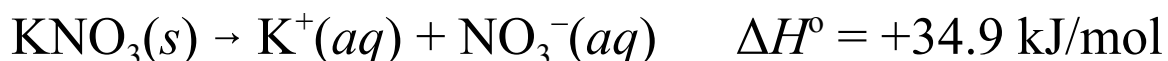
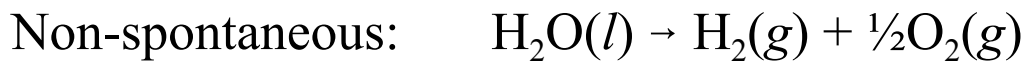


## Spontaneous Change

- Any process, once initiated, that continues without further intervention is **spontaneous**.
- Although exothermic processes tend to be spontaneous, spontaneous reactions can be exothermic or endothermic:



- If under certain conditions a process is spontaneous in a given direction, it will be non-spontaneous in the reverse direction under the same conditions.



- Sometimes, if we change conditions, the direction of spontaneous change can be reversed.

## Spontaneous Change and Equilibrium

☞ Spontaneous change always leads toward a condition of equilibrium.



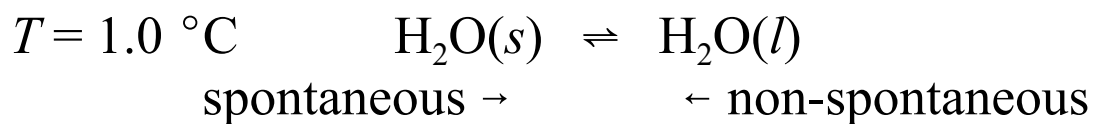
- With partial pressures for which  $Q < K$ , reaction will proceed spontaneously in the forward direction until equilibrium is achieved.
- With partial pressures for which  $Q > K$ , reaction will proceed spontaneously in the reverse direction to reach equilibrium.

☞ By changing conditions, this system can run spontaneously in either direction.

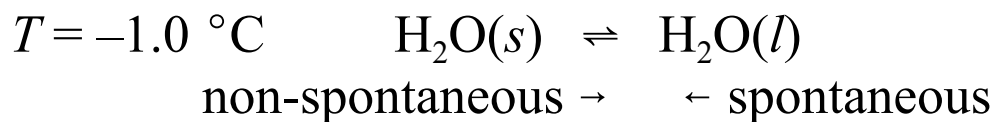
## Spontaneous Phase Changes

☞ Spontaneity of phase changes depends on conditions.

- At +1.0 °C, melting of ice to form liquid water is spontaneous, while the reverse process of freezing is non-spontaneous:



- At -1.0 °C, melting of ice is non-spontaneous, but freezing of water is spontaneous:



- At 0.0 °C, ice and liquid water are in equilibrium, and conversion of one into the other is non-spontaneous.

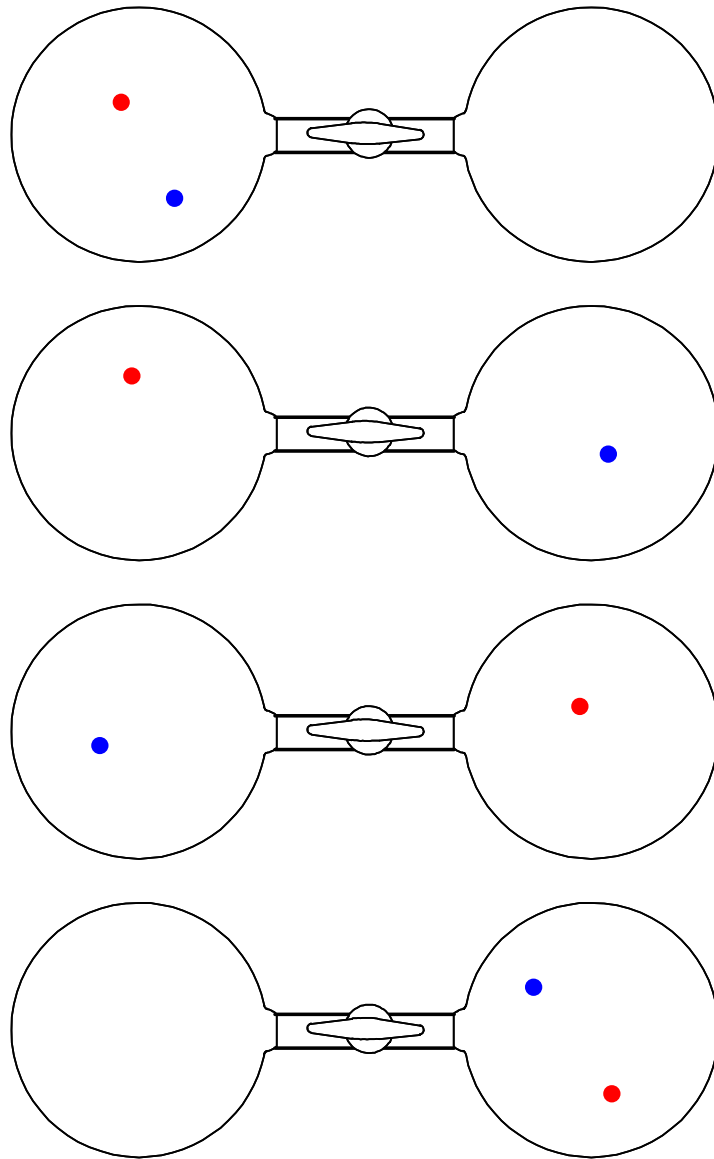
# Entropy

- ☞ The thermodynamic function **entropy**,  $S$ , is a measure of randomness or disorder.
- ☞ The physical state of a substance is related to its entropy.

State	Order	Entropy
solid	high	low
liquid	medium	higher
gas	low	highest

- ☞ A more disordered system is more likely than an ordered one.

# Spontaneous Expansion of Gas Sample



## Possible Arrangements of Three Molecules in Two Connected Flasks

Left	Right
● ● ●	
● ●	●
● ●	●
● ●	●
●	● ●
●	● ●
●	● ●
	● ● ●

## Probability of an Ordered vs. Disordered State

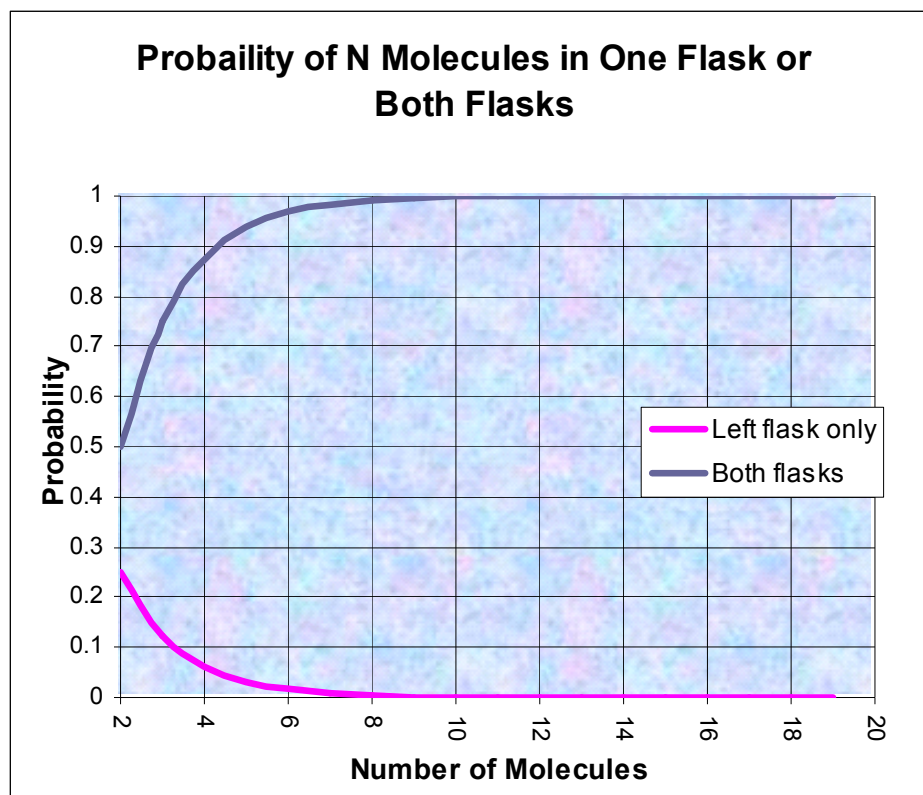
- Probability of finding all  $N$  molecules in one of two flasks (ordered state):

$$P_o = \left(\frac{1}{2}\right)^N$$

- Probability of finding  $N$  molecules distributed between both flasks (disordered state):

$$P_d = 1 - 2 \times \left(\frac{1}{2}\right)^N$$

- As  $N$  increases, the probability of the ordered state is virtually zero and that of the disordered state is virtually one.



## Second Law of Thermodynamics

Every spontaneous change results in an increase in *total* entropy.

- ☞ Total entropy is the sum of the entropy of the system and the surroundings.
- ☞ The total entropy change of a process is the sum of the entropy change of the system and its surroundings.

$$\Delta S_{\text{total}} = \Delta S_{\text{system}} + \Delta S_{\text{surroundings}}$$

- ☞ Overall, the Universe is moving toward greater disorder.



**Rudolph Clausius' (1822-1888)**  
**Classic Statement of the First and Second Laws**

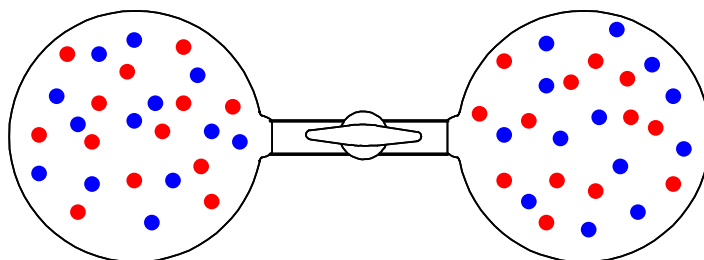
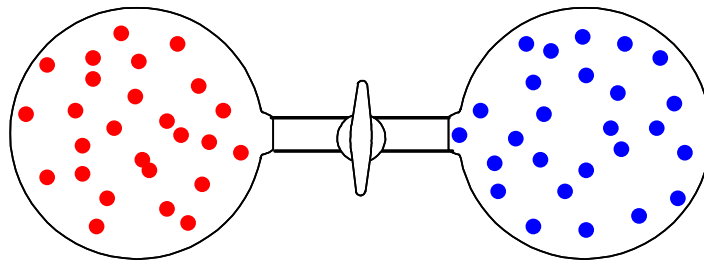
The energy of the world is a constant; the entropy strives  
for a maximum.

- ☞ An enthalpy change of the system,  $\Delta H_{\text{system}}$ , requires an equal and opposite enthalpy change for the surroundings,  $\Delta H_{\text{surroundings}}$ . [First Law]
  
- ☞ An entropy change of the system,  $\Delta S_{\text{system}}$ , *does not* require an equal and opposite change for the surroundings,  $\Delta S_{\text{surroundings}}$ . [Second Law]
  
- ☞ Some total entropy changes only involve  $\Delta S_{\text{system}}$ , while others involve both  $\Delta S_{\text{system}}$  and  $\Delta S_{\text{surroundings}}$ .

## Mixing of Two Non-Reactive Gases

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

$$\Delta S_{\text{total}} = \Delta S_{\text{system}}$$



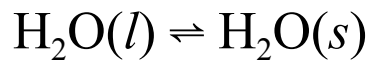
- ☞ Mixing is spontaneous, because it results in greater disorder.

$$\Delta S_{\text{total}} = \Delta S_{\text{system}} > 0$$

- ☞ Separating the mixture into individual gases in their own containers is non-spontaneous.

$$\Delta S_{\text{total}} = \Delta S_{\text{system}} < 0$$

## Water Freezing Below 0 °C



- ☞ Water is going to a more ordered state:

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

- ☞ Water evolves heat (equal to its heat of fusion) to the surroundings, causing greater thermal motion and more disorder in the molecules of the surroundings.

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

- ☞ Increase in entropy for the surroundings is greater than decrease in entropy from the ordering of water molecules in the ice (the system), so total entropy change is positive.

$$\Delta S_{\text{total}} = \Delta S_{\text{system}} + \Delta S_{\text{surroundings}} > 0$$

- ☞ Freezing of water below its f.p. (m.p.) is spontaneous.

**Entropy Changes for Water Freezing**  
**At -1 °C, 0 °C, and +1 °C**  
 $\text{H}_2\text{O}(l) \rightleftharpoons \text{H}_2\text{O}(s)$

Temp. °C	$\Delta S_{\text{system}}$ $\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$	$\Delta S_{\text{surroundings}}$ $\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$	$\Delta S_{\text{total}}$ $\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$	Spontaneity
-1	-21.85	+21.93	+0.08	spontaneous
0	-21.99	+21.99	0	equilibrium
+1	-22.12	+22.05	-0.08	non-spontaneous

- ✓ At -1 °C,  $\Delta S_{\text{total}} > 0$ , and freezing is spontaneous.
- ✓ At 0 °C,  $\Delta S_{\text{total}} = 0$ , and neither freezing nor melting is spontaneous, because water and ice are in equilibrium and no net change occurs.
- ✓ At +1 °C,  $\Delta S_{\text{total}} < 0$ , and freezing is non-spontaneous; melting (the reverse process) is spontaneous.