Chap. 4. The Statistical Interpretation of Entropy.

4.1. Intro.

- From the statement for the 2nd law of Thermo, from Classical Thermo. argue it is difficult to assign a physical significancy or quality to en
  - differe from internal E.

$U = U(T)$ atomic E. $S = (\frac{q}{T})$?

- the 2nd law - law only in that it has not yet been disproved.
  evidence No perpetual motion machine. (degradation $W \to Q$ rev irr

4.2. Entropy and disorder on an atomic scale. - a measure of degree of mix-up-nes Gibb

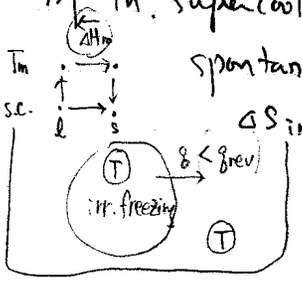
- the more mix up the constituent particles in the sys. the larger the e
  ΔS can be related w/ atomic-scale-randomness or disorder.

- atomic arrangement solid liquid gas → more disorder (entropy p

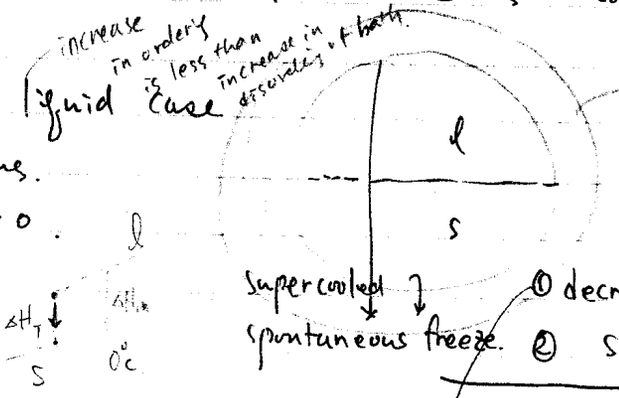
$$\Delta S_{\substack{melting \\ s \to l}} = \frac{q}{T_m} = \frac{\Delta H_m}{T_m} \text{ at } p \text{ const.}$$

$\Delta S > 0$. → means more mix-up-mess.

Ex: In supercooled liquid case spontaneous.



$\Delta S_{irr} > 0$.

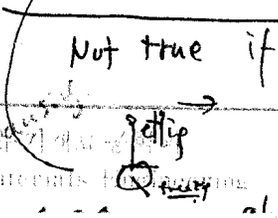


appears less the degree of
① decrease in disorder ($l \to s$
② $S \uparrow$. $\because \Delta S_{irr} > 0$. $\frac{q}{T_{m\,0°C}}$

$\Delta S_{sys} = \frac{q_{rev}}{T}$ $|q_{rev}| > |q|$

$\Delta S_{res} = \frac{q}{T}$

Not true if we consider → the degree of order of the heat bath



7/2 6 - 9 (8)
10 - 12.
13 - 14

(2)

例: If the freezing occurs at the equil^m melting pt.

then, the increase in the degree of order of the freezing sys.

sum of ΔS = the decrease in the degree of order of the heat rese
$= 0$. absorbing the heat of solidification

Disorder is simply been transferred from the sys. to the heat reservoir

∴ The equil^m melting or freezing temp. ≡ temp. at which no change the degree of order of the sys. + heat bath.

only at this temp. → the solid phase in equil^m w/ the liquid p

relationship bet'n S and degree of mix-up-ness =

4.3. The concept of microstate.

statistical mechanics

the effect of quantization of energy ≡ !! book!

3/22 (9) 경험 Most probable = equil^m state

4.4. Determination of the Most Probable Microstate.

$\Omega_1 = 3$ (0/3/0/0/)

$\Omega_2 = 3$ (2/0/0/1/) $= 3$

$\Omega_3 = 6$ (1/1/1/0/)

4 2+2 1 n1
3 n=1 ba

The # of arrangements within a given distribution Ω, is calculated a
If n particles are distributed among the energy level
such that n_0 in level ϵ_0, n_1 in ϵ_1, n_r in ϵ_r

(4.1) $$\Omega = \frac{n!}{n_0!\, n_1!\, n_2! \cdots n_r!} = \frac{n!}{\prod_{i=0}^{i=r} n_i!}$$

When the value for n_i are large, Stirling's approx.

$$\ln x! = x \ln x - x$$

(4.2) $$\ln \Omega = n \ln n - n - \sum_{i=0}^{i=r} (n_i \ln n_i - n_i)$$

As the macro state of a sys. is determined by the fixed values of U, V.
any distribution of particles among the energy levels must conform w/

(4.4) and $n = \text{const.} = n_0 + n_1 + \cdots + n_r = \sum n_i$

From (4.3), (4.4), any interchange of particles among the E. levels must conform w/ the conditions.

(4.5) $$\delta U = \sum \epsilon_i \delta n_i = 0.$$

(4.6) $$\delta n = \sum \delta n_i = 0$$

Also, from Eq (4.2)

$$\delta(n \ln n - n) = 0 \quad \text{const.}$$

$$\delta \ln \Omega = -\sum \left(\delta n_i \ln n_i + \frac{n_i \delta n_i}{n_i} - \delta n_i\right)$$

(4.7) $$= -\sum (\delta n_i \ln n_i)$$

가장 큰 확률.

If Ω has the max. value possible, then a small rearrangement of particles among the energy levels will not change the value of Ω

(4.8) $$(4.7) \rightarrow \therefore \delta \ln \Omega_{max} = -\sum (\delta n_i \ln n_i) = 0.$$

⇒ To ~~satisfy~~ be Ω the max. (4.5), (4.6) (4.8) to be satisfied at the

⇒ Solution for the set of n_i values ··· the most probable distribution

4.9) multiply (4.5) by const β $\left(\propto \frac{1}{\epsilon_i}\right)$ $\sum \beta \epsilon_i \delta n_i = 0$

4.10) multiply (4.6) by const α (dimensionless) $\sum \alpha \delta n_i = 0.$

11) (4.8) + (4.9) + (4.10) $$\sum_{i=0}^{r} (\ln n_i + \alpha + \beta \epsilon_i) \delta n_i = 0.$$

(i.e) $$(\ln n_0 + \alpha + \beta \epsilon_0) \delta n_0 + \cdots + (\ln n_r + \alpha + \beta \epsilon_r) \delta n_r = 0$$

p 13-20. Mach. statistical

4.12). $$\ln n_i + \alpha + \beta \epsilon_i = 0 \quad \text{or} \quad n_i = e^{-\alpha} e^{-\beta \epsilon_i}$$

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Summing $\sum_{0}^{r} n_i = n = e^{-\alpha}\sum_{0}^{r} e^{-\beta\epsilon_i} \rightarrow e^{-\alpha} = \dfrac{n}{\sum e^{-\beta\epsilon_i}}$

when $\sum e^{-\beta\epsilon_i} = e^{-\beta\epsilon_0} + e^{-\beta\epsilon_1} + \cdots + e^{-\beta\epsilon_r} = P$ (= partition

$$e^{-\alpha} = \frac{n}{P}$$

(4.13) (4.12) $\rightarrow$ $n_i = \dfrac{n e^{-\beta\epsilon_i}}{P}$

(2)*

Since P.N. $e^{-\beta}$ const. $\Rightarrow$ energy level 이 낮을수록 # of particle

long calculation

$\beta = \left(1 + \frac{1}{\bar{\epsilon}}\right)$

Q/N average Energy / unit

total # particles. $\bar{\epsilon} \rightarrow 0$ $(T \rightarrow 0)$

$\beta \rightarrow \infty$

또한 온도가 높아질수록 해당하는 ϵ_i 의 n_i 가 크려면 ($\frac{1}{T}$ $\beta \downarrow$ 되어야 한다 if ϵ_i const) 을 1'c는 mole 을 편리한 변경.

$\therefore \beta \propto \frac{1}{T}$ or $\beta = \frac{1}{kT}$ — Boltzman const.

$k = \frac{R}{a} = \frac{8.314}{6.023 \times 10^{23}} = 1.3$ J

$\epsilon_i = (i + \frac{1}{2})h\nu$

joule / deg. atom

Interpret 온도 1°올라갈 때 이 kinetic energy

$\therefore \beta > 0$

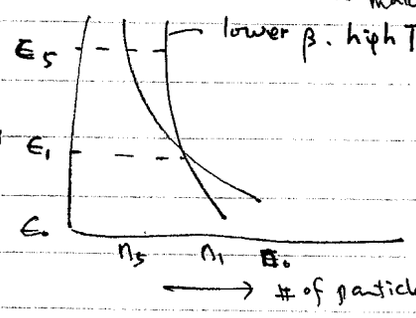
4.5. The Effect of Temp.

As $T \uparrow$, $\beta \left(= \frac{1}{kT}\right) \downarrow$ upper levels become more populated

to make # of particle at high energy increase.

Since Avg. energy of the particles (increase in U/n)

for fixed V, n: $U \uparrow$ as



if the # of particles in the sys. ⇑ extremely large,

then the # of arrangement of the most probable distribution (= Sc

is the only significant term to, Ω_{total}. (= total # of arr

i.e., $\Omega_{max} \simeq \Omega_{total}$.

w/ $\beta = \frac{1}{kT}$ & (4.2) $\ln \Omega_{total} \simeq \ln \Omega_{max} = n \ln n - \sum n_i \ln n_i$

since (4.13) $n_i = \dfrac{n e^{-\beta\epsilon_i}}{P}$

$$\ln \Omega_{max} (\ln \Omega_{total}) = n \ln n - \sum n_i \ln n_i \quad , \quad n_i = \frac{n e^{-\beta \epsilon_i}}{P}$$

Date $\rightarrow \left[\ln \frac{n}{P} + \left(-\frac{\epsilon_i}{kT}\right.\right.$

$$\ln \Omega_{total} = n \ln n - \frac{n}{P} \sum \left[e^{-\epsilon_i/kT} \ln \left(\frac{n}{P} e^{-\epsilon_i/kT} \right) \right]$$

$$= n \ln n - \frac{n}{P} (\ln n - \ln P) \sum e^{-\epsilon_i/kT} + \frac{n}{PkT} \sum \epsilon_i e^{-\epsilon_i/k}$$

$$= n \ln P + \frac{n}{PkT} \sum \epsilon_i e^{-\epsilon_i/kT} \quad U$$

But $U = \sum n_i \epsilon_i = \sum \frac{n}{P} \epsilon_i e^{-\epsilon_i/kT} = \frac{n}{P} \sum \epsilon_i e^{-\epsilon_i}$

(4.15) $\rightarrow \ln \Omega_{total} = n \ln P + \frac{U}{kT}$.

(4.16) Thermal Equil^m within a sys. and the Boltzman Eq.

Suppose the particle sys & the heat bath at in thermal equil^m., small exchange of energy at const U.V.n occur.

$\delta \ln \Omega = \frac{\delta U}{kT}$ as E exchange at const V_{total}.

$\delta U = \delta q$ $\quad$ P is only fn of (ϵ_i, T)

$$\delta \ln \Omega = \frac{\delta q}{kT} \quad \delta S = \frac{\delta S}{k}$$

S, Ω are state fn. (path indept)

가능한 방법이 있는 경우.

(4.16) $\boxed{S = k \ln \Omega} = k \ln \Omega_{max}$ ← $\boxed{\text{Boltzman Eq.}}$

가장 큰 인트로피

render physical significance to entropy

relationship bet'n the entropy of a sys. and its degree of mixe

~~# of ways~~ the ~~most probable state~~ of the sys w/ fixed U.

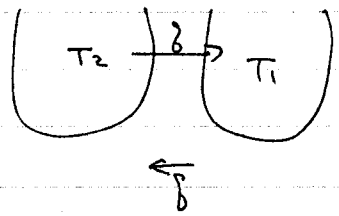
∴ equil^m state = state of S max.

equil^m ← $S_{max} = k \ln \Omega_{max}$.

3/28 ( ) ← 앞에꺼 설명 why?( ) dw = 0

4) Heat flow and the production of Entropy.

Classical Therm.



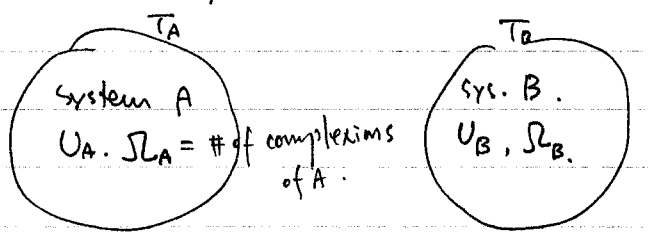
$T_2 > T_1$

irreversible process → ΔS_i pro

reverse process ⇒ impossibl
q from T_1 to T_2.

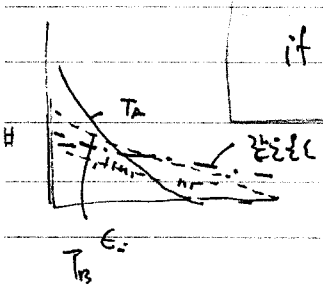
Statistical Thermo w/ micro state

a microstate w/ temp. diff. within a sys. is less probable than that of uniform temp.



$T_A > T_B$.

→ when contacted. $\Omega_A \Omega_B$ Not necessarily its max.



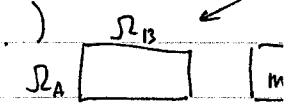
if heat flows from A to B, the increase in Ω_B (from increase is greater than the decrease in Ω_A (from decreas

Heat flow occurs to increase the value of $\Omega_A \times \Omega_B$.

ceases when $\Omega_A \Omega_B$ reaches its max.

(when the increase in Ω_B = the decrease in Ω_A.)

↳ thermal equil.



$\therefore \delta \ln \Omega_A \Omega_B = 0$. (the transfer of a quantity of heat δq does not cause a change in $\Omega_A \times \Omega_B$)

from $\delta \ln \Omega = \dfrac{\delta q}{kT}$ $\quad \delta \ln \Omega_A = \dfrac{\delta q_A}{kT_A}$, $\delta \ln \Omega_B = \dfrac{\delta q_B}{kT_B}$

here $\delta q_A = -\delta q_B$.

$$\delta \ln \Omega_A \Omega_B = \left(\frac{1}{T_A} - \frac{1}{T_B}\right)\frac{\delta q}{k} = 0 \qquad \underline{T_A = T_B.}$$

$\Omega_A \cdot \Omega_B$ 가 max. 가 ∴ 같아진다.

reversible only when $T_A = T_B$ →

micro most probable state ↔ less ~~sta~~ probable = impro

How vast is the sum of them!
Were I to count them, they would outnumber the grains of (7)
(시 1장. 17-18.

3/27/목 (11)

Date

4.8. Configurational Entropy & Thermal Entropy.

~~precedi~~ Previous discussion → based on identical particles, redistrib. thermal energy. → thermal entropy.

entropy. → based on diff. particles, mixing.

Mixing of two ~~x~~tals. → diffusion proceeds until no conc. grad. acl

A A | B B
A A | B B

$\Omega_{4:0} = 1.$ (A)

$\Omega_{3:1} = 4 \times 4 = 16.$ $_4C_1$

$\Omega_{2:2} = (4 \times 3/2)^2 = 36.$ $_4C_2$

$\Omega_{1:3} = 4 \times 4 = 16 = \frac{4 \times 3 \times 2}{3!}$ — indistinguisha config $_4C_3$

$\Omega_{0:4} = 1. = \left(\frac{4 \times 3 \times 2}{4!}\right)\left(\frac{4 \times 3 \times 2}{4!}\right)$ $_4C_4$

B_1 A
A B_2 = B_2 A
A B_1

70 = # of ways = $\frac{8!}{4!4!}$

$\frac{36}{70} = \Omega_{2:2}$ = the most probable. = the elimination of conc. gradients.

from $S = k \ln \Omega.$

as $\Omega \uparrow$, $S \uparrow$. to max.

↓ entropy increase as the reason the increase in the # of spa conf. → S_{conf}.

A+B) unmixed → A + B (mixed)
$n_a + n_b$ → at Const U, V, n.

$$\Delta S_{conf} = S_{conf(2)} - S_{conf(1)} = k \ln \frac{\Omega_{conf(2)}}{\Omega_{conf(1)}}$$

$$\Omega_{conf(2)} = \frac{(n_a+n_b)!}{n_a!\, n_b!} \quad \& \quad \Omega_{conf(1)} = 1.$$

$$\Delta S_{conf} = k \ln \frac{(n_a+n_b)!}{n_a!\, n_b!}$$

• two closed sys. thermal contact
• two open sys. identical in contact.
# of conf = 1

(most probable energy of the sys. × (no. conc. grad.)) → Maximize $\boxed{\Omega_{th}\,\Omega_{conf}}$

$$S_{total} = S_{th} + S_{conf} = k \ln \Omega_{th}\,\Omega_{conf}$$

열에너지 의 보존이 아닌 다른 수단

ideal mix ∋ $\Omega_{th} = \Omega_{th_2}$

$= k \ln \frac{\Omega_{th(2)}\,\Omega_{conf(2)}}{\Omega_{th(1)}\,\Omega_{conf(1)}}$