Statistical Mechanics and Material Properties

By

Kunio TAKAHASHI
Tokyo Institute of Technology,
Tokyo 152-8552, JAPAN
Phone/Fax +81-3-5734-3915
takahak@ide.titech.ac.jp
http://www.ide.titech.ac.jp/~KT-lab/

Statistical Mechanics and Thermodynamics

- Thermodynamics
  (0^{th} low : A.eq.B and B.eq.C -> A.eq.C)
  1^{st} low : Energy conservation
  2^{nd} low : Free energy decreases
  3^{rd} low : Entropy -> 0 at 0K

Interface essential to utilize thermodynamics

- Statistical Mechanics
  Ergodic theorem : time average = space average, (in equilibrium)

Grave-stone of Boltzmann…

You may have learnt Thermodynamics

- Thermodynamics
  (0^{th} low : A.eq.B and B.eq.C -> A.eq.C)
  1^{st} low : Energy conservation
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Everything is derived from these principles…
But !

- Definitions
  - Temperature
  - Free energy
  - Entropy
  - Equilibrium

Please remember when you have heard them first.
How they were defined ?

Could you understand them as you could do in kinetics ?

Definitions

- Temperature
  - °C : water
  - °F : salt water

  } Empirical temp.

  Temp. in science (physics or kinetics) is same as above ?
- Free energy
  - Helmholtz $F = U - TS$
  - Gibbs $G = U + PV - TS$

  Free energy is same as the energy in kinetics ?

  Why they need to be defined as above ?
- Entropy

  What is this ?
- Equilibrium

  What is the definition ?

You may have learnt Thermodynamics

- Thermodynamics
  (0^{th} low : A.eq.B and B.eq.C -> A.eq.C)
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But !

- Definitions
  - Temperature
  - Free energy
  - Entropy
  - Equilibrium

Understanding of them
(= statistical mechanics)
lead you to utilize
thermodynamics
⇩
Material properties

Let's define them step by step !

Temperature (first trial)

Example : Ideal gas (1)

- Assumption

  Number of molecule : N in volume : V

  Velocity of molecule : $\mathbf{c} = (u, v, w)$ → $c^2 = u^2 + v^2 + w^2$

  probability : $F(\mathbf{c}) = f(u)f(v)f(w)$

$$\langle u^2 \rangle = \langle v^2 \rangle = \langle w^2 \rangle$$

$$\langle u^2 \rangle = \frac{1}{3}\langle c^2 \rangle$$

- Momentum change = Pressure on area *A*

$$\int_0^{+\infty} \left(2mu \times f(u) \frac{N}{V} Audt \right) du = PAdt$$

$$PV = \int_0^{+\infty} (2mu \times f(u) Nu) du = mN \int_{-\infty}^{+\infty} u^2 f(u) du = Nm\langle u^2 \rangle$$

- Comparison with eq. of state : $PV = NkT$

$$PV = Nm\frac{1}{3}\langle c^2 \rangle = N\frac{2}{3}\left\langle \frac{1}{2}mc^2 \right\rangle$$

$$\left\langle \frac{1}{2}mc^2 \right\rangle = \frac{3}{2}kT$$

- Law of equi-partition of energy

$$\left\langle \frac{1}{2}mu^2 \right\rangle = \left\langle \frac{1}{2}mv^2 \right\rangle = \left\langle \frac{1}{2}mw^2 \right\rangle = \frac{1}{2}kT$$

Example : Ideal gas (2)

$$c^2 = u^2 + v^2 + w^2$$

- Probability function

$$F(\mathbf{c}) = f(u) f(v) f(w)$$ taking log : $$\ln F(c) = \ln f(u) + \ln f(v) + \ln f(w)$$

diff. with u : $$\frac{d \ln F}{du} = \frac{d \ln f}{du}$$ → $$\frac{d \ln F}{dc}\frac{dc}{du} = \frac{d \ln F}{dc}\frac{u}{c} = \frac{d \ln f}{du}$$

- Const. independent of c, u, v, w : $$\frac{1}{c}\frac{d \ln F}{dc} = \frac{1}{u}\frac{d \ln f}{du} = \frac{1}{v}\frac{d \ln f}{dv} = \frac{1}{w}\frac{d \ln f}{dw} = -\gamma$$

because it is probability... $$f(u) = \sqrt{\frac{\gamma}{2\pi}} e^{-\frac{1}{2}\gamma u^2}$$

- Average kinetic energy (expectated value) :

$$\left\langle \frac{1}{2} m u^2 \right\rangle = \int_{-\infty}^{+\infty} \frac{1}{2} m u^2 f(u) du = \int_{-\infty}^{+\infty} \frac{1}{2} m u^2 \sqrt{\frac{\gamma}{2\pi}} e^{-\frac{1}{2}\gamma u^2} du = \frac{1}{2} m \sqrt{\frac{\gamma}{2\pi}} \int_{-\infty}^{+\infty} u^2 e^{-\frac{1}{2}\gamma u^2} du$$

$$= \frac{1}{2} m \sqrt{\frac{\gamma}{2\pi}} \sqrt{\frac{2\pi}{\gamma^3}} = \frac{m}{2\gamma}$$ using eq. of state $$= \frac{1}{2} kT$$ therefor $$\gamma = \frac{m}{kT}$$

- Maxwell distribution :

$$f(u) = \sqrt{\frac{m}{2\pi kT}} e^{-\frac{m}{2}u^2 / kT}$$

$$F(u, v, w) = \left(\frac{m}{2\pi kT}\right)^{\frac{3}{2}} e^{-\frac{m}{2}(u^2 + v^2 + w^2) / kT}$$

Example : Ideal gas (3)

$$F(u,v,w) = \left(\frac{m}{2\pi kT}\right)^{\frac{3}{2}} e^{-\frac{m}{2}\left(u^2+v^2+w^2\right)/kT}$$

- Maxwell distribution

$$f(u) = \sqrt{\frac{m}{2\pi kT}} e^{-\frac{m}{2}u^2/kT}$$

Probability function $\propto e^{\{\text{kineticenergy}\}/kT}$

- Only for Ideal gas ?

< Remember >

- Empirical knowledge is used.

  Eq. of state for ideal gas

  Relation between Temp. and average Kinetic energy

- This is the definition of Temp. !?

Let's consider more general case !

You may have learnt Thermodynamics

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  Everything is derived from these principles.

- Definitions
  - Temperature
  - Free energy
  - Entropy
  - equilibrium
  - etc…

Temperature is kinetic energy ?
(at equilibrium)

Temperature and equilibrium (general treatment)

Canonical ensemble (1)

- Assumption 1 (a model of system)
  Num. of elements with energy e_i is n_i .
  Total num. of elements (particle, molecule, etc…) : $N = \sum n_i$
  Total energy : $E = \sum n_i e_i$

  N and E are given.

…, therefore
  $n_i(e_i)$ is determined by the state. (density of state)
  States with same $n_i(e_i)$ are indistinguishable.

Why !?

- Assumption 2 (most important !!)
  The state is observed so as to maximize
  the way of shuffling of the density of state $n_i(e_i)$

Canonical ensemble (2)

- the way of shuffling of the state
- To maximize *W*

$$W = \frac{N!}{n_1!n_2!n_3!\Lambda}$$

$$L \equiv \ln W - \lambda_1\left(\sum_i n_i - N\right) - \lambda_2\left(\sum_i n_i e_i - E\right) \to \max$$

Lagrange multiplier

using the definition of *W*

$$L = \left(\ln N! - \sum_i n_i!\right) - \lambda_1\left(\sum_i n_i - N\right) - \lambda_2\left(\sum_i n_i e_i - E\right)$$

$$\frac{\partial L}{\partial n_i} = \frac{\partial L}{\partial \lambda_i} = 0$$

using the Stirling's formula $\ln x! \approx x \ln x - x$

$$L = \left(N \ln N - N - \sum_i (n_i \ln n_i - n_i)\right) - \lambda_1\left(\sum_i n_i - N\right) - \lambda_2\left(\sum_i n_i e_i - E\right) \to \max$$

…,

Canonical ensemble (3)

$$L = \left(N \ln N - N - \sum_i \left(n_i \ln n_i - n_i \right) \right) - \lambda_1 \left(\sum_i n_i - N \right) - \lambda_2 \left(\sum_i n_i e_i - E \right) \to \max$$

- Here, *N* and *E* are constant, therefore

$$\frac{\partial L}{\partial n_i} = -\left(\ln n_i + 1 - 1 \right) - \lambda_1 - \lambda_2 e_i = 0 \quad \Rightarrow \quad n_i = \exp\left(-\lambda_1 - \lambda_2 e_i\right) = \Lambda_1 \exp\left(-\lambda_2 e_i\right)$$

- Using $N = \sum n_i$

$$\frac{n_i}{N} = \frac{1}{\sum_i \exp\left(-\lambda_2 e_i\right)} \exp\left(-\lambda_2 e_i\right) \propto \exp\left(-\lambda_2 e_i\right)$$

- Comparing with Maxwell distribution $f(u) = \sqrt{\frac{m}{2\pi kT}} e^{-\frac{m}{2}u^2 / kT}$

$$\frac{n_i}{N} = \frac{1}{\sum_i \exp\left(-e_i / kT\right)} \exp\left(-e_i / kT\right)$$

: Maxwell-Boltzmann distribution

e_i is not limited to be the kinetic energy.

kinetic energy, potential energy, etc…

Canonical ensemble (3)

$$L = \left(N \ln N - N - \sum_i \left(n_i \ln n_i - n_i \right) \right) - \lambda_1 \left(\sum_i n_i - N \right) - \lambda_2 \left(\sum_i n_i e_i - E \right) \rightarrow \max$$

- Here, N and E are constant, therefore

$$\frac{\partial L}{\partial n_i} = -(\ln$$

$$\exp\left(-\lambda_2 e_i\right)$$

- Using

$$\frac{n_i}{N} = \frac{}{\sum_i e}$$

Temperature is energy !
(used in physics)
in the most probable situation.

- Comparing with l distribution

$$f(u) = \sqrt{\frac{m}{2\pi kT}} e^{-\frac{m}{2}u^2 / kT}$$

$$\frac{n_i}{N} = \frac{1}{\sum_i \exp\left(-e_i / kT\right.} \quad \left(-e_i / kT\right)$$

: Maxwell-Boltzmann distribution

e_i is not limited to be the kinetic energy.
kinetic energy, potential energy, etc...

Canonical ensemble (4)

- Probability of the state of energy E : $\propto \exp(-E/kT)$
- Probability of the state whose energy > E : $\propto \exp(-E/kT)$
- "Assumption 2"

The state is observed so as to maximize
the way of shuffling of the density of state $n_i(e_i)$

The most probable situation

Equilibrium !

Equilibrium is,,,
the most probable state !!

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Everything is derived from these principles.

- Definitions
  - Temperature
  - Free energy
  - Entropy
  - equilibrium
  - etc…

Temperature is energy ! (at equilibrium)

Equilibrium is the most probable state.

Definitions

- Temperature

  Empirical temp. °C : water — defined one or two temp.

  °F : salt water

  T. can be shifted and scaled, so as proportional to energy !

- Free energy

  Helmholtz $F = U - TS$

  Gibbs $G = U + PV - TS$

  Free energy is same as the energy in physics ?

  Why they need to be defined as above ?

- Entropy

  What is this ?

- Equilibrium

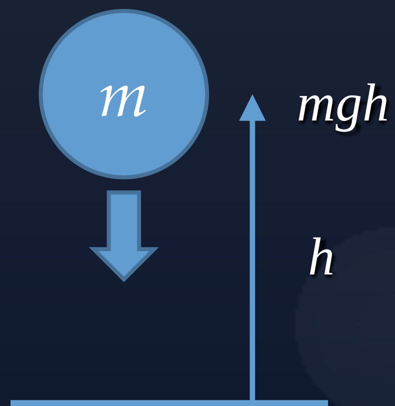
  The most probable state ! So, we can observe always…

Free energy and entropy

Prediction of phenomena

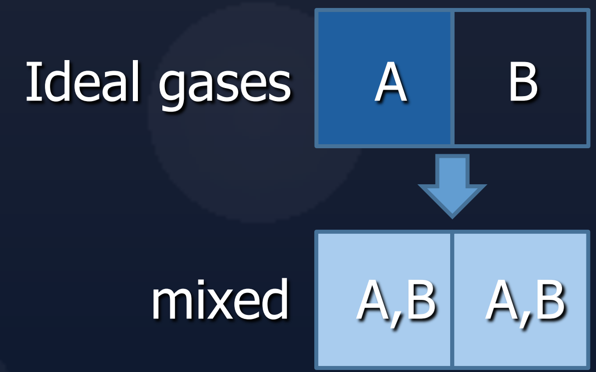
Physicists (kinetics)

- as to decrease Potential Energy



Chemists (chemistry)

- as to decrease Free Energy



After the phenomena

Decreased	Potential Energy	Not changed
Not changed	Total energy	Not changed
? (Not changed)	Free Energy	Decreased

Chemists wanted to introduce **something like potential energy**, to predict the phenomena.

Chemists wanted to introduce something like potential energy, to predict the phenomena.

The something; related to the work or energy, used in thermodynamic technology, (ex. steam engine, chemical reaction, etc…)

Definition of free energy :

Energy that can be converted into a work in a process of

constant temperature and volume (Helmholtz). $F = U - TS$

constant temperature and pressure (Gibbs). $G = U + PV - TS$

(Two of three *T*, *P*, & *V* determine its state.)

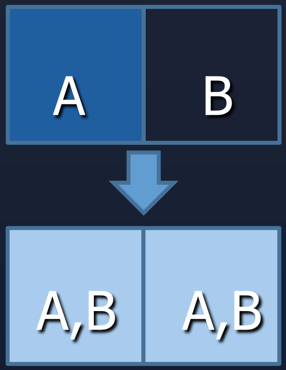
Energy or work in kinetics

What's this ! ??

$$G = U + PV - TS$$

Definition of free energy :

Energy that can be converted into a work in a process



$$G = U + PV - TS$$

What's this ! ??

- The TS term increases in the mixing process, even if kinetic and potential energy never changes.
- The mixing process never goes back.

Increase in TS term $\rightarrow$ Decrease of G

= Increase of the usable energy

= Degrade of energy

Definition of free energy :

Energy that can be converted into a work in a process

$$G = U + PV - TS$$

What's this ! ??

- There exists a part of energy, which we can not take as a work.
- It is proportional to the temperature.

The degrade is proportional to the temp…

Degrade of the energy exits…

Empirical knowledge of chemists

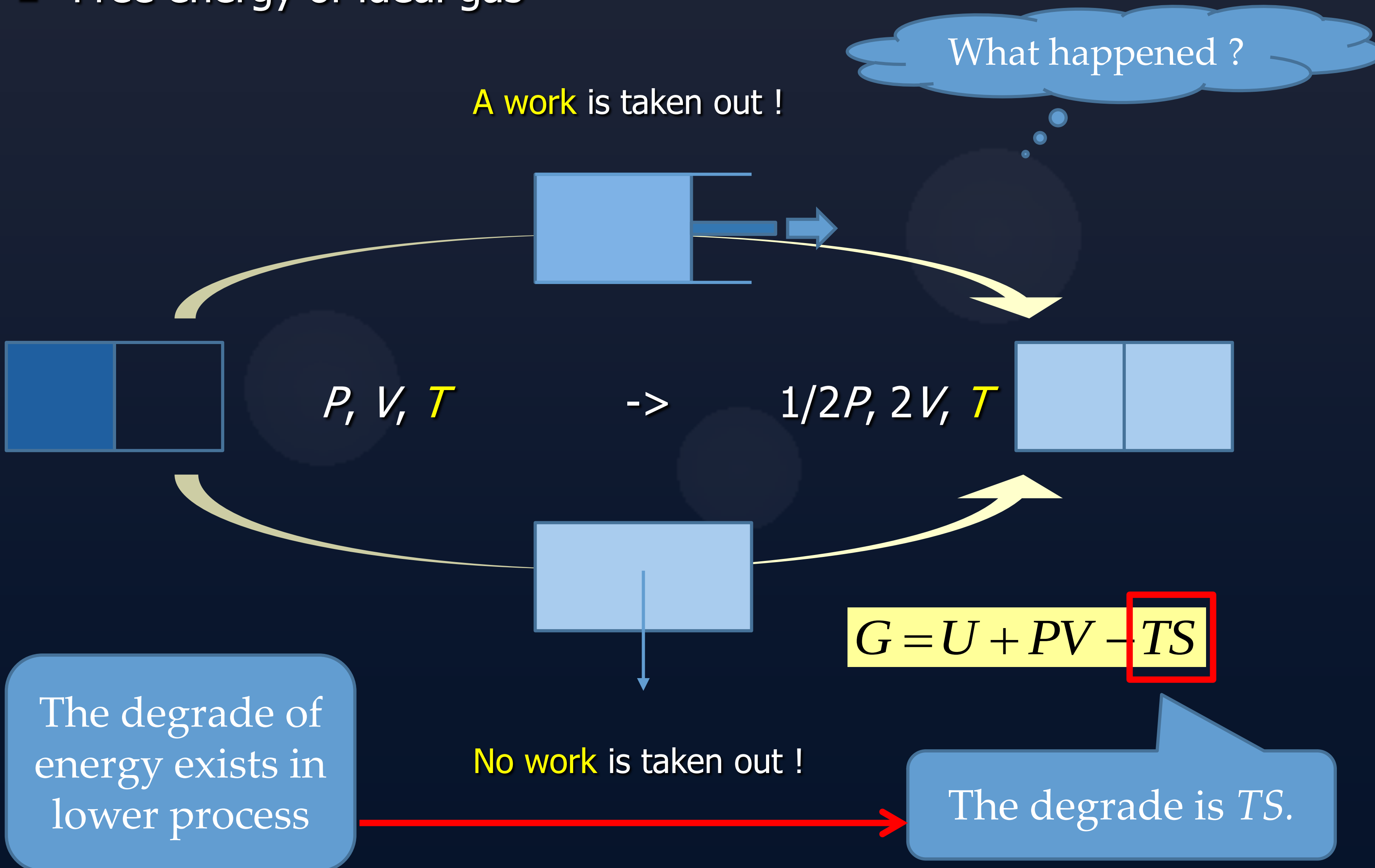
- S is defined as the entropy.

What's the entropy ! ??

This is the definition of entropy in thermodynamics.

Boltzmann's entropy formula & Free energy

- Free energy of ideal gas



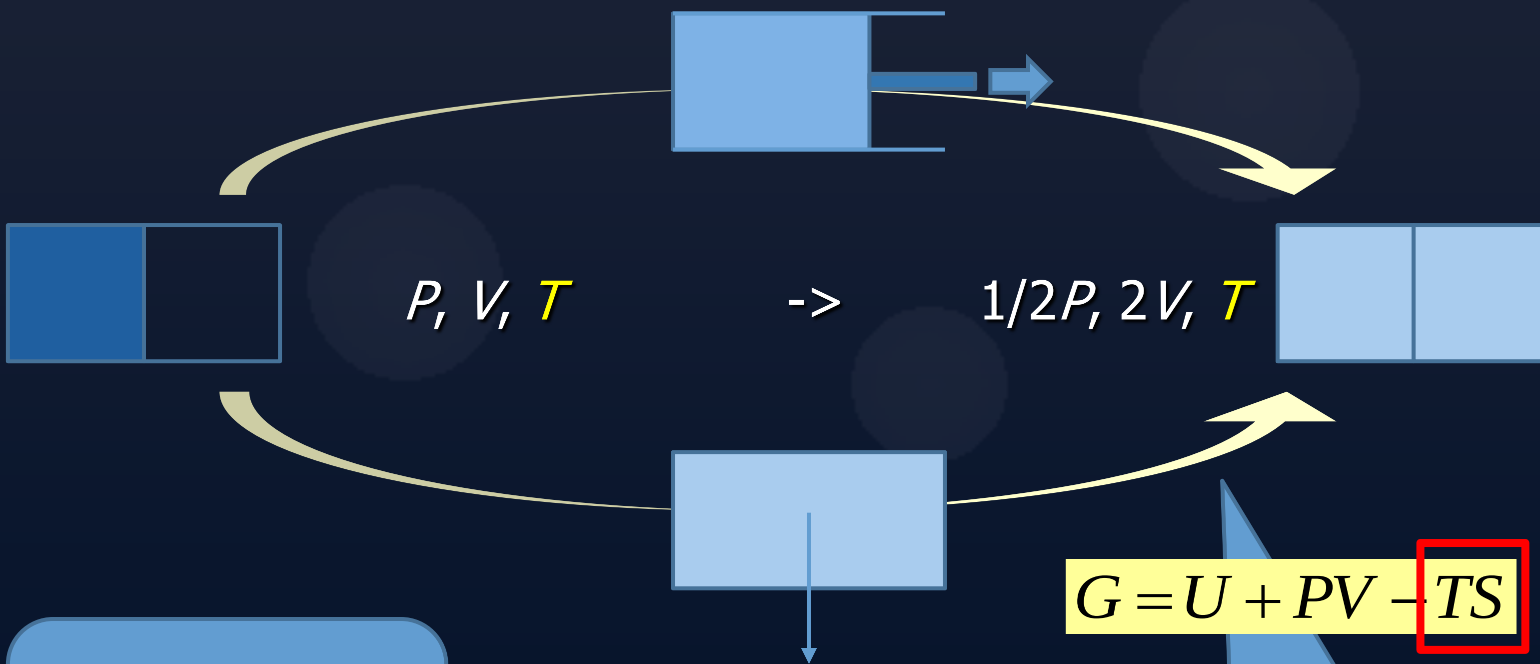
Boltzmann's entropy formula & Free energy

- Free energy of ideal gas

$$PV = NkT$$

A work is taken out !

$$\int_{V}^{2V} PdV = \int_{V}^{2V} \frac{NkT}{V} dV = NkT \ln 2$$



$$G = U + PV - TS$$

The degrade of energy exists in lower process

No work is taken out !

Change in S is $\Delta S = Nk \ln 2$?

Statistical Mechanics
and Thermodynamics

- Thermodynamics
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Boltzmann's entropy formula : $S = k \ln W$

Grave-stone of Boltzmann…

- Statistical Mechanics
  Ergodic theorem : time average = space average, (in equilibrium)

Boltzmann's entropy formula & Free energy

- *W* : Number of state $S = k \ln W$

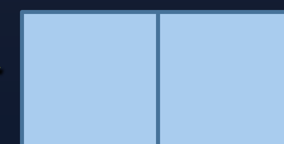
  v : small control volume

  V/v : num. of the c. volume 2*V/v* : num. of the c. volume

Num. of the way to shuffle to distribute the atoms to the each c. volume

$W_0 = (V/v)^N$ $W = (2V/v)^N = W_0 2^N$

P, *V*, *T* -> 1/2*P*, 2*V*, *T*



$S_0 = k \ln W_0$

$$S = S_0 + \Delta S = k \ln\left(W_0 2^N\right) = S_0 + Nk \ln 2$$

$$\Delta S = Nk \ln 2$$

No work is taken out !

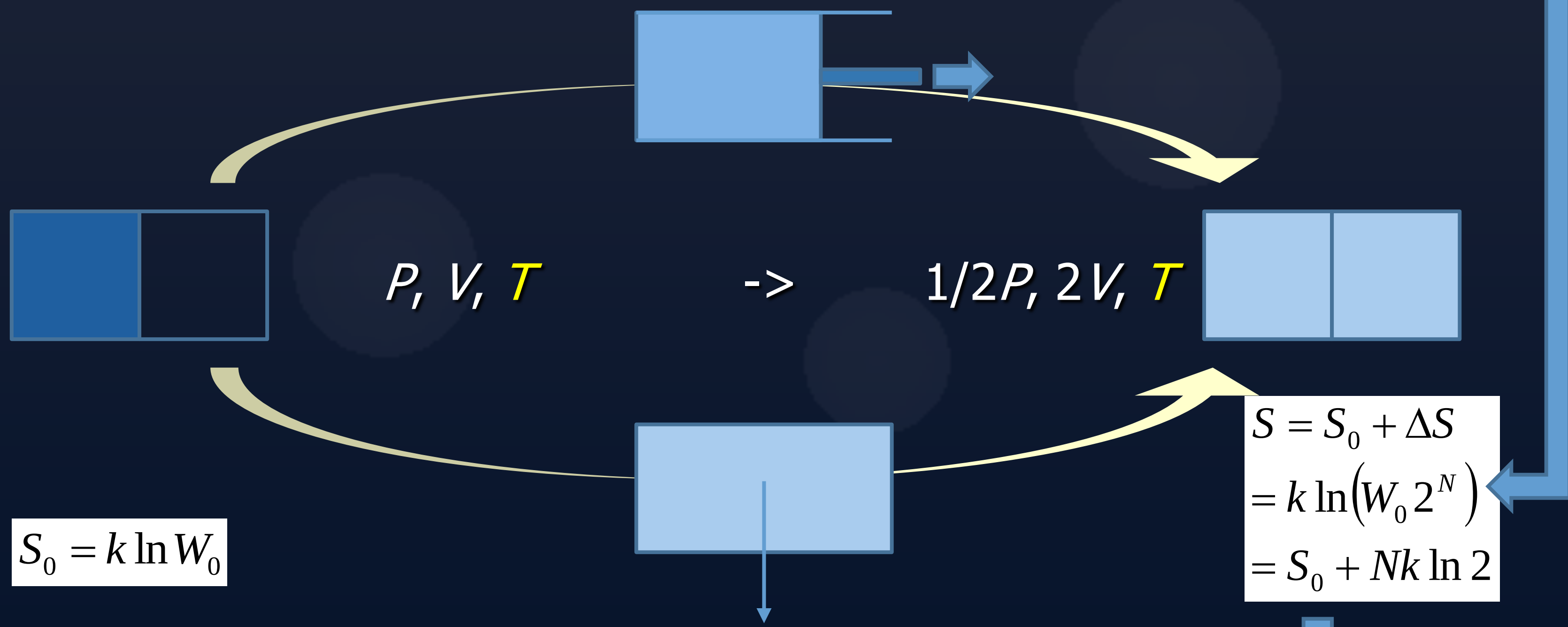
Boltzmann's entropy formula & Free energy

- Free energy of ideal gas

$$PV = NkT$$

A work is taken out !

$$\int_V^{2V} P\,dV = \int_V^{2V} \frac{NkT}{V}\,dV = NkT \ln 2$$



$$S_0 = k \ln W_0$$

$$S = S_0 + \Delta S = k \ln\left(W_0 2^N\right) = S_0 + Nk \ln 2$$

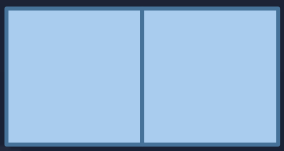
$$\Delta S = Nk \ln 2$$

No work is taken out !

Boltzmann's entropy formula & Free energy

- Free energy of ideal gas

P, V, T -> $1/2P, 2V, T$



Internal E.	U_0	->	U_0
Free E.	$G_0=U_0+PV-TS_0$	->	$G_0-T\Delta S$

No change.

Only entropy term must be changed as

Entropy	S_0	->	$S_0+\Delta S$

Energy taken out : $\int_V^{2V} PdV = \int_V^{2V} \frac{NkT}{V} dV = NkT \ln 2$

Entropy change must be

$\Delta S = Nk \ln 2$

Definition of entropy : $S = k \ln W$

$S_0 = k \ln W_0$

$S_0 + \Delta S = k \ln\left(W_0 2^N\right) = S_0 + Nk \ln 2$

If the entropy is defined as this, it becomes consistent.

Boltzmann's entropy formula & Free

Check of understanding

- Free energy of ideal gas

$$PV = NkT$$

A work is taken out !

$$\int_V^{2V} PdV = \int_V^{2V} \frac{NkT}{V} dV = NkT \ln 2$$

We can take out the infinite work ! ???...
although internal energy must be finite.

P, V, T -> $1/2P$, $2V$, T

W depends on volume ! ???...
Energy never depend on volume…

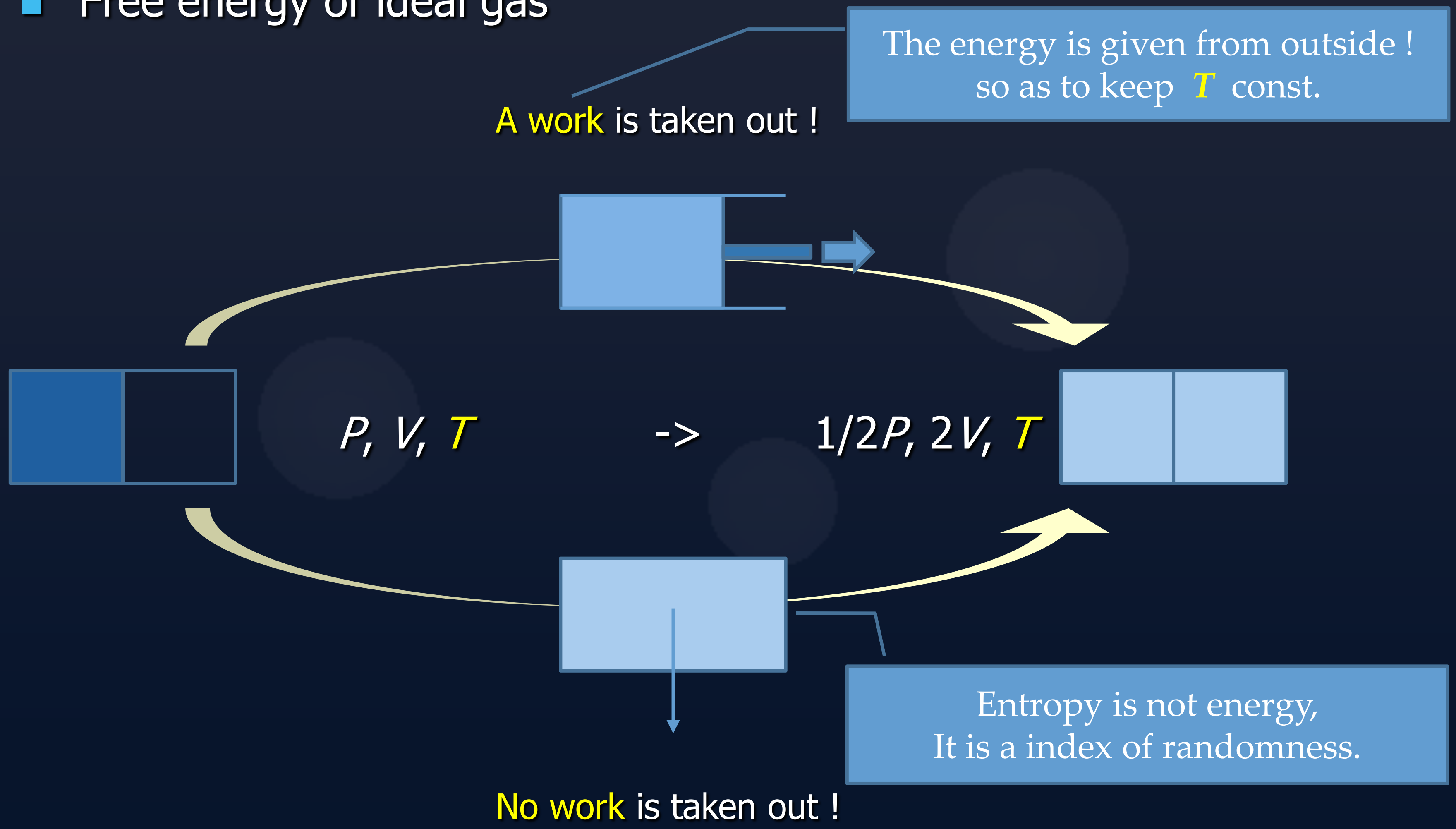
$$S_0 = k \ln W_0$$

No work is taken out !

$$S_0 + \Delta S = k \ln\left(W_0 2^N\right) = S_0 + Nk \ln 2$$

Boltzmann's entropy formula & Free energy

- Free energy of ideal gas



Introduction of Free energy & entropy & temperature

- Definition of **Free Energy** :

  Energy that can be converted into a work.

  (There exist the energy part we can not take out.)

Internal energy = Kinetic energy

we can take out from outside (by heat transfer…)

$$G = U + PV - TS$$

Degrade of the energy…

- Definition of **Entropy** ← Definition of **Temperature**

  Related to the randomness

  $S = k \ln W$

- Temperature

  Empirical temp. °C : water, °F : salt water — defined one or two temp.

  T. can be shifted and scaled, so as proportional to energy !

- Free energy

  Helmholtz $F = U - TS$

  Gibbs $G = U + PV - TS$

  $G = U + PV - TS$

  Free energy is energy that can be converted into work.

  If defined as above, it become consistent.

- Entropy

  $S = k \ln W$ corresponding to number of states, i.e. randomness.

- Equilibrium

  Most probable state ! So, we can observe always…

These are the interface between Thermodynamics and statistical mechanics

Statistical Mechanics
and Thermodynamics

- Thermodynamics

  (0^{th} low : A.eq.B and B.eq.C -> A.eq.C)

  1^{st} low : Energy conservation + …

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  3^{rd} low : Entropy -> 0 at 0K

Boltzmann's entropy formula : $S = k \ln W$

- Statistical Mechanics

  Ergodic theorem : time average = space average, (in equilibrium)

Grave-stone of Boltzmann…

Based of statistical mechanics,

Thermodynamics can be utilized !

Activation energy and Arrhenius plots and rate-determining step

- chemical reaction
- diffusion coefficient
- others… (evaporation, adsorption, etc…)

Arrhenius plots is to know the mechanism of rate-determining step.

Specific heat capacity (1: ideal gasses)

- Remember thermodynamics ! (How have you learnt ?)

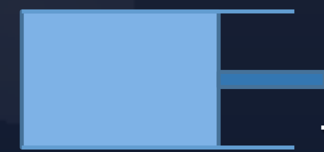
$$C_V = \frac{1}{N}\left(\frac{\partial U}{\partial T}\right)_V$$ why ?

$$C_p = \frac{1}{N}\left(\frac{\partial H}{\partial T}\right)_p$$ why ?

- Definition

  Heat required to increase unit temp.

  - under constant volume



fixed

$$\Delta Q = \Delta G = \Delta U = NC_V \Delta T$$

  - under constant pressure

$$\Delta Q = \Delta G = \Delta U + P\Delta V - \Delta T\Delta S = \Delta U + P\Delta V = NC_P \Delta T$$

$$NC_V \Delta T + P\Delta V = NC_P \Delta T$$

- Mayer's relation

$$C_p - C_V = k$$

$$G = U + PV - TS$$

Specific heat capacity (2: metals)

- Einstein's model
- Dulong-Petit's Low
- Debye model

What is the U?

- Ionic cores

$$U = \langle e_{\mathrm{k}} \rangle + \langle e_{\mathrm{p}} \rangle = 3\frac{1}{2}kT + 3\frac{1}{2}kT = 3kT$$

$$\frac{\Delta Q}{\Delta T} = 3k$$

- Electrons = negligible

Quantum statistical mechanics

Phase diagram

- Stability of phases
- Phase rule
- Phase diagram
- Calculation of Phase Diagram (CALPHAD)