G is the Gibbs free energy, $G=E-TS+PV$. Therefore under constant pressure conditions, if $dG \leq 0$, then the process can occur spontaneously, because the change in system energy exceeds the energy lost to entropy. $dG=0$ is the condition for equilibrium. This is also commonly written in terms of enthalpy, where $H=E+PV$. $G=H-TS$

Gibbs free energy **:** $\boldsymbol{G=E+PV-TS=H-TS}$

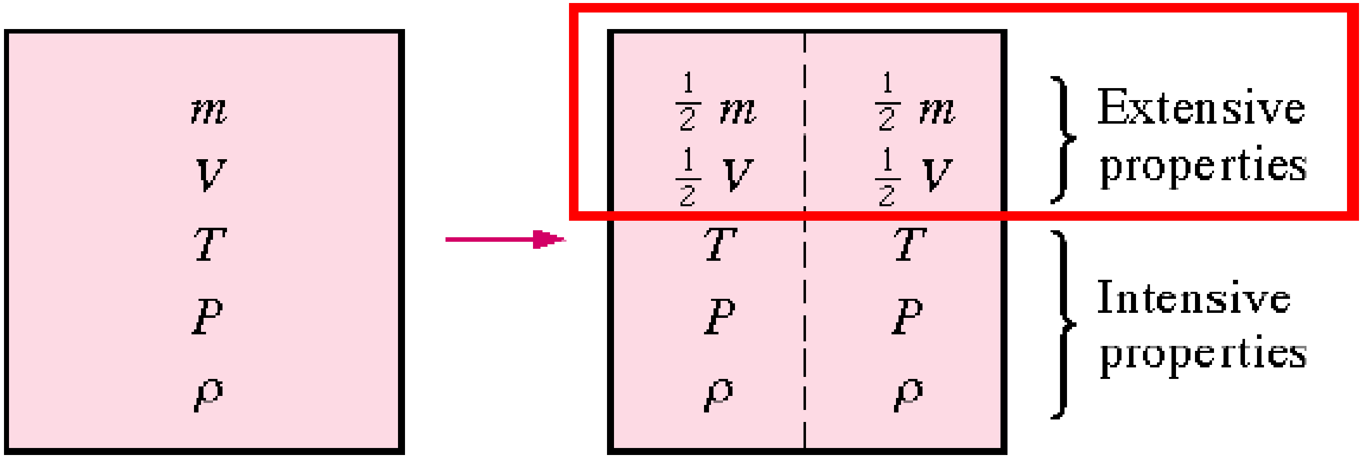
Useful when P is constrained during thermodynamic process.

Properties of a system

Any characteristic of a system in equilibrium is called a ***Property***. The property is independent of the path used to arrive at the system condition.

Intensive Property (강성적 상태량: 질량 무관)
are those that are independent of the size of a system. **Ex) T, P**

Extensive Property(종량적 상태량: 질량에 의존)
are those whose values depend on the size of the system. **Ex) V, E, H, S, G 등**



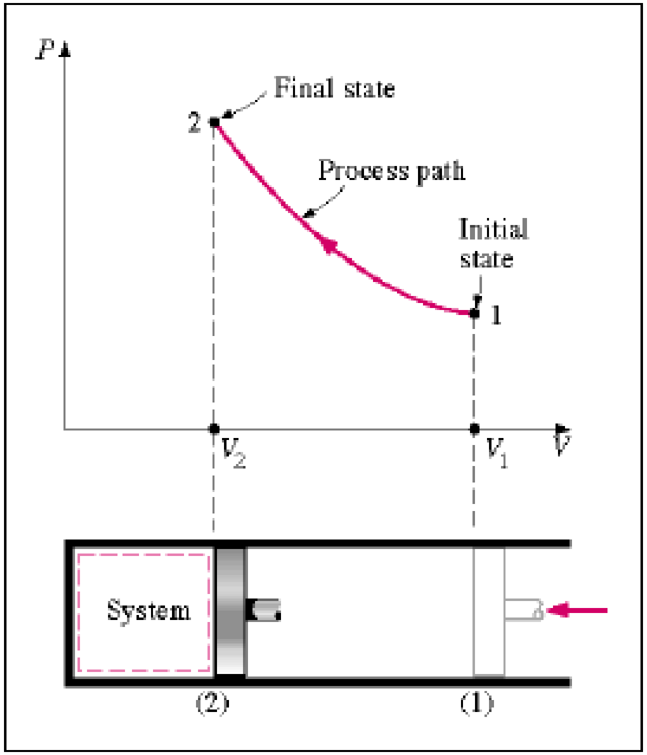
Process & Cycle

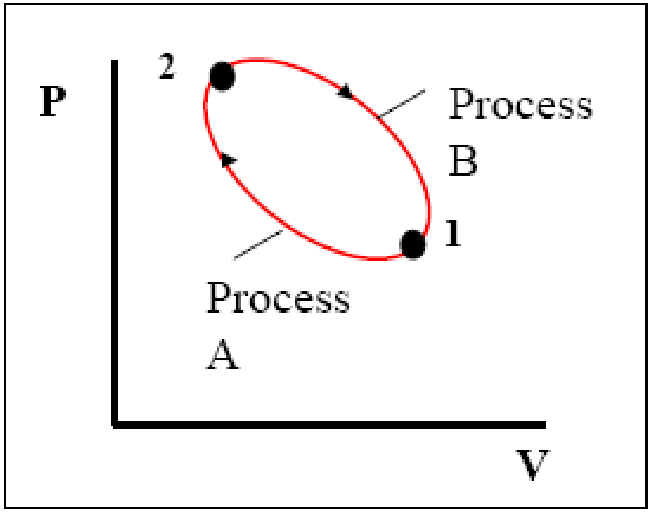
Any change from one state to another is called a ***process***.

During a ***quasi-equilibrium*** or ***quasi-static process*** the system remains practically in equilibrium at all times.

A process with identical end states is called a ***cycle***.

등온(isothermal)
정적 (isochoric)
정압(isobaric)
단열(adiabatic)
가역/비가역(reversible/irreversible)





About the thermodynamical laws :-)

(According to P.W. Atkins "*The Second Law, Energy Chaos, and Form*".)

- There are four laws.
- The third of them, the *Second Law*, was recognized first.
- The first, the *Zeroth Law*, was formulated last.
- The *First Law* was second.
- The *Third Law* might not even be a law in the same sense as the others.

The four laws in thermodynamics

- **Zeroth law :** 열역학적 평형
  - 만약 계 A와 계 B를 접촉하여 열역학적 평형상태를 이루고 있고 계 B와 계 C를 접촉하여 열역학적 평형상태를 이루고 있다면, 계 A와 계 C를 접촉하여도 열역학적 평형을 이룬다.
  - 열역학적 평형은 열적 평형(열교환과 온도와 관계)과 역학적 평형(일교환과 압력 같은 일반화된 힘과 관계)과 화학적 평형(물질교환과 화학퍼텐셜과 관계)을 포함한다

- **First law: :** 에너지 보존 법칙

$$\boxed{dE = \delta Q - \delta w + d(\sum \mu_i N_i)}$$

The change in the internal energy of a closed thermodynamic system is equal to the sum of the amount of heat energy supplied to the system and the work done on the system.

- **Second law :** 엔트로피

$$\boxed{S = \frac{q}{T}}$$

The total entropy of any isolated thermodynamic system tends to increase over time, approaching a maximum value.

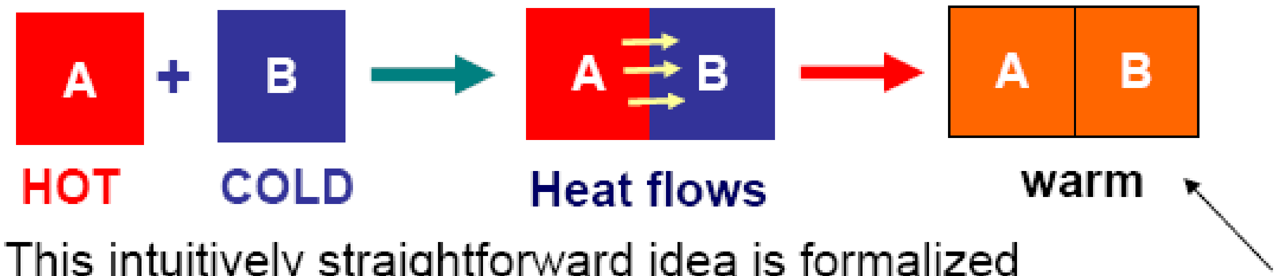
- **Third law of thermodynamics : 절대 0 도**

The entropy of all system and of all states of a system is zero at absolute zero or

It is impossible to reach the absolute zero of temperature by any finite number of processes.

Equality of Temperature (Scales)

Thermal Equilibrium (heat stops flowing)



Same temperature

This intuitively straightforward idea is formalized in the zeroth law of thermodynamics and is made practical through the development of thermometers and temperature scales

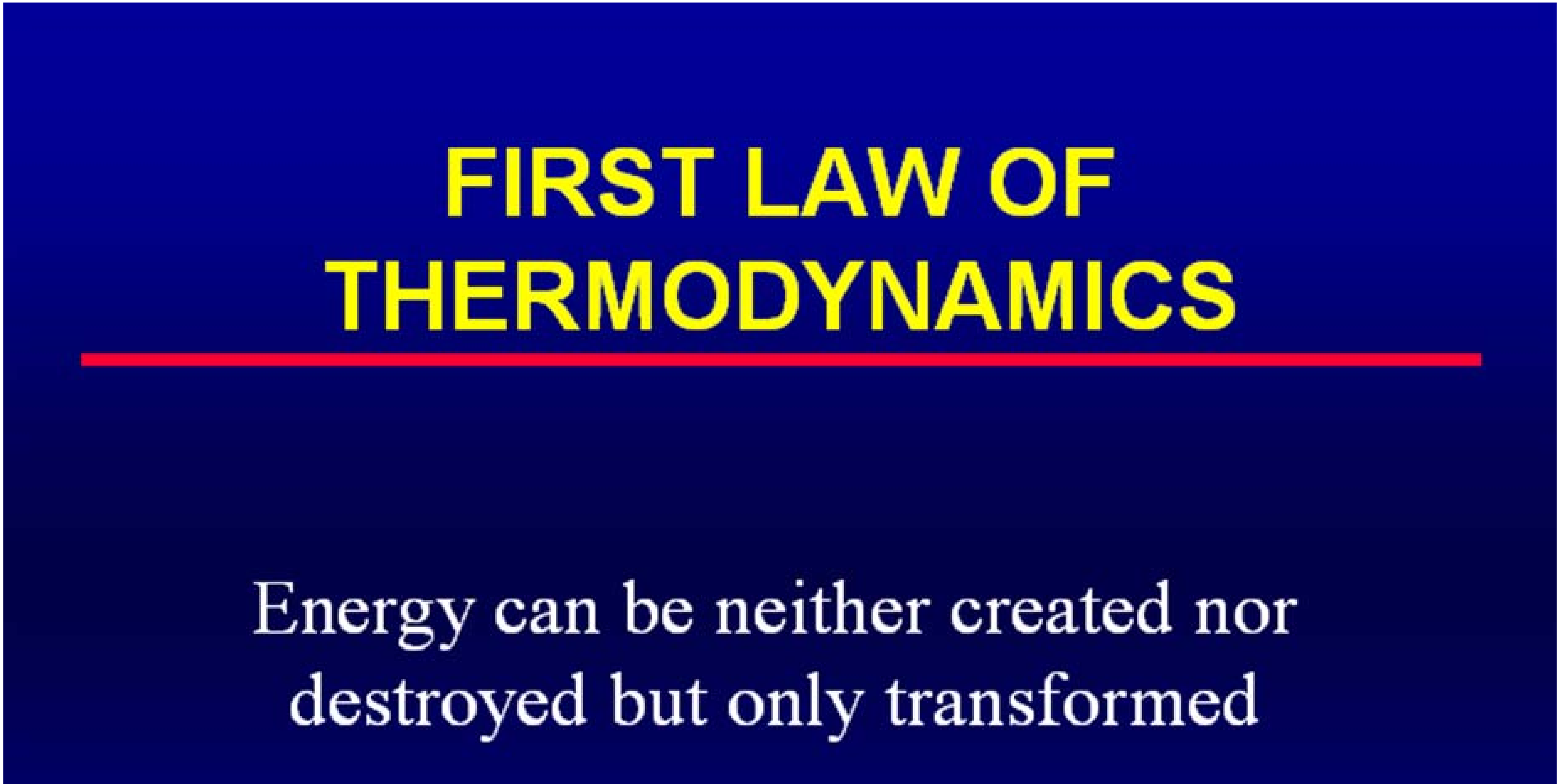
K = °C + 273.15
R = F + 459.67

IF **A** and **B** are in thermal equilibrium and

B and **C** are in thermal equilibrium, **then**

A and **C** are in thermal equilibrium.

ZERO'th Law of Thermodynamics



FIRST LAW OF THERMODYNAMICS

Energy can be neither created nor destroyed but only transformed

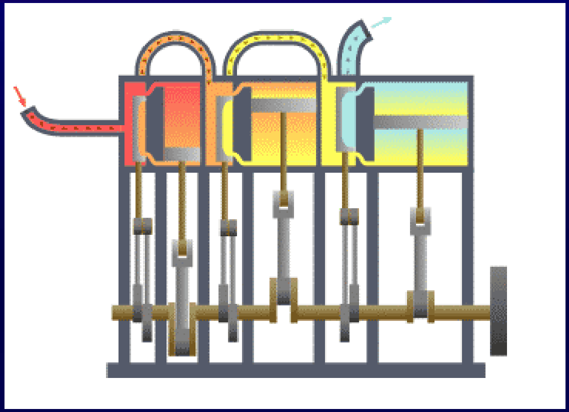
; but it can be transformed from one into another.

; The total amount of energy in the universe is constant for any physical and chemical change.

Chapter 1.2

Internal energy E of a system

: sum of the kinetic and potential energies of all parts of the system.



Energy In = Energy Out

or

$U_2 - U_1 = Q - W$

where

U_1: internal energy of the system at the beginning

U_2: internal energy of the system at the end

Q : net heat flow into the system

W : net work done by the system

$$\boxed{dE = \delta Q - \delta W = \delta Q - P \cdot dV}$$

: Change in the internal energy is equal to the amount added by heating minus the amount lost by doing work on the environment.

Chapter 1.3 HEAT CONTENT OR ENTHALPY

$$H = E + PV \longrightarrow \boxed{dE = \delta Q - P \cdot dV}$$

When V is constant

$$\frac{\delta Q}{dT} = \frac{dE}{dT} + P\cancelto{0}{\frac{dV}{dT}} \qquad C_V = \left(\frac{\partial Q}{\partial T}\right)_V = \left(\frac{\partial E}{\partial T}\right)_V \qquad \boxed{C_V = \left(\frac{\partial E}{\partial T}\right)_V \quad \text{or} \quad E = \int C_V\, dT}$$

실험적으로 V 를 일정하게 하는 것 (Cv)이 어렵기 때문에 V 보다 P를 일정하게 유지하는 것 (Cp)이 편함 → pressure ex)1 atm,

When pressure is const.

$$H \equiv E + PV$$

$$\begin{aligned} dH &= dE + PdV + VdP \\ &= \delta Q - \delta w + PdV + VdP \\ &= \delta Q - PdV + PdV + VdP \\ &= \delta Q + VdP \end{aligned}$$

$$\frac{dH}{dT} = \frac{\delta Q}{dT} + V\frac{dP}{dT}$$

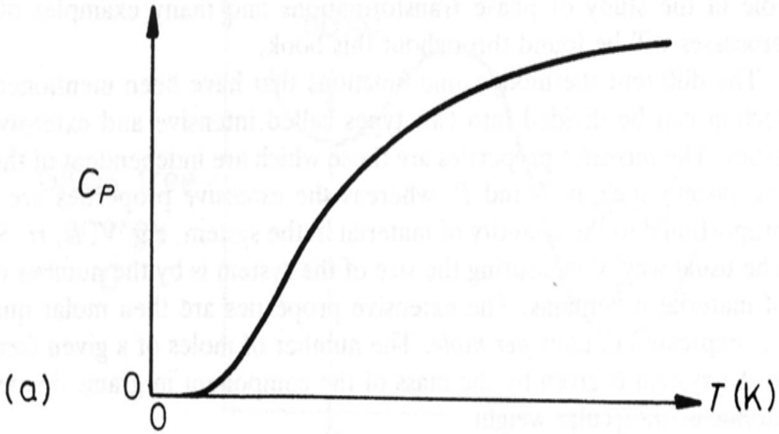
$$\frac{dP}{dT} = 0 \quad \text{when} \quad P \text{ is constant}$$

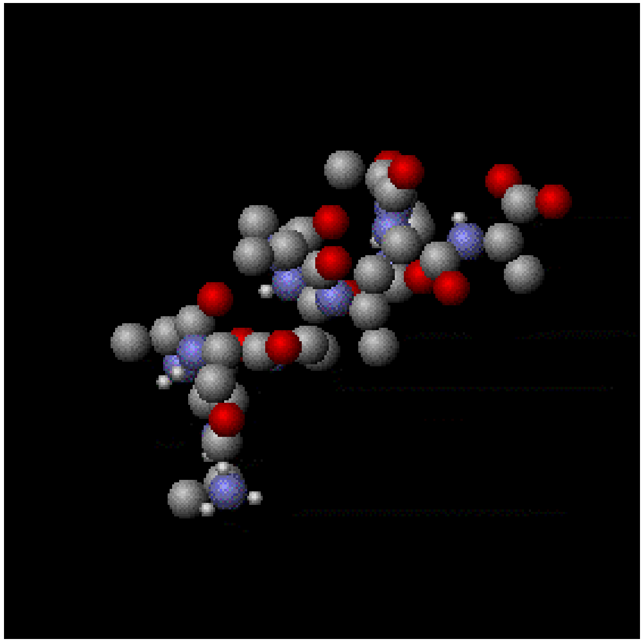
$$\boxed{\left(\frac{dH}{dT}\right)_P = \left(\frac{\delta Q}{dT}\right)_P = C_P} \qquad \boxed{H = \int C_p\, dT}$$

C_P ; 온도에 따라 변함 (온도의 함수)

$$C_P = a + bT + CT^{-2}$$

(경험식 above room temp)





Molecules have internal structure because they are composed of atoms that have different ways of moving within molecules. Kinetic energy stored in these *internal degrees of freedom* contributes to a substance’s specific heat capacity and not to its temperature.

Table of specific heat capacities

Substance	Phase	C_p J / g·K	C_p J / *mol*·K	C_v J / *mol*·K	Volumetric heat capacity J / cm^3·K
Aluminium	Solid	0.897	24.2		2.422
Copper	solid	0.385	24.47		3.45
Diamond	solid	0.5091	6.115		1.782
Gold	solid	0.1291	25.42		2.492
Graphite	solid	0.710	8.53		1.534
Iron	solid	0.450	25.1		3.537
Lithium	solid	3.58	24.8		1.912
Magnesium	solid	1.02	24.9		1.773
Silver	solid	0.233	24.9		
Water	liquid (25 °C)	4.1813	75.327	74.53	4.184
Zinc	solid	0.387	25.2		

All measurements are at 25 °C unless otherwise noted.

- **The *second* law of thermodynamics**

$$\boxed{S = \frac{q}{T}}$$

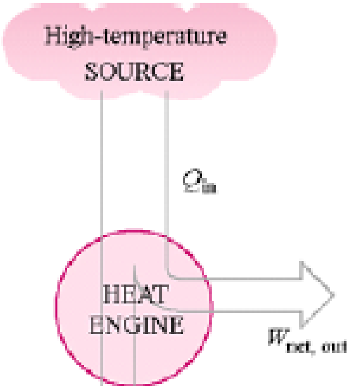
; The disorder of the universe always increase

; all chemical and physical processes occur spontaneously only when disorder is increased.

Two classical statements of the second law

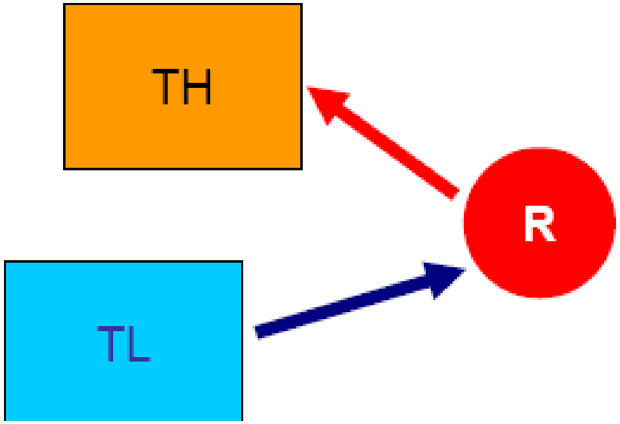
Kelvin-Planck statement

It is impossible for any system to operate in a cycle that takes heat from a hot reservoir and converts it to work in the surroundings without at the same time transferring some heat to a colder reservoir



Clausius

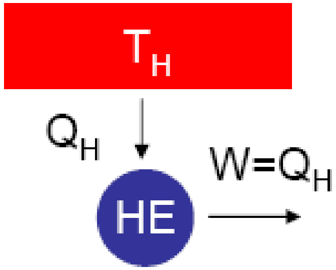
It is impossible for any system to operate in a cycle that takes heat from a cold reservoir and transfer it to a hot reservoir without at the same time converting some work into heat



Thus, two statements

Kelvin-Planck statement

1. 단일 열에너지 저장고로는 사이클로 운전되는 기관은 불가능
2. 즉 반드시 열 손실이 있어야 일이 나온다는 말
3. 한번은 가능하지만 여기서는 사이클 기관
4. 열효율 100 %의 기관은 불가능하다.



$$\beta = \frac{Q_L}{W_{net}}$$

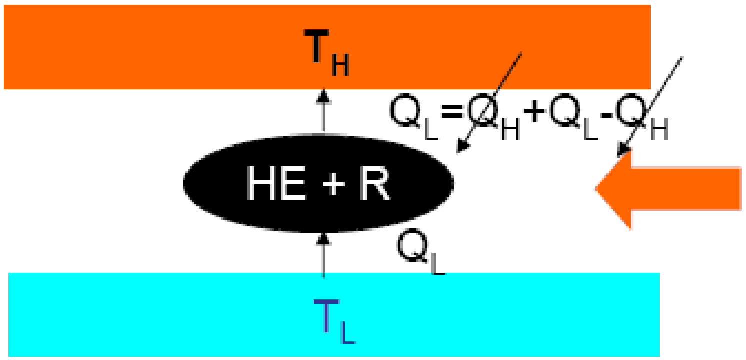
Clausius

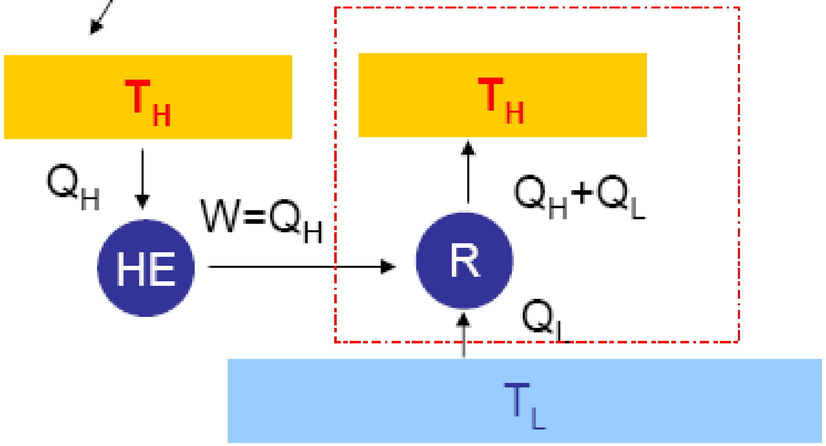
1. 낮은 온도에서 높은 온도로 그냥은 못간다는 것 (일이 필요하다)
2. 모터없는 냉장고는 없다. (압축일이 반드시 필요)
3. 무한대의 COP는 존재하지 않는다.

100 % 효율의 heat engine에 의해 구동됨

Is it possible?

YES NO~!





THE SECOND LAW OF THERMODYNAMICS

(1) All energy received as heat by a heat engine cycle cannot be converted into work (This means that no cycle can have a thermal efficiency of 100%)

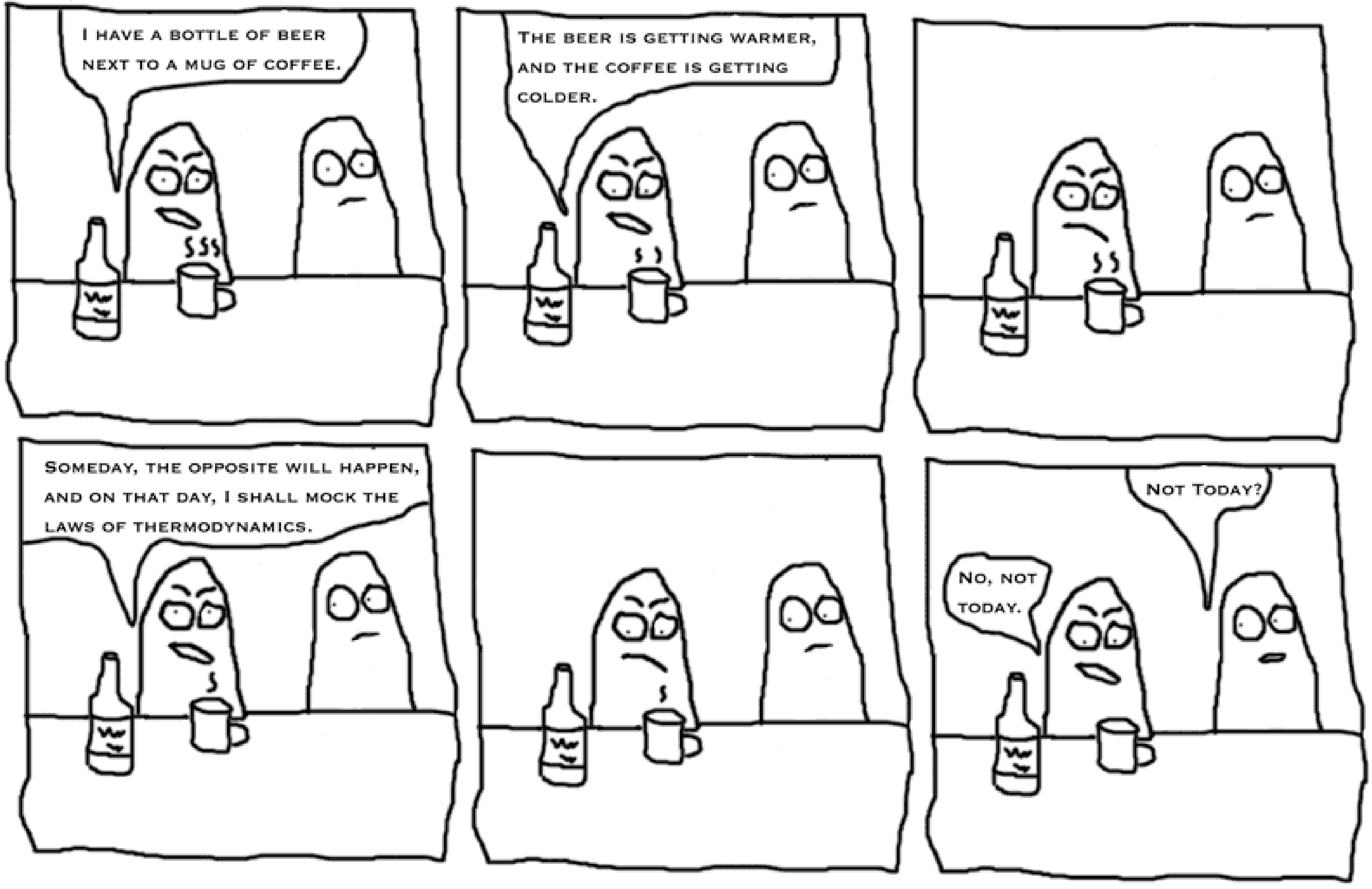
(2) The transformation of heat to work is dependent of a temperature difference and on the flow of heat from a high temperature reservoir to a low temparature reservoir to a low temperature reservoir. (In other word heat must flow from hot to cold)

(3) It is impossible to construct an engine that, operating in a cycle, will produce no effect other than the transfer of heat from a low temperature reservoir to a hight temperature reservoir.

Packin a Punch in a Sack Lunch

by Collin Anderson

“Thermodynamics”



- 2nd law ; Entropy (S) ; irreversibility, disorder

- In an **isolated system**, **a process can occur only if it increases the total entropy of the system**. If a system is at equilibrium, by definition no spontaneous processes occur, and therefore the system is at maximum entropy.
- **Heat cannot spontaneously flow from a material at lower temperature to a material at higher temperature.**
- **It is impossible to convert heat completely into work.**

Enropy : $S = \dfrac{q}{T}$

Ex) A+B → C+D

; toward an equil. state

Spontaneous >> increase in entropy

; degree of irreversibility

→평형에 가까울수록 줄어든다

→ degradation

Ex) mixing of gases

What is reversible process?

→ Continuous maintenance of equil. state

→ 무한히 느리다

→ Degree of irrevesibility가 최소 (≈0)

→ Imaginary process

Chapter 1.4 ENTROPY

Entropy is an extensive quantity.

Entropy is

1) a thermodynamic variable of the system.
2) a measure of the number of ways of arranging the atoms or molecules composing the system

The atomistic approach leads to identical conclusions and it has the great advantage of being comprehensible in terms the metallurgist can appreciate.

Entropy can be computed from randomness by Boltzmann equation, i.e.,

$$\boxed{S = k \ln w}$$

w : degree of randomness, k: Boltzman constant

→ **thermal**; vibration (no volume change)

→ **Configuration**; atom 의 배열 방법 수 (distinguishable)

$$\boxed{S = S_{th} + S_{config}}$$

엔트로피 생성 (disorder 증가)

$$\int_1^2 dS = \frac{\delta Q}{T} + \delta S_{gen},$$

Path dependent
Various processes are present

$$\boxed{S_2 - S_1 = \int_1^2 \frac{\delta Q}{T} + {}_1S_{2,gen}}$$

Entropy equilibrium

Entropy change
= +in – out + generation

	Non-isolated systems	Isolated systems
Reversible	$dS = \frac{\delta Q}{T}$	$dS = \frac{\delta Q}{T} = 0$
Irreversible	$dS > \frac{\delta Q}{T}$	$dS > \frac{\delta Q}{T} > 0$

Where dS is the entropy change of the system only.

Excess mixing Entropy

If there is no volume change or heat change (S_{config}),

$$w_{config} = 1 \quad \rightarrow before\_solution\_(pureA\_pureB)$$

$$w_{config} = \frac{(N_A + N_B)!}{N_A!N_B!} \rightarrow after\_solution\_(N_A, N_B)$$ ⬅ **Number of distinguishable way of atomic arrangement**

$$\Delta S^{mix} = S^{after} - S^{before} = k\ln\frac{(N_A + N_B)!}{N_A!N_B!} - k\ln 1$$

$$\rightarrow N_A = X_A N_0\ ,\ \ N_B = X_B N_0, N_A + N_B = N_0$$ 이므로

using Stirling's approximation $\ln N! \approx N\ln N - N$

and $R = kN_0$

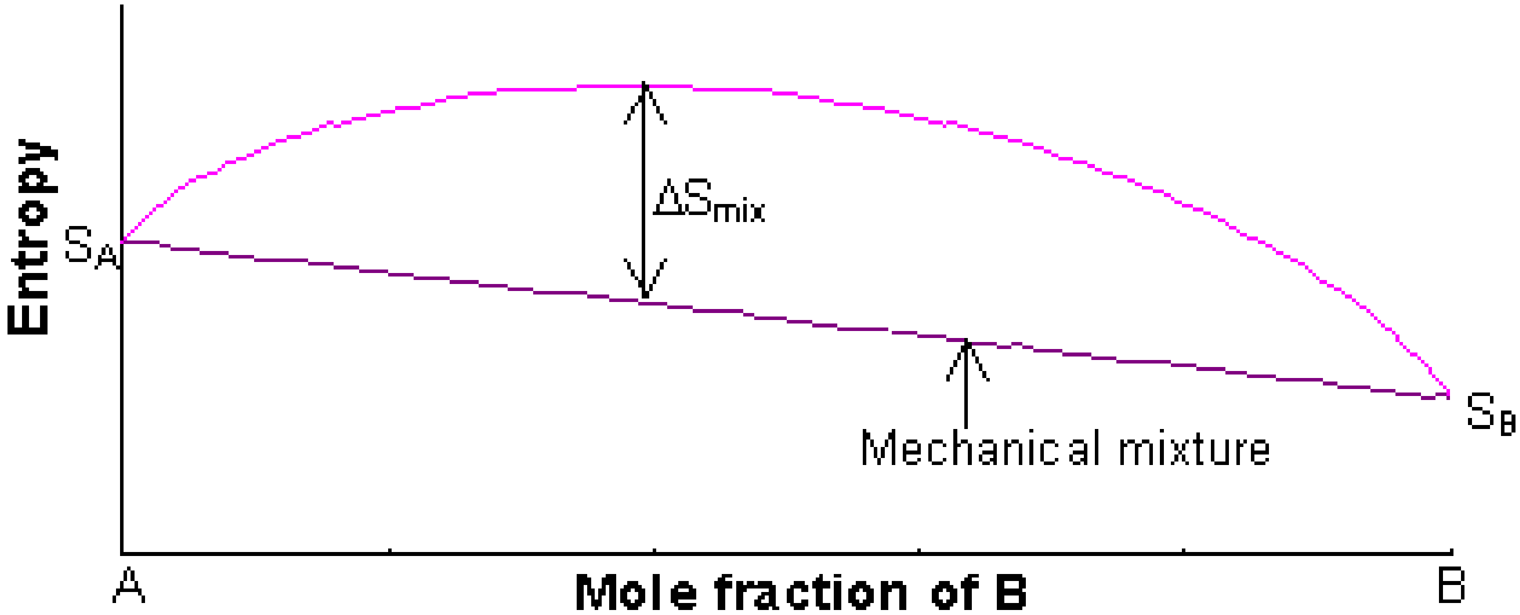
$$= k[(N_o \ln N_o - N_o) - (X_A N_o \ln X_A N_o - X_A N_o) - (X_B N_o \ln X_B N_o - X_B N_o)]$$

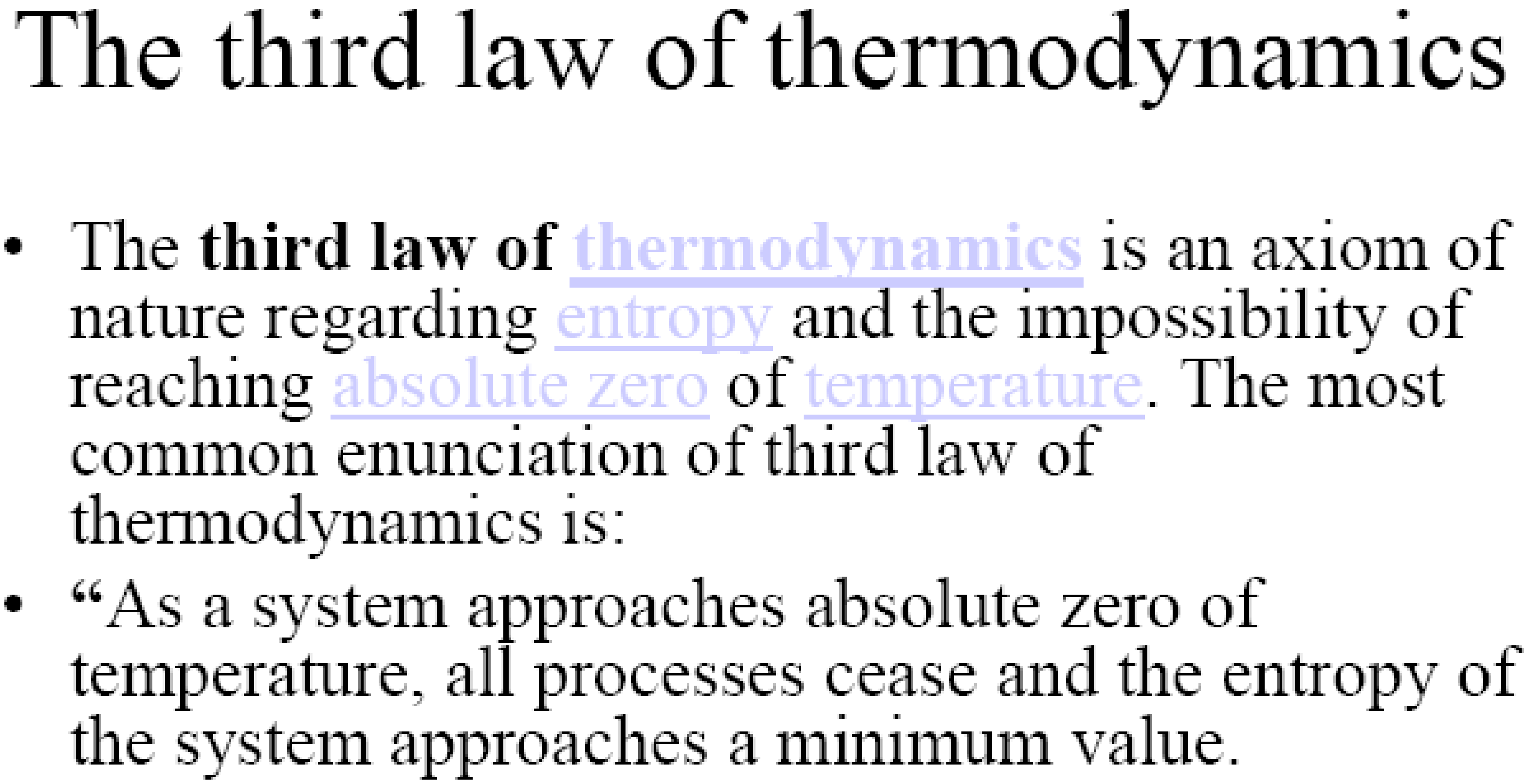
$$\Delta S^{mix} = -R(X_A \ln X_A + X_B \ln X_B)$$

Excess mixing Entropy

If there is no volume change or heat change (S_{config}),

$$\Delta S^{mix} = -R(X_A \ln X_A + X_B \ln X_B)$$





The third law of thermodynamics

- The **third law of** thermodynamics is an axiom of nature regarding entropy and the impossibility of reaching absolute zero of temperature. The most common enunciation of third law of thermodynamics is:
- “As a system approaches absolute zero of temperature, all processes cease and the entropy of the system approaches a minimum value.
- In brief, this postulates that entropy is temperature dependent and leads to the formulation of the idea of absolute zero.