

Enthalpy, Entropy, and Gibbs Free Energy

Chapters 5 and 19

Everything we do is connected

in one way or another with energy. Without energy modern society could not function and life itself would not exist. The issues surrounding energy—its sources, production, distribution, consumption, and environmental impact—pervade conversations in science, politics, economics, and public policy.

The amazing organization of

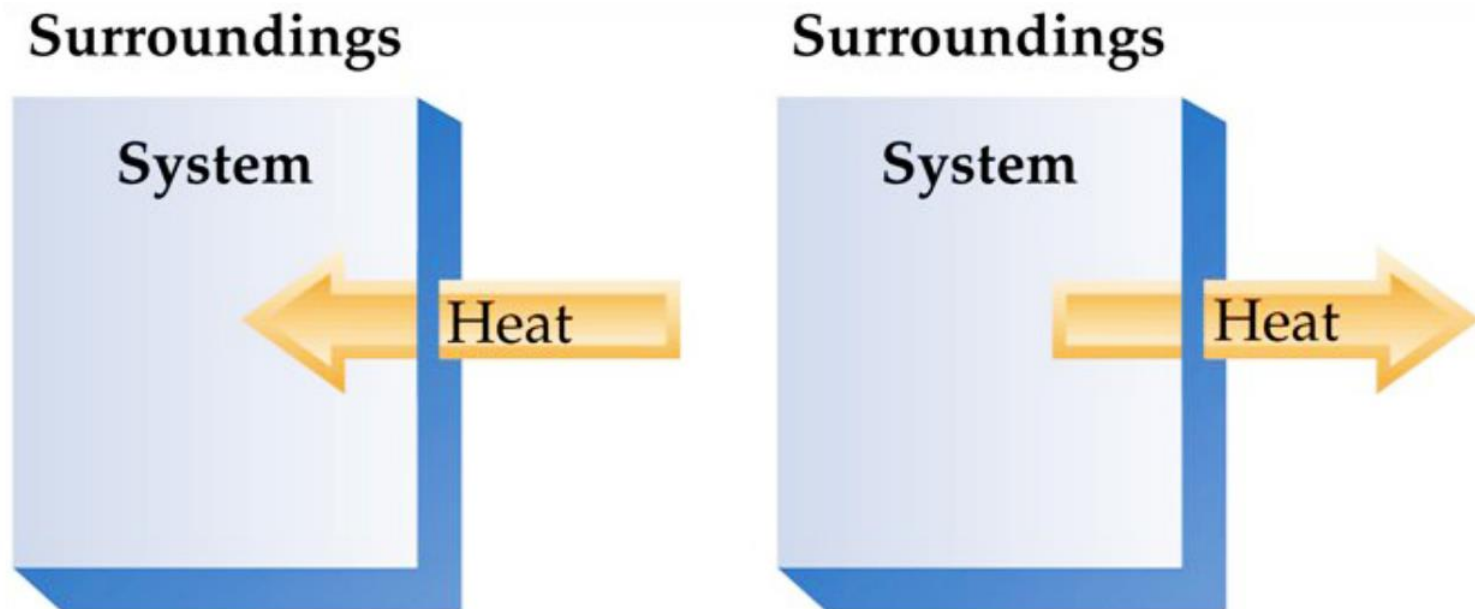
living systems, from complex molecular structures such as those of nucleosomes, to cells, to tissues, and finally to whole plants and animals, is an unending source of wonder and delight to the scientists who study them. Energy must be spent, somehow, to form and maintain these organized systems. But how is that energy channeled to accomplish these tasks?

Understanding natural processes, whether they be DNA replication, photosynthesis, or merely the rusting of a nail, relies on understanding the general laws that govern chemical reactions. There are two

THERMOCHEMISTRY

**CHEMICAL
THERMODYNAMICS**

Thermochemistry is the correlation of chemical processes and energy changes.



1st Law of Thermodynamics

In any process, the total energy of the universe remains unchanged: **energy is conserved**.

A process and its reverse are equally allowed by the first law

$$0 = \Delta E_{\text{forward}} + \Delta E_{\text{reverse}}$$

(Energy is conserved in both directions)

2nd Law of Thermodynamics

Processes that increase $\Delta S_{\text{universe}}$ are **spontaneous**.

$$\Delta S_{\text{univ}} > 0$$

Spontaneous Forward

$$\Delta S_{\text{univ}} = 0$$

At Equilibrium

$$\Delta S_{\text{univ}} < 0$$

Spontaneous Reverse

Spontaneous Processes

- Any process that occurs without outside intervention is spontaneous.
- When two eggs are dropped they spontaneously break.
- The reverse reaction is not spontaneous.

Some classes of spontaneous processes:

Phase transitions (melting, freezing)

Mixing

Expansion

Heat transfer

Movement towards chemical equilibrium

Exothermic Spontaneous Processes

Thermite reaction



aluminium forms stronger bonds with oxygen than iron

$$\Delta H = - 848 \text{ kJ}$$

Thermite contains its own supply of oxygen and does not require any external source of air... it cannot be smothered and may ignite in any environment, given sufficient initial heat. It will burn well while wet and cannot be easily extinguished with water, **thermite is used for welding underwater** (military use: Incendiary bombs)



Copper(II) thermite reactions can be so fast that copper thermite can be considered a type of flash powder.

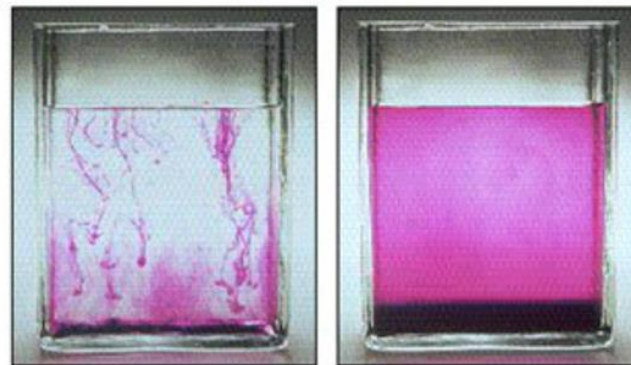


thermite-like mixtures are used as pyrotechnic initiators as in fireworks.

Endothermic Spontaneous Processes



$$\Delta H_{\text{sol}} = +25.7 \text{ kJ/mol}$$



Thermal Decomposition of Ammonium Nitrate

In the molten salt
(m.p. $\sim 169.6^\circ$)



This reaction is carried out industrially for the synthesis of nitrous oxide, N_2O .

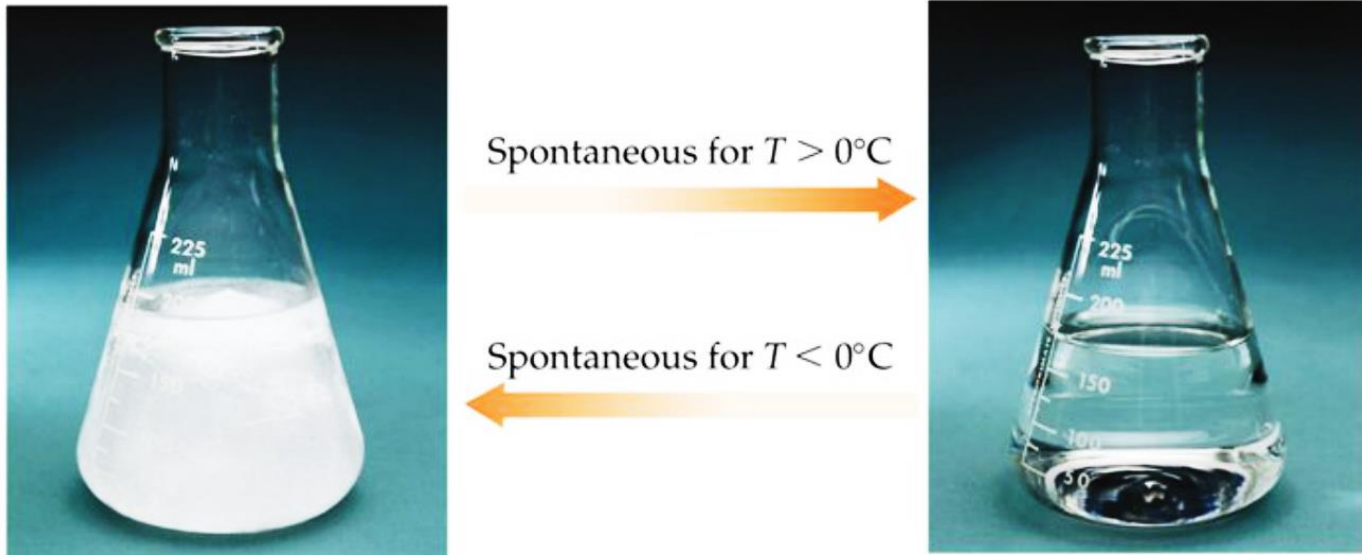
At the same time, ammonium nitrate dissociates easily



These two reactions take place simultaneously within a molten mass of ammonium nitrate, a thermal equilibrium may reach depending on the heat losses of the system

Spontaneous Processes

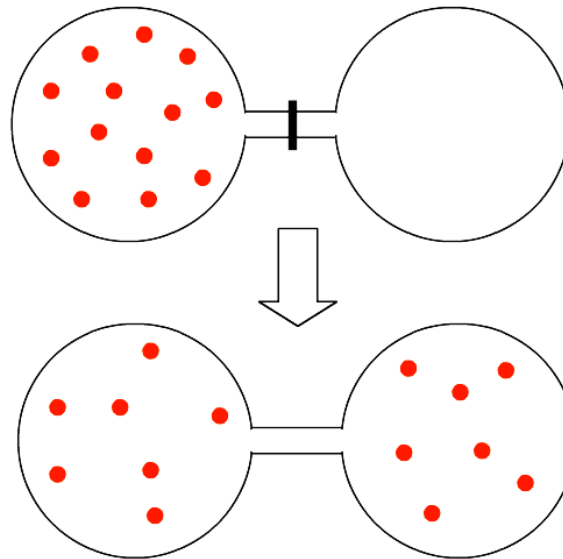
Can be Temperature Dependent!



Which of the following are spontaneous?

- Spreading of the fragrance of perfume through a room
- Formation of CH_4 and O_2 from CO_2 and H_2O at room temp and 1 atm.
- Dissolution of sugar in a cup of hot coffee

Expansion of a gas



Open valve: gas
spontaneously
expands

More probable
state

SYSTEM CHANGES to state of HIGHER PROBABILITY
For entropy-driven reactions - the more RANDOM state

Defining Entropy “S”

- Entropy is related to **probability**
- If a system has several available macrostates, it will spontaneously proceed to the one with the largest number of available microstates.
- The macrostate with the greatest probability (largest number of available microstates) has the highest entropy.

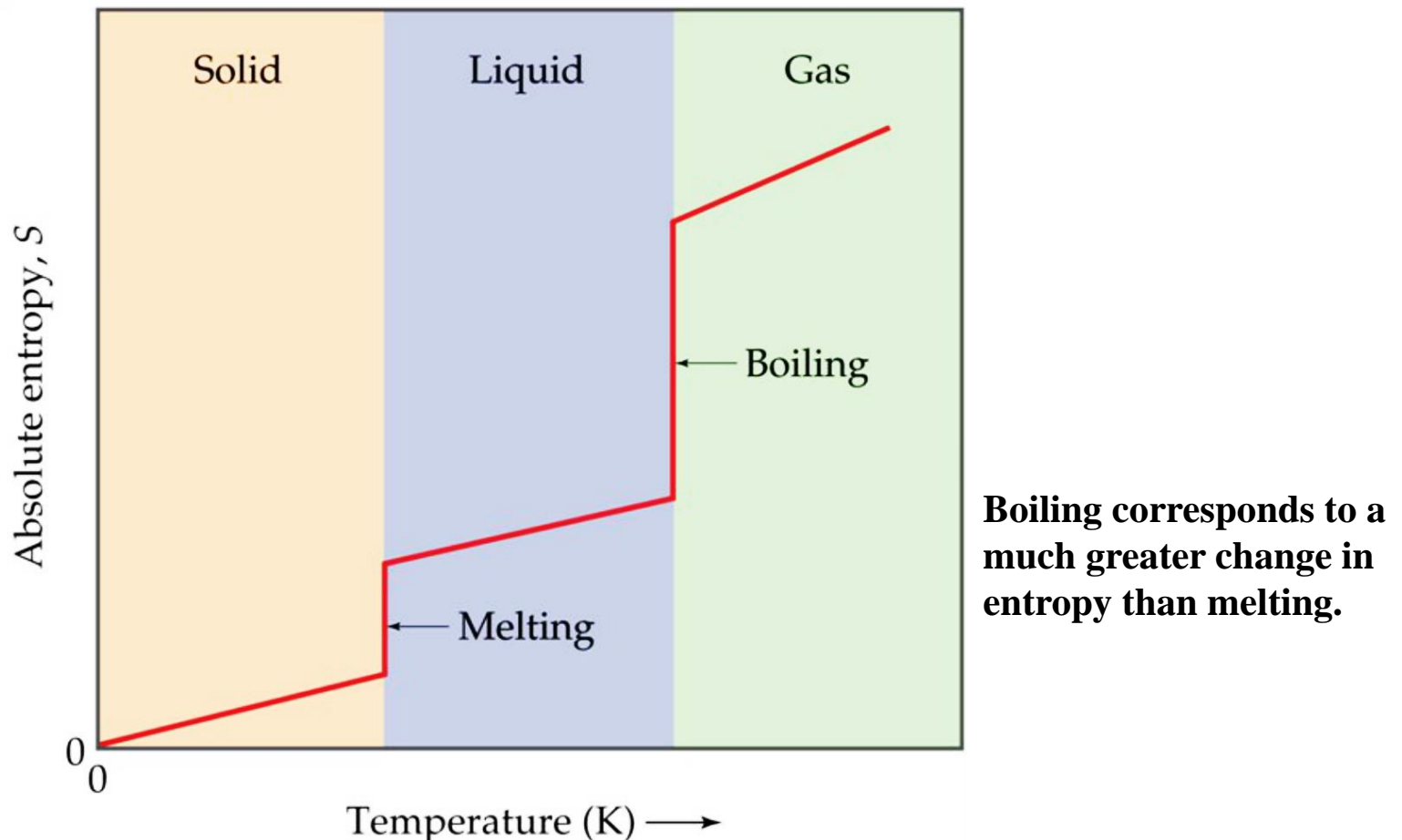
$$S = k_B \ln \Omega \text{ J/K}$$

k_B = Boltzmann's constant, the gas constant per molecule (R/N_A)

Ω = the number of available microstates of a given state

$$\Delta S = q/T \text{ J/mol-K}$$

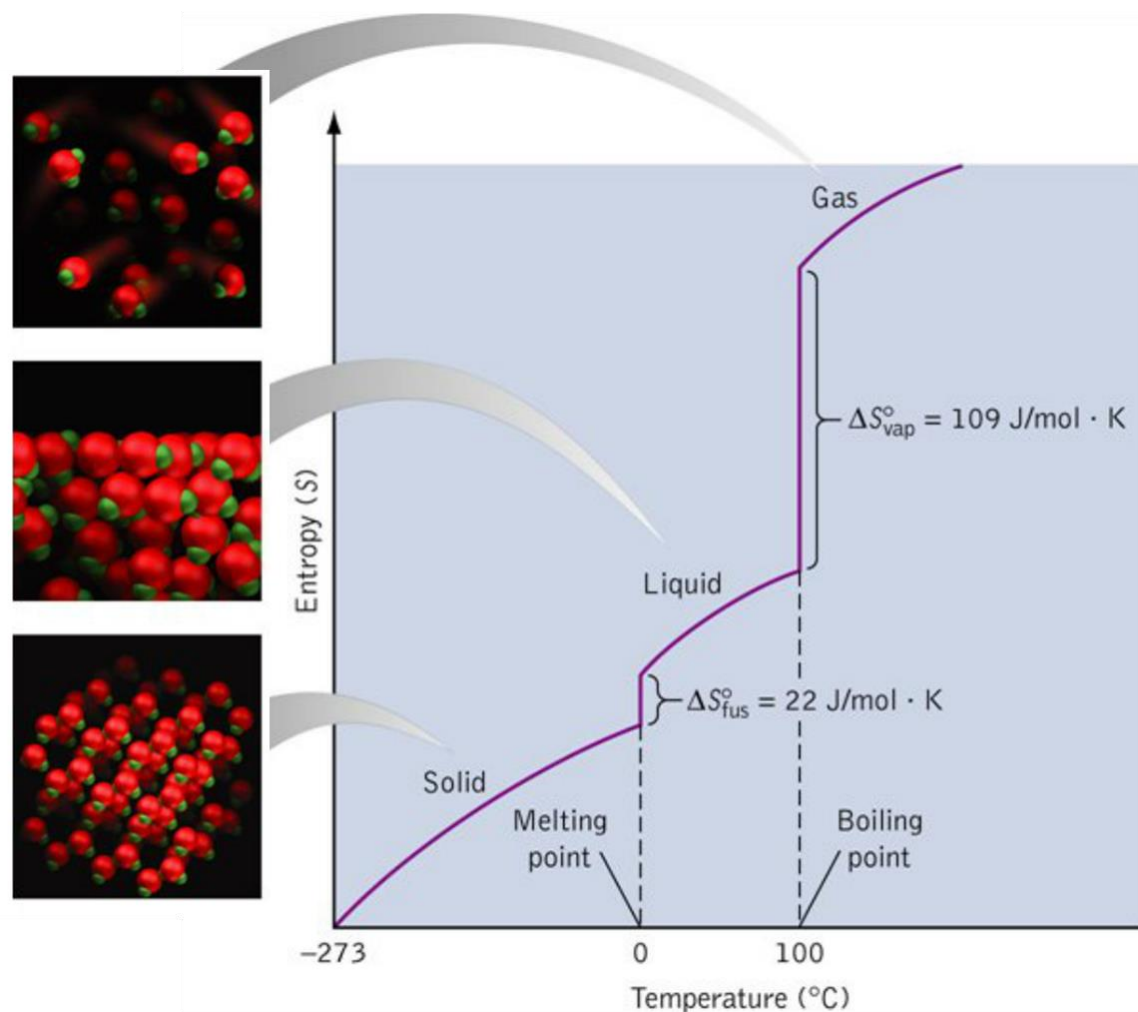
When you heat something you increase its entropy.



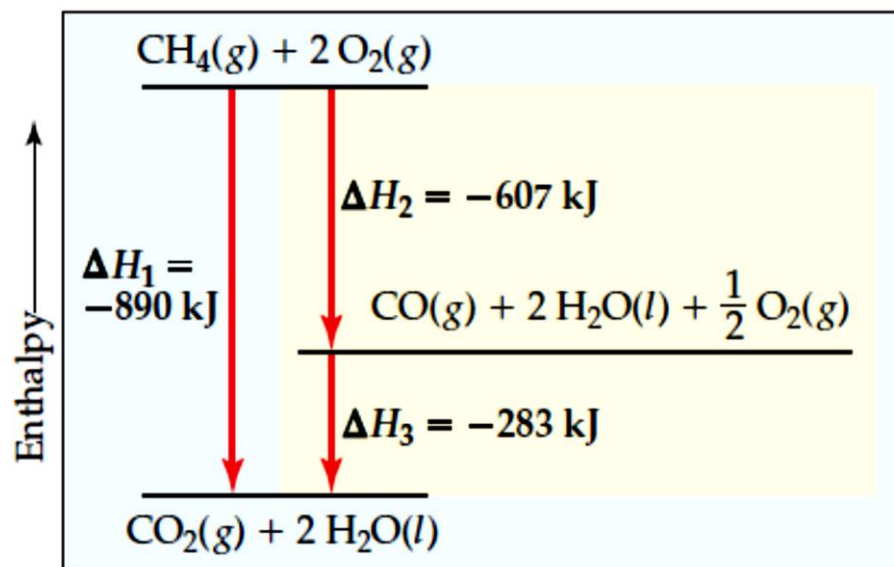
Energy changes dramatically at a phase change.

- A gas is less ordered than a liquid which is less ordered than a solid
- Any process that increases the number of gas molecules leads to an increase in entropy

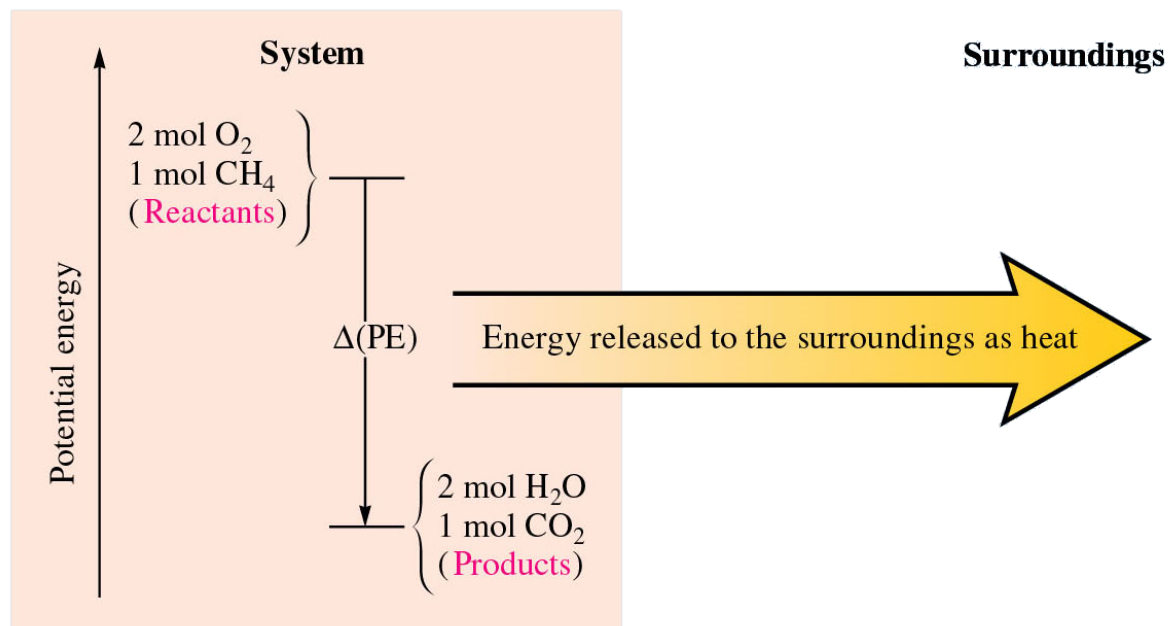
- Entropy is a state function.
- For a system, $\Delta S = S_{\text{final}} - S_{\text{initial}}$.
- If $\Delta S > 0$ the randomness increases
- if $\Delta S < 0$ the order increases.



Combustion of Methane



▲ Figure 5.22 Enthalpy diagram illustrating Hess's law.



The 2nd Law of Thermodynamics

- In any **spontaneous process**, the entropy of the universe increases.

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

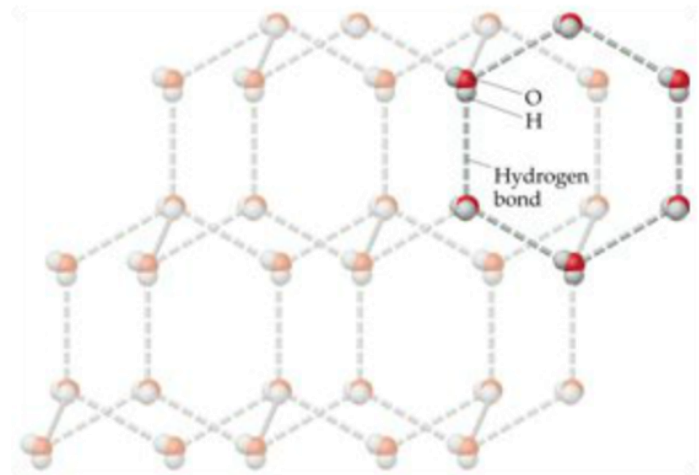
- Entropy is not conserved: ΔS_{univ} is increasing.
- For a reversible process:

$$\Delta S_{\text{univ}} = 0$$

- For a spontaneous process (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.
- 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.

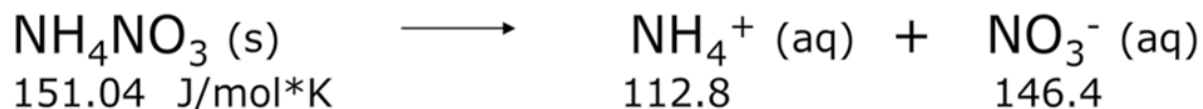


Entropy Changes in Chemical Reactions

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

- Standard molar entropies of elements are not zero.
- S° greater for gases than liquids and solids
- S° generally increases with increasing molar mass
- S° generally increases with increasing number of atoms in a molecule

- Calculate ΔS° for the dissolution of ammonium nitrate, given the following entropy values:



We can calculate Entropy Changes in Chemical Reactions (in the system), what about the surroundings?

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

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

Is the decomposition of calcium carbonate spontaneous under standard conditions?
Calculate ΔS_{univ} to support your answer.

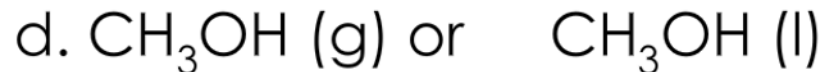
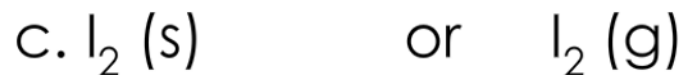


Standard Molar Entropies of selected substances at 298 K

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 ₂ O(g)	188.8	Fe(s)	27.3
NH ₃ (g)	192.5	FeCl ₃ (s)	142.3
CH ₃ OH(g)	237.6	NaCl(s)	72.3
C ₆ H ₆ (g)	269.2		
Liquids			
H ₂ O(l)	69.9		
CH ₃ OH(l)	126.8		
C ₆ H ₆ (l)	172.8		

Conceptual Question:

Which substances in each of the following pairs would you expect to have the higher standard molar entropy? Why?



How to we balance ΔS and ΔH to predict whether a reaction is spontaneous?

For a spontaneous reaction the entropy of the universe must increase.

Reactions with large negative ΔH values are spontaneous.

Gibbs free energy, G , of a state is

$$G = H - TS$$

For a process occurring at constant temperature

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

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

Standard Free-Energy Changes

We can tabulate standard free-energies of formation,

$$\Delta G^\circ_f$$

$\Delta G^\circ = 0$ for elements

ΔG° for a process is given by

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

The quantity ΔG° for a reaction tells us whether a mixture of substances will spontaneously react to produce more reactants ($\Delta G^\circ > 0$) or products ($\Delta G^\circ < 0$).

$\Delta G < 0$: forward reaction is spontaneous.

$\Delta G = 0$: reaction is at equilibrium

$\Delta G > 0$: forward reaction is not spontaneous.

Gibbs Free Energy and Temperature

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

If $\Delta H < 0$ and $\Delta S > 0$, then ΔG is always negative.

If $\Delta H > 0$ and $\Delta S < 0$, then ΔG is always positive.

If $\Delta H < 0$ and $\Delta S < 0$, then ΔG is negative at low temperatures.

If $\Delta H > 0$ and $\Delta S > 0$, then ΔG is negative at high temperatures.

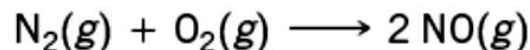
Even though a reaction has a negative ΔG , it may occur too slowly to be observed.

Effect of Temperature on the Spontaneity of Reactions					
ΔH	ΔS	$-T\Delta S$	$\Delta G = \Delta H - T\Delta S$	Reaction Characteristics	Example
-	+	-	Always negative	Spontaneous at all temperatures	$2\text{O}_3(\text{g}) \longrightarrow 3\text{O}_2(\text{g})$
+	-	+	Always positive	Nonspontaneous at all temperatures; reverse reaction always spontaneous	$3\text{O}_2(\text{g}) \longrightarrow 2\text{O}_3(\text{g})$
-	-	+	Negative at low T ; positive at high T	Spontaneous at low T ; becomes nonspontaneous at high T	$\text{H}_2\text{O}(\text{l}) \longrightarrow \text{H}_2\text{O}(\text{s})$
+	+	-	Positive at low T ; negative at high T	Nonspontaneous at low T ; becomes spontaneous at high T	$\text{H}_2\text{O}(\text{s}) \longrightarrow \text{H}_2\text{O}(\text{l})$

Sample Exercise 19.6

Calculating Free-Energy Change from ΔH° , T , and ΔS°

Calculate the standard free-energy change for the formation of $\text{NO}(g)$ from $\text{N}_2(g)$ and $\text{O}_2(g)$ at 298 K:



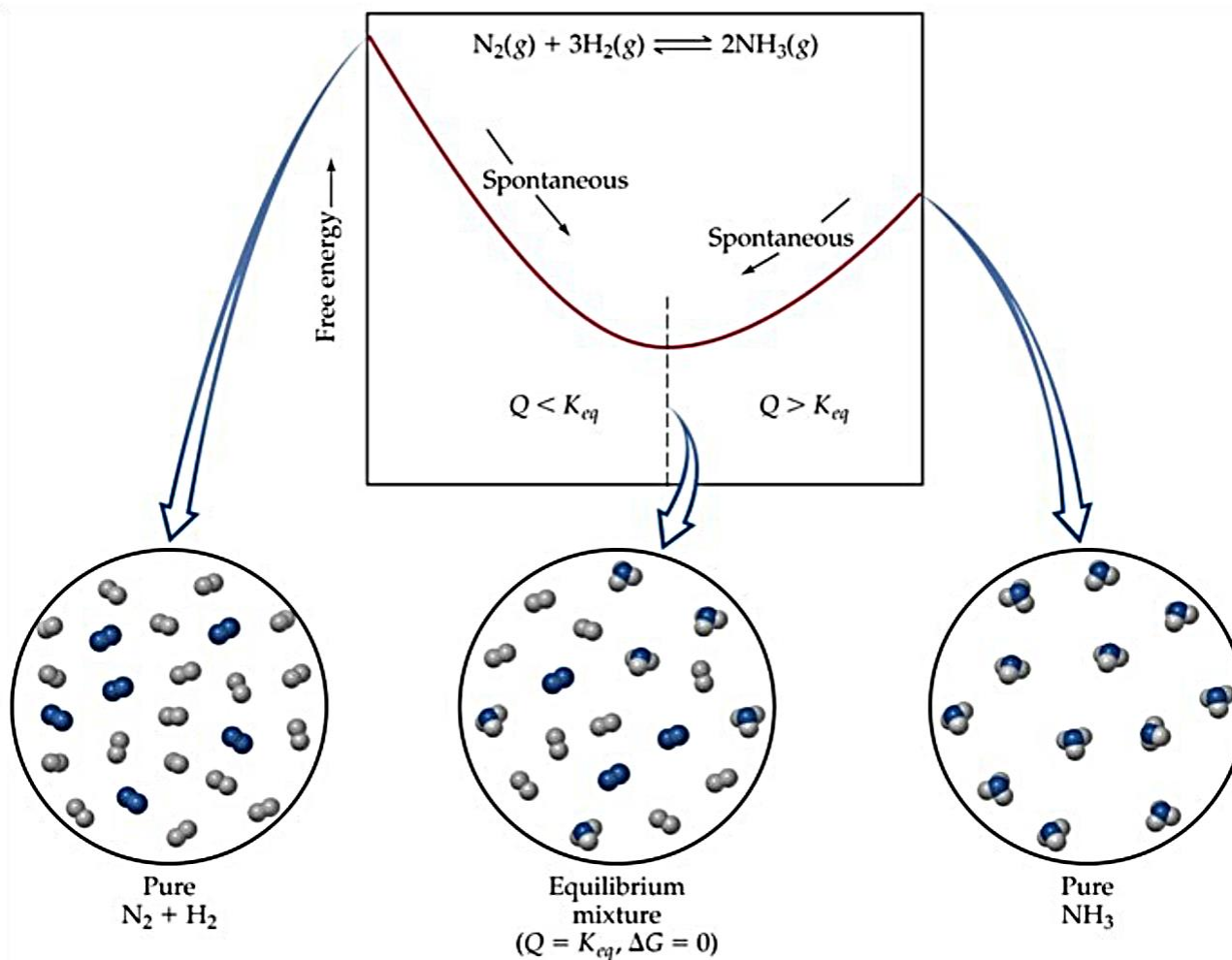
given that $\Delta H^\circ = 180.7 \text{ kJ}$ and $\Delta S^\circ = 24.7 \text{ J/K}$. Is the reaction spontaneous under these conditions?

► Practice Exercise 1

Which of these statements is true? **(a)** All spontaneous reactions have a negative enthalpy change **(b)** All spontaneous reactions have a positive entropy change **(c)** All spontaneous reactions have a positive free-energy change **(d)** All spontaneous reactions have a negative free-energy change **(e)** All spontaneous reactions have a negative entropy change

► Practice Exercise 2

Calculate ΔG° for a reaction for which $\Delta H^\circ = 24.6 \text{ kJ}$ and $\Delta S^\circ = 132 \text{ J/K}$ at 298 K. Is the reaction spontaneous under these conditions?



Initially ammonia will be produced spontaneously ($Q < K_{eq}$).

After some time, the ammonia will spontaneously react to form N_2 and H_2 ($Q > K_{eq}$).

At equilibrium, $\Delta G = 0$ and $Q = K_{eq}$.

Gibbs Free Energy and Equilibrium Constant

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

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

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

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

This equation is one of the most important relationships in thermo because it allows us to calculate K from standard free energy change.

From the above we can conclude:

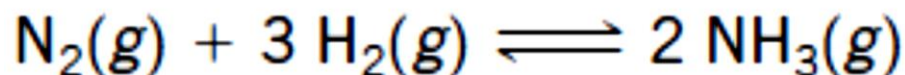
- If $\Delta G^\circ < 0$, then $K > 1$.
- If $\Delta G^\circ = 0$, then $K = 1$.
- If $\Delta G^\circ > 0$, then $K < 1$.

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

Sample Exercise 19.12

Calculating an Equilibrium Constant from ΔG°

The standard free-energy change for the Haber process at 25 °C



$$\Delta G^\circ = -33.3 \text{ kJ/mol}$$

Calculate the equilibrium constant for the process at 25 °C.

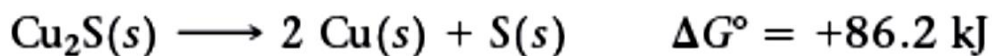
► Practice Exercise 1

The K_{sp} for a very insoluble salt is 4.2×10^{-47} at 298 K. What is ΔG° for the dissolution of the salt in water?

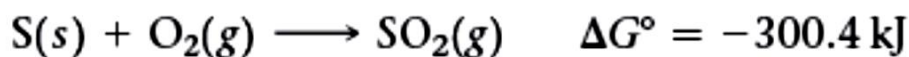
- (a) -265 kJ/mol (b) -115 kJ/mol (c) -2.61 kJ/mol
(d) $+115 \text{ kJ/mol}$ (e) $+265 \text{ kJ/mol}$

Driving Nonspontaneous Reactions: Coupling Reactions

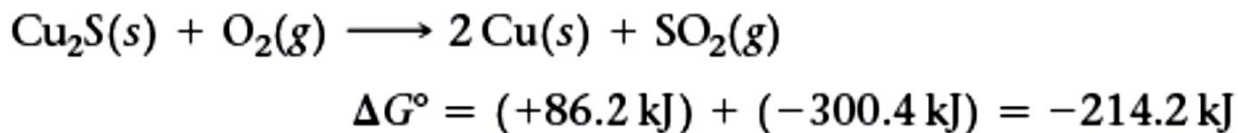
Many desirable chemical reactions, including a large number that are central to living systems, are nonspontaneous as written. For example, consider the extraction of copper metal from the mineral *chalcocite*, which contains Cu_2S . The decomposition of Cu_2S to its elements is nonspontaneous:



Because ΔG° is very positive, we cannot obtain $\text{Cu}(s)$ directly via this reaction. Instead, we must find some way to “do work” on the reaction to force it to occur as we wish. We can do this by coupling the reaction to another one so that the overall reaction *is* spontaneous. For example, we can envision the $\text{S}(s)$ reacting with $\text{O}_2(g)$ to form $\text{SO}_2(g)$:

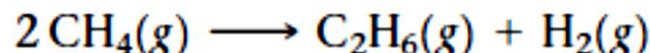


By coupling (adding together) these reactions, we can extract much of the copper metal via a spontaneous reaction:



In essence, we have used the spontaneous reaction of $\text{S}(s)$ with $\text{O}_2(g)$ to provide the free energy needed to extract the copper metal from the mineral.

[19.100] The conversion of natural gas, which is mostly methane, into products that contain two or more carbon atoms, such as ethane (C_2H_6), is a very important industrial chemical process. In principle, methane can be converted into ethane and hydrogen:



In practice, this reaction is carried out in the presence of oxygen:



(a) Using the data in Appendix C, calculate K for these reactions at 25°C and 500°C . **(b)** Is the difference in ΔG° for the two reactions due primarily to the enthalpy term (ΔH) or the entropy term ($-T\Delta S$)? **(c)** Explain how the preceding reactions are an example of driving a nonspontaneous reaction, as discussed in the “Chemistry and Life” box in Section 19.7. **(d)** The reaction of CH_4 and O_2 to form C_2H_6 and H_2O must be carried out carefully to avoid a competing reaction. What is the most likely competing reaction?

ΔG° and Equilibrium

Calculate, ΔG° and K_{eq} at 25°C for:



$$\begin{aligned}\Delta G^\circ &= (1 \text{ mol}) \Delta G^\circ_{f(\text{graphite})} - (1 \text{ mol}) \Delta G^\circ_{f(\text{diamond})} \\ &= 0 - (1 \text{ mol})(2.900 \text{ kJ/mol}) \\ &= -2.900 \text{ kJ}\end{aligned}$$

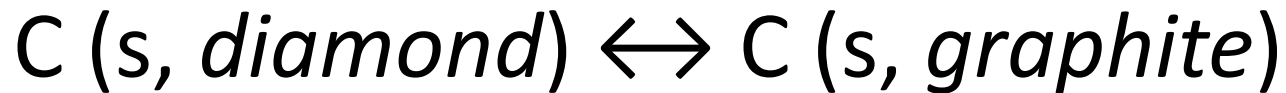
The reaction is spontaneous at 25°C.

$$\Delta G^\circ = -2.900 \text{ kJ} = -RT \ln K$$

$$-2.900 \text{ kJ} = -(8.314 \text{ J/mol-K}) (298.2 \text{ K}) \ln K$$

$$\ln K = 1.170$$

$$K_{eq} = e^{1.170} = 3.22$$



$$\Delta G^\circ = -2.900 \text{ kJ}$$

$$K_{\text{eq}} = 3.22$$

The negative value of ΔG° and the equilibrium constant >1 suggest that diamonds can spontaneously react to form graphite. Although **the reaction is *thermodynamically favored***, the rate constant is extremely small due to a huge activation energy. The disruption of the bonding in the diamond to form planar sp^2 hybridized carbon atoms is ***kinetically unfavorable***.