University of Science
Department of Materials science

Chapter 4

The Statistical Interpretation of Entropy

Assoc.Prof. Le Van Hieu

Msc. Pham Van Viet

Department of Materials science,
University of Science, VNU-HCMC

cuu duong than cong . com

CuuDuongThanCong.com

https://fb.com/tailieudientucntt

Statistical Interpretation of Entropy

- Statistical mechanics bridges between

phenomenological thermodynamics ⟷ underlying microscopic behavior

-Statistical mechanics requires a separate lecture (see textbook part II)

but

abstract nature of entropy asks for an intuitive picture for state function S

➡ Here: heuristic approach to statistical interpretation of entropy by

[Ludwig Boltzman](#)

cuu duong than cong . com

Macro-states and Micro-states

Example:

a two-phase-block case with 6 identical but distinguishable particles

A certain set of numbers of particles in each phase block corresponds to a certain macrostate.

{ab, cdef}and{ab, cedf} are the same macro and microstates.

{ab, cdef}and{ac, bdef} are the same macro but different microstates.

{abc,def}and{def,abc} are the same macro but different microstates.

{ab, cdef}and {abcd,ef} are different macrostates.

The thermodynamic probability of a macrostate is the corresponding number of microstates:

$$W = \frac{N!}{n_1!\, n_2!} \qquad \text{(multiplicity of configuration).}$$

Every microstate is assumed to be equally probable.

cuuduongthancong.com

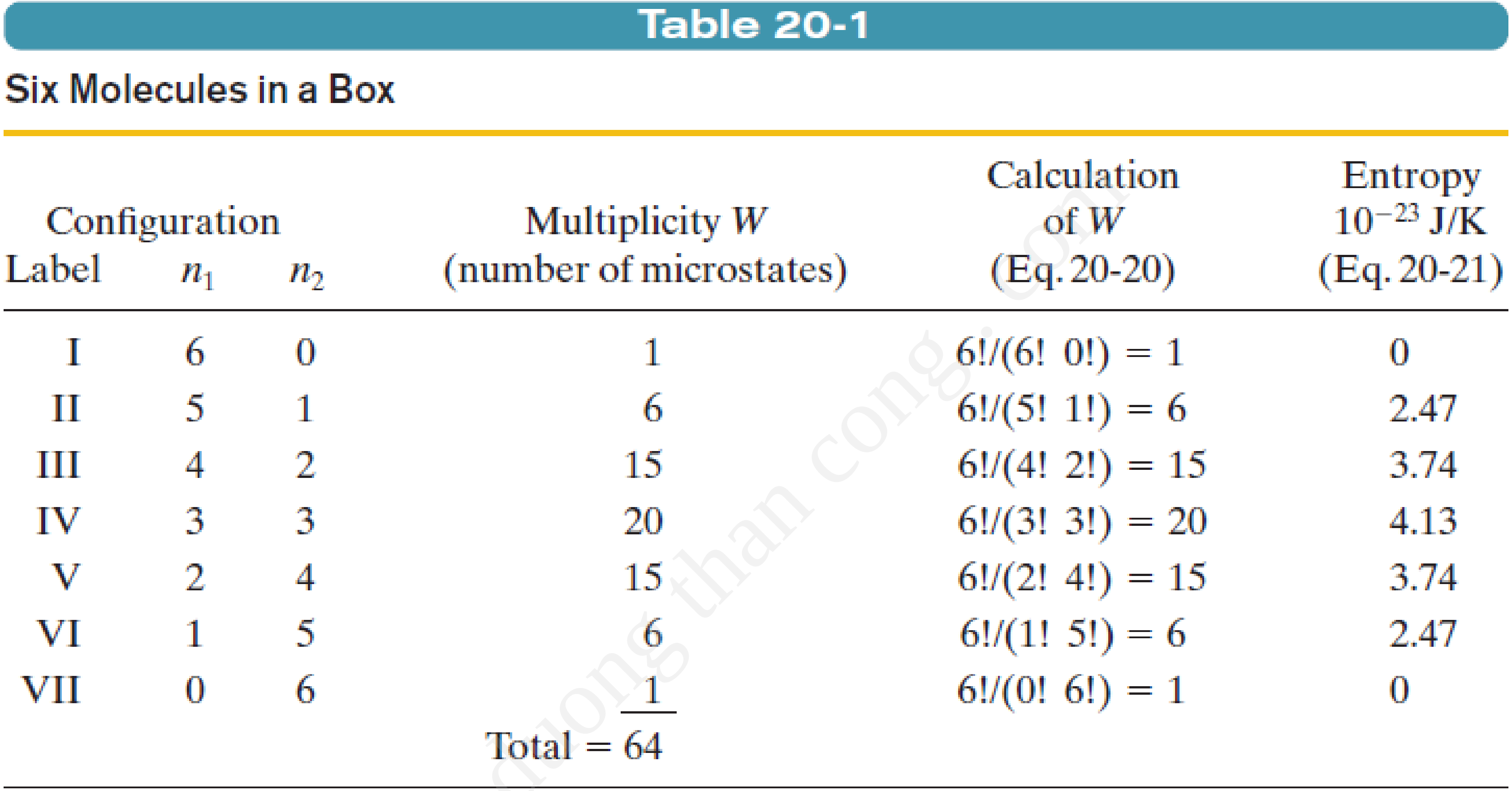


Table 20-1

Six Molecules in a Box

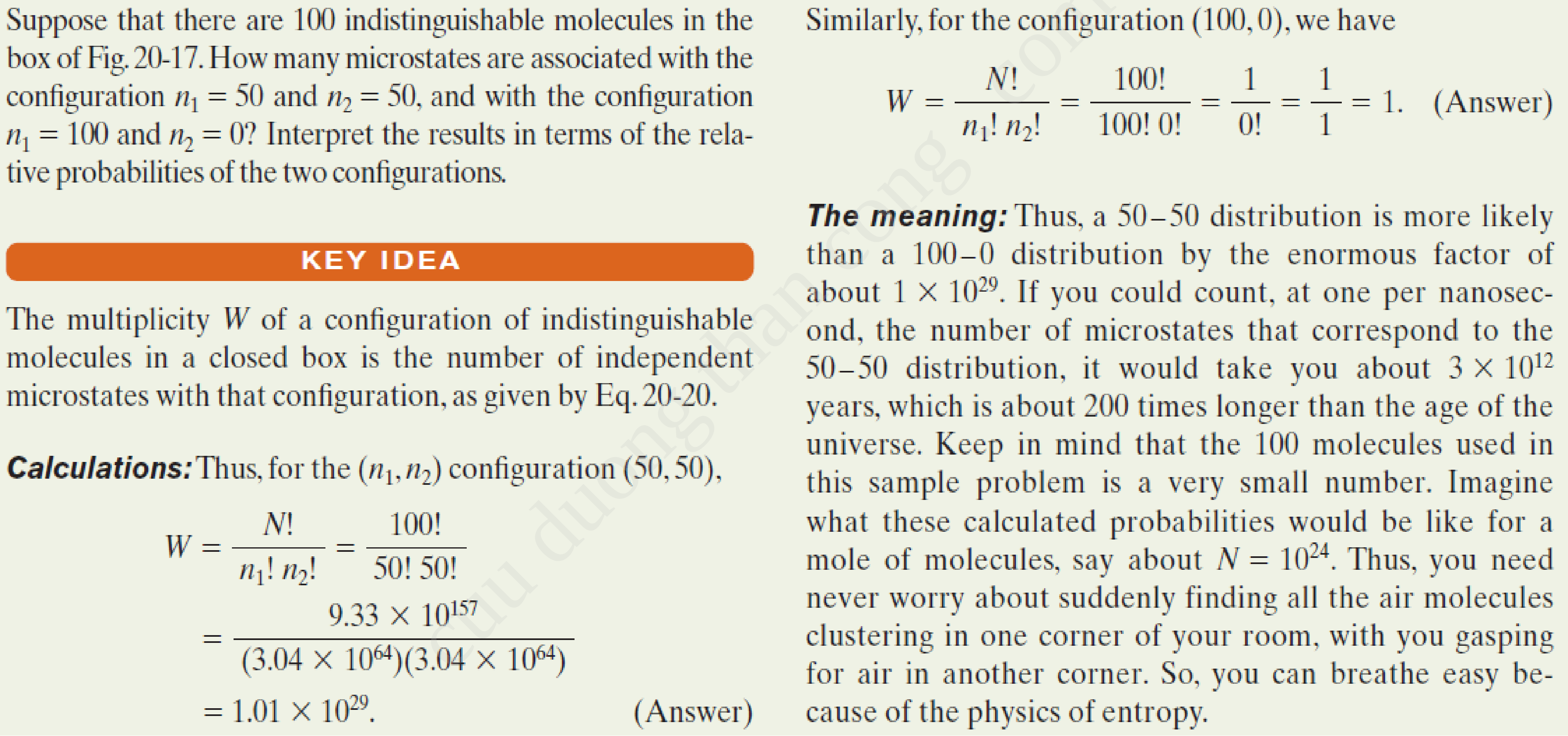
Configuration Label	n_1	n_2	Multiplicity W (number of microstates)	Calculation of W (Eq. 20-20)	Entropy 10^{-23} J/K (Eq. 20-21)
I	6	0	1	$6!/(6!\ 0!) = 1$	0
II	5	1	6	$6!/(5!\ 1!) = 6$	2.47
III	4	2	15	$6!/(4!\ 2!) = 15$	3.74
IV	3	3	20	$6!/(3!\ 3!) = 20$	4.13
V	2	4	15	$6!/(2!\ 4!) = 15$	3.74
VI	1	5	6	$6!/(1!\ 5!) = 6$	2.47
VII	0	6	1	$6!/(0!\ 6!) = 1$	0
			Total = 64		

cuu duong than cong. com

A system changes its microstate all the time.
The equilibrium state is the most probable macrostate.

CuuDuongThanCong.com https://fb.com/tailieudientucntt

Example, Microstates and multiplicity:



Suppose that there are 100 indistinguishable molecules in the box of Fig. 20-17. How many microstates are associated with the configuration $n_1 = 50$ and $n_2 = 50$, and with the configuration $n_1 = 100$ and $n_2 = 0$? Interpret the results in terms of the relative probabilities of the two configurations.

KEY IDEA

The multiplicity W of a configuration of indistinguishable molecules in a closed box is the number of independent microstates with that configuration, as given by Eq. 20-20.

Calculations: Thus, for the (n_1, n_2) configuration (50, 50),

$$W = \frac{N!}{n_1!\,n_2!} = \frac{100!}{50!\,50!}$$

$$= \frac{9.33 \times 10^{157}}{(3.04 \times 10^{64})(3.04 \times 10^{64})}$$

$$= 1.01 \times 10^{29}. \qquad \text{(Answer)}$$

Similarly, for the configuration (100, 0), we have

$$W = \frac{N!}{n_1!\,n_2!} = \frac{100!}{100!\,0!} = \frac{1}{0!} = \frac{1}{1} = 1. \qquad \text{(Answer)}$$

The meaning: Thus, a 50–50 distribution is more likely than a 100–0 distribution by the enormous factor of about 1×10^{29}. If you could count, at one per nanosecond, the number of microstates that correspond to the 50–50 distribution, it would take you about 3×10^{12} years, which is about 200 times longer than the age of the universe. Keep in mind that the 100 molecules used in this sample problem is a very small number. Imagine what these calculated probabilities would be like for a mole of molecules, say about $N = 10^{24}$. Thus, you need never worry about suddenly finding all the air molecules clustering in one corner of your room, with you gasping for air in another corner. So, you can breathe easy because of the physics of entropy.

cuu duong than cong . com

CuuDuongThanCong.com https://fb.com/tailieudientucntt

Example, Entropy change :

When *n* moles of an ideal gas doubles its volume in a free expansion, the entropy increase from the initial state *i to the* final state *f is* $S_f - S_i = nR \ln 2$. Derive this result with statistical mechanics.

Calculations: The molecules are in a closed container, and the multiplicity *W* of their microstates can be found by:

$$W_i = \frac{N!}{N!\,0!} = 1.$$

Here *N* is the number of molecules in the n moles of the gas. Initially, with the molecules all in the left half of the container, their *(n1, n2)* configuration is *(N, 0)*.

Finally, with the molecules spread through the full volume, their *(n1, n2)* configuration is *(N/2, N/2)*.

$$W_f = \frac{N!}{(N/2)!\,(N/2)!}.$$

The initial and final entropies are

$$S_i = k \ln W_i = k \ln 1 = 0$$

$$S_f = k \ln W_f = k \ln(N!) - 2k \ln[(N/2)!]$$

Now,

$$\begin{aligned} S_f &= k \ln(N!) - 2k \ln[(N/2)!] \\ &= k[N(\ln N) - N] - 2k[(N/2)\ln(N/2) - (N/2)] \\ &= k[N(\ln N) - N - N\ln(N/2) + N] \\ &= k[N(\ln N) - N(\ln N - \ln 2)] = Nk \ln 2. \end{aligned}$$

Therefore,

$$S_f = nR \ln 2.$$

The change in entropy from the initial state to the final is thus

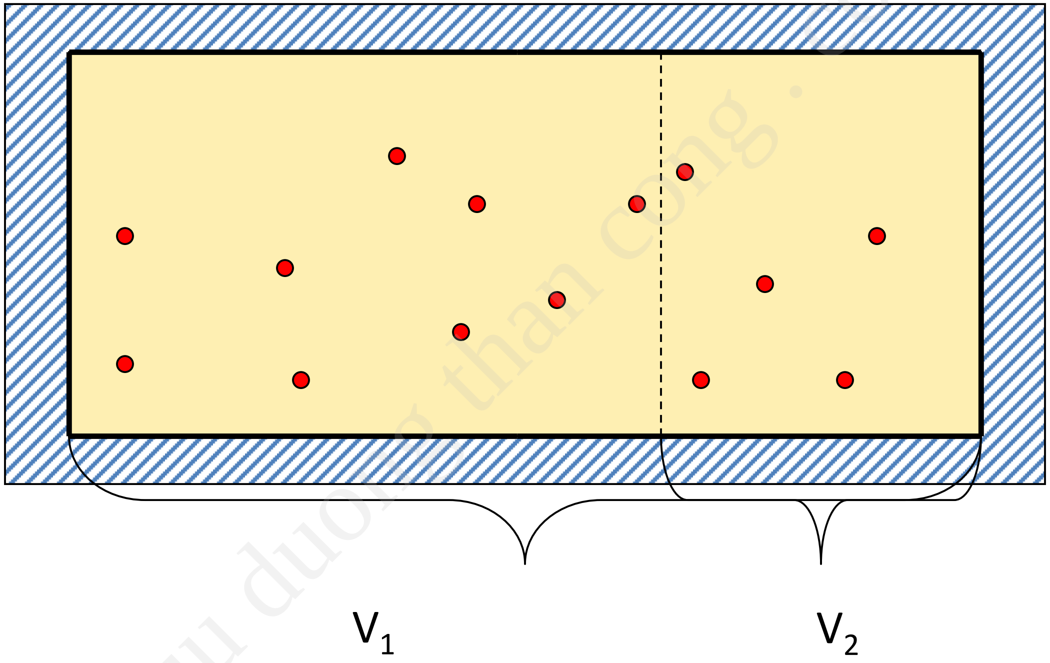
$$\begin{aligned} S_f - S_i &= nR \ln 2 - 0 \\ &= nR \ln 2, \end{aligned}$$

which is what we set out to show.

cuuduongthancong.com

- Consider a gas in a box from an atomistic point of view

atoms (or molecules) are moving in a disordered manner within the box having collisions with the walls



- Probability to find a particular atom in V_2 reads $$p(1) = \bar{p} = \frac{V_2}{V_1}$$

Let's pick two atom:

Probability to find both of them at the same time in V_2 reads $$p(2) = \bar{p} \cdot \bar{p} = \left(\frac{V_2}{V_1} \right)^2$$

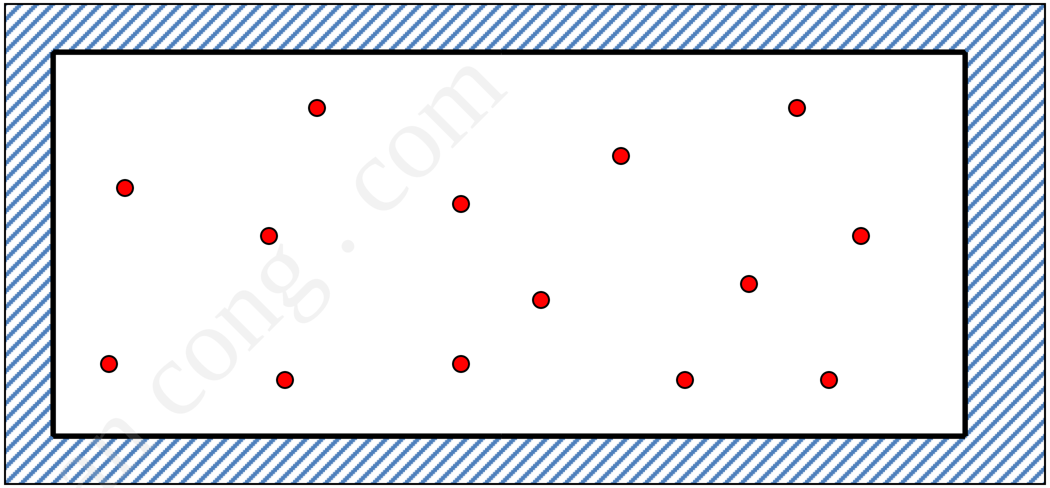
cuu duong than cong . com

CuuDuongThanCong.com https://fb.com/tailieudientucntt

➡ Probability to find all N atom at the same time in V_2 reads

$$p(N) = \bar{p}^N = \left(\frac{V_2}{V_1}\right)^N$$

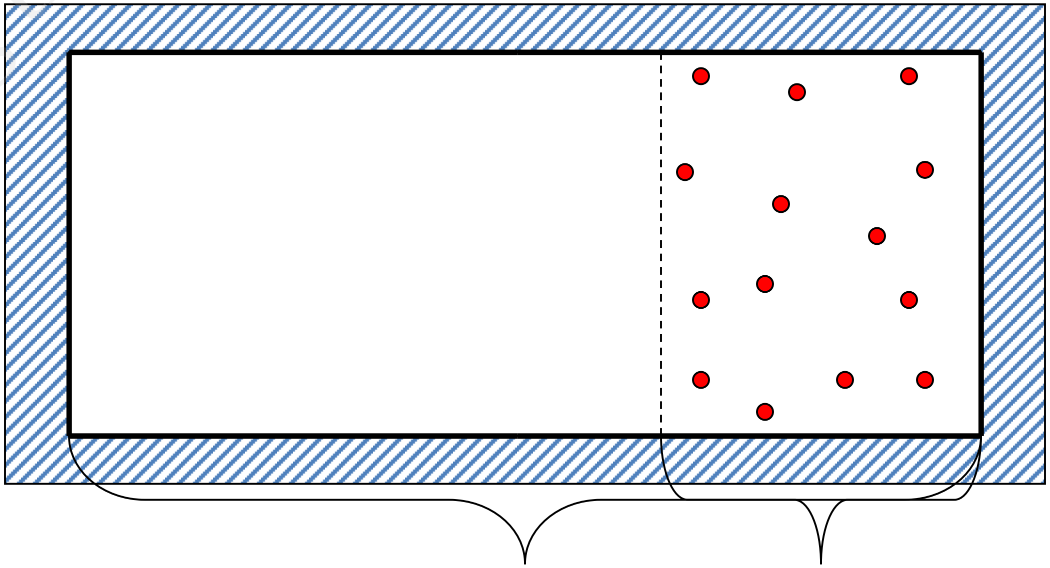
- Let W_1 be the "thermodynamic probability" to find system in the homogeneously occupied state)



- Thermodynamic probability to find system in a state with all atoms in V_2 reads:

$$W_2 = W_1\left(\frac{V_2}{V_1}\right)^N$$ or

$$\frac{W_1}{W_2} = \left(\frac{V_1}{V_2}\right)^N$$



Note: W_1>>W_2 for N large

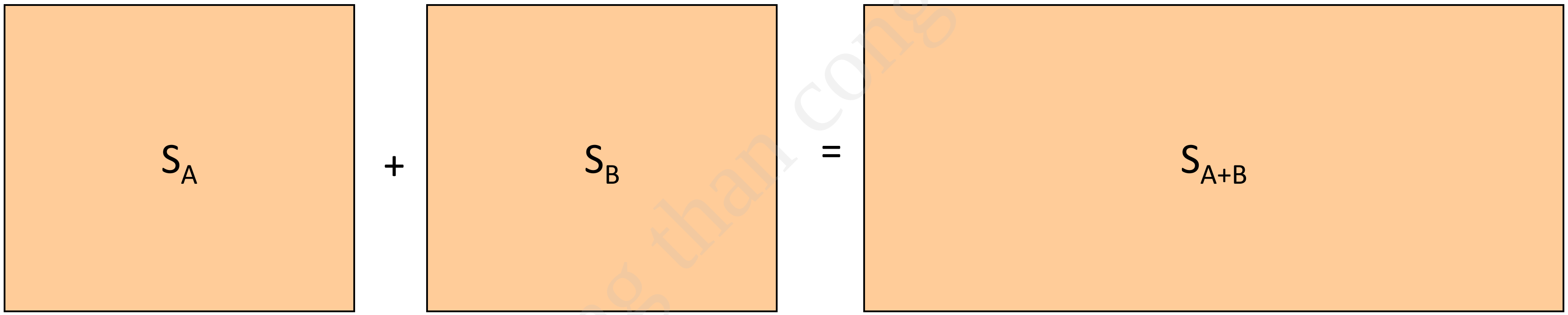
cuu duong than cong . com

CuuDuongThanCong.com https://fb.com/tailieudientucntt

- Entropy S quantifies the thermodynamic probability W of a particular state

➡ $S = \text{function}(W)$

- We know: S extensive ➡ $S_{A+B} = S_A + S_B$



- Thermodynamic probability W_{A+B} to find combined system A+B in a state where subsystem A is in a state of thermodynamic probability W_A
  and
  subsystem B is in a state of thermodynamic probability W_B reads $W_{A+B} = W_A \cdot W_B$

- Which function does the job $f(W_{A+B}) = \boxed{f(W_A \cdot W_B) = f(W_A) + f(W_B)}$

so that $S(W_{A+B}) = S(W_A) + S(W_B)$

cuu duong than cong . com

CuuDuongThanCong.com

https://fb.com/tailieudientucntt

$$S = C \ln W$$

Check: $S_{A+B} = C \ln W_{A+B} = C \ln W_A W_B = C \ln W_A + C \ln W_B$

$$= S_A + S_B$$

- Let's determine C

We know entropy change with volume change $V_0 \rightarrow V_f$ for an ideal gas in an adiabatically isolated box

$$\boxed{\Delta S = nR \ln \frac{V_f}{V_0}}$$

Now we apply $\Delta S = C \ln W_f - C \ln W_0 = C \ln \frac{W_f}{W_0}$

with $\frac{W_f}{W_0} = \left(\frac{V_f}{V_0}\right)^N$

$$\Rightarrow \Delta S = C \ln \left(\frac{V_f}{V_0}\right)^N$$

cuu duong than cong . com

CuuDuongThanCong.com

https://fb.com/tailieudientucntt

$$\Delta S = N\,C\ln\frac{V_f}{V_0} = n\,N_A\,C\ln\frac{V_f}{V_0}$$

comparison with $\Delta S = nR\ln\frac{V_f}{V_0}$

$$C = \frac{R}{N_A} = \frac{k_B N_A}{N_A} = k_B$$

$$S = k_B \ln W$$

W: # of possible microstates

Principle of increase of entropy

↔

Adiabatically insulated system approaches state of maximum probability.

cuuduongthancong.com