CHE 2615
Physical Chemistry

Lecture1: 2nd law of thermodynamics

UNZA

2021

First Law of Thermodynamics

- It states that “Energy cannot be created nor destroyed”.
- During any process, the energy of the universe is constant.

$$dU_{universe} = dU_{sys} + dU_{surroundings} = \text{ZERO !!!}$$

- Therefore, the total energy of the universe is a constant.
- The First Law of thermodynamics led to the introduction of the internal energy, *U.*

First Law of Thermodynamics

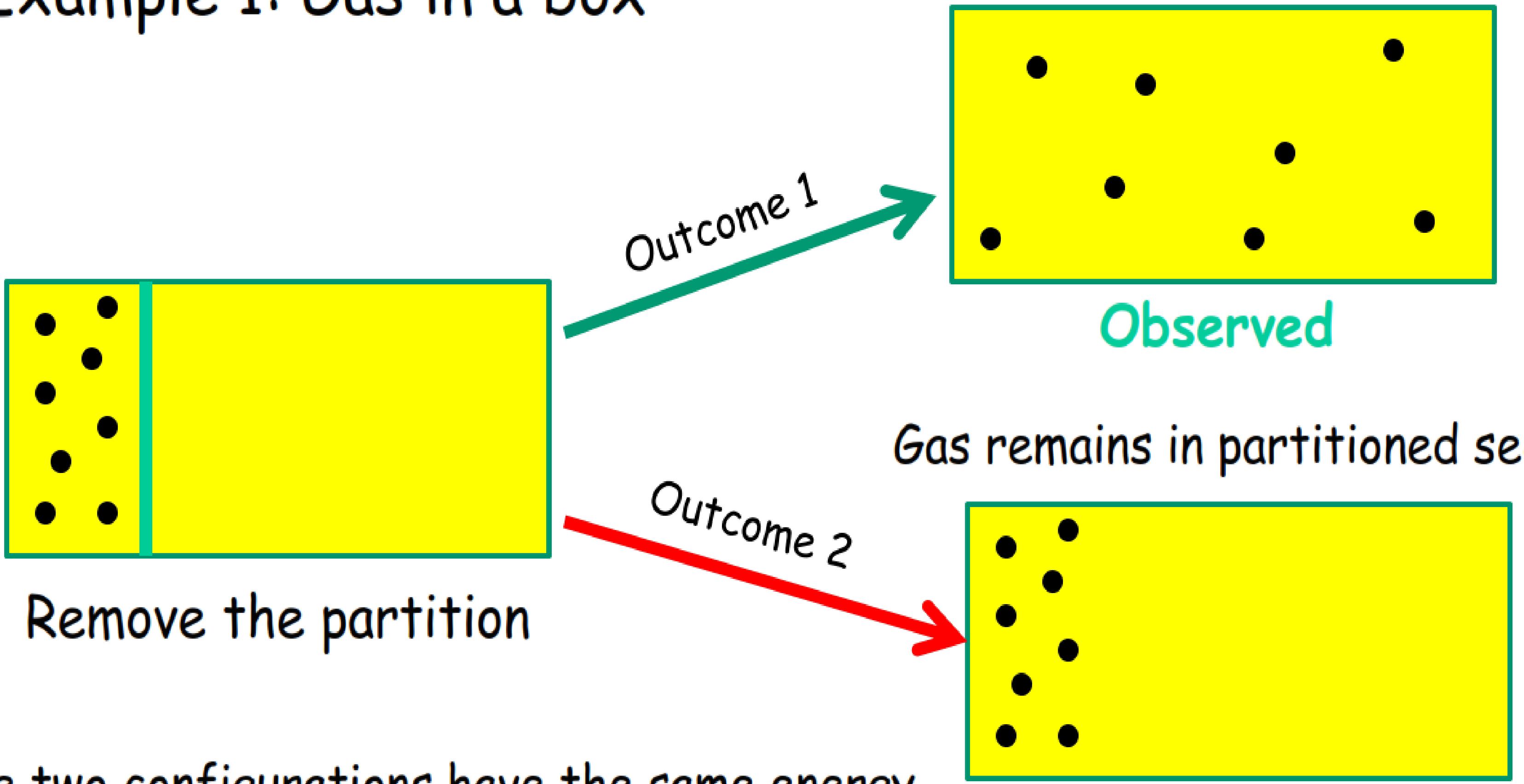
- Energy can, however, be converted from one form to another or transferred from a system to the surroundings or vice versa.
- Any energy transfer between system and surroundings is accomplished via ***work*** or ***transfer of heat***.

$$dU = dq + dw$$

- The internal energy is a state function that ***lets us assess whether a change is permissible***.
- Only those changes may occur for which the internal energy of an isolated system remains constant.

First Law – Limitations

Example 1: Gas in a box



Gas expands to fill volume

Outcome 1

Observed

Remove the partition

Outcome 2

Gas remains in partitioned section

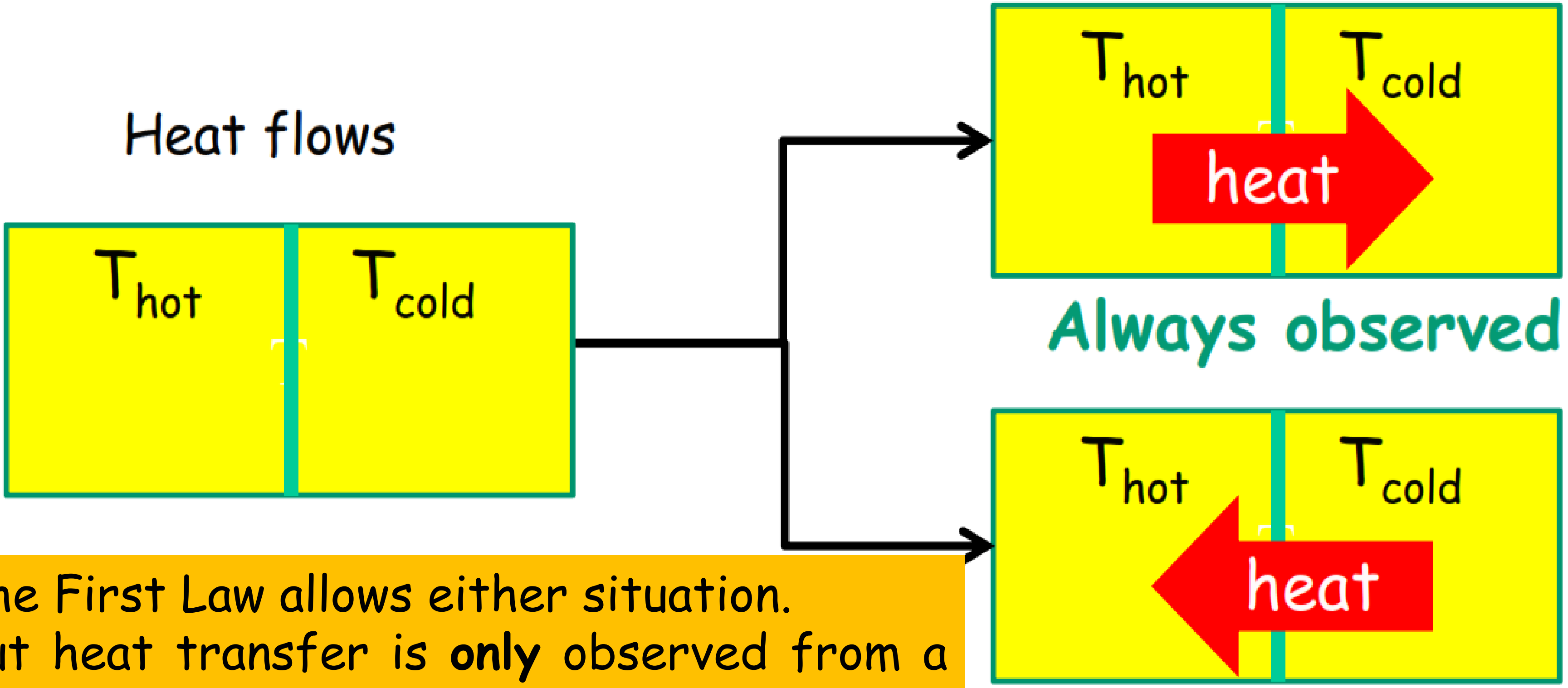
Not Observed

The two configurations have the same energy.
We gain no stability by choosing 1 or 2.
Both are possible!
Why is only 1 observed?

First law is happy with either outcome!

First Law – Limitations

- Example 3: heat flow
- Suppose we place a hot body next to a cold body.



Heat flows

Always observed

Never observed

The First Law allows either situation.
But heat transfer is **only** observed from a hot **body to a cold body**.

The essence of these examples is that just because a process is **POSSIBLE** does **NOT** mean that it is spontaneous.

First Law of Thermodynamics

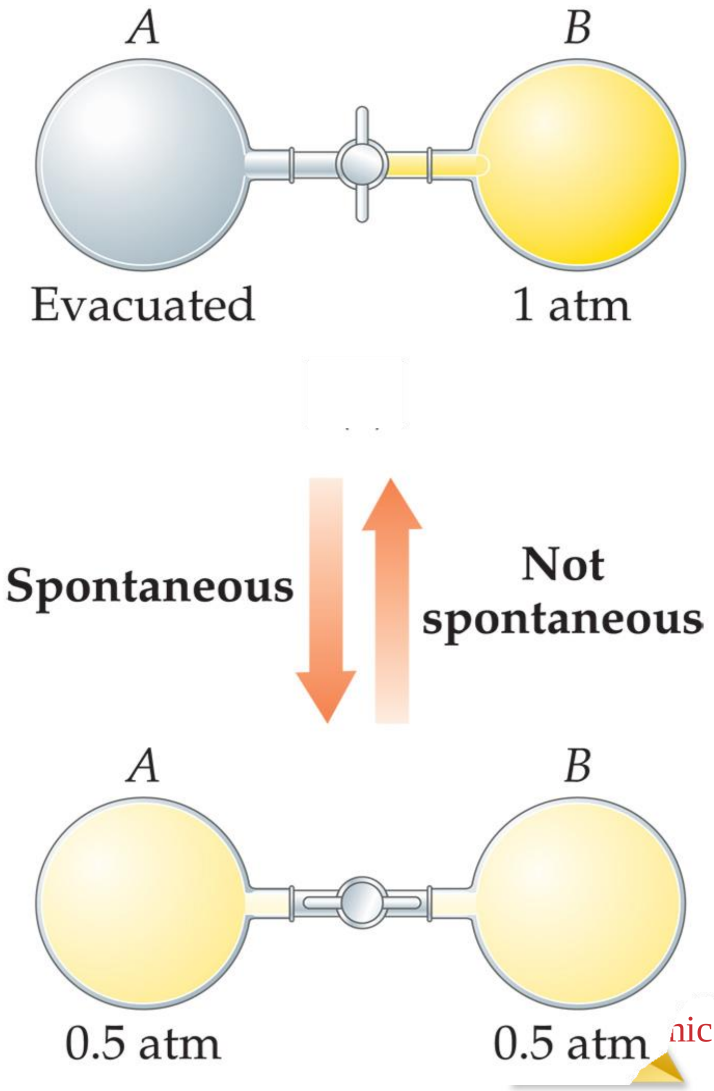
- The First Law uses the internal energy to ***identify permissible changes***; the Second Law uses the entropy to ***identify the spontaneous changes among those permissible changes***.
- We begin by defining the concept of spontaneity

Spontaneous Processes

- A **SPONTANEOUS** process is one that occurs naturally (needs no external source of work).
- Or Spontaneous processes are those that can proceed on there own accord, without any outside assistance, or without any outside intervention.
- A **NON-SPONTANEOUS** process is a possible process (allowed by the 1st Law), BUT an external source of work is required to drive it.
- The 1st Law requires a process to be possible, but says nothing about the spontaneity of the process
- In general, the tendency of a process to occur naturally is called the spontaneity.

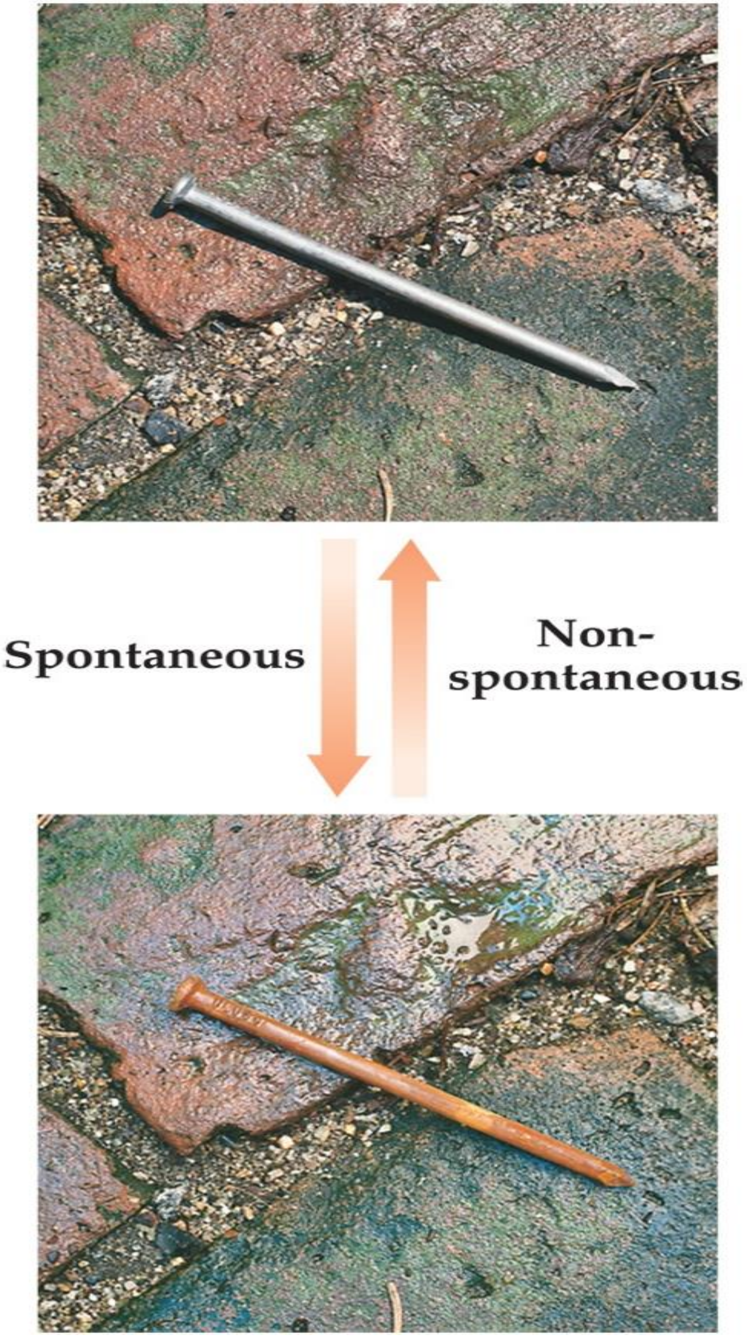
Spontaneous Processes

- Examples of spontaneous processes includes:
  1) Confined gas
     - The gas in vessel *B* will spontaneously effuse into vessel *A* until equilibrium is reached.
     - Once equilibrium is reached, the gas will *not* spontaneously effuse



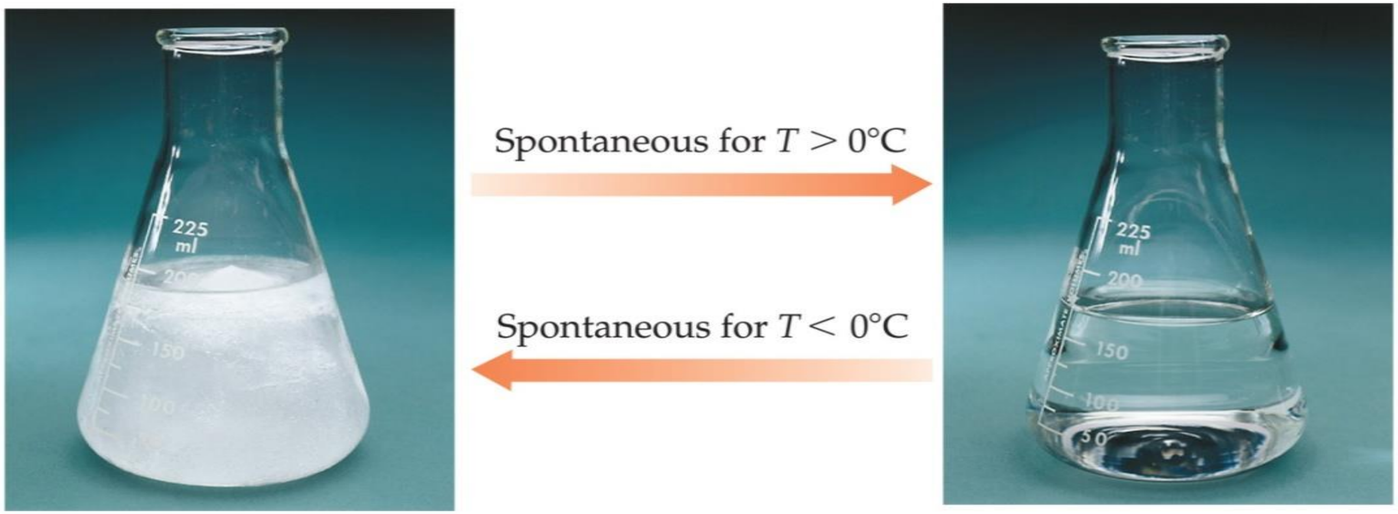
Spontaneous Processes

2. Rusting of iron
    - Processes that are spontaneous in one direction are non-spontaneous in the reverse direction.



Spontaneous Processes

- Processes that are spontaneous at one temperature may be non-spontaneous at other temperatures.
- Above 0°C it is spontaneous for ice to melt.
- Below 0°C the reverse process is spontaneous.



Criteria of spontaneity

- Some important criteria of spontaneous physical and chemical changes are listed below.

(1) **A spontaneous change is one-way or unidirectional. For reverse change to occur, work has** to be done.

(2) **For a spontaneous change to occur, time is no factor. A spontaneous reaction may take** place rapidly or very slowly.

(3) **If the system is not in equilibrium state (unstable), a spontaneous change is inevitable.** The change will continue till the system attains the state of equilibrium.

Criteria of spontaneity

(4) Once a system is in equilibrium state, it does not undergo any further spontaneous change in state if left undisturbed**. To take the system away from equilibrium, some external work** must be done on the system.

(5) A spontaneous change is accompanied by decrease of internal energy or enthalpy (ΔH).

- It implies that only such reactions will occur which are exothermic.

Criteria of spontaneity

- For many years scientists believed that only exothermic changes resulting in a lowering of internal energy or enthalpy could occur spontaneously.
- But the melting of ice and evaporation of rain water are endothermic processes which proceed spontaneously.
- Clearly, there is some other factor in addition to ΔH which governs spontaneity.
- It is the second law of thermodynamics which introduces this new factor that is called *entropy*.

Spontaneity and Randomness

- Careful examination shows that in each of the processes *viz.*, melting of ice and evaporation of water, there is an increase in randomness or disorder of the system.
- The water molecules in ice are arranged in a highly organised crystal pattern which permits little movement.
- As the ice melts, the water molecules become disorganised and can move more freely.
- The movement of molecules becomes freer still when the water evaporates into space as now they can roam about throughout the entire atmosphere.

Spontaneity and Randomness

- In other words, we can say that the randomness of the water molecules increases as ice melts into water or water evaporates into space.

Melting of Ice is a classic example of 'Increasing Entropy'.

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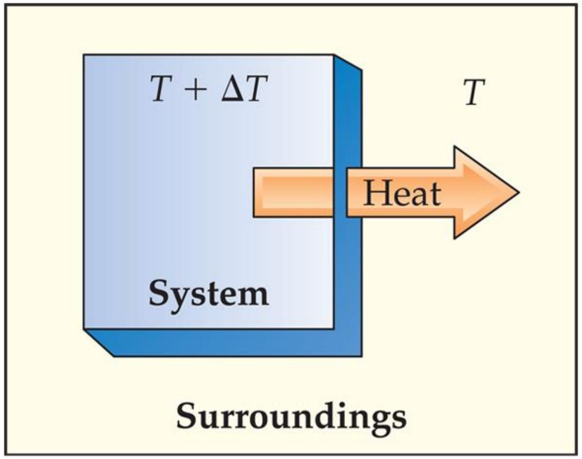
Increase in Randomness Favours a Spontaneous Change

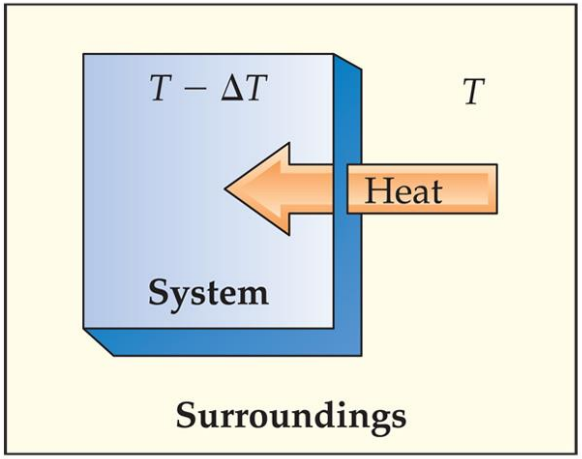
- A change that brings about randomness is more likely to occur than one that brings about order.
- Let us suppose we have a suit of playing cards arranged numerically.
- We can see that *the* sequence of cards is certainly highly organised.
- Now, if we throw the cards into the air, collect them and re-stack them, we will almost surely find that they have been placed at random.

Increase in Randomness Favours a Spontaneous Change

- This is expected because when the cards are tossed, there are many ways for them to be disordered, while there is only one way for them to come together again in their original sequence.
- Thus on the basis of pure chance a disordered sequence is far more probable than the ordered one with which we started.
- The same law of chance applies to any physical or chemical process.

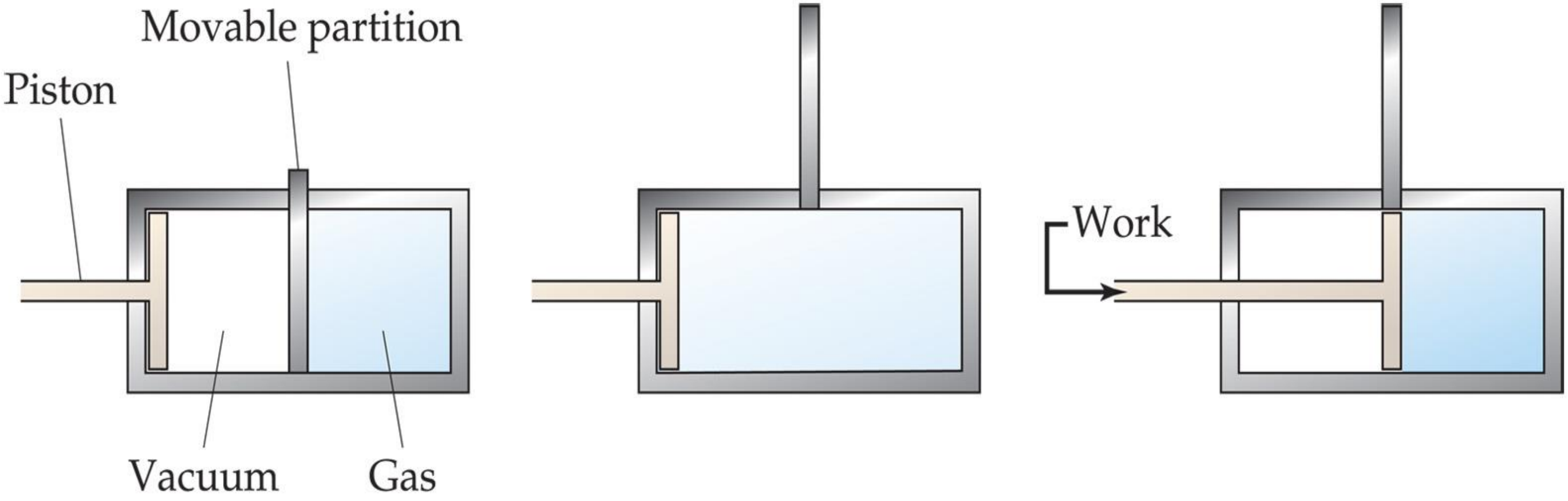
Reversible Processes





- In a reversible process the system changes in such a way that the system and surroundings can be put back in their original states by exactly reversing the process.
- Changes are infinitesimally **small** in a reversible process.

Irreversible Processes



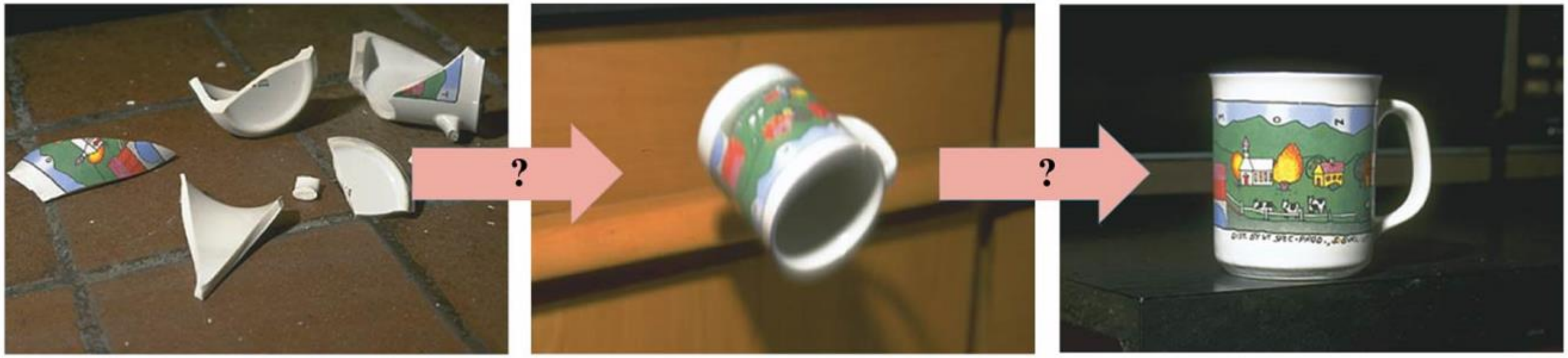
- Irreversible processes cannot be undone by exactly reversing the change to the system.
- All **Spontaneous** processes are **irreversible**.
- All **Real** processes are **irreversible**.

Chemical
Thermodynamics

Second Law - Formulated

- Spontaneity **REQUIRES** us to formulate the 2nd Law.
- You are likely to have already been familiar with the 2nd Law in at least one of several forms

The Second Law of Thermodynamics – Introduction



(a) Initial state.

(b) Later: cup reassembles and rises up.

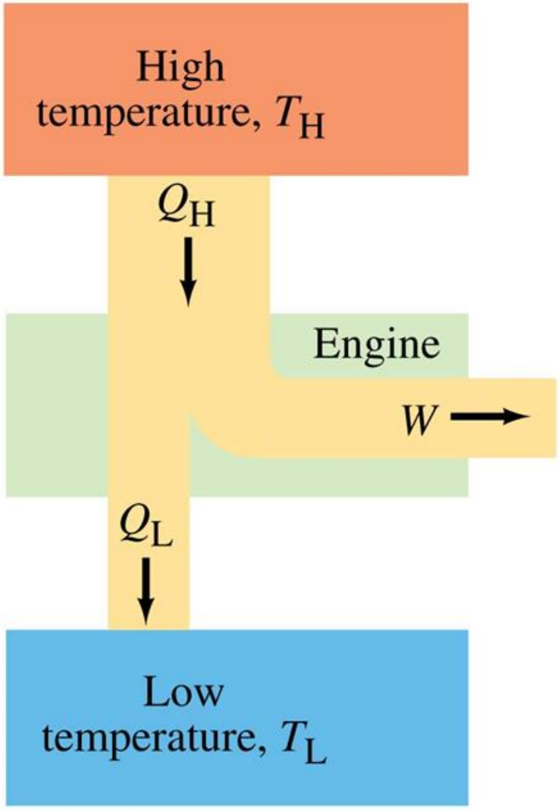
(c) Later still: cup lands on table.

- The absence of the process illustrated above indicates that conservation of energy is not the whole story.
- If it were, movies running backwards would look perfectly normal to us!

Heat Engines

- It is easy to produce thermal energy using work, but how does one produce work using thermal energy?

- This is a heat engine; mechanical energy can be obtained from thermal energy only when heat can flow from a higher temperature to a lower temperature.



The Second Law of Thermodynamics – Introduction

- The second law of thermodynamics is a statement about which processes occur and which do not.

- There are many ways to state the second law; here is one:

1. ***Heat can flow spontaneously from a hot object to a cold object; it will not flow spontaneously from a cold object to a hot object.***

Entropy

- *Entropy* (*S*) is a term coined by Rudolph Clausius in the 19th century.
- Clausius was convinced of the significance of the ratio of heat delivered and the temperature at which it is delivered,

$$\frac{q}{T}$$

- *Entropy can be thought of as a measure of the randomness of a system*.
- It is related to the various modes of motion in molecules.

Order to Disorder

- This gives us yet another statement of the second law:

3. ***Natural processes tend to move toward a state of greater disorder.***

Example 1:

- If you put milk and sugar in your coffee and stir it, you wind up with coffee that is uniformly milky and sweet.
- No amount of stirring will get the milk and sugar to come back out of solution.

Order to Disorder

Example 2:

- When a tornado hits a building, there is major damage.
- You never see a tornado approach a pile of rubble and leave a building behind when it passes.
- Thermal equilibrium is a similar process — the uniform final state has more disorder than the separate temperatures in the initial state.
- Growth of an individual, is a processes of increasing order.

Order to Disorder

- Do they violate the second law of thermodynamics?
- No! These are not isolated systems.
- Energy comes into them in the form of food, sunlight, and air, and energy also leaves them.
- The second law of thermodynamics is the one that defines the arrow of time—processes will occur that are not reversible, and movies that run backward will look silly.

Entropy

- Like total energy, *E*, and enthalpy, *H*, entropy is a state function.
- Therefore,

$$\Delta S = S_{final} - S_{initial}$$

- **A process accompanied by an increase in entropy tends to be spontaneous.**
- Consider a molecular system in states *A and B*
- In state *A* all the molecules are arranged and highly ordered, while in state *B* the molecules are present at random and it is highly disordered.

Entropy

(1) By definition, the entropy of *A* is low and that of *B* high.

Thus an increase of entropy occurs in the change from *A to B.*

(2) According to the law of chance (probability), *A is less probable and B is more probable.*

Therefore, the change from *A to B is spontaneous.*

Entropy

(3) From (1) and (2), it follows that the change from *A to B* which is accompanied by increase of entropy will tend to be spontaneous.

Hence we can say, in general, that a change in a system which is accompanied by an increase in entropy, tends to be spontaneous

Entropy and the Second Law of Thermodynamics

- Definition of the change in entropy *S* when an amount of heat *Q* is added:

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

- Another statement of the second law of thermodynamics:

2. The total entropy of an isolated system never decreases.

Entropy

- For a process occurring at constant temperature (an isothermal process):

$$\Delta S = \frac{q_{rev}}{T}$$

q_{rev} = the heat that is transferred when the process is carried out **reversibly** at a constant temperature.

T = temperature in Kelvin.

Unavailability of Energy; Heat Death

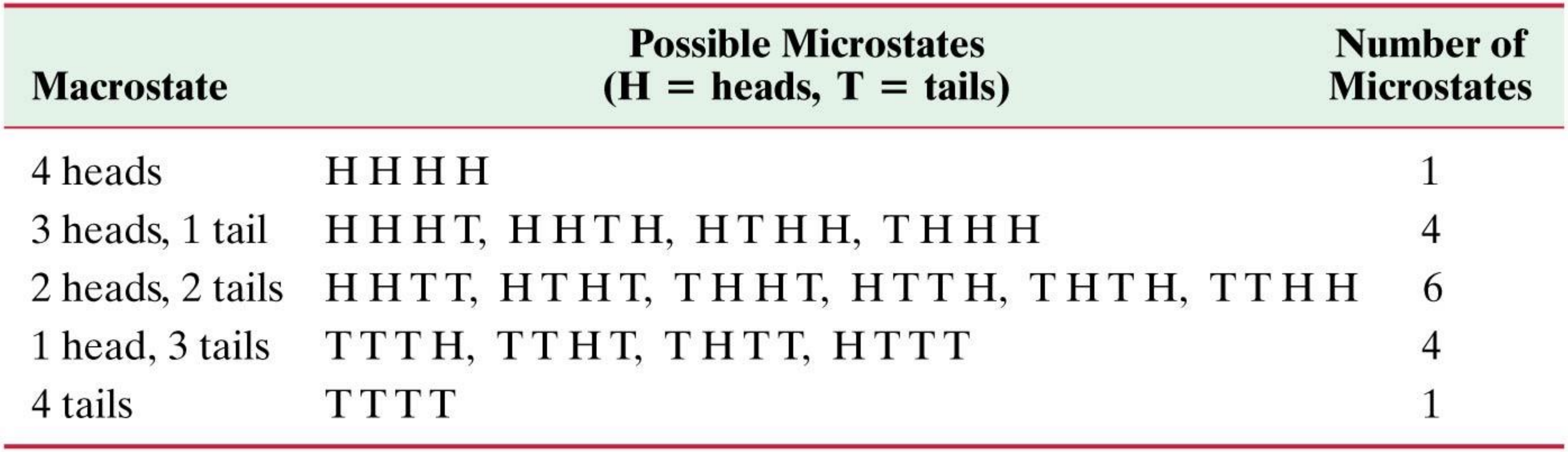
- Another consequence of the second law:
- **In any natural process, some energy becomes unavailable to do useful work**.
- If we look at the universe as a whole, it seems inevitable that, as more and more energy is converted to unavailable forms, the ability to do work anywhere will gradually vanish.
- This is called the heat death of the universe.

Statistical Interpretation of Entropy and the Second Law

- A macrostate of a system is specified by giving its macroscopic properties—temperature, pressure, and so on.
- A microstate of a system describes the position and velocity of every particle.
- For every macrostate, there are one or more microstates.

Statistical Interpretation of Entropy and the Second Law

- A simple example: tossing four coins.
- The macrostates describe how many heads and tails there are; the microstates list the different ways of achieving that macrostate.



Macrostate	Possible Microstates (H = heads, T = tails)	Number of Microstates
4 heads	H H H H	1
3 heads, 1 tail	H H H T, H H T H, H T H H, T H H H	4
2 heads, 2 tails	H H T T, H T H T, T H H T, H T T H, T H T H, T T H H	6
1 head, 3 tails	T T T H, T T H T, T H T T, H T T T	4
4 tails	T T T T	1

Statistical Interpretation of Entropy and the Second Law

- We assume that each microstate is equally probable; the probability of each macrostate then depends on how many microstates are in it.
- The number of microstates quickly becomes very large if we have even 100 coins instead of four; the table on the next slide lists some macrostates, how many microstates they have, and the relative probability that each macrostate will occur. Note that the probability of getting fewer than 20 heads or tails is extremely small.

Statistical Interpretation of Entropy and the Second Law

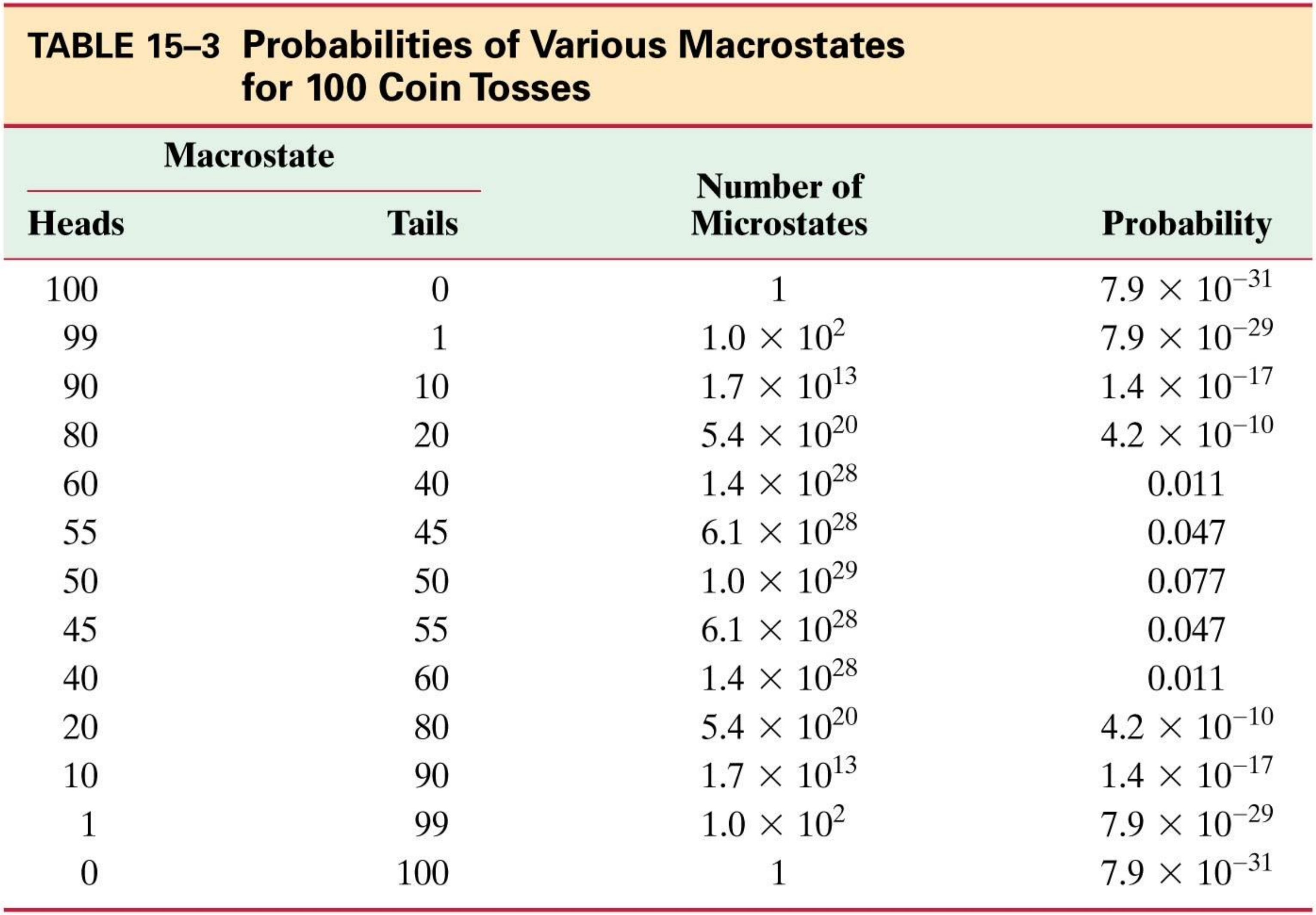


TABLE 15–3 Probabilities of Various Macrostates for 100 Coin Tosses

Macrostate			
Heads	**Tails**	**Number of Microstates**	**Probability**
100	0	1	7.9×10^{-31}
99	1	1.0×10^{2}	7.9×10^{-29}
90	10	1.7×10^{13}	1.4×10^{-17}
80	20	5.4×10^{20}	4.2×10^{-10}
60	40	1.4×10^{28}	0.011
55	45	6.1×10^{28}	0.047
50	50	1.0×10^{29}	0.077
45	55	6.1×10^{28}	0.047
40	60	1.4×10^{28}	0.011
20	80	5.4×10^{20}	4.2×10^{-10}
10	90	1.7×10^{13}	1.4×10^{-17}
1	99	1.0×10^{2}	7.9×10^{-29}
0	100	1	7.9×10^{-31}

Statistical Interpretation of Entropy and the Second Law

- Now we can say that the second law does not forbid certain processes; all microstates are equally likely.

- However, some of them have an extraordinarily low probability of occurring—a lake freezing on a hot summer day, broken crockery re-assembling itself; all the air in a room moving into a single corner.

- Remember how low some probabilities got just in going from four coins to 100—if we are dealing with many moles of material, they can become so rare as to be effectively impossible.

Statement of the second law

- ***"The entropy of the universe does not change for reversible processes and increases for spontaneous processes"*.**

Or

- ***Whenever a spontaneous process takes place, it is accompanied by an increase in the total energy of the universe.***
- More specifically, we take the term 'universe' to mean the system and the surroundings. Thus,

$$\Delta S_{univ} = \Delta S_{system} + \Delta S_{surrounding}$$

Second Law of Thermodynamics

- The second law, as stated above, tells us that when an irreversible spontaneous process occurs, the entropy of the system and the surroundings increases.
- In other words:

$$\Delta S_{univ} > 0$$

- When a reversible process occurs, the entropy of the system remains constant.

$$\Delta S_{univ} = 0$$

Second Law of Thermodynamics

The entropy of the universe increases (real, spontaneous processes).

But, entropy can decrease for individual systems.

Reversible (ideal):

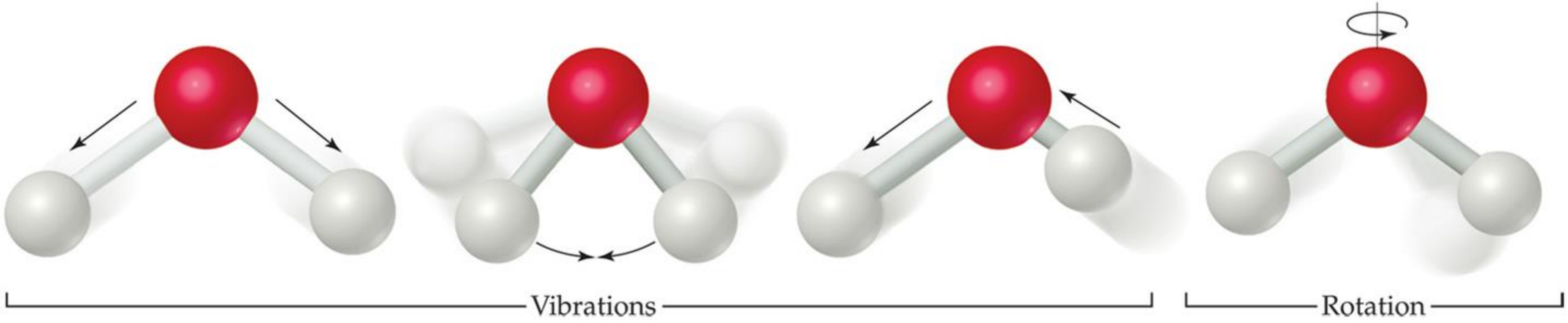
$$\Delta S_{univ} = \Delta S_{system} + \Delta s_{surrounding} = 0$$

Irreversible (real, spontaneous):

$$\Delta S_{univ} = \Delta S_{system} + \Delta S_{surrounding} > 0$$

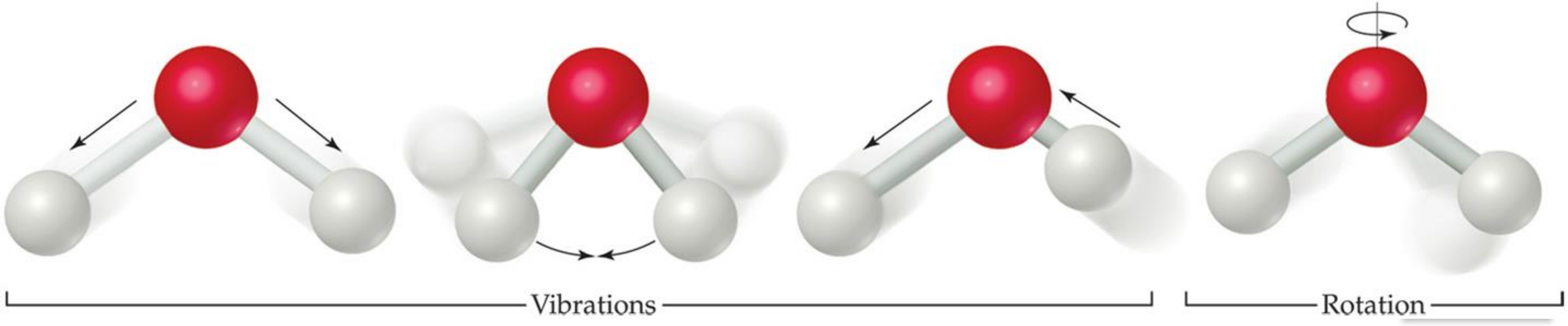
Entropy on the Molecular Scale

- Ludwig Boltzmann described the concept of entropy on the molecular level.
- Temperature is a measure of the average kinetic energy of the molecules in a sample.



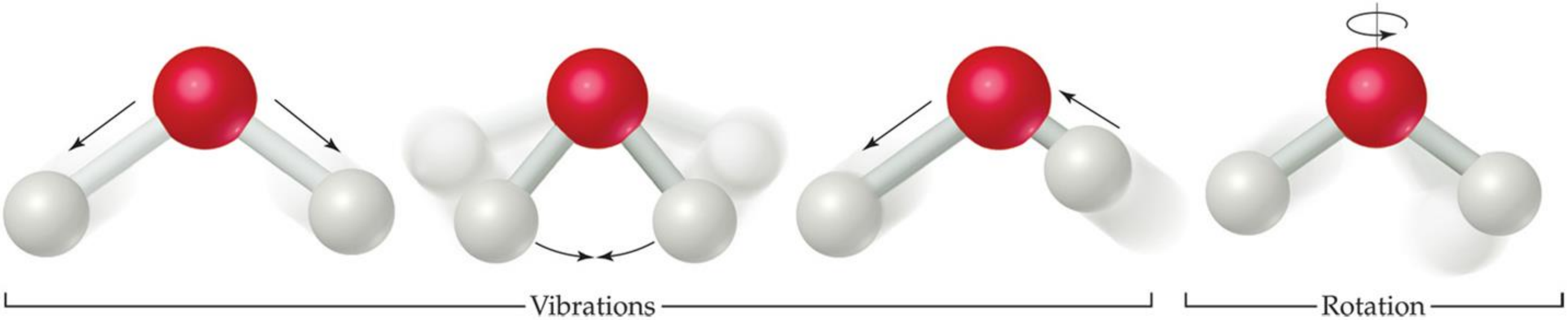
Entropy on the Molecular Scale

- Molecules exhibit several types of motion:
  - Translational: Movement of the entire molecule from one place to another.
  - Vibrational: Periodic motion of atoms within a molecule.
  - Rotational: Rotation of the molecule on about an axis or rotation about σ bonds.



Entropy on the Molecular Scale

- Boltzmann envisioned the motions of a sample of molecules at a particular instant in time.
  - This would be akin to taking a snapshot of all the molecules.
- He referred to this sampling as a microstate of the thermodynamic system.

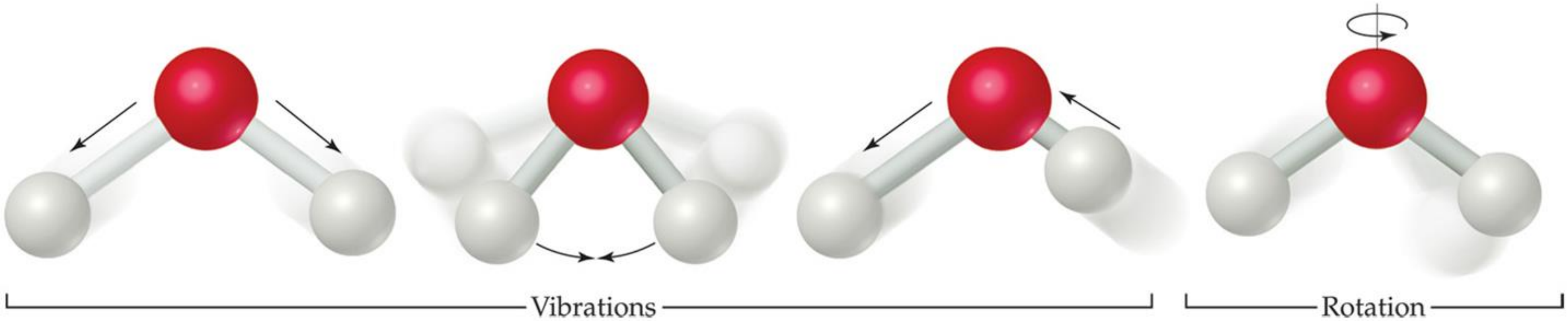


Entropy on the Molecular Scale

- Each thermodynamic state has a specific number of microstates, W, associated with it.
- Entropy is

$$S = k \ln W$$

where k is the Boltzmann constant, 1.38×10^{-23} J/K.



Entropy on the Molecular Scale

Implications:

- more particles

    -> more states -> more entropy

- higher T

    -> more energy states -> more entropy

- less structure (gas vs solid)

    -> more states -> more entropy

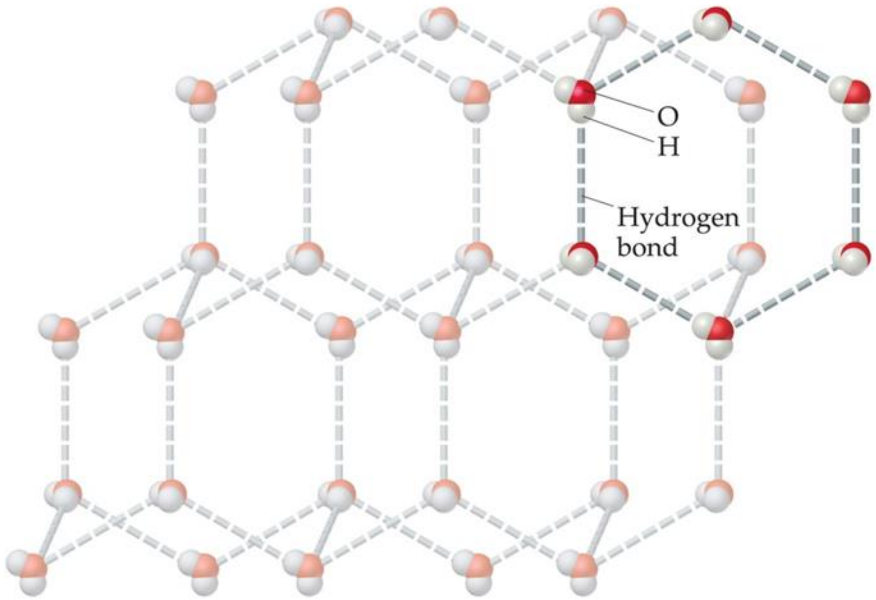
Entropy on the Molecular Scale

- The number of microstates and, therefore, the entropy tends to increase with increases in
  - Temperature.
  - Volume (gases).
  - The number of independently moving molecules.

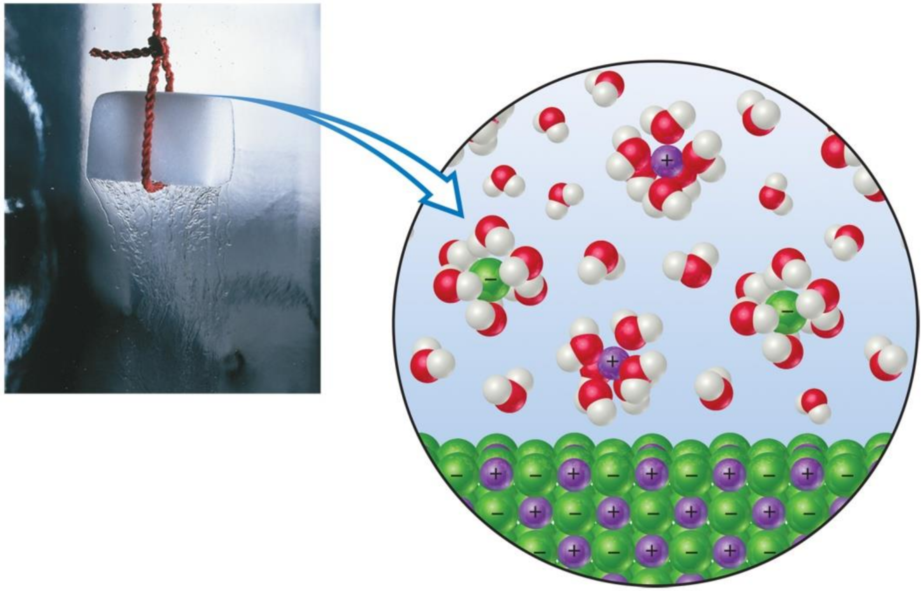
Entropy and Physical States

- Entropy increases with the freedom of motion of molecules.
- Therefore,

  $S(g) > S(l) > S(s)$



Solutions



Dissolution of a solid:

- Ions have more entropy (more states)
- *But,* Some water molecules have less entropy (they are grouped around ions).

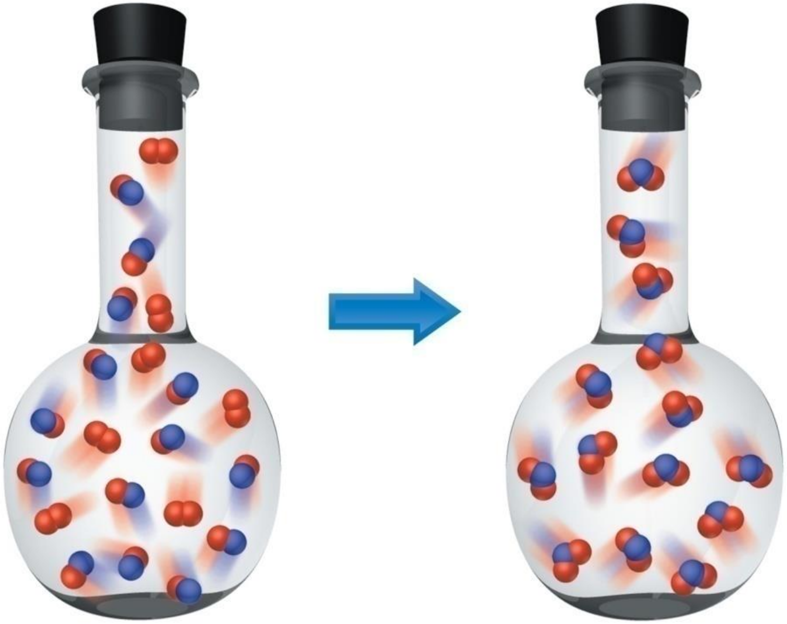
Usually, there is an overall increase in S.

(The exception is very highly charged ions that make a lot of water molecules align around them.)

Entropy Changes

- In general, entropy ***increases*** when

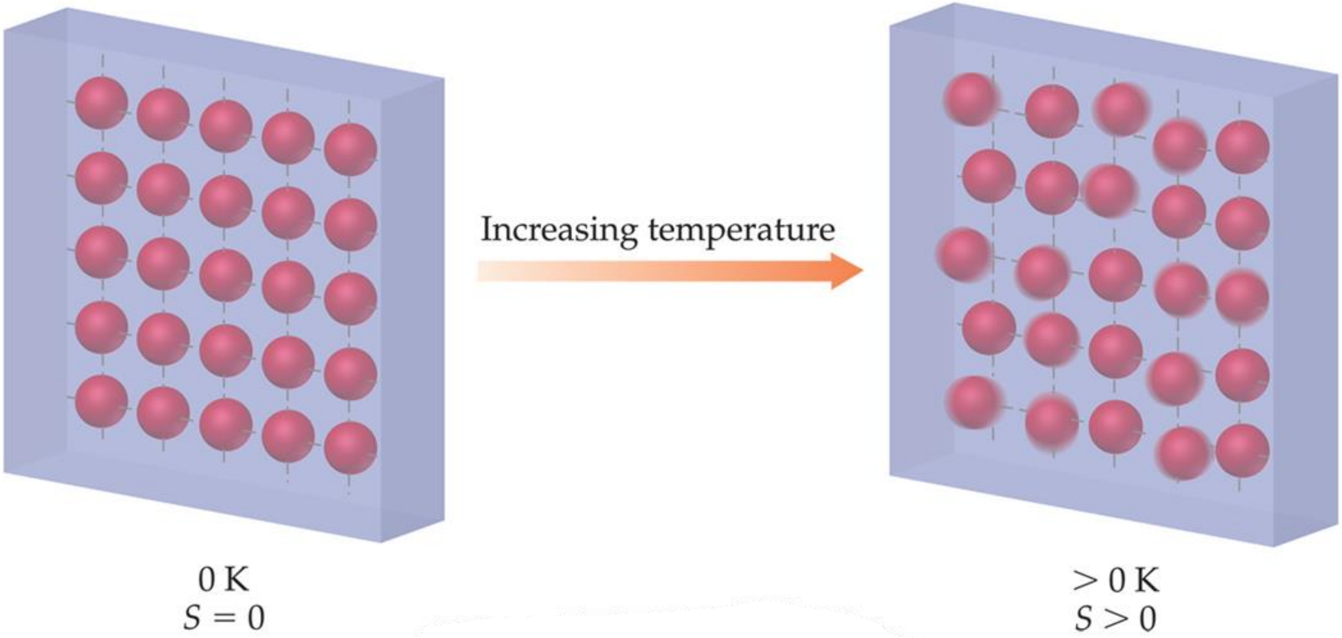
  - Gases are formed from liquids and solids.
  - Liquids or solutions are formed from solids.
  - The number of gas molecules increases.
  - The number of moles increases.



Third Law of Thermodynamics

- **The entropy of a pure crystalline substance at absolute zero is 0.**

$$S = k\ lnW = k\ ln1 = 0$$



Standard Entropies

- These are molar entropy values of substances in their standard states.
- Standard entropies tend to increase with increasing molar mass.

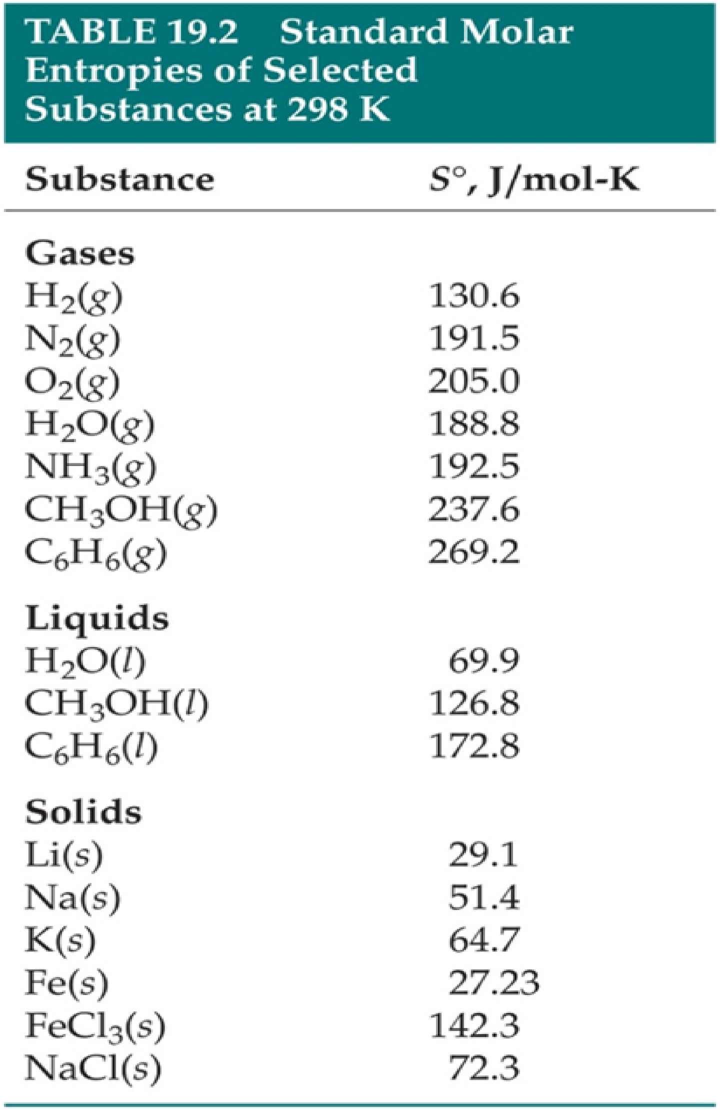
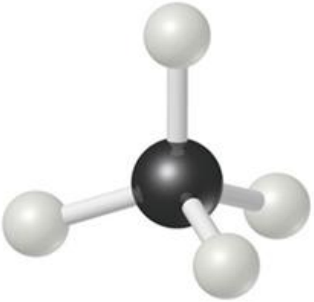


TABLE 19.2 Standard Molar Entropies of Selected Substances at 298 K

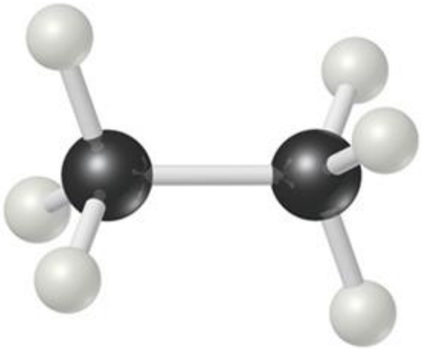
Substance	*S*°, J/mol-K
Gases	
$H_2(g)$	130.6
$N_2(g)$	191.5
$O_2(g)$	205.0
$H_2O(g)$	188.8
$NH_3(g)$	192.5
$CH_3OH(g)$	237.6
$C_6H_6(g)$	269.2
Liquids	
$H_2O(l)$	69.9
$CH_3OH(l)$	126.8
$C_6H_6(l)$	172.8
Solids	
$Li(s)$	29.1
$Na(s)$	51.4
$K(s)$	64.7
$Fe(s)$	27.23
$FeCl_3(s)$	142.3
$NaCl(s)$	72.3

Standard Entropies

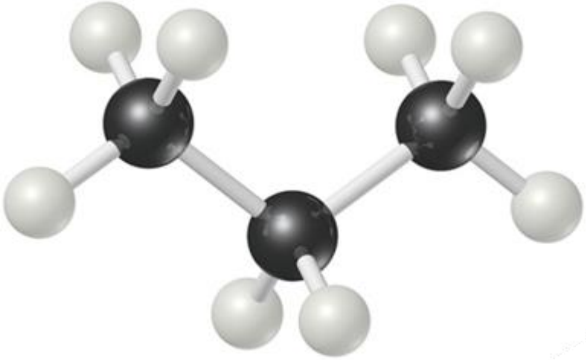
- Larger and more complex molecules have greater entropies.



Methane, CH_4
$S° = 186.3\ J\ mol^{-1}\ K^{-1}$



Ethane, C_2H_6
$S° = 229.6\ J\ mol^{-1}\ K^{-1}$



Propane, C_3H_8
$S° = 270.3\ J\ mol^{-1}\ K^{-1}$

Entropy Changes

- Entropy changes for a reaction can be calculated the same way we used for Δ*H:*

$$\Delta S_{rxn} = \Sigma S^{\circ}_{reactants} - \Sigma S^{\circ}_{products}$$

S° for each component is found in a table.

Note for pure elements:

$$S^{\circ} \neq 0$$

$$\Delta H^{\circ} = 0$$

Practical uses: surroundings & system

Entropy Changes in Surroundings

- Heat that flows into or out of the system also changes the entropy of the surroundings.
- For an isothermal process:

$$\Delta S_{surr} = \frac{-q_{sys}}{T}$$

Practical uses: surroundings & system

Entropy Changes in Surroundings

- Heat that flows into or out of the system also changes the entropy of the surroundings.
- For an isothermal process:

$$\Delta S_{surr} = \frac{-q_{sys}}{T}$$

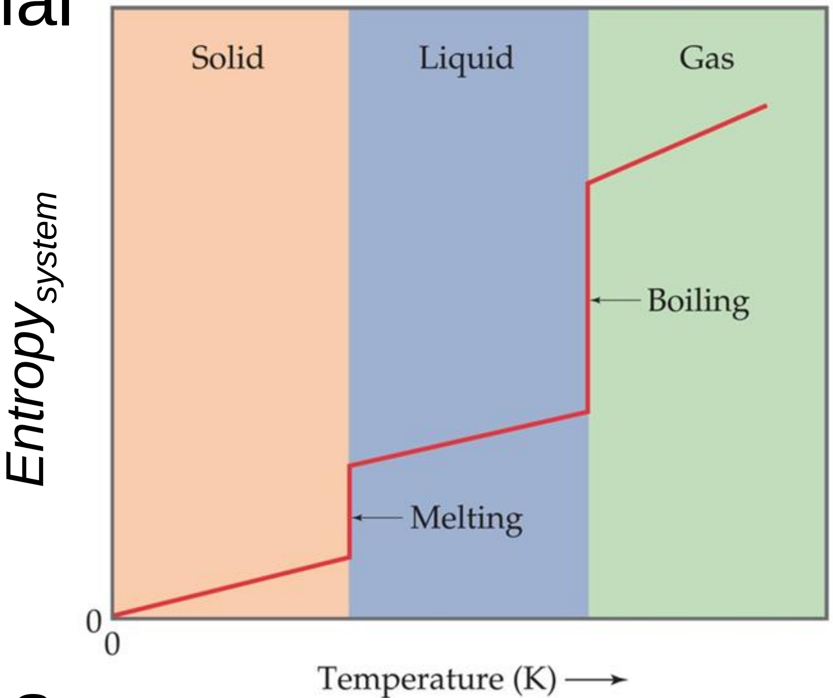
- At constant pressure, q_{sys} is simply ΔH° for the system.

$$\Delta S_{surr} = \frac{-q_{sys}}{T} = \frac{-\Delta H^\circ}{T}$$

Link S and ΔH: Phase changes

$$\Delta S_{surr} = \frac{-q_{sys}}{T} = \frac{-\Delta H^\circ_{sys}}{T}$$

- A phase change is isothermal (no change in T).



For water:

ΔH_{fusion} = 6 kJ/mol

ΔH_{vap} = 41 kJ/mol

If we do this reversibly: $\Delta S_{surr} = -\Delta S_{sys}$

Practical uses: surroundings & system

Entropy Change in the Universe

- The universe is composed of the system and the surroundings.
- Therefore,

$$\Delta S_{\text{universe}} = \Delta S_{\text{system}} + \Delta S_{\text{surroundings}}$$

- For spontaneous processes

$$\Delta S_{\text{universe}} > 0$$

Practical uses: surroundings & system

$$\Delta S_{universe} = \Delta S_{system} + \Delta S_{surround}$$

$$\Delta S_{surr} = \frac{-\Delta H^{\circ}_{sys}}{T}$$

$$\Delta S_{universe} = \Delta S_{system} + \frac{-\Delta H^{\circ}_{sys}}{T}$$

$$\underbrace{T\Delta S_{universe}}_{} = T\Delta S_{system} + -\Delta H^{\circ}_{sys}$$

= – Gibbs Free Energy

Practical uses: surroundings & system

$$\underbrace{T\Delta S_{universe}} = T\Delta S_{system} + -\Delta H^{\circ}_{sys}$$

= – Gibbs Free Energy

Make this equation nicer:

$$-T\Delta S_{universe} = \Delta H^{\circ}_{sys} - T\Delta S_{system}$$

$$\boxed{\Delta G = \Delta H^{\circ}_{sys} - T\Delta S_{system}}$$

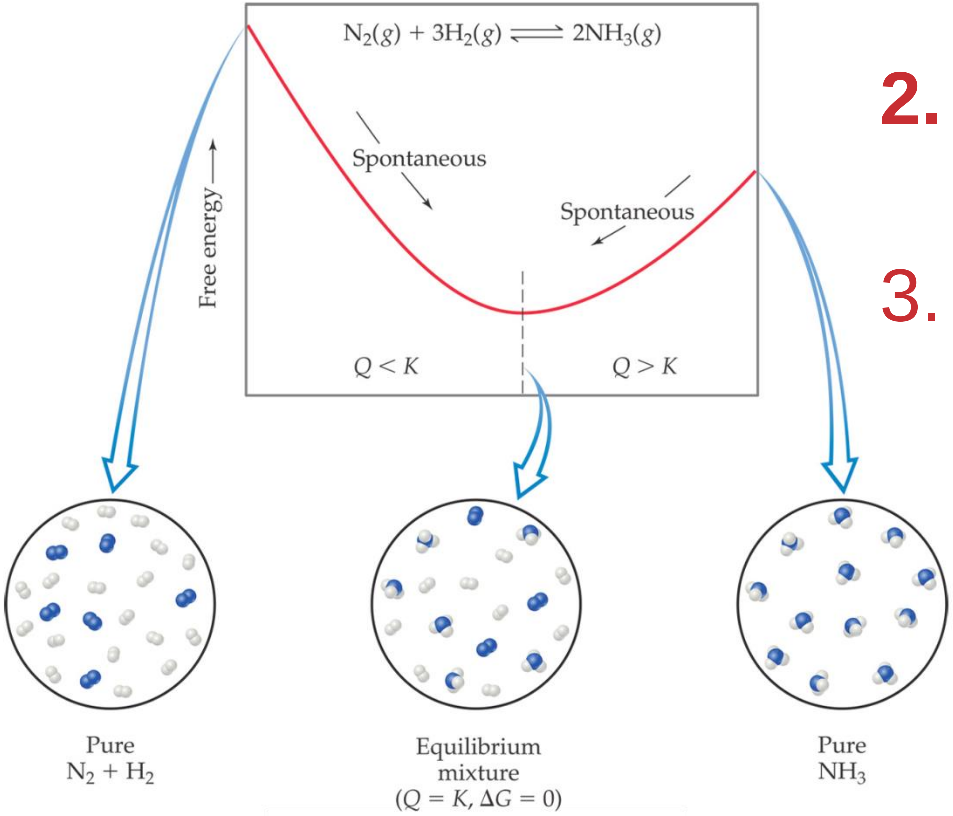
Chemical Thermodynamics

Practical uses: surroundings & system …Gibbs Free Energy

- $-T\Delta S_{\text{universe}}$ is defined as the Gibbs free energy, ΔG.
- For spontaneous processes: $\boldsymbol{\Delta S_{\text{universe}} > 0}$
- And therefore: $\boldsymbol{\Delta G < 0}$

- *ΔG is easier to determine than $\Delta S_{\text{universe}}$*
- *So* Use ΔG to decide if a process is spontaneous.

Gibbs Free Energy



1. If ΔG is negative, the forward reaction is spontaneous.
2. **If ΔG is 0, the system is at equilibrium.**
3. If ΔG is positive, the reaction is spontaneous in the reverse direction.

Standard Free Energy Changes

- Standard free energies of formation, ΔG_f° are analogous to standard enthalpies of formation, ΔH_f°.

$$\Delta G_f^\circ = \Sigma\Delta G^\circ_{reactants} - \Sigma\Delta G^\circ_{products}$$

- ΔG° can be looked up in tables, *Or* calculated from S° and ΔH°.

Free Energy Changes

- Very key equation:

$$\Delta G = \Delta H^\circ_{sys} - T\Delta S_{system}$$

- This equation shows how ΔG° changes with temperature.
- (We assume S° & ΔH° are independent of T.)

Free Energy and Temperature

- There are two parts to the free energy equation:
    - ΔH°— the enthalpy term
    - $T\Delta S^\circ$ — the entropy term
- The temperature dependence of free energy comes from the entropy term.

Free Energy and Temperature

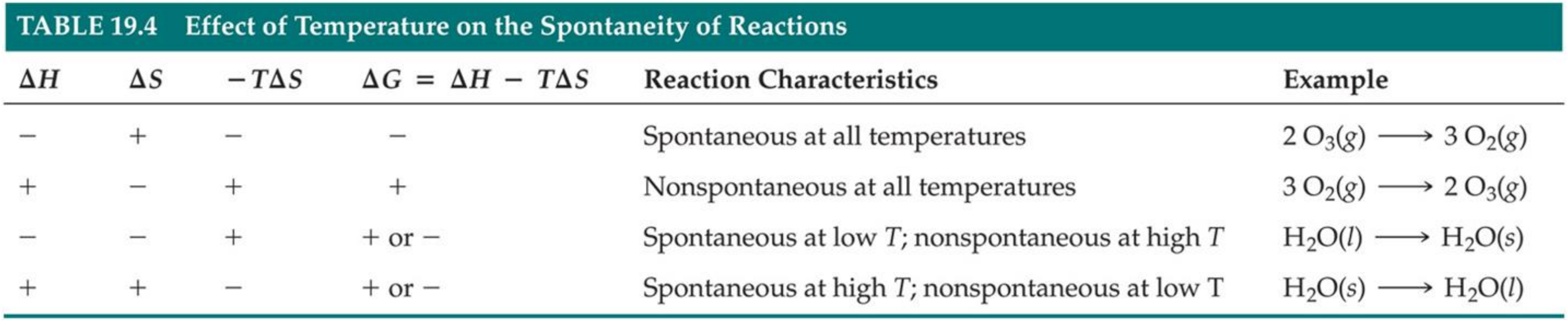


TABLE 19.4 Effect of Temperature on the Spontaneity of Reactions

ΔH	ΔS	$-T\Delta S$	$\Delta G = \Delta H - T\Delta S$	Reaction Characteristics	Example
−	+	−	−	Spontaneous at all temperatures	$2\,O_3(g) \longrightarrow 3\,O_2(g)$
+	−	+	+	Nonspontaneous at all temperatures	$3\,O_2(g) \longrightarrow 2\,O_3(g)$
−	−	+	+ or −	Spontaneous at low *T*; nonspontaneous at high *T*	$H_2O(l) \longrightarrow H_2O(s)$
+	+	−	+ or −	Spontaneous at high *T*; nonspontaneous at low T	$H_2O(s) \longrightarrow H_2O(l)$

- By knowing the sign (+ or -) of ΔS and ΔH, we can get the sign of ΔG and determine if a reaction is spontaneous.

Free Energy and Equilibrium

- Remember from above:

  - ✓ **If ΔG is 0, the system is at equilibrium.**

- So **Δ*G*** must be related to the equilibrium constant, K (chapter 15).
- The ***standard*** free energy, **Δ*G*°**, is directly linked to K_{eq} by:

$$\Delta G^\circ = -RT \ln K$$

Free Energy and Equilibrium

- Under non-standard conditions, we need to use **ΔG** instead of **ΔG° .**

$$\Delta G^\circ = -RT \ln K$$

$$\Delta G = \Delta G^\circ + RT \ln Q$$

- Q is the reaction quotient from chapter 15.

- **Note**: at equilibrium: *$\Delta G = 0$.*
- away from equilibrium, sign of **ΔG** tells which way rxn goes spontaneously.

Gibbs Free Energy

1. If ΔG is negative, the forward reaction is spontaneous.
2. **If ΔG is 0, the system is at equilibrium.**
3. If ΔG is positive, the reaction is spontaneous in the reverse direction.

Gibbs Free Energy