

# CH365 Chemical Engineering Thermodynamics

## Lesson 25

### 3<sup>rd</sup> Law and Entropy from the Microscopic Viewpoint

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# What is Entropy?

entropy - Wiktionary - Internet Explorer

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**Noun** [ edit ]

**entropy** (*countable and uncountable*, plural **entropies**)

Wikipedia has an article on: **entropy**

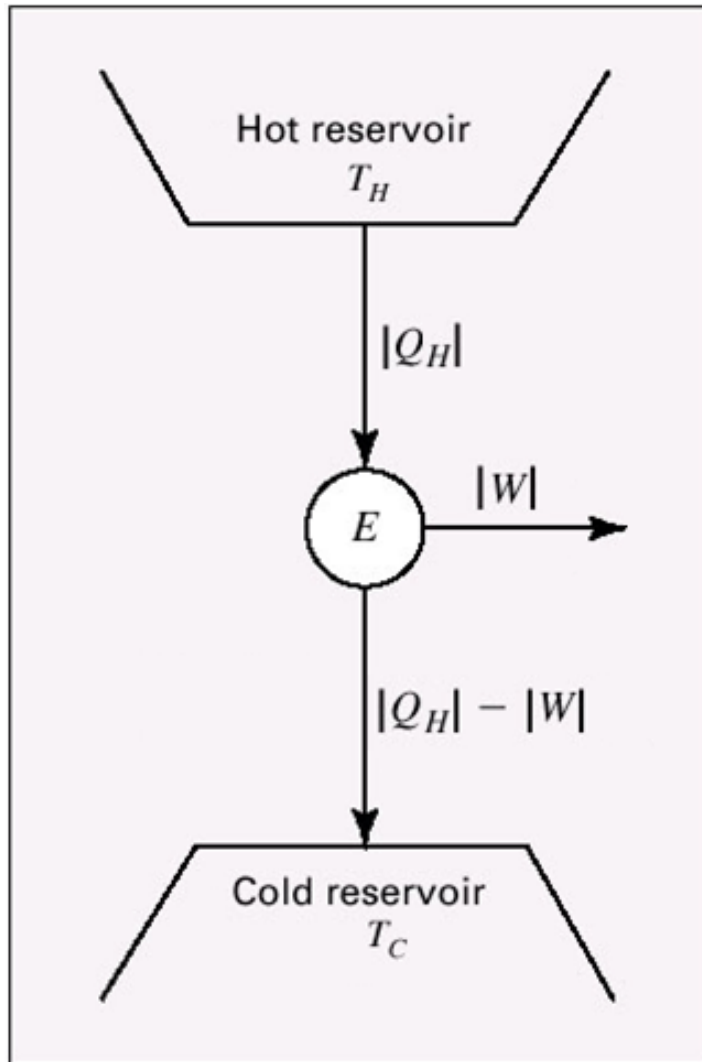
- (*thermodynamics, countable*)
  - strictly **thermodynamic entropy**. A **measure** of the **amount** of **energy** in a **physical system** that cannot be used to do **work**.
 
$$A = U - TS \text{ (Helmholtz Free Energy; A is for "arbeit")}$$

$$G = H - TS \text{ (Gibbs Free Energy)}$$
  - A measure of the **disorder present** in a system.
 

*Ludwig Boltzmann defined **entropy** as being directly proportional to the natural logarithm of the number of microstates*

<https://en.wiktionary.org/wiki/entropy>

# Implications



$$\eta = \frac{|W|}{|Q_H|} = 1 - \frac{T_C}{T_H} \quad (\text{Eq. 5.8})$$

What happens to  $\eta$  as  $T_C$  goes to zero?

As  $T_C$  goes to zero, the amount of “lost work” goes to zero.

# Third Law of Thermodynamics

**The absolute entropy is zero for all perfect crystalline substances at absolute zero temperature.**

$$S = S(T) = \int_0^{T_f} \frac{(C_P)_S}{T} dT + \frac{\Delta H_f}{T_f} + \int_{T_f}^{T_v} \frac{(C_P)_L}{T} dT + \frac{\Delta H_v}{T_v} + \int_{T_v}^T \frac{(C_P)_G}{T} dT$$

(Eq. 5.40)

**This equation allows calculation of absolute entropy.**

**The 3<sup>rd</sup> Law repairs an important problem.**

In[1]:= (\*CaO(s) m.p. 2845 K\*)

(\*Cp from Appendix C page 670\*)

$$C_p = 6.104 + .443 * 10^{-3} * T - 1.047 * 10^5 * T^{-2};$$

$$\text{In[2]:= } \int_0^{273} \frac{C_p}{T} dT$$

Integrate: Integral of  $0.000443 - \frac{104700.}{T^3} + \frac{6.104}{T}$  does not converge on {0, 273}.

$$\text{Out[2]= } \int_0^{273} \frac{6.104 - \frac{104700.}{T^2} + 0.000443 T}{T} dT$$

$$\text{In[3]:= } s[T_] = \int \frac{C_p}{T} dT$$

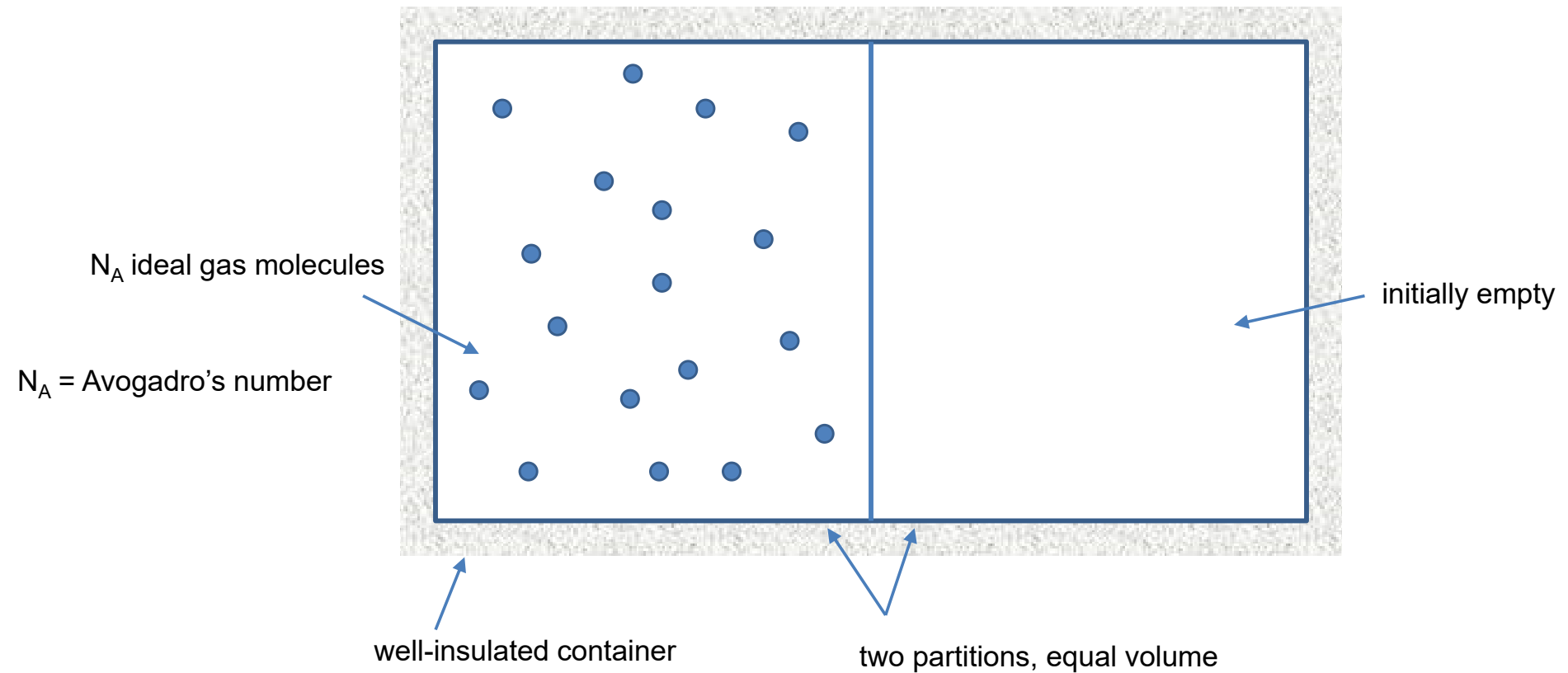
$$\text{Out[3]= } \frac{52350.}{T^2} + 0.000443 T + 6.104 \text{ Log}[T]$$

$$\text{In[4]:= } s[273]$$

$$\text{Out[4]= } 35.0635659798$$

# Statistical Interpretation

- ideal gas
  - molecules do not interact
  - internal energy resides within the individual molecules



$$U = U(T, V) \quad \text{ch. 4, p. 138, (un-numbered equation)}$$

$$dU = \underbrace{\left( \frac{\partial U}{\partial T} \right)_V}_{\text{definition of } C_V} dT + \underbrace{\left( \frac{\partial U}{\partial V} \right)_T}_{0 \text{ } \rightarrow \text{Because molecules don't interact}} dV$$

$$\frac{\Delta S}{R} = \underbrace{\int_{T_{\text{before}}}^{T_{\text{after}}} \frac{C_P^{\text{ig}}}{R} \frac{dT}{T}}_{0, \text{ no change in } T} - \ln \left( \frac{P_{\text{final}}}{P_{\text{initial}}} \right) \quad \underbrace{\quad}_{P \text{ drops by half}} \quad (\text{Eq. 5.10})$$

ch. 3, p. 79, (Eq. 3.13a)

$$dU = C_V dT$$

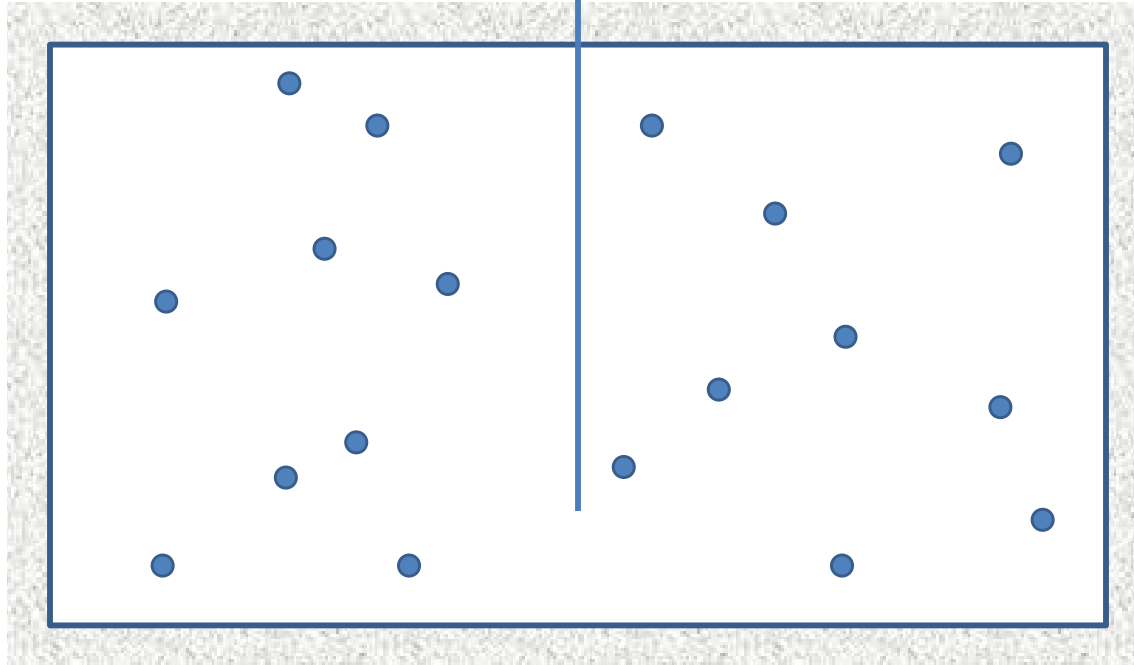
Recall:

ch. 3, p. 79, (Eq. 3.14a)

$$dH = C_P dT$$

definition of  $C_P$ :

$$C_P \equiv \left( \frac{\partial H}{\partial T} \right)_P$$



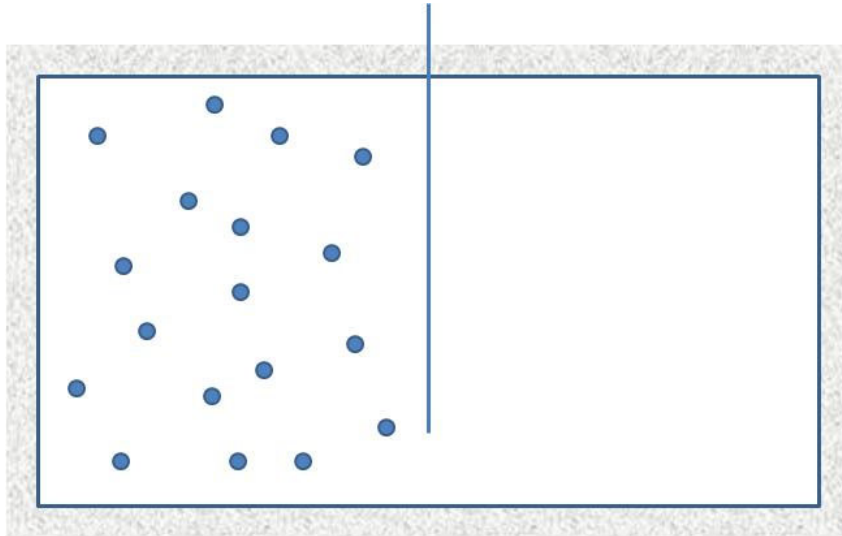
$$\Delta U = C_V \Delta T = 0$$

But if  $\Delta U=0$ , then  $T$  does not change.

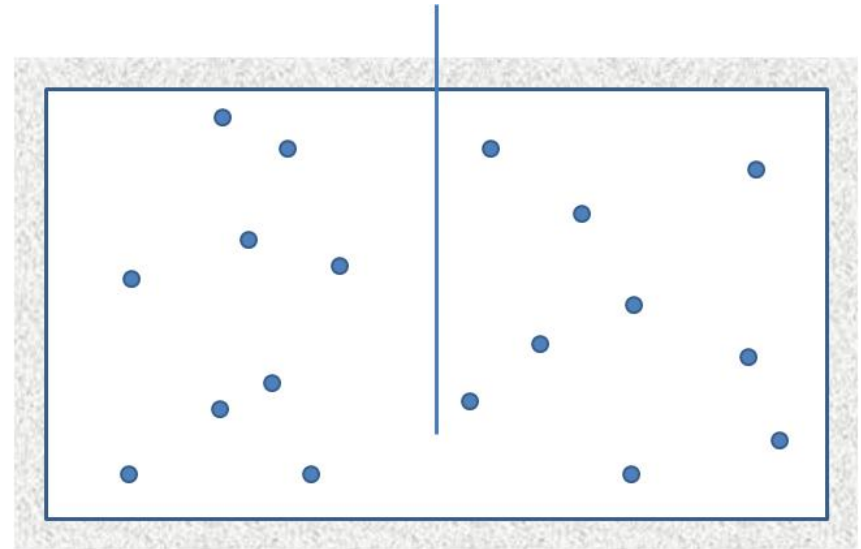
$$\Delta S = -R \cdot \ln \left( \frac{P_{\text{after}}}{P_{\text{before}}} \right) = R \cdot \ln(2) \quad \underbrace{\quad}_{>0 \text{ (irreversible)}}$$

Result of *classical* thermodynamics

more ordered → less random → less disordered



less ordered → more random → more disordered



- immediately after opening
- molecules are not randomly distributed over the total volume
- crowded into half the space

Increasing disorder (or decreasing structure) on the molecular level corresponds to increasing entropy.

Expression for disorder postulated by J.W. Gibbs and L. Boltzmann, 1878.



# Quantitative Expression of Disorder

Formulation of J.W. Gibbs and L. Boltzmann

$$\Omega = \frac{N!}{(N_1!)(N_2!)(N_3!)\cdots} \quad (\text{Eq. 5.36})$$

$\Omega$  = number of different ways that microscopic particles can be distributed among the "states" accessible to them.

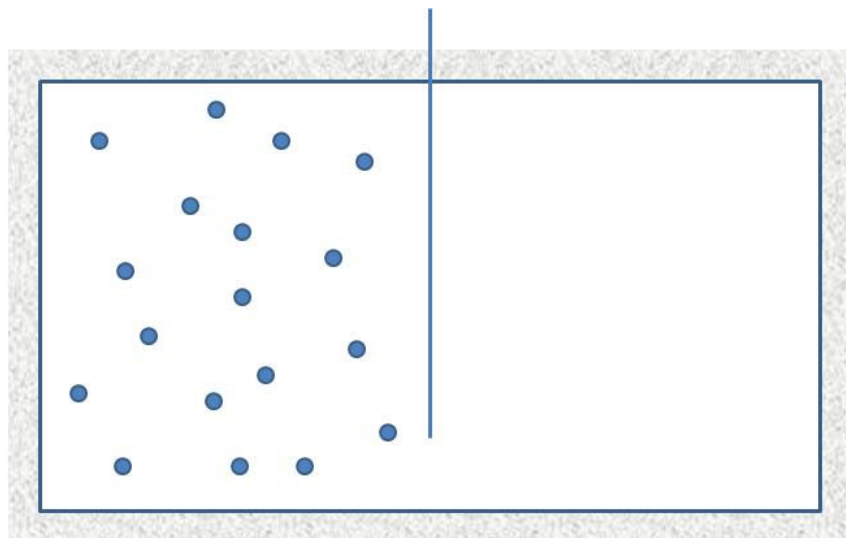
$N$  = total number of particles

$N_1$  = number of particles in state 1

$N_i$  = number of particles in state  $i$

Boltzmann used "W" for "Wahrscheinlichkeit"

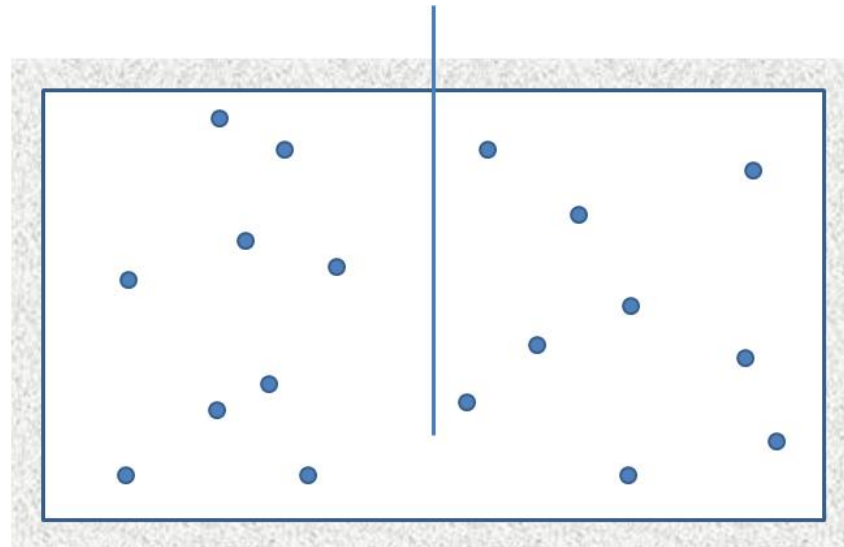
more ordered = less random = less disordered



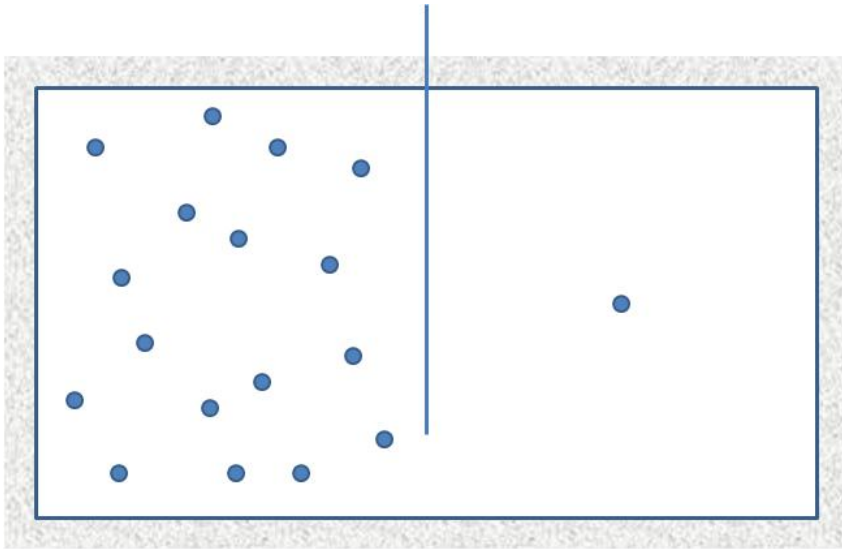
All molecules are in one of the two states.

$$\begin{aligned}\Omega_{\text{initial}} &= \frac{N_A!}{(N_A!)(0!)} \\ &= \frac{18!}{(18!)(0!)} \\ &= 1\end{aligned}$$

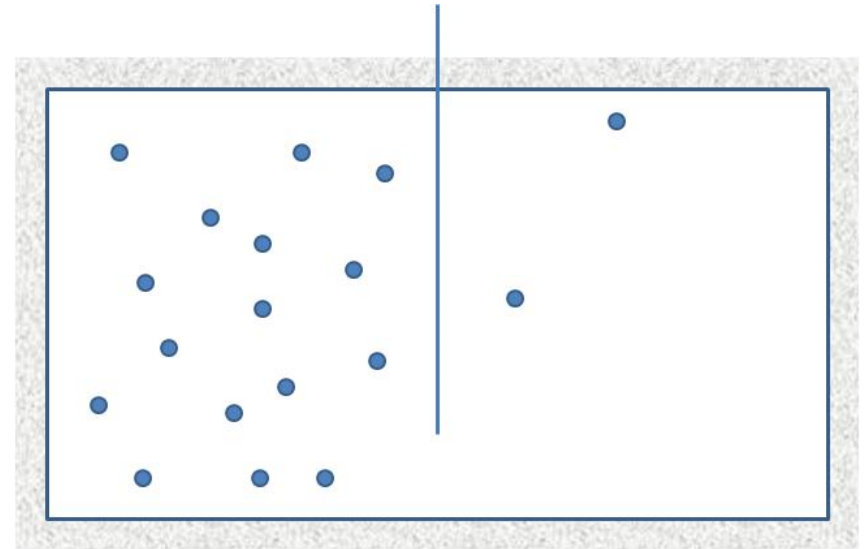
less ordered = more random = more disordered



$$\begin{aligned}\Omega_{\text{final}} &= \frac{N_A!}{\left(\frac{N_A}{2}!\right)\left(\frac{N_A}{2}!\right)} \\ &= \frac{18!}{9! \cdot 9!} \\ &= 48,620\end{aligned}$$



$$\Omega_1 = \frac{18!}{(17!)(1!)} = 18$$



$$\Omega_2 = \frac{18!}{(16!)(2!)} = 153$$

unbounded as  $N_A$  increases

for the 18 particles,  $\Omega_{\text{final}} = 48,620$

How about  $N_A = 10^{23}$ ?

There are a large number of ways that particles can distribute themselves *uniformly* between the two states.

There are also a large number of ways that particles can distribute themselves *non-uniformly* between the two states.

The ratio of a specific  $\Omega_i$  to the total  $\Omega$  is the probability of that distribution.

Boltzmann's connection:

(Eq. 5.37)

$$S_i = k \cdot \ln(\Omega_i)$$

Equations 5.36 and 5.37 are the basis of modern statistical thermodynamics

Boltzmann's constant



Boltzmann had what Jules Winnfield called “a moment of clarity.” He realized that equation 5.37 unified the statistical and classical approaches to entropy.

$$S_i = k \cdot \ln(\Omega_i) \quad \Rightarrow \quad S_{\text{final}} - S_{\text{initial}} = k \cdot \ln\left(\frac{\Omega_{\text{final}}}{\Omega_{\text{initial}}}\right)$$

(Eq. 5.37)

$$\Omega_{\text{final}} = \frac{N_A!}{\left(\frac{N_A}{2}\right)!^2} \quad \Omega_{\text{initial}} = 1$$

$$S_{\text{final}} - S_{\text{initial}} = k \cdot \ln\left(\frac{N_A!}{\left(\frac{N_A}{2}\right)!^2}\right) = k \left[ \ln(N_A!) - \ln\left(\left(\frac{N_A}{2}\right)!^2\right) \right] = k \left[ \ln(N_A!) - 2 \cdot \ln\left(\frac{N_A}{2}\right)! \right]$$

James Stirling  
(1692-1770)

Stirling's Formula:  $\ln(x!) = x \cdot \ln(x) - x$

Limit of large x

$$S_{\text{final}} - S_{\text{initial}} = k \left[ (N_A \cdot \ln(N_A) - N_A) - 2 \cdot \left( \frac{N_A}{2} \ln\left(\frac{N_A}{2}\right) - \frac{N_A}{2} \right) \right]$$

$$S_{\text{final}} - S_{\text{initial}} = k \left[ (N_A \cdot \ln(N_A) - N_A) - 2 \cdot \left( \frac{N_A}{2} \ln \left( \frac{N_A}{2} \right) - \frac{N_A}{2} \right) \right]$$

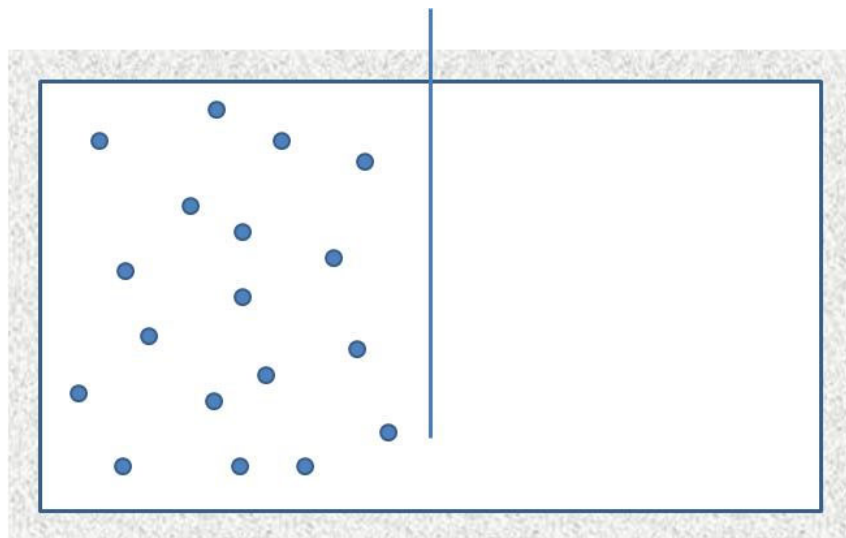
$$= k \left[ N_A \cdot \ln(N_A) - N_A - N_A \cdot \ln \left( \frac{N_A}{2} \right) + N_A \right]$$

$$= k \left[ N_A \cdot \ln(N_A) - N_A \cdot \ln \left( \frac{N_A}{2} \right) \right]$$

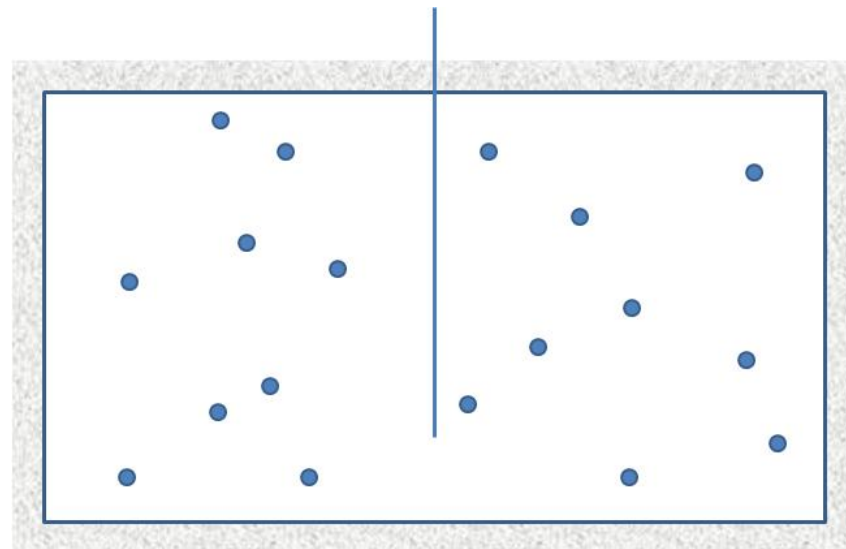
$$= k \cdot N_A \cdot \left[ \ln(N_A) - \ln \left( \frac{N_A}{2} \right) \right]$$

$$= k \cdot N_A \cdot \ln \left( \frac{N_A}{\frac{N_A}{2}} \right) = k \cdot N_A \cdot \ln(2)$$

more ordered  $\Rightarrow$  less random  $\Rightarrow$  less disordered



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# Homework

## Problem 5.44

A nuclear power plant generates 750 MW; the reactor temperature is 315 deg C and a river with water temperature of 20 deg C is available.

(a) What is the maximum possible thermal efficiency of the plant, and what is the minimum rate at which heat must be discarded to the river?

(b) If the actual thermal efficiency of the plant is 60% of the maximum, at what rate must heat be discarded to the river, and what is the temperature rise of the river if it has a flow rate of 165 cubic meters per second?

# Problem 5.50

Ethylene vapor is cooled at atmospheric pressure from 830 to 35 deg C by direct heat transfer to the surroundings at 25 deg C. With respect to this surroundings temperature, what is the lost work of the process in kJ/mol?

Show that the same result is obtained as the work which can be derived from reversible heat engines operating with the ethylene vapor as the heat source and the surroundings as the sink.

The heat capacity of ethylene is given in Table C.1 of App. C.