

Thermodynamics

Work, Entropy, Free Energy, and the Direction of Chemical Reactions

The First Law of Thermodynamics: Energy Conservation/ Work

•The Second Law of Thermodynamics: Entropy

•The Third Law of Thermodynamics: Entropy @ Absolute Zero

•Calculating the Change in Entropy of a Reaction

•Entropy, Free Energy, and Work

•Free Energy, Equilibrium, and Reaction Direction



# The First Law of Thermodynamics Work vs. Energy Flow

#### Spontaneous Processes

- Thermodynamics addresses the question: can a reaction occur?
- Any process that occurs without outside intervention is spontaneous.
- When an egg is dropped, it spontaneously breaks.
- The reverse reaction is not spontaneous. (Humpty Dumpty couldn't be put back together again.)
- A spontaneous process therefore occurs in only one direction. (At a given set of conditions: temperature & pressure.)



#### **Spontaneous Processes**

- A process that is spontaneous in one direction is not spontaneous in the opposite direction.
- Example: At 1 atm ice turns to water spontaneously at *T* > 0°C, Water turns to ice spontaneously at *T* < 0°C.



#### **Spontaneous Processes**

- Chemical systems in equilibrium are reversible and are **not** spontaneous.
- In any spontaneous process, the path between reactants and products is irreversible.
- Thermodynamics provides the direction of a process. *It cannot predict the speed (rate) at which the process will occur.*
- Endothermic and exothermic reactions can both be spontaneous.





# Entropy and the Second Law of Thermodynamics

#### Entropy (S) is a measure of disorder

- A system with little freedom, such as a crystalline solid or a deck of cards in a specific sequence, has relatively small disorder and low entropy.
- A system with many degrees of freedom (possible arrangements), such as a gas or a shuffled deck of cards, has relatively *large disorder and high entropy*.

 $S_{
m disorder} > S_{
m order}$ 

$$\Delta S_{\rm sys} = S_{\rm final} - S_{\rm initial}$$



#### QUESTION # T.1

The sign on  $\Delta S$  for the system in a certain chemical change is negative. The  $\Delta S$  value for the surroundings for the same reaction is positive. What would have to be true to make the reaction represent a spontaneous change?

- A. The  $\Delta S$  of the system would have to have a greater magnitude than  $\Delta S$  of the surroundings.
- B. The  $\Delta S$  of the surroundings would have to have a greater magnitude than the  $\Delta S$  of the system.
- C. This change could never be spontaneous as written. However, the reverse reaction will be spontaneous.
- D. My spontaneous answer? I don't know yet.























and  $\Delta S_{svs} > 0$  for a spontaneous process.







### Molecular Motion & Entropy

- Heat increases molecular motion, and therefore entropy must increase.
- Entropy increases markedly at the temperature of a phase change.
- 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.



The Third Law of Thermodynamics: the entropy of a perfect crystal at 0 K is zero.

## Ouestions #T.8-T.13 Which member has the higher entropy in each of the following pairs? [Assume constant temperature, except in (6).] Consider: The less ordered a system, the greater the entropy. (1) A: 1 mol NaCl<sub>(s)</sub> or B: 1 mol NaCl<sub>(aq)</sub>

- (2) A: 1 mol SF<sub>6</sub> or B: 1 mol SCl<sub>6</sub>
- (3) A: 1 mol  $CO_{2 (g)}$  or B: 1 mol  $CO_{(g)}$ (4) A: 1 mol  $S_8$  or B: 4 mol  $S_2$
- (5) A: 1 mol H<sub>2</sub>O<sub>(g)</sub> or B: 1 mol H<sub>2</sub>O<sub>(s)</sub>
  (6) Chicken noodle soup at A: 24°C or at B: 95°C

#### **Entropy & Entropy Changes**

- Absolute entropy can be determined from complicated experimental measurements.
- Standard molar entropy, S°: entropy of a substance in its standard state. Similar in concept to ΔH°.
- + Units: J/mol·K Note units of  $\Delta H$ : kJ/mol.
- Standard molar entropies of elements are not zero.

	Standard Molar Entr	opies of Sele	cted Substances at		
298 K					
Substance	S°, J/mol-K	Substance	S°, J/mol-K		
Gases		Solids			
$H_2(g)$	130.7	Li(s)	29.1		
$N_2(g)$	191.6	Na(s)	51.3		
$O_2(g)$	205.2	K(s)	64.7		
$H_2O(g)$	188.8	Fe(s)	27.3		
$NH_3(g)$	192.5	FeCl <sub>3</sub> (s)	142.3		
CH <sub>3</sub> OH(g)	237.6	NaCl(s)	72.3		
$C_6H_6(g)$	<sup>269.2</sup> Fo	or a chemica	l reaction which		
Liquids	produces n products from m				
$H_2O(l)$	69.9	reactants.			
CH <sub>3</sub> OH(I)	126.8	-	-		
$C_6H_6(I)$	172.8 ΔS°	$=\sum nS^{\circ}(\text{produ})$	$acts$ ) – $\sum mS^{\circ}(reactants)$		

The Standard Entropy of Reaction, 
$$\Delta S^{o}_{rxn}$$
For many chemical reactions:  $\Delta S^{o} = S^{o}_{products} - S^{o}_{reactants} > 0$ But for reactions in which the total # of moles of products decrease,  
particularly gases which have very high entropy, we predict that the  
entropy of the products is less than that of the reactants. Therefore,  
the entropy will decrease during the reaction:  
 $N_{2(g)} + 3 H_{2(g)} \longrightarrow 2 NH_{3(g)} \Delta S^{o} = S^{o}_{products} - S^{o}_{reactants} < 0$ **Standard entropy of reaction**,  $\Delta S^{o}_{rxn}$ :  
 $\Delta S^{o}_{rxn} = \sum m S^{o}_{products} - \sum n S^{o}_{reactants}$  $\Delta S^{o}_{rxn} = (2 \text{ mol NH}_{3} \times S^{o} \text{ of NH}_{3}) - [(1 \text{ mol x 191.5 J/mol K}) + (3 \text{ mol x 130.6 J/mol-K})]$  $\Delta S^{o}_{rxn} = -197 \text{ J/K}$ As predicted,  $\Delta S^{o} < 0$ 











#### Entropy Changes in the Surroundings

The second law of thermodynamics restated says:

Decreases in the entropy of the system can occur only if **increases** in the entropy of the surroundings outweigh them.

•The surroundings either add energy to the system or remove energy from it.

•Therefore there are two possible types of enthalpy changes in chemical reactions.





#### QUESTION # T.15

To produce hydrogen gas through electrolysis at 25°C the following reaction is used: H<sub>2</sub>O (*l*)  $\rightarrow$  H<sub>2</sub>(*g*) + 1/2O<sub>2</sub>(*g*). The reaction has a  $\Delta H$  value of 286 kJ. What is the value for  $\Delta S$  of the surroundings for this process?

- A. 11.4 kJ/K
- B. -11.4 kJ/K
- C. 960 J/K
- D. -960 J/K

Interplay of $\Delta S_{sys}$ and $\Delta S_{surr}$ in Determining the Sign of $\Delta S_{univ}$				
Signs of Entropy Changes				
$\Delta S_{sys}$	$\Delta S_{\rm surr}$	$\Delta S_{univ}$	Process Spontaneous?	
+	+	+	Yes	
-	-	_	No (reaction will occur in opposite direction)	
+	-	?	Yes, if $\Delta S_{sys}$ has a larger magnitude than $\Delta S_{surr}$	
-	+	?	Yes, if $\Delta S_{surr}$ has a large magnitude than $\Delta S_{sys}$	

