TABLE 8.4 Average Bond Enthalpies (kJ/mol)

Single Bonds

C—H	413	N—H	391	O—H	463	F—F	155
C—C	348	N—N	163	O—O	146		
C—N	293	N—O	201	O—F	190	Cl—F	253
C—O	358	N—F	272	O—Cl	203	Cl—Cl	242
C—F	485	N—Cl	200	O—I	234		
C—Cl	328	N—Br	243			Br—F	237
C—Br	276			S—H	339	Br—Cl	218
C—I	240	H—H	436	S—F	327	Br—Br	193
C—S	259	H—F	567	S—Cl	253		
		H—Cl	431	S—Br	218	I—Cl	208
Si—H	323	H—Br	366	S—S	266	I—Br	175
Si—Si	226	H—I	299			I—I	151
Si—C	301						
Si—O	368						
Si—Cl	464						

Multiple Bonds

C=C	614	N=N	418	O_2	495
C≡C	839	N≡N	941		
C=N	615	N=O	607	S=O	523
C≡N	891			S=S	418
C=O	799				
C≡O	1072				

Bond Enthalpies and the Enthalpies of Reactions

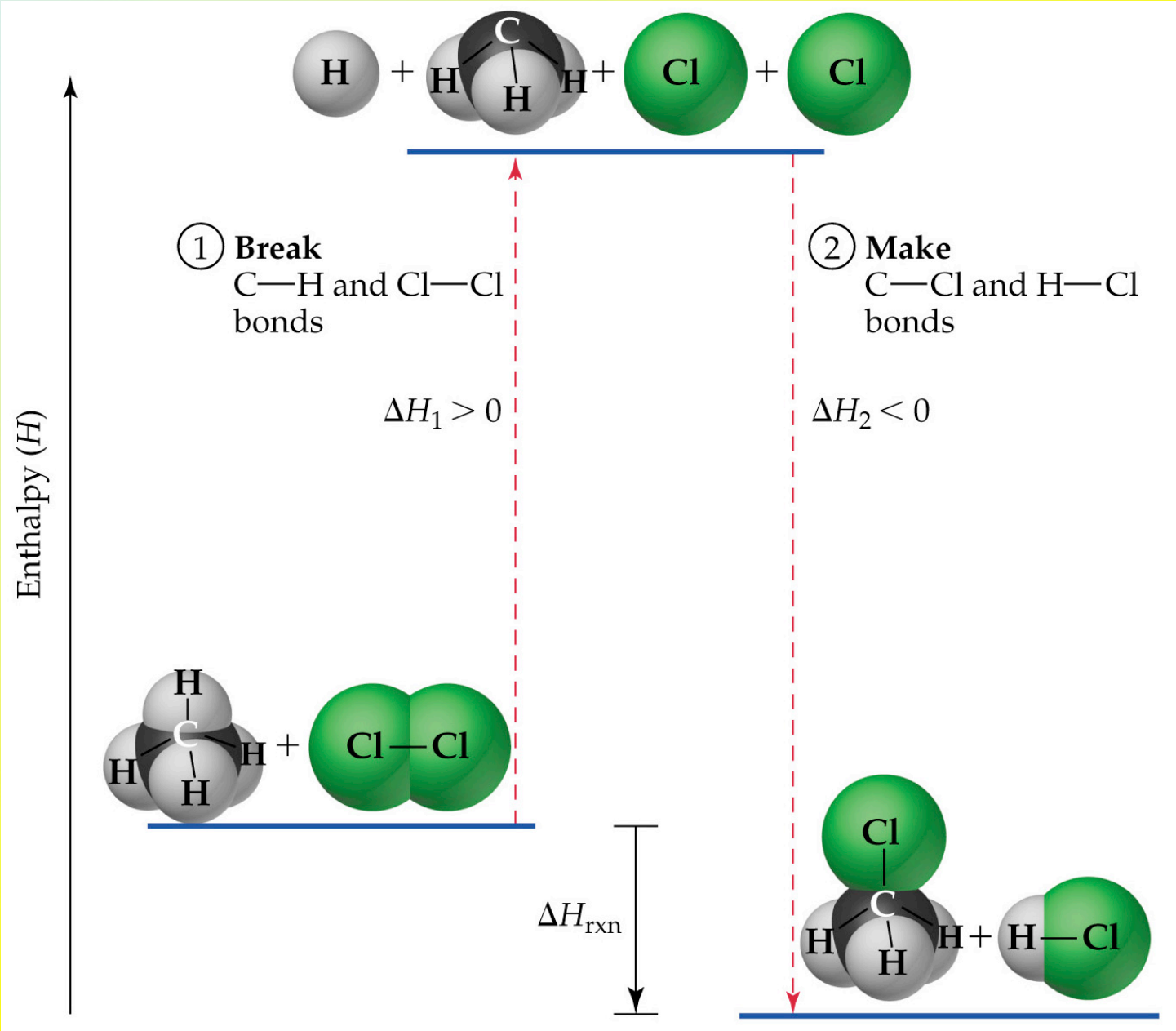
- We can use bond enthalpies to calculate the enthalpy for a chemical reaction.
- We recognize that in any chemical reaction bonds need to be broken and then new bonds get formed.
- The enthalpy of the reaction is given by the sum of bond enthalpies for bonds broken less the sum of bond enthalpies for bonds formed.

- Mathematically, if ΔH_{rxn} is the enthalpy for a reaction, then

$$\Delta H_{rxn} = \sum D(\text{bonds broken}) - \sum D(\text{bonds formed})$$

- We illustrate the concept with the reaction between methane, CH_4, and chlorine:

$$CH_4(g) + Cl_2(g) \rightarrow CH_3Cl(g) + HCl(g) \qquad \Delta H_{rxn} = ?$$

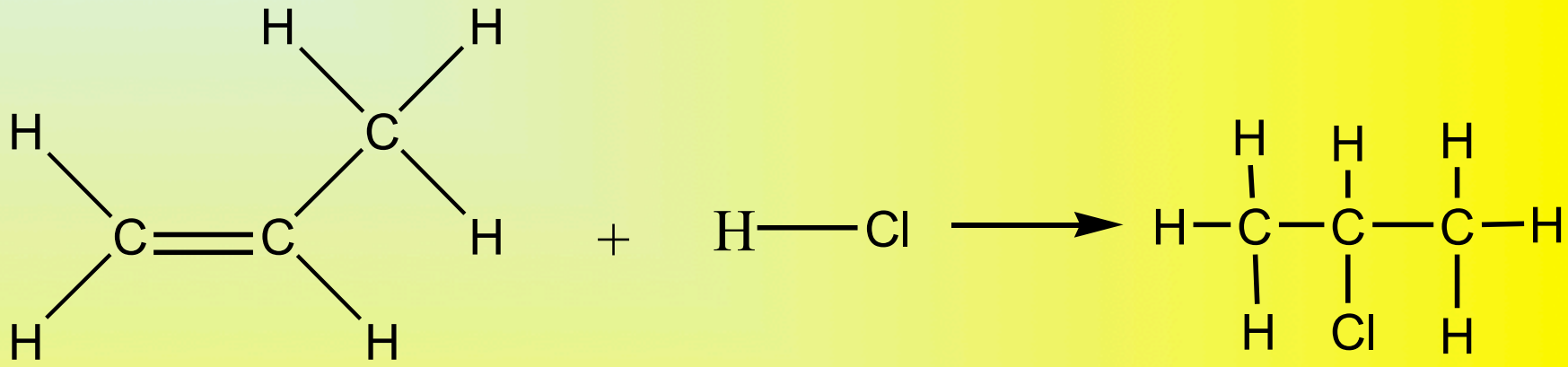

H
C
H
H
H
Cl
Cl
1 Break
C—H and Cl—Cl
bonds
2 Make
C—Cl and H—Cl
bonds
Enthalpy (H)
$\Delta H_1 > 0$
$\Delta H_2 < 0$
H
C
H
H
H
Cl—Cl
ΔH_{rxn}
Cl
C
H
H
H
H—Cl

- In this reaction one C-H bond and one Cl-Cl bond are broken while one C-Cl bond and one H-Cl bond are formed.

$$\Delta H_{rxn} = \{[D(\text{C-H}) + D(\text{Cl-Cl})] - [D(\text{C-Cl}) + D(\text{H-Cl})]\}$$
$$= -104\ \text{kJ}$$

- The overall reaction is exothermic which means that the bonds formed are stronger than the bonds broken.
- The above result is consistent with Hess's law.

- Example – Use bond energies from the table in your text to calculate ΔH for the following reaction:



Bond Enthalpy and Bond Length

- We know that multiple bonds are shorter than single bonds.
- We can show that multiple bonds are stronger than single bonds.
- As the number of bonds between atoms increases, the atoms are held closer and more tightly together.
- NOTE: A double bond between two atoms is not twice as strong as a single bond between the same two atoms.

TABLE 8.5 Average Bond Lengths for Some Single, Double, and Triple Bonds

Bond	Bond Length (Å)	Bond	Bond Length (Å)
C—C	1.54	N—N	1.47
C=C	1.34	N=N	1.24
C≡C	1.20	N≡N	1.10
C—N	1.43	N—O	1.36
C=N	1.38	N=O	1.22
C≡N	1.16		
		O—O	1.48
C—O	1.43	O=O	1.21
C=O	1.23		
C≡O	1.13		

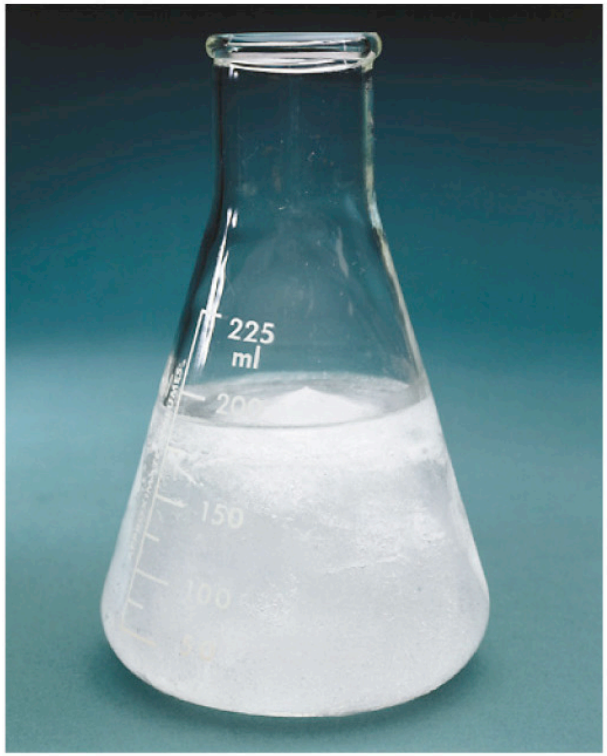
Spontaneous Processes

- 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.

- 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 $T > 0°C$, Water turning to ice is spontaneous at $T < 0°C$.

Reversible and Irreversible Processes

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



Spontaneous for $T > 0°C$

Spontaneous for $T < 0°C$

- When 1 mol of water is frozen at 1 atm at 0°C to form 1 mol of ice, $q = \Delta H_{fus}$ of heat is removed.
- To reverse the process, $q = \Delta H_{fus}$ must be added to the 1 mol of ice at 0°C and 1 atm to form 1 mol of water at 0°C.
- Therefore, converting between 1 mol of ice and 1 mol of water at 0°C is a reversible process.

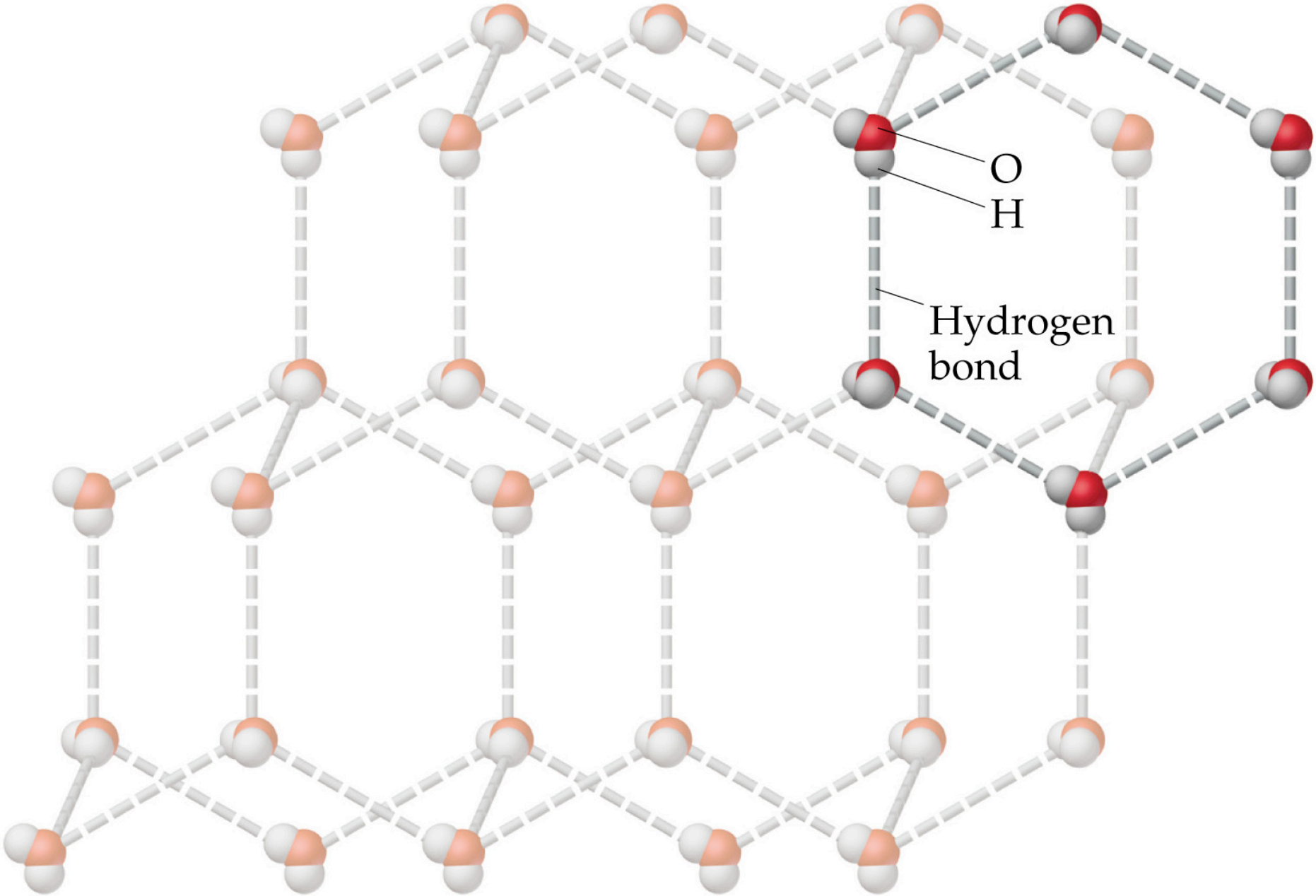
- Allowing 1 mol of ice to warm is a reversible process. To get the reverse process to occur, the water temperature must be lowered to 0°C.

- Chemical systems in equilibrium are reversible.
- Thermodynamics gives us the direction of a process. It cannot predict the speed at which the process will occur.
- Why are some endothermic reactions spontaneous?

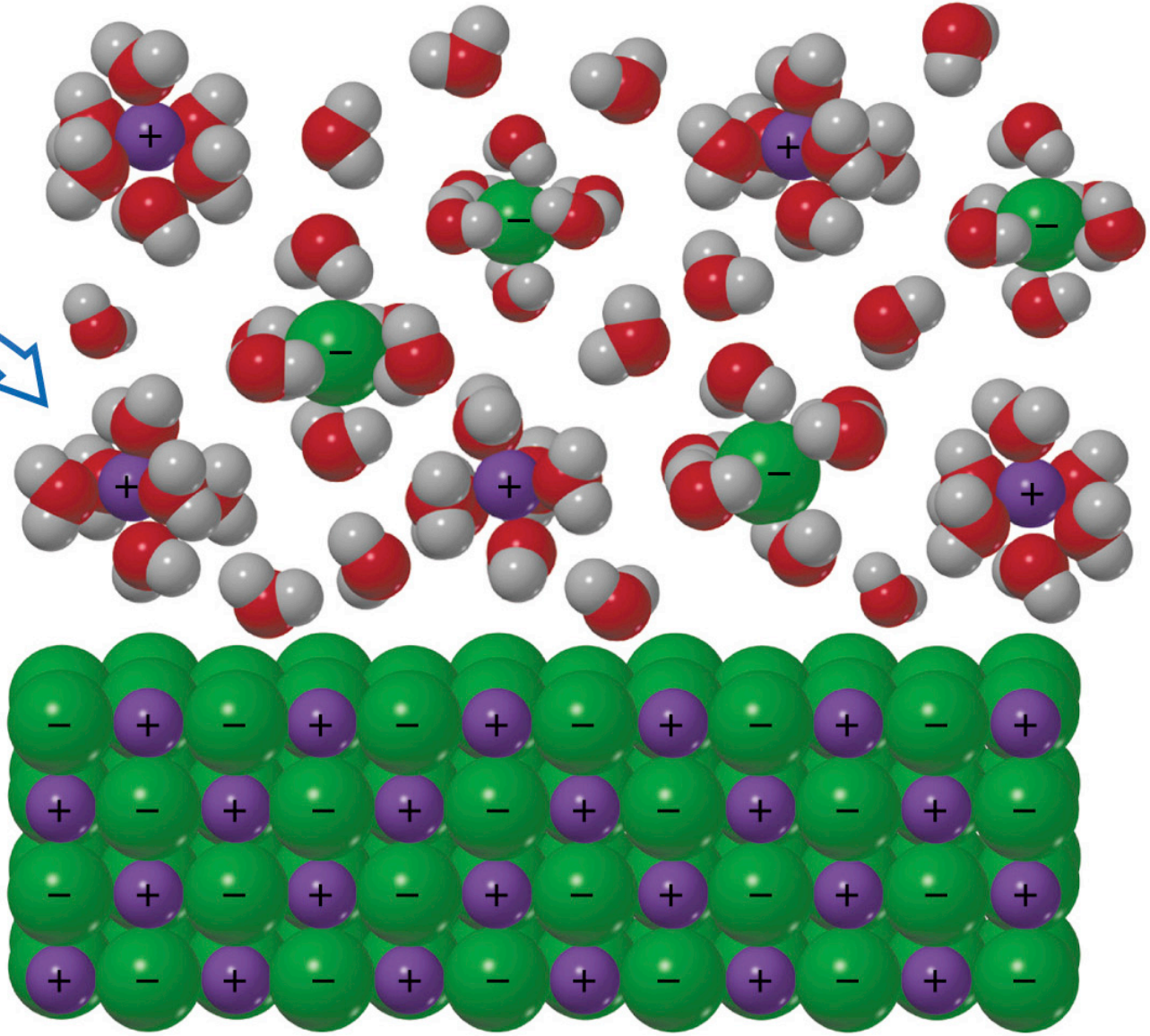
Entropy

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


O
H
Hydrogen
bond

- 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).



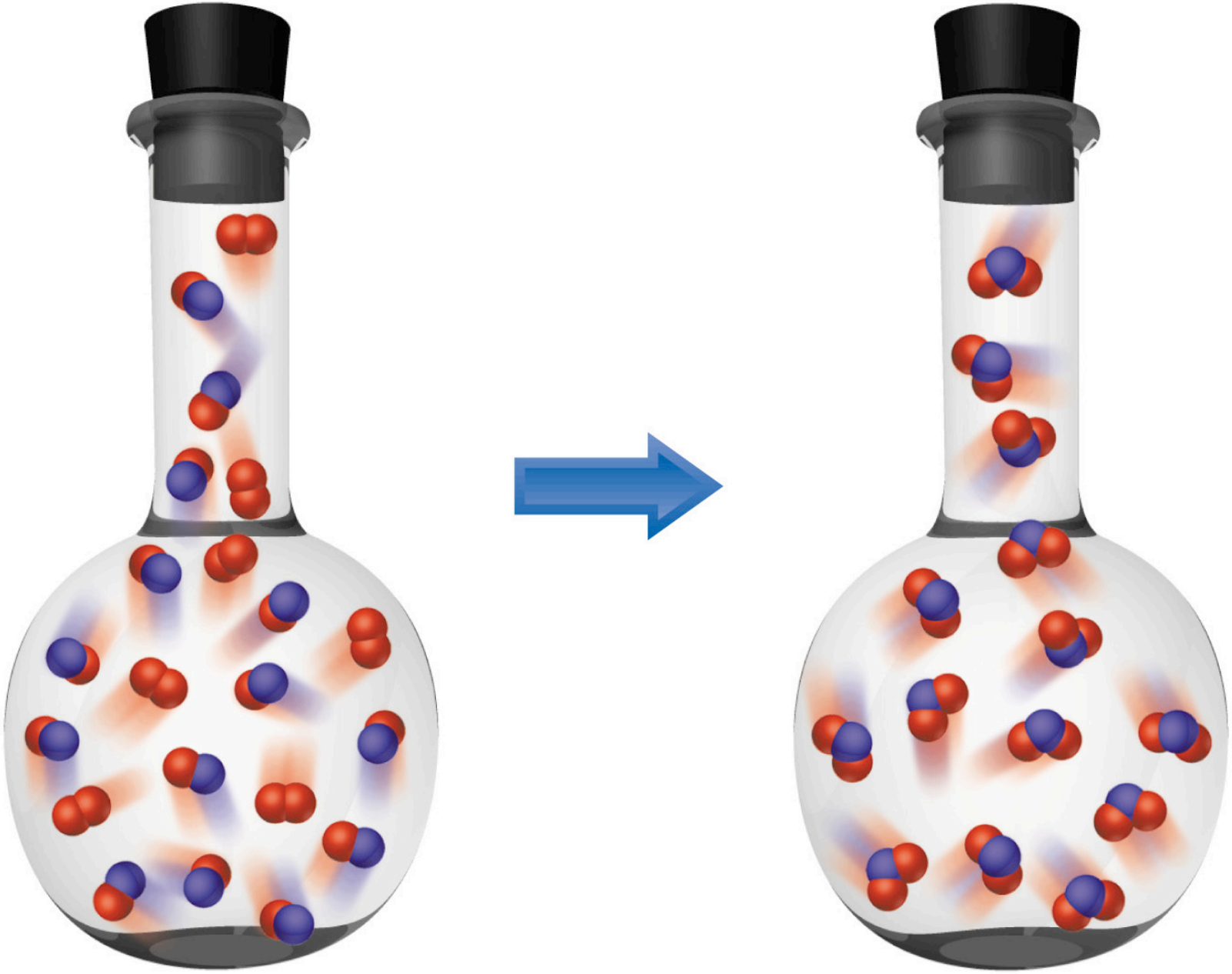
- Generally, when an increase in entropy in one process is associated with a decrease in entropy in another, the increase in entropy dominates.
- Entropy is a state function.
- For a system, $\Delta S = S_{\text{final}} - S_{\text{initial}}$.
- If $\Delta S > 0$ the disorder increases, if $\Delta S 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

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.
- $\Delta S_{univ} = \Delta S_{sys} + \Delta S_{surr}$: 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: ΔS_{univ} is increasing.

The Molecular Interpretation of Entropy

- A gas is less ordered than a liquid that is less ordered than a solid.
- Aqueous ions are less ordered than pure solids and liquids, but more ordered than gases
- Any process that increases the number of gas molecules leads to an increase in entropy.
- When NO(*g*) reacts with O_2(*g*) to form NO_2(*g*), the total number of gas molecules decreases, and the entropy decreases.



(a) (b)

Examples – Determine the sign of ΔS for each of the following:

1. $Na\ (s) + \frac{1}{2}\ Cl_2\ (g) \rightarrow NaCl\ (s)$

2. $N_2\ (g) + 3\ H_2\ (g) \rightarrow 2\ NH_3\ (g)$

3. $2\ H_2\ (g) + O_2\ (g) \rightarrow 2\ H_2O\ (l)$

4. $H_2O\ (l) \rightarrow H_2O\ (g)$

5. $NaCl\ (s) \rightarrow Na^+\ (aq) + Cl^-\ (aq)$

Examples – Determine the sign of ΔS for each of the following:

1. $Na\ (s) + \frac{1}{2}\ Cl_2\ (g) \rightarrow NaCl\ (s)$ negative

2. $N_2\ (g) + 3\ H_2\ (g) \rightarrow 2\ NH_3\ (g)$ negative

3. $2\ H_2\ (g) + O_2\ (g) \rightarrow 2\ H_2O\ (l)$ negative

4. $H_2O\ (l) \rightarrow H_2O\ (g)$ positive

5. $NaCl\ (s) \rightarrow Na^+\ (aq) + Cl^-\ (aq)$ positive