

# Lecture 9

## Examples and Problems

- Counting microstates of combined systems
- Volume exchange between systems
- Definition of Entropy and its role in equilibrium
- The second law of thermodynamics
- Statistics of energy exchange
- General definition of temperature
- Why heat flows from hot to cold

# Exercise: Microstates and Entropy

Pretend we are playing a coin-tossing game. We will toss 100 pennies (all distinguishable) into the air, and there is an equal chance they will land on the table or on the floor.

What is the probability that all 100 pennies will land on the table?

What is the dimensionless entropy associated with the situation that 70 pennies land on the table, and 30 land on the floor (accounting for the fact that each penny can land heads or tails, but ignoring the various places on the table or floor that each penny can land)?

# Exercise: Microstates and Entropy

Pretend we are playing a coin-tossing game. We will toss 100 pennies (all distinguishable) into the air, and there is an equal chance they will land on the table or on the floor.

What is the probability that all 100 pennies will land on the table?

$$P(100 \text{ on table}) = 0.5^{100} = 7.9 \times 10^{-31}$$

What is the dimensionless entropy associated with the situation that 70 pennies land on the table, and 30 land on the floor (accounting for the fact that each penny can land heads or tails, but ignoring the various places on the table or floor that each penny can land)?

This is one macrostate, and we want to know how many microstates correspond to it. There are three parts:

1. how many ways to have a 70/30 split:  $100!/(70!30!)$
2. how many ways for the 70 to be configured:  $2^{70}$
3. how many ways for the 30 to be configured:  $2^{30}$

$$\text{Therefore: } \Omega(70 \text{ on table}) = 100!/(70!30!) 2^{70} 2^{30} = 100!/(70!30!) 2^{100}$$

$$\sigma = \ln \Omega = \ln[100!/(70!30!) 2^{100}] = 100 \ln 2 + \ln(100!) - \ln(70!) - \ln(30!) \\ \{\text{We'll see later that } \ln x! \approx x \ln x - x\} \rightarrow \sigma = 130$$

# Summary of Bin Counting

Number of microstates for  $N$  objects in  $M$  bins:

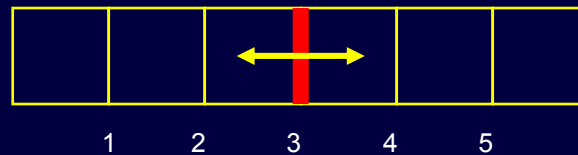
	Unlimited occupancy	Single occupancy	$N \ll M$ Dilute gas
Distinguishable	$M^N$	$\frac{M!}{(M-N)!}$	$M^N$
Identical	$\frac{(N+M-1)!}{(M-1)!N!}$	$\frac{M!}{(M-N)!N!}$	$\frac{M^N}{N!}$

Needed at high densities  
(liquids and solids)  
OK for gases, too.
 
 OK at low densities  
(gases only)

# Exercise: Microstates and Entropy

When the numbers are small, and the whole distribution matters, the average and the most likely may not be very close.

Consider 3 particles (A, B, C) in a system with 6 multiple occupancy cells partitioned by a movable barrier:



Take  $N_L=1$  (particle A) and  $N_R=2$  (particles B and C).

Some possible microstates:



1) Calculate the entropy for each partition position.

2) What are the most likely and average partition positions?

Note: We are interested in the volume on the left and right,  $V_L$  and  $V_R$ , so we'll express our answers in terms of them.  $V_L + V_R = 6$ .

# Worksheet for this problem

1 particle on left

2 (distinguishable) on right  
multiple-occupancy bins



$\Omega_L$	$\Omega_R$	$\Omega = \Omega_L \Omega_R$	$\sigma = \ln(\Omega)$
1	$5^2 = 25$	25	3.22

# Solution

1 particle on left  
2 (distinguishable) on right  
multiple-occupancy bins



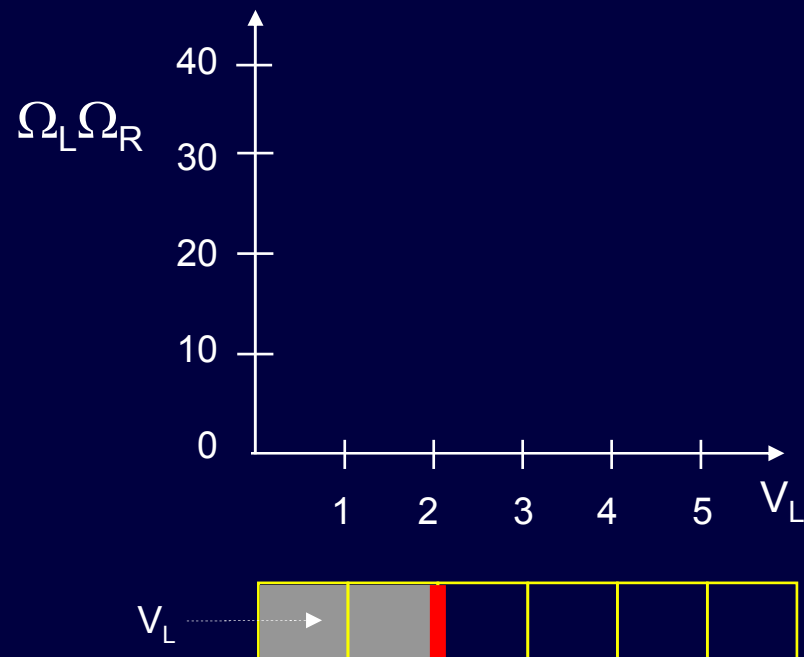
$\Omega_L$	$\Omega_R$	$\Omega = \Omega_L \Omega_R$	$\sigma = \ln(\Omega)$
1	$5^2 = 25$	25	3.22
2	$4^2 = 16$	32	3.47
3	$3^2 = 9$	27	3.30
4	$2^2 = 4$	16	2.77
5	$1^2 = 1$	5	1.61

$$\Omega_{\text{tot}} = 105$$

The most likely  $V_L = 2$ .

$$\begin{aligned} \text{The average } \langle V_L \rangle &= (1 \cdot 25 + 2 \cdot 32 + 3 \cdot 27 + 4 \cdot 16 + 5 \cdot 5) / 105 \\ &= 259 / 105 = 2.47 \end{aligned}$$

# Graph the Results



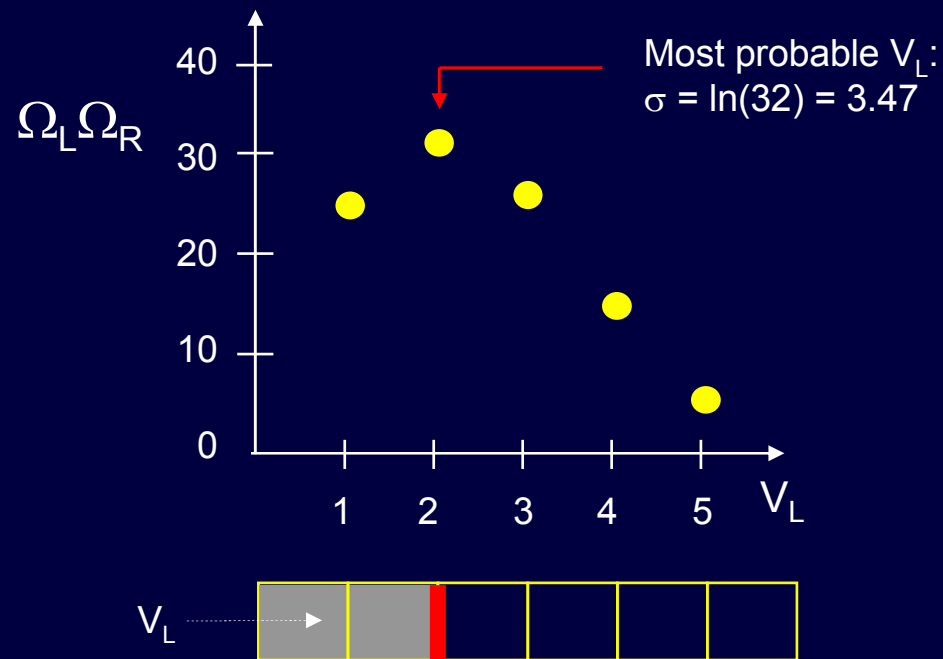
Notice that the most likely position occurs when:

$$\frac{N_L}{V_L} = \frac{N_R}{V_R} \left( = \frac{1}{2} \text{ in this example} \right)$$

What is the probability,  $P(2)$ , that  $V_L = 2$ ?



# Graph the Results



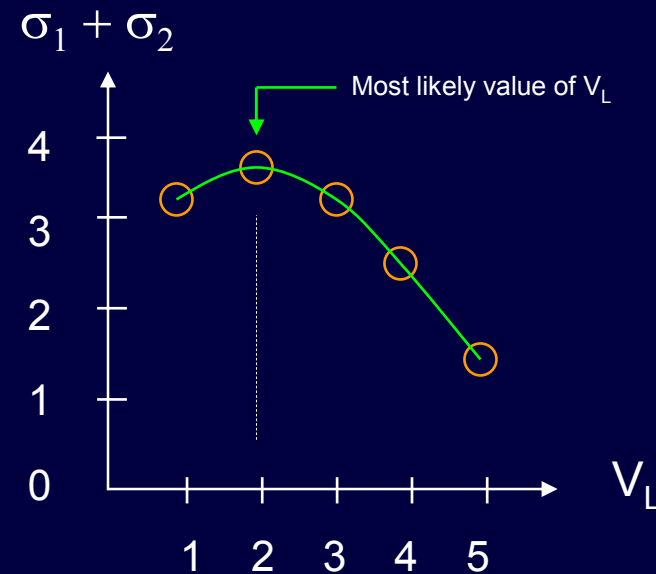
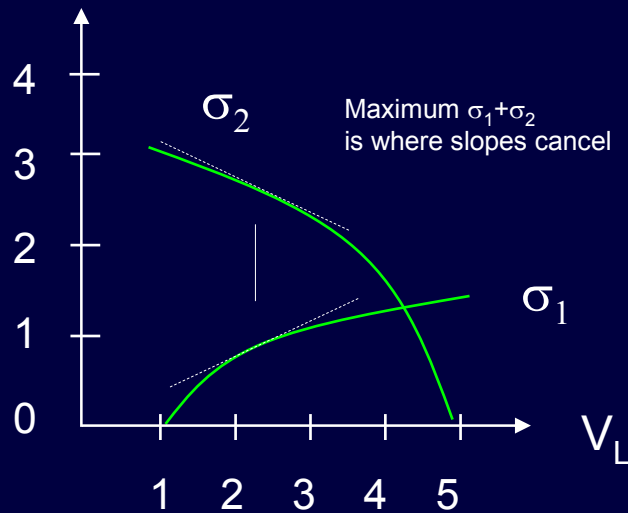
Notice that the most likely position occurs when:

$$\frac{N_L}{V_L} = \frac{N_R}{V_R} \left( = \frac{1}{2} \text{ in this example} \right)$$

What is the probability,  $P(2)$ , that  $V_L = 2$ ?

$$P(2) = \frac{32}{105} = 30.5\%$$

# Maximizing the Total Entropy



If the partition is allowed to move freely, the most likely macrostate occurs at maximum total entropy,  $\sigma_{\text{tot}} = \sigma_L + \sigma_R$ . This is equivalent to maximizing  $\Omega$ .

This corresponds to  $\frac{\partial \sigma_1}{\partial V_1} = \frac{\partial \sigma_2}{\partial V_2}$  **not**  $\sigma_1 = \sigma_2$ .

Entropy will be more convenient to calculate than  $\Omega$ .

# Summary

- The total entropy of an isolated system is maximum in equilibrium.
- So if two parts (1 and 2) can exchange  $V$ , equilibrium requires:

$$\frac{\partial \sigma_1}{\partial V_1} = \frac{\partial \sigma_2}{\partial V_2}$$

This is a general equilibrium condition.  
A similar relation holds for any  
exchanged quantity.

Entropy of an ideal gas:

For  $N$  distinguishable particles in volume  $V$ :  $\Omega \propto V^N \Rightarrow \sigma = N \ln V + \text{const}$

You can't calculate the constant (that requires quantum mechanics),  
but it drops out of problems where one only needs the entropy change.

For example, if the temperature is constant:

$$\sigma_f - \sigma_i = N \ln V_f - N \ln V_i = N \ln(V_f/V_i)$$

# Act 1: Isothermal Expansion

We isothermally compress 1 mole of  $O_2$  from 2 liters to 1 liter.

1. How much does the (dimensionless) entropy of the gas change?

- A) 0
- B)  $6 \times 10^{23} \ln(2)$
- C)  $-6 \times 10^{23} \ln(2)$

2. How much does the (dimensionless) entropy of the environment change?

- A) 0
- B)  $6 \times 10^{23} \ln(2)$
- C)  $-6 \times 10^{23} \ln(2)$

# Solution

We isothermally compress 1 mole of  $O_2$  from 2 liters to 1 liter.

1. How much does the (dimensionless) entropy of the gas change?

A) 0

B)  $6 \times 10^{23} \ln(2)$

C)  $-6 \times 10^{23} \ln(2)$

There are half as many places for each gas particle:

$$\Omega_i \propto V^N \rightarrow \Omega_f \propto (V/2)^N$$

$$\begin{aligned}\sigma_f - \sigma_i &= (N \ln V_f + \text{const}) - (N \ln V_i + \text{const}) = N \ln(V_f/V_i) \\ &= N_A \ln(1/2) = -6 \times 10^{23} \ln 2\end{aligned}$$

2. How much does the (dimensionless) entropy of the environment change?

A) 0

B)  $6 \times 10^{23} \ln(2)$

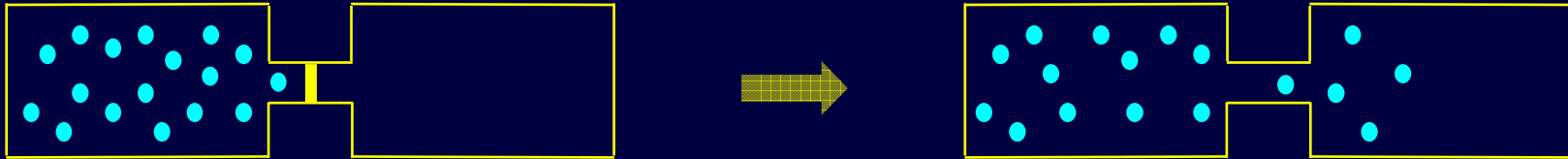
C)  $-6 \times 10^{23} \ln(2)$

According to the 2<sup>nd</sup> Law, the entropy of an isolated system must stay the same or increase.

Considering the (gas + environment) as the 'system', the reduction in  $\sigma_{\text{gas}}$  must be matched by an increase in  $\sigma_{\text{env}}$ . We will see later that for isothermal processes,  $\Delta\sigma_{\text{total}} = 0$  (i.e., they are reversible!).

# Act 2: Free Expansion

Now we let the gas 'free' expand back to 2 liters.

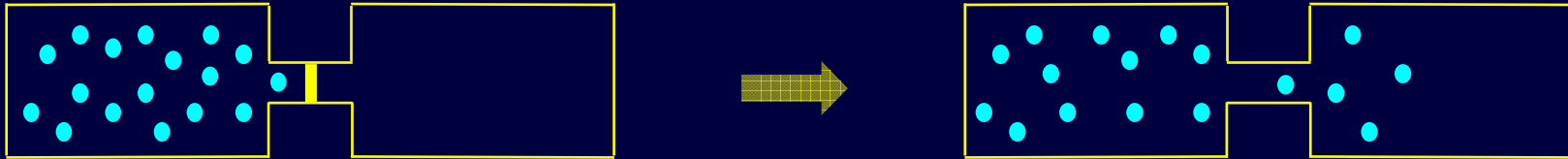


How much does the total entropy change?

- A) 0
- B)  $6 \times 10^{23} \ln(2)$
- C)  $-6 \times 10^{23} \ln(2)$

# Solution

Now we let the gas 'free' expand back to 2 liters.



How much does the total entropy change?

A) 0

B)  $6 \times 10^{23} \ln(2)$

C)  $-6 \times 10^{23} \ln(2)$

There are twice as many places for each gas particle:

$$\Omega_i \propto V^N \rightarrow \Omega_f \propto (2V)^N$$

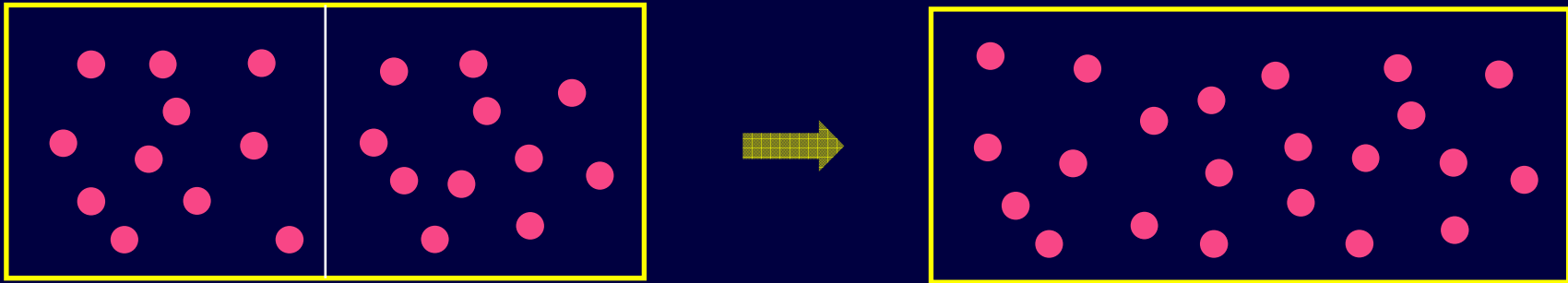
$$\sigma_f - \sigma_i = (N \ln V_f + \text{const}) - (N \ln V_i + \text{const}) = N \ln(V_f/V_i)$$

$$= N_A \ln(2) = 6 \times 10^{23} \ln 2$$

This *is* an isothermal process (why?), but not quasi-static, i.e., the gas is not in equilibrium throughout the expansion. In fact, the gas does not interact with the environment at all, so  $\sigma_{\text{env}}$  doesn't change.

Because this is an irreversible expansion (the particles will never randomly all go back into the 1-liter box!),  $\sigma_{\text{tot}}$  increases.

# Act 3

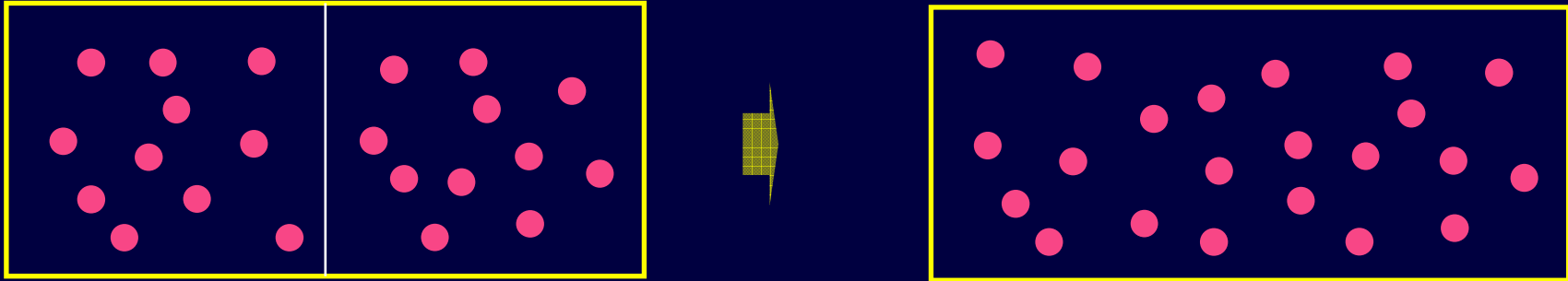


A partition separates two equal halves of a container, each containing  $N$  atoms of He. What is the change in the dimensionless entropy after the partition is removed?

- A)  $\Delta\sigma \sim 0$
- B)  $\Delta\sigma = N \ln 2$
- C)  $\Delta\sigma = 2N \ln 2$



# Solution (Gibbs Paradox)



A partition separates two equal halves of a container, each containing  $N$  atoms of He. What is the change in the dimensionless entropy after the partition is removed?

A)  $\Delta\sigma \sim 0$

B)  $\Delta\sigma = N \ln 2$

C)  $\Delta\sigma = 2N \ln 2$

The system before removing the partition is nearly identical to the system after removing it, i.e., the number of microstates changes very little (there are small fluctuations, fractionally  $\sim 1/\sqrt{N}$ )

Therefore  $\Delta\sigma \sim 0$ . Let's calculate it (incorrectly...)

Initial entropy

$$\Omega_L = \Omega_R = (n_T V)^N$$

$$\sigma_i = \sigma_L + \sigma_R$$

$$\sigma_i = 2N \ln(V) + 2N \ln(n_T)$$

final entropy

$$\Omega_f = (2n_T V)^{2N}$$

$$\sigma_f = 2N \ln(2V) + 2N \ln(n_T)$$

$$\Delta\sigma = \sigma_f - \sigma_i = 2N \ln(2)$$

What did we do wrong?

# Gibbs Paradox (2)

- So far we have dealt with situations where the number of particles in each subsystem is fixed. Here, after the partition is removed, particles can move freely between the two halves.
- To correctly calculate the change in entropy, we must account for the fact that the particles are identical.

Initial entropy

$$\Omega_L = \Omega_R = (n_T V)^N / N!$$

$$\sigma_i = \sigma_L + \sigma_R$$

$$\sigma_i = 2N \ln(n_T V) - 2 \ln(N!)$$

final entropy

$$\Omega_f = (2n_T V)^{2N} / (2N)!$$

$$\sigma_f = 2N \ln(2n_T V) - \ln((2N)!)$$

$$\text{Use: } \ln(N!) \approx N \ln N - N$$

$$\Delta\sigma = \sigma_f - \sigma_i \sim 0$$

# General Definition of Temperature

Start with the energy sharing result: Two systems that are allowed to exchange energy will do so until the total entropy is maximized  $\rightarrow$

$$\frac{d\sigma_{\text{tot}}}{dU_1} = 0 = \frac{d(\sigma_1 + \sigma_2)}{dU_1} = \frac{\partial\sigma_1}{\partial U_1} - \frac{\partial\sigma_2}{\partial U_2} \quad \Rightarrow \quad \frac{\partial\sigma_1}{\partial U_1} = \frac{\partial\sigma_2}{\partial U_2}$$

By definition,  $T_1 = T_2$  in equilibrium.

Define the absolute temperature  $T$ :

$$\frac{1}{kT} \equiv \left( \frac{\partial\sigma}{\partial U} \right)_v$$

With this definition, out of equilibrium, heat flows from hot to cold.

Under everyday conditions (large objects, not near absolute zero) we have equipartition of energy:  $U = \frac{1}{2}kT$  for each energy mode.

# Entropy, T, and $C_V$

A conventional entropy,  $S \equiv k \sigma$ , is often used.

Our basic definition of T is then:  $\longrightarrow$

S has dimensions energy/temperature (J/K).

$$\frac{1}{T} \equiv \left( \frac{\partial S}{\partial U} \right)_V$$

For fixed-V processes:

$$\left( \frac{\partial S}{\partial T} \right)_V = \left( \frac{\partial S}{\partial U} \right)_V \left( \frac{\partial U}{\partial T} \right)_V \equiv C_V / T$$

So:

$$S(T_f) - S(T_0) = \int_{T_0}^{T_f} \frac{C_V(T')}{T'} dT'$$

Or:

$$\sigma(T_f) - \sigma(T_0) = \int_{T_0}^{T_f} \frac{C_V(T')}{kT'} dT'$$

One can use this to calculate absolute entropy (no arbitrary constants).

# Exercise:

## A Large Collection of Oscillators

Consider  $10^{24}$  oscillators at 300 K with  $\varepsilon \ll kT$ .

1) What's  $C_V$ ?

2) If 1 J of  $U$  is added, how much does  $T$  go up?

3) How much does that 1 J make  $\sigma$  go up?

# Solution

Consider  $10^{24}$  oscillators at 300 K with  $\varepsilon \ll kT$ .

1) What's  $C_V$ ?

Equipartition holds, so  $C_V = Nk = 13.8 \text{ J/K}$ .

2) If 1 J of U is added, how much does T go up?

$$\Delta T = \Delta U / C_V = 0.07 \text{ K}$$

3) How much does that 1 J make  $\sigma$  go up?

$$d\sigma/dU = 1/kT$$

T is almost constant here, so:

$$\Delta\sigma = \Delta U/kT = 1 \text{ J} / (4.2 \times 10^{-21} \text{ J}) = 2.4 \times 10^{20}$$

$\Delta\Omega$  is the exponential of this, a gigantic number.

Note:

$$\begin{aligned}\Delta S &= k\Delta\sigma = \Delta U/T \\ &= 1/300 \text{ J/K}\end{aligned}$$

# FYI: Absolute Entropy

There is a natural method to determine absolute entropy (no arbitrary constants).

- At  $T=0$ , an object in equilibrium has only one accessible state (maybe two) (the lowest energy level, or two if there is degeneracy).

⇒ Entropy is  $\sim 0$  at  $T=0$ .

- As  $T \rightarrow 0$ , the entropy falls smoothly to that limit.  
This is sometimes called the “Third Law of Thermodynamics”
- So, the absolute  $S(T)$  can be calculated by setting  $S(0) = 0$ :

$$S(T) = \int_0^T \frac{C_V(T')}{T'} dT'$$

This integral does not diverge, because  $C_V \rightarrow 0$  as  $T \rightarrow 0$ .

- Absolute entropies are computed for many substances.  
For example,  $S_{O_2}(T=25^\circ \text{ C}, p=1\text{Atm}) = 205.04 \text{ J/mol.K}$

<http://www.egr.msu.edu/classes/me417/somerton/FCTables.pdf>

# Exercise

Consider a  $\sim 1$  liter container of  $N_2$  at STP. What fractional increase in the volume of the box  $V$  will double the number of microstates?

1) What is  $N$ ?

2) What is  $\Omega$ ?

3) What is  $\Omega_f/\Omega_i$ ?



# Exercise

Consider a ~1 liter container of  $N_2$  at STP. What fractional increase in the volume of the box  $V$  will double the number of microstates?

1) What is  $N$ ?

At STP, 1 mole of a gas occupies 22.4 liter. Therefore, in 1 liter there is  $N = 1 \text{ liter} \times (6 \times 10^{23} / 22.4 \text{ liter}) = 2.7 \times 10^{22}$

2) What is  $\Omega$ ?

$$\Omega = (n_T V)^N$$

3) What is  $\Omega_f / \Omega_i$ ?

$$\Omega_f / \Omega_i = 2 = (n_T V_f)^N / (n_T V_i)^N = (V_f / V_i)^N$$

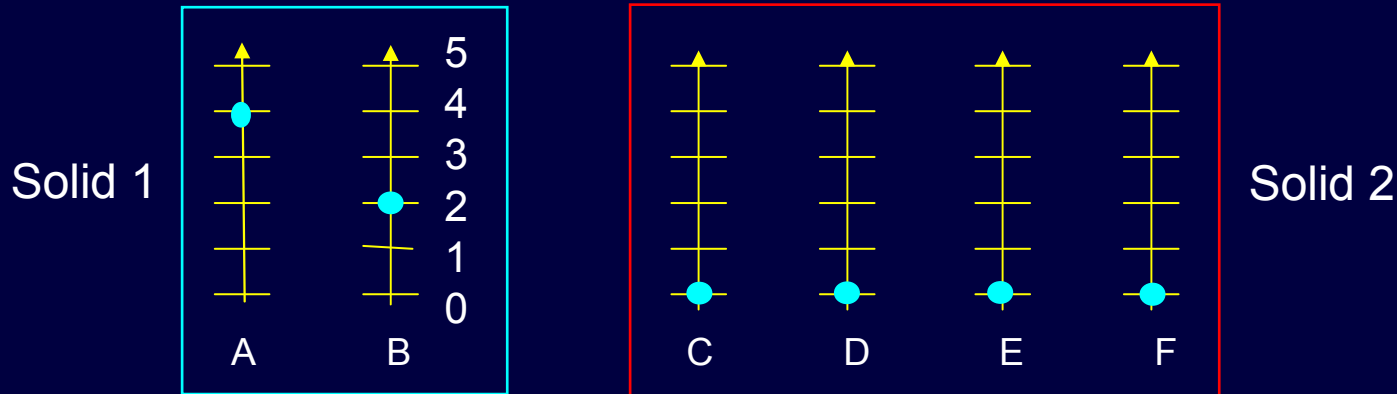
$$(V_f / V_i) = 2^{1/N} = 2^{(3.7 \times 10^{-23})} = 1.0 \text{ according to my calculator.}$$

$$= 1 + 2.56 \times 10^{-23} \text{ according to Mathematica}$$

The lesson: the number of microstates increases mind-bogglingly fast – that's why the gas fills the space.

# Example: Exchanging Energy

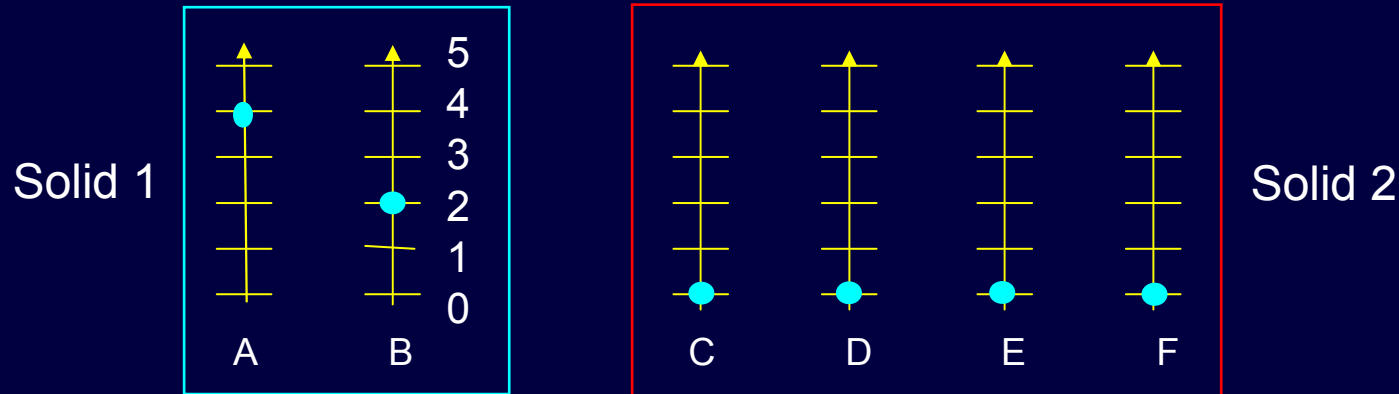
Two oscillators, A and B (“solid 1”) with energy level spacing  $\varepsilon$  share a total of 6 quanta. One possible microstate is shown in the figure below. They are brought into contact with four oscillators, C, D, E and F (“solid 2”) which initially share no quanta.



- 1) Initially, what is the entropy of solid 1? Solid 2?
- 2) If solid 2 is brought into contact with solid 1, what is the total entropy after equilibrium is reached?
- 3) What is the average energy in oscillator A, before and after?

# Solution

Two oscillators, A and B (“solid 1”) with energy level spacing  $\varepsilon$  share a total of 6 quanta. One possible microstate is shown in the figure below. They are brought into contact with four oscillators, C, D, E and F (“solid 2”) which initially share no quanta.



1) Initially, what is the entropy of solid 1? Solid 2?

$$\Omega_1 = \frac{(q_1 + N_1 - 1)!}{q_1! (N_1 - 1)!} = 7 \Rightarrow \sigma_1 = 1.95 \quad \sigma_2 = \ln(1) = 0$$

2) If solid 2 is brought into contact with solid 1, what is the total entropy after equilibrium is reached?

$$\Omega_{\text{tot}} = \frac{(q_{\text{tot}} + N_{\text{tot}} - 1)!}{q_{\text{tot}}! (N_{\text{tot}} - 1)!} = 462 \Rightarrow \sigma_{\text{tot}} = 6.14$$

3) What is the average energy in oscillator A, before and after?

Before: 2 oscillators share  $6\varepsilon$ .  $\langle U_{\text{av}} \rangle = 3\varepsilon$ .

After: 6 oscillators share  $6\varepsilon$ .  $\langle U_{\text{av}} \rangle = \varepsilon$ .

# Example: Energy Exchange

Consider this situation:

$$N_1 = 3, \quad N_2 = 4$$

$$q = q_1 + q_2 = 8 \quad (\text{i.e., } U = 8\varepsilon)$$

What is the most likely energy for each of the two systems?



# Solution

Consider this situation:

$$N_1 = 3, \quad N_2 = 4$$

$$q = q_1 + q_2 = 8 \quad (\text{i.e., } U = 8\varepsilon)$$

What is the most likely energy for each of the two systems?

I am not going to work it out in detail.

Here's a graph of the solution.

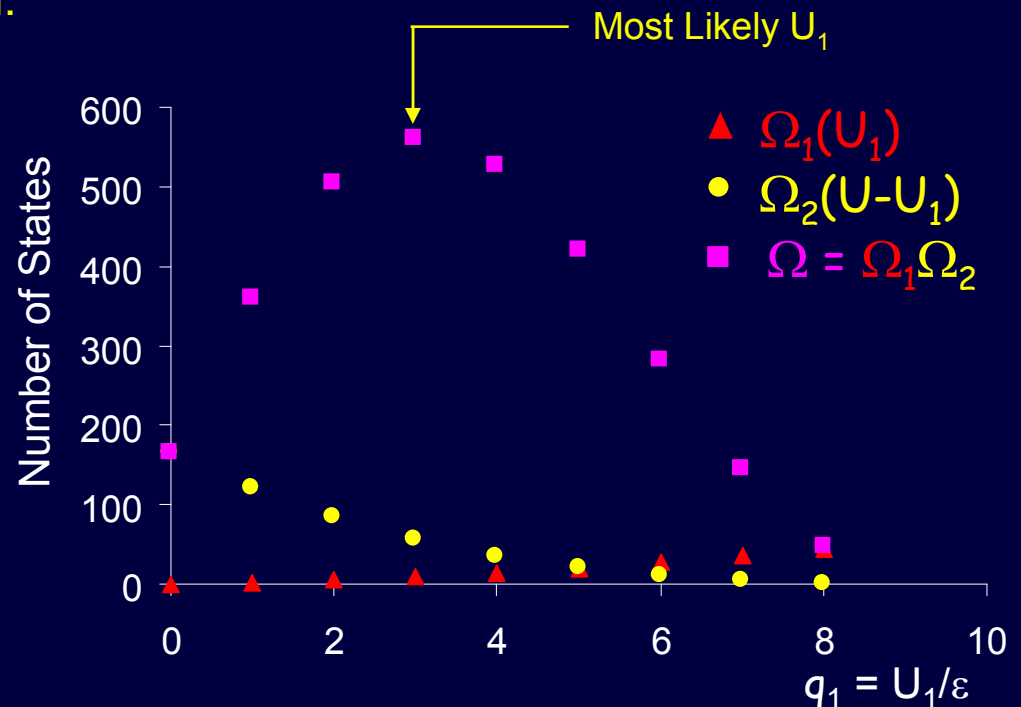
Sample calculation:  $q_1=1, q_2 = 7$ .

$$\text{Use: } \Omega_i = \frac{(q_i + N_i - 1)!}{q_i! (N_i - 1)!}$$

$$\text{Then: } \Omega_1 = \frac{3!}{1!2!} = 3$$

$$\Omega_2 = \frac{10!}{7!3!} = 120$$

$$\Omega = 360$$



Most likely macrostate:  $U_1/N_1 = 3/3 \approx U_2/N_2 = 5/4$ . ~ Equipartition. N is not large.