Entropy

Entropy (s):→Is a degree of disorder of the reaction.

→Is a measure of how spread out or dispersed the energy of a system among the different possible ways that system can contain energy.

- It used to predict the spontaneity of a process.
- The greater the dispersal, the greater is the entropy.

Most process are accompanied by a change in entropy

Example

- Consider the suitable depicted in the above figure, before the valve is opened, the system possesses a certain amount of entropy. Upon opening the valve, the gas molecules now have access to the combined volume of both bulbs.
- A large volume for movement results in a narrowing of the gap between translational energy levels of the molecules.

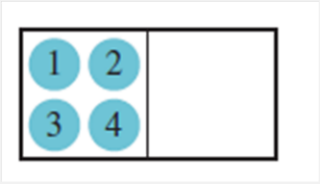
Consequently

The entropy of the system increases because closely spaced energy levels leads to a greater dispersal among the energy levels.

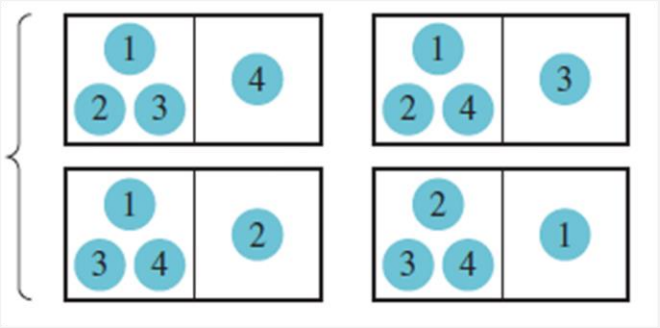
Microstate and entropy

To provide a propel definition of (entropy) we consider a simple system of four molecules distributed between two equal compartment.

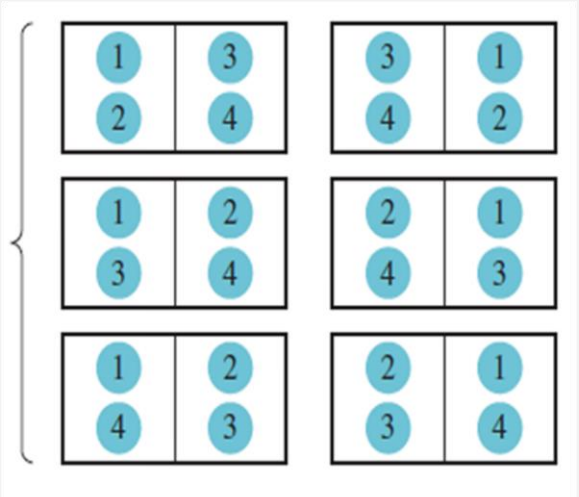
1) There is only one way to arrange all the molecules in the left compartment.



2) Four ways to have three molecules in the left compartment and one in the right compartment.



3) Six ways to have two molecules in each of two compartments.



Microstate →The above eleven possible ways of distributing the molecules.

- ✓ **Distribution** → each set of similar microstates.

Distribution (III) → is the most probable because there are six ways to achieve it.

Distribution (II) → is the least probable because it has one microstate.

Conclusion

The probability of occurrence of a particle distribution depends on the number of ways in which the distribution can be achieved.

Boltzmann law of entropy

$S = K \ln w$

W → number of microstates.

K→ Boltzmann constant ($1.38*10^{-23}$ J/K).

- Larger the W, greater is the entropy of a system.
- Entropy is a state function.

Consider a certain process in a system, the entropy change for the process(ΔS)

$$\Delta S = S_f - S_i$$

$$\therefore \Delta S = K \ln w_f - K \ln w_i$$

$$= K \ln \frac{w_f}{w_i}$$

S_f → final entropy

S_i → initial entropy

If wf > wi

$\therefore \Delta S > 0$ and the entropy of the system increases.

Changes in entropy

There is a connection between the qualitative description of entropy in terms of dispersal of energy and the quantitative definition of entropy in terms of microstates. We conclude that.

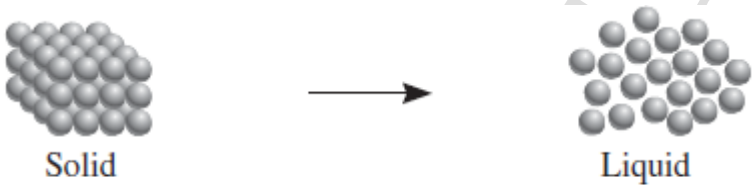
- A system with fewer microstates (smaller W), has a lower entropy.
- A system with more microstates (larger W), has a higher entropy.

Process that lead to a change in entropy of a system in terms of the change in the number of microstates of the system.

1) Melting

- ✓ In solid, the atoms or molecules are confined to fixed positions and the number of microstates is small.
- ✓ These atom or molecules can occupy many more position as they move away from the lattice point.

The number of microstate increases



(a)

2) Vaporization

- ✓ Will also lead to an increase in the entropy of the system.
- ✓ The increase will be considerably greater than that melting.
- ✓ molecules in the gas phase occupy much more space
- ✓ There are far more microstates than in the liquid phase.

(b)

3)Solution Procces

✓ Lead to an increase in entropy.

Example "sugar crystal dissolved in water"

✓ The highly ordered structure of the solid and part of the ordered structure of water break down.

✓ The solution has greater number of microstates than the pure solute and pure solvent combined.

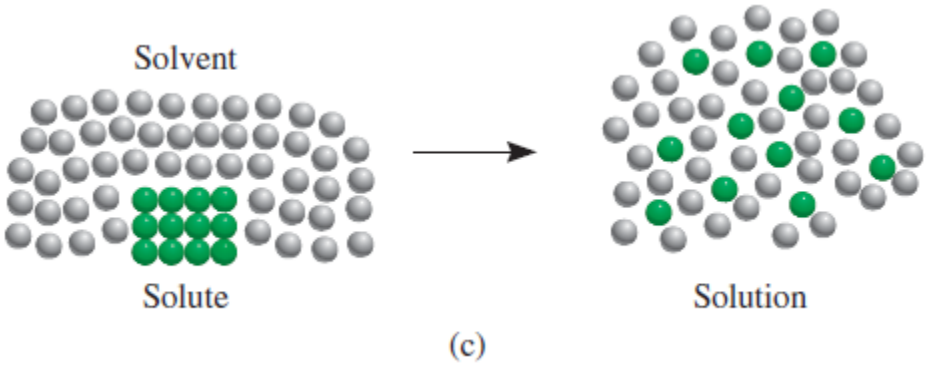
another Example" when an ionic solid such as NaCl dissolved in water".

There are two contributions to entropy increase kkkincreaseincrease.

(1) Solution process "mixing of solute with solvent"

(2) Dissociation of compound into ions.

$$"NaCl_{(s)} \xrightarrow{H2O} Na^{+}_{(aq)} + Cl^{-}_{(aq)}"$$



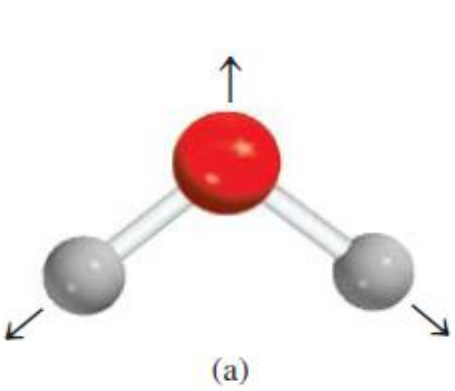
(c)

4) Hydration

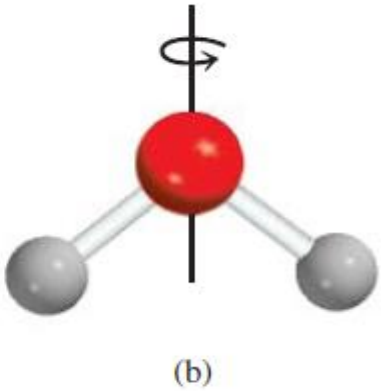
- ✓ Causes water molecules to become more ordered a round the ions.
- ✓ This process decreases entropy because it reduces the number of microstates of the solvent.

5) Heating

- ✓ Also increases the entropy of a system.
- ✓ In addition to translational motion, molecules can also execute rotational motions and vibrational motions.
- ✓ As the temperature is increased, the energies associated with all types of molecular motion increase.
- ✓ This increase in energy is distributed among the quantized energy levels.
- ✓ More microstates become available at higher temperature.



(a)



(b)

Standard entropy

- ✓ Is the absolute entropy of a substance at "1atm" and "25°C".

- Not used to calculate the entropy of the system? because it's difficult to determine the number of microstate for a macroscopic system containing many molecules.
- Entropy is obtained by calorimetric method.
- The units of entropy are J/k or J/k.mol for 1 mole of the substance.

Why we use Joules rather than kilo Joules?!

Because entropy values are typically quite small.

Entropies of elements and compounds are all positive.

Standard Entropy Values (S°) for Some Substances at 25°C

Substance	S° (J/K · mol)
$H_2O(l)$	69.9
$H_2O(g)$	188.7
$Br_2(l)$	152.3
$Br_2(g)$	245.3
$I_2(s)$	116.7
$I_2(g)$	260.6
C (diamond)	2.4
C (graphite)	5.69
CH_4 (methane)	186.2
C_2H_6 (ethane)	229.5
$He(g)$	126.1
$Ne(g)$	146.2

That is , $S° > 0$

"$\Delta H°F$" Standard enthalpy of formation "for elements in their stable form is equal to zero and for compounds it may be positive or negative".

Note that

- Standard entropy of water vapor is greater than that of water.
- Bromine vapor has higher standard entropy than liquid bromine.
- Iodine vapor has greater standard entropy than solid Iodine.
- For different substances in the same phase, molecular complexity determines which ones have higher entropies.

❖Which one of the following has greater entropy?!

(1) Graphite or diamond?!

Both graphite and diamond are solid, but diamond has a more ordered structure and hence a smaller number of microstates.

Therefore, diamond has smaller standard entropy than graphite.

(2) Natural gases" methane and ethane"?!

Ethane has a more complex structure and hence more ways to execute molecular motions, which also increase its microstates.

Therefore, ethane has greater standard entropy than methane.

(3) Non atomic gases "helium and neon"?!

Neon has a greater standard entropy than helium because its molar mass is greater.

Choose

1) Degree of disorder of the reaction is …….

A) enthalpy
B) Gibbs free energy
C) standard Entropy
D) Entropy

2) Is a measure of how spread out the energy of a system among the different possible ways that system can contain energy .

A) enthalpy
B) standard Entropy
C) Entropy
D) Gibbs free energy

3) Greater the dispersal, ……. the entropy.

A) Not change
B) smaller
C) greater
D) all of the above

4) Possible ways of distributing the molecules.

A) microstate
B) distribution
C) entropy
D) enthalpy

5)……. Is a set of similar microstate.

A) entropy
B) enthalpy
C) distribution
D) Gibbs free energy

6) When a solid melts the entropy……

A) increase
C) not change
B) decrease
D) none of the above

7) When ice melts entropy……

A) increase
C) not change
B) decrease
D) none of the above

8) When water frozen to ice the entropy……..

A) increase
C) not change
B) decrease
D) none of the above

9) When a vapor is converted to a solid the entropy…….

A) increase
C) not change
B) decrease
D) none of the above

10) When a solid sublimes, the entropy……

A) increase
C) not change
B) decrease
D) none of the above

11) When sugar dissolves in water, the entropy…… .

A) increase
B) decrease
C) not change
D) none of the above

12) The unit of entropy is…….

A) J/ºC
B) J/K
C) J/Kg
D) KJ/mole

13) The unit of entropy is…….

A) J/K
B) J/K.mole
C) KJ/K
D) both A and B

14) Entropy is determined by ……..Method

A) Gravimetric
B) Calorimetric
C) titration
D) all of the above

15) entropy of element and compound are all……..

A) Positive
B) Negative
C) zero
D) equal

16) The entropy of substance at "1atm" and "25ºC"is called…….

A) Normal entropy
C) standard entropy
B) enthalpy
D) Gibbs free energy

17) The standard entropy is The entropy of substance at "…… atm "

A) 1
C) 1.5
B) 2
D) 3

18) The standard entropy for elements in their stable form is equal to…….

A) 1
C) Negative value
B) zero
D) positive value

19) The process that is accompanied by decrease in entropy is …….

A) Sublimation
C) hydration
B) heating
D) evaporation

20) Solution process lead to an ……. in entropy

A) increase
C) Not change
B) decrease
D) all of the above

21) Hydration process lead to ……. entropy.

A) increase
B) decrease
C) Not change
D) all of the above

22) More microstate become available at……Temp.

A) Lower
B) constant
C) higher
D) all of the above

23) The standard enthalpy for compounds may be ……..

A) Positive
B) Negative
C) Zero
D) both A and B

24) The standard entropy for water vapor is …….. water

A) greater than
B) equal
C) smaller than
D) none of them

25) Graphite has …….. entropy than diamond.

A) greater
B) smaller
C) equal
D) all the above

26) Which of the following has the highest entropy (S^o) at 25ºC

A) $CH_3OH_{(L)}$

B) $CO_{(g)}$

C) $MgCO_{3(s)}$

D) $H_2O_{(L)}$

27) Which of these species has the highest entropy (S^o) at 25ºC

A) $CO_{(g)}$

B) $CH_{4(g)}$

C) $NaCl_{(s)}$

D) $H_2O_{(L)}$

28) Arrange these compounds in order of increasing standard molar entropy at 25ºC , $C_3H_{8(g)}$, $C_2H_{4(g)}$, $ZnS_{(s)}$ and $H_2O_{(L)}$

A) $ZnS_{(s)} < H_2O_{(L)} < C_3H_{8(g)} < C_2H_{4(g)}$

B) $C_2H_{4(g)} < H_2O_{(L)} < C_3H_{8(g)} < NaCl_{(s)}$

C) $ZnS_{(s)} < C_3H_{8(g)} < C_2H_{4(g)} < H_2O_{(L)}$

D) $ZnS_{(s)} < H_2O_{(L)} < C_2H_{4(g)} < C_3H_{8(g)}$

29) Arrange the following substances in the order of increasing entropy at 25°C.

$HF(g)$, $NaF(s)$, $SiF_4(g)$, $SiH_4(g)$, $Al(s)$

lowest → highest

A) $SiF_4(g) < SiH_4(g) < NaF(s) < HF(g) < Al(s)$

B) $HF(g) < Al(s) < NaF(s) < SiF_4(g) < SiH_4(g)$

C) $Al(s) < NaF(s) < HF(g) < SiH_4(g) < SiF_4(g)$

D) $Al(s) < HF(g) < NaF(s) < SiF_4(g) < SiH_4(g)$

30) Which response includes *all* the following processes that are accompanied by an *increase* in entropy?

1. $2SO_2(g) + O_2(g) \rightarrow SO_3(g)$
2. $H_2O(l) \rightarrow H_2O(s)$
3. $Br_2(l) \rightarrow Br_2(g)$
4. $H_2O_2(l) \rightarrow H_2O(l) + (1/2)O_2(g)$

A) 1, 2, 3, 4

B) 1, 2

C) 2, 3, 4

D) 3, 4

31) Which response includes *all* of the following processes that are accompanied by an *increase* in entropy?

1. $I_2(s) \rightarrow I_2(g)$
2. $2I(g) \rightarrow I_2(g)$
3. $2NH_3(g) \rightarrow N_2(g) + 3H_2(g)$
4. $Mg^{2+}(aq) + 2OH^-(aq) \rightarrow Mg(OH)_2(s)$

A) 1, 2

B) 1, 3

C) 3, 4

D) 3