

CHAPTER 18. ENTROPY, FREE ENERGY AND EQUILIBRIUM

Thermodynamics: Study of energy changes accompanying chemical or physical processes.

⇒ Thermodynamics tells us the direction and extent of the reaction, but it does not tell us how fast the reaction occurs.

THE FIRST LAW OF THERMODYNAMICS

Law of Conservation of Energy: The total amount of energy in the universe is constant. Energy can be converted from one form to another, but energy cannot be created or destroyed in ordinary chemical and physical processes.

$$\text{1st Law of Thermodynamics: } \Delta E = q + w$$

E = internal energy; sum of the kinetic and potential energies of the particles in a system.

q = heat absorbed by the system (+) or heat released by the system to the surroundings (-).

w = work done on the system (+) or by the system (-); work is the energy used when a force moves an object through a distance d.

$$q \text{ at constant pressure: } q_p = \Delta H$$

ΔH = Enthalpy: Heat gained or lost by a system at constant pressure.

State Function: Property of a system that depends only on its present state, which is determined by variables such as temperature and pressure. ΔE and ΔH are state functions.

ΔH_f° = Standard Molar Enthalpy of Formation: The heat change for the formation of 1 mole of a compound from its elements in their most stable forms under standard conditions.

⇒ $\Delta H_f^\circ = 0$ for an element in its most stable form at 25 °C (298 K) and 1 atm pressure.

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

18.2 SPONTANEOUS PROCESSES

Types of processes:

- 1) Spontaneous– naturally occurs under a given set of conditions.
- 2) Nonspontaneous - does not occur under a given set of conditions.

⇒ If a process is spontaneous in the forward direction, then the reverse process will be nonspontaneous.

Examples of spontaneous processes:

- Iron rusts when exposed to air and water.
- A waterfall runs downhill, not up.
- Ice melts at $T > 0^\circ\text{C}$.

What makes a process spontaneous?

- Tendency for a system to go to a lower state of energy.
⇒ Many spontaneous processes are exothermic (e.g. combustion reactions have $\Delta H < 0$), but some spontaneous processes are endothermic (e.g. ice melting has $\Delta H > 0$).
- Tendency for a system to become more disordered or random.
⇒ Entropy of a system typically increases, $\Delta S > 0$ (+ ΔS : increase in disorder)

Thus, spontaneity is a balance between enthalpy and entropy.

18.3 ENTROPY

Entropy, S: a measure of the disorder or randomness of a system. Entropy increases as the number of possible microstates increases.

Microstate: microscopic arrangement of atoms or particles.

What is the order of entropy values for solid, liquid and gaseous states?

Solid state is highly ordered \Rightarrow smallest number of microstates \Rightarrow lowest entropy.

Gas molecules move randomly in a disorderly manner \Rightarrow largest number of microstates \Rightarrow highest entropy.

Standard Entropy, S° , the absolute entropy of a substance at 1 atm and 25 °C.

$$\text{Units: } \frac{J}{K \cdot mol}$$

\Rightarrow Entropy of an element in its most stable form is NOT zero.

Trends for Standard Entropy values

- entropy of solid < liquid < gas
- more complex molecules have higher entropies (\uparrow vibrational energy)

E.g. Which do you predict to have the highest standard entropy, S° ?

A. $H_2O(s)$ B. $Na(s)$ C. $Br_2(l)$ D. $H_2O(g)$ E. $C_3H_8(g)$

18.4 THE SECOND LAW OF THERMODYNAMICS

Second Law of Thermodynamics - The entropy of the universe always increases for a spontaneous process.

\Rightarrow For a spontaneous process: $\Delta S_{univ} = \Delta S_{sys} + \Delta S_{surr} > 0$.

\Rightarrow For an equilibrium process: $\Delta S_{univ} = \Delta S_{sys} + \Delta S_{surr} = 0$.

Entropy Changes in the System

Standard Entropy of Reaction:

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

ΔS is usually + ($\Delta S > 0$) when

1. A solid changes to a liquid or gas, or a liquid changes to a gas.
2. The number of gas molecules increases (# product gas molecules than reactant gas molecules).
3. A molecule is broken into 2 or more smaller molecules.

E.g. Predict whether ΔS is + or – for the following reactions

A. $2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$ ΔS is _____

B. $CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$ ΔS is _____

C. $AgBr(s) \rightleftharpoons Ag^+(aq) + Br^-(aq)$ ΔS is _____

Entropy Changes in the Surroundings

Entropy of the surroundings is related to the heat gained or lost by the system:

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

Third Law of Thermodynamics - The entropy of a perfect crystal is zero at 0 K.

- At 0 K there are no translational, vibrational or rotational motions.
- As a substance is heated, entropy increases due to increased molecular motion and increased kinetic energy.
- Entropy of a substance is determined by measuring the specific heat of a substance at different temperatures.

18.5 GIBBS FREE ENERGY

For spontaneous processes: $\Delta S_{\text{univ}} = \Delta S_{\text{sys}} - \frac{\Delta H_{\text{sys}}}{T} > 0$

Multiplying both sides by $-T$ gives us:

$$-T\Delta S_{\text{univ}} = \Delta H_{\text{sys}} - T\Delta S_{\text{sys}} < 0$$

ΔG = Gibbs free energy change

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

ΔG is the maximum amount of energy available to do work on the surroundings.

Relationship between ΔG and spontaneity

1. $\Delta G < 0$, spontaneous process in the forward direction; the process releases energy.
2. $\Delta G > 0$, nonspontaneous process in the forward direction.
3. $\Delta G = 0$, system is at equilibrium; no net change occurs.

Standard Free Energy Changes

ΔG_f° = standard free energy of formation: the free energy change that occurs when 1 mole of a compound is formed from its elements in their standard states.

$\Rightarrow \Delta G_f^\circ = 0$ for an element in its most stable form at 1 atm pressure and 25 °C.

$\Delta G_{\text{rxn}}^\circ$ = standard free energy of reaction: the free energy change that results when reactants in their standard states are converted to products in their standard states.

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

The Gibbs equation provides another way to obtain the standard free energy for a reaction:

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

Affect of Temperature on Spontaneity

ΔH	ΔS	ΔG	Reaction Outcome
-	+	Always negative	Reaction is spontaneous at all temperatures
+	-	Always positive	Reaction is nonspontaneous at all temperatures.
-	-	- at low T + at high T	Reaction is spontaneous at low T, but becomes nonspontaneous at high T.
+	+	+ at low T - at high T	Reaction is nonspontaneous at low T, but becomes spontaneous at high T.

How do we determine the temperature at which a process goes from nonspontaneous to spontaneous (or vice versa)?

Set $\Delta G^\circ = 0$: $0 = \Delta H^\circ - T\Delta S^\circ$

$$T = \Delta H^\circ / \Delta S^\circ$$

⇒ Note that this temperature is an approximation because we are assuming that ΔH° and ΔS° don't change with temperature.

Phase Transitions Between Physical States

At the temperature at which the phase transition occurs, the system is at equilibrium:

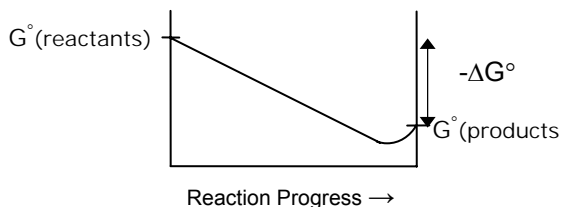
$$\Delta H - T\Delta S = 0 \Rightarrow \Delta S = \frac{\Delta H}{T}$$

18.6 FREE ENERGY AND CHEMICAL EQUILIBRIUM

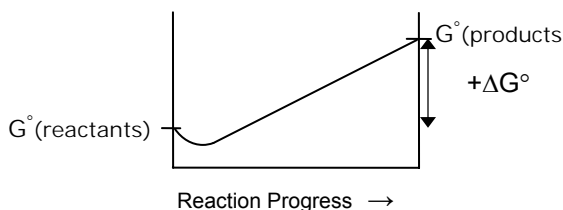
ΔG = actual free energy change; free energy change that results when reactants and products are not in their standard states.

Free Energy, ΔG , Changes During the Course of a Reaction:

1. ΔG° is a large negative number ($\Delta G^\circ < 0$). Spontaneous process; reaction mix is mostly products.



2. ΔG° is a large positive number ($\Delta G^\circ > 0$). Nonspontaneous process; reaction mix is mostly reactants.



⇒ $G = 0$ at the minimum point; this is the equilibrium mixture of reactants and products.

⇒ ΔG (actual amount of free energy) changes as the reaction progresses; but ΔG° (standard free energy) has a fixed value.

Relationship between ΔG and ΔG° :

$$\Delta G = \Delta G^\circ + RT \ln Q$$

At equilibrium, $\Delta G = 0$ and $Q = K$:

$$\Delta G^\circ = -RT \ln K$$

or rearranging

$$K = e^{-\Delta G^\circ / RT}$$

Relationship between ΔG° and K

1. ΔG° is negative: $K > 1$ (product favored)
2. ΔG° is zero: $K = 1$
3. ΔG° is positive: $K < 1$ (reactant favored)