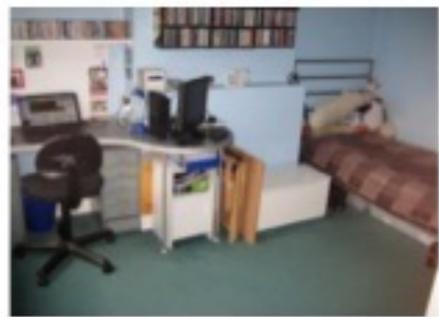
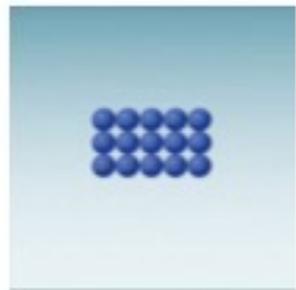
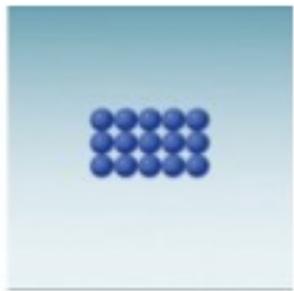


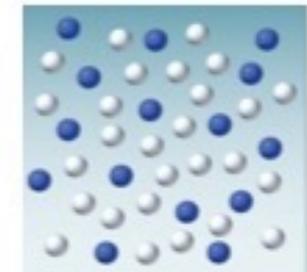
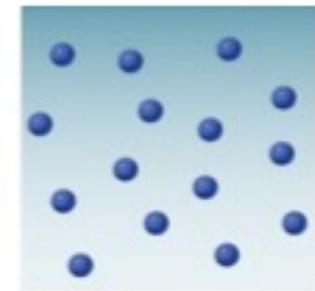
15.2 Entropy and spontaneity

Entropy (S): A measure of randomness (disorder).

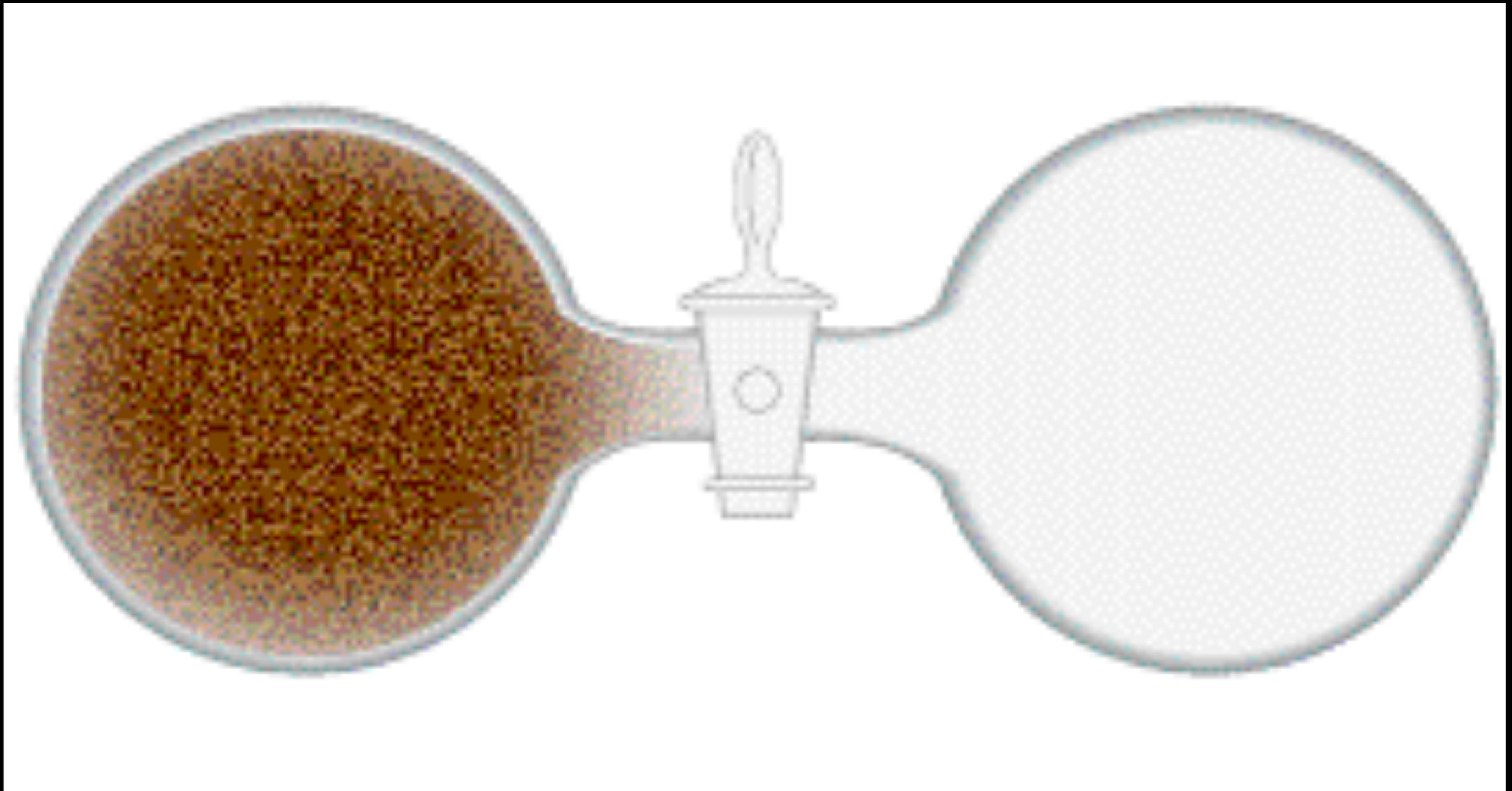
LOW ENTROPY



HIGH ENTROPY



Key idea: Nature spontaneously proceeds towards those states that have the highest probabilities of existing.



Lower Entropy

Higher Entropy

Slow moving particles

Fast moving particles

Particles close together

Particles spread out

Fewer particles

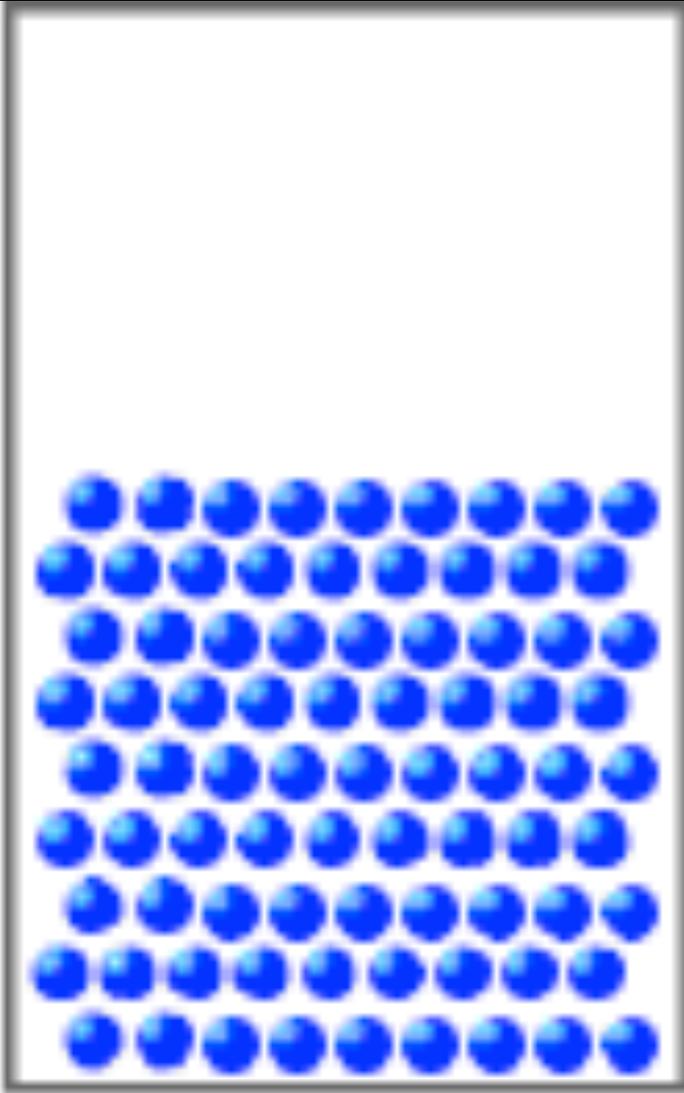
More particles

Solids

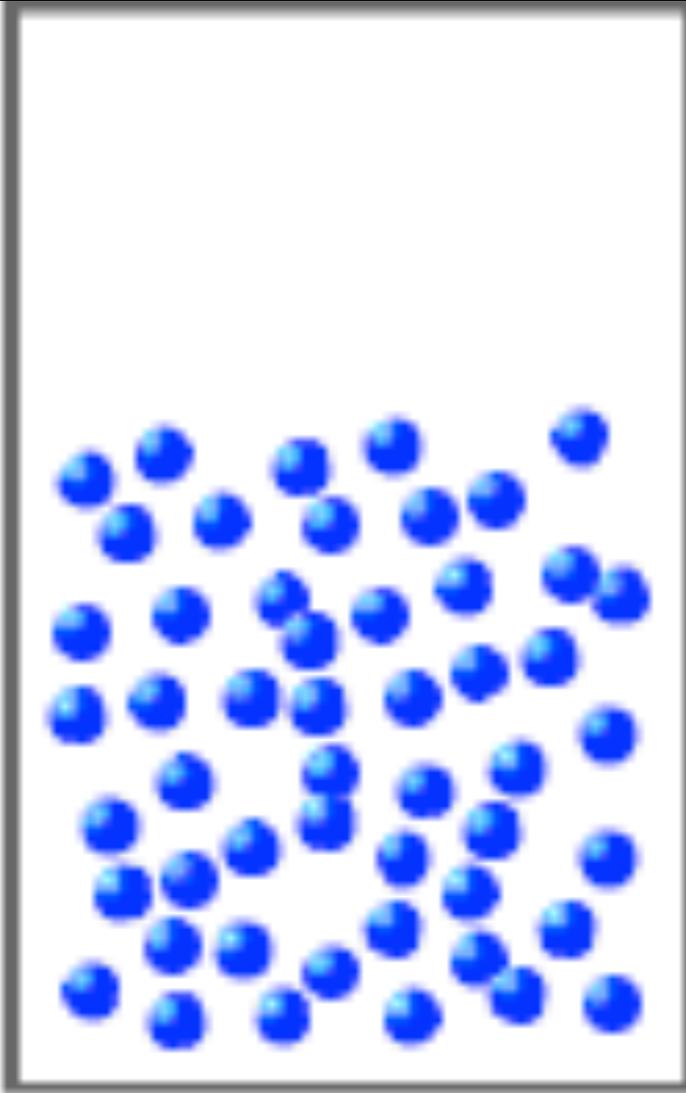
Gases

For changes of state:

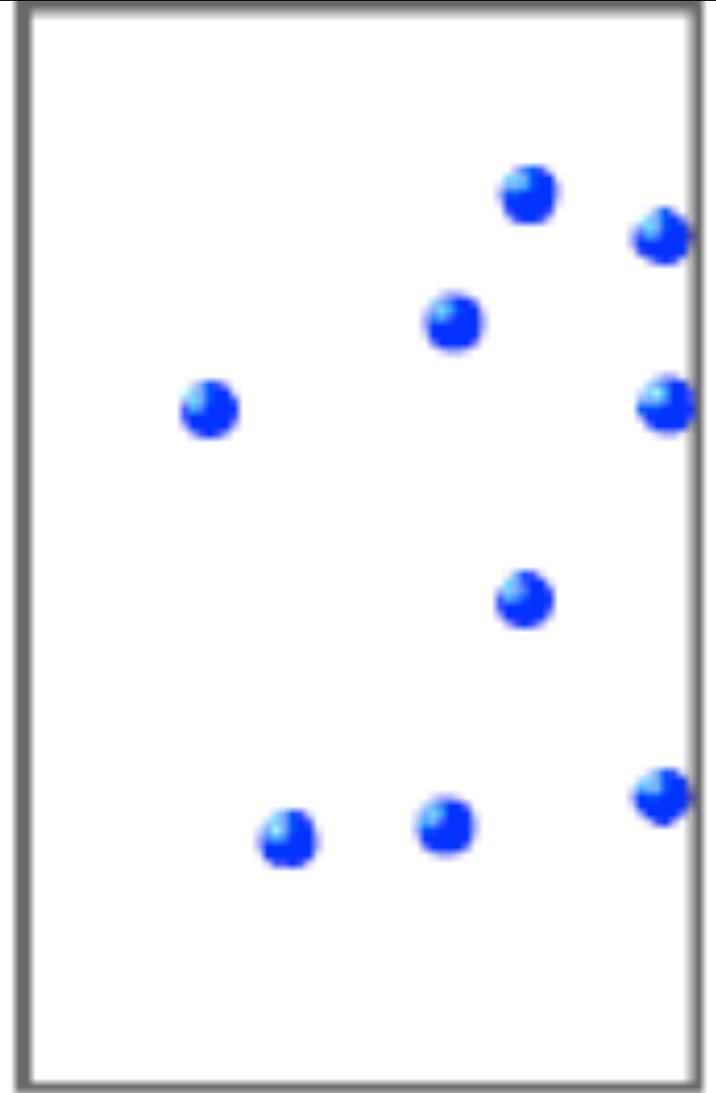
$$S_{\text{solid}} < S_{\text{liquid}} < S_{\text{gas}}$$



Solid



Liquid



Gas

Entropy will increase when:

- Temperature increases
- More particles (moles) form in a chemical reaction
- These changes of state:
 - solid → liquid
 - liquid → gas
 - solid → gas

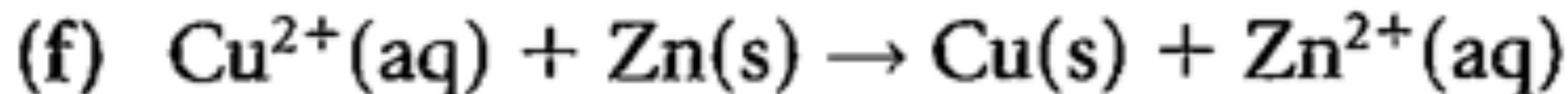
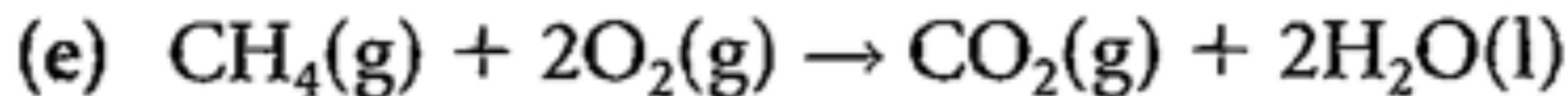
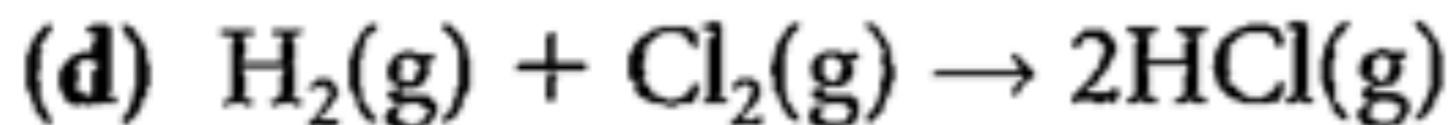
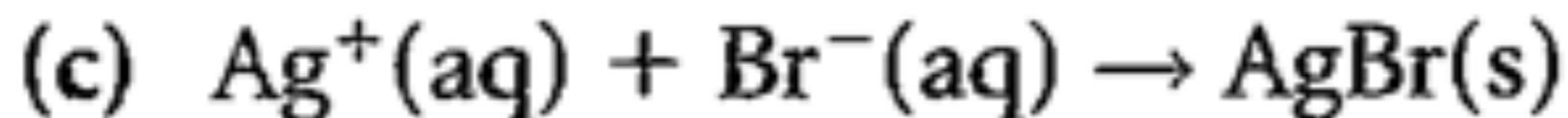
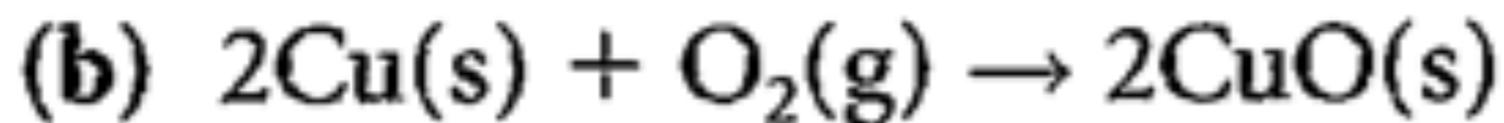
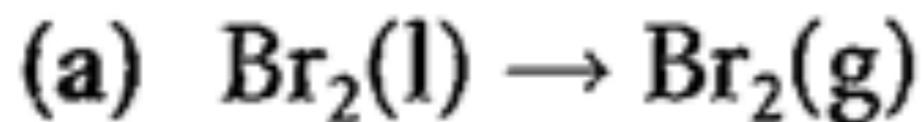
Predict the sign for entropy:

Change	ΔS
solid \rightarrow liquid	
solid \rightarrow gas	
liquid \rightarrow gas	
liquid \rightarrow solid	
gas \rightarrow solid	
gas \rightarrow liquid	

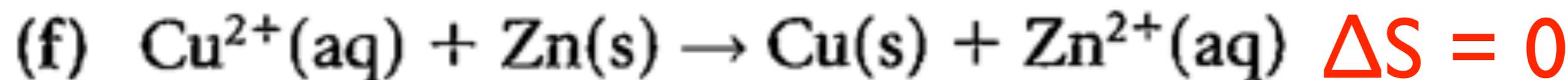
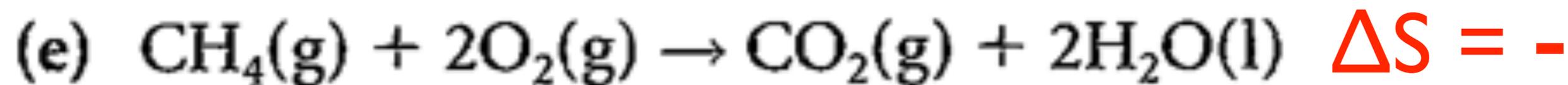
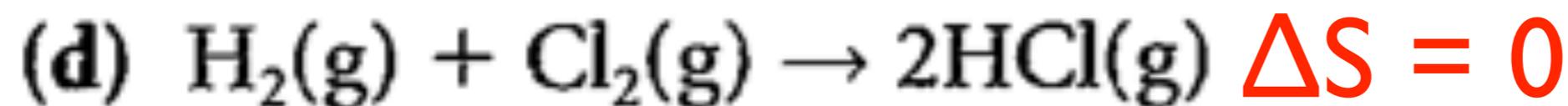
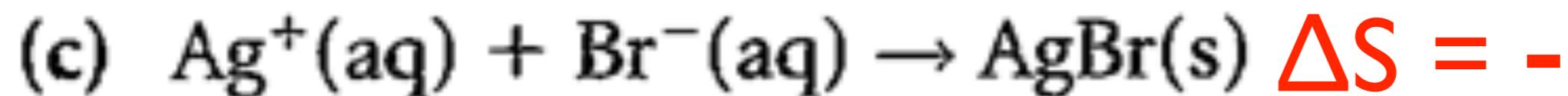
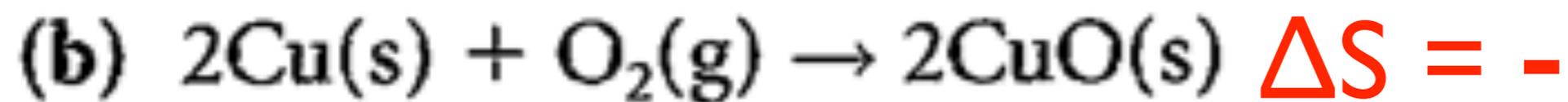
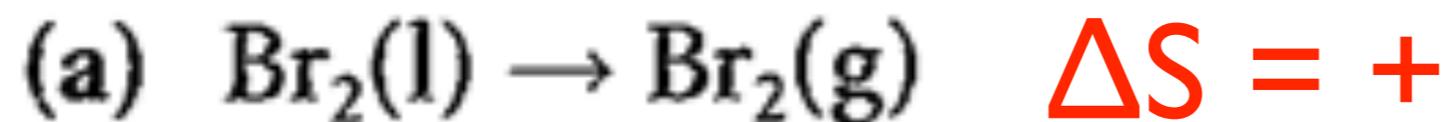
Predict the sign for entropy:

Change	ΔS
solid \rightarrow liquid	increase (+)
solid \rightarrow gas	increase (+)
liquid \rightarrow gas	increase (+)
liquid \rightarrow solid	decrease (-)
gas \rightarrow solid	decrease (-)
gas \rightarrow liquid	decrease (-)

Predict the entropy change ΔS for the following changes.



Predict the entropy change ΔS for the following changes.



Calculating entropy:

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

(see handout: thermodynamic values)

Spontaneity:

A spontaneous process occurs naturally on its own.

(does not refer to the length of time for a process to occur)

The First Law of Thermodynamics:

In any chemical or physical process, energy is neither created nor destroyed.

The Second Law of Thermodynamics:

In any spontaneous process there is always an increase in the entropy of the universe.

The Third Law of Thermodynamics:

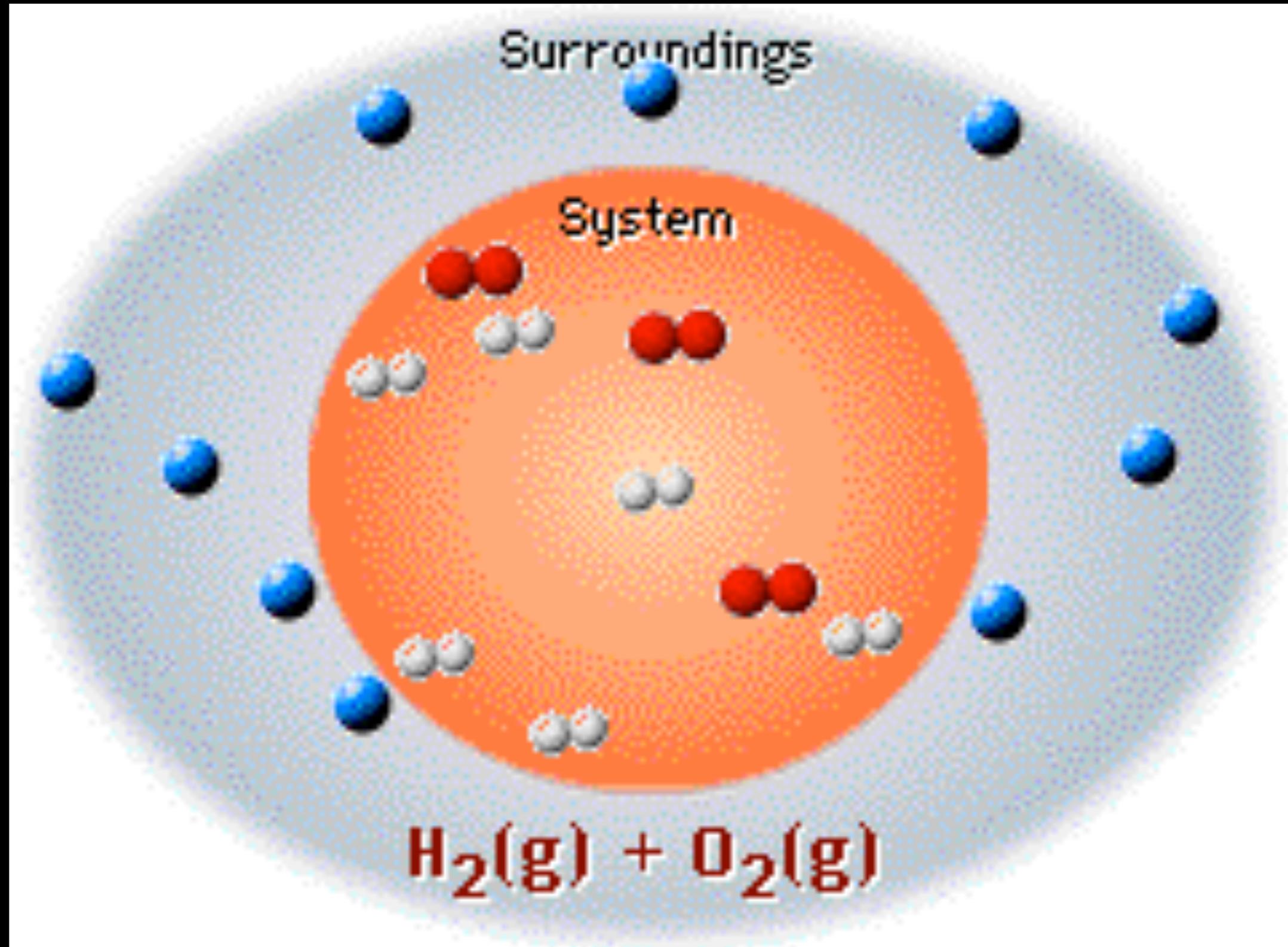
The entropy of a perfect crystal at absolute zero is exactly equal to zero.

If $\Delta S_{\text{universe}} = \text{positive (+)}$,
the process is spontaneous.

If $\Delta S_{\text{universe}} = \text{negative (-)}$,
the process does not take place
(spontaneous in the opposite direction).

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

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



Gibbs Free Energy

The sign of ΔS_{sur} depends on the direction of heat flow.

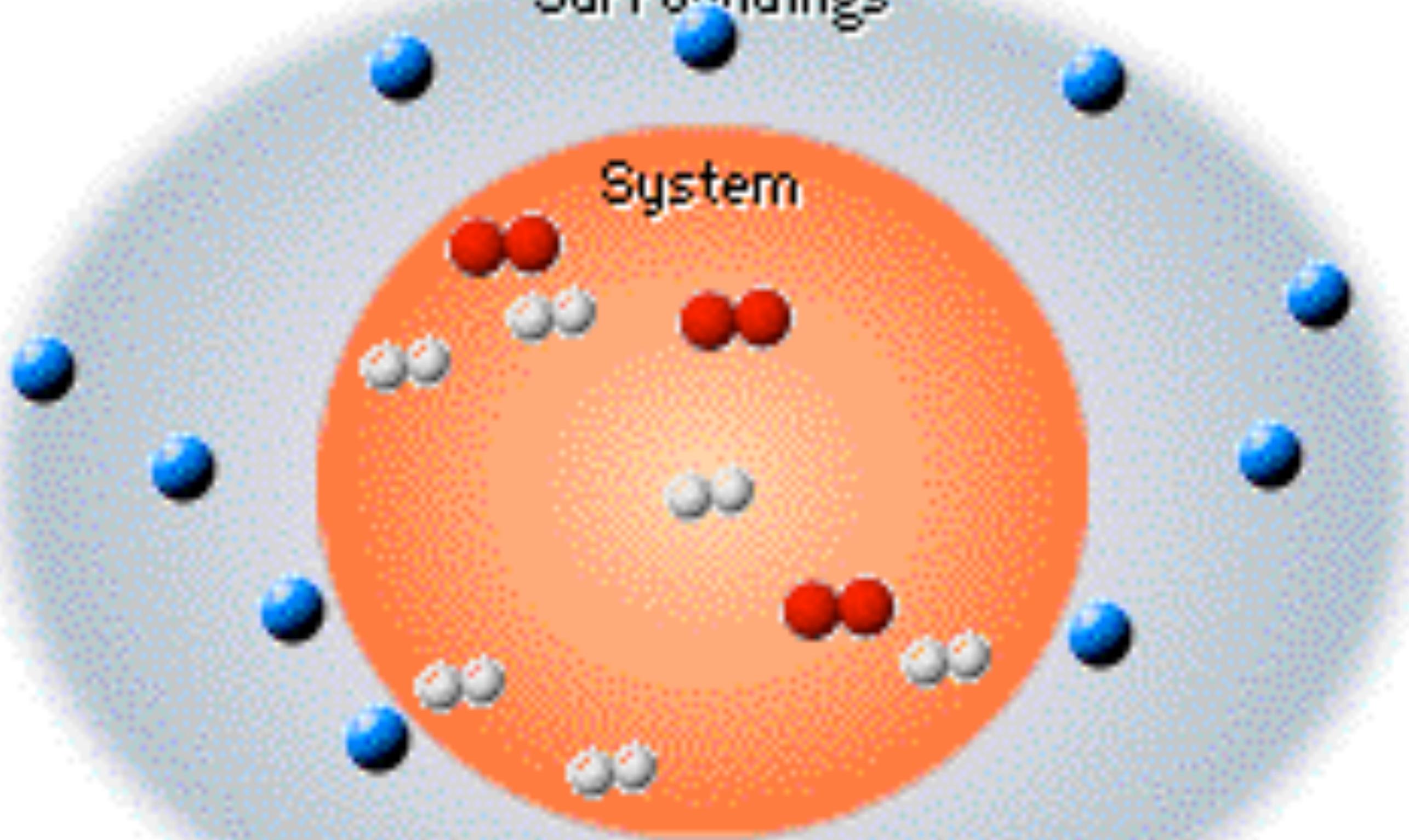
$$\Delta S_{\text{sur}} \propto -\Delta H_{\text{system}}$$

The magnitude of ΔS_{sur} depends on the temperature.

$$\Delta S_{\text{sur}} \propto 1/T \quad (\text{where } T \text{ is in kelvins})$$

Surroundings

System



Therefore,

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

Substituting into,

$$\Delta S_{\text{uni}} = \Delta S_{\text{sys}} + \Delta S_{\text{sur}}$$

becomes,

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

multiplying through by $-T$ gives,

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

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

ΔG

Called “Gibbs free energy”

$$\boxed{\Delta G = \Delta H - T\Delta S}$$

Note: all values refer to the system

Gibbs free energy (trivia):

- aka “available energy”
- derived in the 1870s by the American mathematician Josiah Willard Gibbs

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

Recall,

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

Therefore,

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

From this we can conclude,

1. If ΔG is negative then ΔS_{uni} is positive and the process is spontaneous.

2. If ΔG is positive then ΔS_{uni} is negative and the process is not spontaneous.

Thermodynamics Summary: The Driving Forces

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

	ΔH		ΔS		ΔG	Spontaneous?
1	-		+		-	Always
2	+		+		?	Only at high temperatures
3	-		-		?	Only at low temperatures
4	+		-		+	Never