

First Law of Thermodynamics

The first law of thermodynamics states that the energy of the universe is conserved. If one object loses energy, another has to gain that energy.

The mathematical relationship for this is:

$$\Delta E = q + w$$

However, some reactions always occur even though the energy of the reaction is conserved. A reaction that occurs on its own even though energy is conserved is spontaneous.

Example of Spontaneous Rxns

An egg cracking when dropped to the ground is spontaneous. The reverse reaction is not spontaneous.

Iron rusting is spontaneous. The reverse reaction is not spontaneous.

Water freezing is spontaneous at a temperature below 0 °C. Water melting is spontaneous at a temperature above 0 °C.

Reversible and Irreversible

In a reversible process, a change in a system can be restored by exactly reversing the change. Example: melting and freezing ice.

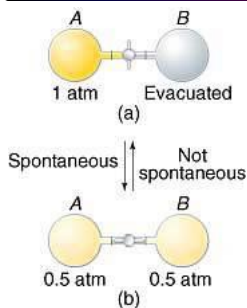
In an irreversible process, the system can still be restored, but through a different process.

Rules for reversibility

Whenever a chemical system is in equilibrium, we can go reversibly between the reactants and products.

In any spontaneous process, the path between reactants and products is irreversible.

Spontaneous Expansion of a Gas



In this spontaneous expansion, the gas will expand without generating any heat ($q = 0$) and without doing any work ($w = 0$). So, since there is no ΔE , there is some other factor causing the expansion.

Entropy

A common thread through all reversible processes is that the process is heading to a state of more disorder.

Entropy is the measure of the amount of disorder, or randomness, in a system.

The change in entropy (ΔS) is calculated by:

$$\Delta S = q_{\text{rev}}/T \text{ (when } T \text{ is constant)}$$

Second Law of Thermodynamics

An increase in entropy of the surroundings of a system must be greater than the decrease in entropy of the system:

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

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

We are going to focus on just an isolated system, so:

$$\text{Reversible: } \Delta S_{\text{sys}} = 0$$

$$\text{Irreversible: } \Delta S_{\text{sys}} > 0$$

Changing Entropy

Since entropy is randomness, a decrease in the randomness of a system means the system has become more ordered.

To increase the order, the system must decrease the number of degrees of freedom. Ways to change the degrees of freedom include:

- 1) Forming or breaking bonds
- 2) Translational motion- movement of whole molecule
- 3) Rotational motion - spinning of molecule
- 4) Vibrational motion - atoms within molecule moving closer and farther apart

Third Law of Thermodynamics

If we decrease the thermal energy of a substance, degrees of freedom decrease as well, lowering the entropy.

If we lower the temperature to the point where there is perfect order in the system, or no entropy or randomness, the substance is at absolute zero.

Standard Molar Entropies

By using lab data of enthalpy, heat capacity and temperature, it is possible to determine the standard entropies of substances (found in Appendix 4)

Trends in standard entropy:

- 1) Standard molar entropies for elements are not zero.
- 2) Standard molar entropies of gases are greater than liquids which are greater than solids
- 3) Standard molar entropies increase with molar mass
- 4) Standard molar entropies increase with the number of atoms in a formula

Standard Molar Entropies

The entropy change of a chemical reaction can be determined using the equation:

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

Where n and m are the coefficients in the chemical reaction.

Gibbs Free Energy

J. Williard Gibbs developed a way to relate the enthalpy (ΔH) and the entropy (ΔS) of a reaction in order to determine the reaction's spontaneity. Free energy (ΔG) will tell whether a reaction is spontaneous or not through the following equation:

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

When $\Delta G < 0$, the forward reaction is spontaneous

When $\Delta G = 0$, the reaction is at equilibrium

When $\Delta G > 0$, the reverse reaction is spontaneous

Standard Free Energy

The standard free energy of a reaction can be determined in the same way as the standard enthalpy and entropy.

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

Predicting ΔG

A certain chemical reaction is exothermic and increases its randomness. Is the reaction

- Always spontaneous
- Never spontaneous
- Spontaneous only at high temperatures
- Spontaneous only at low temperatures

Predicting Free Energy

TABLE 19.4 Effect of Temperature on Reaction Spontaneity

ΔH	ΔS	ΔG	Reaction Characteristics	Example
-	+	Always negative	Reaction is spontaneous at all temperatures; reverse reaction is always nonspontaneous	$2\text{O}_2(g) \rightarrow \text{O}_3(g)$
+	-	Always positive	Reaction is nonspontaneous at all temperatures; reverse reaction is always spontaneous	$3\text{O}_2(g) \rightarrow 2\text{O}_3(g)$
-	-	Negative at low temperatures; positive at high temperatures	Reaction is spontaneous at low temperatures but becomes nonspontaneous at high temperatures	$\text{CaO}(s) + \text{CO}_2(g) \rightarrow \text{CaCO}_3(s)$
+	+	Positive at low temperatures; negative at high temperatures	Reaction is nonspontaneous at low temperatures but becomes spontaneous at high temperatures	$\text{CaCO}_3(s) \rightarrow \text{CaO}(s) + \text{CO}_2(g)$

Non-Standard Free Energy

When conditions are not standard, it is still possible to calculate the free energy provided you know some information about the reaction:

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

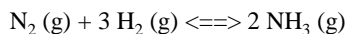
For this reaction to work, R must be

$$8.314 \times 10^{-3} \text{ kJ/mol K}$$

And Q values must involve pressures of gases.

Example

Calculate the ΔG at 250 K for a reaction that consists of 1.0 atm N_2 , 3.0 atm H_2 , and 0.25 atm NH_3 for the reaction:



K from ΔG°

Provided you know the standard free energy ΔG° of a reaction, you can determine the equilibrium constant (K) by using the equation:

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

Again, R needs to be $8.314 \times 10^{-3} \text{ kJ/mol K}$.

State Functions

A state function are properties that define a state and do not depend on how we reach that state. Examples are temperature and enthalpy.

Heat transfer is not a state function because it is dependent on which way the transfer goes.
