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[TP] How many distinguishable ways can 4 ink molecules be arranged among 21 water molecules?

17% 1. 1450
17% 2. 3260
17% 3. 8890
17% 4. 12650
17% 5. 14950
17% 6. 65780

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Lecture 28 CH102 A1 (MWF 9:05 am)

Wednesday, April 4, 2018

- Counting particle dispersal
- Maximum particle dispersal = uniform pressure
- Arrangements ⟶ Entropy
- Counting energy dispersal

Next lecture: Heat (energy) flow → entropy change. Spontaneity of phase transitions: water ⇌ steam. ΔS in colligative properties: Freezing point depression.

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Counting distinguishable (unique) arrangements

The number of distinguishable arrangements of
j identical objects of one kind (water molecules, say) and
k identical objects of another kind (ink molecules, say) is …

$$W(j,k) = \frac{(j+k)!}{j! \times k!}$$

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Counting distinguishable (unique) arrangements

The number of distinguishable arrangements of
j identical objects of one kind, say $j = 4$ water molecules, and
k identical objects of another kind, say $k = 3$ ink molecules …

$$W(4,3) = \frac{(4+3)!}{4!\,3!} = \cdots$$

$$\frac{7 \times 6 \times 5 \times 4!}{4!\,3!} = \frac{7 \times 6 \times 5}{3 \times 2} = 7 \times 5 = 35$$

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[TP] How many distinguishable ways can 4 ink molecules be arranged among 21 water molecules?

1. 1450
2. 3260
3. 8890
4. 12650
5. 14950
6. 65780

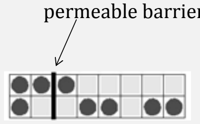
0 of 0

10

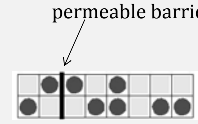
Maximum particle dispersal = uniform pressure

The goal: To see that what "happens" corresponds to the maximum number of arrangements

Pressure in a gas is unequal



Pressure in a gas is uniform



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Pressure in a gas becomes uniform

Why?

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Lattice gas model of pressure

$$\frac{P}{RT} = n/V = \text{gas density}$$

$$n = \text{particles}$$

$$V = \text{lattice positions}$$

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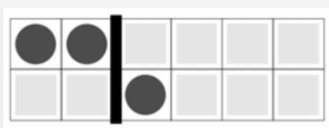
$P_{\text{left}} > P_{\text{right}}$



Left side: $n/V = 2/4$, $W_{\text{left}} = \ldots$

6

Right side: $n/V = 1/8$, $W_{\text{right}} = \ldots$

8

$$W_{\text{total}} = W_{\text{left}} \times W_{\text{right}} = 6 \times 8 = 48$$

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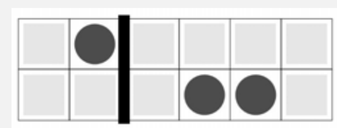
$P_{\text{left}} = P_{\text{right}}$



Left side: $n/V = 1/4$, $W_{\text{left}} = \ldots$

4

Right side: $n/V = 2/8$, $W_{\text{right}} = \ldots$

28

$$W_{\text{total}} = W_{\text{left}} \times W_{\text{right}} = 4 \times 28 = 112$$

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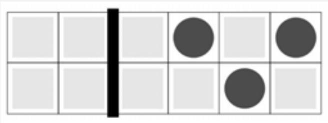
$P_{left} < P_{right}$



Left side: $n/V = 0/4$, W_{left} …

1

Right side: $n/V = 3/8$, $W_{right} = $ …

56

$W_{total} = W_{left} \times W_{right} = 1 \times 56 = 56$

17

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Pressure in a gas becomes uniform

Why?

$P_{left} > P_{right}$ has $W_{total} = 48$

$P_{left} = P_{right}$ has $W_{total} = 112$

$P_{left} < P_{right}$ has $W_{total} = 56$

Uniform pressure maximizes W!

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Arrangements → Entropy

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$S = k_B \ln(W)$

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$S = k_B \ln(W)$

$k_B = R/N_A = 1.4 \times 10^{-23}$ J/K

Why natural log?

Doubling size of system: $W \longrightarrow W \times W = W^2$

Doubling size of system: $S \rightarrow k_B \ln(W^2) = 2k_B \ln(W) = 2S$, so …

Boltzmann's definition in terms of natural log makes S …

scale with size of system (extensive).

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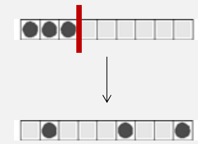
Spontaneous?



Calculate the entropy change.

$W_i = 1 \rightarrow W_f = (6+3)!/(6!\,3!) = 84$

$\Delta S = S_f - S_i = k_B \ln(W_f / W_i) = k_B \ln(84/1) > 0$

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Counting energy dispersal

The goal: Entropy change is
proportional to enthalpy change and
inversely proportional to absolute temperature …

$$\Delta S = \frac{\Delta H}{T}$$

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Counting energy dispersal

Unique (distinguishable) arrangements of
q identical quanta distributed among
m identical molecules

For example, four quanta among three molecules …

$q|q|qq$, $q||qqq$, $|qqqq|$, $q|qq|q$, etc.

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Counting energy dispersal

Four quanta among three molecules …

$q|q|qq$, $q||qqq$, $|qqqq|$, $q|qq|q$, etc.

How many unique such arrangements, $W_e(4,3)$?

$W_e(4,3) = 6!/(4!\,2!)$

$= 15$

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Counting energy dispersal

Unique (distinguishable) arrangements of

q identical quanta among

m identical molecules …

$$W_e(q,m) = \frac{(q+m-1)!}{q!\,(m-1)!}$$

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