

## Spontaneous Processes

- Thermodynamics is concerned with the question: can a reaction occur?
- First Law of Thermodynamics: energy is conserved.
- Any process that occurs without outside intervention is spontaneous.
- When two eggs are dropped they spontaneously break.
- The reverse reaction is not spontaneous.
- We can conclude that a spontaneous process has a direction.

## Spontaneous Processes

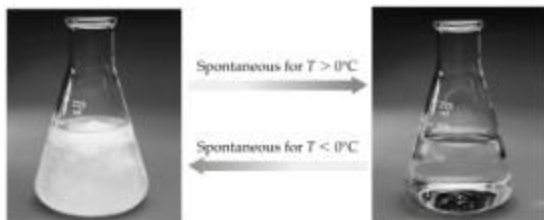
- A process that is spontaneous in one direction is not spontaneous in the opposite direction.
- The direction of a spontaneous process can depend on temperature: Ice turning to water is spontaneous at  $T > 0^\circ\text{C}$ , Water turning to ice is spontaneous at  $T < 0^\circ\text{C}$ .

### Reversible and Irreversible Processes

- A reversible process is one that can go back and forth between states along the same path.



## Spontaneous Processes



## Spontaneous Processes

### Reversible and Irreversible Processes

- When 1 mol of water is frozen at 1 atm at  $0^\circ\text{C}$  to form 1 mol of ice,  $q = \Delta H_{\text{vap}}$  of heat is removed.
- To reverse the process,  $q = \Delta H_{\text{vap}}$  must be added to the 1 mol of ice at  $0^\circ\text{C}$  and 1 atm to form 1 mol of water at  $0^\circ\text{C}$ .
- Therefore, converting between 1 mol of ice and 1 mol of water at  $0^\circ\text{C}$  is a reversible process.
- Allowing 1 mol of ice to warm is an irreversible process. To get the reverse process to occur, the water temperature must be lowered to  $0^\circ\text{C}$ .

## Spontaneous Processes

### Reversible and Irreversible Processes



## Spontaneous Processes

### Reversible and Irreversible Processes

- Chemical systems in equilibrium are reversible.
- In any spontaneous process, the path between reactants and products is irreversible.
- Thermodynamics gives us the direction of a process. It cannot predict the speed at which the process will occur.
- Why are endothermic reactions spontaneous?

## Entropy and the Second Law of Thermodynamics

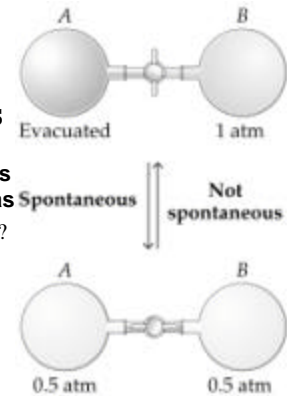
### The Spontaneous Expansion of a Gas

- Why do spontaneous processes occur?
- Consider an initial state: two flasks connected by a closed stopcock. One flask is evacuated and the other contains 1 atm of gas.
- The final state: two flasks connected by an open stopcock. Each flask contains gas at 0.5 atm.
- The expansion of the gas is isothermal (i.e. constant temperature). Therefore the gas does no work and heat is not transferred.

## Entropy and the Second Law of Thermodynamics

### The Spontaneous Expansion of a Gas

- Why does the gas expand?



## Entropy and the Second Law of Thermodynamics

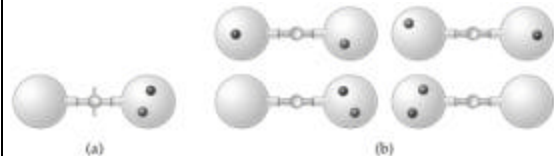
### The Spontaneous Expansion of a Gas

- Consider the simple case where there are two gas molecules in the flasks.
- Before the stopcock is open, both gas molecules will be in one flask.
- Once the stopcock is open, there is a higher *probability* that one molecule will be in each flask than that both molecules will be in the same flask.

## Entropy and the Second Law of Thermodynamics

### The Spontaneous Expansion of a Gas

- When there are many molecules, it is much more probable that the molecules will distribute among to the two flasks than all remain in only one flask.



## Entropy and the Second Law of Thermodynamics

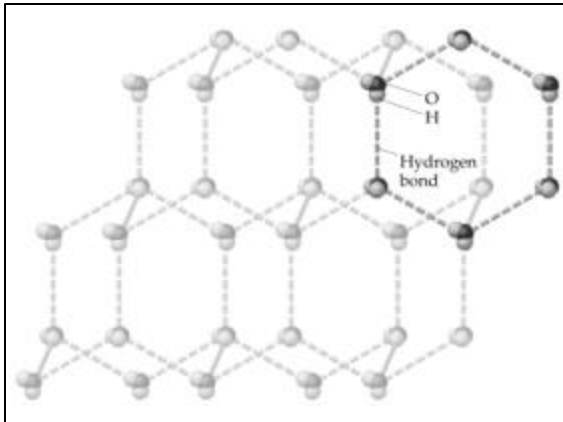
### Entropy

- Entropy,  $S$ , is a measure of the disorder of a system.
- Spontaneous reactions proceed to lower energy or higher entropy.
- In ice, the molecules are very well ordered because of the H-bonds.
- Therefore, ice has a low entropy.

## Entropy and the Second Law of Thermodynamics

### Entropy

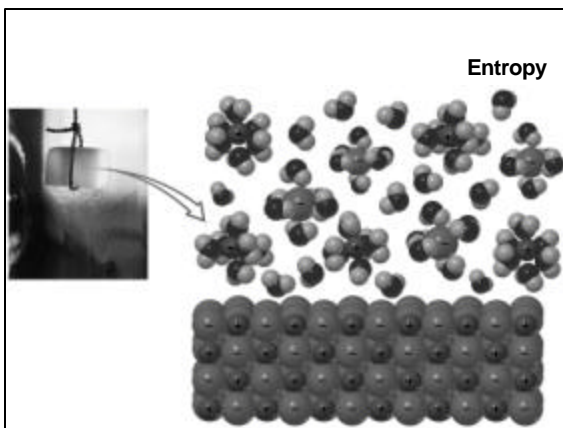
- As ice melts, the intermolecular forces are broken (requires energy), but the order is interrupted (so entropy increases).
- Water is more random than ice, so ice spontaneously melts at room temperature.



## Entropy and the Second Law of Thermodynamics

### Entropy

- There is a balance between energy and entropy considerations.
- When an ionic solid is placed in water two things happen:
  - the water organizes into hydrates about the ions (so the entropy decreases), and
  - the ions in the crystal dissociate (the hydrated ions are less ordered than the crystal, so the entropy increases).



## Entropy and the Second Law of Thermodynamics

### Entropy

- Generally, when an increase in entropy in one process is associated with a decrease in entropy in another, the increase in entropy dominates.
- Entropy is a state function.
- For a system,  $\Delta S = S_{\text{final}} - S_{\text{initial}}$ .
- If  $\Delta S > 0$  the randomness increases, if  $\Delta S < 0$  the order increases.

## Entropy and the Second Law of Thermodynamics

### Entropy

- Suppose a system changes reversibly between state 1 and state 2. Then, the change in entropy is given by

$$\Delta S_{\text{sys}} = \frac{q_{\text{rev}}}{T} \text{ (constant } T\text{)}$$

- at constant  $T$  where  $q_{\text{rev}}$  is the amount of heat added reversibly to the system. (Example: a phase change occurs at constant  $T$  with the reversible addition of heat.)

## Entropy and the Second Law of Thermodynamics

### The Second Law of Thermodynamics

- The second law of thermodynamics explains why spontaneous processes have a direction.
- In any spontaneous process, the entropy of the universe increases.
- $\Delta S_{\text{univ}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}}$ ; the change in entropy of the universe is the sum of the change in entropy of the system and the change in entropy of the surroundings.
- Entropy is not conserved:  $\Delta S_{\text{univ}}$  is increasing.

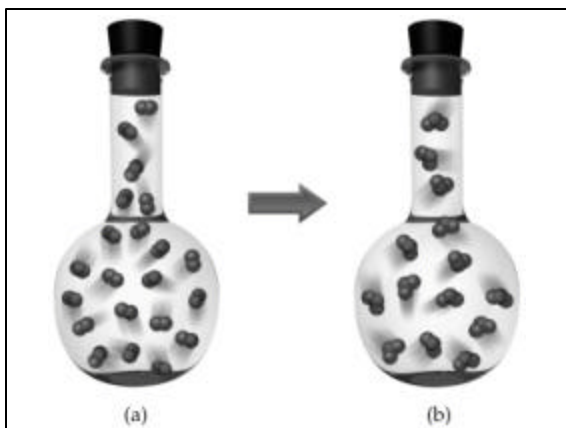
## Entropy and the Second Law of Thermodynamics

### The Second Law of Thermodynamics

- For a reversible process:  $\Delta S_{\text{univ}} = 0$ .
- For a spontaneous process (i.e. irreversible):  $\Delta S_{\text{univ}} > 0$ .
- Note: the second law states that the entropy of the universe must increase in a spontaneous process. It is possible for the entropy of a system to decrease as long as the entropy of the surroundings increases.
- For an isolated system,  $\Delta S_{\text{sys}} = 0$  for a reversible process and  $\Delta S_{\text{sys}} > 0$  for a spontaneous process.

## The Molecular Interpretation of Entropy

- A gas is less ordered than a liquid that is less ordered than a solid.
- Any process that increases the number of gas molecules leads to an increase in entropy.
- When  $\text{NO}(g)$  reacts with  $\text{O}_2(g)$  to form  $\text{NO}_2(g)$ , the total number of gas molecules decreases, and the entropy decreases.



## The Molecular Interpretation of Entropy

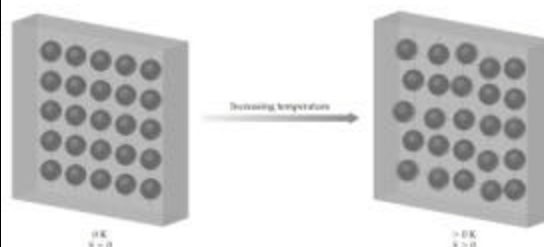
- There are three atomic modes of motion:
  - translation (the moving of a molecule from one point in space to another),
  - vibration (the shortening and lengthening of bonds, including the change in bond angles),
  - rotation (the spinning of a molecule about some axis).



## The Molecular Interpretation of Entropy

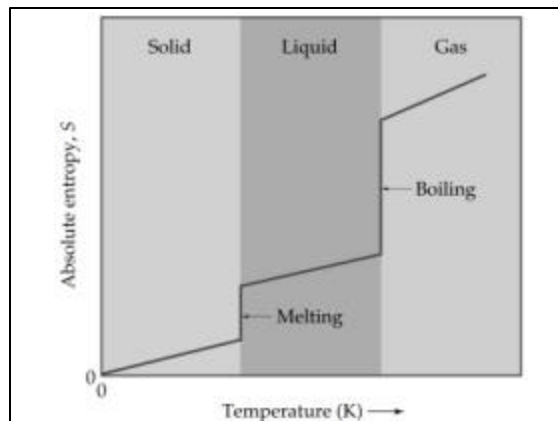
- Energy is required to get a molecule to translate, vibrate or rotate.
- The more energy stored in translation, vibration and rotation, the greater the degrees of freedom and the higher the entropy.
- In a perfect crystal at 0 K there is no translation, rotation or vibration of molecules. Therefore, this is a state of perfect order.

## The Molecular Interpretation of Entropy



## The Molecular Interpretation of Entropy

- Third Law of Thermodynamics: the entropy of a perfect crystal at 0 K is zero.
- Entropy changes dramatically at a phase change.
- As we heat a substance from absolute zero, the entropy must increase.
- If there are two different solid state forms of a substance, then the entropy increases at the solid state phase change.



## The Molecular Interpretation of Entropy

- Boiling corresponds to a much greater change in entropy than melting.
- Entropy will increase when
  - liquids or solutions are formed from solids,
  - gases are formed from solids or liquids,
  - the number of gas molecules increase,
  - the temperature is increased.

## Entropy Changes in Chemical Reactions

- Absolute entropy can be determined from complicated measurements.
- Standard molar entropy,  $S^\circ$ : entropy of a substance in its standard state. Similar in concept to  $\Delta H^\circ$ .
- Units: J/mol-K. Note units of  $\Delta H$ : kJ/mol.
- Standard molar entropies of elements are not zero.
- For a chemical reaction which produces  $n$  moles of products from  $m$  moles of reactants:
 
$$\Delta S^\circ = \sum nS^\circ(\text{products}) - \sum mS^\circ(\text{reactants})$$

TABLE 19.2 Standard Molar Entropies of Selected Substances at 298 K

Substance	$S^\circ$ , J/mol-K	Substance	$S^\circ$ , J/mol-K
<b>Gases</b>		<b>Solids</b>	
H <sub>2</sub> (g)	130.7	Li(s)	29.1
N <sub>2</sub> (g)	191.6	Na(s)	51.3
O <sub>2</sub> (g)	205.2	K(s)	64.7
H <sub>2</sub> O(g)	188.8	Fe(s)	27.3
NH <sub>3</sub> (g)	192.5	FeCl <sub>2</sub> (s)	142.3
CH <sub>3</sub> OH(g)	237.6	NaCl(s)	72.3
C <sub>6</sub> H <sub>6</sub> (g)	269.2		
<b>Liquids</b>			
H <sub>2</sub> O(l)	69.9		
CH <sub>3</sub> OH(l)	126.8		
C <sub>6</sub> H <sub>6</sub> (l)	172.8		

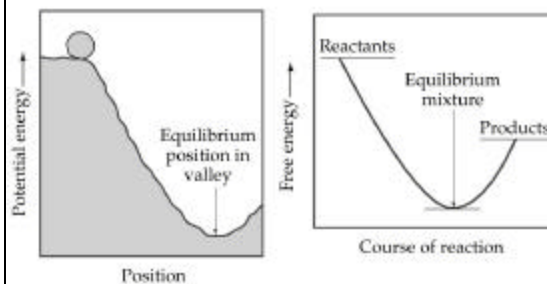
## Gibbs Free Energy

- For a spontaneous reaction the entropy of the universe must increase.
- Reactions with large negative  $\Delta H$  values are spontaneous.
- How do we balance  $\Delta S$  and  $\Delta H$  to predict whether a reaction is spontaneous?
- Gibbs free energy,  $G$ , of a state is
 
$$G = H - TS$$
- For a process occurring at constant temperature
 
$$\Delta G = \Delta H - T\Delta S$$

## Gibbs Free Energy

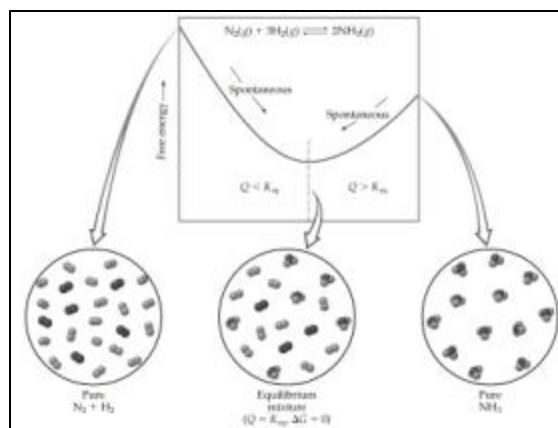
- There are three important conditions:
  - If  $\Delta G < 0$  then the forward reaction is spontaneous.
  - If  $\Delta G = 0$  then reaction is at equilibrium and no net reaction will occur.
  - If  $\Delta G > 0$  then the forward reaction is not spontaneous. If  $\Delta G > 0$ , work must be supplied from the surroundings to drive the reaction.
- For a reaction the free energy of the reactants decreases to a minimum (equilibrium) and then increases to the free energy of the products.

## Gibbs Free Energy



## Gibbs Free Energy

- Consider the formation of ammonia from nitrogen and hydrogen:
 
$$\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \rightleftharpoons 2\text{NH}_3(\text{g})$$
- Initially ammonia will be produced spontaneously ( $Q < K_{eq}$ ).
- After some time, the ammonia will spontaneously react to form  $\text{N}_2$  and  $\text{H}_2$  ( $Q > K_{eq}$ ).
- At equilibrium,  $\Delta G = 0$  and  $Q = K_{eq}$ .



## Gibbs Free Energy

### Standard Free-Energy Changes

- We can tabulate standard free-energies of formation,  $\Delta G_f^\circ$  (c.f. standard enthalpies of formation).
- Standard states are: pure solid, pure liquid, 1 atm (gas), 1 M concentration (solution), and  $\Delta G^\circ = 0$  for elements.
- $\Delta G^\circ$  for a process is given by
 
$$\Delta G^\circ = \sum n\Delta G_f^\circ(\text{products}) - \sum m\Delta G_f^\circ(\text{reactants})$$
- The quantity  $\Delta G^\circ$  for a reaction tells us whether a mixture of substances will spontaneously react to produce more reactants ( $\Delta G^\circ > 0$ ) or products ( $\Delta G^\circ < 0$ ).

## Free Energy and Temperature

- Focus on  $\Delta G = \Delta H - T\Delta S$ :
  - If  $\Delta H < 0$  and  $\Delta S > 0$ , then  $\Delta G$  is always negative.
  - If  $\Delta H > 0$  and  $\Delta S < 0$ , then  $\Delta G$  is always positive. (That is, the reverse of 1.)
  - If  $\Delta H < 0$  and  $\Delta S < 0$ , then  $\Delta G$  is negative at low temperatures.
  - If  $\Delta H > 0$  and  $\Delta S > 0$ , then  $\Delta G$  is negative at high temperatures.
- Even though a reaction has a negative  $\Delta G$  it may occur too slowly to be observed.

## Free Energy and Temperature

TABLE 19.4. Effect of Temperature on the Spontaneity of Reactions

$\Delta H$	$\Delta S$	$-T\Delta S$	$\Delta G = \Delta H - T\Delta S$	Reaction Characteristics	Example
-	+	-	Always negative	Spontaneous at all temperatures	$2O_3(g) \rightarrow 3O_2(g)$
+	-	+	Always positive	Nonspontaneous at all temperatures; reverse reaction always spontaneous	$3O_2(g) \rightarrow 2O_3(g)$
-	-	+	Negative at low T; positive at high T	Spontaneous at low T; becomes nonspontaneous at high T	$H_2O(l) \rightarrow H_2O(g)$
+	+	-	Positive at low T; negative at high T	Nonspontaneous at low T; becomes spontaneous at high T	$H_2O(s) \rightarrow H_2O(l)$



## Free Energy and The Equilibrium Constant

- Recall that  $\Delta G^\circ$  and  $K$  (equilibrium constant) apply to standard conditions.
- Recall that  $\Delta G$  and  $Q$  (equilibrium quotient) apply to any conditions.
- It is useful to determine whether substances under any conditions will react:

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

## Free Energy and The Equilibrium Constant

- At equilibrium,  $Q = K$  and  $\Delta G = 0$ , so

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

$$0 = \Delta G^\circ + RT \ln K_{eq}$$

$$\Delta G^\circ = -RT \ln K_{eq}$$

- From the above we can conclude:
  - If  $\Delta G^\circ < 0$ , then  $K > 1$ .
  - If  $\Delta G^\circ = 0$ , then  $K = 1$ .
  - If  $\Delta G^\circ > 0$ , then  $K < 1$ .