Chapter 18

Entropy, Free Energy, and Equilibrium

Part I

18.1

Spontaneous Processes

- Chemical processes can be classifies as :
  - ***Spontaneous processes***: processes that occur "naturally" under a specific set of conditions.
    - Combustion of hydrocarbons:

    $CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(l)$ $\Delta H° = -890$ kJ/mol

    A spontaneous process involves a decrease in the energy of the system. it is usually "but not always" exothermic.
  - ***Nonspontaneous processes***: processes that do not occur "naturally" under a specific set of conditions.

    $CO_2(g) + 2H_2O(l) \rightarrow CH_4(g) + 2O_2(g)$ $\Delta H° = +890$ kJ/mol

    A *non*spontaneous process involves an increase in the energy of the system. it is usually "but not always" endothermic.

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Spontaneous Processes

TABLE 18.1 Familiar Spontaneous and Nonspontaneous Processes

Spontaneous	Nonspontaneous
Ice melting at room temperature	Water freezing at room temperature
Sodium metal reacting violently with water to produce sodium hydroxide and hydrogen gas [⏮ Section 7.7]	Sodium hydroxide reacting with hydrogen gas to produce sodium metal and water
A ball rolling downhill	A ball rolling uphill
The rusting of iron at room temperature	The conversion of rust back to iron metal at room temperature
Water freezing at −10°C	Ice melting at −10°C

Reaction of sodium with water is so vigorous such that water catches fire!!

http://www.youtube.com/watch?v=uqDWbknpiVk&feature=related

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Spontaneous Processes

- At room temperature :
  - Freezing of water:

    $H_2O(l) \rightarrow H_2O(s)$ $\Delta H° = -6.01$ kJ/mol

  is a nonspontaneous process although it is exothermic.

  - Melting of ice:

    $H_2O(s) \rightarrow H_2O(l)$ $\Delta H° = +6.01$ kJ/mol

  is a spontaneous process although it is endothermic.

- To predict spontaneity, it is not enough to consider only the reaction energy or enthalpy. Another important thermodynamic quantity called ***entropy*** helps in predicting the spontaneity of a given system.

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What is Entropy?

- ***Entropy (S)***: is a thermodynamic quantity that measures the *disorder* of a system.

  In general, a greater disorder means a greater entropy, and a greater order means a smaller entropy.
- Like enthalpy (H) and internal energy (U), entropy (S) is a *state function*.

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Probability

- An ***improbable*** event can happen in only a small number of ways (may be only one way).
- A ***probable*** event can happen in many different ways.

Very highly ordered

Disordered

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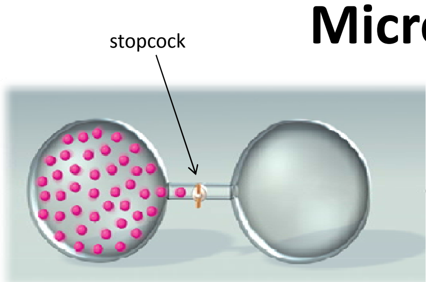
Microstates



The state of problem:
A sample of gaseous molecules is confined in the left bulb, and the molecules are not allowed to go to the other bulb

- What will happen if the stopcock between the two bulbs is opened?

  The molecules originally confined in the left-side bulb expand and evenly occupy both bulbs. *"a spontaneous process"*

- Let us inspect this more carefully by considering the microscopic states "***microstates***" of a system starting with a very small number of molecules.

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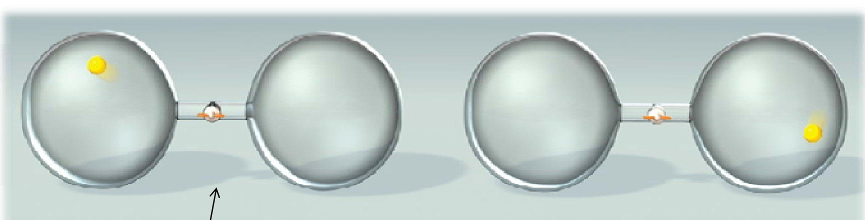
Microstates



Probability of finding the molecule in the left side bulb is **1/2** .

The number of molecules is 1

The number of possible positions (*left or right*) is 2

The number of microstates is 2

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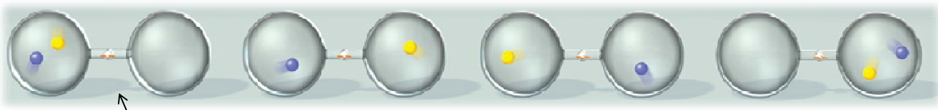
Microstates



Probability of finding the molecule in the left side bulb is **1/4** .

The number of molecules is 2

The number of possible positions is 2

The number of microstates is 4

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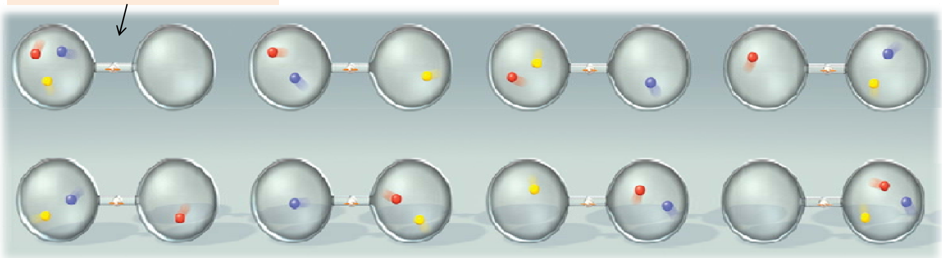
Probability of finding the molecule in the left side bulb is **1/8** .

Microstates



The number of molecules is 3

The number of possible positions is 2

The number of microstates is 8

Number of microstates = n^x

x : number of molecules

n : number of possible positions

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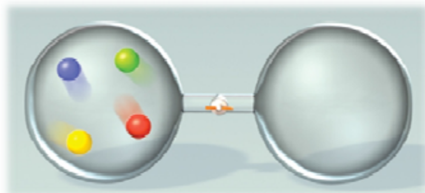
Microstates and Most Probable Distribution

Distribution I

4 | 0

Probability of finding the molecule in the left side bulb is **1/16** .



The number of molecules is 4

The number of possible positions is 2

The number of microstates for this distribution 1

Number of microstates = $\boldsymbol{n}^x = 2^4 = 16$

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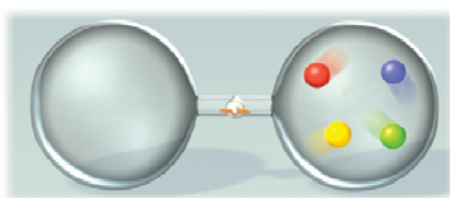
Microstates and Most Probable Distribution

Distribution II

0 | 4



The number of molecules is 4

The number of possible positions is 2

The number of microstates for this distribution 1

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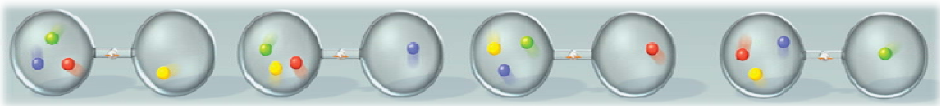
Microstates and Most Probable Distribution

Distribution III 3 1



The number of molecules is 4

The number of possible positions is 2

The number of microstates for this distribution 4

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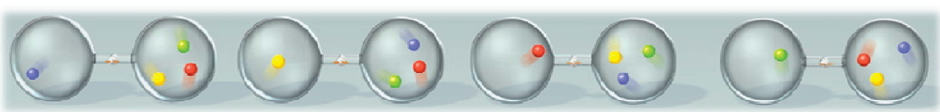
Microstates and Most Probable Distribution

Distribution IV 1 3



The number of molecules is 4

The number of possible positions is 2

The number of microstates for this distribution 4

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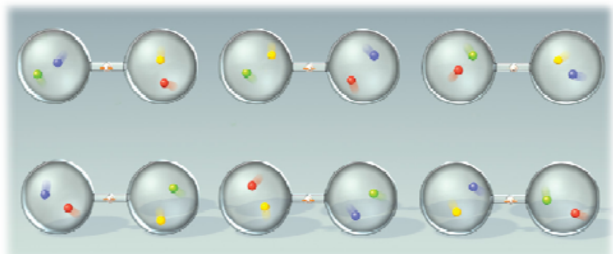
Microstates and *Most* Probable Distribution

Distribution V

2 2

The most probable distribution because more microstates are involved →



Does this make sense??

Yes, the gas molecules are more probably going to split evenly between the two bulbs.

The number of molecules is	4
The number of possible positions is	2
The number of microstates for this distribution	6

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Microstates and *Least* Probable Distribution

- It is *very highly improbable* for the gas molecules to stay in the left bulb and not distributed between the two bulbs (*nonspontaneous* process). This will almost *never* occur if you have 1 mole of molecules.
- The gas will spontaneously expand so that the molecules will fill up both bulbs evenly. This satisfies a larger number of microstates for the gas molecules.

TABLE 16.2 Probability of Finding All the Molecules in the Left Bulb as a Function of the Total Number of Molecules

Number of Molecules	Relative Probability of Finding All Molecules in the Left Bulb
1	$\frac{1}{2}$
2	$\frac{1}{2} \times \frac{1}{2} = \frac{1}{2^2} = \frac{1}{4}$
3	$\frac{1}{2} \times \frac{1}{2} \times \frac{1}{2} = \frac{1}{2^3} = \frac{1}{8}$
5	$\frac{1}{2} \times \frac{1}{2} \times \frac{1}{2} \times \frac{1}{2} \times \frac{1}{2} = \frac{1}{2^5} = \frac{1}{32}$
10	$\frac{1}{2^{10}} = \frac{1}{1024}$
n	$\frac{1}{2^n} = \left(\frac{1}{2}\right)^n$
6×10^{23} (1 mole)	$\left(\frac{1}{2}\right)^{6\times10^{23}} \approx 10^{-(2\times10^{23})}$

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Entropy and Microstates

- In 1868, Boltzmann showed that the entropy of a system is related to the natural log of the number of microstates (W)

$$S = k \ln W$$

k : Boltzmann constant (1.38 x 10^{-23} J/K)

The larger the value of W for a system (more microstates), the greater its entropy.

- The entropy change (ΔS) for a process is given by:

$$\Delta S = S_f - S_i$$

$$\Delta S = k \ln W_f - k \ln W_i$$

When the number of microstates increases during a process, the entropy of that process increases ($\Delta S > 0$).

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Entropy and Macrostates

- The previous equation can <u>not</u> be used to calculate the entropy for *macroscopic systems*.

$$S = k \ln W$$

$$W = \boldsymbol{n^x}$$

Normal calculators can't handle x > 500.

- Entropy is normally determined using calorimetry experiments.

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Standard Entropy

- The ***standard entropy*** ($S°$) is the absolute entropy of a substance at 1 atm (typically at 25°C). Its units is (J/K·mol).

TABLE 18.2 Standard Entropy Values ($S°$) for Some Substances at 25°C

Substance	$S°$ (J/K · mol)	Substance	$S°$ (J/K · mol)
$H_2O(l)$	69.9	C(diamond)	2.4
$H_2O(g)$	188.7	C(graphite)	5.69
$Br_2(l)$	152.3	$CH_4(g)$ (methane)	186.2
$Br_2(g)$	245.3	$C_2H_4(g)$ (ethane)	229.5
$I_2(s)$	116.7	$He(g)$	126.1
$I_2(g)$	260.6	$Ne(g)$	146.2

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General Trends for Entropy

- Entropy for the gas phase is greater than that of the liquid or solid phase of the same substance.
- More complex structures have a greater entropy.
- For allotropes, more ordered forms have a lower entropy.
- Heavier monoatomic elements have a greater entropy than lighter ones.

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Entropy Change in a System

- One can predict *qualitatively* whether the entropy of a system increases ($\Delta S > 0$) or decreases ($\Delta S < 0$).

(a) *Melting:*

$\Delta S > 0$ →

solid

liquid

Particles are confined to fixed positions. They are highly ordered and occupy a small number of microstates.

Particles can now occupy more possible positions. They become less ordered and occupy a greater number of microstates compared to the solid state.

$S_{solid} < S_{liquid}$

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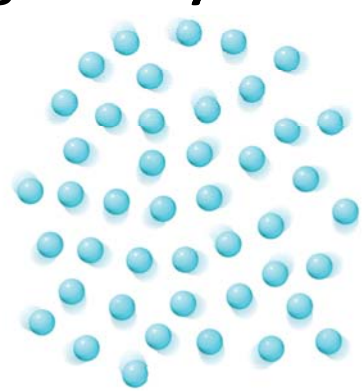
Entropy Change in a System

(b) *Vaporization:*

$\Delta S > 0$ →



liquid

gas

Particles in the gaseous phase occupy far more microstates than the liquid phase.

$S_{liquid} << S_{gas}$

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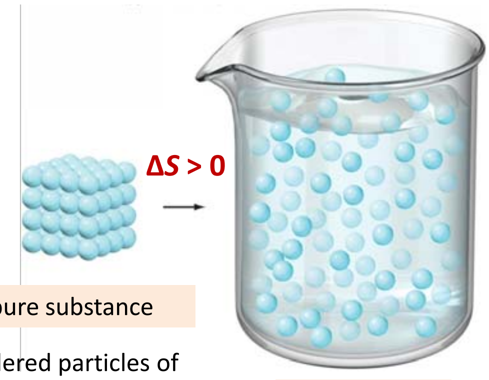
Entropy Change in a System

(c) *Dissolving:*



pure substance

solution

When the highly ordered particles of the pure substance and the ordered solvent molecules are mixed, the order in both are disrupted. The molecules in the solution, as a result, will have a grater number of microstates.

$S_{\text{pure substance}} < S_{\text{solution}}$

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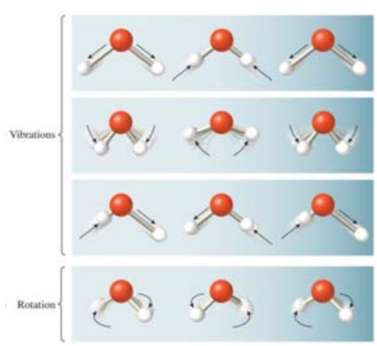
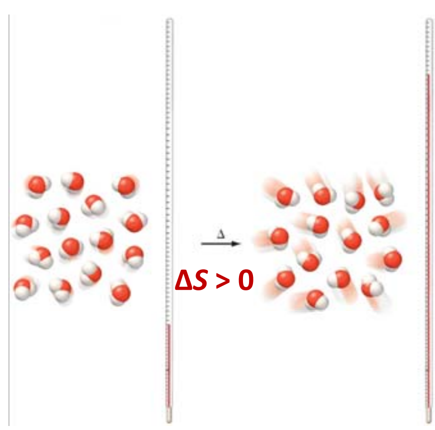
Entropy Change in a System

(d) *Heating:*

Heating always increases both the energy and the entropy of a system.





$S_{\text{lower temp.}} < S_{\text{higher temp.}}$

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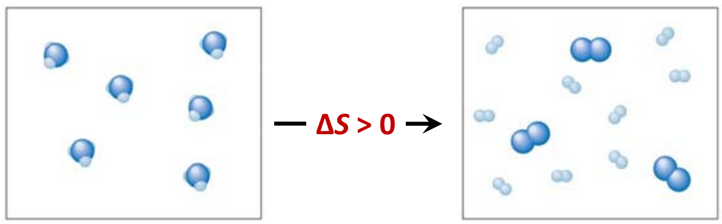
Entropy Change in a System

(e) *Chemical reactions:*

A reaction that results in an increase in the number of moles of gas always increases the entropy of the system.

$$2NH_3 \longrightarrow N_2 + 3H_2$$



$S_{\text{fewer moles}}$ < $S_{\text{more moles}}$

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Entropy

- Exercise:

  Determine the sign of ΔS for the following processes:

  - Liquid nitrogen evaporates.

    $\Delta S > 0$
  - Two clear liquids are mixed and a solid yellow precipitate forms.

    $\Delta S > 0$ for mixing of the two liquids.

    $\Delta S < 0$ for formation of precipitation.
  - Liquid water is heated from 22.5 °C to 55.8 °C

    $\Delta S > 0$

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The Universe, the System, and the Surroundings

- The universe is made up of two parts:

  the system and ***the surroundings***

System

Reactants and products

Surroundings

Reaction container, room, everything else

$$\Delta S_{univ} = \Delta S_{sys} + \Delta S_{surr}$$

Second Law of Thermodynamics

- There are two types of processes:
  - ***Spontaneous processes***: They occur under a specific set of conditions.

    In a spontaneous process, the entropy of the universe increases.

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

  - ***Equilibrium processes***: They do not tend to occur. However, They can be made to occur by the addition or removal of energy. (e.g. melting of ice at 0°C)

    In an equilibrium process, the entropy of the universe remains unchanged.

    $$\Delta S_{univ} = \Delta S_{sys} + \Delta S_{surr} = 0$$

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Entropy Change in a System (ΔS_{rxn})

- For a system represented by the following equation:

$$a\text{A} + b\text{B} \rightarrow c\text{C} + d\text{D}$$

The change in *standard* entropy of this reaction ($\Delta S°_{rxn}$) is:

$$\Delta S°_{rxn} = [c\,S°(\text{C}) + d\,S°(\text{D})] - [a\,S°(\text{A}) + b\,S°(\text{B})]$$

In general, the change of entropy of a chemical reaction (a system) is given by:

$$\Delta S°_{rxn} = \Sigma nS°(\text{products}) - \Sigma mS°(\text{reactants})$$

where *n* and *m* are the stoichiometric coefficients of the reactants and products in a given equation.

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Entropy Change in a System (ΔS_{rxn})

- Exercise:

Calculate the standard entropy change ($\Delta S°$) for the following reaction. First, predict the sign for ΔS_{rxn} qualitatively.

$$2NH_3(g) \rightarrow N_2(g) + 3H_2(g)$$

The entropy is expected to increase (2 mol → 4 mol)

$$\Delta S°_{rxn} = \Sigma nS°(\text{products}) - \Sigma mS°(\text{reactants})$$

The values of $S°$ can be found in Appendix 2

$$= [(1)(191.5\text{ J/K·mol}) + (3)(131.0\text{ J/K·mol})] - [(2)(193.0\text{ J/K·mol})]$$

$$= 584.5\text{ J/K·mol} - 386\text{ J/K·mol}$$

$$= 198.5\text{ J/K·mol}$$ (*Entropy increases*)

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18.3

Entropy Change in a System (ΔS_{rxn})

- The ΔS°_{rxn} values of the following reactions are calculated from the standard entropy values.

	ΔS°_{rxn} (J/K·mol)
$N_2(g) + 3H_2(g) \rightarrow 2NH_3(g)$	– 198.5
$CaCO_3(s) \rightarrow CaO(s) + CO_2(g)$	160.5
$H_2(g) + Cl_2(g) \rightarrow 2HCl(g)$	20.0

Recall that the reaction that results in an increase in the number of moles of gas always increases the entropy of the system. The opposite is also true. When there is *no change in the number of moles of gas*, the calculated ΔS°_{rxn} will be a relatively a small value with a positive or negative sign.

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Entropy Change in the Surroundings (ΔS_{surr})

- Change in entropy of the surroundings is directly proportional to the enthalpy of the system. At constant temperature:
  - an *exothermic* process corresponds to an increase of the entropy of the surroundings. ($\Delta S_{surr} > 0$)
  - an *endothermic* process corresponds to a decrease of the entropy of the surroundings. ($\Delta S_{surr} < 0$)

$$\Delta S_{surr} \; \alpha \; -\Delta H_{sys} \qquad ①$$

☝ *Just think about it*. Any system naturally tends to lower its energy (lose energy). This is in consistent with the second law of thermodynamics which states that the entropy of the universe is always positive.

A broken egg **could** repair itself - it would just be incredibly unlikely!

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Entropy Change in the Surroundings (ΔS_{surr})

- The transfer of a given quantity of energy from the system to the surroundings as heat produces a greater disorder in the surrounding at a low temperature that it does at a high temperature. Thus, the magnitude of change in entropy of the surroundings is *inversely* proportional to the temperature.

$$\Delta S_{surr} \propto 1/T \qquad ②$$

- Combining ① and ② gives:

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

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18.3

Entropy Change in the Surroundings (ΔS_{surr})

- Exercise:

Consider the following two reactions at 25°C:

$Sb_2S_3(s) + 3Fe(s) \rightarrow 2Sb(s) + 3FeS(s)$ $\Delta H° = -125$ kJ/mol

$Sb_4O_6(s) + 6C(s) \rightarrow 4Sb(s) + 6CO(g)$ $\Delta H° = 778$ kJ/mol

Calculate $\Delta S°_{surr}$ for each reaction at 1 atm and 25°C.

We use:

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

For the first reaction: $\Delta S°_{surr} = \frac{-(-125 \text{ KJ/mol})}{298 \text{ K}} = +419$ J/K·mol

For the second reaction: $\Delta S°_{surr} = \frac{-(778 \text{ KJ/mol})}{298 \text{ K}} = -2610$ J/K·mol

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18.3

Calculating ΔS_{univ}

- Exercise:
  For the reaction: $2NH_3(g) \rightarrow N_2(g) + 3H_2(g)$, $\Delta S°_{rxn}$ and $\Delta H°_{rxn}$ are 198.5 J/K·mol and – 92.6 kJ/mol , respectively. Calculate $\Delta S°_{univ}$ associated with the reaction above at 25°C.

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

$$\Delta S_{univ} = \Delta S_{sys} + \Delta S_{surr}$$

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Predicting Spontaneity of a Process

- Here are the possible combinations of entropy changes, and how to predict whether a chemical process is spontaneous or not.

$$\Delta S_{univ} = \Delta S_{sys} + \Delta S_{surr}$$

TABLE 16.3 Interplay of ΔS_{sys} and ΔS_{surr} in Determining the Sign of ΔS_{univ}

Signs of Entropy Changes			
ΔS_{sys}	ΔS_{surr}	ΔS_{univ}	*Process Spontaneous?*
+	+	+	Yes
−	−	−	No (reaction will occur in opposite direction)
+	−	?	Yes, if ΔS_{sys} has a larger magnitude than ΔS_{surr}
−	+	?	Yes, if ΔS_{surr} has a larger magnitude than ΔS_{sys}

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Predicting Spontaneity of a Process

- Exercise:

  Predict if a process is most likely spontaneous when a highly exothermic reaction is undergone at a low temperature.

$$\Delta S_{univ} = \Delta S_{sys} + \Delta S_{surr}$$

TABLE 16.3 Interplay of ΔS_{sys} and ΔS_{surr} in Determining the Sign of ΔS_{univ}

Signs of Entropy Changes			
ΔS_{sys}	ΔS_{surr}	ΔS_{univ}	*Process Spontaneous?*
+	+	+	Yes
−	−	−	No (reaction will occur in opposite direction)
+	−	?	Yes, if ΔS_{sys} has a larger magnitude than ΔS_{surr}
−	+	?	Yes, if ΔS_{surr} has a larger magnitude than ΔS_{sys}

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Third Law of Thermodynamics

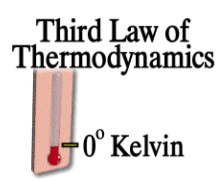
- For a perfect crystalline substance at absolute zero (0 K), there is only one way to arrange its constituents. They are not moving at all (the number of microstates is just one).

  $S = k \ln W$

  with $W = 1$

  $S = k \ln (1) = 0$

- The *third law of thermodynamic* states that entropy of a perfect crystalline substance at absolute zero temperature is zero.



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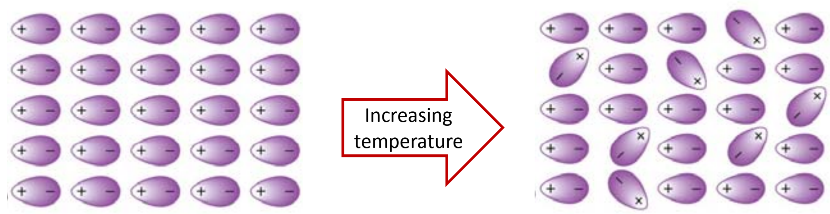
Third Law of Thermodynamics

- As the temperature of a perfect crystal is raised, the random vibrational motions increase, and disorder (*and number of microstates*) increases within the crystal.



A perfect crystal of HCl at 0 K. (S = 0)

More vibrations, more disorder and a greater number of microstates. (S = +ve)

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Third Law of Thermodynamics

- The *absolute* entropy of a substance at any given temperature can be determined using the third law of thermodynamics.

$$\Delta S = S_f - S_i$$

S_i is zero if the substance starts at 0 K.

$$\Delta S = S_f$$

The measured change in entropy is equal to the absolute entropy at the new temperature.

☞ Unlike enthalpy and internal energy, the *absolute value* of entropy of any substance can be determined. We usually refer to the standard entropies ($S°$)

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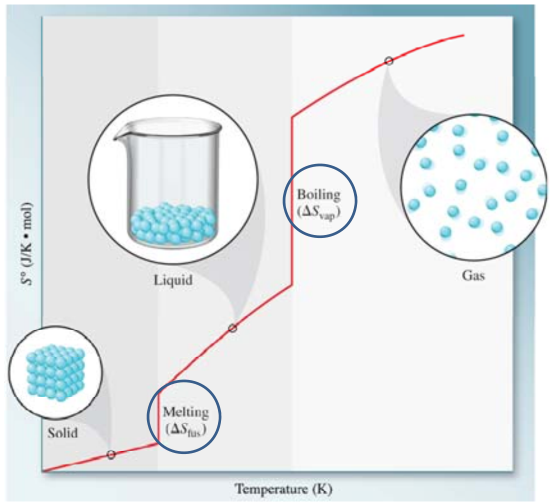
Entropy Change as a Function of Temperature



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