

Chapter VI :  
Enthalpy, Helmholtz Energy,  
and Gibbs Energy

## Helmholtz Energy

In thermodynamics, the Helmholtz free energy (or Helmholtz energy) is a thermodynamic potential that measures the useful work obtainable from a closed thermodynamic system at a constant temperature (isothermal). The change in the Helmholtz energy during a process is equal to the maximum amount of work that the system can perform in a thermodynamic process in which temperature is held constant. At constant temperature, the Helmholtz free energy is minimized at equilibrium.

## Reversible process

According to the first law of thermodynamics:

$$dU = \delta Q + \delta W$$

where  $U$  is the internal energy,  $\delta Q$  is the energy added as heat, and  $\delta W$  is the work done on the system. The second law of thermodynamics for a reversible process yields  $\delta Q_{rev} = TdS$

$$V = cte \Rightarrow \delta W = 0, dU = \delta Q, \quad \delta Q = TdS \Rightarrow dU = TdS \Rightarrow dU - TdS = 0$$

$$T = cte \Rightarrow dU - Tds = 0 \Rightarrow d(U - TS) = 0$$

$U$  and  $S$ : state functions

$$\Delta F = \Delta U - T\Delta S$$

**If  $T$  and  $V$  constant  $dF = 0 \Rightarrow F_1 = F_2$**

## Irreversible process

$$\delta Q_{rev} = TdS$$

$$V = cte \Rightarrow \delta W = 0, dU = \delta Q, \quad \delta Q < TdS \Rightarrow dU < TdS \Rightarrow dU - TdS < 0$$

$$T = cte \Rightarrow dU - Tds < 0 \Rightarrow d(U - TS) < 0$$

$$\Delta F = \Delta U - T\Delta S < 0$$

**If  $T$  and  $V$  constant  $dF < 0 \Rightarrow F_1 < F_2$**

## Enthalpy free (Gibbs free energy)

In thermodynamics, the Gibbs free energy (or Gibbs energy as the recommended name; symbol  $G$  is a thermodynamic potential that can be used to calculate the maximum amount of work, other than pressure-volume work, that may be performed by a thermodynamically closed system at constant temperature and pressure. It also provides a necessary condition for processes such as chemical reactions that may occur under these conditions.

## Reversible process

According to the first law of thermodynamics:

$$dU = \delta Q + \delta W$$

$$\delta Q_{rev} = TdS$$

$$dU = \delta Q - PdV \Rightarrow \delta Q = dU + PdV = TdS \Rightarrow dU + PdV - TdS = 0$$

$$d(U + PV - TS) = 0 \Rightarrow U + PV = H \Rightarrow d(H - TS) = 0$$

$S$  and  $H$ : state functions

$$G = H - TS \Rightarrow \Delta G = \Delta H - T\Delta S = 0, \quad \Delta G = \Delta H - T\Delta S$$

**If  $T$  and  $P$  constant  $dG = 0 \Rightarrow G_1 = G_2$**

## Irreversible process

$$\delta Q_{rev} = TdS$$

$$dU = \delta Q - PdV \Rightarrow \delta Q = dU + PdV < TdS \Rightarrow dU + PdV - TdS < 0$$

$$d(U + PV - TS) < 0 \Rightarrow U + PV = H \Rightarrow d(H - TS) < 0$$

$$\Delta G = \Delta H - T\Delta S < 0$$

**If  $T$  and  $P$  constant  $dG < 0 \Rightarrow G_1 < G_2$**

Based on the equation  $\Delta G = \Delta H - T\Delta S$ , we can be predicted if the reaction is spontaneous or not:

	<b>Sign of <math>\Delta H</math></b>	<b>Sign of <math>\Delta S</math></b>	<b>Sign of <math>\Delta G</math></b>	<b>remark</b>
<b>1</b>	Negative (-) Exothermic	Positive (+) Endothermic	Always Negative (-)	Reaction is spontaneous at all temperatures
<b>2</b>	Positive (+) Endothermic	Negative (-) Decrease in entropy	Always Positive (+)	Reaction is non-spontaneous at all temperatures
<b>3</b>	Negative (-) Exothermic	Positive (+) Decrease in entropy	Depends upon temperature: 1) At low temperature $T\Delta S < \Delta H$ 2) At high temperature at $T > T_i$ where, $T_i = \frac{\Delta H}{\Delta S}$	Reaction is spontaneous at low temperature. Reaction is non-spontaneous at high temperature.
<b>4</b>	Positive (+) Endothermic	Negative (-) Decrease in entropy	Depends upon temperature: 1) At low temperature $T\Delta S < \Delta H$ 2) At high temperature $T\Delta S > \Delta H$	Reaction is non-spontaneous at low temperatures Reaction is spontaneous at high temperature

### Variation of enthalpy free

$$dG = VdP - SdT$$

- $T = cte$ :  $dG = VdP$
- $V = cte$ :  $dG = -SdT$

### Variation of energy free

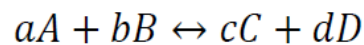
$$dF = -pdV - SdT$$

- $T = cte$ :  $dF = -PdV$
- $V = cte$ :  $dF = -SdT$

- **Application in chemical reaction**

-  $\Delta G_R^0$  for the reaction

We have the following reaction



### $\Delta G_R^0$ of this reaction

The standard Gibbs free energy for any reaction is just the sum of the standard Gibbs free energies of formation of the products minus the sum of the standard Gibbs free energies of formation of the reactants.

$$\Delta G_R^0 = \sum n_p (\Delta G_f^0)_p - \sum n_R (\Delta G_f^0)_R$$

$$\Delta G_f^0(N_2) = \Delta G_f^0(O_2) = \Delta G_f^0(H_2) = \Delta G_f^0(C) = 0$$

### Calculate $\Delta G^0$

$$\Delta G^0 = \Delta H^0 - T\Delta S^0$$

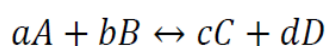
$$\Delta H_R^0 = \sum n_p (\Delta H_f^0)_p - \sum n_R (\Delta H_f^0)_R$$

$$\Delta S_R^0 = \sum n_p (S^0)_p - \sum n_R (S^0)_R$$

### Chemical Equilibrium

In a chemical reaction, chemical equilibrium is the state in which both the reactants and products are present in concentrations which have no further tendency to change with time, so that there is no observable change in the properties of the system. This state results when the forward reaction proceeds at the same rate as the reverse reaction. The reaction rates of the forward and backward reactions are generally not zero, but they are equal. Thus, there are no net changes in the concentrations of the reactants and products. Such a state is known as dynamic equilibrium.

For the following reactions:



$$K_c = \frac{[C]^c [D]^d}{[A]^a [B]^b}$$

### Relation between Thermodynamics and equilibrium chemical

$$\Delta G^0 = -RT \ln K_p$$

Where:  $K_p$ : partial pressure equilibrium

$$K_p = \frac{P_C^c P_D^d}{P_A^a P_B^b}$$

$$\Delta G^0 = -RT \ln K_c$$

### Relation between $k_c$ and $k_p$

$$K_p = K_c \cdot (RT)^{\Delta n}$$

Where :

$$\Delta n = \sum (n)_{\text{products(gaz)}} - \sum (n)_{\text{Reactants(gaz)}}$$

### Van't Hoff Equation

The Van 't Hoff equation relates the change in the equilibrium constant  $K$ , of a chemical reaction to the change in temperature  $T$ , given the standard enthalpy change. The Van 't Hoff equation has been widely utilized to explore the changes in state functions in a thermodynamic system. The Van't Hoff plot, which is derived from this equation, is especially effective in estimating the change in enthalpy and entropy of a chemical reaction.

For the **Van 't Hoff** equation, which is:

$$\frac{d \ln k_p}{dT} = -\frac{1}{R} \frac{\Delta H^0}{T^2}$$

$$\Rightarrow \ln \frac{K_{T_2}}{K_{T_1}} = -\frac{\Delta H^0}{R} \left( \frac{1}{T_2} - \frac{1}{T_1} \right)$$