<u>CHAPTER 20.</u> <u>Thermodynamics: Entropy and Free Energy</u> <u>Section 20.1. The Second Law of Thermodynamics</u>

We must now address <u>why</u> reactions occur, and what controls the equilibrium constant K of a reaction. To do this, we must introduce the idea of a spontaneous process.

"spontaneous" means it occurs by itself

"non-spontaneous" means it can occur only if external energy is continuously input.

Consider a falling object, such as a tennis ball or chalk-board eraser.

Now consider chemical reactions:

(i) Reactions with K_c >>>1, therefore ~100% to the right (products)

e.g., sodium metal, Na(s), will <u>spontaneously</u> react with Cl_2 gas to give NaCl, but NaCl will <u>not</u> spontaneously give Na(s) and Cl_2 unless we input energy to drive it backwards. 2 Na (s) + $Cl_2(g) \rightarrow 2$ NaCl (s)

This example is obvious, but what about:

 $Ca(s) + 2 Ag^{+}(aq) \rightarrow or \leftarrow Ca^{2+}(aq) + 2 Ag(s)$

Which is the spontaneous direction, and which is the direction we must force it to go?

(ii) Reactions with $0.1 < K_c < 10$, therefore both reactants and products at equilibrium. The spontaneous direction is towards equilibrium, and the non-spontaneous one is away from equilibrium.



So, why are reactions spontaneous in one direction (or towards equilibrium) and non-spontaneous in the other (or away from equilibrium)??? The answer lies in the 2nd Law of Thermodynamics.

Let's first refresh our memory of the First Law. First Law of Thermodynamics = Conservation of Energy $\Delta E = q + w$ E = internal energy of system (sum of potential and kinetic energies) q = heat w = work

As chemists, our "system" is usually a reaction in a beaker—everything else is "surroundings"

 $\therefore E_{universe} = E_{system} + E_{surroundings}$

The universe consists of everything \therefore its energy is constant ($\Delta E_{univ} = 0$) $\therefore \Delta E_{univ} = \Delta E_{sys} + \Delta E_{surr} = 0$

i.e., ΔE_{sys} and ΔE_{surr} cancel each other out \therefore energy (E) cannot be created or destroyed. This is the **First Law of Thermodynamics**

However, the First Law does <u>not</u> by itself help us to understand and predict the spontaneous direction.



Can we predict spontaneity from the sign of ΔH ?

i.e., are all exothermic rxns ($\Delta H < 0$) spontaneous?

are all endothermic rxns ($\Delta H > 0$) non-spontaneous?

19th century scientists used to think so for a long time, but the answer is NO.

$$\begin{array}{ll} CH_4\left(g\right)+2\ O_2\left(g\right)\rightarrow CO_2\left(g\right)+2\ H_2O\left(g\right) & \Delta H^\circ_{rxn}=-802\ kJ\\ Na\left(s\right)+\frac{1}{2}\ Cl_2\left(g\right)\rightarrow NaCl\left(s\right) & \Delta H^\circ_{rxn}=-411\ kJ \end{array}$$

These are spontaneous as written (left to right), and their $\Delta H < 0$. But, <u>in general</u>, $\Delta H < 0$ does <u>not</u> define spontaneity. There are reactions with $\Delta H > 0$ (endothermic) that are also spontaneous.

(i.e. spontaneous reactions are often also exothermic, but not always!!)

 $\begin{array}{ll} \mbox{melting of ice:} & H_2O\left(s\right) \to H_2O\left(l\right) & \Delta H^{\circ}_{r\times n} = +6.02 \ \mbox{kJ} \\ \mbox{evaporation of } H_2O: & H_2O\left(l\right) \to H_2O\left(g\right) & \Delta H^{\circ}_{r\times n} = +44.0 \ \mbox{kJ} \\ \mbox{dissolution of many salts} & NaCl(s) \to Na^{*}(aq) + Cl^{-}(aq) & \Delta H^{\circ}_{sol} = +3.9 \ \mbox{kJ} \end{array}$

 $\Delta H > 0$ for all of them, yet all occur spontaneously.

 \therefore ** ΔH by itself does not determine spontaneity! **

We must keep looking to find the law that determines spontaneity!



Figure 20.1 A spontaneous endothermic chemical reaction. $Ba(OH)_2 \cdot 8H_2O(s) + 2NH_4NO_3(s) \rightarrow Ba^{2+}(aq) + 2NO_3^{-}(aq) + 2NH_3(aq) + 10H_2O(l)$ $\Delta H^{\circ}_{rxn} = +62.3 \text{ kJ}$



This reaction occurs spontaneously when the solids are mixed. The reaction mixture absorbs heat from the surroundings so quickly that the beaker freezes to a wet block.



Freedom of Particle Motion

All spontaneous endothermic processes result in an *increase* in the *freedom of motion* of the particles in the system.

solid \rightarrow liquid \rightarrow gas

crystalline solid + liquid \rightarrow ions in solution

less freedom of particle motion → more freedom of particle motion
localized energy of motion → dispersed energy of motion

A change in the freedom of motion of particles in a system is a key factor affecting the *direction* of a spontaneous process. Important clue to what leads to spontaneity!



The Concept of ENTROPY

= a measure of the disorder in a system OR ways of arranging the components OR degree of dispersal of the energy of the system.

Consider a new pack of playing cards = order Start shuffling = disorder

Box: layer of blue balls, layer of red, layer of green... = order Shake \Rightarrow disorder

Gas in one container distributes between it and an empty container when connected: order \rightarrow disorder = smaller area of dispersal \rightarrow greater area of dispersal (Figs 20.2 and 20.3)

i.e., the gas molecules have more ways/places to arrange themselves.

For all the above examples, we say <u>the system achieves an increased number of</u> <u>microstates</u> (see textbook)

Order	Disorder
solid	liquid
liquid	gas
molecules	atoms
protein	amino acids
house	pile of bricks

Other examples:



Figure 20.2 Spontaneous expansion of a gas.



When the stopcock is opened, the gas spontaneously expands to fill both flasks.

Increasing the volume increases the number of translational energy levels the particles can occupy. The number of microstates – and the entropy – increases.



Figure 20.4 Expansion of a gas and the increase in number of microstates.



Nature has an inherent tendency towards disorder! Increasing disorder = increasing number of ways of arranging components of a system without changing its energy.

e.g., gas vs solid. A gas is <u>much</u> more disordered than a solid

A measure of disorder in a system is ENTROPY (S). Increasing entropy (S) = increasing disorder

i.e. $S_{disordered system} > S_{ordered system}$ e.g. $S_{gas} \gg S_{solid}$

S is a state function, like enthalpy H or energy E - depends on the state of the system, not how it got there. Units of S are Joules/Kelvin (J/K)

Now we can define the rule for a spontaneous process!! -- it involves the system <u>and</u> its surroundings

> ** For a spontaneous process, $\Delta S_{universe} > 0$ This is the **Second Law of Thermodynamics** **

i.e., spontaneous processes occur in the direction that increases the entropy of the universe. i.e., $\Delta S_{universe} > 0$





Now, $\Delta S_{universe} = \Delta S_{system} + \Delta S_{surroundings}$ $\therefore \Delta S_{sys} + \Delta S_{surr} > 0$ for a spontaneous process.

First, let's look at ΔS_{sys} in more detail. We'll return to ΔS_{surr} laterEntropy S is related to disorder = number of equivalent ways of arranging system =number of microstates. In 1877, Boltzmann defined SS = k InWW = Number of ways system can be arranged.k = k_B = Boltzmann's Constant

Interesting, but rarely can we know or measure W on a molecular level.

Standard Molar Entropies (S°)

20-10

Remember that enthalpy H cannot be determined absolutely, only changes ΔH . However, absolute entropies can be determined because of the

> <u>Third Law of Thermodynamics.</u> "A perfect crystal has zero entropy at absolute zero."

 $S_{sys} = k \ln W = k \ln 1 = 0$ *i.e.*, $S_{sys} = 0$ at 0 K

As with ΔH , we normally quote S at standard conditions for molar amounts, *i.e.*, S^o = standard molar entropy (J/mol.K or J.mol⁻¹K⁻¹)



Standard Molar Entropies

S° is the *standard molar entropy* of a substance, measured for a substance in its *standard state* in units of J/mol·K.

The conventions for defining a standard state include:

- 1 atm for gases
- 1 *M* for solutions, and
- the pure substance in its most stable form for solids and liquids.

