

# Entropy, Free Energy, and Equilibrium

Source:  
Raymond Chang, Chemistry, 7<sup>th</sup> edition  
Mc Graw Hill

# Three Law of Thermodynamic

1<sup>st</sup>

- Energy can be converted to one form to another
- But energy cannot be created or destroyed

2<sup>nd</sup>

- Explains why chemical processes tends to favor one direction.

3<sup>rd</sup>

- Is an extension of the second law...?????????

# *Spontaneous Reaction*

is a reaction that does occur under the given set of conditions.

# Spontaneous of Physical and Chemical Process

- ▶ A waterfall runs downhill.
- ▶ Heat flows from a hotter object to a colder one.
- ▶ Iron exposed to water and oxygen form rust, but rust does not spontaneously change back to iron.
- ▶ A piece of sodium metals reacts violently with water to form rust, but rust does not spontaneously change back to iron.

*Processes that occur spontaneously in one direction can not, under the same conditions, also take place spontaneously in the opposite direction*

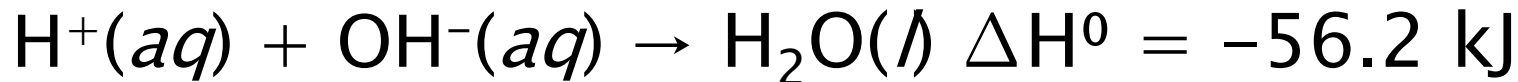
# Spontaneous Reaction

Large number of exothermic reaction

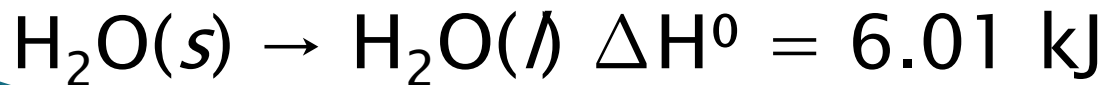
**Combustion of methane:**




**Acid–base neutralization:**



**Solid–to–liquid phase transition:**

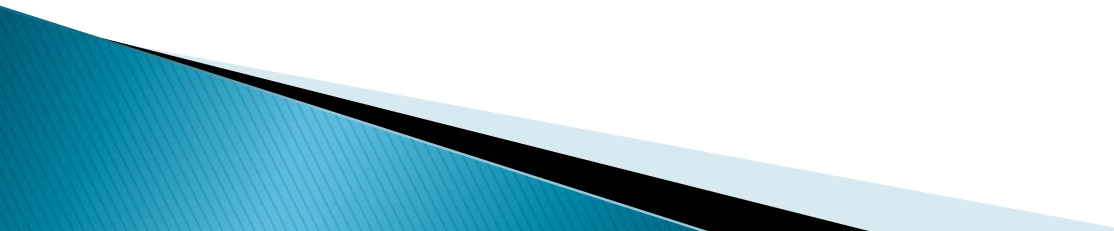


- ▶ Exothermicity favors the spontaneity of a reaction but does not guarantee it.
  - ▶ We cannot decide whether or not a chemical reaction will occur spontaneously solely on the basis of energy changes in the system.
  - ▶ We need another thermodynamic quantity to make this kind of prediction.
  - ▶ Which is turns out to be *entropy*.
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Two things to know about the system to predict spontaneity of a process

- ▶ The change in enthalpy, nearly equivalent to  $\Delta E$  for most processes.
- ▶ Entropy (S), a measure of the randomness or disorder of a system.

The greater the disorder of a system, the greater its entropy. The more ordered a system, the smaller its entropy.



## Standard Entropy Values ( $S^\circ$ ) for Some Substance at 25°C

Substance	$S^\circ$ (J/K.mol)
$\text{H}_2\text{O}(l)$	69.9
$\text{H}_2\text{O}(g)$	188.7
$\text{Br}_2(l)$	152.3
$\text{Br}_2(g)$	245.3
$\text{I}_2(s)$	116.7
$\text{I}_2(g)$	260.6
C(diamond)	2.44
C(graphite)	5.69
$\text{He}(g)$	126.1
$\text{Ne}(g)$	146.2

*Standard entropy is the absolute entropy of a substance at 1 atm and 25°C.*



Like energy and enthalpy, entropy is a state function. Consider a certain process in which a system changes from some initial state to some final state. The entropy change for the process,  $\Delta S$ , is

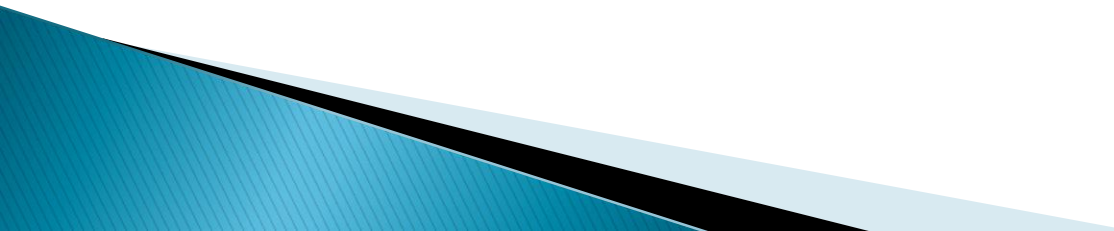
$$\Delta S = S_f - S_i$$

$S_f$  : entropies of the system in the final

$S_i$  : entropies of the system in the initial state

If the change results in an increase in randomness, or disorder, then  $S_f > S_i$  or  $\Delta S > 0$ .

# Process with $\Delta S > 0$

- ▶ Melting
  - ▶ Vaporization
  - ▶ Dissolving
  - ▶ Heating
- 

Process	$\Delta S$
Freezing ethanol	$\Delta S < 0$
Evaporating a beaker of liquid bromine at room temperature	$\Delta S > 0$
Dissolving sucrose in water	$\Delta S > 0$
Cooling nitrogen gas from 80°C to 20°C.	$\Delta S < 0$
Condensing water vapor	$\Delta S < 0$
Forming sucrose crystals from a supersaturated solution	$\Delta S < 0$
Heating hydrogen gas from 60°C to 80°C	$\Delta S > 0$
Subliming dry ice	$\Delta S > 0$

# The second law of Thermodynamics

- ▶ The entropy of the universe increases in a spontaneous process and remains unchanged in an equilibrium process

- ▶ For spontaneous process:

$$\Delta S_{\text{univ}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}} > 0$$

- ▶ For an equilibrium process:

$$\Delta S_{\text{univ}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}} = 0$$

# Standard entropy of reaction ( $\Delta S^\circ_{\text{rxn}}$ )

For the reaction  $aA + bB \rightarrow cC + dD$

$$\Delta S^\circ_{\text{rxn}} = [cS^\circ(\text{C}) + dS^\circ(\text{D})] - [aS^\circ(\text{A}) + bS^\circ(\text{B})]$$

In general,

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

From the absolute entropy values in Appendix 3, calculate the standard entropy changes for the following reactions at 25°C.

- ▶  $\text{CaCO}_3(s) \rightarrow \text{CaO}(s) + \text{CO}_2(g)$
- ▶  $\text{N}_2(g) + 3\text{H}_2(g) \rightarrow 2\text{NH}_3(g)$
- ▶  $\text{H}_2(g) + \text{Cl}_2(g) \rightarrow 2\text{HCl}(g)$
- ▶  $2\text{CO}_2(g) + \text{O}_2(g) \rightarrow 2\text{CO}_2(g)$
- ▶  $3\text{O}_2(g) \rightarrow 2\text{O}_3(g)$
- ▶  $2\text{NaHCO}_3(s) \rightarrow \text{Na}_2\text{CO}_3(s) + \text{H}_2\text{O}(l) + \text{CO}_2(g)$

