Chapter – 5

Thermodynamics

2marks:

1. For the process to occur under adiabatic conditions, the correct condition is:

(i) $\Delta T = 0$

(ii) $\Delta p = 0$

(iii) q = 0

(iv) w = 0

Answer:

A system is said to be under adiabatic conditions if there is no exchange Of heat between the system and its surroundings. Hence, under adiabatic conditions, q = 0.

Therefore, alternative (iii) is correct,

2. The enthalpies of all elements in their standard states are:
(i) unity

(ii) zero

(iii) < 0

(iv) different for each element

Answer:

The enthalpy of all elements in their standard state is zero. Therefore, alternative (ii) is correct

3. $\Delta U^{\ominus}$ of combustion of methane is $-X$ kJ mol^{-1}. The value of $\Delta H^{\ominus}$ is

(i)$=\Delta U^{\ominus}$

(ii) $>\Delta U^{\ominus}$

(iii) $<=\Delta U^{\ominus}$

(iv) $= 0$

Answer:

Since$\Delta H^{\theta}=\Delta U^{\theta}+\Delta n_g RT$ and $\Delta U^{\theta}=-X kmol^{-1}$

$\Delta H^{\theta}=(-X)+\Delta n_g RT$
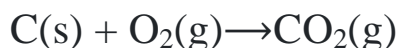
$\Rightarrow \triangle H^{\theta}<\Delta U^{\theta}$

Therefore, alternative (iii) is correct.

4. Enthalpy of combustion of carbon to CO_2 is $-393.5-7.151 kJmol^{-1}$. Calculate the heat released upon formation

of 35.2 g ofCO_2 from carbon and dioxygen gas.

Answer:

Formation of CO_2 from carbon and dioxygen gas can be represented as:

$C(s) + O_2(g) \longrightarrow CO_2(g)$

$\Delta_f H = -393.5 \text{kJmol}^{-1}$

(1 mole =44g) Heat released on formation
of $44g CO_2 = -393.5 \text{kJmol} -1$

∴ Heat released on formation of $35.2g CO_2$

$= -314.8 \text{kJmol}^{-1}$

5. For an isolated system, ΔU = 0, what will be ΔS ?

Answer:
ΔS will be positive i.e., greater than zero
Since ΔU = 0, ΔS will be positive and the reaction will be spontaneous.

6. For the reaction,$2Cl(g) \rightarrow Cl_2(g)$, what are the signs of ΔH and ΔS ?

Answer:

ΔH and ΔS are negative

The given reaction represents the formation of chlorine molecule from chlorine atoms. Here, bond formation is taking place. Therefore, energy Is being released. Hence ΔH is negative.

Also, two moles of atoms have more randomness than one mole of a molecule. Since spontaneity is decreased, ΔS is negative for the given reaction.

7. The equilibrium constant for a reaction is 10. What will be the value of $\Delta G^{\ominus}$? R = 8.314JK^{-1} mol^{-1}

T = 300 K.

Answer:

From the expression, $\Delta G^{\theta} = -2.303$ RT logk $_{eq}$

ΔG^{θ} for the reaction,

$= (2.303) (8.314JK^{-1}mol^{-1}) (300K) \log 10 = -5744.14 Jmol^{-1}$

$= -5.744 kkmol^{-1}$

8. Choose the correct answer. A thermodynamic state function is a quantity

(i) used to determine heat changes

(ii) whose value is independent of path

(iii) used to determine pressure volume work

(iv) whose value depends on temperature only

Answer:

A thermodynamic state function is a quantity Whose value is independent of a path. Functions like p, V, T etc. depend only on the state of a system and not on the path.

Hence, alternative (ii) is correct.

4marks:

1. The enthalpy of combustion of methane, graphite and dihydrogen at 298 K are, – 890.3kJmol^{-1}−393.5kJmol^{-1}, and −285.8kJmol^{-1} respectively. Enthalpy of formation of CH$_4$ will be
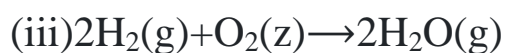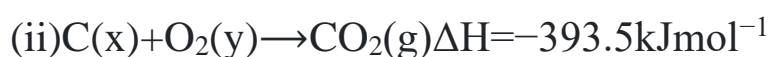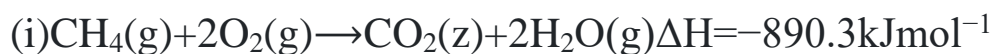
(i)−74.8kJmol^{-1}

(ii)−52.27kJmol^{-1}

(iii)+74.8kJmol^{-1}

(iv)+52.26kJmol^{-1}

Answer:

According to the question,

(i)$CH_4(g)+2O_2(g)\rightarrow CO_2(z)+2H_2O(g)\Delta H=-890.3kJmol^{-1}$

(ii)$C(x)+O_2(y)\rightarrow CO_2(g)\Delta H=-393.5kJmol^{-1}$

(iii)$2H_2(g)+O_2(z)\rightarrow 2H_2O(g)$

$\Delta H=-285.8kJmol^{-1}$

Thus, the desired equation is the one that represents the formation of $CH_4(g)$ i.e..,

$$C_{(s)} + 2H_{2(g)} \longrightarrow CH_{4(g)}$$
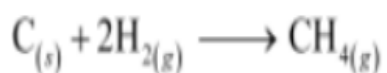
$$\Delta_f H_{CH_4} = \Delta_c H_c + 2\Delta_c H_{H_2} - \Delta_c H_{CO_2}$$

= [-395.5 + 2(-285.8) - (-890.3)] kJ Mol^{-1}

= -74.8 kJ Mol^{-1}

∴ Enthalpy of formation of CH$_4$(g)$=-74.8$kJmol^{-1} Hence, alternative (i) is correct.

2. A reaction, A + B → C + D + q is found to have a positive entropy change. The reaction will be

(i) possible at high temperature

(ii) possible only at low temperature

(iii) not possible at any temperature

(iv) possible at any temperature

Answer:

For a reaction to be spontaneous, ΔG should be negative.

ΔG = ΔH – TΔS

According to the question, for the given reaction,

ΔS = positive

ΔH = negative (since heat is evolved)

⇒ ΔG = negative

Therefore, the reaction is spontaneous at any temperature.

Hence, alternative (iv) is correct.

3. In a process, 701 J of heat is absorbed by a system and 394 J of work is done by the system. What is the change in internal energy for the process?

Answer:

According to the first law of thermodynamics,

$\Delta U = q + W$ (i)

Where,

ΔU = change in internal energy for a process

q = heat

W = work

Given,

$q = + 701$ J (Since heat is absorbed)

$W = –394$ J (Since work is done by the system)

Substituting the values in expression (i), we get

$\Delta U = 701$ J $+ (–394$ J$)$

$\Delta U = 307$ J

Hence, the change in internal energy for the given process is 307 J.

4. Calculate the number of kJ of heat necessary to raise the temperature of 60.0 g of aluminium from 35°C to 55°C. Molar heat capacity of Al is 24 Jmol^{-1}K^{-1}.

Answer:

From the expression of heat (q) $q = m \cdot c \cdot \Delta T$

Where,

c= molar heat capacity
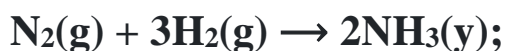
m= mass of substance

ΔT= change in temperature

Substituting the values in the expression of q:

$q=(60/27 \text{mol})(24 \text{Jmol}^{-1}\text{K}^{-1})(20\text{K})$

q=1066.7J

q=1.07k

5. Given

$N_2(g) + 3H_2(g) \rightarrow 2NH_3(y)$;

$\Delta_r H\theta=-92.4\text{kJmol}^{-1}$

What is the standard enthalpy of formation ofNH_3 gas?

Answer:

Standard of formation of a compound is the charge in enthalpy that takes place during the formation of 1 mole Of a substance in its standard form from its constituent elements in their standard state.
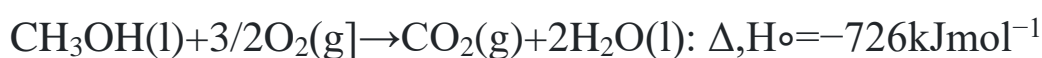
Re-writing the given equation for 1 mole of $NH_{3(g)}$.

$1/2N_2(g)+3/2H_2(g)\rightarrow NH_{3(g)}$

$\therefore$ Standard enthalpy of formation of $NH_{3(g)}$

$=1/2\ \Delta_rH\theta = 1/2(-92.4\ \text{kJmol}^{-1}) = -46.2\text{kJmol}^{-1}$

6. Calculate the standard enthalpy of formation of$CH_3OH(l)$ from the following data:

$CH_3OH(l)+3/2O_2(g]\rightarrow CO_2(g)+2H_2O(l)$: $\Delta,H\circ = -726\text{kJmol}^{-1}$

$C(\text{graphite}) +O_2(g)\rightarrow CO2(g)$: $\Delta eH = -393\text{kJmol}^{-1}$

$H_2(g)+1/2O_2(g)\rightarrow H_2O(1)$; $\Delta,H = -286\text{kJmol}^{-1}$

Answer:

The reaction that takes place during the formation of$CH_3OH(l)$ can be written as:

$C(s) + 2H_2O(g) + 1/2O_2(G), \longrightarrow CH_3OH_{(\eta)}(1)$

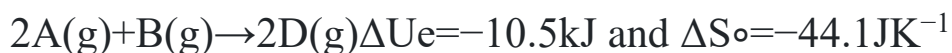The reaction (I) can be obtained from the given reactions by following the algebraic calculations as:

Equation (ii) + 2 × equation (iii) – equation (i)

$\Delta_fH\theta\ [CH_3OH(l)] = \Delta cH^\theta + 2\Delta_fH^\theta\ [H_2O(l)] - \Delta_rH^\theta$

$= (-393\ \text{kJ mol}^{-1}) + 2(-286\ \text{kJ mol}^{-1}) - (-726\ \text{kJ mol}^{-1})$

$= (-393 - 572 + 726)\ \text{kJ mol}^{-1}$

$\Delta_fH^\theta\ [CH_3\ OH(l)] = -239\ \text{kJ mol}^{-1}$

7. For the reaction

$2A(g)+B(g)\rightarrow 2D(g)$ $\Delta U^e=-10.5kJ$ and $\Delta S^\circ=-44.1JK^{-1}$

Calculate $\Delta G^\ominus$ for the reaction, and predict whether the reaction may occur spontaneously

Answer:

For the given reaction,

$2A(g)+B(g)\rightarrow 2D(g)$ $\Delta \eta_g=2-(3)=-1$ mole

Substituting the value of ΔU^θ

in the expression of ΔH:

$\Delta H^\theta=\Delta U^\theta+\Delta n_g RT$

$=(-10.5kJ)-(-1)(8.314\times10^{-3}\,kJK{-1}\,mol^{-1})\,(298K) =$ $-10.5kJ^{-2}.48kJ$ $\Delta H^\ominus=-12.98kJ$

Substituting the values of $\Delta H^\ominus$ and $\Delta S^\ominus$ in the expression of $\Delta G^\ominus$

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

$=-12.98kJ - (298K)(-44.1JK^{-1}) = -12.98kJ + 13.14\ kJ$ $\Delta G^\ominus =+0.16kJ$

Since ΔG^θ for the reaction is positive, the reaction will not occur spontaneously.

8. Calculate the entropy change in surroundings when 1.00 mol ofH₂O(l) is formed under standard conditions. $\Delta H^0 = -286kJ\ mol^{-1}$

Answer:

It is given that 286 kJmol^{-1} of heat is evolved the formation of 1 mol ofH₂O(l).

Thus, an equal amount of heat will be absorbed by the surroundings.

$q_{surr} = +286$ kJmol^{-1}

Entropy change(ΔS_{surr}) for the surroundings = q_{surr} / 7

$= 286kJmol^{-1} / 298k$

$\therefore \Delta S_{surt} = 959.73\ Jmol^{-1}K^{-1}$

7marks:

1. The reaction of cyanamide, $NH_2CN(s)$ with dioxygen was carried out in a bomb calorimeter, and ΔU was found to be $-742.7 kJmol^{-1}$ at 298 K. Calculate enthalpy change for the reaction at 298 K.

$NH_2CN(g) + 3/2O_2(g) \rightarrow N_2(g)+CO_2(g)+H_2O(l)$
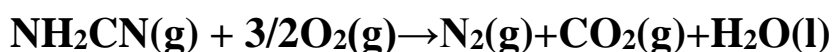
Answer:

Enthalpy change for a reaction (ΔH) is given by the expression,

$\Delta H = \Delta U + \Delta n_g RT$

Where,

ΔU = change in internal energy

Δn_g = change in number of moles

For the given reaction,

$\Delta ng = \sum n_g$ (products) $- \sum n_g$ (reactants)

$= (2 - 1.5)$ moles

$\Delta n_g = 0.5$ moles

And,

$\Delta U = -742.7$ kJ mol^{-1}

$T = 298$ K

$R = 8.314 \times 10^{-3}$ kJ mol^{-1} K^{-1}

Substituting the values in the expression of ΔH:

$\Delta H = (-742.7$ kJ mol$^{-1}) + (0.5$ mol$) (298$ K$) (8.314 \times 10^{-3}$ kJ mol^{-1} K$^{-1})$

$= -742.7 + 1.2$

$\Delta H = -741.5 \text{ kJ mol}^{-1}$

2. Calculate the enthalpy change on freezing of 1.0 mol of water at10.0°C to ice at

−10.0°C.ΔfusH=6.03kJmol−1 at 0°C

$C_p[H_2O(I)]=75.3Jmol_{-1}K-1$

$C_\rho[H_2O(s)]=36.8Jmol^{-1}K^{-1}$

Answer:

Total enthalpy change involved in the transformation is the of the following changes:

(a) Energy change involved in the transformation of 1 mol of water at 10° C to 1 mol of water at 0 C.

(b) Energy change involved in the transformation of 1 mol of water at 0° to 1 mol of ice at 0°C

(c) Energy change involved in the transformation of 1 mol of ice at0°C to 1 mol of ice at−10°C.

$\Delta H = C_p[\ H_2OCl]\Delta T + \Delta H \text{ fivering} + C_\rho[H_2O_{(s)}]\Delta T$

$= (75.3] \text{ mol}^{-1}K^{-1})\ (0-10)\ K + (-6.03 \times 10^3 Jmol^{-1}) + (36.8]$
$\text{mol}^{-1}\ K^{-1}\ )\ (-10 - 0)K$

$=-7533 \text{ mol}^{-1} - 6030 \text{Jmol}^{-1} - 368 \text{Jmol}^{-1}$
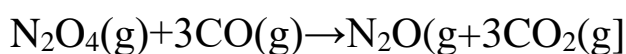
$=-7151 \text{J mol}^{-1}$

$=-7.151 \text{kJmol}^{-1}$

Hence, the enthalpy change involved in the transformation is-7.151kJmol^{-1}.

3. Enthalpies of formation of CO(g), CO$_2$(g), N$_2$O(g) and N$_2$O$_4$(g) are −110,−393,81 and 9.7kJmol^{-1} respectively.

Find the value of ΔH for the reaction:
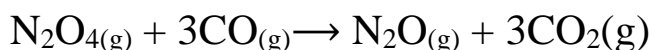
$N_2O_4(g)+3CO(g)\rightarrow N_2O(g+3CO_2(g]$

Answer:

Δ_rH for a reaction is defined as the difference between ΔH value of products and ΔH value of reactants.

$\Delta_r H=\sum\Delta_r H(\text{ products })-\sum\Delta_f H(\text{ reactants })$

For the given reaction,

$N_2O_{4(g)} + 3CO_{(g)} \longrightarrow N_2O_{(g)} + 3CO_2(g)$

$\Delta_r H=[\ \{\Delta f H(N_2O)+3\Delta J H(CO_2)\}-\{\Delta f H\ (N_2O_4) + 3\Delta j H(CO)\}\ ]$

Substituting the values of ΔH for N_2O, CO_2, N_2O_4 , and CO

From the question, we get:

$\Delta_rH = [\ \{\ 81kJmol^{-1} + 3(-393)kJmol^{-1}\} - \{9.7kJmol^{-1} + 3(-110)$ $kJmol^{-1}\}]$

$\Delta_rH = -7777kJmol^{-1}$

Hence, the value of Δ_rH

for the reaction is $-777.7\ kJmol^{-1}$.

4. Calculate the enthalpy change for the process CCl4(g)→C(g)+4Cl(g) and calculated bond enthalpy of C−Cl in CCl4(g)

$\Delta_{vap}pH^{\theta}\ (CC|4) = 30.5kJmol^{-1}\ \Delta_fH^{\theta}(CCl4) = -135.5kJmol-1$

$\Delta_aH^{\theta}(C) = 715.0kJmol^{-1}$, where Δ_aH^{θ} is enthalpy of atomisation

$\Delta_2H^{\theta}(Cl_2) = 242kJmol^{-1}$

Answer:

The chemical equations implying to the given values of enthalpies" are:

(1) $CCl_{4(l)}$ à $CCl_{4(g)}$; $\Delta vapH^{\ominus} = 30.5\ kJmol^{-1}$

(2) $C_{(s)}$ à $C_{(g)}$ $\Delta aH^{\ominus} = 715\ kJmol^{-1}$

(3) $Cl2_{(g)}$ à $2Cl_{(g)}$; $\Delta_aH^{\ominus} = 242\ kJmol^{-1}$

(4) $C_{(g)} + 4Cl_{(g)}$ à $CCl_{4(g)}$; $\Delta fH^{\ominus}$

= -135.5 kJmol^{-1} ΔH for the process $CCl_{4(g)}$ à $C_{(g)}$ + $4Cl_{(g)}$ can be measured as:

$\Delta H = \Delta_a H^{\Theta}(C) + 2\Delta a H^{\Theta}(Cl_2) - \Delta_{vap}H^{\Theta} - \Delta fH$

= $(715kJmol^{-1}) + 2(kJmol^{-1}) - (30.5kJmol^{-1}) - (-135.5kJmol^{-1})$

Therefore, H= 1304kJmol^{-1}

The value of bond enthalpy for C-Cl in $CCl_4(g)$

= 1304/4kJmol^{-1}

= 326 kJmol^{-1}

5. For the reaction at 298 K,

$2A + B \rightarrow C$

$\Delta H = 400kJmol^{-1}$

and $\Delta S = 0.2kJmol^{-1}$

At what temperature will the reaction become spontaneous considering ΔH and ΔS to be constant over the temperature range.

Answer:

From the expression

$\Delta G = \Delta H - T\Delta S$
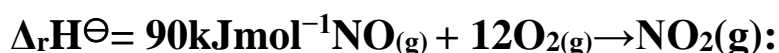
Assuming the reaction at equilibrium,δ

T for the reaction would be:

T=(ΔH−ΔG)1/ΔS=ΔH/ΔS(ΔG=0 at equilibrium)

=400kJmol^{-1} 0.2 kJK^{-1} mol^{-1} T=2000K

For the reaction to be spontaneous, ΔG must be negative. Hence, for the given reaction to be spontaneous, T should be greater than 2000 K.

6. Comment on the thermodynamic stability of NO(g), given

12N$_{2(g)}$+12O$_{2(g)}$→NO$_{(g)}$;

Δ$_r$H$^\ominus$= 90kJmol^{-1}NO$_{(g)}$ + 12O$_{2(g)}$→NO$_2$(g):

Δ$_r$H^e= −74kJmol^{-1}

Answer:

The positive value of Δ$_r$H indicates that heat is absorbed during the formation of NO(g), j. This means that NO(g) has higher than the reactants(N2 and O2) .

Hence, NO$_{(g)}$ is unstable. The negative value o$_f$Δ$_r$H

H indicates that heat is evolved during the formation ofNO$_{2(g)}$ from NO$_{(g)}$ and O$_{2(g)}$

. The product, NO$_{2(g)}$ is stabilized with minimum energy.

Hence, unstable NO$_{(g)}$ changes to unstableNO$_{2(g)}$.

This equation represents the formation of NO(g) from its elements (o2(g))and the positive value of ΔrH (enthalpy change of reaction under standard conditions) indicates that heat is absorbed during this process. The positive value suggests that the reactants have a higher enthalpy than the product, NO(g).

7.Explain the First Law of Thermodynamics and its significance in chemical processes. Provide an example to illustrate the application of this law.

Answer:

The First Law of Thermodynamics, also known as the Law of Conservation of Energy, states that energy cannot be created or destroyed in an isolated system; it can only be converted from one form to another. In the context of chemical processes, the total energy of a system and its surroundings remains constant.

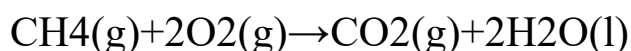Significance of the First Law of Thermodynamics in Chemical Processes:

Energy Conservation: The law emphasizes the conservation of energy, implying that the total energy content of a system and its surroundings remains constant. This principle is crucial in understanding and predicting energy changes during chemical reactions.

Heat and Work Transfer: The law helps in understanding how heat and work are exchanged between a system and its surroundings. It allows the calculation of the energy changes associated with chemical reactions, providing insights into the feasibility and spontaneity of processes.

Internal Energy: The concept of internal energy (U) is introduced, representing the total energy content of a system. Changes in internal energy are related to heat exchange and work done during a process.

Example Illustrating the First Law:

Consider the combustion of methane (4CH4):

$CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(l)$

In this reaction, methane reacts with oxygen to form carbon dioxide and water. The First Law of Thermodynamics can be applied to analyze the energy changes during this process:

$\Delta U = q + w$

Fill in the blanks:

1. In thermodynamics, the _____ law states that energy cannot be created or destroyed, only converted from one form to another.

Answer: First

2. The internal energy of a system is the sum of its _____ and _____ energies.

Answer: kinetic; potential

3. The change in internal energy of a system is equal to the heat added to the system minus the work done by the system, according to the _____ law of thermodynamics.

Answer: first

4. The _____ law of thermodynamics states that the entropy of an isolated system will never decrease over time.

Answer: second

5. Enthalpy is defined as the sum of the internal energy of a system and the product of its pressure and _____.

Answer: volume

6. According to the _____ law of thermodynamics, it is impossible to reach absolute zero in a finite number of steps.

Answer: third

7. The process in which a system exchanges both heat and work with its surroundings is called a _____ process.

Answer: cyclic

8. The equation $\Delta U = Q - W$ represents the _____ law of thermodynamics, where ΔU is the change in internal energy, Q is the heat added to the system, and W is the work done by the system.

Answer: first

9. The Gibbs free energy (G) is defined as the enthalpy minus the product of the temperature and _____.

Answer: entropy

10. According to the _____ law of thermodynamics, the entropy of a perfect crystal approaches zero as the temperature approaches absolute zero.

Answer: third

Multiple choice:

1. Which law of thermodynamics states that energy cannot be created or destroyed, only converted from one form to another?

a. Zeroth law

b. First law

c. Second law

d. Third law

Answer:

b. First law

2. The internal energy of a system is the sum of its:

a. Kinetic and potential energies

b. Pressure and volume

c. Heat and work

d. Entropy and enthalpy

Answer:

a.Kinetic and potential energies

3. Enthalpy is defined as:

a. Heat content of a system

b. Internal energy of a system

c. Work done by a system

d. Entropy of a system

Answer:

a. Heat content of a system

4. According to the second law of thermodynamics, entropy of an isolated system will:

a. Increase

b. Decrease

c. Remain constant

d. Approach zero

Answer:

a.Increase

5. The equation ΔU = Q – W represents which law of thermodynamics?

a. Zeroth law

b. First law

c. Second law

d. Third law

Answer:

b. First law

6. The process in which a system exchanges both heat and work with its surroundings is called a:

a. Isobaric process

b. Adiabatic process

c. Isothermal process

d. Cyclic process

Answer:

d. Cyclic process

7. The Gibbs free energy (G) is defined as:

a. Enthalpy minus temperature

b. Internal energy minus entropy

c. Enthalpy minus entropy multiplied by temperature

d. Entropy minus temperature

Answer:

c. Enthalpy minus entropy multiplied by temperature

8. According to the third law of thermodynamics, the entropy of a perfect crystal approaches zero as:

a. Temperature increases

b. Temperature decreases

c. Pressure increases

d. Pressure decreases

Answer:

b. Temperature decreases

9. The work done by a system in an isothermal process is equal to:

a. Zero

b. Change in internal energy

c. Heat added to the system

d. Change in enthalpy

Answer:

c. Heat added to the system

10. Which thermodynamic state function is a measure of the disorder or randomness of a system?

a. Internal energy

b. Enthalpy

c. Entropy

d. Gibbs free energy

Answer:

c. Entropy

<u>Summary:</u>

Thermodynamics, a foundational branch of physical science, delves into the intricate relationships between heat, energy, and work within diverse systems. The discipline is guided by four fundamental laws. The Zeroth Law establishes the concept of temperature and thermal equilibrium between systems. The First Law, rooted in the principle of energy conservation, asserts that energy can neither be created nor destroyed, only transformed. It introduces the concept of internal energy and its relation to heat and work. The Second Law, a cornerstone of thermodynamics, introduces entropy as a measure of system disorder, emphasizing its natural tendency to increase. Heat spontaneously flows from higher to lower temperatures, and not all energy can be converted into work.

The Third Law posits that entropy approaches zero as temperature approaches absolute zero. Crucial concepts such as enthalpy, Gibbs free energy, and entropy play pivotal roles in understanding the spontaneity and feasibility of processes. Overall, thermodynamics provides essential insights into energy transformations, chemical reactions, and the behaviour of matter, making it indispensable in scientific and engineering applications.