

E-Text in Chemistry

Chapter 6

Thermodynamics T.D

Thermodynamics is a branch of chemistry that deals with the heat changes associated with chemical reactions.

Applications of T.D

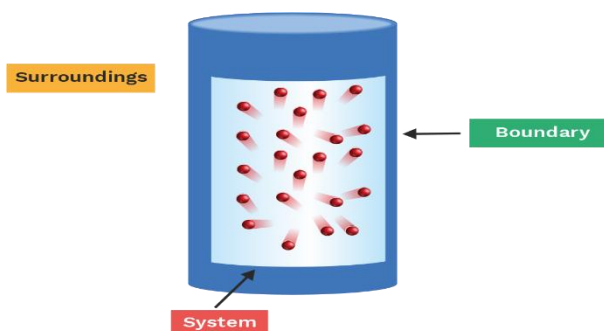
Thermodynamics is extremely useful in understanding and predicting the behavior of chemical reactions occurring in daily life.

Limitations of T.D

1. It doesn't give information about the rate of reaction.
2. Thermodynamics process is not applicable for micro system – electron, proton and neutron.

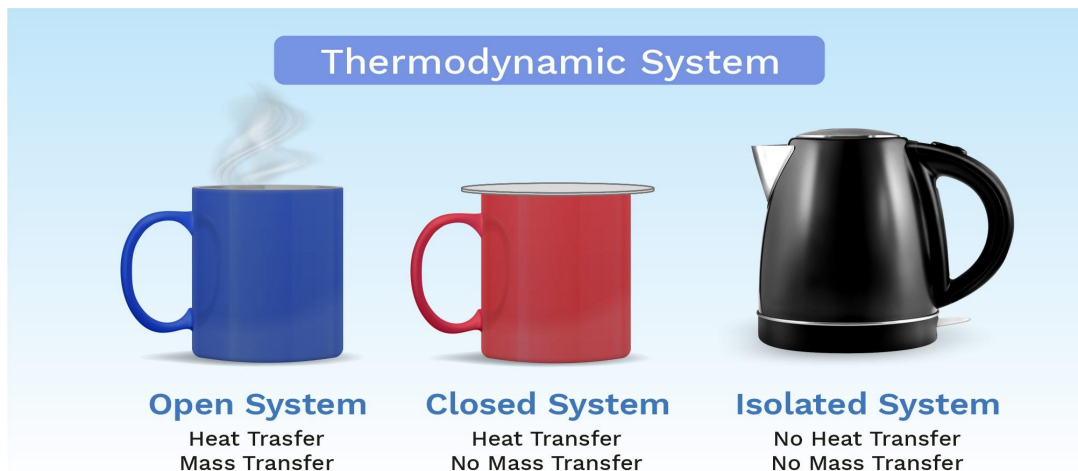
System and Surroundings

System is the part of the universe which is under investigation. The part of the universe other than system is called surroundings.



Types of Thermodynamic systems

1. **Open system:** It is a system that can exchange both energy and matter with the surroundings.
Eg. Hot water taken in an open vessel.
2. **Closed system:** It is a system that can exchange only energy and not matter with the surroundings.
Eg. Hot water taken in a closed vessel.
3. **Isolated system:** It is a system that cannot exchange both energy and matter with the surroundings.
Eg. Hot water taken in a thermoflask.



Extensive and Intensive Properties

1. Extensive properties: These are properties which depend on the amount of matter present in the system. Here system is divided.

Eg: Volume (v), length (l), breadth (b), height (h), internal energy (U), enthalpy (H), entropy (S), Gibb's energy (G), heat capacity.

2. Intensive properties: These are properties which are independent of the amount of matter present in the system. Or, these are the properties which do not change when a system is divided.

Eg: Temperature (T), Pressure (P), Volume (V), density, refractive index, molar heat capacity, viscosity, surface tension.

State and Path functions

A property that depends only on the initial and final state of a system and not on the path followed is called a state function.

Eg. T, P, V, U, H, S, G.

The properties which depend on the path followed is called Path functions.

Eg. heat (q) and work (w)

Thermodynamic process

1. Isothermal process: It is a process that occurs at constant temperature. $\Delta T = 0$ but $\Delta q \neq 0$

2. Isobaric process: It is a process that occurs at constant Pressure. $\Delta P = 0$

3. Isochoric process: It is a process that occurs at constant volume. $\Delta V = 0$

4. Adiabatic process: It is a process that occurs at constant heat energy. Here no heat enters into or leaves from the system. $\Delta q = 0$ but $\Delta T \neq 0$

5. Cyclic process: The system undergoes a series of changes and finally returns to its initial state. $\Delta U = 0$ and $\Delta H = 0$

6. Reversible process: The driving force favours the process while opposing force opposes it. If the driving and opposing forces are differed by an infinitesimally small quantity the process takes place in both directions. Such a process is called reversible process.

7. Irreversible process: If the driving and opposing forces are differed by a large quantity, then the process takes place in only one direction. Such a process is called irreversible process.

Expansion work and Non-Expansion work

1. Expansion work (W_{exp}): It is related to gaseous systems. It is the product of pressure and change in volume. $(W_{\text{exp}}) = -P\Delta V$

For irreversible process, $(W_{\text{exp}}) = -P\Delta V$

For reversible process, $(W_{\text{exp}}) = -2.303nRT \log(V_2/V_1)$

2. Non-expansion work ($W_{\text{non-exp}}$): It is related to electrochemical cells. It is the product of potential difference (E) and charge (Q). $W_{\text{non-exp}} = E \times Q$

Internal Energy U

It is the energy possessed by a body. It is the sum of different types of molecular energies - translational kinetic energy, rotational kinetic energy, vibrational kinetic energy, electronic energy, nuclear energy. The change in internal energy ΔU during a process is measured by using an apparatus called *Bomb Calorimeter*.

First law of thermodynamics

It is same as law of conservation of energy. It states that energy can neither be created nor be destroyed. The total energy in the universe is always a constant. The total energy of an isolated system is always a constant.

$$\text{Mathematically } \Delta U = q + w$$

Where q is the amount of heat absorbed by the system and w is the amount of work done on the system.

If there is only expansion work, the above equation becomes $\Delta U = q - P\Delta V$
since, $W_{\text{exp}} = -P\Delta V$

For a system containing only solids or liquids, $\Delta V = 0$. So $\Delta U = q$

For an isothermal reversible process, $\Delta U = 0$.

$$\text{So, } q = -w = 2.303nRT \log V_2/V_1$$

For an adiabatic process, $q = 0$, so $\Delta U = w$.

Significance of change in Internal energy ΔU

$$\text{We know that } \Delta U = q - P\Delta V$$

For a process taking place at constant volume, $\Delta V = 0$. So $\Delta U = q_v$

That is, ΔU gives the amount of heat absorbed or evolved by a system at constant volume.

Enthalpy (H)

It is the total heat content of a system. It is the sum of internal energy and pressure-volume energy of a system. $H = U + PV$

Relation between ΔH and ΔU

$$H_1 = U_1 + PV_1 \dots \dots \dots (1)$$

$$H_2 = U_2 + PV_2 \dots \dots \dots (2)$$

$$\text{Equation (2) - (1)}$$

$$\Delta H = \Delta U + P\Delta V$$

From ideal gas equation, $PV = nRT$

If n_1 and n_2 are the total no. of moles of reactants and products, then $PV_1 = n_1RT$ and $PV_2 = n_2RT$

$$P(V_2 - V_1) = (n_2 - n_1)RT$$

$$P\Delta V = \Delta nRT$$

$$\Delta H = \Delta U + \Delta nRT$$

Significance of ΔH

We know that $\Delta H = \Delta U + P\Delta V$ at constant pressure

From first law of thermodynamics, $\Delta U = q - P\Delta V$

$$\text{So, } q = \Delta U + P\Delta V$$

$$\Delta H = q_p$$

Enthalpy change in a chemical reaction is equal to the amount of heat evolved or absorbed at constant pressure.

Standard enthalpy of reactions ($\Delta_r H^0$)

The standard enthalpy of reaction is the enthalpy change for a reaction when all the substances are in their standard states at 1 bar pressure and at 298 K temperature.

Standard enthalpy of formation ($\Delta_f H^0$)

It is the standard enthalpy change for the formation of one mole of a compound from its elements in their most stable state. The standard enthalpy of formation of CO_2 is the enthalpy change when 1 mole of CO_2 is formed from C and O_2 at 298K temperature, 1 bar pressure and all the substances are in their stable state.

Enthalpies of phase transition

It is the enthalpy change when one mole of a substance changes from one phase to another phase at a particular temperature.

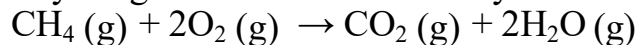
1. **Enthalpy of fusion ($\Delta_{\text{fus}} H^0$):** It is the enthalpy change when one mole of a solid substance changes to liquid state at its melting point. Melting of a solid is endothermic, so all enthalpies of fusion are positive.
2. **Enthalpy of vaporization ($\Delta_{\text{vap}} H^0$):** It is the enthalpy change when one mole of a liquid substance changes to its vapour state at its boiling point.
3. **Enthalpy of sublimation ($\Delta_{\text{sub}} H^0$):** It is the enthalpy change when one mole of a solid substance is directly converted to gaseous state at a particular temperature below its melting point.

Hess's Law of Constant Heat Summation

The law states that the total enthalpy change for a physical or chemical process is the same whether the reaction taking place in a single step or in several steps.

Standard enthalpy of combustion ($\Delta_c H^0$)

It is defined as the enthalpy change when 1 mole of a substance is completely burnt in presence of excess of air or oxygen and all the reactants and products being in their standard states. It is always negative since heat is always evolved during combustion.



Enthalpy of atomization ($\Delta_a H^0$)

It is the enthalpy change on breaking one mole of bonds completely to obtain atoms in the gas phase. In the case of diatomic molecules, the enthalpy of atomization is same as the bond dissociation enthalpy.



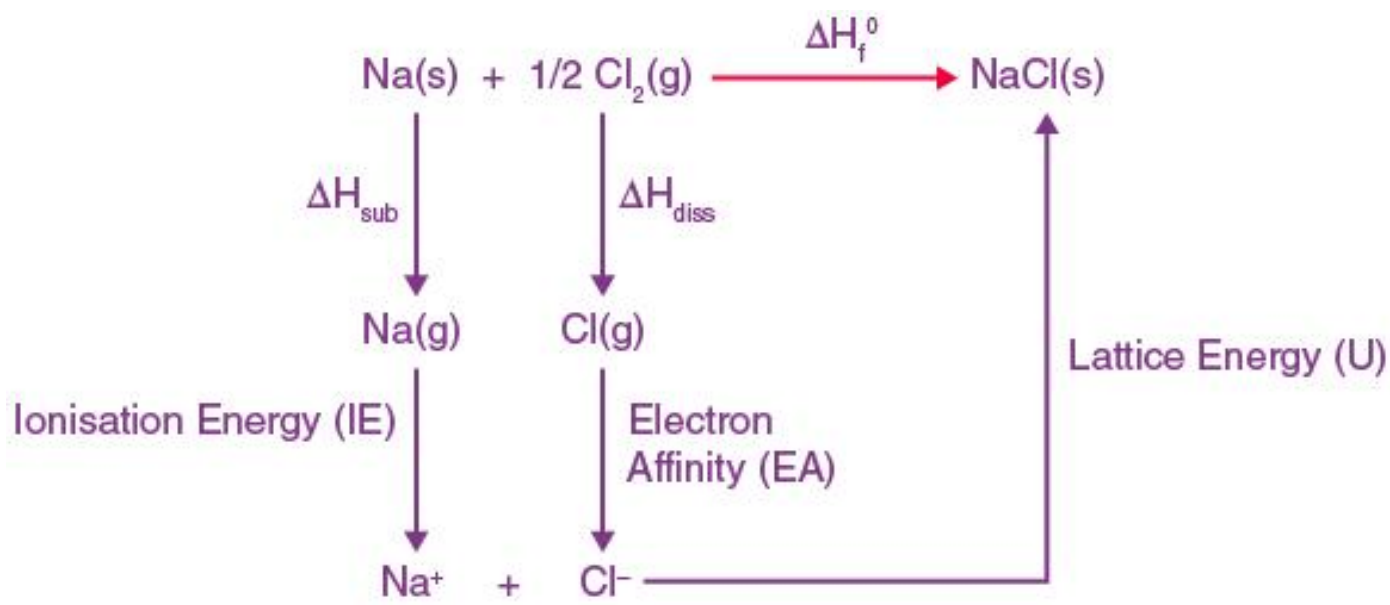
Enthalpy of Solution ($\Delta_{\text{sol}} H^0$)

Enthalpy of solution is the enthalpy change when one mole of a substance is dissolved in a specified amount of solvent. For most of the ionic compounds, $\Delta_{\text{sol}} H^0$ is positive and the dissociation process is endothermic. Therefore, the solubility of most salts in water increases with rise of temperature.

Lattice enthalpy

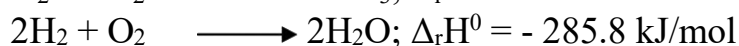
The lattice enthalpy of an ionic compound is the enthalpy change when one mole of an ionic compound dissociates into gaseous ions.

Born-Haber Cycle of NaCl



Spontaneous Process

It is a process that takes place without the help of any external agency. All natural processes are spontaneous. The examples are the flow of water from high level to low level, flow of heat from hot body to cold body, inter mixing of gases, burning of fuels, melting of ice, evaporation of water. A spontaneous process cannot reverse its direction by its own. Spontaneous chemical reactions are also called feasible or probable or irreversible reactions.



A process that takes place with the help of an external agency is called non-spontaneous process. The flow of water from low level to high level.

Criteria for spontaneity

During spontaneous processes like burning of fuels, flow of heat from hot body to cold body, flow of water from high level to low level. The energy of the system decreases. Hence the criteria for spontaneity is *decrease in energy*.

But for some spontaneous processes like melting of ice, evaporation of water, heat is absorbed. The energy of the system increases during the process. The above processes are accompanied with increase in disorder (entropy) of the system. Thus another criterion for spontaneity is *increase in disorderness or randomness of the system*.

Entropy (S)

It is *a measure of degree of disorderness or randomness of a system*. As the disorderness increases, entropy also increases. It is an extensive property and state function.

If a system absorbs 'q' amount of heat reversibly at a temperature T, then the change in entropy, $\Delta S = \frac{q_{\text{rev.}}}{T}$.

Where $q_{\text{rev.}}$ is the amount of heat absorbed reversibly.

Entropy and spontaneity

During a spontaneous process, disorderness of the system increases. Thus, entropy increases and hence ΔS becomes positive.

The total entropy change for the system and surroundings is given by $\Delta S_{\text{Total}} = \Delta S_{\text{syst.}} + \Delta S_{\text{surr.}}$

For a spontaneous process, $\Delta S_{\text{Total}} > 0$

When a system attains *equilibrium*, the entropy becomes maximum and there is no further change in entropy.

$$\Delta S_{\text{Total}} = 0$$

If $\Delta S_{\text{Total}} < 0$, the process is non-spontaneous.

Second Law of Thermodynamics:

It can be stated as the entropy of the universe always increases during every spontaneous process.

Third law of Thermodynamics:

It states that the entropy of any perfectly crystalline substance becomes zero at absolute zero of temperature.

Gibb's energy (G)

It is defined as *the maximum amount of available energy that can be converted to useful work*. $G = H - TS$

It is an extensive property and a state function. If G_1 is the initial Gibb's energy and G_2 is its final value, then the change in Gibb's energy (ΔG) = $G_2 - G_1$

The unit of Gibb's energy is kJ/mol.

Relation between ΔG , ΔH and ΔS (Gibb's Equation)

$$\Delta G = \Delta H - \Delta TS$$

Gibb's energy and Spontaneity

For a spontaneous process, ΔS_{Total} is positive. So ΔG_{sys} is negative. ($\Delta G_{\text{sys}} < 0$)

For a non-spontaneous process, ΔS_{Total} is negative, so ΔG_{sys} is positive. ($\Delta G_{\text{sys}} > 0$)

For a process at equilibrium, $\Delta S_{\text{Total}} = 0$. So $\Delta G_{\text{sys}} = 0$

Conditions for ΔG to be negative

We know that for a spontaneous process, ΔG_{sys} is negative. Also $\Delta G = \Delta H - T\Delta S$.

- 1) If ΔH is negative and ΔS is +ve, ΔG is always -ve and the process is always spontaneous.
- 2) If both ΔH and ΔS are positive, ΔG will be -ve when $T\Delta S > \Delta H$. This is possible at high temperature.
- 3) If both ΔH and ΔS are negative, ΔG will be -ve when $T\Delta S < \Delta H$. This is possible at low temperature. If ΔH is +ve and ΔS -ve, then ΔG will be always +ve and the process will be always non-spontaneous.

Gibb's energy change (ΔG) and Equilibrium constant (K)

The standard Gibb's energy change of a reaction ($\Delta_r G^0$) is related to equilibrium constant (K) by the equation

$$\Delta G = -2.303RT \log K$$
