

[TP] Evaluate W_e(9 quanta, 4 molecules).

25% 1. 11 x 10 = 110
25% 2. 10 x 22 = 220
25% 3. 13 x 11 = 143
25% 4. None of the above

BOSTON UNIVERSITY

Response Counter

10

1

Lecture 31 CH102 A1 (MWF 9:05 am)

Wednesday, April 12, 2017

- Review: Practice with particle dispersal
- Maximum particle dispersal = uniform pressure
- Arrangements ⟶ Entropy
- Counting energy dispersal
- Heat (energy) flow → entropy change

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

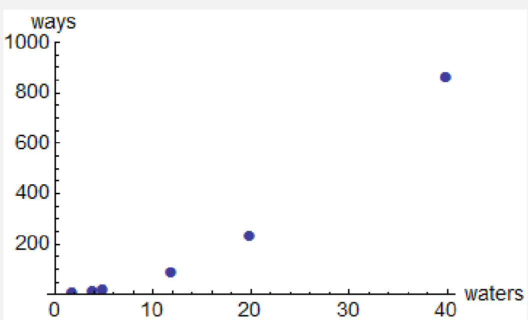
Notes: Spontaneity: Second law of thermodynamics

http://quantum.bu.edu/courses/ch102-spring-2017/handouts.html

BOSTON UNIVERSITY

The more water, the more ways ink disperses

2 ink particles in water



BOSTON UNIVERSITY

9

Maximum particle dispersal = uniform pressure

The goal: What "happens" corresponds to the maximum number of arrangements

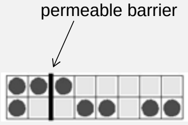
BOSTON UNIVERSITY

15

Lecture 31 CH102 A1 (MWF 9 am) Spring 2017 Copyright © 2017 Dan Dill dan@bu.edu

Pressure in a gas is unequal

permeable barrier

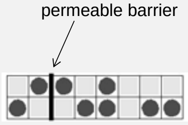


BOSTON UNIVERSITY 16

Lecture 31 CH102 A1 (MWF 9 am) Spring 2017 Copyright © 2017 Dan Dill dan@bu.edu

Pressure in a gas is uniform

permeable barrier



BOSTON UNIVERSITY 17

Lecture 31 CH102 A1 (MWF 9 am) Spring 2017 Copyright © 2017 Dan Dill dan@bu.edu

Pressure in a gas becomes uniform

Why?

BOSTON UNIVERSITY 18

Lecture 31 CH102 A1 (MWF 9 am) Spring 2017 Copyright © 2017 Dan Dill dan@bu.edu

Lattice gas model of pressure

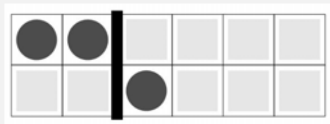
$1/(R\,T)\;P = n\,/\,V =$ gas density

$n =$ particles

$V =$ lattice positions

BOSTON UNIVERSITY 19

$P_{left} > P_{right}$



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

6

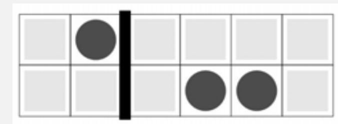
Right side: $n / V = 1/8$, $W_{right} = \ldots$

8

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

BOSTON UNIVERSITY 20

$P_{left} = P_{right}$



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

4

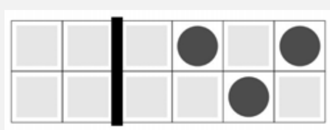
Right side: $n / V = 2/8$, $W_{right} = \ldots$

28

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

BOSTON UNIVERSITY 21

$P_{left} < P_{right}$



Left side: $n / V = 0/4$, $W_{left} \ldots$

1

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

56

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

BOSTON UNIVERSITY 22

Pressure in a gas becomes uniform

Why?

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

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

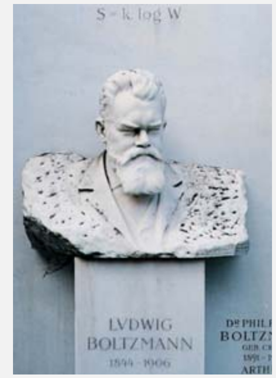
$P_{left} < P_{right}$ has $W_{total} = 56$

Uniform pressure maximizes W!

BOSTON UNIVERSITY 23

Arrangements → Entropy

$S = k_B \ln(W)$



$S = k_B \ln(W)$

Why natural log?

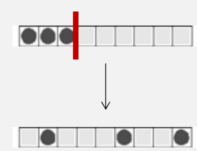
Doubling size of system: $W \to W \times W = W^2$

Doubling size of system: $S \to 2\,S$, so …

Boltzmann's definition makes S scale with size of system (extensive).

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

Spontaneous?



Calculate the entropy change.

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

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

Counting energy dispersal

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

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

BOSTON UNIVERSITY 29

Counting energy dispersal

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

For example, four quanta among three molecules …
q|q|qq, q||qqq, |qqqq|, q|qq|q, etc.

BOSTON UNIVERSITY 30

Counting energy dispersal

Four quanta among three molecules …
q|q|qq, q||qqq, |qqqq|, q|qq|q, etc.

How many unique such arrangements, $W_e(4,3)$?
total = uniques × degeneracies
6! = $W_e(4,3)$ × (4! 2!)
$W_e(4,3)$ = 6!/(4! 2!)
= 15

BOSTON UNIVERSITY 31

Counting energy dispersal

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

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

BOSTON UNIVERSITY 32