

Lecture Presentation

**Chapter 18**

**Free Energy and**

**Thermodynamics**

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## First Law of Thermodynamics

- You can't win!
- *The first law of thermodynamics is that energy cannot be created or destroyed.*
  - The total energy of combustion equals the energy that goes to propel the car and the amount dissipated as heat.

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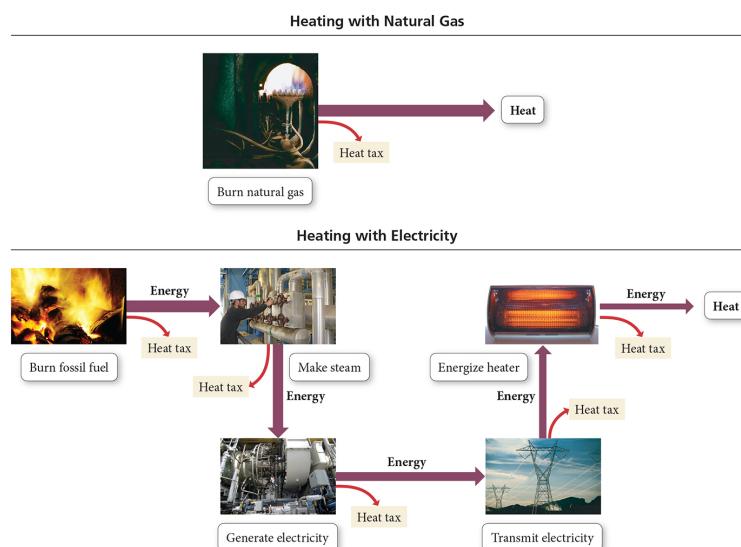
## The Energy Tax

- You can't break even!
- To recharge a battery with 100 kJ of useful energy will require more than 100 kJ because of the second law of thermodynamics.
- Every energy transition results in a “loss” of energy.
  - An “energy tax” demanded by nature
  - Conversion of energy to heat, which is “lost” by heating up the surroundings



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## Heat Tax



Fewer steps generally results in a lower total heat tax.

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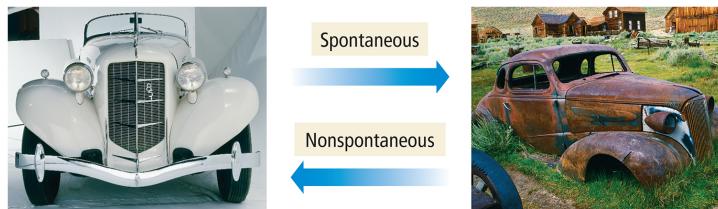
## Thermodynamics and Spontaneity

- Thermodynamics predicts whether a process will occur under the given conditions.
  - Processes that occur without ongoing outside intervention are called **spontaneous**.
    - Nonspontaneous processes require energy input to occur.
- Spontaneity is determined by comparing the **chemical potential energy** of the system before the reaction with the free energy of the system after the reaction.
  - If the system after reaction has less potential energy than before the reaction, the reaction is thermodynamically favorable.
- Spontaneity ≠ fast or slow

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## Reversibility of Process

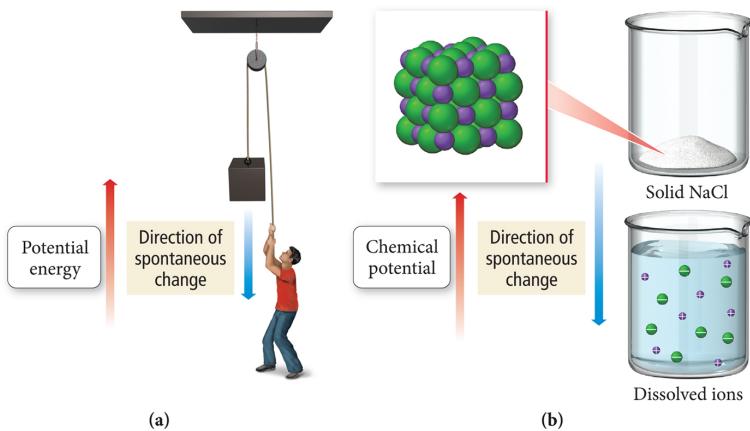
- Any spontaneous process is irreversible because there is a net release of energy when it proceeds in that direction.
  - It will proceed in only one direction.
- A reversible process will proceed back and forth between the two end conditions.
  - Any reversible process is at equilibrium.
  - This results in no change in free energy.
- If a process is spontaneous in one direction, it *must* be nonspontaneous in the opposite direction.



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## Comparing Potential Energy

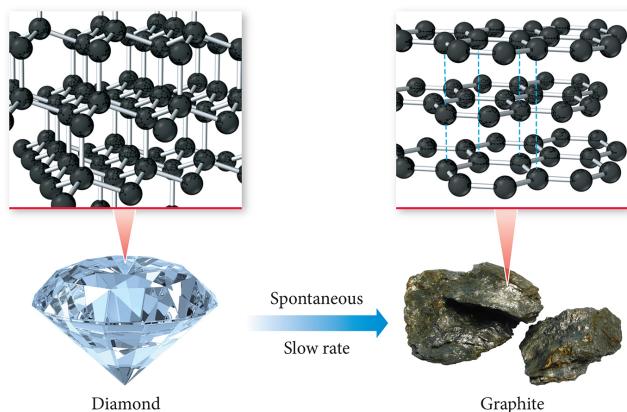
### The Concept of Chemical Potential



The direction of spontaneity can be determined by comparing the potential energy of the system at the start and the end.

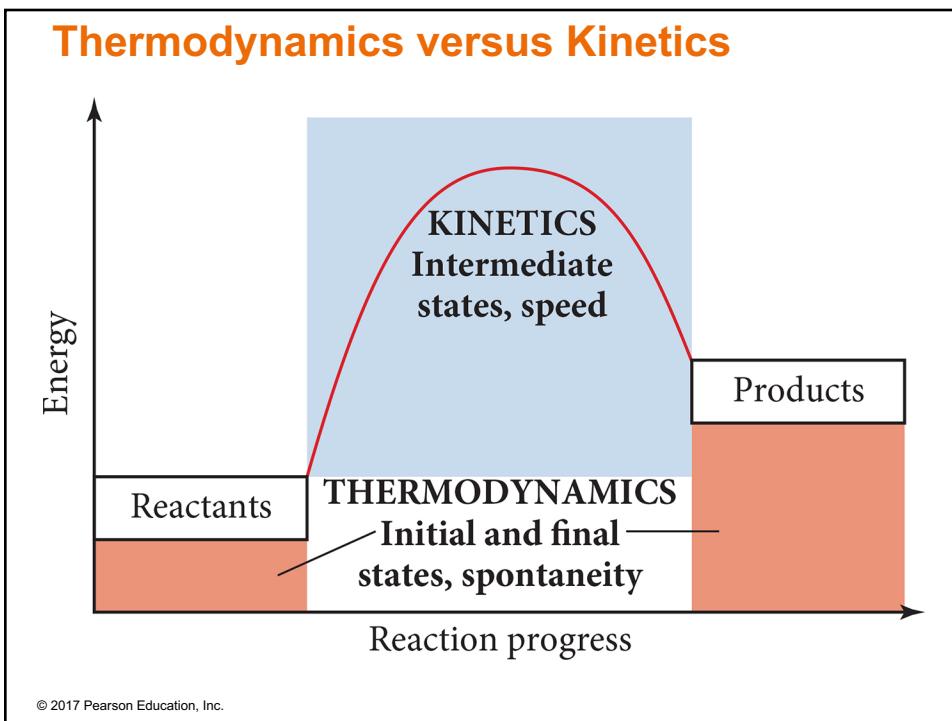
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## Diamond → Graphite



Graphite is more stable than diamond, so the conversion of diamond into graphite is spontaneous. But don't worry: It's so slow that your ring won't turn into pencil lead in your lifetime (or through many of your generations).

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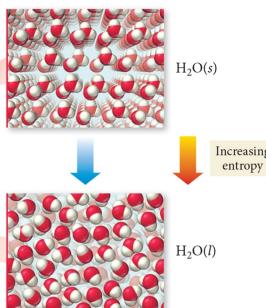
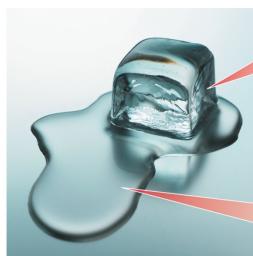
## Spontaneous Processes

- Spontaneous processes occur because they release energy from the system.
- Most spontaneous processes proceed from a system of higher potential energy to a system at lower potential energy.
  - **Exothermic**
- But there are some spontaneous processes that proceed from a system of lower potential energy to a system at higher potential energy.
  - **Endothermic**
- How can something absorb potential energy, yet have a net release of energy?

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## Melting Ice

Melting is an endothermic process, yet ice will spontaneously melt above 0 °C.

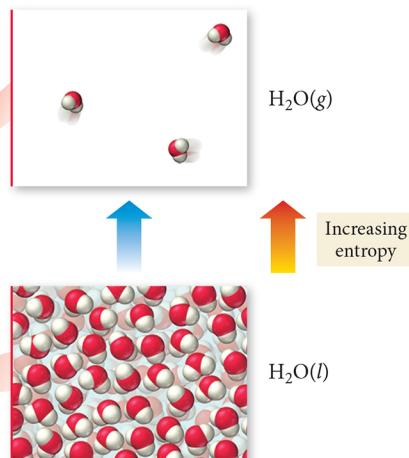


When a solid melts, the particles have more freedom of movement.

More freedom of motion increases the randomness of the system. When systems become more random, energy is released. We call this energy, **entropy**.

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## Water Evaporating



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## The Second Law of Thermodynamics

- The **second law of thermodynamics** states for any spontaneous process, the entropy of the universe increases.  
 $-\Delta S_{\text{univ}} > 0$
- Processes that increase the entropy of the universe occur spontaneously.
- Entropy is a state function.
- $\Delta S = \Delta S_{\text{final}} - \Delta S_{\text{initial}}$

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## Heat Transfer and Changes in Entropy of the Surroundings

- The second law demands that the entropy of the universe increases for a spontaneous process.
- Yet processes like water vapor condensing are spontaneous, even though the water vapor is more random than the liquid water.
- If a process is spontaneous, but the entropy change of the process is unfavorable, there must have been a large increase in the entropy of the surroundings.
- The entropy increase must come from heat released by the system; the process must be exothermic!

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## Factors Affecting Whether a Reaction Is Spontaneous

- There are two factors that determine whether a reaction is spontaneous. They are the **enthalpy change** and the **entropy change** of the system.
- The enthalpy change,  $\Delta H$ , is the difference in the sum of the internal energy and PV work energy of the reactants to the products.
- The entropy change,  $\Delta S$ , is the difference in randomness of the reactants compared to the products.

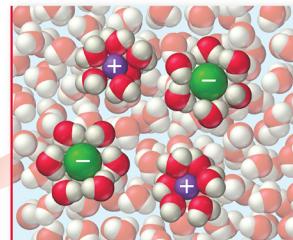
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## Entropy

- **Entropy** is a thermodynamic function that increases as the number of energetically equivalent ways of arranging the components increases,  $S$ .
  - $S$  generally J/mol•K
- $S = k \ln W$ 
  - $k$  = Boltzmann constant =  $1.38 \times 10^{-23}$  J/K
  - $W$  is the number of energetically equivalent ways a system can exist.
    - Unitless

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## Salt Dissolving in Water



$\text{NaCl}(aq)$

Increasing entropy



$\text{NaCl}(s)$

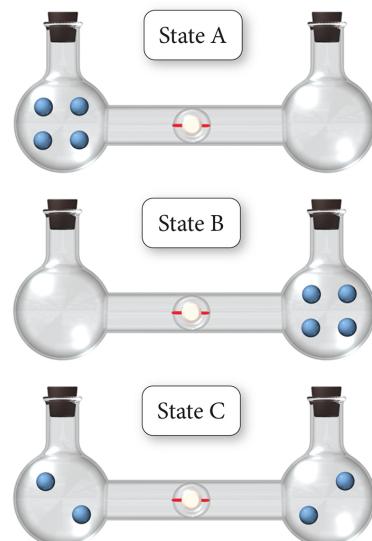
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**W**

These are energetically equivalent states for the expansion of a gas.

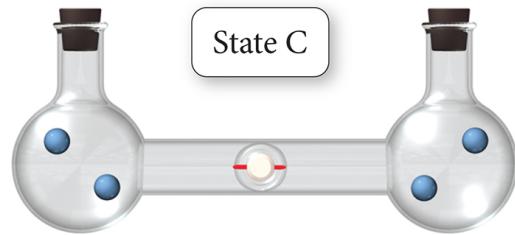
It doesn't matter, in terms of potential energy, whether the molecules are all in one flask or evenly distributed.

But one of these states is more probable than the other two.



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## Macrostates → Microstates



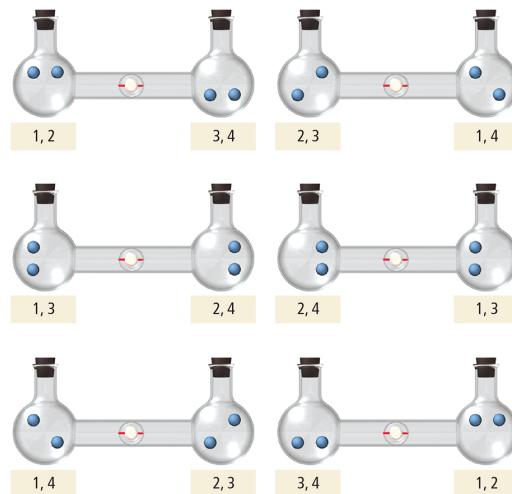
This macrostate can be achieved through several different arrangements of the particles.

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## Macrostates → Microstates

These microstates all have the same macrostate.

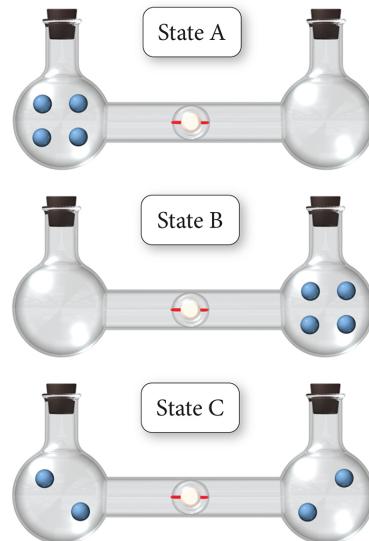
So there are six different particle arrangements that result in the same macrostate.



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## Macrostates and Probability

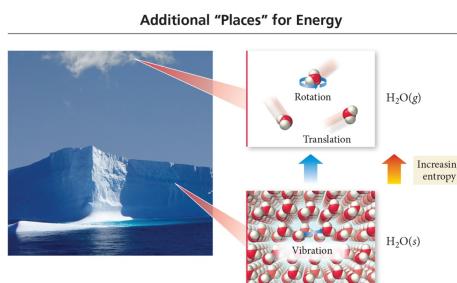
- There is only one possible arrangement that gives state A and one that gives state B.
- There are six possible arrangements that give state C.
- The macrostate with the highest entropy also has the greatest dispersal of energy.
- Therefore, state C has higher entropy than either state A or state B.
- *There is six times the probability of having the state C macrostate than either state A or state B.*



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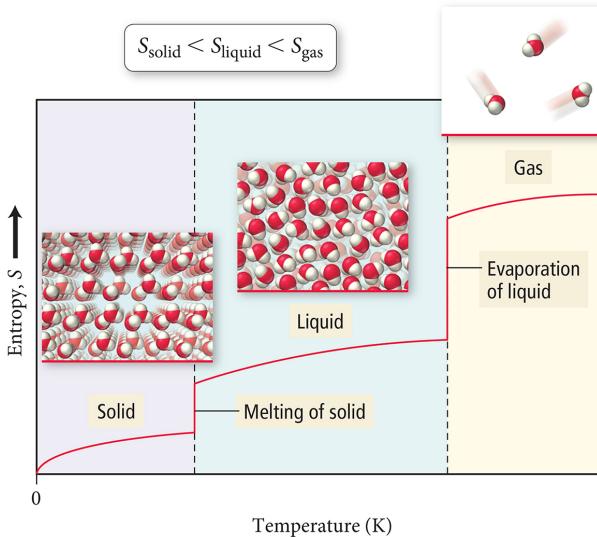
## Entropy Change in State Change

- When materials change state, the number of macrostates it can have changes as well.
  - The more energetically equivalent configurations the molecules have, the more macrostates are possible.
  - Gases have greater macrostates than liquids, which have greater macrostates than solids.



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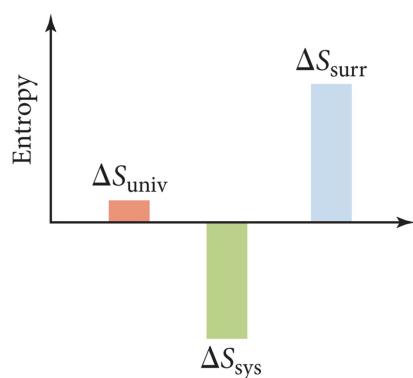
## Entropy Change and State Change



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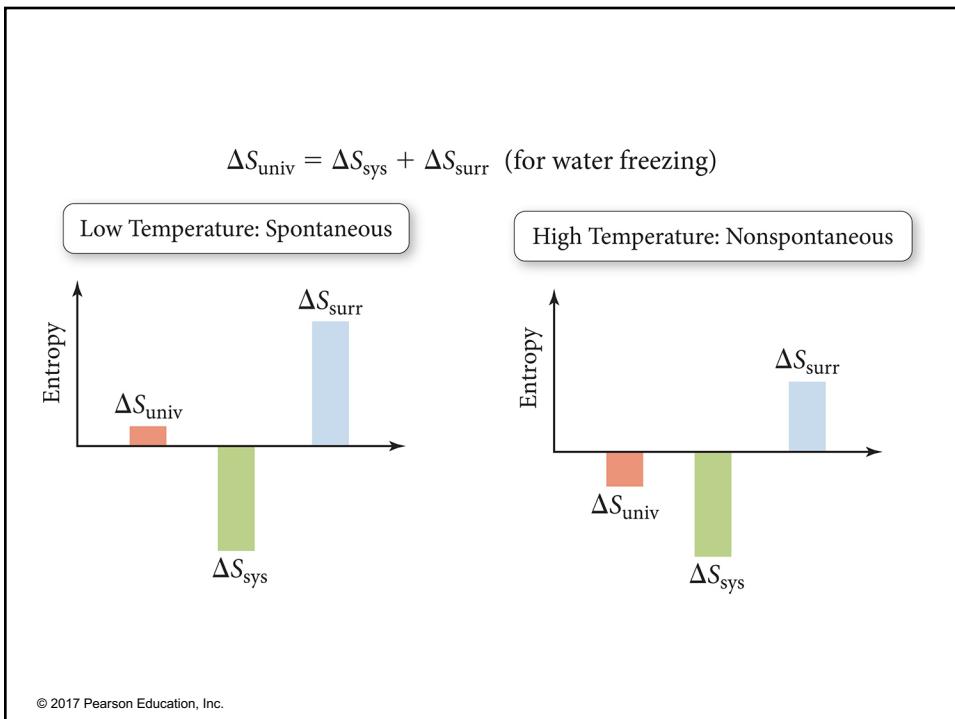
## Entropy Change in the System and Surroundings

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



When the entropy change in a system is unfavorable (negative), the entropy change in the surroundings must be favorable (positive) and large in order to allow the process to be spontaneous.

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## Heat Exchange and $\Delta S_{\text{surroundings}}$

- When a system process is exothermic, it adds heat to the surroundings, increasing the entropy of the surroundings.
- When a system process is endothermic, it takes heat from the surroundings, decreasing the entropy of the surroundings.
- The amount the entropy of the surroundings changes depends on its original temperature.
  - The higher the original temperature, the less effect addition or removal of heat has.

## Temperature Dependence of $\Delta S_{\text{surroundings}}$

- There is greater impact on entropy when heat is added to surroundings that are at lower temperature than at higher temperature.
- Water freezes spontaneously below 0 °C because the heat released on freezing increases the entropy of the surroundings enough to make  $\Delta S$  positive.
  - Above 0 °C the increase in entropy of the surroundings is insufficient to make  $\Delta S$  positive.

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## Quantifying Entropy Changes in Surroundings

- The entropy change in the surroundings is proportional to the amount of heat gained or lost.  $q_{\text{surroundings}} = -q_{\text{system}}$
- The entropy change in the surroundings is also inversely proportional to its temperature.
- At constant pressure and temperature, the overall relationship is as follows:

$$\Delta S_{\text{surr}} = \frac{-\Delta H_{\text{sys}}}{T} \quad (\text{constant } P, T)$$

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## Gibbs Free Energy

- From the previous relationships of  $\Delta S_{\text{univ}}$ , we can derive that  $-T\Delta S_{\text{univ}} = \Delta H_{\text{sys}} - T\Delta S_{\text{sys}}$ .
- The **Gibbs free energy**, **G**, is the maximum amount of work energy that can be released to the surroundings by a system for a constant temperature and pressure system.
  - Gibbs free energy is often called the **chemical potential** because it is analogous to the storing of energy in a mechanical system.
- $\Delta G_{\text{sys}} = \Delta H_{\text{sys}} - T\Delta S_{\text{sys}}$
- Because  $\Delta S_{\text{univ}}$  determines if a process is spontaneous,  $\Delta G$  also determines spontaneity.  $\Delta S_{\text{univ}}$  is positive when spontaneous, so  $\Delta G$  is negative.

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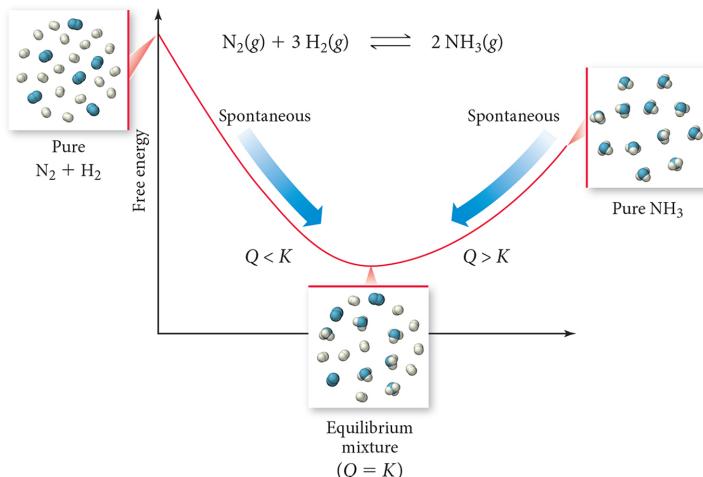
## Gibbs Free Energy, $\Delta G$

- A process will be spontaneous when  $\Delta G$  is negative.**
- $\Delta G$  will be negative when
  - $\Delta H$  is negative and  $\Delta S$  is positive.
    - Exothermic and more random
  - $\Delta H$  is negative and large, and  $\Delta S$  is negative but small.
    - At low temperature
  - $\Delta H$  is positive but small, and  $\Delta S$  is positive and large.
    - At high temperature
  - $\Delta G$  will be positive when  $\Delta H$  is positive and  $\Delta S$  is negative.
    - Never spontaneous at any temperature.
- When  $\Delta G = 0$  the reaction is at **equilibrium**.

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## Free Energy Change and Spontaneity

Gibbs Free Energy Determines the Direction of Spontaneous Change



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## $\Delta G$ , $\Delta H$ , and $\Delta S$

TABLE 18.1 The Effect of  $\Delta H$ ,  $\Delta S$ , and  $T$  on Spontaneity

$\Delta H$	$\Delta S$	Low Temperature	High Temperature	Example
-	+	Spontaneous ( $\Delta G < 0$ )	Spontaneous ( $\Delta G < 0$ )	$2 N_2O(g) \longrightarrow 2 N_2(g) + O_2(g)$
+	-	Nonspontaneous ( $\Delta G > 0$ )	Nonspontaneous ( $\Delta G > 0$ )	$3 O_2(g) \longrightarrow 2 O_3(g)$
-	-	Spontaneous ( $\Delta G < 0$ )	Nonspontaneous ( $\Delta G > 0$ )	$H_2O(l) \longrightarrow H_2O(s)$
+	+	Nonspontaneous ( $\Delta G > 0$ )	Spontaneous ( $\Delta G < 0$ )	$H_2O(l) \longrightarrow H_2O(g)$

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## Standard Conditions

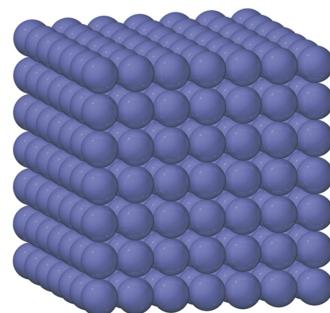
- The **standard state** is the state of a material at a defined set of conditions.
- For a gas: pure gas at exactly 1 atm
- For a liquid or solid: pure substance in its most stable form at exactly 1 atm pressure and temperature of interest
  - Usually 25 °C
- Solution = substance in a solution with concentration 1 M

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## The Third Law of Thermodynamics: Absolute Entropy

- The **absolute entropy** of a substance is the amount of energy it has due to dispersion of energy through its particles.
- The third law states that the entropy for a perfect crystal at 0 K is zero.
- Absolute entropy = 0 J/mol · K
  - A substance that isn't a perfect crystal at absolute zero has some energy from entropy.
  - The absolute entropy of substances is always positive.

Perfect crystal at 0 K  
 $W = 1$     $S = 0$



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## Standard Molar Entropy

- $S^\circ$
- Extensive property
- Standard molar entropy values are for 1 mole of substance at 298 K for a particular state, a particular allotrope, a particular molecular complexity, a particular molar mass, and a particular degree of dissolution.

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## Standard Molar Entropy

**TABLE 18.2** Standard Molar Entropy Values ( $S^\circ$ ) for Selected Substances at 298 K

Substance	$S^\circ$ (J/mol · K)	Substance	$S^\circ$ (J/mol · K)	Substance	$S^\circ$ (J/mol · K)
<b>Gases</b>		<b>Liquids</b>		<b>Solids</b>	
$\text{H}_2(g)$	130.7	$\text{H}_2\text{O}(l)$	70.0	$\text{MgO}(s)$	27.0
$\text{Ar}(g)$	154.8	$\text{CH}_3\text{OH}(l)$	126.8	$\text{Fe}(s)$	27.3
$\text{CH}_4(g)$	186.3	$\text{Br}_2(l)$	152.2	$\text{Li}(s)$	29.1
$\text{H}_2\text{O}(g)$	188.8	$\text{C}_6\text{H}_6(l)$	173.4	$\text{Cu}(s)$	33.2
$\text{N}_2(g)$	191.6			$\text{Na}(s)$	51.3
$\text{NH}_3(g)$	192.8			$\text{K}(s)$	64.7
$\text{F}_2(g)$	202.8			$\text{NaCl}(s)$	72.1
$\text{O}_2(g)$	205.2			$\text{CaCO}_3(s)$	91.7
$\text{Cl}_2(g)$	223.1			$\text{FeCl}_3(s)$	142.3
$\text{C}_2\text{H}_4(g)$	219.3				

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## Relative Standard Entropies: States

- The gas state has much larger entropy than the liquid state at a particular temperature.
- The liquid state has a larger entropy than the solid state at a particular temperature.

$S^\circ$  (J/mol · K)

$H_2O(l)$	70.0
$H_2O(g)$	188.8

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## Relative Standard Entropies: Molar Mass

- The larger the molar mass, the larger the entropy.
- Heavier atoms are closer to each other, allowing more dispersal of energy through the states.

$S^\circ$ (J/mol·K)		
He(g)	126.2	
Ne(g)	146.1	
Ar(g)	154.8	
Kr(g)	163.8	
Xe(g)	169.4	

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## Relative Standard Entropies: Allotropes

- The less constrained the structure of an allotrope is, the larger its entropy.
- The fact that the layers in graphite are not bonded together makes it less constrained.

S° (J/mol·K)		
C(s, diamond)	2.4	
C(s, graphite)	5.7	

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## Relative Standard Entropies: Molecular Complexity

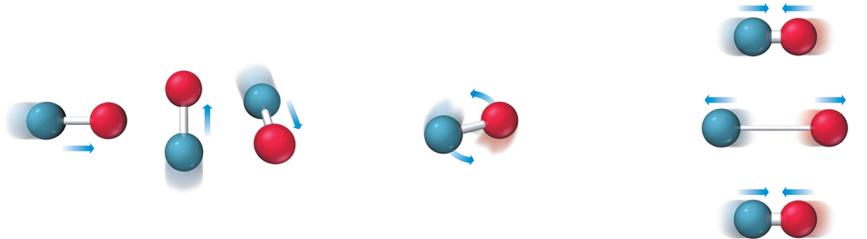
- Larger, more complex molecules generally have larger entropy.
- More energy states are available, allowing more dispersal of energy through the states.

	Molar Mass (g/mol)	S° (J/mol·K)
Ar(g)	39.948	154.8
NO(g)	30.006	210.8

	Molar Mass (g/mol)	S° (J/mol·K)
CO(g)	28.01	197.7
C <sub>2</sub> H <sub>4</sub> (g)	28.05	219.3

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## “Places” for Energy in Gaseous NO



Translational motion

Rotational motion

Vibrational motion

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## Relative Standard Entropies' Dissolution

- Dissolved solids generally have larger entropy, distributing particles throughout the mixture.

$S^\circ(\text{J/mol} \cdot \text{K})$

$\text{KClO}_3(\text{s})$	143.1
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$\text{KClO}_3(\text{aq})$	265.7
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## The Standard Entropy Change, $\Delta S$

- The standard entropy change is the difference in absolute entropy between the reactants and products under standard conditions.

$$\Delta S_{\text{rxn}}^{\circ} = \sum n_p S^{\circ}(\text{products}) - \sum n_r S^{\circ}(\text{reactants})$$

- Remember, although the standard enthalpy of formation,  $\Delta H_f^{\circ}$ , of an element is 0 kJ/mol, the absolute entropy at 25 °C,  $S^{\circ}$ , is always positive.

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## Calculating $\Delta G^{\circ}$

- At 25 °C

$$\Delta G_{\text{rxn}}^{\circ} = \sum n_p \Delta G_f^{\circ}(\text{products}) - \sum n_r \Delta G_f^{\circ}(\text{reactants})$$

- At temperatures other than 25 °C

- Assuming the change in  $\Delta H^{\circ}_{\text{reaction}}$  and  $\Delta S^{\circ}_{\text{reaction}}$  is negligible

$$\Delta G_{\text{rxn}}^{\circ} = \Delta H_{\text{rxn}}^{\circ} - T \Delta S_{\text{rxn}}^{\circ}$$

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## Standard Free Energies of Formation

- The free energy of formation ( $\Delta G_f^\circ$ ) is the change in free energy when 1 mol of a compound forms from its constituent elements in their standard states.
- The free energy of formation of pure elements in their standard states is zero.

**TABLE 18.3** Standard Molar Free Energies of Formation  $\Delta G_f^\circ$  for Selected Substances at 298 K

Substance	$\Delta G_f^\circ$ (kJ/mol)	Substance	$\Delta G_f^\circ$ (kJ/mol)
$\text{H}_2(g)$	0	$\text{CH}_4(g)$	-50.5
$\text{O}_2(g)$	0	$\text{H}_2\text{O}(g)$	-228.6
$\text{N}_2(g)$	0	$\text{H}_2\text{O}(l)$	-237.1
C(s, graphite)	0	$\text{NH}_3(g)$	-16.4
C(s, diamond)	2.900	$\text{NO}(g)$	+87.6
$\text{CO}(g)$	-137.2	$\text{NO}_2(g)$	+51.3
$\text{CO}_2(g)$	-394.4	NaCl(s)	-384.1

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## $\Delta G$ Relationships

- If a reaction can be expressed as a series of reactions, the sum of the  $\Delta G$  values of the individual reaction is the  $\Delta G$  of the total reaction.
  - $\Delta G$  is a state function.
- If a reaction is reversed, the sign of its  $\Delta G$  value reverses.
- If the amount of materials is multiplied by a factor, the value of the  $\Delta G$  is multiplied by the same factor.
  - The value of  $\Delta G$  of a reaction is extensive.

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## Why Free Energy Is “Free”

- The free energy is the maximum amount of energy available to do work.
- For many exothermic reactions, some of the heat released due to the enthalpy change goes into increasing the entropy of the surroundings, so it is not available to do work.
- And even some of this free energy is generally lost to heating up the surroundings.

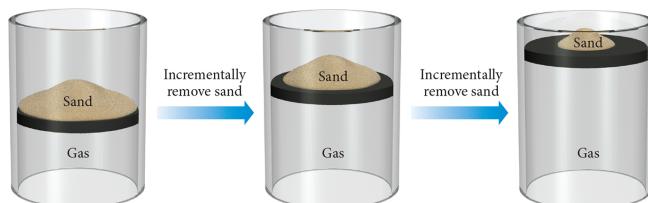
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## Free Energy and Reversible Reactions

- The change in free energy is a theoretical limit as to the amount of work that can be done.
- If the reaction achieves its theoretical limit, it is a reversible reaction.

### Reversible Process

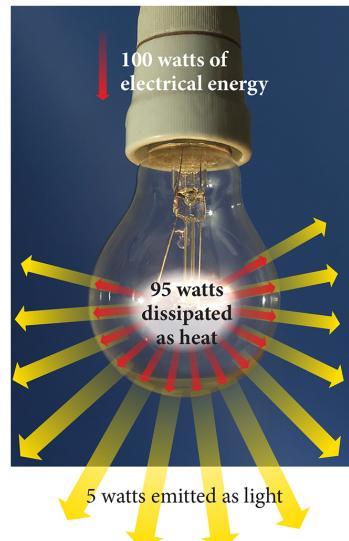
Weight of sand exactly matches pressure at each increment.



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## Real Reactions

- In a real reaction, some (if not most) of the free energy is “lost” as heat.
- Therefore, real reactions are irreversible.



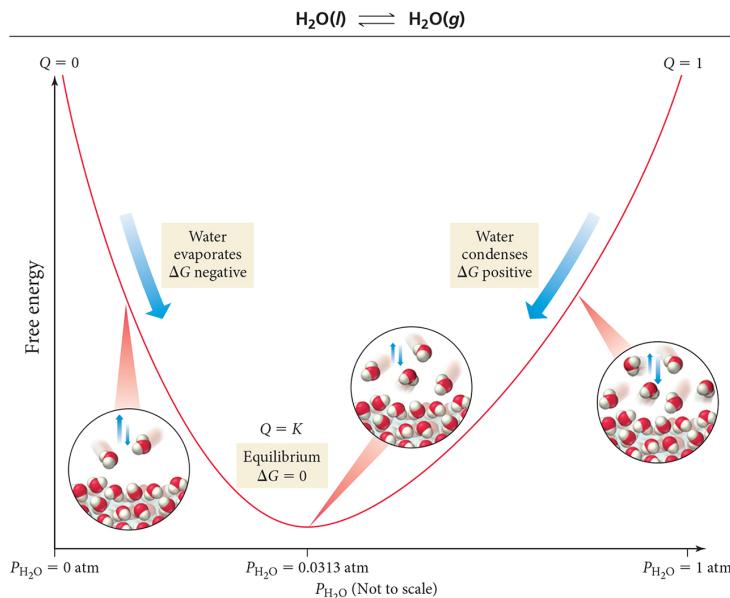
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## $\Delta G$ under Nonstandard Conditions

- $\Delta G = \Delta G^\circ$  only when the reactants and products are in their standard states.
  - Their normal state at that temperature
  - Partial pressure of gas = 1 atm
  - Concentration = 1 M
- Under nonstandard conditions,  $\Delta G = \Delta G^\circ + RT\ln Q$ .
  - Q is the reaction quotient.
- At equilibrium,  $\Delta G = 0$ .

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## Free Energy versus Pressure for Water

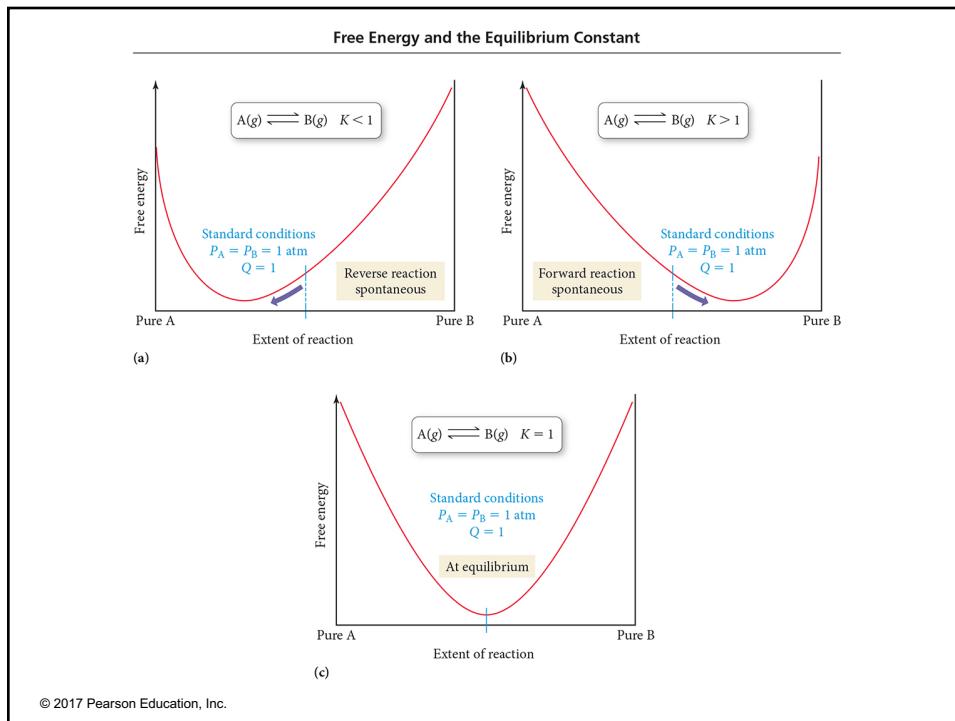


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## $\Delta G^\circ$ and $K$

- Because  $\Delta G_{\text{rxn}} = 0$  at equilibrium, then  $\Delta G^\circ = -RT\ln(K)$ .
- When  $K < 1$ ,  $\Delta G^\circ$  is positive, and the reaction is spontaneous in the reverse direction under standard conditions.
  - Nothing will happen until there are products present!
- When  $K > 1$ ,  $\Delta G^\circ$  is negative, and the reaction is spontaneous in the forward direction under standard conditions.
- When  $K = 1$ ,  $\Delta G^\circ$  is 0, and the reaction is at equilibrium under standard conditions.

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## Why Is the Equilibrium Constant Temperature-Dependent?

- Combining these two equations  
 $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$   
 $\Delta G^\circ = -RT\ln(K)$
  - It can be shown that
- $$\ln(K) = \frac{\Delta H_{rxn}^\circ}{R} \left( \frac{1}{T} \right) + \frac{\Delta S_{rxn}^\circ}{R}$$
- This equation is in the form  $y = mx + b$ .
  - The graph of  $\ln(K)$  versus inverse  $T$  is a straight line with slope  $\frac{\Delta H_{rxn}^\circ}{R}$  and  $y$ -intercept  $\frac{\Delta S_{rxn}^\circ}{R}$ .

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