Entropy, Free Energy, and Equilibrium

Source:
Raymond Chang, Chemistry, 7th edition
Mc Graw Hill

Three Law of Thermodynamic

1st	• Energy can be converted to one form to another • But energy cannot be created or destroyed
2nd	• Explains why chemical processes tends to favor one direction.
3rd	• 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:

$CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(l)\ \ \Delta H^0 = -890.4\ kJ$

Acid-base neutralization:

$H^+(aq) + OH^-(aq) \rightarrow H_2O(l)\ \Delta H^0 = -56.2\ kJ$

Solid-to-liquid phase transition:

$H_2O(s) \rightarrow H_2O(l)\ \Delta H^0 = 6.01\ kJ$

- 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*.

Two things to know about the system to predict spontaneity of a process

- The change in enthalpy, nearly equivalent to ΔE 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°) for Some Substance at 25°C

Substance	S° (J/K.mol)
$H_2O(l)$	69.9
$H_2O(g)$	188.7
$Br_2(l)$	152.3
$Br_2(g)$	245.3
$I_2(s)$	116.7
$I_2(g)$	260.6
C(diamond)	2.44
C(graphite)	5.69
He(*g*)	126.1
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, ΔS, 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	ΔS
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 80ºC to 20ºC.	$\Delta S < 0$
Condensing water vapor	$\Delta S < 0$
Forming sucrose crystals from a supersaturated solution	$\Delta S < 0$
Heating hydrogen gas from 60ºC to 80ºC	$\Delta S > 0$
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 equilibriium process:
  $\Delta S_{\text{univ}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}}$

Standard entropy of reaction (ΔS^o_{rxn})

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

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

In general,

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

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

- $CaCO_3(s) \rightarrow CaO(s) + CO_2(g)$
- $N_2(g) + 3H_2(g) \rightarrow 2NH_3(g)$
- $H_2(g) + Cl_2(g) \rightarrow 2HCl(g)$
- $2CO_2(g) + O_2(g) \rightarrow 2CO_2(g)$
- $3O_2(g) \rightarrow 2O_3(g)$
- $2NaHCO_3(s) \rightarrow Na_2CO_3(s) + H_2O(l) + CO_2(g)$