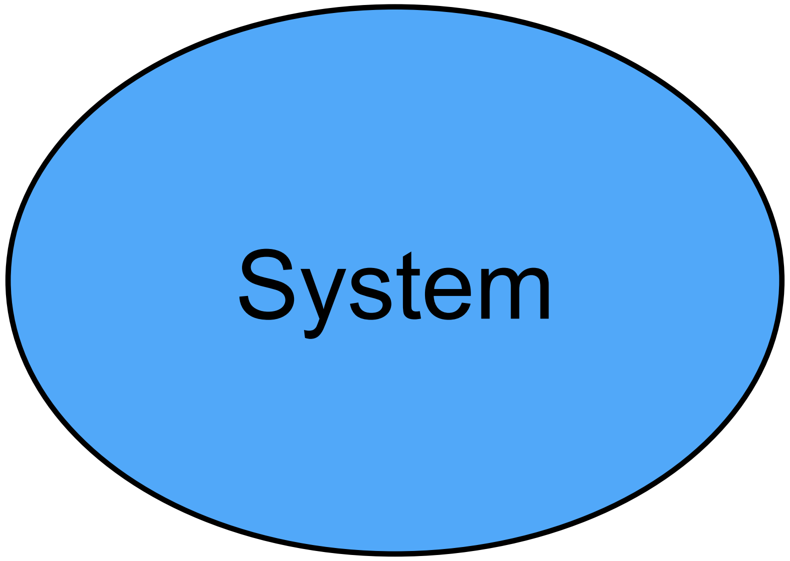
Chapter 19: Free Energy and Thermodynamics I

Chem 102
Jussi Eloranta

Thermochemistry

- Study of energy and heat associated with chemical reactions and physical changes
- Quantify heat and work transfer between system and surroundings
- System: Arbitrary designation of the reaction or whatever you decide


System

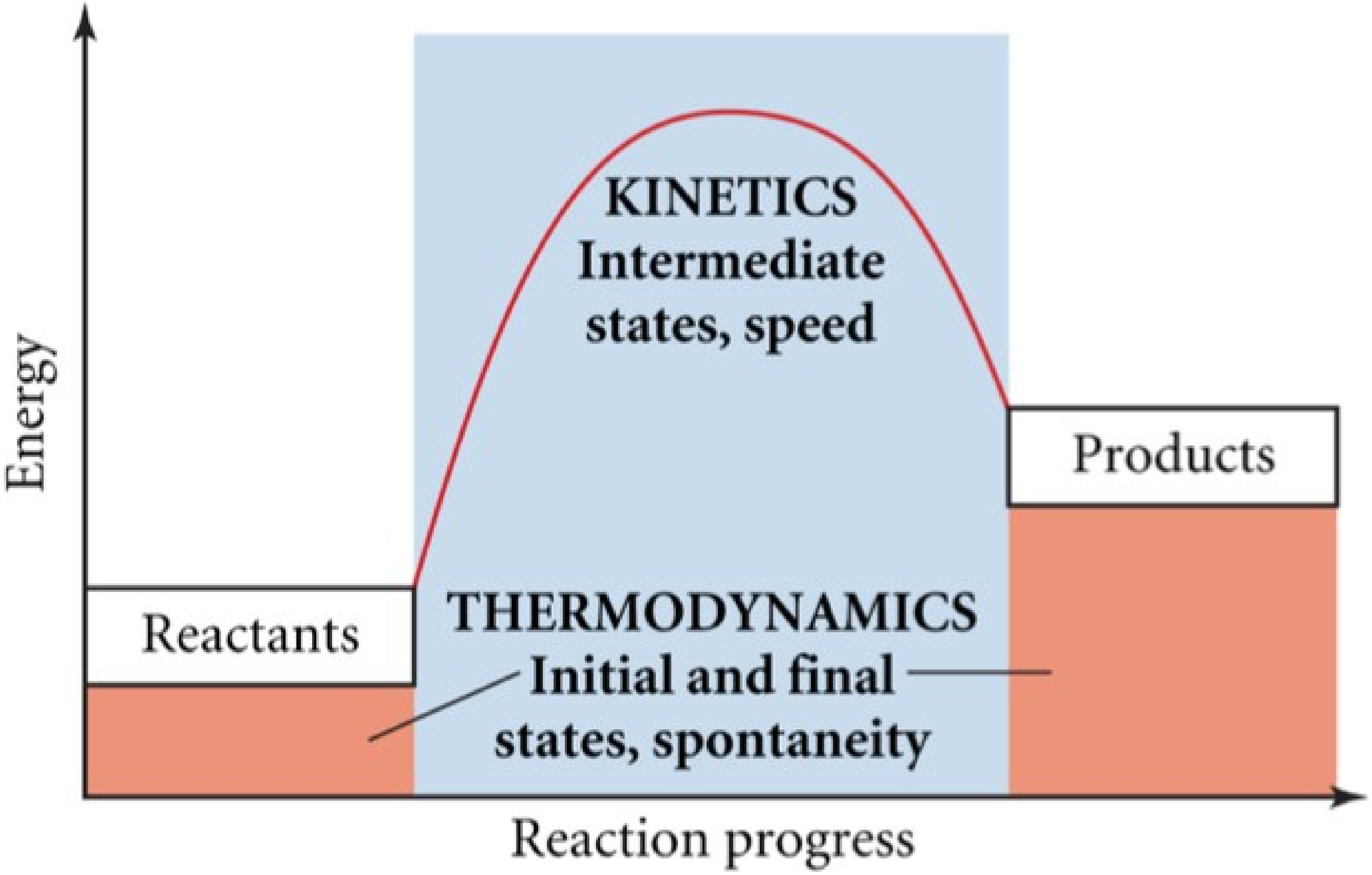
Surroundings
(everything else)
(rest of the universe)

Thermochemistry

- Thermodynamics: Study of how much energy is exchanged
- Enthalpy (heat of reaction)
  - Will the reaction be favored in terms of energy?
  - Many processes in the universe trend towards lower energy
- Entropy
  - Measure of the disorder in matter
  - Disorder in the universe increases (higher entropy)
- Free energy
  - Will a process (reaction) occur **spontaneously**?
  - Considers both enthalpy and entropy

Thermodynamics vs. Kinetics

Thermodynamics (spontaneity) can tell us whether a process will happen, but **not** how fast!

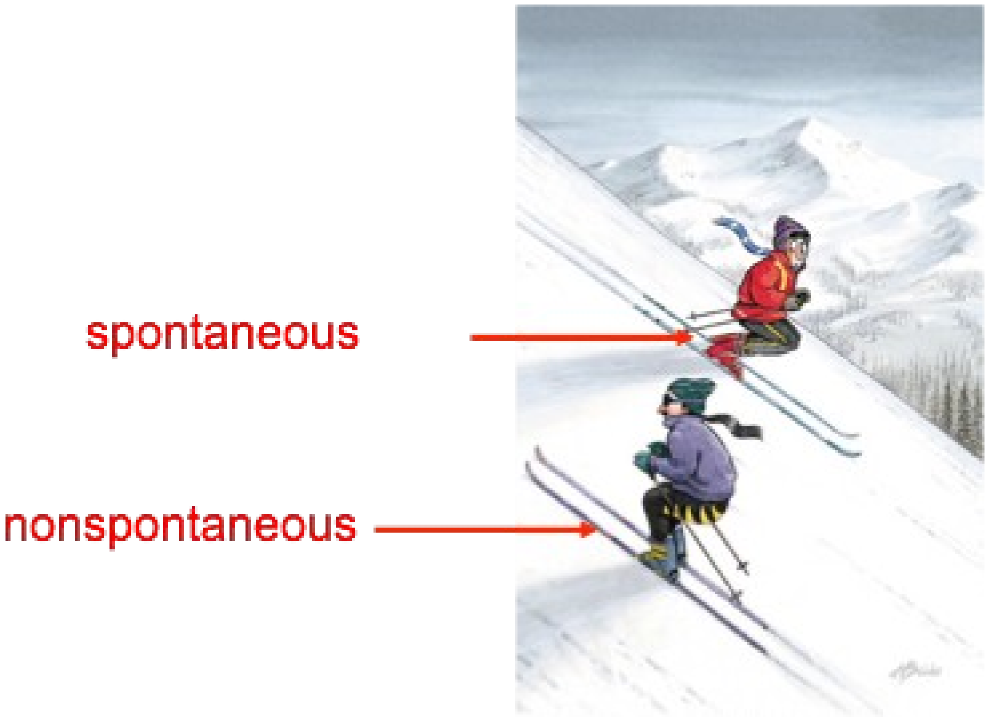


Spontaneity

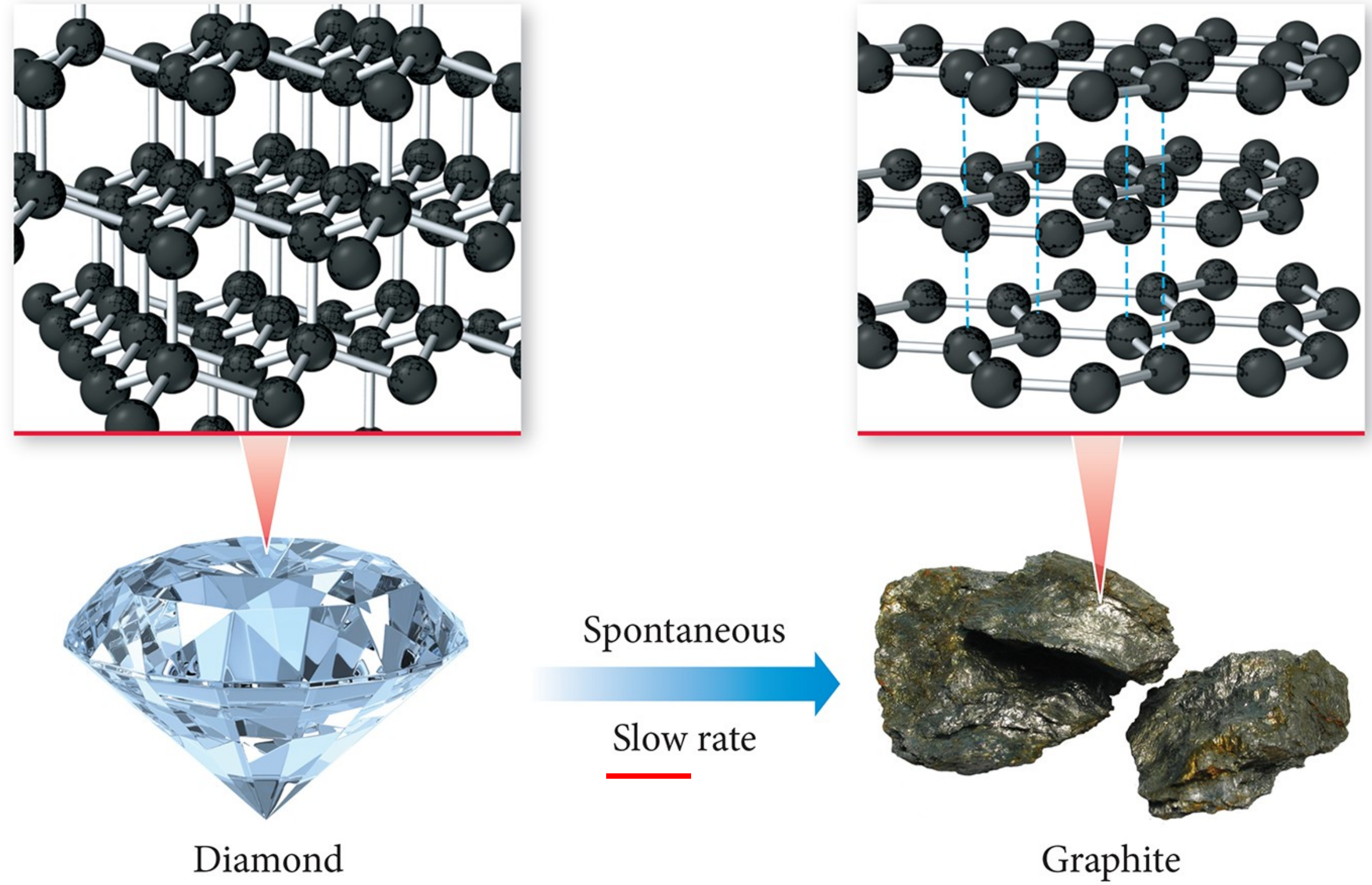
- Spontaneous chemical or physical processes proceed in a given direction without being driven by an outside source of energy
- In the universe, processes often go to **lower potential energy:**
  - Chemical potential energy
  - Free energy is released (more later)

<u>Examples of spontaneous processes:</u>

- A waterfall runs downhill
- A lump of sugar dissolves in a cup of coffee
- At 1 atm, water freezes below 0 ^{0}C and ice melts above 0 ^{0}C
- Heat flows from a hotter object to a colder object
- A gas expands in an evacuated bulb
- Iron exposed to oxygen and water forms rust



Spontaneity does not indicate speed!



© 2017 Pearson Education, Inc.

Non-spontaneous processes are still possible, they just require external energy.

Laws of Thermodynamics

First Law: **Energy is conserved**

Energy can be stored, for example, as:

- Motion of atoms / molecules (kinetic energy)
- Chemical bonds or interaction between atoms/molecules (potential energy)

$$\boxed{\Delta E_{sys} = q + w}$$

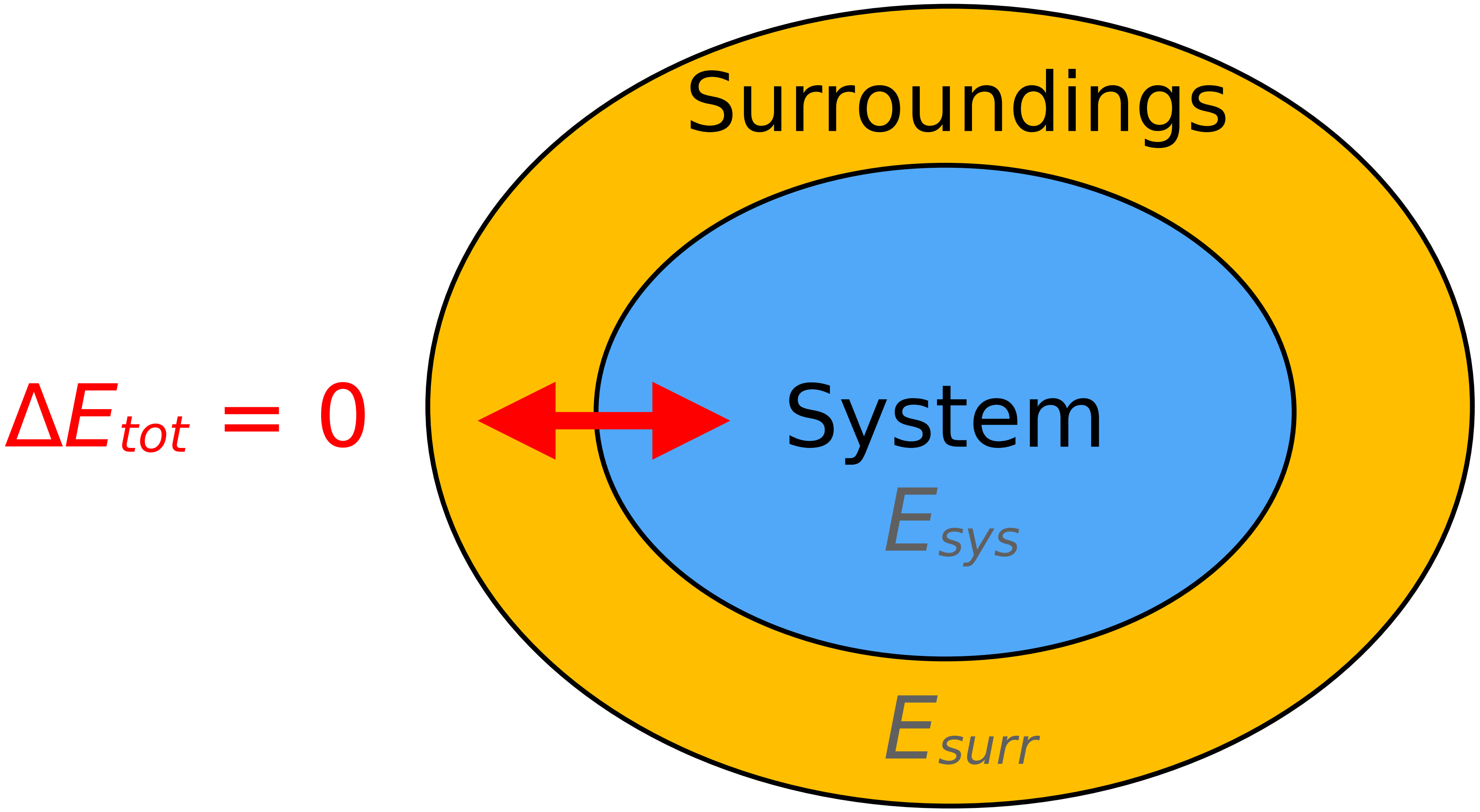
- Change in internal energy (ΔE_{sys}) of a system is the heat (q) exchanged with the surroundings plus the work (w) done by the system on the surroundings.
- Note: Sometimes symbol U (instead of E) is used for internal energy.

1st law of thermodynamics

Energy is conserved: $\Delta E_{tot} = \Delta E_{sys} + \Delta E_{surr} = 0$

This means that $\Delta E_{sys} = -\Delta E_{surr}$:

- Total energy of the universe is constant
- Energy cannot be created or destroyed



1st law of thermodynamics

- When $\Delta E_{sys} > 0$:
  - Energy transferred from surroundings to system
  - System gains energy (“positive thing”)
- When $\Delta E_{sys} < 0$:
  - Energy transferred from system to surroundings
  - System loses energy (“negative thing”)
- Energy exchange between sys and surr: $\Delta E_{sys} = q + w$
- Energy exchange by heat (q) or work (w):

$q = mC\Delta T$ (C = specific heat capacity)

$w = -P\Delta V$ (“pressure-volume work”)

Enthalpy (*H*)

- At constant pressure ($\Delta P = 0$): $\Delta H_{sys} = q$
- The first law then gives: $\Delta H_{sys} = \Delta E_{sys} + P\Delta V$
- Endothermic: $\Delta H_{sys} > 0$ Exothermic: $\Delta H_{sys} < 0$

  system gains heat system loses heat

$$\Delta H^\circ_{rxn} = \sum(n\Delta H^\circ_{f,products}) - \sum(m\Delta H^\circ_{f,reactants})$$

- Review: Hess's Law, Heat of Formation, Work by a system
- Recall: $^\circ$ denotes thermodynamic standard state
  - Pure gases, solids, liquids: 1 atm pressure (often 25 $^\circ$C)
  - Aqueous solutions: 1 M

Enthalpy alone <u>does not</u> indicate spontaneity

Recall Enthalpy (ΔH): Does a decrease in enthalpy mean a reaction proceeds spontaneously?

<u>Spontaneous reactions</u>

$CH_4\,(g) + 2O_2\,(g) \longrightarrow CO_2\,(g) + 2H_2O\,(l) \quad \Delta H^0 = -890.4\text{ kJ}$

$H^+\,(aq) + OH^-\,(aq) \longrightarrow H_2O\,(l) \quad \Delta H^0 = -56.2\text{ kJ}$

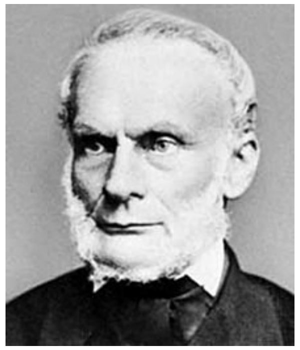
$H_2O\,(s) \longrightarrow H_2O\,(l) \quad \Delta H^0 = 6.01\text{ kJ}$

$NH_4NO_3\,(s) \xrightarrow{H_2O} NH_4^+(aq) + NO_3^-\,(aq) \quad \Delta H^0 = 25\text{ kJ}$

<u>NO</u>

Entropy (*S*)

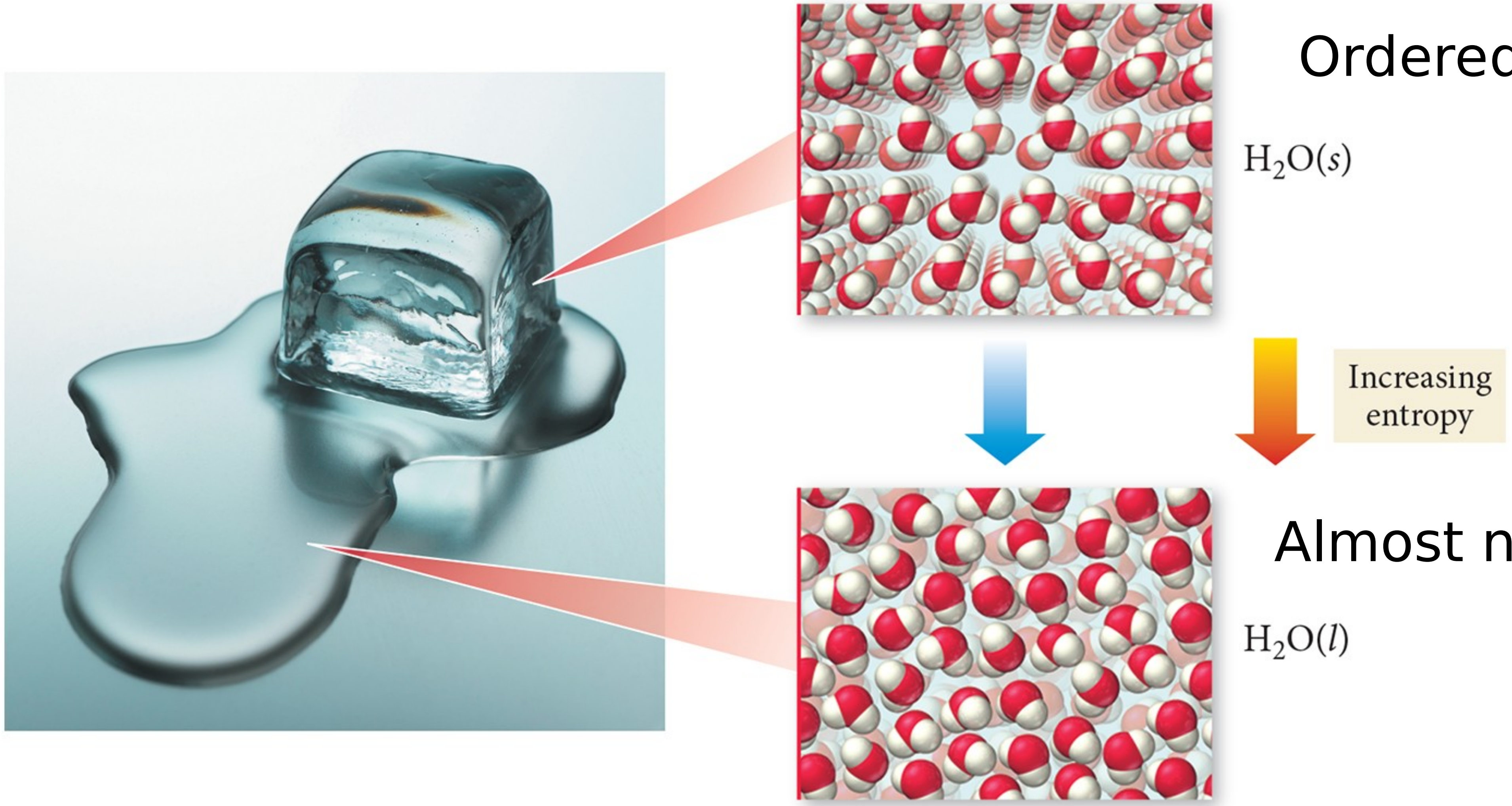
- **Entropy** is a measure of how disordered a system is
- *S* increases with the number of energetically equivalent ways to arrange a system
- *S* is a state function (does not depend on the path how to get from initial to final state)



Rudolph Klausius
Germany, 1822 - 1888

Entropy example 1

Ice melting is an endothermic process at room temperature, but the entropy increases (**Δ*S* > 0**), making it **spontaneous.**

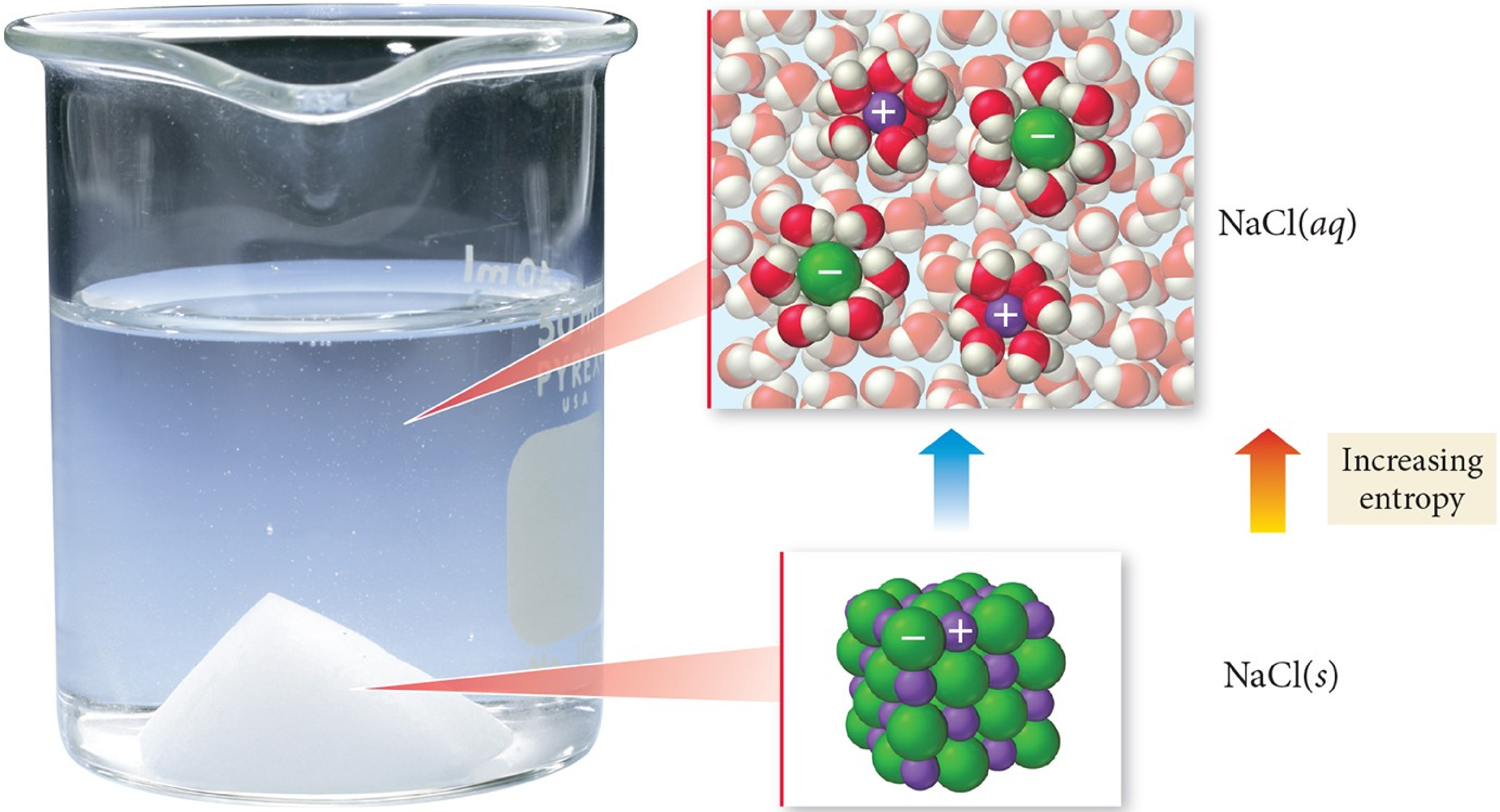


Ordered

Almost no order

Entropy example 2

Dissolving NaCl(s) increases entropy (highly ordered crystal structure is broken down).



Laws of Thermodynamics

Second Law: **For any spontaneous process, the entropy of the universe increases.**

- In the universe, everything tends toward less order
- In a cyclic process, entropy must increase or stay the same but cannot decrease! (Rudolf Clausius)
- Some energy is always lost as heat

- Within a system entropy can decrease, but the overall entropy of the universe (= sys + surr) must increase

Laws of Thermodynamics

Third Law: **As temperature approaches absolute zero, entropy approaches constant value. The entropy of a perfectly ordered crystal at absolute zero temperature is zero.**

However, nothing in the universe has zero entropy (cannot reach absolute zero temperature)!

2nd Law of Thermodynamics examples

- Charging your phone battery:

  Some energy goes to charging, but some is lost as heat to the surroundings

- Car engine:

  Some energy from combustion goes to moving your car, but some is lost as heat or sound

- Generating electricity:

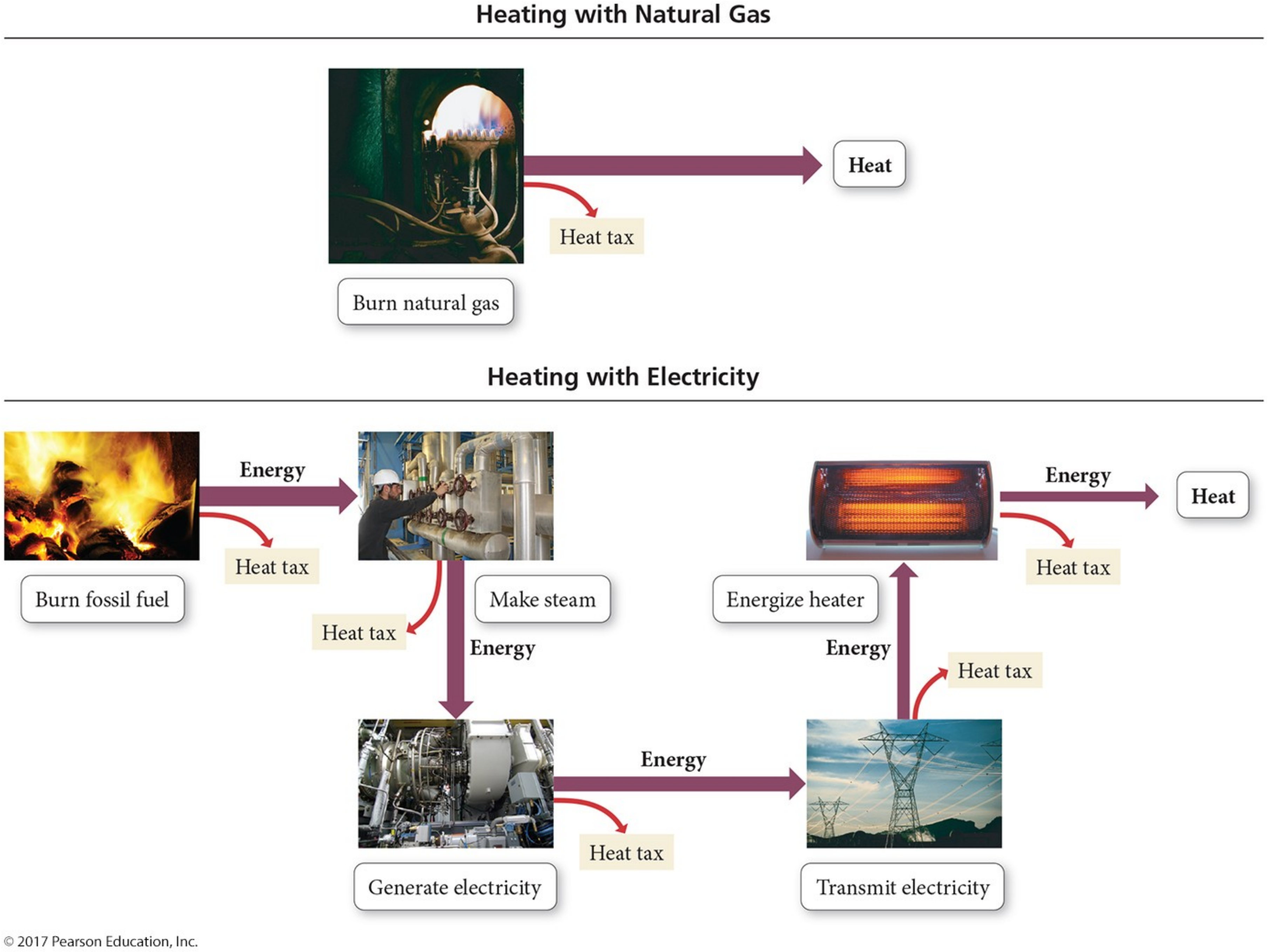
  Some energy from combustion goes to produce electricity, but some is lost as heat

- Pool ball:

  Collision between pool balls would be exact transfer of energy, but some is lost as heat and sound

- Thermodynamics: perpetual motion machines do not exist

2nd Law of Thermodynamics examples



© 2017 Pearson Education, Inc.

Nature’s heat tax

You can decrease S_{sys}, but energy input is required

- Office tends toward disorder:

  But you can clean your office by putting in work

  In that process, some energy is converted to heat, so the entropy of the universe increases

- Life:

  Life represents an ordered system, but the entropy of the universe increases during photosynthesis, digestion, respiration, etc.

Entropy (*S*)

S is a thermodynamic function that increases with the number of energetically equivalent ways to arrange the particles of a system.

Ludwig Boltzmann defined this as:

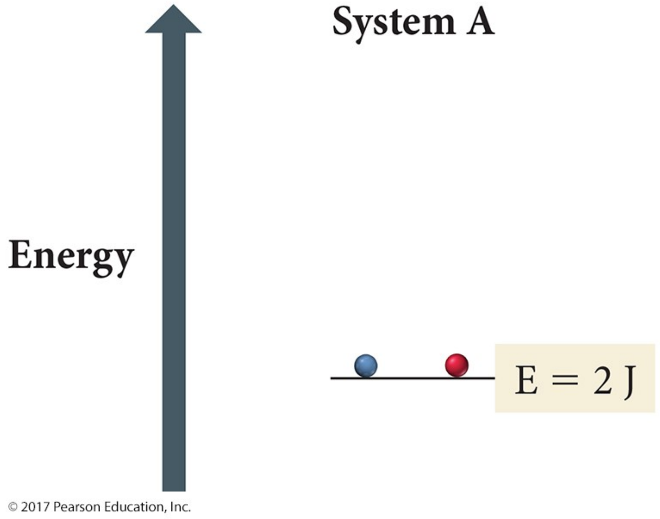
$$\boxed{S = k \ln W}$$

Ludwig Boltzmann
1844 - 1906
Vienna, Austria

- W = number of ways to arrange (no unit)
- S has units of J / K (or J / (K mol) for molar entropy)
- k = Boltzmann constant (= R/N_A) = 1.38 x 10^{-23} J / K

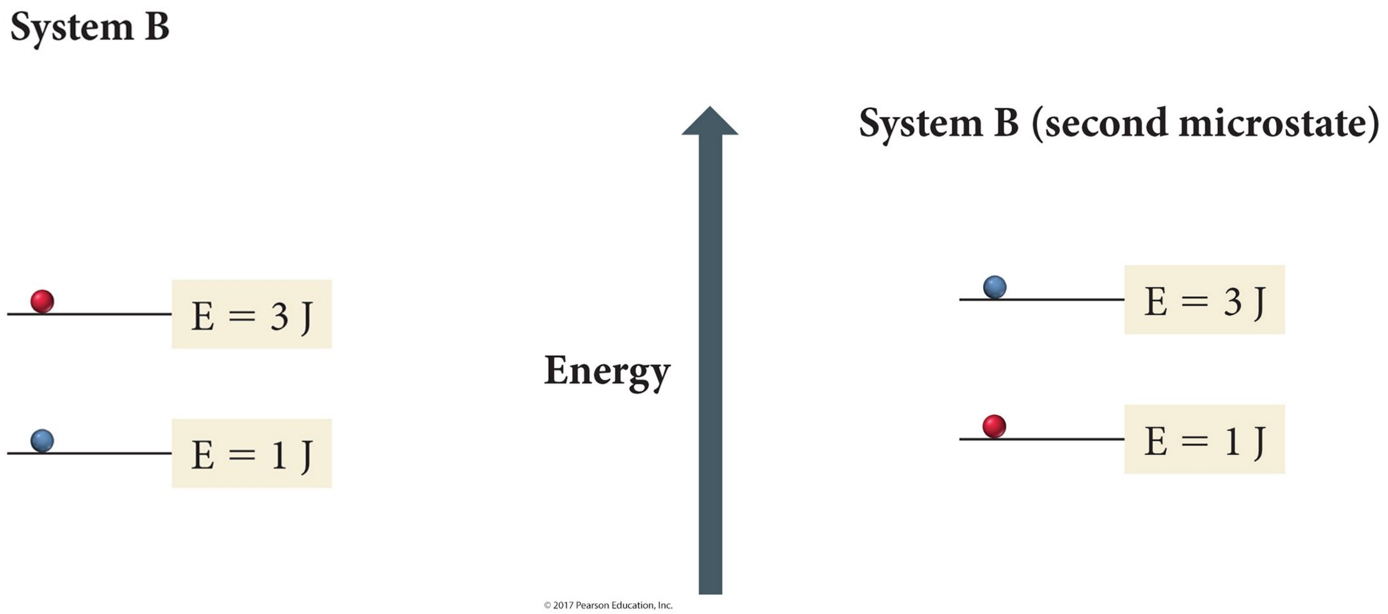
What does function *W* represent?

W is the number of possible “microstates” in a system



© 2017 Pearson Education, Inc.

Energy = 4 *J*



© 2017 Pearson Education, Inc.

Energy = 4 *J*

System A: 1 possible state, ***W* = 1**

System B: 2 possible states (both with energy 4*J*), ***W* = 2**

According to Boltzmann, B has higher entropy than A.

Macrostates vs. Microstates

- **Macro: Large view**

  Example: a gas in a flask

- **Micro: Small view**

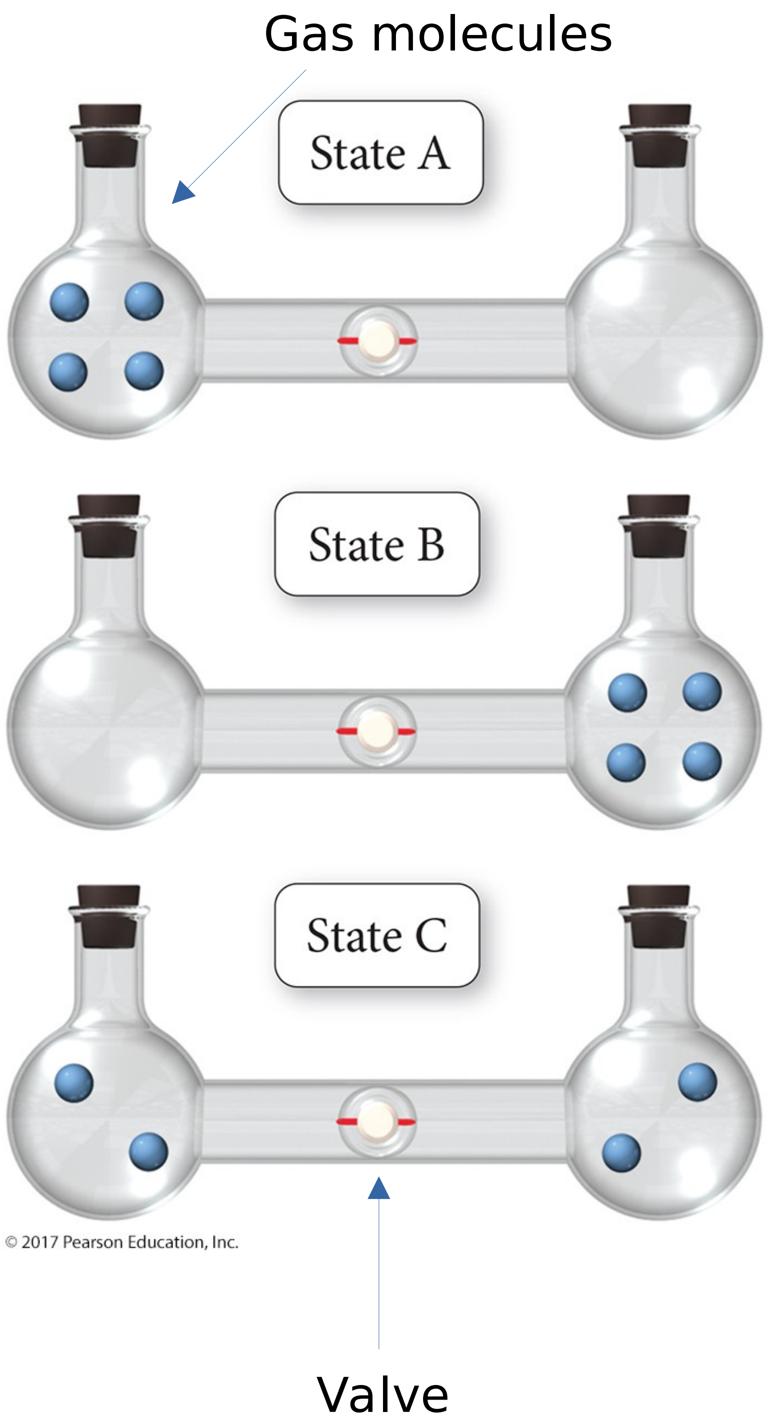
  Example: look at the individual molecules in the flask

- Many microstates may contribute to macrostate
- The more microstates there are for a given macrostate, the higher the entropy

Example: Gas flask

- Start with valve closed: One possible configuration (either A or B).
- Open the valve: More possible configurations (C).

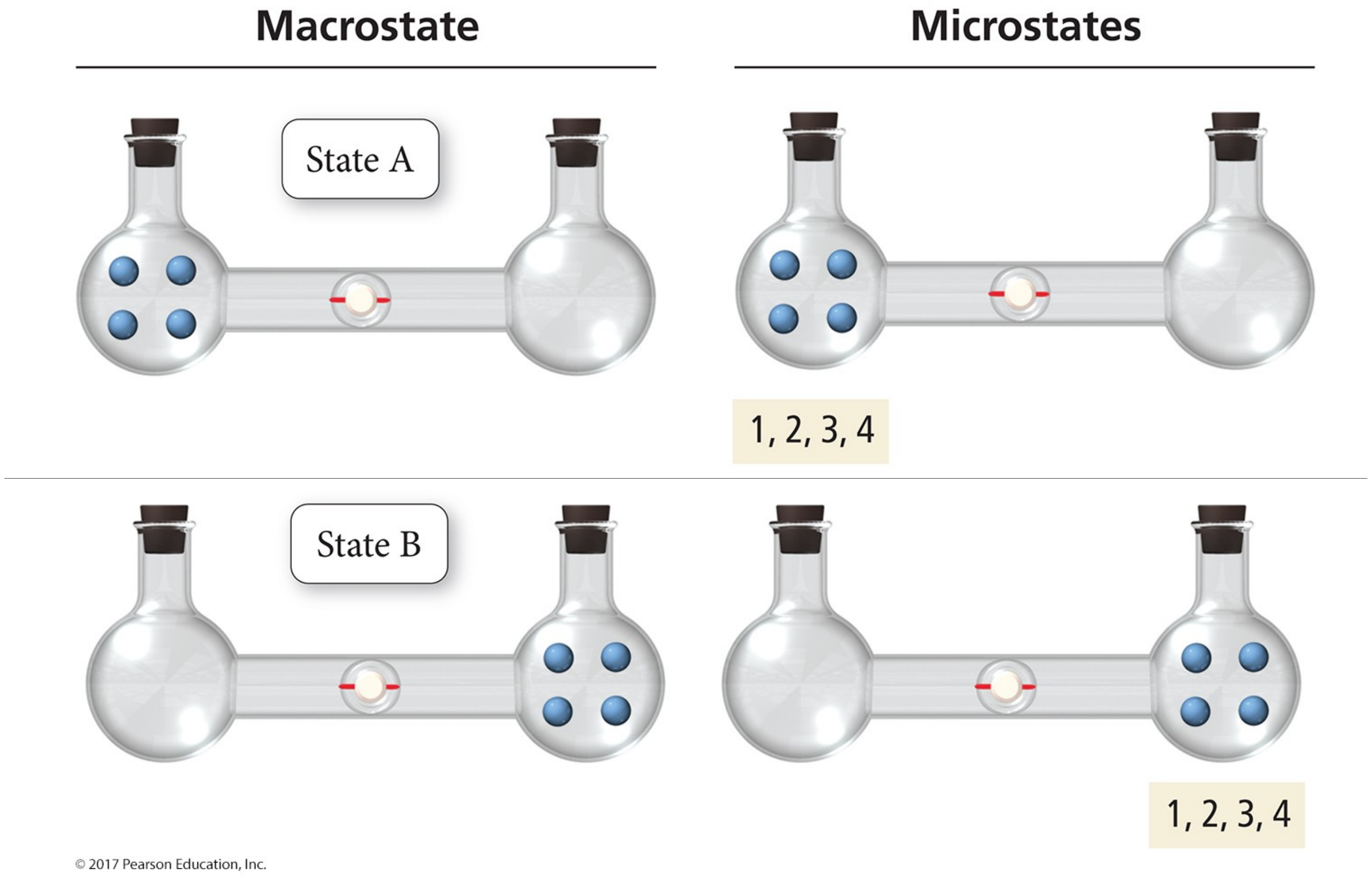
Does the entropy increase after opening the valve? YES?



© 2017 Pearson Education, Inc.

Example: Gas flask

For both State A and State B, there is only one possible microstate:

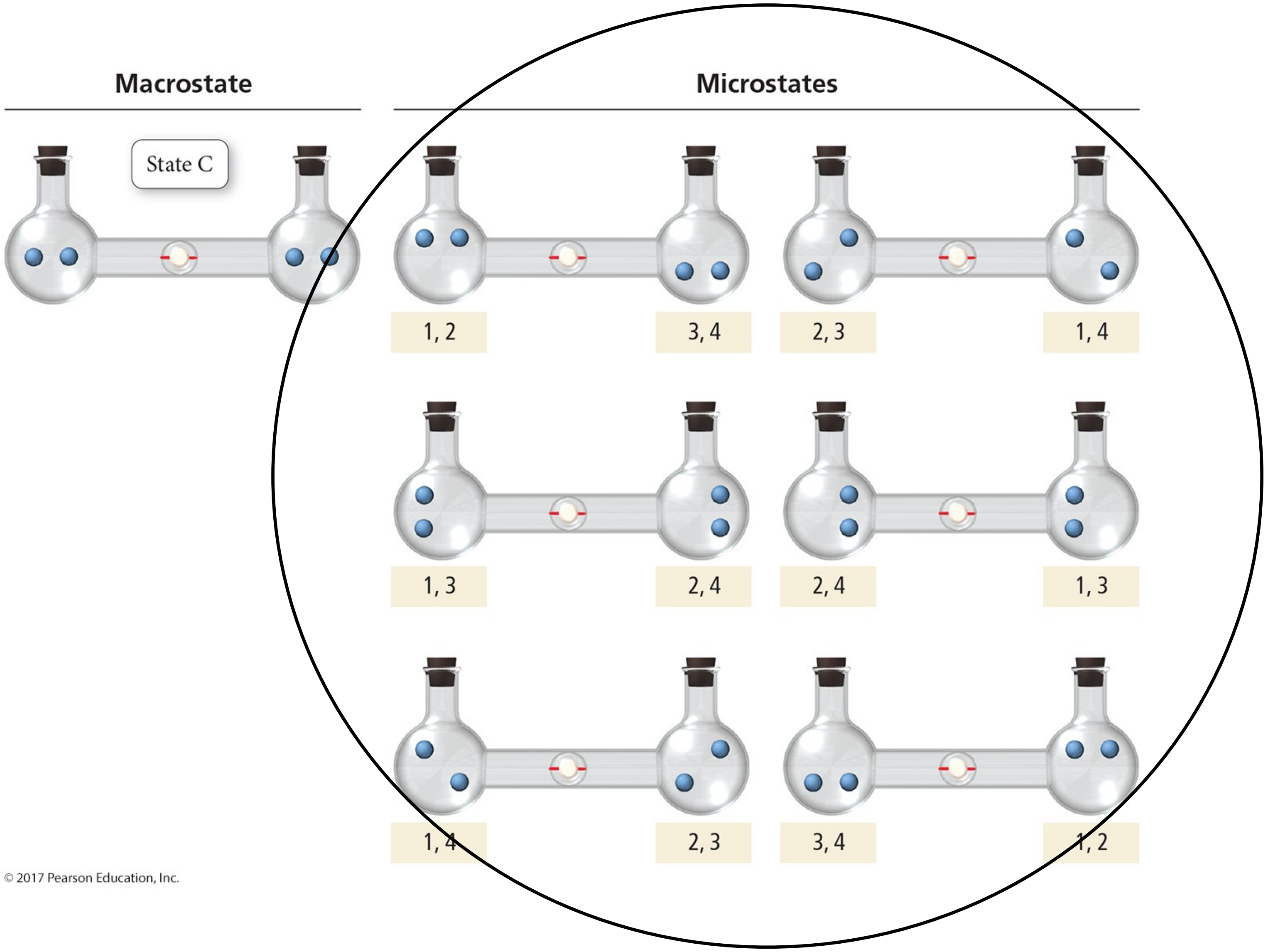


© 2017 Pearson Education, Inc.

$W = 1$

Example: Gas flask

For State C, there are six possible microstates!



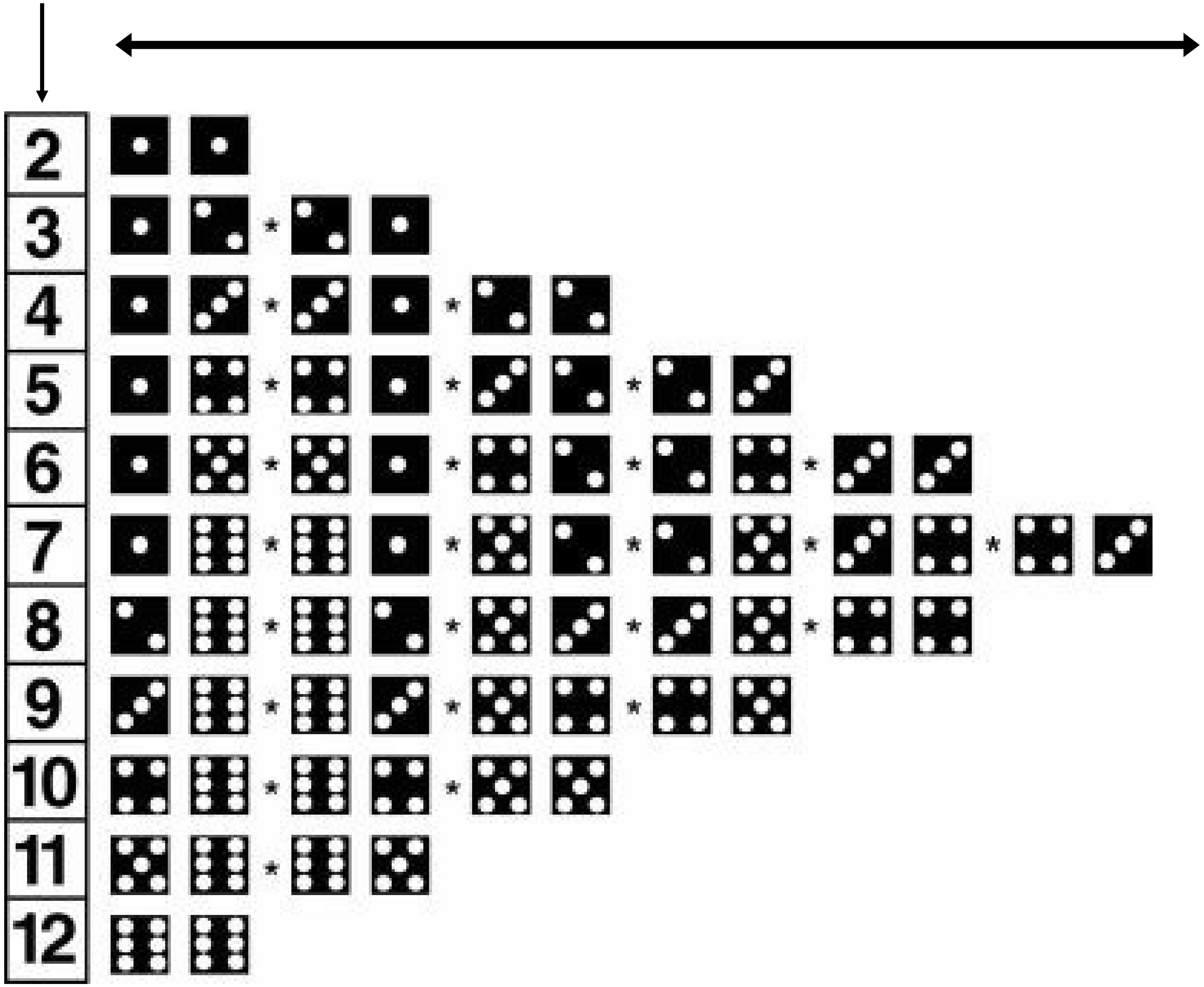
© 2017 Pearson Education, Inc.

$W = 6$

So, State C (6) has higher entropy than A (1) or B (1).

Similar to possible combinations of dice

macrostate microstates



Change in entropy (Δ*S*)

- Think in terms of energy dispersal or randomization
- For a given amount of energy, if the energy can be dispersed more randomly, it will have higher entropy

- The **change** in entropy during a process is important:

$$\boxed{\Delta S = S_{fin} - S_{ini}}$$

(ini = Initial state; fin = Final state)

Back to the 2nd Law of Thermodynamics

- Second Law: **For any spontaneous process, the entropy of the universe must increase,**

$$\Delta S_{tot} = \Delta S_{sys} + \Delta S_{surr} > 0$$

- A chemical system **proceeds in the direction that increases the entropy of the universe** (ΔS_{tot})
- It goes toward the state that has the largest number of energetically equivalent ways to arrange (for the universe)
- For the system this means changing its energy/entropy (often to minimize the energy and increase entropy)

Entropy and change of state

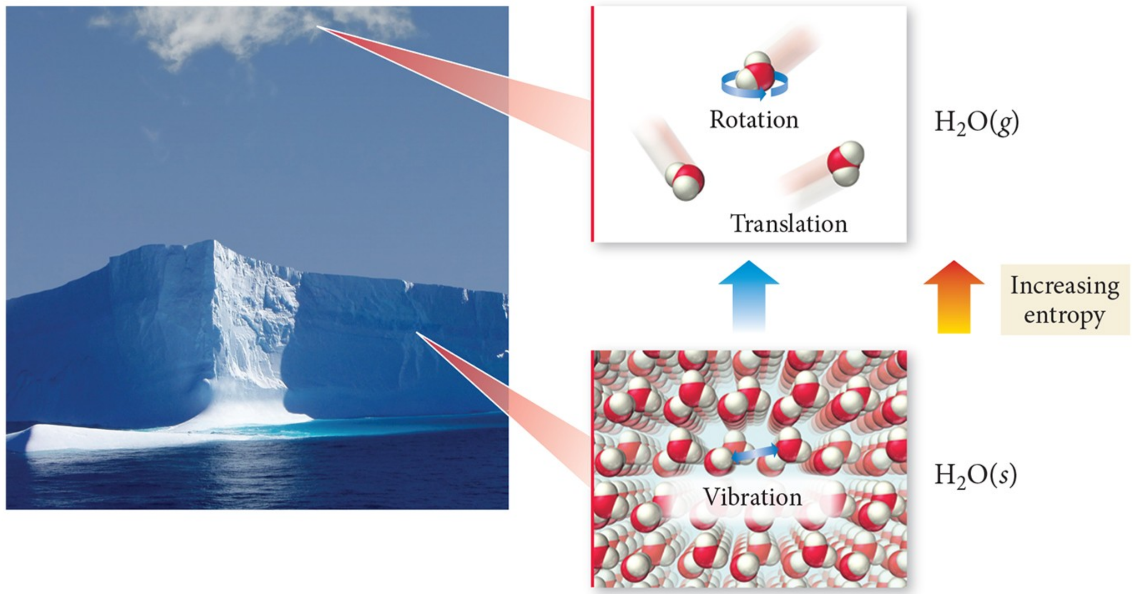
- Solids: Molecules/atoms are locked in their positions

  Location of Energy: **vibration within the bonds / lattice**

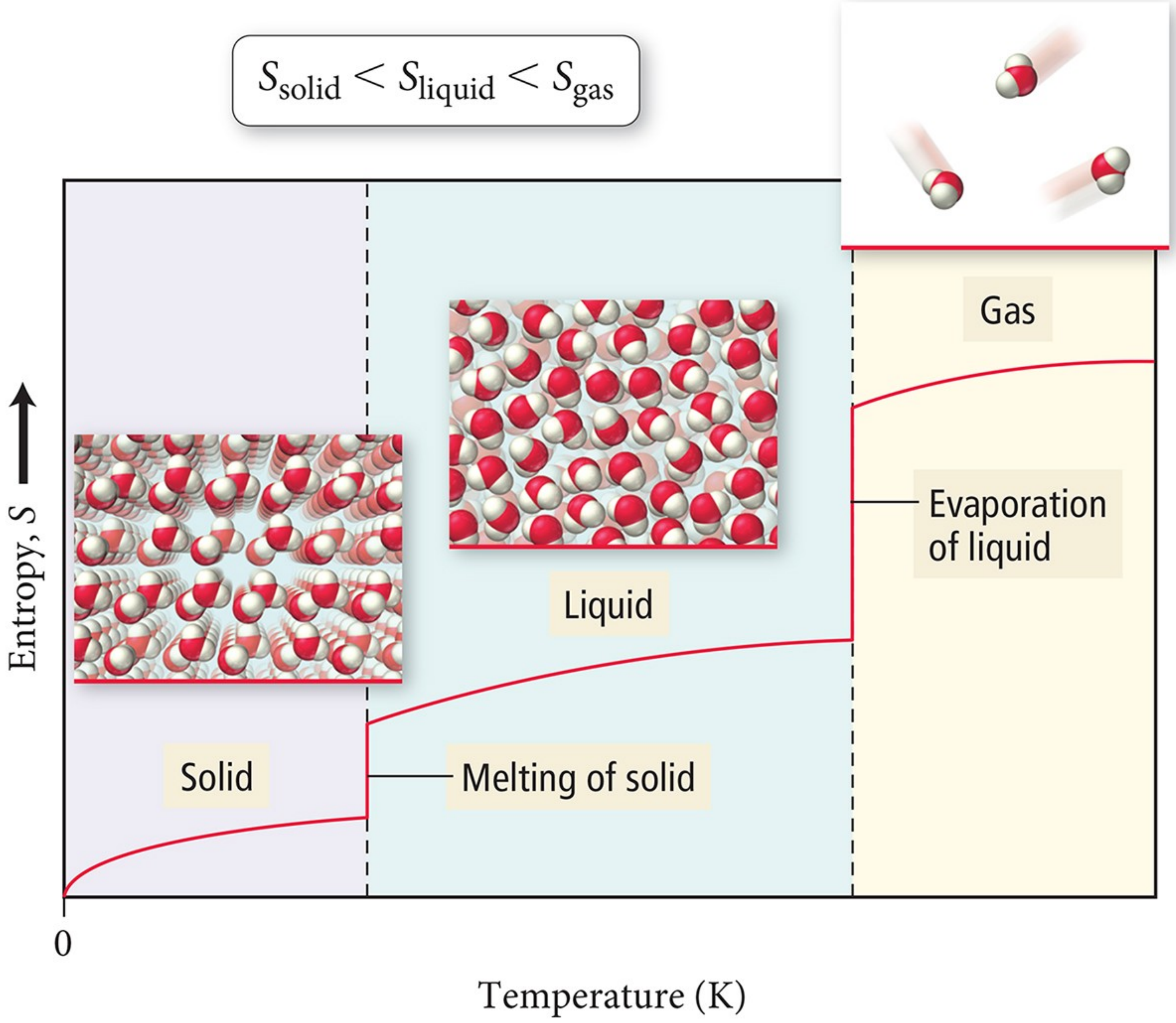
- Liquids and Gases: Molecules are not locked in their positions

  Location of Energy: **vibration within the bonds** + **translation** (molecules move) + **rotation** (molecules spin around their center of mass)

Additional "Places" for Energy



Entropy and change of state (phase transitions)



- Melting and evaporation can be spontaneous even though they are endothermic

- Entropy jumps at phase transition points

Entropy, reactions, and molecules

General trends:

- *S* increases when the number of gas molecules increases:

  For example: A(*g*) → 2B(*g*)
- *S* decreases: gas → liquid → solid
- More atoms in a molecule results in higher *S*:

  $CH_3OH(g)$ vs. $O_2(g)$
- Higher molar mass (for a given number of atoms in the molecule) tends to increase *S*:

  $O_2(g)$ (32 g/mol) vs. $N_2(g)$ (28 g/mol)

Predict the sign of ΔS_{sys} for each process

- $H_2O(g) \rightarrow H_2O(l)$
- $H_2O(s) \rightarrow H_2O(l)$
- $Mg(s) + Cl_2(g) \rightarrow MgCl_2(s)$
- $N_2(g) + 3H_2(g) \rightarrow 2NH_3(g)$
- $2O_3(g) \rightarrow 3O_2(g)$