

الباب

الديناميكا الحرارية الإحصائية للحالات المجهرية

Statistical Thermodynamics of Microstates

162		I
174		II
176		

Statistical Thermodynamics of Microstates

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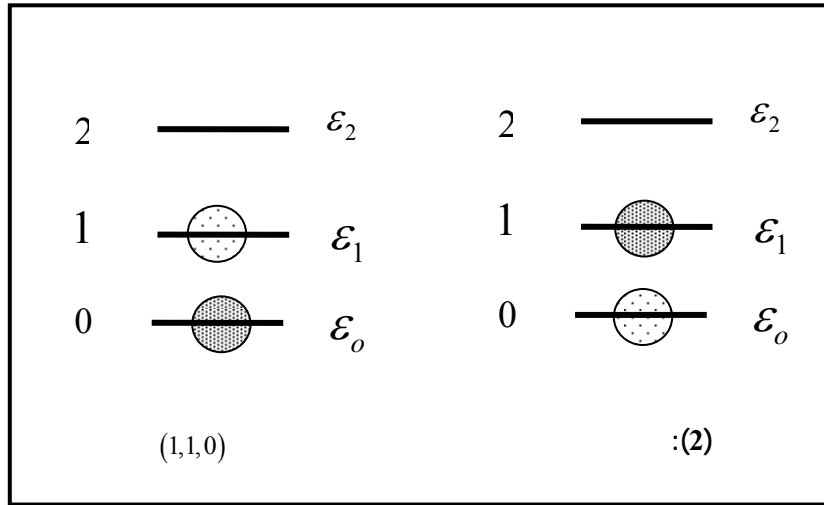
"S"

"Ω"

$$S = k_B \ln \Omega, \tag{1}$$

Ω S k_B

(Hypothetical) (1) -1



" :

" ()

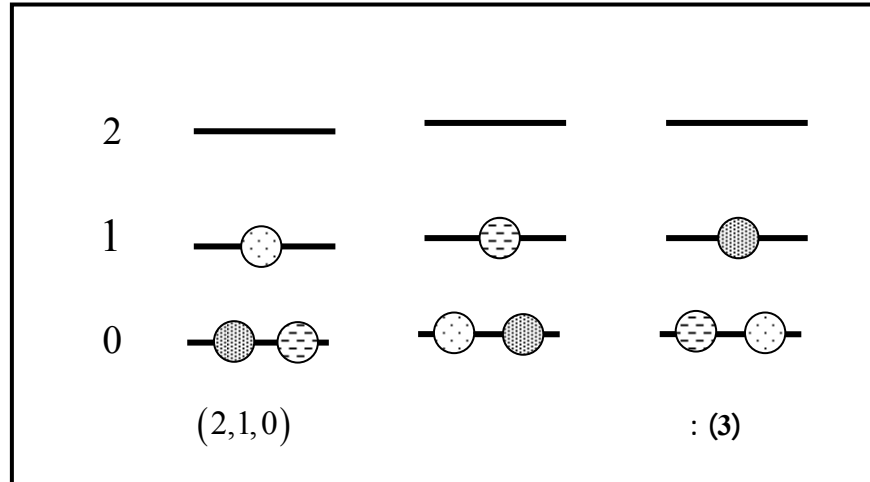
ω

(2,1,0)

:

:

(3)



:

N

$$N = \sum_j n_j$$

:

n_2

n_1

j

n_j

: j

$$\omega\{n_i\} = \frac{N!}{n_1!n_2!\cdots n_j!} = \frac{N!}{\prod_{i=1}^j n_i!} \quad (2)$$

:

:

N n_1

$$\omega_1 = \binom{N}{n_1} = \frac{N!}{n_1!(N-n_1)!}$$

chapter 7

Statistical thermodynamics of Microstates

$$\binom{N - n_1}{n_2}$$

:

$$\omega_2 = \binom{N - n_1}{n_2} = \frac{(N - n_1)!}{n_2!(N - n_1 - n_2)!}$$

$$\binom{N - n_1 - n_2}{n_3}$$

:

$$\omega_3 = \binom{N - n_1 - n_2}{n_3} = \frac{(N - n_1 - n_2)!}{n_3!(N - n_1 - n_2 - n_3)!}$$

.

:

$$\omega\{n_i\} = \omega_1 \times \omega_2 \times \omega_3 \times \dots \times \omega_j = \frac{N!}{n_1!n_2!\dots n_j!} = \frac{N!}{\prod_{i=1}^j n_i!}$$

:

Π

$$\prod_{i=1}^r n_i! = n_1! \times n_2! \times \dots \times n_r!$$

.

ω_i

:

"

"

ω_i

(Statistical weight)

"

(Thermodynamic Probability)

p_i

,

:

chapter 7

Statistical thermodynamics of Microstates

$$p_i = \frac{\omega_i}{\sum_{i=1}^j \omega_i}, \quad 0 \leq p_i \leq 1 \quad (3)$$

:

$$\sum_{i=1}^j p_i = \sum_{i=1}^j \frac{\omega_i}{\sum_{i=1}^j \omega_i} = \frac{\sum_{i=1}^j \omega_i}{\sum_{i=1}^j \omega_i} = 1$$

(4,3,2,1,0)

:

(4,3,2,1,0)

:

:

"N"

$$N = \sum_{n_i=1}^5 n_i = 4 + 3 + 2 + 1 + 0 = 10$$

:

$$\omega\{n_i\} = \frac{N!}{n_1!n_2!n_3!n_4!n_5!} = \frac{10!}{4!3!2!1!0!} = 12600$$

:

:

:

$$S = k_B \ln \omega\{n_i\} \\ = (1.38 \times 10^{-23} \text{ Jk}^{-1}) \times \ln(12600) = 1.30 \times 10^{-22} \text{ Jk}^{-1}$$

.

:

"N = 10"

$$. 7.8 \text{ Jk}^{-1} \text{ mol}^{-1}$$

:

:

-1

$$\lim_{T \rightarrow 0} S = 0$$

.()
Ω

T → 0

:

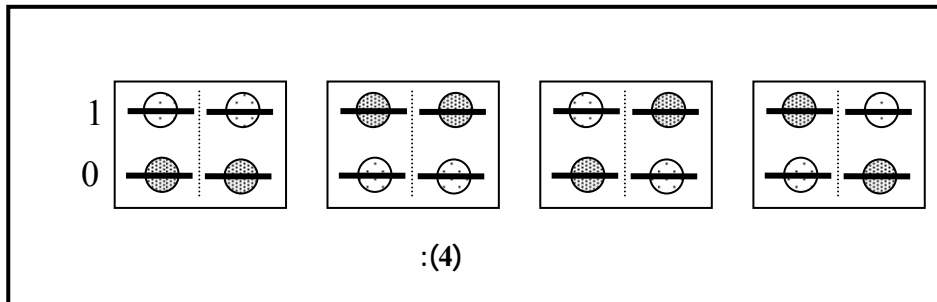
1

$$\lim_{T \rightarrow 0} S = k_B \ln \Omega = k_B \ln 1 = 0$$

(Extensive "Additive" property)

-2

(1,1,0)



(4)

$$S = k_B \ln 2$$

$$S = k_B \ln 4 = k_B \ln 2^2 = 2k_B \ln 2$$

$$S = k_B \ln 2^N = Nk_B \ln 2$$

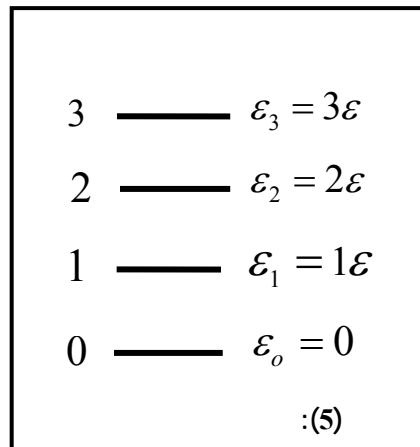
$$\Omega_{total} = \Omega_1 \times \Omega_2$$

$$S_{total} = S_1 + S_2,$$

"N = 3"

(5)

$$\varepsilon_i = i \varepsilon \text{ Joule, } i = 0, 1, 2, 3$$



$$. U = 3\varepsilon \text{ J}$$

A, B, C

:

()

$$\sum_{i=0}^3 n_i = 3,$$

$$U = \sum_{i=0}^3 n_i \epsilon_n = 3\epsilon,$$

:

ω_k

n_i

k

(1)

P_k

(1)

k	n_0	n_1	n_2	n_3	n_0	n_1	n_2	n_3	U (J)	$\omega_k \{n_i\}$	P_k
1	2	0	0	1	AB	0	0	C	3ϵ	3	$\frac{3}{10}$
					AC	0	0	B			
					BC	0	0	A			
2	1	1	1	0	A	B	C	0	3ϵ	6	$\frac{6}{10}$
					B	C	A	0			
					C	A	B	0			
					A	C	B	0			
					B	A	C	0			
					C	B	A	0			
3	0	3	0	0	0	ABC	0	0	3ϵ	1	$\frac{1}{10}$

$k = 1, 2, 3$

(1)

:

$$\Omega = \sum_k \omega_k \{n_i\} = 10$$

$$\epsilon_i = i \times 10^{-20} \text{ Joule}, \quad i = 0, 1, 2, 3, 4$$

$$.4 \times 10^{-20} \text{ J} \quad "U"$$

.(2)

: (2)

(10 ⁻²⁰ Joule)					
4	●				
3		●			
2			●●	●	
1		●		●●	●●●●
0	●●●●●	●●●●●	●●●●●	●●●●	●●
$U (10^{-20} \text{ J})$	4	3+1	2×2	2+1+1	4×1
k	1	2	3	4	5

: $U (4 \times 10^{-20} \text{ J})$

(minimize)

.(298.15 K)

" $F = U - TS$ "

$$\omega_k = \frac{6!}{n_0!n_1!n_2!n_3!n_4!} \quad (3)$$

(3)

k	$\{n_0, n_1, n_2, n_3, n_4\}$	ω_k	$S (10^{-23} \text{ JK}^{-1})$	$U (10^{-20} \text{ J})$	$F (10^{-20} \text{ J})$
1	{5, 0, 0, 0, 1}	6	2.47	4.00	3.26
2	{4, 1, 0, 1, 0}	30	4.70	4.00	2.60
3	{4, 0, 2, 0, 0}	15	3.74	4.00	2.89
4	{3, 2, 1, 0, 0}	60	5.65	4.00	2.32
5	{2, 4, 0, 0, 0}	15	3.74	4.00	2.89

"k = 4" (3)

F S

:

()

:

-1

N

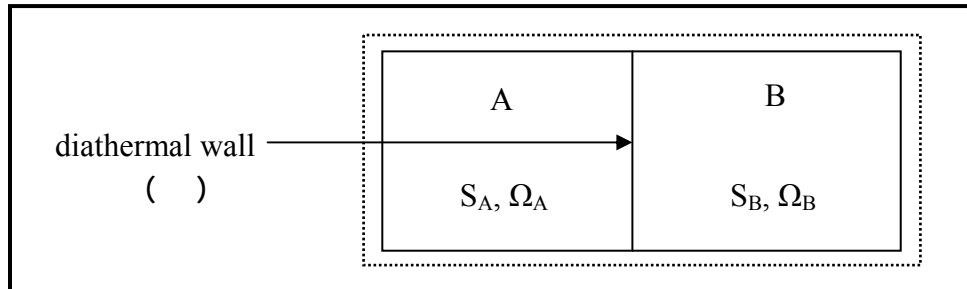
(i

$$U \quad (ii)$$

$$S = k_B \ln \Omega$$

A, B :

S_B, Ω_B S_A, Ω_A



$$S_{total} = S_A + S_B \quad (I)$$

:

$$\Omega_{total} = \Omega_A \times \Omega_B \quad (II)$$

: Ω S

$$S = f(\Omega) \quad (III)$$

(I)

$$f(\Omega_{total}) = f(\Omega_A) + f(\Omega_B) \quad (IV)$$

(II)

$$f(\Omega_{total}) = f(\Omega_A \times \Omega_B) \quad (V)$$

(V) (IV)

$$f(\Omega_A) + f(\Omega_B) = f(\Omega_A \times \Omega_B) \tag{VI}$$

:

(VI)

$$S = k_B \ln \Omega$$

-II

()

-1

.(A,B,C,D)

.10

.() 2

k				
1				••
2			••	
3		••		
4	••			
5			•	•
6		•		•
7		•	•	
8	•			•
9	•		•	
10	•	•		
	A	B	C	D

() -2

:

$$\epsilon_i = i \times \epsilon, \quad i = 0, 1, 2$$

$$.U = 2\epsilon$$

. 1.63

2

. 2

$$U = 2\epsilon$$

.2 1

ϵ_i	1	2
2		⊗
1	⊕ ⊗	
0		⊕
ω_i	$\frac{2!}{2!0!0!} = 1$	$\frac{2!}{1!0!1!} = 2$

:

$$. \Omega_1 = \omega_1 + \omega_2 = 1 + 2 = 3$$

:

$$S_1 = k_B \ln \Omega_1 = (1.38 \times 10^{-23} \text{ JK}^{-1}) \ln 3$$

$$= 1.5 \times 10^{-23} \text{ JK}^{-1}$$

⊙

$$:\Omega_2 = \omega_1 + \omega_2 = 3 + 3 = 6$$

ε_i	1	2
2		⊕
1	⊕ ⊗	
0	⊙	⊗ ⊙
ω_i	$\frac{3!}{2!1!0!} = 3$	$\frac{3!}{2!0!1!} = 3$

:

$$S_2 = k_B \ln \Omega_2 = (1.38 \times 10^{-23} \text{ JK}^{-1}) \ln 6$$

$$= 2.5 \times 10^{-23} \text{ JK}^{-1}$$

:

$$\frac{S_2}{S_1} = \frac{\ln 6}{\ln 3} = 1.63$$

()

-1

:

$$\varepsilon_i = i \times \varepsilon, \quad i = 0, 1, 2, 3$$

$$.U = 6\varepsilon$$

-

$$.44 =$$

-

$$.0.91, 0.91, 1.09, 1.09$$

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