

Before we begin the new Ch 18 material we will review some of the Thermodynamics topics (ch 6) covered in chm151

The First Law of Thermodynamics:

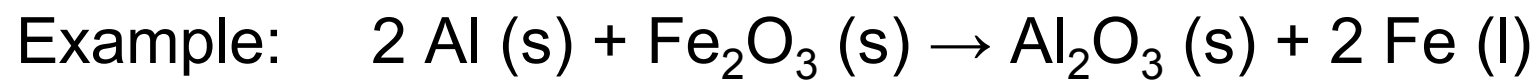
A system can exchange energy with its surrounds two ways:

Calorimetry and thermal energy exchange:

Enthalpy (H):

Calculating enthalpy change (ΔH) from tabulated data:

$$\Delta H^{\circ}_{\text{rxn}} = \sum n \Delta H^{\circ}_{\text{f}}(\text{products}) - \sum n \Delta H^{\circ}_{\text{f}}(\text{reactants})$$



Calculate $\Delta H^\circ_{\text{rxn}}$

	ΔH°_f (kJ/mol)
Al (s)	0
Fe_2O_3 (s)	-822.2
Al_2O_3 (s)	-1699.8
Fe (l)	12.40

Chapter 18: Entropy and Free Energy

Reading: pgs 783-802

Learning Goals

First Law of Thermodynamics

-Energy can not be created nor destroyed, during a reaction or process it can be converted from one form to another

-For reactions/processes which take place at constant pressure, the thermal energy released or absorbed is a measure of the change in Enthalpy (ΔH).

Second Law of Thermodynamics

-Why reactions tend to favor one direction over the other.

-The connection to Entropy

Third Law of Thermodynamics

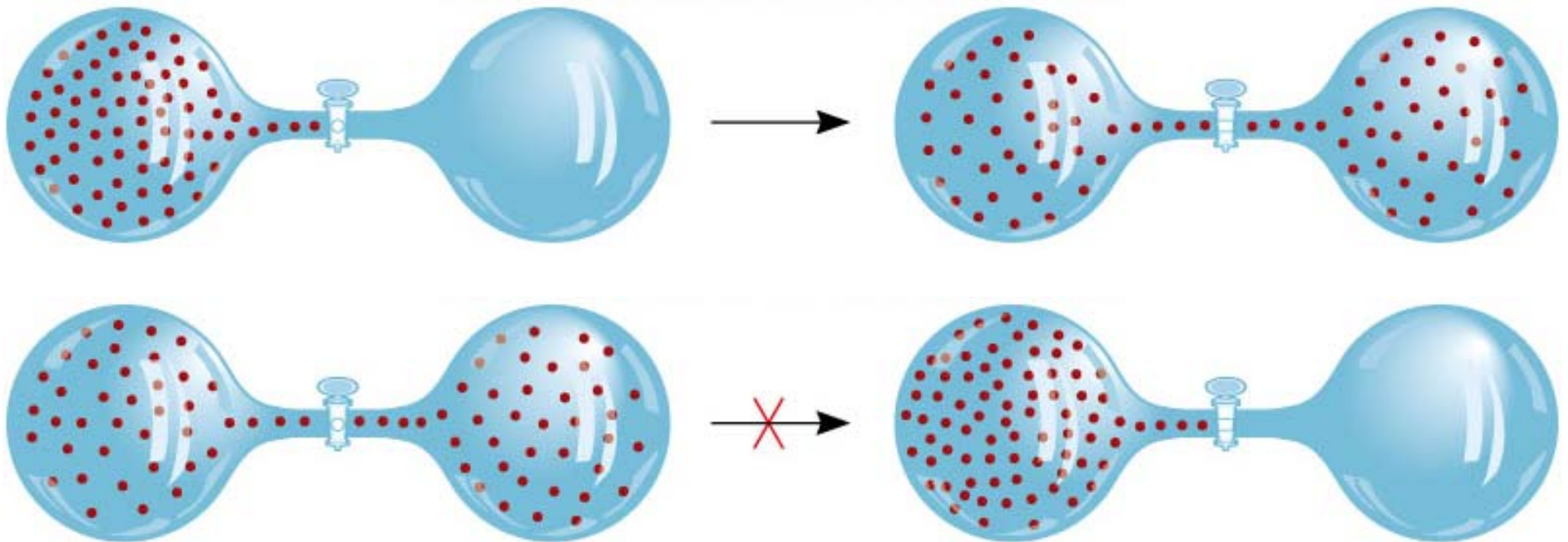
-At absolute zero ($T = 0 \text{ K}$), the entropy of a system is zero.

Spontaneous Processes

Thermodynamics helps us to predict if a given reaction will occur under a given set of conditions.

If the reaction or process occurs under the given conditions then it is said to be SPONTANEOUS.

If it does NOT occur then it is said to be NON-spontaneous, under those conditions.



Examples of spontaneous physical/chemical processes:

Spontaneity and changes in Enthalpy (ΔH)

-In general, spontaneous processes occur in order to decrease the energy of the system

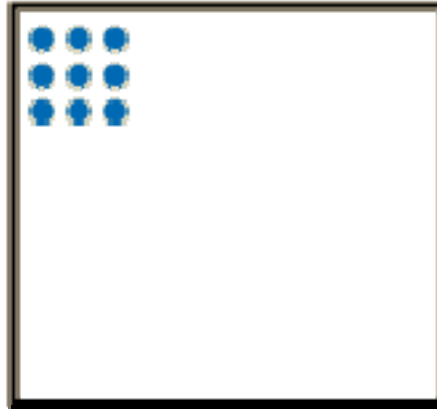
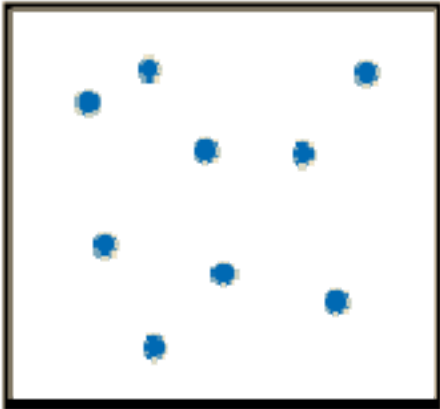
Solid-Liquid Phase Transition



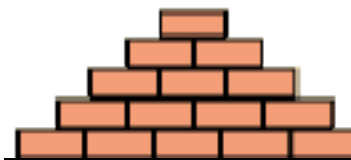
At temperatures above 0 °C, this process occurs spontaneously.

How can this **ENDOTHERMIC** process occur spontaneously?

Entropy (S): a measure of randomness (disorder) within a system
-the greater the disorder, the greater the entropy



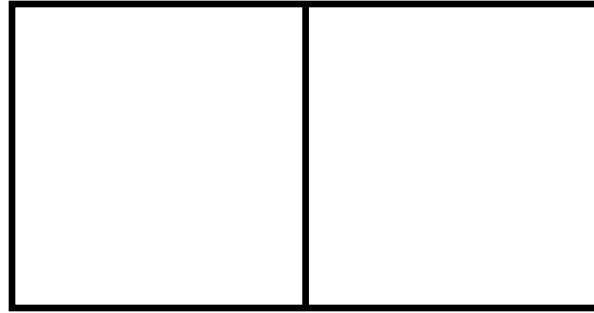
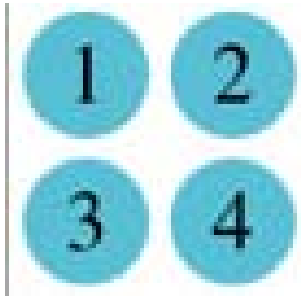
If you tossed bricks off a truck, which kind of pile of bricks would you more likely produce?



Disorder is more probable than order.



Microstates of a system and Entropy (S)



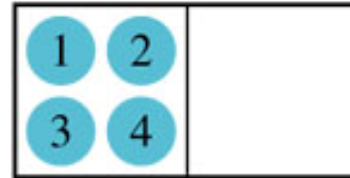
You are given a system which is made up of four gas particles and two boxes of equal size.

How many different ways can you arrange this system?

Distribution

I

Microstates



The eleven possible configurations are called the MICROSTATES of the system.

-You have a higher probability of forming a distribution with a large number of microstates than a distribution with only a few microstates.

-The probability of occurrence of a particular distribution (state) depends on the number of ways (microstates) in which the distribution can be achieved.

Tossing two coins:

The entropy (S) of a system is related to the number of microstates (W) the system can obtain.

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

Entropy is a state function

Entropy (S) and disorder



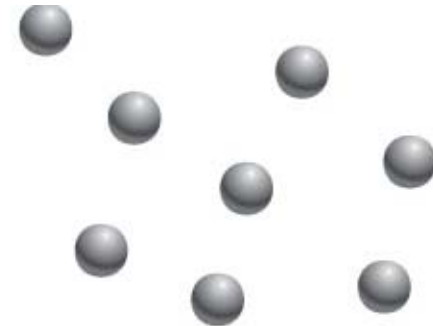
Solid



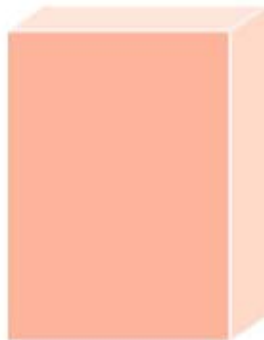
Liquid



Liquid



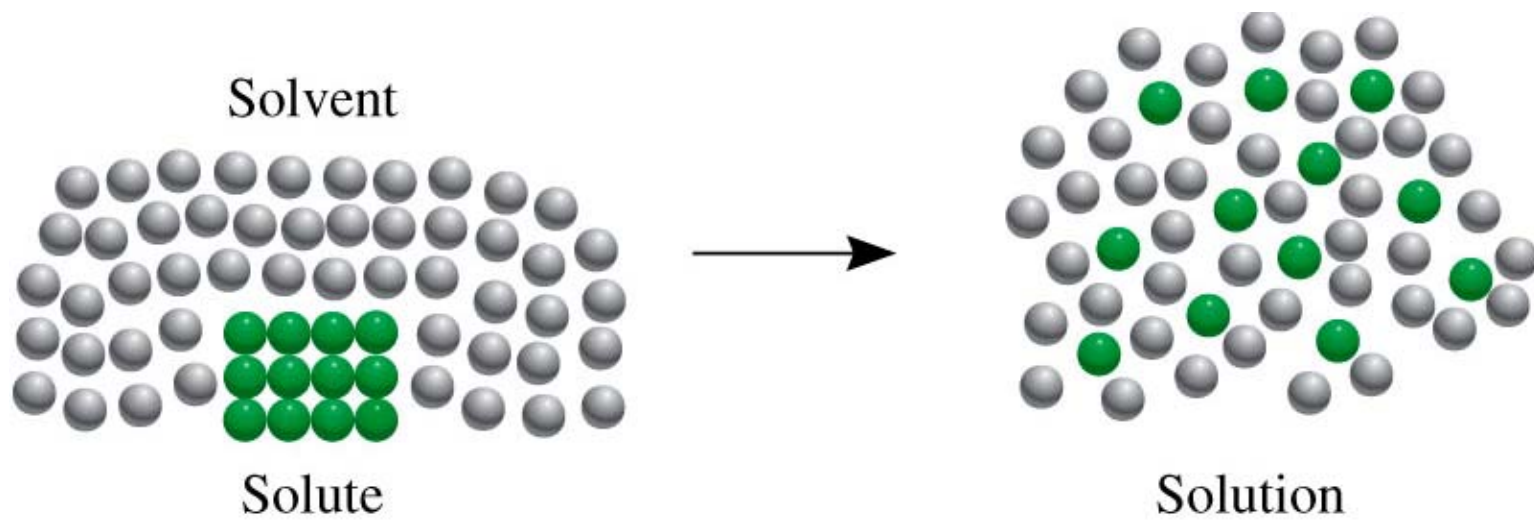
Vapor



System at T_1



System at T_2 ($T_2 > T_1$)



Entropy steps for dissolving Sodium Chloride:

Standard Entropy (S°): Entropy of a substance at 1 atm and 25 °C

TABLE 18.1

Standard Entropy Values (S°) for Some Substances at 25°C

Substance	S° (J/K · mol)
H ₂ O(<i>l</i>)	69.9
H ₂ O(<i>g</i>)	188.7
Br ₂ (<i>l</i>)	152.3
Br ₂ (<i>g</i>)	245.3
I ₂ (<i>s</i>)	116.7
I ₂ (<i>g</i>)	260.6
C (diamond)	2.4
C (graphite)	5.69
CH ₄ (methane)	186.2
C ₂ H ₆ (ethane)	229.5
He(<i>g</i>)	126.1
Ne(<i>g</i>)	146.2

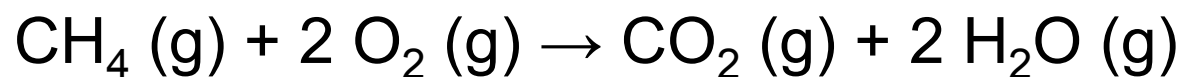
Second Law of Thermodynamics: The entropy of the universe increases in a spontaneous process and remains unchanged during equilibrium.

To calculate $\Delta S_{\text{universe}}$, we need to know ΔS_{system} and $\Delta S_{\text{surroundings}}$

Calculating ΔS_{system} :

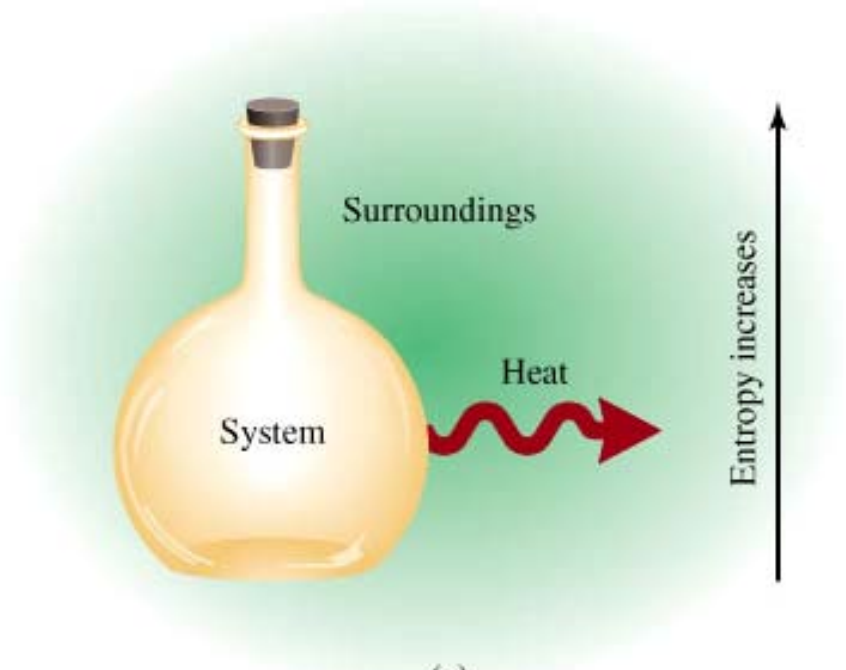
$$\Delta S^{\circ}_{\text{rxn}} = \sum n S^{\circ}(\text{products}) - \sum m S^{\circ}(\text{reactants})$$

Example: Calculate $\Delta S^{\circ}_{\text{rxn}}$ for the combustion of methane

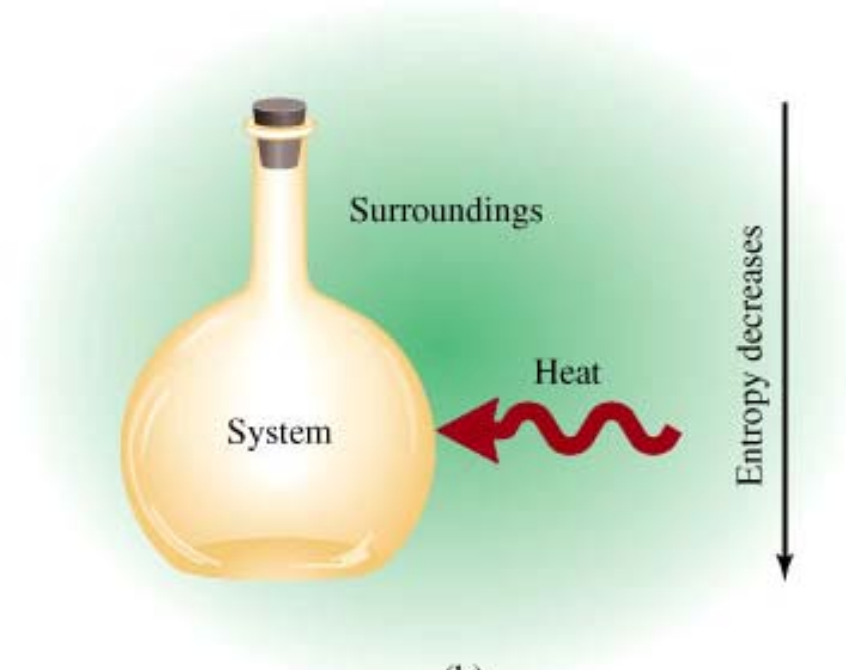


Substance	S° (J/K*mol)
CH ₄ (g)	186.2
O ₂ (g)	0
CO ₂ (g)	213.6
H ₂ O (g)	188.7

Calculating $\Delta S_{\text{surroundings}}$:



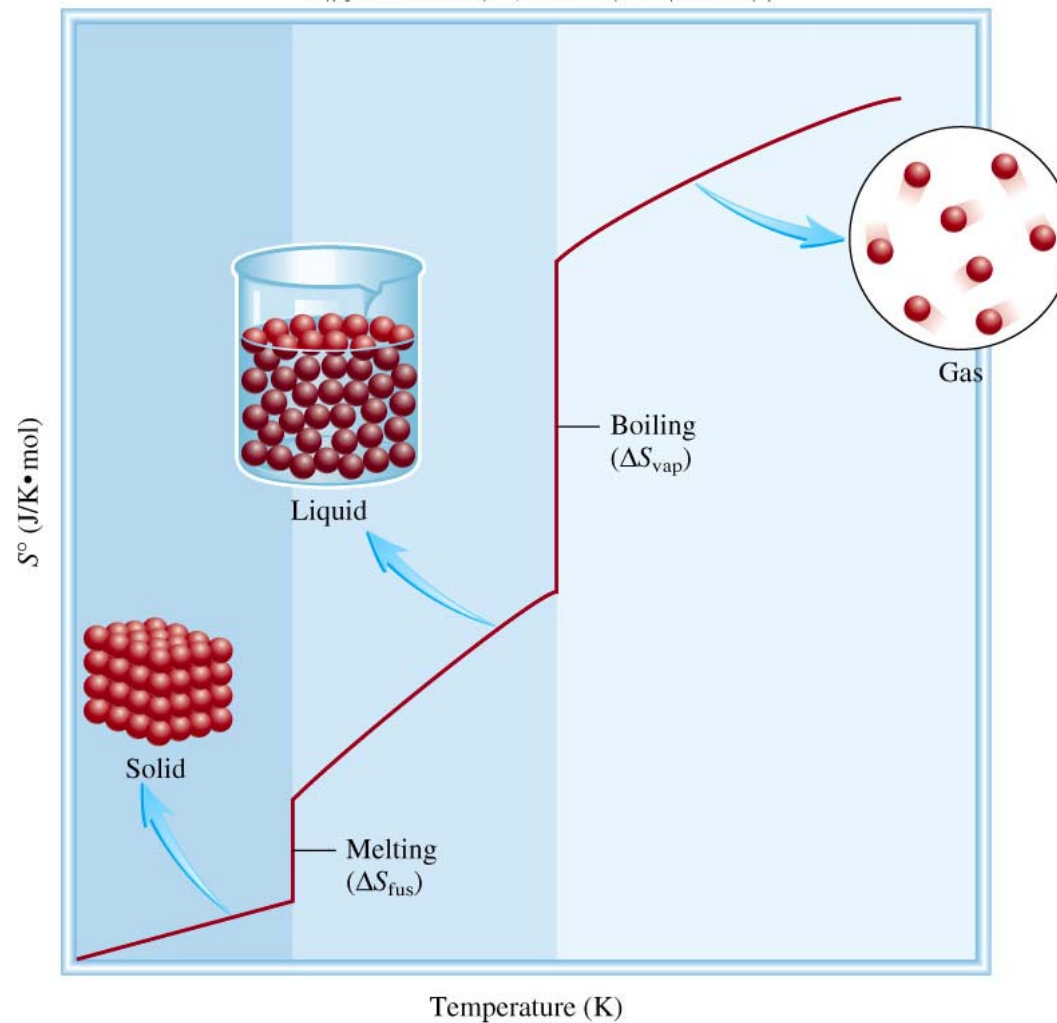
(a)



(b)

Third Law of Thermodynamics: the entropy (S) of a perfect crystalline solid at absolute zero ($T = 0 \text{ K}$) is zero.

-there is only one way to arrange the atoms in the crystal, therefore, there is only ONE microstate



Reaction Spontaneity

-Most favorable reactions and processes increase entropy as they proceed ($\Delta S > 0$) and release thermal energy ($\Delta H < 0$).

-However, a reaction or process may proceed spontaneously even if there is a decrease in entropy ($\Delta S < 0$) OR an input of energy ($\Delta H > 0$).

To determine the spontaneity of a reaction we must consider all of the following properties:

Entropy (S)

Enthalpy (H)

Temperature (T)

To do this we introduce a new thermodynamic property called the Gibbs Free Energy (G).

Gibbs Free Energy (G)

$$G = H - TS$$

As a reaction or process proceeds, we can evaluate how the free energy changes:

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

There are various combinations of ΔH and ΔS which lead to a reaction or process being spontaneous.

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

ΔH	ΔS	ΔG

For the combinations of ΔH and ΔS that are temperature dependent, what temperature leads to a change in spontaneity?

Example: Calculate ΔG for the decomposition of CaCO_3 under standard conditions (1 atm, 25 °C).



	ΔH°_f (kJ/mol)	ΔS° (J/K*mol)
CaO (s)	-635.6	39.8
CO ₂ (g)	-393.5	213.6
CaCO ₃ (s)	-1206.9	92.9

At what temperature does the decomposition of CaCO_3 become spontaneous?

Entropy change at a phase transition

-At the boiling point or the freezing point, the system is in equilibrium and $\Delta G = 0$.

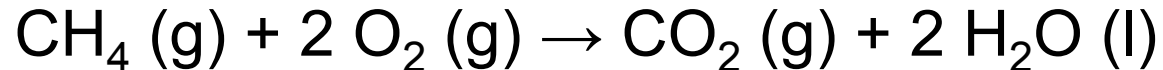
$$\Delta S_{(\text{ice} \rightarrow \text{water})} =$$

$$\Delta H_{\text{fus}} = 6010 \text{ J/mol}$$

$$\Delta S_{(\text{water} \rightarrow \text{ice})} =$$

Calculating the standard free-energy change ($\Delta G^\circ_{\text{rxn}}$)
(standard = 1 atm and 25 °C)

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



	ΔG_f° (kJ/mol)
CH ₄ (g)	-50.8
O ₂ (g)	0
CO ₂ (g)	-394.4
H ₂ O (l)	-237.2