

Section 16.1

Spontaneity



Michael Stogsdill

Mott Community College

Learning Objectives



- Distinguish between spontaneous and nonspontaneous processes
- Describe the dispersal of matter and energy that accompanies certain spontaneous processes

Spontaneity



- Processes have a natural tendency to occur in one direction under a given set of conditions.
 - Water will naturally flow downhill, but uphill flow requires a pump.
 - Iron exposed to air will corrode, but rust is not converted to iron requires smelting
- A **spontaneous process** is one that occurs naturally under certain conditions.
- A **nonspontaneous process** will not take place without the continual input of energy from an external source.

Reversible Processes

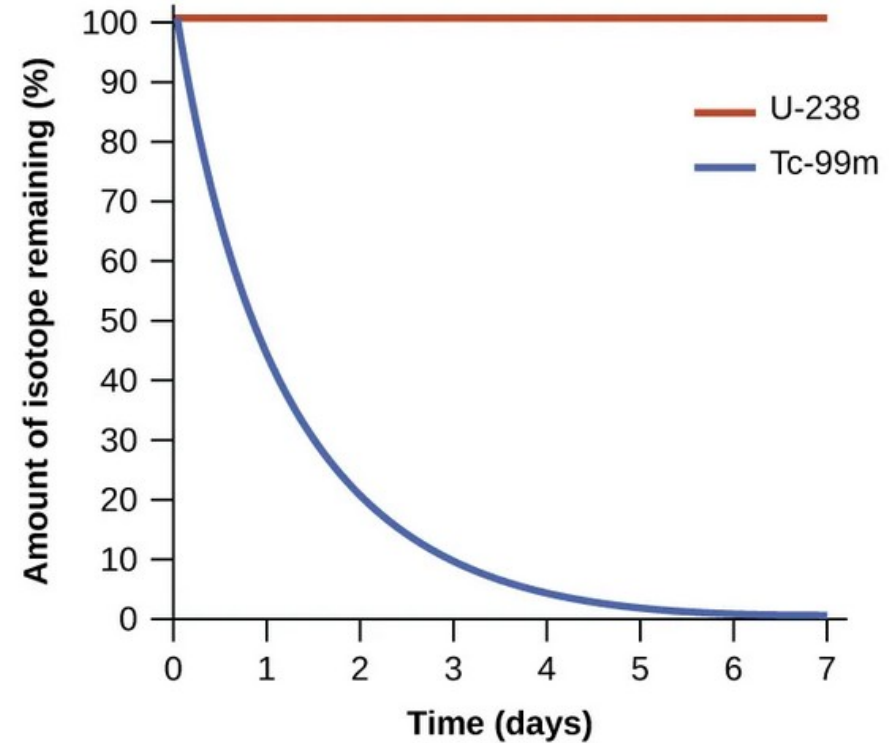


- A process that is spontaneous in one direction under a particular set of conditions is nonspontaneous in the reverse direction.
- At room temperature and typical atmospheric pressure, ice will spontaneously melt, but water will not spontaneously freeze.

Spontaneity and Rates



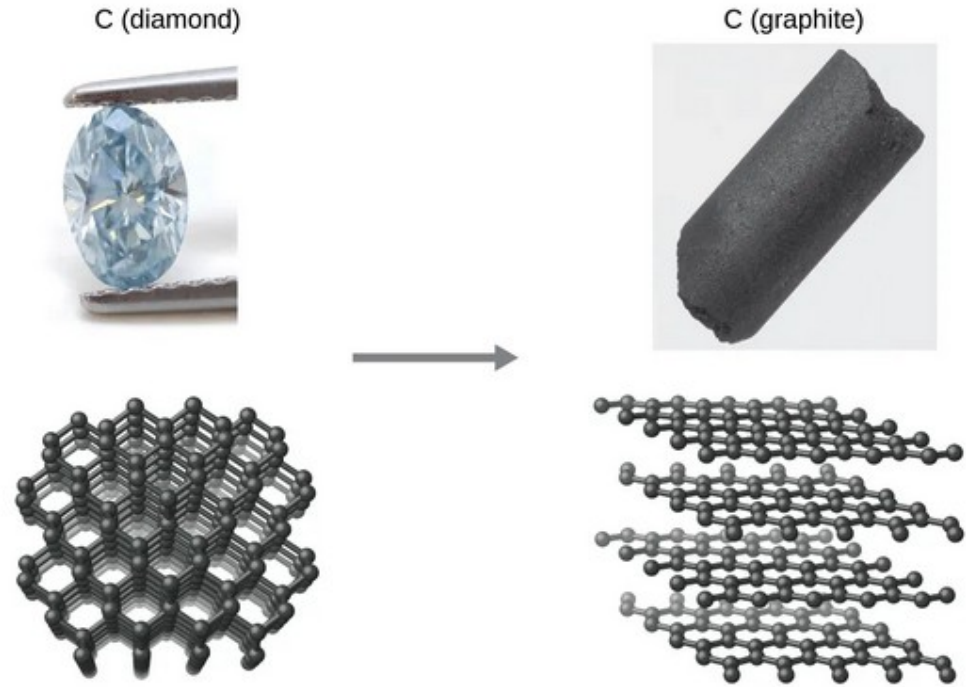
- The spontaneity of a process is *not* correlated to the speed of the process.
- A spontaneous change may be so rapid that it is essentially instantaneous or so slow that it cannot be observed over any practical period of time.



Spontaneity and Rates



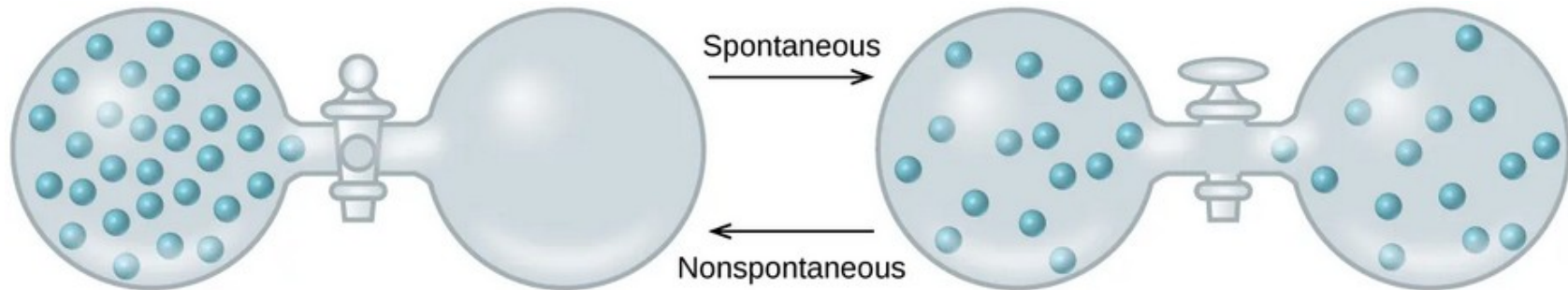
- Graphite is the stable form of carbon under ambient atmospheric pressure.
- Diamond is the stable allotrope at very high pressures.
- Yet diamonds are observed to exist, and persist, under ambient conditions.



Dispersal of Matter and Energy



- Consider an isolated system consisting of two flasks connected with a closed valve.
 - Initially there is an ideal gas in one flask and the other flask is empty ($P = 0$).
 - When the valve is opened, the gas spontaneously expands to fill both flasks equally. But why?



Considering Internal Energy



- No work has been done because the pressure in a vacuum is zero.

$$w = -P\Delta V = 0 \quad (P = 0 \text{ in a vacuum})$$

- Since the system is isolated, no heat has been exchanged with the surroundings ($q = 0$).
- The first law of thermodynamics confirms that there has been no change in the system's internal energy

$$\Delta U = q + w = 0 + 0 = 0$$

Dispersal of Matter is Spontaneous

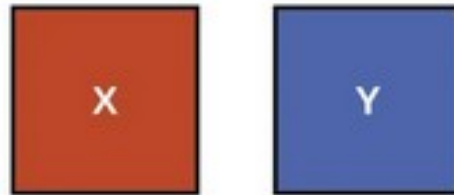


- The spontaneity of this process is not a consequence of any change in energy.
- Instead, the driving force is related to the *greater, more uniform dispersal of matter* that results when the gas is allowed to expand.
- After the spontaneous expansion took place, the matter was distributed both more widely and more uniformly.
 - Occupying twice its original volume
 - Present in equal amounts in each flask

Dispersal of Energy is Spontaneous



- Consider two objects at different temperatures
- When these objects come into contact, heat spontaneously flows from the hotter object to the colder one.
 - One object loses energy and the other gains it.
 - There was no net gain or loss of thermal energy
 - The available thermal energy was redistributed among the two objects.



$$T_X > T_Y$$



X and Y in contact

Section 16.2

Entropy



Michael Stogsdill

Mott Community College

Learning Objectives



- Define entropy
- Explain the relationship between entropy and the number of microstates
- Predict the sign of the entropy change for chemical and physical processes

Reversible Processes

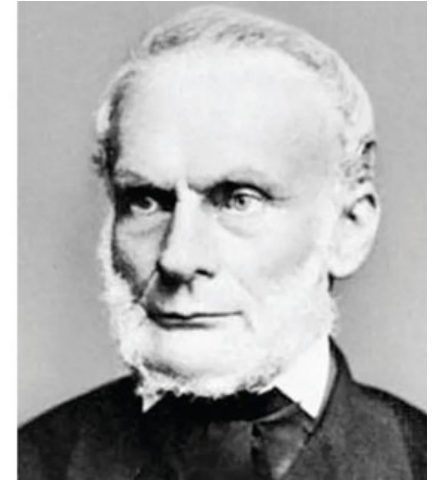


- A **reversible process** is one that takes place at such a slow rate that it is always at equilibrium
- Its direction can be changed (it can be “reversed”) by an infinitesimally small change in some condition.
- The idea of a reversible process is a formalism required to support the development of various thermodynamic concepts
 - No real processes are truly reversible
 - They are classified as irreversible

Hinting at Entropy



- In 1824, Nicolas Léonard Sadi Carnot published the results of an extensive study regarding the efficiency of steam heat engines.
- Rudolf Clausius introduced a new thermodynamic property that relates the spontaneous heat flow accompanying a process to the temperature at which the process takes place.



Entropy



- In 1865, Clausius named this property **entropy** (S) and defined its change for any process as the following:

$$\Delta S = \frac{q_{\text{rev}}}{T}$$

- Similar to other thermodynamic properties, this new quantity is a state function
 - Its change depends only upon the initial and final states of a system.

Entropy and Microstates



- Ludwig Boltzmann developed a statistical model that relates the entropy of a system to the **number of microstates** (W).
- A **microstate** is a specific configuration of all the locations and energies of the atoms or molecules that make up a system.
- The relation between a system's entropy and the number of possible microstates is

$$S = k \ln W$$

- Where k is the Boltzmann constant, 1.38×10^{-23} J/K.

Entropy as a State Function



- The change in entropy for a process is the difference between its final (S_f) and initial (S_i) values:

$$\Delta S = S_f - S_i = k \ln W_f - k \ln W_i = k \ln \frac{W_f}{W_i}$$

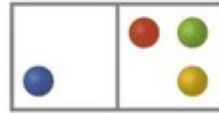
- The change in entropy does not depend on the path only on the final and initial states.
- This is not just a property of entropy, all thermodynamic state functions operate this way.

Microstates



- An increase in the number of microstates, $W_f > W_i$, yields an increase in system entropy, $\Delta S > 0$.
- A reduction in the number of microstates, $W_f < W_i$, yields a decrease in system entropy, $\Delta S < 0$.
- Microstates with equivalent particle arrangements (not considering individual particle identities) are grouped together and are called **distributions**.
- *The most probable distribution is the one of greatest entropy.*

Microstates and Probability



Scaling Microstates

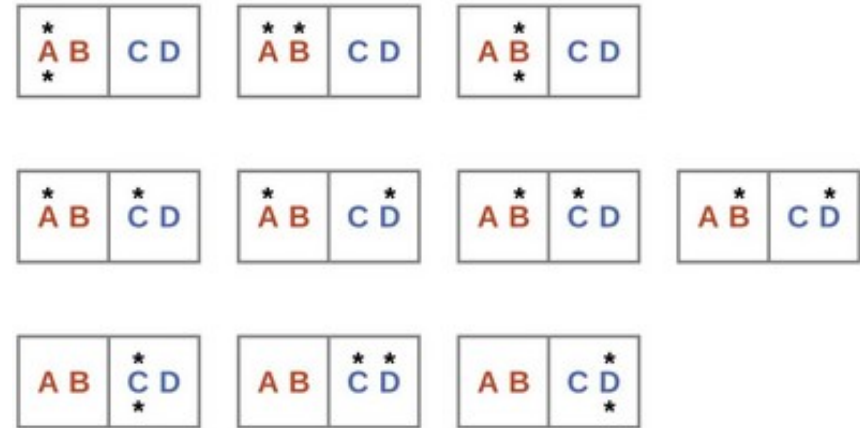


- Adding more particles to the previous system would result in an exponential increase in microstates (2^N).
- Having even one mole of particles would result in an extremely large number of microstates ($N \approx 10^{23}$).
- Regardless of the number of particles in the system the distributions in which roughly equal numbers of particles are found in each box are always the most probable configurations.

Heat as Microstates



- Consider a system consisting of two objects, each containing two particles and two units of thermal energy, “*”
- The hot object is comprised of particles **A** and **B** and initially contains both energy units.
- The most likely result is the flow of heat to yield the uniform dispersal of energy.



Predicting the Sign of ΔS



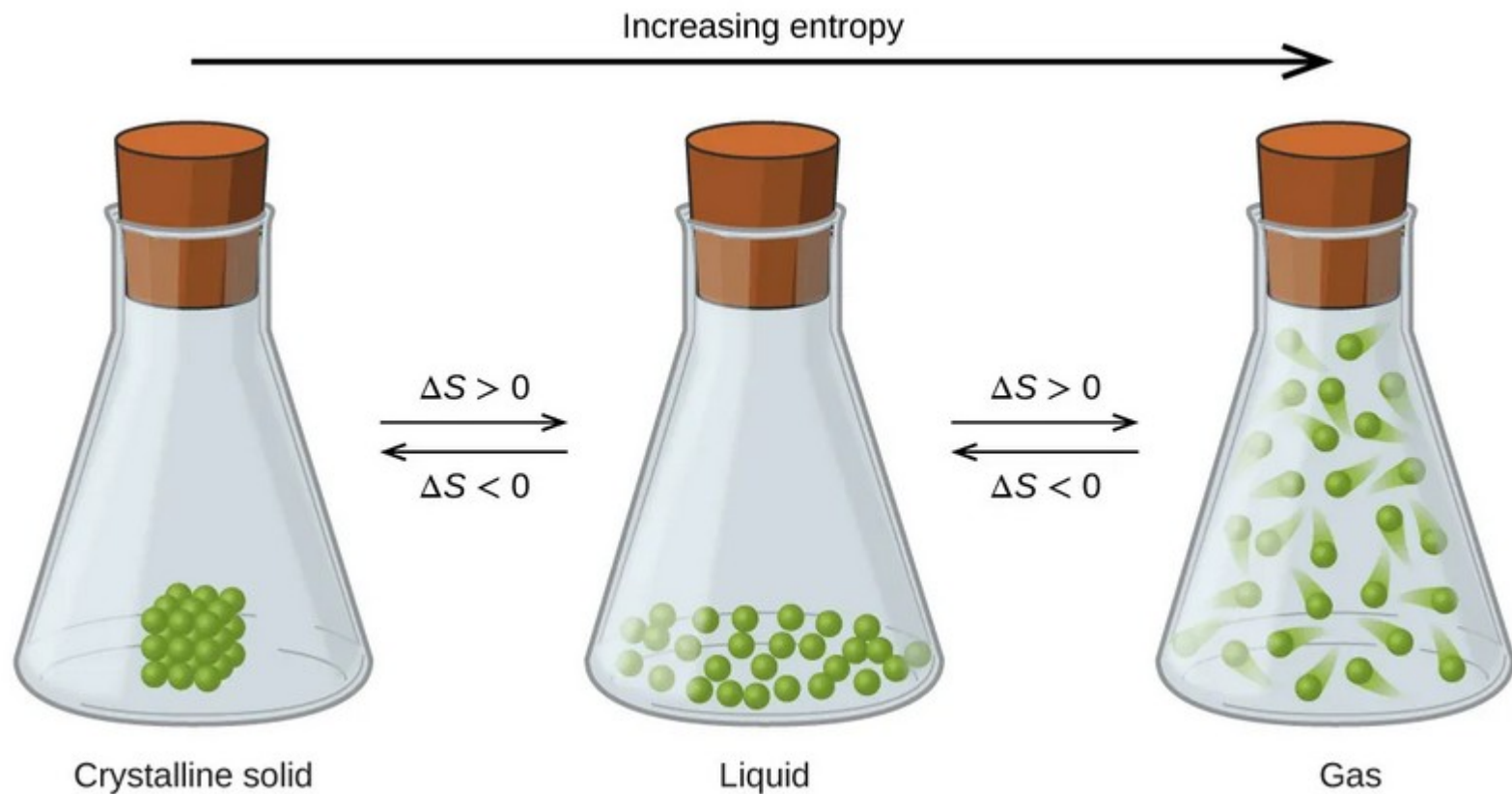
- In the solid phase, the atoms or molecules are restricted to nearly fixed positions, oscillating around these positions.
 - The number of microstates is relatively small.
- In the liquid phase, the atoms or molecules are free to move, though they remain in relatively close proximity to one another.
 - The number of microstates is greater than for solids, $S_{\text{liquid}} > S_{\text{solid}}$.
 - Melting results in an increase in entropy, $\Delta S > 0$.
 - Freezing results in a decrease in entropy, $\Delta S < 0$.

Entropy of Gases



- Atoms or molecules in the gas phase occupy a much greater volume than the liquid phase.
- Each atom or molecule can be found in many more locations, corresponding to a much greater number of microstates.
 - For any substance, $S_{\text{gas}} > S_{\text{liquid}} > S_{\text{solid}}$
 - Vaporization and sublimation result in an increase entropy, $\Delta S > 0$.
 - Condensation and deposition result in a decreases in entropy, $\Delta S < 0$.

Predicting the Sign of ΔS

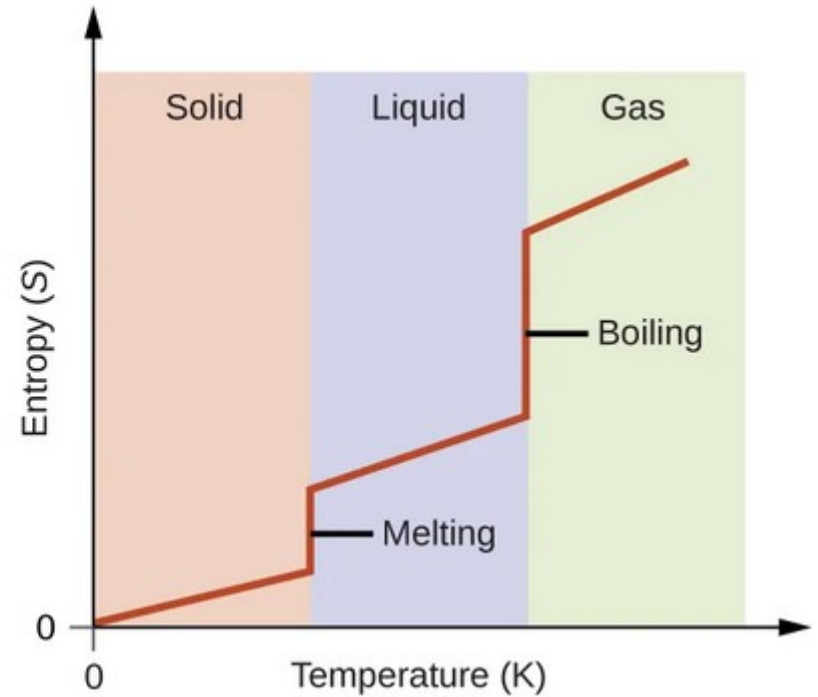
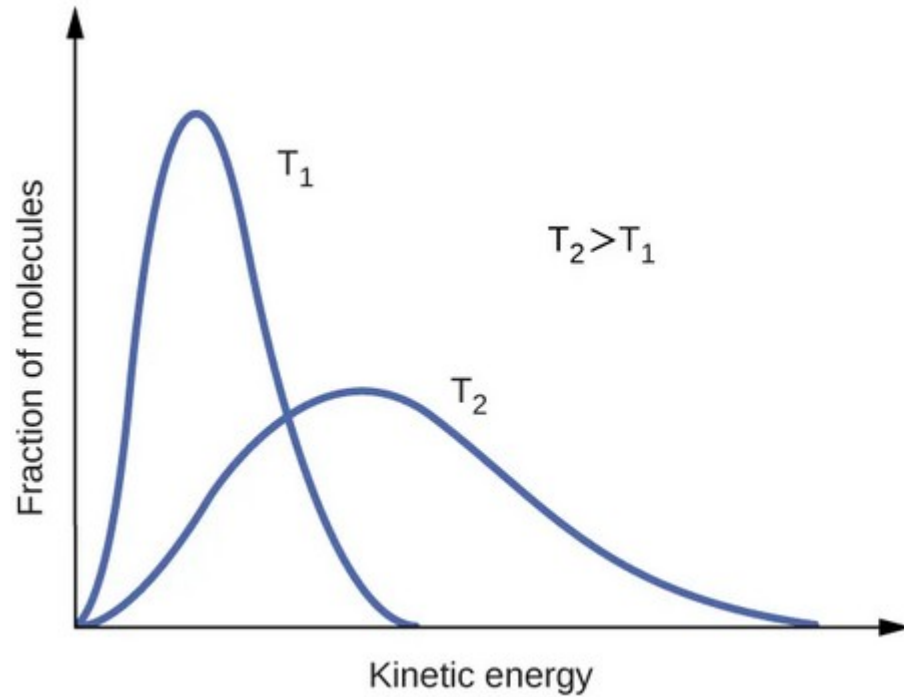


Entropy of Temperature



- The temperature of a substance is proportional to the average kinetic energy of its particles.
 - Solids have more extensive vibrations.
 - Liquids and gases have more rapid translation of particles.
- At higher temperatures, the distribution of kinetic energies among the atoms or molecules of the substance is also broader than at lower temperatures.
 - Kinetic energies are more dispersed.
- The entropy for any substance increases with temperature

Entropy of Temperature



Section 16.3

The Second and Third Laws of Thermodynamics



Michael Stogsdill

Mott Community College

Learning Objectives



- State and explain the second and third laws of thermodynamics
- Calculate entropy changes for phase transitions and chemical reactions under standard conditions

The Second Law of Thermodynamics



- Processes that involve an increase in entropy of the system ($\Delta S > 0$) are very often spontaneous. But not always.
- To identify a property that reliably predicts spontaneity we must also consider the effect a process has on the surroundings.
- Together the change of entropy of a system and the surroundings encompasses the change to the universe.

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

Heat Flow and ΔS



- Consider the three possible outcomes of the process of heat flow between two objects, the *system* and the *surroundings*.
 - 1) The objects are at different temperatures
 - Heat flows from the hotter to the cooler object.
 - This is always spontaneous.
 - 2) The objects are at different temperatures
 - Heat flows from the cooler to the hotter object.
 - This is never observed to occur spontaneously.
 - 3) The objects are at essentially the same temperature, $T_{\text{sys}} \approx T_{\text{surr}}$
 - This means the system is at equilibrium.

Outcome One



- Designating the hotter object as the system and invoking the definition of entropy yields the following:

$$\Delta S_{\text{sys}} = \frac{-q_{\text{rev}}}{T_{\text{sys}}} \quad \text{and} \quad \Delta S_{\text{surr}} = \frac{q_{\text{rev}}}{T_{\text{surr}}}$$

- The magnitudes of $-q_{\text{rev}}$ and q_{rev} are equal
- Since $T_{\text{sys}} > T_{\text{surr}}$, the entropy decrease of the system will be less than the entropy increase of the surroundings. The entropy of the universe will increase:

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

Outcome Two



- Designating the hotter object as the system and invoking the definition of entropy yields the following:

$$\Delta S_{\text{sys}} = \frac{q_{\text{rev}}}{T_{\text{sys}}} \quad \text{and} \quad \Delta S_{\text{surr}} = \frac{-q_{\text{rev}}}{T_{\text{surr}}}$$

- The arithmetic signs of q_{rev} denote the gain of heat by the system and the loss of heat by the surroundings.
- The direction of the heat flow will yield a negative value for ΔS_{univ} .
- This process involves a decrease in the entropy of the universe.*

Outcome Three



- The objects are at essentially the same temperature, $T_{\text{sys}} \approx T_{\text{surr}}$, the magnitudes of the entropy changes are essentially the same for both the system and the surroundings.

$$|\Delta S_{\text{sys}}| \approx |\Delta S_{\text{surr}}|$$

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

Second Law of Thermodynamics



- *All spontaneous changes cause an increase in the entropy of the universe.*

The Second Law of Thermodynamics

$\Delta S_{\text{univ}} > 0$	spontaneous
$\Delta S_{\text{univ}} < 0$	nonspontaneous (spontaneous in opposite direction)
$\Delta S_{\text{univ}} = 0$	at equilibrium

A Convenient Approximation



- Determining the *reversible heat* transferred can be practically very difficult.
- However, because the surroundings usually represents a huge thermal sink, the heat transferred from or to the surroundings can all be considered reversible.
- This allows us a convenient approximation.

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

The Third Law of Thermodynamics



- Consider the entropy of a pure, perfectly crystalline solid at absolute zero (0 K).
 - This system would have zero kinetic energy.
 - There is one possible location for each atom or molecule ($W = 1$).

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

- This limiting condition represents the **third law of thermodynamics**
 - *The entropy of a pure, perfect crystalline substance at 0 K is zero.*

Standard Entropies



- Careful calorimetric measurements can be made to determine the temperature dependence of a substance's entropy and to derive absolute entropy values under specific conditions.
- **Standard entropies** (S°) are for one mole of substance under standard conditions
 - A pressure of 1 bar and a temperature of 298.15 K

Standard Entropy Change



- The **standard entropy change** (ΔS°) for a reaction may be computed using:

$$\Delta S^\circ = \sum \nu S^\circ(\text{products}) - \sum \nu S^\circ(\text{reactants})$$

- where ν represents stoichiometric coefficients in the balanced equation representing the process.



$$= [xS^\circ(\text{C}) + yS^\circ(\text{D})] - [mS^\circ(\text{A}) + nS^\circ(\text{B})]$$

Finding Standard Entropies



- A table of standard entropy values for various substances can be found in [Appendix G](#).
- Don't forget that these values are only valid at standard temperatures and pressures.

Substance	S° (J mol ⁻¹ K ⁻¹)
carbon	
C(s, graphite)	5.740
C(s, diamond)	2.38
CO(g)	197.7
CO ₂ (g)	213.8
CH ₄ (g)	186.3
C ₂ H ₄ (g)	219.3
C ₂ H ₆ (g)	229.2
CH ₃ OH(l)	126.8
C ₂ H ₅ OH(l)	160.7
hydrogen	
H ₂ (g)	130.7
H(g)	114.7
H ₂ O(g)	188.8
H ₂ O(l)	70.0
HCl(g)	186.8
H ₂ S(g)	205.7
oxygen	
O ₂ (g)	205.2

Section 16.4

Free Energy



Michael Stogsdill

Mott Community College

Learning Objectives



- Define Gibbs free energy, and describe its relation to spontaneity
- Calculate free energy change for a process using free energies of formation for its reactants and products
- Calculate free energy change for a process using enthalpies of formation and the entropies for its reactants and products
- Explain how temperature affects the spontaneity of some processes
- Relate standard free energy changes to equilibrium constants

Gibbs Free Energy



- Determining Spontaneity with entropy alone can be difficult.
 - We need to measure the entropy change of both the system and the surroundings.
- Josiah Willard Gibbs proposed an alternative property capable of predicting spontaneity called **Gibbs Free Energy**.
- It is defined in terms of a *system's* enthalpy and entropy

$$G = H - TS$$

Free Energy Change



- Free energy is a state function
- At constant temperature and pressure, the **free energy change** (ΔG) may be expressed as:

$$\Delta G = \Delta H - T\Delta S$$

$\Delta S_{\text{univ}} > 0$	$\Delta G < 0$	spontaneous
$\Delta S_{\text{univ}} < 0$	$\Delta G > 0$	nonspontaneous
$\Delta S_{\text{univ}} = 0$	$\Delta G = 0$	at equilibrium

Deriving Gibbs Free Energy



- Beginning with the Second Law of Thermodynamics

$$\Delta S_{\text{univ}} = \Delta S + \frac{q_{\text{surr}}}{T}$$

- The first law requires that $q_{\text{surr}} = -q_{\text{sys}}$, and at constant pressure $q_{\text{sys}} = \Delta H$, so this expression may be rewritten as:

$$\Delta S_{\text{univ}} = \Delta S - \frac{\Delta H}{T}$$

Deriving Gibbs Free Energy



- Multiplying both sides of this equation by $-T$, and rearranging yields the following:

$$-T\Delta S_{\text{univ}} = \Delta H - T\Delta S$$

- Comparing this equation to the previous one for free energy change shows the following relation:

$$\Delta G = -T\Delta S_{\text{univ}}$$

What's “Free” about ΔG ?



- ΔG may be interpreted as representing the difference between the energy produced by the process, ΔH , and the energy lost to the surroundings, $T\Delta S$.

$$\Delta G = \Delta H - T\Delta S$$

- This difference is the energy available (or “free”) to do useful work by the process.
 - If the process could somehow be made to take place reversibly.

$$\Delta G = w_{\max}$$

- where w_{\max} refers to all types of work except expansion (pressure-volume) work.

Calculating Free Energy Change



- **Standard Gibb's Free Energy Change (ΔG°)** can be calculated from the standard enthalpy (ΔH°) and standard entropy (ΔS°).

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$

Free Energy of Formation ΔG_f°



- The standard free energy change for a reaction may also be calculated from **standard free energy of formation** (ΔG_f°) values of the reactants and products involved in the reaction.
 - The free energy change that accompanies the formation of one mole of a substance from its elements in their standard states.
 - ΔG_f° is by definition zero for elemental substances in their standard states.



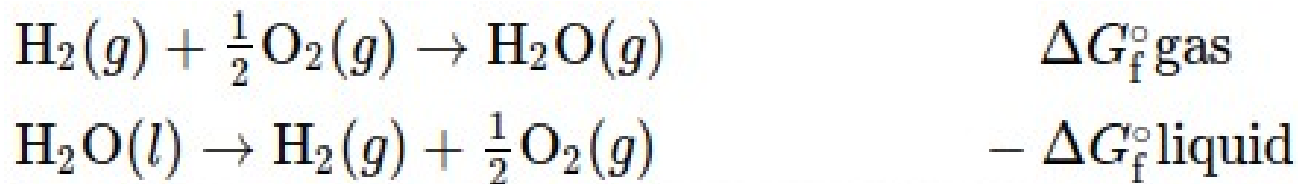
$$\Delta G^\circ = \sum \nu \Delta G^\circ (\text{products}) - \sum \nu \Delta G^\circ (\text{reactants})$$

$$= [x\Delta G_f^\circ (C) + y\Delta G_f^\circ (D)] - [m\Delta G_f^\circ (A) + n\Delta G_f^\circ (B)]$$

Free Energy Changes for Coupled Reactions



- Just like we used *Hess's Law* to calculate the enthalpy of a reaction, we can use the same technique to find the free energy change of a reaction.



Temperature Dependence of Spontaneity



$$\Delta G = \Delta H - T\Delta S$$

	$\Delta H > 0$ (endothermic)	$\Delta H < 0$ (exothermic)
$\Delta S > 0$ (increase in entropy)	$\Delta G < 0$ at high temperature $\Delta G > 0$ at low temperature Process is spontaneous at high temperature	$\Delta G < 0$ at any temperature Process is spontaneous at any temperature
$\Delta S < 0$ (decrease in entropy)	$\Delta G > 0$ at any temperature Process is nonspontaneous at any temperature	$\Delta G < 0$ at low temperature $\Delta G > 0$ at high temperature Process is spontaneous at low temperature

Critical Temperature of Spontaneity

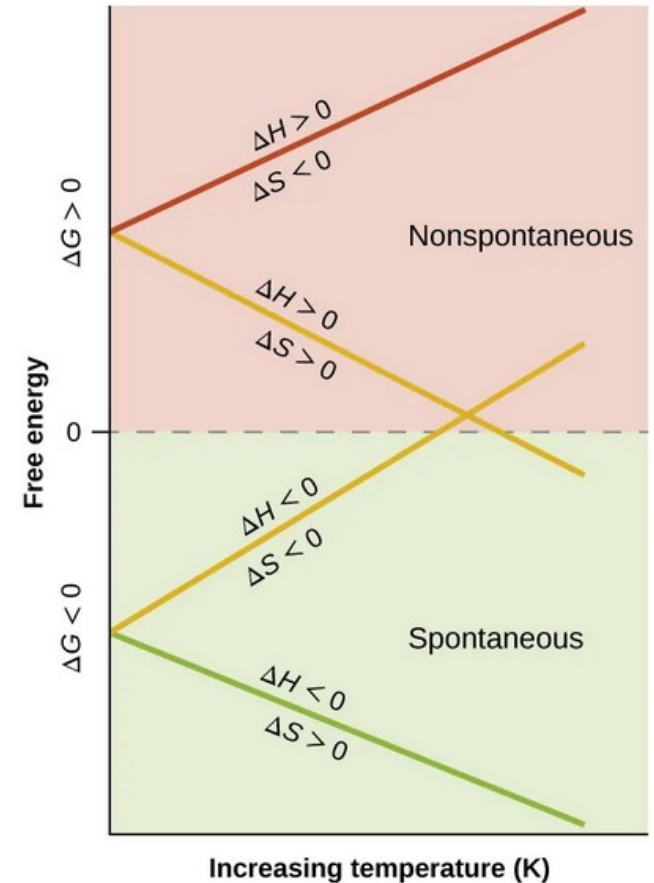


$$\Delta G = \Delta H - T\Delta S$$

$$y = b + mx$$

$$\Delta G = 0 = \Delta H - T\Delta S$$

$$T = \frac{\Delta H}{\Delta S}$$



Free Energy and Nonstandard Conditions



- The free energy change for a process with reactants and products present under nonstandard conditions is:

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

- Pressures other than 1 bar; concentrations other than 1 M
- R is the gas constant (8.314 J/K mol), T is the kelvin or absolute temperature, and Q is the reaction quotient.

Free Energy and Equilibrium



- When ΔG is zero, the forward and reverse driving forces are equal, and the process occurs in both directions at the same rate.
 - $Q = K$ and $\Delta G = 0$

$$0 = \Delta G^\circ + RT \ln K \quad (\text{at equilibrium})$$

$$\Delta G^\circ = -RT \ln K \quad \text{or} \quad K = e^{-\frac{\Delta G^\circ}{RT}}$$

- This form of the equation provides a useful link between these two essential thermodynamic properties,

Relations between ΔG° and K



K	ΔG°	Composition of an Equilibrium Mixture
> 1	< 0	Products are more abundant
< 1	> 0	Reactants are more abundant
$= 1$	$= 0$	Reactants and products are comparably abundant

Visualizing Reaction Progress

