Counting Total Number of Microstates of the Combined System in the Microcanonical Ensemble

The Subsystem 'A' has $\Omega_A = 6$ accessible *Microstates*.

The Subsystem 'B' has $\Omega_B = 2$ accessible *Microstates*.

Total No of *Microstates* Ω_{tot} of the composite system.

$$\Omega_{tot} = \Omega_A \times \Omega_B = 12$$

The Partition prevents the transfer of energy from one subsystem to another and in this case keeps $E_A = 5$ and $E_B = 1$.

$$\overbrace{\underbrace{S}_{\text{Entropy}}}^{\text{Macrostate}} = \underbrace{k}_{\text{Boltzmann Constant}} \ln \overbrace{\underbrace{\Omega\,(E, V, N)}_{\text{Accessible Microstates}}}^{\text{Microstate}}$$

Thermodynamics

$$\frac{1}{T} = \left(\frac{\partial S}{\partial E}\right)_{V,N}$$

$$\frac{P}{T} = \left(\frac{\partial S}{\partial V}\right)_{E,N}$$

$$\frac{\mu}{T} = -\left(\frac{\partial S}{\partial N}\right)_{E,V}$$

Canonical Ensemble: Counting the Number of Microstates

The Microstates are given in the table for all the possible values of E_A and E_B

E_A	E_B	Microstates of E_A	Microstates of E_B	$\Omega_A(E_A)$	$\Omega_A(E_B)$	$\Omega_A \Omega_B$	$P_A(E_A)$
6	0	(6,0) (5,1) (4,2) (3,3) (2,4) (1,5) (0,6)	(0,0)	7	1	7	7/84
5	1	(5,0) (4,1) (3,2) (2,3) (1,4) (0,5)	(1,0) (0,1)	6	2	12	12/84
4	2	(4,0) (3,1) (2,2) (1,3) (0,4)	(2,0) (1,1) (0,2)	5	3	15	15/84
3	3	(3,0) (0,3) (2,1) (1,2)	(3,0) (0,3) (2,1) (1,2)	4	4	16	16/84
2	4	(2,0) (1,1) (0,2)	(4,0) (3,1) (2,2) (1,3) (0,4)	3	5	15	15/84
1	5	(1,0) (0,1)	(5,0) (4,1) (3,2) (2,3) (1,4) (0,5)	2	6	12	12/84
0	6	(0,0)	(6,0) (5,1) (4,2) (3,3) (2,4) (1,5) (0,6)	1	7	7	7/84

$\boxed{\Omega_{tot} = 84}$

The Microstates are given in the table for all the possible values of E_A and E_B

E_A	E_B	Microstates of E_A	Microstates of E_B	$\Omega_A(E_A)$	$\Omega_A(E_B)$	$\Omega_A\,\Omega_B$	**$P_B(E_B)$**
6	0	(6,0) (5,1) (4,2) (3,3) (2,4) (1,5) (0,6)	(0,0)	7	1	7	7/84
5	1	(5,0) (4,1) (3,2) (2,3) (1,4) (0,5)	(1,0) (0,1)	6	2	12	12/84
4	2	(4,0) (3,1) (2,2) (1,3) (0,4)	(2,0) (1,1) (0,2)	5	3	15	15/84
3	3	(3,0) (0,3) (2,1) (1,2)	(3,0) (0,3) (2,1) (1,2)	4	4	16	16/84
2	4	(2,0) (1,1) (0,2)	(4,0) (3,1) (2,2) (1,3) (0,4)	3	5	15	15/84
1	5	(1,0) (0,1)	(5,0) (4,1) (3,2) (2,3) (1,4) (0,5)	2	6	12	12/84
0	6	(0,0)	(6,0) (5,1) (4,2) (3,3) (2,4) (1,5) (0,6)	1	7	7	7/84

- The Total Number of Microstates $\Omega_{tot}(E_A + E_B)$ accessible to the isolated composite system whose subsystems have energy E_A and E_B is

  - $\Omega_{tot}(E_A + E_B) = \Omega_A(E_A)\, \Omega_B(E_B)$

- For example if $E_A = 4$ and $E_B = 2$, then 'A' can be any one of the 5 microstates and 'B' can be in an one of 3 microstates. There are two sets of microstates that can be combined to give 15 microstates.

- The Total Number of Microstates Ω_{tot} accessible to the composite system can be found by summing $\Omega_A(E_A)\, \Omega_B(E_B)$ for the possible ways of E_A and E_B consistent with the condition $E_A + E_B = 6$.

$$\Omega = \sum_{E_A} \Omega_A(E_A)\, \Omega_B(E_B)$$

$$= \Sigma \Omega_A(E_A)\, \Omega_B(E_{tot} - E_A)$$

From Table,

- $\Omega_{tot} = (7 \times 1) + (6 \times 2) + (5 \times 3) + (4 \times 4) + (3 \times 5) + (2 \times 6) + (1 \times 7)$

  $= 84$

The ***Composite System*** is isolated. So all accessible ***Microstates*** are equally probable.

That is the composite is equally likely to be in any of its 84 accessible ***Microstates***.

- Let $P_A(E_A)$ = Probability that subsystem **'A'** has energy E_A .

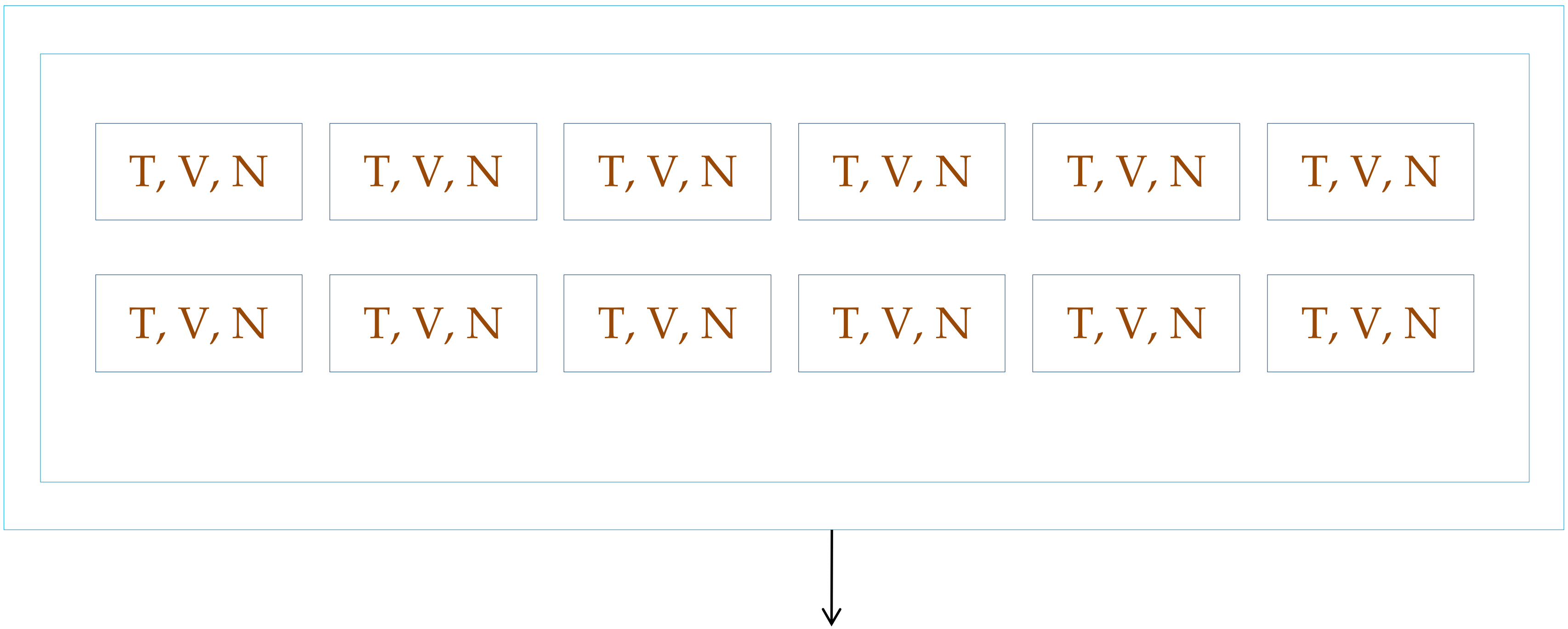
$$P_A(E_A) = \frac{\Sigma\Omega_A(E_A)\,\Omega_B(E_{tot} - E_B)}{\Omega_{tot}}$$

- The mean energy of subsystem **'A'** is found by calculating the ***Ensemble*** average over the 84 ***Microstates*** of the ***Composite System***.

$$\begin{aligned} < E_A > = \bar{E}_A &= \sum E_{A,i} P(E_{A,i}) \\ &= \left(6 \text{ x } \frac{7}{84}\right) + \left(5 \text{ x } \frac{12}{84}\right) + \left(4 \text{ x } \frac{15}{84}\right) + \left(3 \text{ x } \frac{16}{84}\right) + \left(2 \text{ x } \frac{15}{84}\right) \\ &\quad + \left(1 \text{ x } \frac{12}{84}\right) + \left(0 \text{ x } \frac{7}{84}\right) \\ &= 3 \end{aligned}$$

Hence, it is reasonable to assume that when a closed isolated system had time to reach internal ***Thermodynamic Equilibrium***, we are likely to find the closed system in any one of the microstates.

At ***Thermal Equilibrium***, the probability of finding the ***Composite System*** in any one of the **84** accessible ***Microstates*** of the ***Composite System*** is **1/84**.



Canonical Ensemble

In this example, the Ensemble consists of *84* systems each of which is in one of the *84* accessible Microstates.

Probability of finding the particle in a particular microstate

$$p_i = \frac{e^{-\beta\varepsilon_i}}{\Sigma e^{-\beta\varepsilon_i}} = \frac{e^{-\beta\varepsilon_i}}{z}$$

$$z = \Sigma e^{-\beta\varepsilon_i} \longrightarrow \text{Partition function}$$

- The partition function 'Z' contains all the information about the energies of the states of the system.
- All thermodynamical quantities can be obtained from it.
- From 'Z', we can get thermodynamics functions energy, entropy, Helmholtz function, or heat capacity to simply drop out.

Thermodynamic quantities derived from the partition function Z

Function of states	Statistical mechanical expression
U F	$-\dfrac{d \ln Z}{d\beta}$ $-k_B\, T \log Z$
$S = -\left(\dfrac{\partial F}{\partial T}\right)_V = \dfrac{U - F}{T}$	$k_B \ln Z + k_B T\left(\dfrac{\partial \ln Z}{\partial T}\right)_V$
$p = -\left(\dfrac{\partial F}{\partial V}\right)_T$	$k_B T\left(\dfrac{\partial \ln Z}{\partial V}\right)_T$
$H = U + pV$	$k_B T\left[T\left(\dfrac{\partial \ln Z}{\partial V}\right)_V + V\left(\dfrac{\partial \ln Z}{\partial V}\right)_T\right]$
$G = F + pV = H - TS$	$k_B T\left[-\ln Z + V\left(\dfrac{\partial \ln Z}{\partial V}\right)_T\right]$
$C_V = \left(\dfrac{\partial U}{\partial V}\right)_V$	$k_B T\left[2\left(\dfrac{\partial \ln Z}{\partial T}\right)_V + T\left(\dfrac{\partial^2 \ln Z}{\partial T^2}\right)_V\right]$