

CHEMICAL THERMODYNAMICS

Background Information

Thermodynamics deals with the relations between the energies and the properties of the systems at equilibrium. The zeroth law of thermodynamics defines the temperature of a system, the first law, the energy; and the second law the entropy.

The First Law of Thermodynamics:

The energy of the universe which is the sum of the energies of the system and the surroundings is a constant. It can neither be created nor destroyed. But the energy may be transformed from one form into another.

$$\Delta E = Q - W$$

where Q is the heat absorbed by the system and W is the work done by the system. E is a state function but Q and W are path functions.

$$W = P' .dV$$

P' is the external pressure. For a reversible operation P'=P the pressure of the system.

Definition of the Enthalpy:

$$H = E + PV$$

$$Q_p = \Delta H$$

Heat Capacities:

$$\text{At constant volume : } C_v = \frac{dQ_v}{dT} = \left(\frac{\partial E}{\partial T} \right)_v$$

$$\text{At constant pressure : } C_p = \frac{dQ_p}{dT} = \left(\frac{\partial H}{\partial T} \right)_p$$

$$C_p > C_v \quad \text{for an ideal gas : } C_p - C_v = R$$

For an ideal gas :

$$\left(\frac{\partial E}{\partial V}\right)_T = 0 \quad \text{Joule's Law}$$

For a reversible isothermal expansion/compression:

$$W = nRT \ln \frac{V_2}{V_1}$$

Heat of Reaction:

$$\Delta H_r = \sum_{\text{Products}} n_i \Delta H_{f,i} - \sum_{\text{Reactants}} n_i \Delta H_{f,i}$$

$\Delta H_{f,i}$ is the heat of formation of compound i.

Effect of Temperature:

$$\Delta H_{r,T} = \Delta H_{r,T_0} + \int_{T_0}^T \Delta C_p \cdot dT$$

The Second Law of Thermodynamics :

The second law of thermodynamics determines the natural direction of all phenomena.

Definition of Entropy :

$$dS = \frac{dQ_{rev}}{T}$$

For a reversible cycle :

$$\oint dS = \oint \frac{dQ_{rev}}{T} = 0$$

For an irreversible cycle :

$$\oint \frac{dQ_{rev}}{T} < 0 \quad \text{Clausius Inequality}$$

The entropy of an isolated system is increased by any natural change which occurs within it, and the entropy of an isolated system has a maximum value at equilibrium.

The Third Law of Thermodynamics :

The entropy of a pure, crystalline substance is zero at the absolute zero of temperature.

Entropy Change for a Chemical Reaction :

$$\Delta S = \sum_{\text{Products}} S - \sum_{\text{Reactants}} S \quad \text{by using the absolute entropies at } 25^{\circ}\text{C}$$

$$\Delta S_T = \Delta S_{T_0} + \int_{T_0}^T \frac{\Delta C_p}{T} dT$$

Definition of Helmholtz Energy :

$$A = E - TS$$

Definition of Gibbs Free Energy :

$$G = H - TS$$

Gibbs Free Energy Change for a Chem. Rxn.

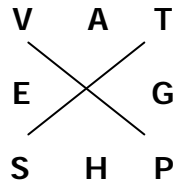
$$\Delta G = \Delta H - T\Delta S$$

In a natural change, the system attempts to achieve the lowest energy and the highest entropy. Entropy is a measure of disorderness of the system.

Gibbs-Helmholtz Equation :

$$\left[\frac{\partial \left(\frac{\Delta G}{T} \right)}{\partial T} \right]_P = -\frac{\Delta H}{T^2}$$

Thermodynamic Cycle:



4 Fundamental Equations of Thermodynamics :

$$dE = TdS - PdV$$

$$dH = TdS + VdP$$

$$dA = -SdT - PdV$$

$$dG = -SdT + VdP$$

Maxwell Relations

$$\left(\frac{\partial T}{\partial V} \right)_S = \left(\frac{\partial P}{\partial S} \right)_V$$

$$\left(\frac{\partial S}{\partial V} \right)_T = \left(\frac{\partial P}{\partial T} \right)_V$$

$$\left(\frac{\partial T}{\partial P} \right)_S = \left(\frac{\partial V}{\partial S} \right)_P$$

$$-\left(\frac{\partial S}{\partial P} \right)_T = \left(\frac{\partial V}{\partial T} \right)_P$$

Conditions for Equilibrium :

$$dG = 0 \quad \text{at constant T and P}$$

$$dA = 0 \quad \text{at constant T and V}$$

Spontaneous changes can continue to occur as long as the Gibbs free energy of the system decreases that is until the Gibbs free energy of the system reaches a minimum value. At equilibrium, the system has a minimum value of Gibbs free energy. So, there are three possibilities;

- $\Delta G < 0$ the transformation can occur spontaneously
- $\Delta G = 0$ the system is at equilibrium
- $\Delta G > 0$ the natural direction is opposite to the direction we thought