

**Spontaneous** Physical and Chemical Processes

- A waterfall runs downhill
- A lump of sugar dissolves in a cup of coffee
- At 1 atm, water freezes below 0 °C and ice melts above 0 °C
- Heat flows from a hotter object to a colder object
- Iron exposed to oxygen and water forms rust
- Some processes are **nonspontaneous**
- A balloon pops, but cannot un-pop



## Formal definitions

• **Spontaneous process:**

– A process that proceeds in a given direction without outside intervention

• **Nonspontaneous process:**

– A process that occurs only as long as energy is added to the system

• **Spontaneity ≠ fast or slow**

**Entropy (S)** is a measure of the **randomness or disorder** of a system.

order ↑ S ↓      disorder ↑ S ↑

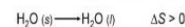
$$\Delta S = S_f - S_i \quad \text{or} \quad \Delta S = S_{\text{products}} - S_{\text{reactants}}$$

If the change from initial to final results in an increase in randomness

$$S_f > S_i \quad \Delta S > 0$$

For any substance, the solid state is more ordered than the liquid state and the liquid state is more ordered than gas state.

$$S_{\text{solid}} < S_{\text{liquid}} < S_{\text{gas}}$$



## Thermodynamics: Entropy

• **Second Law of Thermodynamics:**

– The total entropy of the universe increases in any spontaneous process

• **Entropy (S):**

– In P. Chem terms: A measure of the distribution of energy in a system at a specific T

– Energy distribution affected by

- Molecular motion
- Volume



## Motion of molecules

## • Three types:

a) Translational — movement through space



b) Rotational — spinning motion around center of mass



c) Vibrational — movement of atoms toward/away from each other



## Entropy and Microstates

The motion of molecules is **quantized**:

– Different states related to molecular motion are separated by specific energies

**Energy state or energy level:**

– An allowed value of energy

**Microstate:**

– A unique distribution of particles among energy levels

**Statistical mechanics:**

– Predicting the motion of particles involves some **chance and probability**



$$S = k \ln W$$

• **k** is not rate constant, but **Boltzmann constant**

- $S$  = entropy
- $W$  = # of microstates
- $k$  = Boltzmann constant ( $1.38 \times 10^{-23} \text{ J/K}$ )  
=  $R/N_A$

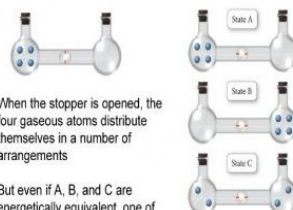
• Entropy increases as # of microstates increases

• Disorder and number of “possibilities” are directly proportional!



## Entropy: Expansion of Gas in a Vacuum

Consider the following situation:



• When the stopper is opened, the four gaseous atoms distribute themselves in a number of arrangements

• But even if A, B, and C are energetically equivalent, one of these states is more probable than the other two

**First Law of Thermodynamics**

Energy can be converted from one form to another but energy cannot be created or destroyed.

**Second Law of Thermodynamics**

The entropy of the **universe** increases in a spontaneous (irreversible) process and remains unchanged in an equilibrium (reversible) process.

$$\text{Spontaneous process:} \quad \Delta S_{\text{univ}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}} > 0$$

$$\text{Equilibrium process:} \quad \Delta S_{\text{univ}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}} = 0$$

If the entropy of the system decreases, then the entropy of the surroundings must increase by a larger amount:

When  $\Delta S_{\text{sys}} < 0$ , then  $\Delta S_{\text{surr}} > 0$  and large for a spontaneous process.

# CHEM 1120- 19.3.8

[SPELL CARD]

## Macrostates and Probability

- State A and state B each have only **ONE** possible arrangement
- Whereas state C has **SIX** possible arrangements

Therefore, state C has higher **entropy** than either state A or state B



37192641

© 2017 TRAVIS

B-0A  
YU-6

# CHEM 1120- 19.3.9

[SPELL CARD]

## Entropy

**State functions** are properties that are determined by the state of the system, regardless of how that condition was achieved.

Examples:

energy, enthalpy, pressure, volume, temperature, **entropy**

Copyright © The McGraw-Hill Companies, Inc. Permission is granted for reproduction or display.

Review



Potential energy of hiker 1 and hiker 2 is the same even though they took different paths.

37192641

© 2017 TRAVIS

B-0A  
YU-6

# CHEM 1120- 19.4.1

[SPELL CARD]

## Entropy Changes in the System ( $\Delta S_{\text{sys}}$ )

The **standard entropy of reaction** ( $\Delta S_{\text{rxn}}^\circ$ ) is the entropy change for a reaction carried out at 1 atm and 25°C.



$$\Delta S_{\text{rxn}}^\circ = [cS^\circ(C) + dS^\circ(D)] - [aS^\circ(A) + bS^\circ(B)]$$

$$\Delta S_{\text{rxn}}^\circ = \sum nS^\circ(\text{products}) - \sum mS^\circ(\text{reactants})$$

37192641

© 2017 TRAVIS

B-0A  
YU-6

# CHEM 1120- 19.4.2

[SPELL CARD]

## Entropy Changes in the System ( $\Delta S_{\text{sys}}$ )

When gases are produced (or consumed)

- Generally, if a reaction produces more gas molecules than it consumes,  $\Delta S^\circ > 0$
- If the total number of gas molecules diminishes,  $\Delta S^\circ < 0$
- If there is no net change in the total number of gas molecules, then  $\Delta S^\circ$  may be positive or negative BUT  $\Delta S^\circ$  will be a small number.

37192641

© 2017 TRAVIS

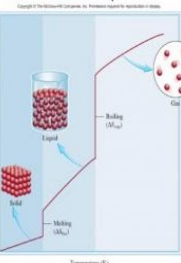
B-0A  
YU-6

# CHEM 1120- 19.4.3

[SPELL CARD]

## Third Law of Thermodynamics

The entropy of a perfect crystalline substance is zero at the absolute zero of temperature.



$$S = k_B \ln W$$

$$W = 1$$

$$S = 0$$

Every substance that is not a perfect crystal at absolute zero has **some** energy from entropy

Therefore, the absolute entropy of substances is **always** positive

37192641

© 2017 TRAVIS

B-0A  
YU-6

# CHEM 1120- 19.4.4

[SPELL CARD]

## Second Law of Thermodynamics

The entropy of the **universe** increases in a spontaneous process and remains unchanged in an equilibrium process.

Spontaneous process:  $\Delta S_{\text{univ}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}} > 0$

Equilibrium process:  $\Delta S_{\text{univ}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}} = 0$

At equilibrium, there is no observable change

No spontaneity in either direction!

37192641

© 2017 TRAVIS

B-0A  
YU-6

# CHEM 1120- 19.5.1

[SPELL CARD]

## Quantifying Entropy Changes in Surroundings

- The entropy change in the surroundings is proportional to the amount of heat gained or lost

$$q_{\text{surr}} = -q_{\text{sys}}$$

- The entropy change in the surroundings is also inversely proportional to the temperature

- At constant pressure and temperature, the overall relationship is:

$$\Delta S_{\text{surr}} = \frac{-q_{\text{sys}}}{\text{Temperature (T)}} = \frac{-\Delta H_{\text{sys}}}{T}$$

37192641

© 2017 TRAVIS

B-0A  
YU-6

# CHEM 1120- 19.5.2

[SPELL CARD]

Recall the second law of thermodynamics

Spontaneous process:  $\Delta S_{\text{univ}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}} > 0$

Equilibrium process:  $\Delta S_{\text{univ}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}} = 0$

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

**Gibbs free energy (G)** For a constant temperature and constant pressure process:

$$\Delta G = \Delta H_{\text{sys}} - T\Delta S_{\text{sys}}$$

$\Delta G < 0$  The reaction is spontaneous in the forward direction.

$\Delta G > 0$  The reaction is nonspontaneous as written. The reaction is spontaneous in the reverse direction.

$\Delta G = 0$  The reaction is at equilibrium.

37192641

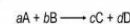
© 2017 TRAVIS

B-0A  
YU-6

# CHEM 1120- 19.5.3

[SPELL CARD]

The **standard free-energy of reaction** ( $\Delta G_{\text{rxn}}^\circ$ ) is the free-energy change for a reaction when it occurs under standard-state conditions.



$$\Delta G_{\text{rxn}}^\circ = [c\Delta G_f^\circ(C) + d\Delta G_f^\circ(D)] - [a\Delta G_f^\circ(A) + b\Delta G_f^\circ(B)]$$

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

**Standard free energy of formation** ( $\Delta G_f^\circ$ ) is the free-energy change that occurs when **1 mole** of the compound is formed from its elements in their standard states.

$\Delta G_f^\circ$  of any element in its **most** stable form in standard state is zero.

37192641

© 2017 TRAVIS

B-0A  
YU-6



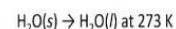


## What makes a reaction spontaneous?

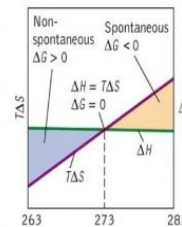
- $\Delta G = \Delta H - T\Delta S$
- Always if:
  - $\Delta H_{\text{rxn}} < 0$
  - And there is an increase in entropy
  - $\Delta S_{\text{rxn}} > 0$
- Sometimes if:
  - $\Delta S_{\text{rxn}} < 0$  and  $\Delta H_{\text{rxn}} < 0$  [ $T\Delta S < \Delta H$ ]
  - $\Delta S_{\text{rxn}} > 0$  and  $\Delta H_{\text{rxn}} > 0$  [ $T\Delta S > \Delta H$ ]
- Never if:
  - $\Delta S_{\text{rxn}} < 0$  and  $\Delta H_{\text{rxn}} > 0$

TABLE 19.2 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 ( $\Delta G < 0$ )	$2\text{N}_2\text{O(g)} \rightarrow 2\text{N}_2\text{(g)} + \text{O}_2\text{(g)}$
+	–	Nonspontaneous ( $\Delta G > 0$ )	Nonspontaneous ( $\Delta G > 0$ )	$3\text{O}_2\text{(g)} \rightarrow 2\text{O}_3\text{(g)}$
–	–	Spontaneous ( $\Delta G < 0$ )	Nonspontaneous ( $\Delta G > 0$ )	$\text{H}_2\text{O(l)} \rightarrow \text{H}_2\text{O(g)}$
+	+	Nonspontaneous ( $\Delta G > 0$ )	Spontaneous ( $\Delta G < 0$ )	$\text{H}_2\text{O(l)} \rightarrow \text{H}_2\text{O(s)}$

When can  $-T\Delta S$  counteract  $\Delta H$ ?

$\Delta H$  = positive  
 $\Delta S$  = positive  
 $\Delta G = \Delta H - T\Delta S$   
 becomes negative  
 above a certain  
 temperature  
 when  $T\Delta S > \Delta H$



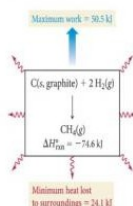
## What's "Free" about Free Energy?

- The free energy is the maximum amount of energy released from a system that is available to do work on the surroundings
- For many exothermic reactions, the  $\Delta G_{\text{rxn}}$  is less than the  $\Delta H_{\text{rxn}}$ 
  - Some of the heat released as a result of the enthalpy change goes into increasing the entropy of the surroundings
  - It is not available to do work



## Free Energy of an Exothermic Reaction

- $\text{C(s, graphite)} + 2\text{H}_2\text{(g)} \rightarrow \text{CH}_4\text{(g)}$
- $\Delta H_{\text{rxn}}^\circ = -74.6 \text{ kJ}$  = exothermic
- $\Delta S_{\text{rxn}}^\circ = -80.8 \text{ J/K}$  = unfavorable
- $\Delta G_{\text{rxn}}^\circ = -50.5 \text{ kJ}$  = spontaneous



$\Delta G^\circ$  is less than  $\Delta H^\circ$  because some of the released heat energy is lost to increase the entropy of the surroundings.



## Gibbs Free Energy and Chemical Equilibrium

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

$R$  is the gas constant (8.314 J/K·mol)

$T$  is the absolute temperature (K)

$Q$  is the reaction quotient

At Equilibrium

$$\Delta G = 0 \quad Q = K$$

$$0 = \Delta G^\circ + RT \ln K$$

$$\Delta G^\circ = -RT \ln K$$

Table 17.4 Relation Between  $\Delta G^\circ$  and  $K$  as Predicted by the Equation  $\Delta G^\circ = -RT \ln K$ 

$K$	$\ln K$	$\Delta G^\circ$	Comments
$> 1$	Positive	Negative	Products are favored over reactants at equilibrium.
$= 1$	0	0	Products and reactants are equally favored at equilibrium.
$< 1$	Negative	Positive	Reactants are favored over products at equilibrium.

$\Delta G < 0$  is spontaneous, also called **exergonic**

$\Delta G > 0$  is non-spontaneous, also called **endergonic**



## Thermodynamics versus Kinetics

