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Contents of Free Sample Book

Class XI

Hints & Solutions (Class 11th)

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Mock Tests

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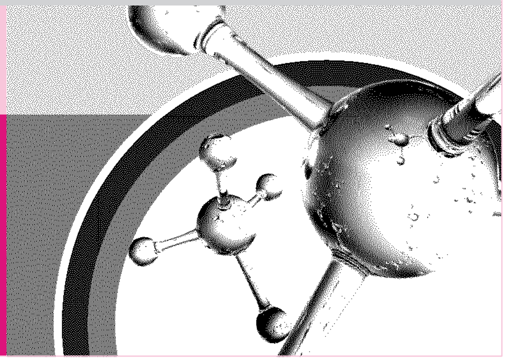
Sample Chapter

CHAPTER- 06

Thermodynamics



Trend Analysis NEET & JEE Main

	NEET	JEE	Remarks
Number of Questions from 2022-16	10	9	Minimum 1 and maximum 2 questions have been asked.
Weightage	3.0%	4.3%	

			NEET		JEE	
Year	**Topic Name**	**Concept Used**	**No. of Ques.**	**Difficulty Level**	**No. of Ques.**	**Difficulty Level**
2022	First law and basic fundamentals of thermodynamics/ Thermo chemistry	Pressure-Volume Curve/ Enthalpy of Formation	1	Easy	1	Average
2021	Entropy and second law of thermodynamics	Second law of thermody-namics	1	Average	1	Average
2020	Applications / Spontaneity, Gibbs energy change and equilibrium constant	First law of thermody-namics/ Second law of thermody-namics	2	Average	1	Average
2019	Applications / Thermodynamics/ Spontaneity, gibbs energy change and equilibrium constant	Reversible isothermal expansion / First law of thermody-namics / Path function / Entropy	2	Average	2	Difficulty/ Easy
2018	Spontaneity, gibbs energy change and equilibrium constant / Applications / Reaction enthalpy	Temperature dependence of equilibrium constant/First law of thermody-namics / ΔH formation	1	Difficulty	2	Average/ Difficulty
2017	Thermodynamics/ Spontaneity, gibbs energy change and equilibrium constant / Application	Internal energy change / Spontaneous reactions/First law of thermody-namics	2	Easy / Average	1	Easy
2016	Reaction enthalpy / Spontaneity, gibbs energy change and equilibrium constant	Heat of formation / Thermody-namic conditions for spontaneous reactions	1	Average	1	Average

NCERT ONE-LINERS
(Important Points to Remember)

6.0 Introduction

- Various forms of energy are interrelated and under certain conditions, these may be transformed from one form into another.
- The laws of thermodynamics deal with energy changes of macroscopic systems involving a large number of molecules rather than microscopic systems containing a few molecules.
- Laws of thermodynamics apply only when a system is in equilibrium or moves from one equilibrium state to another equilibrium state.

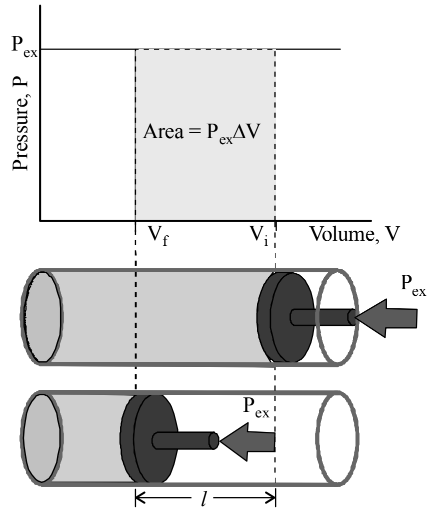
6.1 Thermodynamic Terms

- A **system** in thermodynamics refers to that part of universe in which observations are made and remaining universe constitutes the **surroundings**.
- System and the surroundings together constitute the **universe**.
- The wall that separates the system from the surroundings is called **boundary**.
- **Types of the System :**
  - **Open System :** In an open system, there is exchange of energy and matter between system and surroundings.
  - **Closed System :** In a closed system, there is no exchange of matter, but exchange of energy is possible between system and the surroundings.
  - **Isolated System :** In an isolated system, there is no exchange of energy or matter between the system and the surroundings.

- **The State of the System :**
  - The system must be described. By specifying quantitatively each of the properties such as its pressure (p), volume (V), and temperature (T) as well as the composition of the system.
  - The state of a thermodynamic system is described by its measurable or macroscopic (bulk) properties.
  - The state of a gas can be described by quoting its pressure (p), volume (V), temperature (T), amount (n) etc. Variables like p, V, T are called **state variables** or **state functions** because their values depend only on the state of the system and not on how it is reached. NEET 2008; JEE M 2019
- **The Internal Energy as a State Function :** The total energy of the system may be chemical, electrical, mechanical or any other type of energy. The sum of all these is the energy of the system is called internal energy in thermodynamics (U) of the system.
- **Work :**
  - Adiabatic process is a process in which there is no transfer of heat between the system and surroundings.
  - Internal energy, U, of the system is a state function.
  - By conventions of IUPAC in chemical thermodynamics, **w_{ad} is positive when work is done on the system** and the internal energy of system increases.
  - If **the work is done by the system, w_{ad} will be negative** because internal energy of the system decreases.
- **Heat :**
  - Exchange of energy, which is a result of temperature difference is called heat, q.
  - By conventions of IUPAC in chemical thermodynamics. The q is positive, when heat is transferred from the surroundings to the system and the internal energy of the system increases.
  - q is negative when heat is transferred from system to the surroundings resulting in decrease of the internal energy of the system.
  - A change of state is brought about both by doing work and by transfer of heat. We can write change in internal energy. NEET 2017; JEE M 2019 & 2018
    $\Delta U = q + w$
  - ΔU will depend only on initial and final state. It will be independent of the path.
  - If there is no transfer of energy as heat or as work (isolated system) i.e., if $w = 0$ and $q = 0$, then $\Delta U = 0$.
    In a thermally insulated container a gas expands by 2.0 L under 2.5 atm, P.
    $\therefore\ w = -2 \times 2.5 = -5$ atm – L
    $\therefore\ \Delta U = -5$ atm – L as $\Delta q = 0$
  - $\Delta U = q + w$ is mathematical statement of the **first law of thermodynamics**, which states that the energy of an isolated system is constant.

6.2 Applications

- **Work :** Let us consider a cylinder which contains one mole of an ideal gas fitted with a frictionless piston. Total volume of the gas is V_i and pressure of the gas inside is p. If external pressure is p_{ex} which is greater than p, piston is moved inward till the pressure inside becomes equal to p_{ex}. Let this change be achieved in a single step and the final volume be V_f.



  - If w is the work done on the system by movement of the piston then NEET 2019; JEE M 2019 & 2016
    $w = p_{ex}(-\Delta V) = -p_{ex}\,\Delta V = -p_{ex}(V_f - V_i)$
    e.g., a gas expands from 1 L to 25 L at 300 K against a constant pressure of 1 bar, the work done
    $= 1 \times (25 - 1) = 24 \times 100 = 2400$ J
  - It indicates that in case of compression work is done on the system.
  - If the pressure is not constant at every stage of compression, but changes in number of finite steps, work done on the gas will be summed over all the steps and will be equal to $-\sum p\Delta V$ NEET 2022

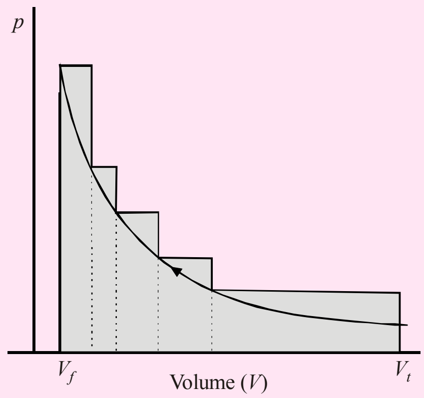


Fig.: *pV-plot when pressure is not constant and changes in finite steps during compression from initial volume, V_i to final volume, V_f. Work done on the gas is represented by the shaded area.*

❖ **Reversible Process :** A process or change is said to be reversible, if a change is brought out in such a way that the process could, at any moment, be reversed by an infinitesimal change. NEET 2022,

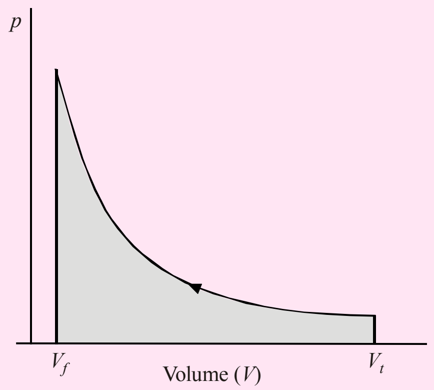


Fig.: *pV-plot when pressure is not constant and changes in infinite steps (reversible conditions) during compression from initial volume, V_i to final volume, V_f. Work done on the gas is represented by the shaded area.*

❖ **Irreversible Processes :** Processes other than reversible processes which are fast and can not be reversed, are known as irreversible processes.

❖ **Work Done Under Reversible Condition :** If the pressure changes during the process such that it is always infinitesimally greater than the pressure of the gas, then, at each stage of compression, the volume decreases by an infinitesimal amount, dV. In such a case. JEE M 2022

$$w = -\int_{V_i}^{V_f} p_{ex}\, dV$$

$$w_{rev} = -\int_{V_i}^{V_f} p_{ex}\, dV = -\int_{V_i}^{V_f} (p_{in} \pm dp)\, dV$$

$$w_{rev} = -\int_{V_i}^{V_f} p_{in}\, dV \quad (dp \times dV \text{ is very small})$$

For n mol of an ideal gas i.e., $pV = nRT \Rightarrow p = \frac{nRT}{V}$

Therefore, at constant temperature **(isothermal process)**

$$w_{rev} = -\int_{V_i}^{V_f} nRT\frac{dV}{V} = -nRT\ln\frac{V_f}{V_i} = -2.303\, nRT\log\frac{V_f}{V_i}$$

❖ **Free expansion:** Expansion of a gas in vacuum ($p_{ex} = 0$) is called free expansion. No work is done during free expansion of an ideal gas whether the process is reversible or irreversible. NEET 2020; AIPMT 2010

❖ **Isothermal and Free Expansion of an Ideal Gas :** For isothermal (T = constant) expansion of an ideal gas into vacuum ; w = 0 since $p_{ex} = 0$. JEE M 2022 & 2020
e.g., 5 moles of an ideal gas at 1 bar and 298 K is expanded into vacuum to triple the volume. The work done, w = 0 as $p_{ext} = 0$.

❖ For isothermal irreversible change
$q = -w = p_{ex}(V_f - V_i)$

❖ For isothermal reversible change

$$q = -w = nRT\ln\frac{V_f}{V_i} = 2.303\, nRT\log\frac{V_f}{V_i}$$

❖ For adiabatic change, $q = 0$,
$\Delta U = w_{ad}$ NEET 2017; AIPMT 2011; JEE M 2017

♦ **Enthalpy, H (A Useful New State Function) :**

❖ The heat absorbed at constant volume is equal to change in the internal energy i.e., $\Delta U = q_V$.

❖ $\Delta H = \Delta U + p\Delta V$ JEE M 2022 & 2019

❖ When heat is absorbed by the system at constant pressure, we are actually measuring changes in the enthalpy.

❖ $\Delta H = q_p$, heat absorbed by the system at constant pressure.

❖ ΔH is negative for exothermic reactions which evolve heat during the reaction and ΔH is positive for endothermic reactions which absorb heat from the surroundings.

❖ $\Delta H = \Delta U + \Delta n_g RT$ JEE M 2022 & 2017
e.g., $H_2(g) + Br_2(g) \rightarrow 2HBr(g)$
$\Delta n_g = 2 - 2 = 0$
$\therefore\ \Delta H = \Delta U$

♦ **Extensive and Intensive Properties :**

❖ An **extensive property** is a property whose value depends on the quantity or size of matter present in the system. For example, mass, volume, internal energy, enthalpy, heat capacity, etc. are extensive properties.

❖ Those properties which do not depend on the quantity or size of matter present are known as **intensive properties**. For example temperature, density, pressure etc. are intensive properties. A molar property, χ_m, is the value of an extensive property χ of the system for 1 mol of the substance.

♦ **Heat Capacity :**

❖ Heat appears as a rise in temperature of the system in case of heat absorbed by the system.

❖ The increase of temperature is proportional to the heat transferred

$$q = \text{coeff.} \times \Delta T$$

- The magnitude of the coefficient depends on the size, composition and nature of the system. We can also write it as $q = C\,\Delta T$

  The coefficient, C is called the heat capacity.
- The molar heat capacity of a substance, $C_m = \left(\frac{C}{n}\right)$, is the heat capacity for one mole of the substance and is the quantity of heat needed to raise the temperature of one mole by one degree celsius (or one kelvin).
- Specific heat, also called specific heat capacity is the quantity of heat required to raise the temperature of one unit mass of a substance by one degree celsius (or one kelvin).

  $q = C \times m \times \Delta T = C\Delta T$
- **The Relationship between C_p and C_V for an Ideal Gas :** At constant volume, the heat capacity, C is denoted by C_V and at constant pressure, this is denoted by C_p.

  $C_p - C_V = R$ NEET 2021

6.3 Measurement of ΔU and ΔH : Calorimetry

- We can measure energy changes associated with chemical or physical processes by an experimental technique called calorimetry.
- In calorimetry, the process is carried out in a vessel called calorimeter.
- **ΔU Measurements :** For chemical reactions, heat absorbed at constant volume, is measured in a bomb calorimeter. JEE M 2021
- **ΔH Measurements :** Measurement of heat change at constant pressure (generally under atmospheric pressure) can be done in a calorimeter
  - $\Delta H = C_p$ (at constant p) and, therefore, heat absorbed or evolved, q_p at constant pressure is also called the heat of reaction or enthalpy of reaction, $\Delta_r H$.

6.4 Enthalpy Change, $\Delta_r H$ of a Reaction – Reaction Enthalpy

- The enthalpy change accompanying a reaction is called the **reaction enthalpy**. The enthalpy change of a chemical reaction, is given by the symbol $\Delta_r H$.
- $\Delta_r H$ = (sum of enthalpies of products) – (sum of enthalpies of reactants)

  $$= \sum_i a_i H_{\text{products}} - \sum_i b_i H_{\text{reactants}}$$

  e.g., $H_2(g) + Br_2(g) \rightarrow 2HBr(g)$

  Bond energies : H – H, Br – Br, H – Br are 433, 192, 364 kJ mol^{-1} respectively, the ΔH° for the reaction $= (2 \times 364) - (433 + 192) = 103$ kJ mol^{-1}

  where a and b represent the coefficients of the product and and reactants in the balanced equation. NEET 2020, 2018

- **Standard Enthalpy of Reactions : The standard enthalpy of reaction** is the enthalpy change for a reaction when all the participating substances are in their standard states.
  - The standard state of a substance at a specified temperature is its pure form at 1 bar.
- **Enthalpy Changes during Phase Transformations :**
  - The enthalpy change that accompanies melting of one mole of a solid substance in standard state is called standard enthalpy of fusion or molar enthalpy of fusion, $\Delta_{fus}H°$.

    $H_2O(s) \longrightarrow H_2O(l);\ \Delta_{fus}H° = 6.00\ \text{kJ mol}^{-1}$
  - Amount of heat required to vaporize one mole of a liquid at constant temperature and under standard pressure (1bar) is called its **standard enthalpy of vaporization** or molar enthalpy of vaporization, $\Delta_{vap}H°$.

    $H_2O(l) \longrightarrow H_2O(g);\ \Delta_{vap}H° = +\,40.79\ \text{kJ mol}^{-1}$

    AIPMT 2012 & 2011; JEE M 2022 & 2021
  - **Standard enthalpy of sublimation,** $\Delta_{sub}H°$ is the change in enthalpy when one mole of a solid substance sublimes at a constant temperature and under standard pressure (1bar).
  - Sublimation is direct conversion of a solid into its vapour. Solid CO_2 or 'dry ice' sublimes at 195K with $\Delta_{sub}H° = 25.2$ kJ mol^{-1}; naphthalene sublimes slowly and for this $\Delta_{sub}H° = 73.0$ kJ mol^{-1}.
  - **Standard Enthalpy of Formation :** The standard enthalpy change for the formation of one mole of a compound from its elements in their most stable states of aggregation (also known as reference states) is called Standard Molar Enthalpy of Formation. Its symbol is $\Delta_f H°$. NEET 2013
  - **Thermochemical Equations :** A balanced chemical equation together with the value of its $\Delta_r H$ is called a thermochemical equation.
  - **Hess's Law of Constant Heat Summation :** If a reaction takes place in several steps then its standard reaction enthalpy is the sum of the standard enthalpies of the intermediate reactions into which the overall reaction may be divided at the same temperature.

    $$\text{Reactant} \xrightarrow{\Delta_r H_1} A \xrightarrow{\Delta_r H_2} B \xrightarrow{\Delta_r H_3} \text{Product}$$

    $$\text{Reactant} \xrightarrow{\Delta_r H} \text{Product}$$

    $\Delta_r H = \Delta_r H_1 + \Delta_r H_2 + \Delta_r H_3$

6.5 Enthalpies for Different Types of Reactions

- **Standard Enthalpy of Combustion ($\Delta_c H°$) :** It is defined as the enthalpy change per mole (or per unit amount) of a substance, when it undergoes combustion and all the **reactants and products** being in their standard states at the specified temperature. AIPMT 2015; JEE M 2018

  $$C_4H_{10}(g) + \frac{13}{2}O_2(g) \longrightarrow 4CO_2(g) + 5H_2O(l);$$

  $$\Delta_c H° = -2658.0\ \text{kJ mol}^{-1}$$

- **Enthalpy of Atomization (symbol: $\Delta_a H°$) :** It is the enthalpy change on breaking one mole of bonds completely to obtain atoms in the gas phase.
  $H_2(g) \rightarrow 2H(g); \Delta_a H° = 435.0$ kJ mol^{-1}
- **Bond Enthalpy (symbol: $\Delta_{bond} H°$) :** It is the amount of energy which is required to break one mole bond or energy is released when one mole of bond is formed.
  The standard enthalpy of reaction, $\Delta_r H°$ is related to bond enthalpies of the reactants and products in gas phase reactions as:
  $\Delta_r H° = \sum$bond enthalpies$_R$ – $\sum$bond enthalpies$_P$
  NEET 2020 Ph II, 2018
- **Lattice Enthalpy :** The lattice enthalpy of an ionic compound is the enthalpy change which occurs when one mole of an ionic compound dissociates into its ions in gaseous state.
  $Na^+Cl^-(s) \rightarrow Na^+(g) + Cl^-(g); \Delta_{lattice} H° = +788$ kJ mol^{-1}
  Since it is impossible to determine lattice enthalpies directly by experiment, we use an indirect method where we construct an enthalpy diagram called a **Born-Haber Cycle**.

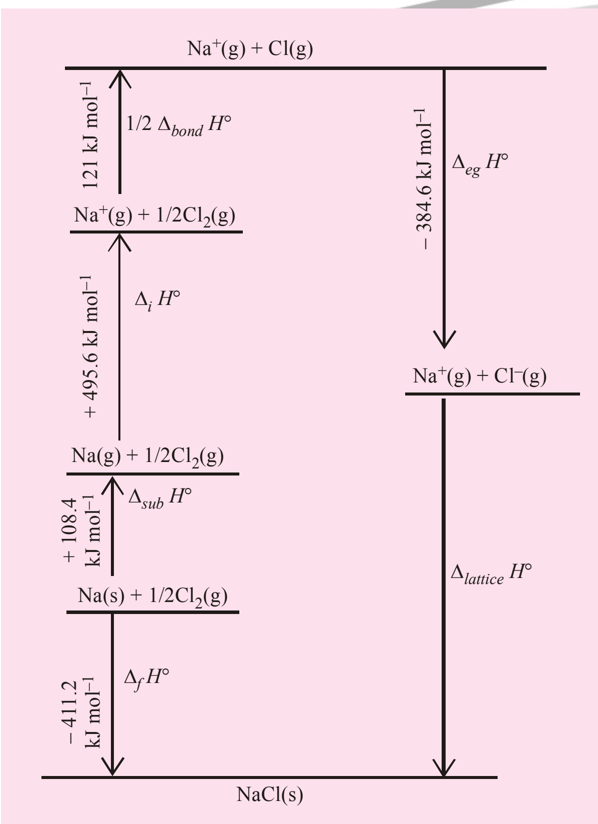


Fig. : *Enthalpy diagram for lattice enthalpy of NaCl*

- **Enthalpy of Solution (symbol : $\Delta_{sol} H°$) :** Enthalpy of solution of a substance is the enthalpy change when one mole of it dissolves in a specified amount of solvent.
  $$\Delta_{sol} H° = \Delta_{lattice} H° + \Delta_{hyd} H°$$
  For most of the ionic compounds, $\Delta_{sol} H°$ is positive and the dissociation process is endothermic. Therefore the solubility of most salts in water increases with rise of temperature.
- **Enthalpy of Dilution :** It is the heat withdrawn from the surroundings when additional solvent is added to the solution. The enthalpy of dilution of a solution is dependent on the original concentration of the solution and the amount of solvent added.

6.6 Spontaneity

- Spontaneity means '*having the potential to proceed without the assistance of external agency*'.
- A spontaneous process is an irreversible process and may only be reversed by some external agency.
- **Entropy and Spontaneity :**
  - Entropy as a measure of the degree of randomness or disorder in the system. The greater the disorder in an isolated system, the higher is the entropy.
  - ΔS is related with q and T for a reversible reaction as :
    $$\Delta S = \frac{q_{rev}}{T}$$
  - The total entropy change (ΔS_{total}) for the system and surroundings of a spontaneous process is given by $\Delta S_{total} = \Delta S_{system} + \Delta S_{surr} > 0$
  - When a system is in equilibrium, the entropy is maximum, and the change in entropy, $\Delta S = 0$.
  - Since entropy is a state property, we can calculate the change in entropy of a reversible process by
    $$\Delta S_{sys} = \frac{q_{sys,\,rev}}{T}$$
- **Gibbs Energy and Spontaneity :**
  - Gibbs function, $G = H - TS$
    Gibbs function, G is an extensive property and a state function.
    The change in Gibbs energy for the system,
    $$\Delta G = \Delta H - T\Delta S$$
    NEET 2021, 2020, 2019; JEE M 2022, 2021 & 2020
  - ΔG is the net energy available to do useful work and is thus a measure of the 'free energy'.
  - ΔG gives a criteria for spontaneity at constant pressure and temperature. NEET 2016
  - If ΔG is negative (< 0), the process is spontaneous.
  - If ΔG is positive (> 0), the process is non spontaneous.
  - **Entropy and Second Law of Thermodynamics :** For an isolated system the change in energy remains constant. Therefore, increase in entropy in such systems is the natural direction of a spontaneous change. This is known as the second law of thermodynamics.

- **Absolute Entropy and Third Law of Thermodynamics :** The entropy of any pure crystalline substance approaches zero as the temperature approaches absolute zero. This is called third law of thermodynamics.

6.7 Gibb's Energy Change and Equilibrium

- $\Delta_r G°$ is related to the equilibrium constant of the reaction as follows:

or $\Delta_r G° = -RT \ln K$

$\Delta_r G° = -2.303\, RT \log K$

Table : Effect of Temperature on Spontaneity of Reactions

$\Delta_r H°$	$\Delta_r S°$	$\Delta_r G°$	Description
–	+	–	Reaction spontaneous at all temperatures
–	–	–	(at low T) Reaction spontaneous at low temperature
–	–	+	(at high T) Reaction nonspontaneous at high temperature
+	+	+	(at low T) Reaction nonspontaneous at low temperature
+	+	–	(at high T) Reaction spontaneous at high temperature
+	–	+	(at all T) Reaction nonspontaneous at all temperatures

NEET 2016

Tips/Tricks/Techniques ONE-Liners
(Exam Special)

- (i) $C_p - C_v = R = 2\text{ cal} = 8.314\text{ J}$

(ii) $\frac{C_p}{C_v} = \frac{3}{2}R$

(iii) For monoatomic gases, $\frac{C_p}{C_v} = \frac{3}{5} = 1.66$

(iv) For diatomic gases, $\frac{C_p}{C_v} = 1.40$

(v) For Triatomic gases $\frac{C_p}{C_v} = 1.33$

- **Entropy Change for an Ideal Gas :**

(i) $\Delta S = C_V \ln\frac{T_2}{T_1} + R\ln\frac{V_2}{V_1}$

(when T and V are two variables)

(ii) $\Delta S = C_P \ln\frac{T_2}{T_1} + R\ln\frac{P_1}{P_2}$ (when T and P are two variables)

- **Work Done (Adiabatic Reversible Expansion)**

$W = \frac{nR(T_2 - T_1)}{\gamma - 1}$ where γ is Poisson's ratio which is equal to $\frac{C_p}{C_v}$ and $C_p - C_v = R$

If we put the value of γ we get the expression for workdone

$W = nC_v(T_2 - T_1)$

- For isothermal process ($\Delta T = 0$),

$\Delta S = R\ln\frac{V_2}{V_1} = R\ln\frac{P_1}{P_2}$

- For isobaric process ($\Delta P = 0$), $\Delta S = C_P \ln\frac{T_2}{T_1}$

- Efficiency of heat engine,

$\eta = \frac{W}{q_2} = \frac{T_2 - T_1}{T_2} = \frac{q_2 - q_1}{q_2}$

where q_2 = heat absorbed by the system at temperature T_2 of the source q_1 = heat rejected by the system at temperature T_1 of the sink

W = net work done.

Exercise 1 : NCERT Based Topic-wise MCQs

6.0 Introduction

1. Which of the following statements is not true regarding the laws of thermodynamics ? NCERT Page-160
(a) It deals with energy changes of macroscopic systems.
(b) It deals with energy changes of microscopic systems.
(c) It does not depends on the rate at which these energy transformations are carried out.
(d) It depends on initial and final states of a system undergoing the change.

6.1 Thermodynamic Terms

2. Which of the following is closed system? NCERT Page-161
(a) Jet engine
(b) Tea placed in a steel kettle
(c) Pressure cooker
(d) Rocket engine during propulsion

3. The state of a thermodynamic system is described by its measurable or macroscopic (bulk) properties. These are
(a) Pressure and volume
(b) Pressure, volume, temperature and amount
(c) Volume, temperature and amount
(d) Pressure and temperature

4. Enthalpy change (ΔH) of a system depends upon its
(a) Initial state NCERT Page-167
(b) Final state
(c) Both on initial and final state
(d) None of these

5. Which of the following factors affect the internal energy of the system ? NCERT Page-162
(a) Heat passes into or out of the system.
(b) Work is done on or by the system.
(c) Matter enters or leaves the system.
(d) All of the above

6. Adiabatic expansions of an ideal gas is accompanied by
(a) decrease in ΔE
(b) increase in temperature
(c) decrease in ΔS
(d) no change in any one of the above properties

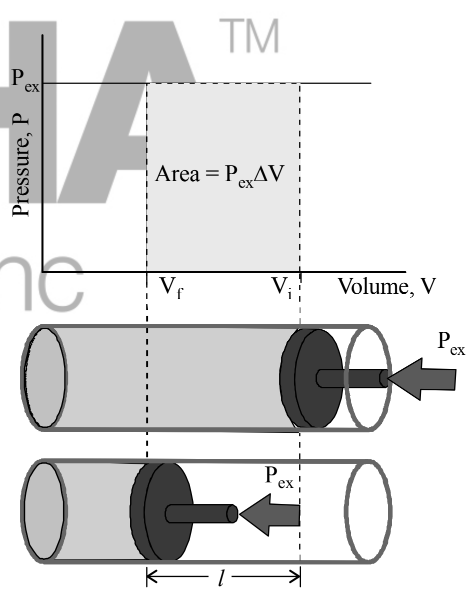
7. Among the following, the state function(s) is (are)
(i) Internal energy NCERT Page-162
(ii) Irreversible expansion work
(iii) Reversible expansion work
(iv) Molar enthalpy
(a) (ii) and (iii) (b) (i), (ii) and (iii)
(c) (i) and (iv) (d) (i) only

8. According to the first law of thermodynamics which of the following quantities represents change in a state function? NCERT Page-164
(a) q_{rev} (b) $q_{rev} - W_{rev}$
(c) q_{rev}/W_{rev} (d) $q_{rev} + W_{rev}$

9. According to the first law of thermodynamics, $\Delta U = q + W$. In special cases the statement can be expressed in different ways. Which of the following is not a correct expression ?
(a) At constant temperature $q = -W$ NCERT Page-164
(b) When no work is done $\Delta U = q$
(c) In gaseous system $\Delta U = q + P\Delta V$
(d) When work is done by the system : $\Delta U = q + W$

6.2 Applications

10. Figure below is showing that one mole of an ideal gas is fitted with a frictionless piston. Total volume of the gas is V_i and pressure of the gas inside is p. If external pressure is P_{ex} which is greater than p, is applied, piston is moved inward till the pressure inside becomes equal to P_{ex}. NCERT Page-164



What does the shaded area represents in the figure ?
(a) Work done (b) Pressure change
(c) Volume change (d) Temperature change

11. When 1 mol of a gas is heated at constant volume, temperature is raised from 298 to 308 K. If heat supplied to the gas is 500 J, then which statement is correct ?
(a) $q = w = 500$ J, $\Delta U = 0$ (b) $q = \Delta U = 500$ J, $w = 0$
(c) $q = -w = 500$ J, $\Delta U = 0$ (d) $\Delta U = 0$, $q = w = -500$ J

12. Which of the following statements/relationships is **not** correct in thermodynamic changes ? NCERT Page-166
(a) $\Delta U = 0$ (isothermal reversible expansion of a gas)
(b) $w = -nRT\ln\frac{V_2}{V_1}$ (isothermal reversible expansion of an ideal gas)
(c) $w = nRT\ln\frac{V_2}{V_1}$ (isothermal reversible expansion of an ideal gas)
(d) For a system of constant volume, heat involved directly changes to internal energy.

13. An ideal gas expands in volume from 1×10^{-3} to 1×10^{-2} m^3 at 300 K against a constant pressure of 1×10^5 Nm^{-2}. The work done is NCERT Page-165
(a) 270 kJ (b) –900 kJ
(c) – 900 J (d) 900 kJ

14. The difference between ΔH and ΔU is usually significant for systems consisting of NCERT Page-167
(a) only solids
(b) only liquids
(c) both solids and liquids
(d) only gases

15. Assume each reaction is carried out in an open container. For which reaction will $\Delta H = \Delta E$? NCERT Page-167
(a) $C(s) + 2H_2O(g) \rightarrow 2H_2(g) + CO_2(g)$
(b) $PCl_5(g) \rightarrow PCl_3(g) + Cl_2(g)$
(c) $2CO(g) + O_2(g) \rightarrow 2CO_2(g)$
(d) $H_2(g) + Br_2(g) \rightarrow 2HBr(g)$

16. For the reaction $CO(g) + \frac{1}{2}O_2(g) \rightarrow CO_2(g)$
Which one of the statement is correct at constant T and P? NCERT Page-167
(a) $\Delta H = \Delta E$
(b) $\Delta H < \Delta E$
(c) $\Delta H > \Delta E$
(d) ΔH is independent of physical state of the reactants

17. For the reaction
$C_3H_8(g) + 5O_2(g) \rightarrow 3CO_2(g) + 4H_2O(l)$
at constant temperature, $\Delta H - \Delta E$ is
(a) $-RT$ (b) $+RT$
(c) $-3RT$ (d) $+3RT$

18. Which is an extensive property of the system ? NCERT Page-168
(a) Volume
(b) Viscosity
(c) Temperature
(d) Refractive index

19. If ΔH is the change in enthalpy and ΔE, the change in internal energy accompanying a gaseous reaction, then
(a) ΔH is always greater than ΔE
(b) $\Delta H < \Delta E$ only if the number of moles of the products is greater than the number of moles of the reactants
(c) ΔH is always less than ΔE
(d) $\Delta H < \Delta E$ only if the number of moles of products is less than the number of moles of the reactants

20. Calorie is equivalent to :
(a) 0.4184 Joule (b) 4.184 Joule
(c) 41.84 Joule (d) 418.4 Joule

21. Equal volumes of two monoatomic gases, A and B, at same temperature and pressure are mixed. The ratio of specific heats (C_p/C_v) of the mixture will be :
(a) 0.83 (b) 1.50
(c) 3.3 (d) 1.67

22. If a reaction involves only solids and liquids which of the following is true ?
(a) $\Delta H < \Delta E$ (b) $\Delta H = \Delta E$
(c) $\Delta H > \Delta E$ (d) $\Delta H = \Delta E + RT\Delta n$

23. During isothermal expansion of an ideal gas, its
(a) internal energy increases NCERT Page-166
(b) enthalpy decreases
(c) enthalpy remains unaffected
(d) enthalpy reduces to zero.

24. Consider the reaction : $N_2 + 3H_2 \rightarrow 2NH_3$ carried out at constant temperature and pressure. If ΔH and ΔU are the enthalpy and internal energy changes for the reaction, which of the following expressions is true ?
(a) $\Delta H > \Delta U$ (b) $\Delta H < \Delta U$
(c) $\Delta H = \Delta U$ (d) $\Delta H = 0$

25. Among the following, the intensive properties are NCERT Page-168
(i) molar conductivity (ii) electromotive force
(iii) resistance (iv) heat capacity
(a) (i) and (ii) (b) (i), (ii) and (iii)
(c) (i) and (iv) (d) (i) only

26. Which of the following factors do not affect heat capacity? NCERT Page-168
(a) Size of system
(b) Composition of system
(c) Nature of system
(d) Temperature of the system

27. Which of the following relation is not correct?
(a) $\Delta H = \Delta U - P\Delta V$ (b) $\Delta U = q + W$
(c) $\Delta S_{sys} = \Delta S_{surr} \geq 0$ (d) $\Delta G = \Delta H - T\Delta S$

28. The internal energy change when a system goes from state A to B is 40 kJ/mol. If the system goes from A to B by a reversible path and returns to state A by an irreversible path, what would be the net change in internal energy ?
(a) > 40 kJ (b) < 40 kJ
(c) Zero (d) 40 kJ

29. Under isothermal condition for one mole of ideal gas what is the ratio of work done under reversible to irreversible process, initially held at 20 atm undergoes expansion from 1L to 2L, at 298K, under external pressure of 10 atm?
(a) 1.7 (b) 2.0
(c) 1.4 (d) 1.0

30. Five moles of an ideal gas at 1 bar and 298 K is expanded into vacuum to double the volume. The work done is : NCERT Page-166
(a) $C_V(T_2 - T_1)$ (b) $-RT(V_2 - V_1)$
(c) $-RT \ln V_2/V_1$ (d) zero

31. How many molecules of ATP, undergo hydrolysis to raise the temperature of 180 kg of water which was originally at room temperature by 1°C ? $C\{P,m\}$ water = 75.32 J/mol/K, $\Delta H\{P\}$ for ATP hydrolysis= 7 kcal/mol NCERT Page-168
(a) 1.5×10^{25} (b) 2.00×10^{23}
(c) 3.4×10^{25} (d) 4.0×10^{24}

32. What is the amount of heat (in Joules) absorbed by 18 g of water initially at room temperature heated to 100°C ? If 10 g of Cu is added to this water , than decrease in temperature (in Kelvin) of water was found to be? $C(p,m)$ for water 75.32 J/mol K ; $C(p,m)$ for Cu = 24.47 J/mol K.
(a) 5649, 369 (b) 5544, 324
(c) 5278, 342 (d) 3425, 425

33. The molar heat capacity of water at constant pressure is 75 JK^{-1} mol^{-1}. When 1kJ of heat is supplied to 100 g of water, which is free to expand, the increase in temperature of water is NCERT Page-168
(a) 6.6 K (b) 1.2 K
(c) 2.4 K (d) 4.8 K

6.3 Measurement of ΔU and ΔH : Calorimetry

34. In the bomb calorimeter, the energy changes are measured at constant volume, under these conditions mark the correct options. NCERT Page-169
(a) work done w = 0
(b) work done w < 0
(c) work done w > 0
(d) either (b) or (c)

35. 2 g of carbon is burnt in a bomb calorimeter in excess of oxygen at 298 K and 1 atmospheric pressure. During the reaction, temperature rises from 298 K to 300 K. If the heat capacity of the bomb calorimeter is 20.7 kJ/K, what is the enthalpy change for the above reaction at 298 K and 1 atm ? $C(graphite) + O_2(g) \rightarrow CO_2(g)$
(a) –20.7 kJ/mol (b) -2.48×10^2 kJ/mol
(c) –41.4 kJ/mol (d) -4.96×10^2 kJ/mol

6.4 Enthalpy Change $\Delta_r H$ of Reaction – Reaction Enthalpy

36. Which of the following is not true regarding thermo-chemical equations?
(a) The coefficients in a balanced thermo-chemical equation refer to the number of moles of reactants and products involved in the reaction
(b) The coefficients in a balanced thermo-chemical equation refer to the number of molecules of reactants and products involved in the reaction
(c) The numerical value of $\Delta_r H$ refers to the number of moles of substances specified by an equation.
(d) Standard enthalpy change $\Delta_r H^{\ominus}$ will have units as kJ mol^{-1}.

37. If enthalpies of formation of $C_2H_4(g)$, $CO_2(g)$ and $H_2O(l)$ at 25°C and 1atm pressure are 52, – 394 and – 286 kJ/mol respectively, the change in enthalpy for combustion of C_2H_4 is equal to NCERT Page-176
(a) – 141.2 kJ/mol (b) – 1412 kJ/mol
(c) + 14.2 kJ/mol (d) + 1412 kJ/mol

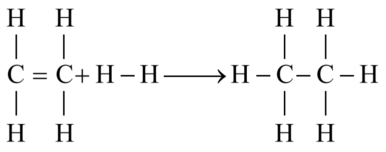
38. The following two reactions are known :
$Fe_2O_3(s) + 3CO(g) \longrightarrow 2Fe(s) + 3CO_2(g);\ \Delta H = -26.8$ kJ
$FeO(s) + CO(g) \longrightarrow Fe(s) + CO_2(g);\ \Delta H = -16.5$ kJ
The value of ΔH for the following reaction
$Fe_2O_3(s) + CO(g) \longrightarrow 2FeO(s) + CO_2(g)$ is;
(a) + 6.2 kJ (b) + 10.3 kJ
(c) – 43.3 kJ (d) – 10.3 kJ

39. Hess's law is used to calculate : NCERT Page-175
(a) enthalpy of reaction.
(b) entropy of reaction
(c) work done in reaction
(d) All of the above

40. Given that bond energies of H – H and Cl – Cl are 430 kJ mol^{-1} and 240 kJ mol^{-1} respectively and ΔH_f for HCl is – 90 kJ mol^{-1}, bond enthalpy of HCl is NCERT Page-177
(a) 380 kJ mol^{-1}
(b) 425 kJ mol^{-1}
(c) 245 kJ mol^{-1}
(d) 290 kJ mol^{-1}

41. From the following bond energies: NCERT Page-178
H – H bond energy: 431.37 kJ mol^{-1}
C = C bond energy: 606.10 kJ mol^{-1}
C – C bond energy: 336.49 kJ mol^{-1}
C – H bond energy: 410.50 kJ mol^{-1}

Enthalpy for the reaction,



will be:

(a) $-243.6\ kJ\ mol^{-1}$ (b) $-120.0\ kJ\ mol^{-1}$
(c) $553.0\ kJ\ mol^{-1}$ (d) $1523.6\ kJ\ mol^{-1}$

42. At 25°C and 1 atm pressure, the enthalpy of combustion of benzene (l) and acetylene (g) are $-3268\ kJ\ mol^{-1}$ and $-1300\ kJ\ mol^{-1}$, respectively. The change in enthalpy for the reaction $3\ C_2H_2(g) \rightarrow C_6H_6(l)$, is **NCERT Page-178**

(a) $+324\ kJ\ mol^{-1}$ (b) $+632\ kJ\ mol^{-1}$
(c) $-632\ kJ\ mol^{-1}$ (d) $-732\ kJ\ mol^{-1}$

6.5 Enthalpies for Different Types of Reactions

43. What is the internal energy (kJ) change occurs when 36 g of $H_2O(l)$ at 100°C converted to $H_2O(g)$?
$\Delta H°$ (vapourisation) = 40.79kJ/mol **NCERT Page-172**

(a) 75.38 (b) 80.98
(c) 70.98 (d) 45.89

44. Consider the reaction :

$4NO_2(g) + O_2(g) \rightarrow 2N_2O_5(g)$,
$\Delta_r H = -111 kJ$.

If $N_2O_5(s)$ is formed instead of $N_2O_5(g)$ in the above reaction, the $\Delta_r H$ value will be :
(given, ΔH of sublimation for N_2O_5 is $-54\ kJ\ mol^{-1}$)

(a) +54 kJ (b) +219 kJ
(c) −219 J (d) −165 kJ

45. Standard enthalpy of vapourisation $\Delta_{vap}H°$ for water at 100°C is $40.66\ kJ\ mol^{-1}$. The change in internal energy of vaporisation of water at 100°C (in $kJ\ mol^{-1}$) is : **NCERT Page-172**

(a) +37.56 (b) −43.76
(c) +43.76 (d) +40.66

(Assume water vapour to behave like an ideal gas).

46. Consider the following reactions: **NCERT Page-173**

(i) $H^+(aq) + OH^-(aq) = H_2O(l)$,
$\Delta H = -X_1\ kJ\ mol^{-1}$

(ii) $H_2(g) + \frac{1}{2}O_2(g) = H_2O(l)$,
$\Delta H = -X_2\ kJ\ mol^{-1}$

(iii) $CO_2(g) + H_2(g) = CO(g) + H_2O(l)$
$\Delta H = -X_3\ kJ\ mol^{-1}$

(iv) $C_2H_2(g) + \frac{5}{2}O_2(g) = 2CO_2(g) + H_2O(l)$'
$\Delta H = +4X_4\ kJ\ mol^{-1}$

Enthalpy of formation of H_2O (l) is

(a) $+X_3\ kJ\ mol^{-1}$ (b) $-X_4\ kJ\ mol^{-1}$
(c) $+X_1\ kJ\ mol^{-1}$ (d) $-X_2\ kJ\ mol^{-1}$

47. Which of the following statements is true for the given reaction? **NCERT Page-177**

$Na(s) \rightarrow Na(g); \Delta H^{\ominus} = 108.4\ kJ\ mol^{-1}$

(a) The enthalpy of atomization is same as the enthalpy of vaporisation
(b) The enthalpy of atomization is same as the enthalpy of sublimation.
(c) The enthalpy of atomization is same as the bond enthalpy
(d) The enthalpy of atomization is same as the enthalpy of solution

48. Diborane is a potential rocket fuel which undergoes combustion according to the equation **NCERT Page-176**

$B_2H_6(g) + 3O_2(s) \longrightarrow B_2O_3(s) + 3H_2O(g)$

Calculate the enthalpy change for the combustion of diborane. Given

(i) $2B(s) + \frac{3}{2}O_2(g) \longrightarrow B_2O_3(s); \Delta H = -1273$ kJ per mol

(ii) $H_2(g) + \frac{1}{2}O_2(g) \longrightarrow H_2O(l); \Delta H = -286$ kJ per mol

(iii) $H_2O(l) \longrightarrow H_2O(g); \Delta H = 44$ kJ per mol

(iv) $2B(s) + 3H_2(g) \longrightarrow B_2H_6(g); \Delta H = 36$ kJ per mol

(a) +2035 kJ per mol (b) −2035 kJ per mol
(c) +2167 kJ per mol (d) −2167 kJ per mol

6.6 Spontaneity

49. In which of the following, entropy decreases? **NCERT Page-182 & 183**

(a) Crystallization of sucrose solution
(b) Rusting of iron
(c) Melting of ice
(d) Vaporization of camphor

50. Choose the reaction with negative ΔS value.

(a) $2NaHCO_3(s) \rightarrow Na_2CO_3(s) + CO_2(g) + H_2O(g)$
(b) $Cl_2(g) \rightarrow 2Cl(g)$
(c) $2SO_2(g) + O_2(g) \rightarrow 2SO_3(g)$
(d) $2KClO_3(s) \rightarrow 2KCl(s) + 3O_2(g)$

51. For the gas phase reaction,

$PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$

which of the following conditions are correct ?

(a) $\Delta H = 0$ and $\Delta S < 0$

(b) $\Delta H > 0$ and $\Delta S > 0$

(c) $\Delta H < 0$ and $\Delta S < 0$

(d) $\Delta H > 0$ and $\Delta S < 0$

52. Unit of entropy is

(a) $JK^{-1}\ mol^{-1}$ (b) $J\ mol^{-1}$

(c) $J^{-1}\ K^{-1}\ mol^{-1}$ (d) $JK\ mol^{-1}$

53. Considering entropy (S) as a thermodynamic parameter, the criterion for the spontaneity of any process is

(a) $\Delta S_{system} + \Delta S_{surroundings} > 0$ NCERT Page-183

(b) $\Delta S_{system} - \Delta S_{surroundings} > 0$

(c) $\Delta S_{system} > 0$ *only*

(d) $\Delta S_{surroundings} > 0$ only

54. A reaction is spontaneous at low temperature but non-spontaneous at high temperature. Which of the following is true for the reaction?

(a) $\Delta H > 0, \Delta S > 0$ (b) $\Delta H < 0, \Delta S > 0$

(c) $\Delta H > 0, \Delta S = 0$ (d) $\Delta H < 0, \Delta S < 0$

6.7 Gibb's Energy Change and Equilibrium

55. At the sublimation temperature, for the process

$CO_2(s) \rightleftharpoons CO_2(g)$ NCERT Page-186

(a) ΔH, ΔS and ΔG are all positive

(b) $\Delta H > 0, \Delta S > 0$ and $\Delta G < 0$

(c) $\Delta H < 0, \Delta S > 0$ and $\Delta G < 0$

(d) $\Delta H > 0, \Delta S > 0$ and $\Delta G = 0$

56. What is the equilibrium constant if ATP hydrolysis by water produces standard free energy of –50 kJ/mol under normal body conditions ?

(a) 2.66×10^8 (b) 5.81×10^8

(c) 1.18×10^7 (d) 1.98×10^8

57. A reaction with $\Delta H = 0$, is found to be spontaneous. This is due to

(a) ΔS is negative (b) ΔS is positive

(c) $T\Delta S$ is positive (d) Both (b) and (c)

58. For the reaction $2NO_2(g) \rightleftharpoons N_2O_4(g)$, when $\Delta S = -176.0\ JK^{-1}$ and $\Delta H = -57.8\ kJ\ mol^{-1}$, the magnitude of ΔG at 298 K for the reaction is_____ $kJ\ mol^{-1}$. (Nearest integer)

NCERT Page-184

(a) 2 (b) –5

(c) 8 (d) 10

59. A reaction occurs spontaneously if

(a) $T\Delta S < \Delta H$ and both ΔH and ΔS are + ve

(b) $T\Delta S > \Delta H$ and ΔH is + ve and ΔS is – ve

(c) $T\Delta S > \Delta H$ and both ΔH and ΔS are + ve

(d) $T\Delta S = \Delta H$ and both ΔH and ΔS are + ve

60. Identify the correct statement for change of Gibbs energy for a system (ΔG_{system}) at constant temperature and pressure

NCERT Page-186

(a) If $\Delta G_{system} = 0$, the system has attained equilibrium

(b) If $\Delta G_{system} = 0$, the system is still moving in a particular direction

(c) If $\Delta G_{system} < 0$, the process is not spontaneous

(d) If $\Delta G_{system} > 0$, the process is not spontaneous

61. In an irreversible process taking place at constant T and P and in which only pressure-volume work is being done, the change in Gibbs free energy (dG) and change in entropy (dS), satisfy the criteria

(a) $(dS)_{V,E} > 0, (dG)_{T,P} < 0$

(b) $(dS)_{V,E} = 0, (dG)_{T,P} = 0$

(c) $(dS)_{V,E} = 0, (dG)_{T,P} > 0$

(d) $(dS)_{V,E} < 0, (dG)_{T,P} < 0$

62. A process has $\Delta H = 200\ J\ mol^{-1}$ and $\Delta S = 40\ JK^{-1}mol^{-1}$. Out of the values given below, choose the minimum temperature above which the process will be spontaneous:

(a) 20 K (b) 12 K

(c) 5 K (d) 4 K

63. In conversion of lime-stone to lime,

$CaCO_3(s) \rightarrow CaO(s) + CO_2(g)$ the values of $\Delta H°$ and $\Delta S°$ are $+179.1\ kJ\ mol^{-1}$ and 160.2 J/K respectively at 298 K and 1 bar. Assuming that $\Delta H°$ and $\Delta S°$ do not change with temperature, temperature above which conversion of limestone to lime will be spontaneous is

(a) 1118 K (b) 1008 K

(c) 1200 K (d) 845 K.

Exercise 2 : NCERT Exemplar & Past Years NEET & JEE Main

NCERT Exemplar Questions

1. Thermodynamics is not concerned about NCERT Page-160
(a) energy changes involved in a chemical reaction
(b) the extent to which a chemical reaction proceeds
(c) the rate at which a reaction proceeds
(d) the feasibility of a chemical reaction

2. Which of the following statement is correct? NCERT Page-161
(a) The presence of reacting species in a covered beaker is an example of open system.
(b) There is an exchange of energy as well as matter between the system and the surroundings in a closed system.
(c) The presence of reactants in a closed vessel made up of copper is an example of a closed system.
(d) The presence of reactants in a thermos flask or any other closed insulated vessel is an example of a closed system.

3. The state of a gas can be described by quoting the relationship between
(a) pressure, volume, temperature
(b) temperature, amount, pressure
(c) amount, volume, temperature
(d) pressure, volume, temperature, amount

4. The volume of gas is reduced to half from its original volume. The specific heat will be
(a) reduce to half (b) be doubled
(c) remain constant (d) increase four times

5. During complete combustion of one mole of butane, 2658 kJ of heat is released. The thermochemical reaction for above change is NCERT Page-176
(a) $2C_4H_{10}(g) + 13O_2(g) \rightarrow 8CO_2(g) + 10H_2O(l);$ $\Delta_c H = -2658.0 \text{ kJ mol}^{-1}$
(b) $C_4H_{10}(g) + \frac{13}{2}O_2(g) \rightarrow 4CO_2(g) + 5H_2O(l);$ $\Delta_c H = -1329.0 \text{ kJ mol}^{-1}$
(c) $C_4H_{10}(g) + \frac{13}{2}O_2(g) \rightarrow 4CO_2(g) + 5H_2O(l);$ $\Delta_c H = -2658.0 \text{ kJ mol}^{-1}$
(d) $C_4H_{10}(g) + \frac{13}{2}O_2(g) \rightarrow 4CO_2(g) + 5H_2O(l);$ $\Delta_c H = +2658.0 \text{ kJ mol}^{-1}$

6. $\Delta_f U^\circ$ of formation of $CH_4(g)$ at certain temperature is -393 kJ mol^{-1}. The value of $\Delta_f H^\circ$ is
(a) zero (b) $< \Delta_f U^\circ$
(c) $> \Delta_f U^\circ$ (d) equal to $\Delta_f U^\circ$

7. In an adiabatic process, no transfer of heat takes place between system and surroundings. Choose the correct option for free expansion of an ideal gas under adiabatic condition from the following.
(a) $q = 0, \Delta T \neq 0, W = 0$ (b) $q \neq 0, \Delta T = 0, W = 0$
(c) $q = 0, \Delta T = 0, W = 0$ (d) $q = 0, \Delta T < 0, W \neq 0$

8. The pressure-volume work for an ideal gas can be calculated by using the expression $W = -\int_{V_i}^{V_f} p_{ex} dV$. The work can also be calculated from the pV-plot by using the area under the curve within the specified limits. When an ideal gas is compressed (a) reversibly or (b) irreversibly from volume V_i to V_f. Choose the correct option. NCERT Page-166
(a) W(reversible) $= W$(irreversible)
(b) W(reversible) $< W$(irreversible)
(c) W(reversible) $> W$(irreversible)
(d) W(reversible) $= W$(irreversible) $+ p_{ex}.\Delta V$

9. The entropy change can be calculated by using the expression $\Delta S = \frac{q_{rev}}{T}$. When water freezes in a glass beaker, choose the correct statement amongst the following. NCERT Page-183
(a) ΔS (system) decreases but ΔS (surroundings) remains the same
(b) ΔS (system) increases but ΔS (surroundings) decreases
(c) ΔS (system) decreases but ΔS (surroundings) increases
(d) ΔS (system) decreases but ΔS (surroundings) also decreases

10. On the basis of theromochemical equations (1), (2) and (3), find out which of the algebraic relationships given in options (a) to (d) is correct
1. C (graphite) + $O_2(g) \rightarrow CO_2(g)$; $\Delta_r H = x$ kJ mol^{-1}
2. C (graphite) + $\frac{1}{2}O_2(g) \rightarrow CO(g)$; $\Delta_r H = y$ kJ mol^{-1}
3. $CO(g) + \frac{1}{2}O_2(g) \rightarrow CO_2(g)$; $\Delta_r H = z$ kJ mol^{-1}

(a) $z = x + y$ (b) $x = y - z$
(c) $x = y + z$ (d) $y = 2z - x$

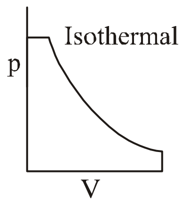
11. Consider the reactions given below. On the basis of these reactions find out which of the algebraic relationship given in options (a) to (d) is correct? NCERT Page-176

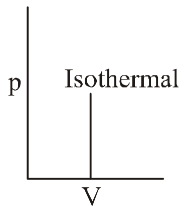
1. C (graphite) + 4 H (g) $\rightarrow$ CH_4 (g); $\Delta_r H = x$ kJ mol^{-1}
2. C (graphite) + $2H_2$ (g) $\rightarrow$ CH_4 (g); $\Delta_r H = y$ kJ mol^{-1}

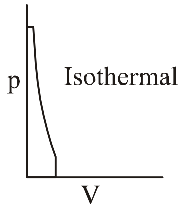
(a) $x = y$ (b) $x = 2y$
(c) $x > y$ (d) $x < y$

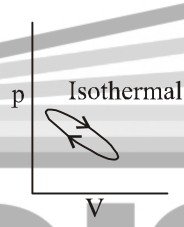
Past Years NEET & JEE Main

12. Which of the following p-V curve represents maximum work done? NCERT Page-165 | NEET 2022

(a)


(b)


(c)


(d)


13. For irreversible expansion of an ideal gas under isothermal condition, the correct option is: NCERT Page-169 & 185 | NEET 2021, C

(a) $\Delta U \neq 0, \Delta S_{total} = 0$ (b) $\Delta U = 0, \Delta S_{total} = 0$
(c) $\Delta U \neq 0, \Delta S_{total} \neq 0$ (d) $\Delta U = 0, \Delta S_{total} \neq 0$

14. The correct option for free expansion of an ideal gas under adiabatic condition is NCERT Page-166 | NEET 2020, C

(a) $q = 0, \Delta T < 0$ and $w > 0$
(b) $q < 0, \Delta T = 0$ and $w = 0$
(c) $q > 0, \Delta T > 0$ and $w > 0$
(d) $q = 0, \Delta T = 0$ and $w = 0$

15. For the reaction, $2Cl(g) \longrightarrow Cl_2(g)$, the correct option is : NCERT Page-184 & 185 | NEET 2020, C

(a) $\Delta_r H > 0$ and $\Delta_r S < 0$ (b) $\Delta_r H < 0$ and $\Delta_r S > 0$
(c) $\Delta_r H < 0$ and $\Delta_r S < 0$ (d) $\Delta_r H > 0$ and $\Delta_r S > 0$

16. Under isothermal condition, a gas at 300 K expands front 0.1 L to 0.25 L against a constant external pressure of 2 bar. The work done by the gas is [Given that 1 L bar = 100 J] NCERT Page-165 | NEET 2019, A

(a) –30 J (b) 5 kJ (c) 25 J (d) 30 J

17. In which case change in entropy is negative ? NCERT Page-185 | NEET 2019, C

(a) Evaporation of water
(b) Expansion of a gas at constant temperature
(c) Sublimation of solid to gas
(d) $2H(g) \rightarrow H_2(g)$

18. The bond dissociation energies of X_2, Y_2 and XY are in the ratio of 1 : 0.5 : 1. ΔH for the formation of XY is –200 kJ mol^{-1}. The bond dissociation energy of X_2 will be NCERT Page-178 | NEET 2018, S

(a) 200 kJ mol^{-1} (b) 100 kJ mol^{-1}
(c) 400 kJ mol^{-1} (d) 800 kJ mol^{-1}

19. For a given reaction, $\Delta H = 35.5$ kJ mol^{-1} and $\Delta S = 83.6$ JK^{-1} mol^{-1}. The reaction is spontaneous at : (Assume that ΔH and ΔS do not vary with tempearature) NCERT Page-185 | NEET 2017, S

(a) $T > 425$ K (b) All temperatures
(c) $T > 298$ K (d) $T < 425$ K

20. A gas is allowed to expand in a well insulated container against a constant external pressure of 2.5atm from an initial volume of 2.50 L to a final volume of 4.50L. The change in internal energy ΔU of the gas in joules will be:- NCERT Page-164 & 165 | NEET 2017, S

(a) – 500 J (b) – 505 J
(c) + 505 J (d) 1136.25 J

21. The correct thermodynamic conditions for the spontaneous reaction at all temperatures is NCERT Page-186 | NEET 2016, C

(a) $\Delta H < 0$ and $\Delta S = 0$ (b) $\Delta H > 0$ and $\Delta S < 0$
(c) $\Delta H < 0$ and $\Delta S > 0$ (d) $\Delta H < 0$ and $\Delta S < 0$

22. At 25°C and 1 atm pressure, the enthalpies of combustion are as given below:

Substance	H_2	C (graphite)	C_2H_6(g)
$\frac{\Delta_c H^{\ominus}}{kJmol^{-1}}$	–286.0	–394.0	–1560.0

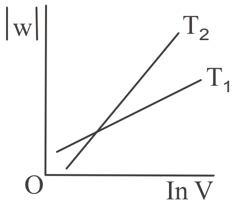
The enthalpy of formation of ethane is NCERT Page-176 | JEE M 2022

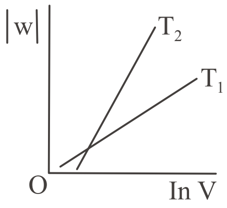
(a) + 54.0 kJ mol^{-1} (b) – 68.0 kJ mol^{-1}
(c) – 86.0 kJ mol^{-1} (d) + 97.0 kJ mol^{-1}

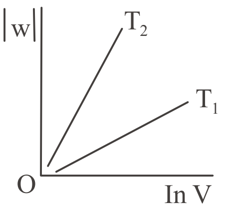
23. For a given chemical reaction $A \rightarrow B$ at 300 K the free energy change is –49.4 kJ mol^{-1} and the enthalpy of reaction is 51.4 kJ mol^{-1}. The entropy change of the reaction is ______ J K^{-1} mol^{-1}. NCERT Page-186 | JEE M 2021, A

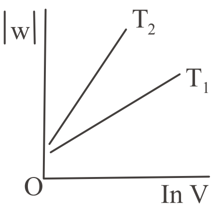
24. For the reaction ; $A(l) \longrightarrow 2B(g)$
$\Delta U = 2.1$ kcal, $\Delta S = 20$ cal K^{-1} at 300 K.
Hence G in kcal is ________. NCERT Page-167, 168 & 185 | JEE M 2020, A

25. Consider the reversible isothermal expansion of an ideal gas in a closed system at two different temperatures T_1 and T_2 ($T_1 < T_2$). The correct graphical depiction of the dependence of work done (w) on the final volume (V) is: NCERT Page-166 | JEE M 2019, S

(a) 

(b) 

(c) 

(d) 

26. Among the following, the set of parameters that represents path functions, is: NCERT Page-162, 184 | JEE M 2019, S

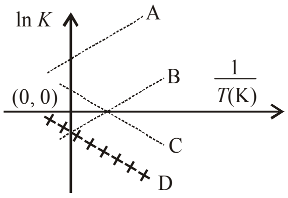
A. $q + w$ B. q

C. w D. H – TS

(a) B and C (b) B, C and D

(c) A and D (d) A, B and C

27. Which of the following lines correctly show the temperature dependence of equilibrium constant, K, for an exothermic reaction? NCERT Page-186 | JEE M 2018, S, BN



(a) A and B (b) B and C

(c) C and D (d) A and D

28. The combustion of benzene (l) gives CO_2 (g) and H_2O (l). Given that heat of combustion of benzene at constant volume is –3263.9 kJ mol^{-1} at 25°C; heat of combustion (in kJ mol^{-1}) of benzene at constant pressure will be : (R = 8.314 JK^{-1} mol^{-1}) NCERT Page-176 | JEE M 2018, S

(a) 4152.6 (b) –452.46

(c) 3260 (d) –3267.6

29. ΔU is equal to NCERT Page-162 & 163 | JEE M 2017, C

(a) Isochoric work (b) Isobaric work

(c) Adiabatic work (d) Isothermal work

30. The heats of combustion of carbon and carbon monoxide are –393.5 and –283.5 kJ mol^{-1}, respectively. The heat of formation (in kJ) of carbon monoxide per mole is : NCERT Page-173 | JEE M 2016, S

(a) 676.5 (b) –110.5 (c) 110.5 (d) 676.5

Exercise 3 : Matching, Statement & Assertion Reason Type

Match the Followings

1. Match Column-I with Column-II.

Column-I	Column-II
(A) C_m	(p) $C_v \Delta T$
(B) q	(q) C/n
(C) ΔU	(r) $C_p \Delta T$
(D) ΔH	(s) $C \Delta T$

(a) A – (q), B – (s), C – (r), D – (p)

(b) A – (q), B – (s), C – (p), D – (r)

(c) A – (s), B – (q), C – (p), D – (r)

(d) A – (q), B – (p), C – (r), D – (s)

2. Match Column-I with Column-II.

Column-I	Column-II
(A) $p_{ext} = 0$	(p) Free expansion of an ideal gas
(B) $q = p_{ext}(V_f - V_i)$	(q) Adiabatic change
(C) $q = 2.303\, nRT \log (V_f / V_i)$	(r) Isothermal reversible change
(D) $\Delta U = W_{ad}$	(s) Isothermal irreversible change

(a) A – (p), B – (s), C – (r), D – (q)

(b) A – (p), B – (q), C – (r), D – (s)

(c) A – (p), B – (r), C – (s), D – (q)

(d) A – (p), B – (r), C – (q), D – (s)

3. Match Column-I with Column-II.

Column-I	Column-II
(A) Spontaneous process	(p) $\Delta H < 0$
(B) Process with $\Delta P = 0$, $\Delta T = 0$	(q) $\Delta G_{T,P} < 0$
(C) $\Delta H_{reaction}$	(r) Isothermal and isobaric process
(D) Exothermic process	(s) [Bond energies of molecules in reactants]- [Bond energies of product molecules

Choose the correct answer from the options given below:

(a) A – (r), B – (q), C – (s), D – (p)

(b) A – (q), B – (r), C – (s), D – (p)

(c) A – (q), B – (r), C – (p), D – (s)

(d) A – (q), B – (p), C – (r), D – (s)

4. Match Column-I with Column-II.

Column-I	Column-II
(A) $C_4H_{10}+\frac{13}{2}O_2 \rightarrow 4CO_2+5H_2O; \Delta H=-w$	(p) Enthalpy of atomisation
(B) $CH_4 \rightarrow C+4H; \Delta H=x$	(q) Enthalpy of formation
(C) $H_2+Br_2 \rightarrow 2HBr; \Delta H=y$	(r) Enthalpy of combustion
(D) $CO_2(s) \rightarrow CO_2(g); \Delta H=z$	(s) Enthalpy of sublimation

(a) A – (s), B – (p), C – (q), D – (r)
(b) A – (q), B – (r), C – (p), D – (s)
(c) A – (r), B – (p), C – (q), D – (s)
(d) A – (p), B – (q), C – (s), D – (r)

5. Match Column-I with Column-II.

Column-I	Column-II
(A) $\Delta H=-ve$; $\Delta S=-ve$ $\Delta G=-ve$	(p) Reaction will be non-spontaneous at high temperature
(B) $\Delta H=-ve$; $\Delta S=-ve$ $\Delta G=+ve$	(q) Reaction will be non-spontaneous at low temperature
(C) $\Delta H=+ve$; $\Delta S=+ve$ $\Delta G=+ve$	(r) Reaction will be spontaneous at low temperature
(D) $\Delta H=+ve$; $\Delta S=+ve$ $\Delta G=-ve$	(s) Reaction will be spontaneous at high temperature

(a) A – (q), B – (r), C – (p), D – (s)
(b) A – (r), B – (p), C – (q), D – (s)
(c) A – (r), B – (q), C – (s), D – (p)
(d) A – (q), B – (s), C – (p), D – (r)

Two-Statement Type Questions

DIRECTIONS : *Read the statements carefully and answer the question on the basis of following options.*

(a) Both statement I and II are correct.
(b) Both statement I and II are incorrect.
(c) Statement I is correct but statement II is incorrect.
(d) Statement II is correct but statement I is incorrect.

6. **Statement I :** Internal energy, U, of the system is a state function.
Statement II : –w shows, that work is done on the system.

7. **Statement I :** In case of expansion maximum amount of work can be obtained under isothermal conditions by reversibly carrying out the process rather than through irreversible route.
Statement II : In case of isothermal compression, work done is positive and the internal energy of the system increases.

8. **Statement I :** When enthalpy factor is absent then randomness factor decides spontaneity of a process.
Statement II : When randomness factor is absent then enthalpy factor decides spontaneity of a process.

Four / Five Statement Type Questions

9. Which of the following statement is incorrect ?
(i) The standard enthalpy of reaction is the enthalpy change for a reaction when all the participating substances are in their standard states.
(ii) The standard state of a substance at a specified temperature is its pure form at 1 bar.
(iii) The standard state of solid iron at 298 K is pure iron at 1 atm
(iv) Standard conditions are denoted by adding the superscript $\ominus$ to the symbol ΔH *e.g.*, $-\Delta H^{\ominus}$
(a) (i) and (ii) (b) (ii) and (iii)
(c) (iii) only (d) (iv) only

10. Pick out the wrong statement
(i) The standard free energy of formation of all elements is zero
(ii) A process accompanied by decrease in entropy is spontaneous under certain conditions
(iii) The entropy of a perfectly crystalline substance at absolute zero is zero
(iv) A process that leads to increase in free energy will be spontaneous
(a) (i) and (ii) (b) (ii) and (iii)
(c) (iii) only (d) (iv) only

11. Identify the correct statement regarding entropy.
(i) At absolute zero temperature, entropy of a perfectly crystalline substance is taken to be zero.
(ii) At absolute zero temperature, the entropy of a perfectly crystalline substance is positive.
(iii) Absolute entropy of a substance cannot be determined.
(iv) At 0°C, the entropy of a perfectly crystalline substance is taken to be zero
(a) only (i) (b) (ii) and (iv)
(c) (i) and (ii) (d) (i) and (iii)

12. Identify the correct statement regarding a spontaneous process:
(i) Lowering of energy in the process is the only criterion for spontaneity.
(ii) For a spontaneous process in an isolated system, the change in entropy is positive.
(iii) Endothermic processes are never spontaneous.
(iv) Mostly of the exothermic processes are spontaneous.
(a) only (i) (b) (ii) and (iv)
(c) (i) and (ii) (d) (i) and (iii)

13. Which of the following statements is correct for the spontaneous adsorption of a gas ?
(i) ΔS is negative and, therefore, ΔH should be highly positive

(ii) ΔS is negative and therefore, ΔH should be highly negative
(iii) ΔS is positive and, therefore, ΔH should be negative
(iv) ΔS is positive and, therefore, ΔH should also be highly positive

(a) (i) and (ii) (b) only (ii)
(c) (iii) and (iv) (d) only (iv)

Assertion & Reason Questions

DIRECTIONS : *These questions consist of two statements, each printed as Assertion and Reason. While answering these questions, you are required to choose any one of the following four responses.*

(a) If both Assertion and Reason are correct and the Reason is a correct explanation of the Assertion.
(b) If both Assertion and Reason are correct but Reason is not a correct explanation of the Assertion.
(c) If the Assertion is correct but Reason is incorrect.
(d) If the Assertion is incorrect and Reason is correct.

14. **Assertion :** Absolute value of internal energy of a substance cannot be determined.
Reason : It is impossible to determine exact values of constitutent energies of the substances.

15. **Assertion :** A process is called adiabatic if the system does not exchange heat with the surroundings.
Reason : It does not involve increase or decrease in temperature of the system.

16. **Assertion :** The mass and volume of a substance are the extensive properties and are proportional to each other.
Reason : The ratio of mass of a sample to its volume is an intensive property.

17. **Assertion :** First law of thermodynamics is applicable to an electric fan or a heater.
Reason : In an electric fan, the electrical energy is converted into mechanical work that moves the blades. In a heater, electrical energy is converted into heat energy.

18. **Assertion :** For an isothermal reversible process $Q = -W$ *i.e.* work done by the system equals the heat absorbed by the system.
Reason : Enthalpy change (ΔH) is zero for isothermal process.

19. **Assertion :** The value of enthalpy of neutralization of weak acid and strong base is numerically less than 57.1 kJ.
Reason : All the OH^- ions furnished by 1 g equivalent of strong base are not completely neutralized.

20. **Assertion :** Many endothermic reactions that are not spontaneous at room temperature become spontaneous at high temperature.
Reason : Entropy of the system increases with increase in temperature.

Exercise 4 : Skill Enhancer MCQs

1. Enthalpy of sublimation of iodine is 24 cal g^{-1} at 200°C. If specific heat of $I_2(s)$ and $I_2(vap)$ are 0.055 and 0.031 cal $g^{-1}K^{-1}$ respectively, then enthalpy of sublimation of iodine at 250°C in cal g^{-1} is :
(a) 2.85 (b) 5.7 (c) 22.8 (d) 11.4

2. Which of the following expressions is true for an ideal gas?
(a) $\left(\frac{dV}{dT}\right)_P = 0$ (b) $\left(\frac{dP}{dT}\right)_V = 0$
(c) $\left(\frac{dU}{dV}\right)_T = 0$ (d) $\left(\frac{dU}{dT}\right)_V = 0$

3. 0.5 mole each of two ideal gases $A\left(C_{v,m} = \frac{5}{2}R\right)$ and B $(C_{v,m} = 3R)$ are taken in a container and expanded reversibly and adiabatically, during this process temperature of gaseous mixture decreased from 350 K to 250 K. Find ΔH (in cal/mol) for the process:
(a) – 100 R (b) – 137.5 R
(c) – 375 R (d) None of these

4. A heating coil is immersed in a 100 g sample of H_2O (l) at 1 atm and 100°C in a closed vessel. In this heating process, 60% of the liquid is converted into gaseous form at constant pressure of 1 atm. Densities of liquid and gaseous water under these conditions are 1000 kg/m^3 and 0.60 kg/m^3 respectively. Magnitude of the work done for the process is :
(a) 4997 J (b) 4970 J
(c) 9994 J (d) None of these

5. For the reaction taking place at certain temperature
$$NH_2COONH_4(s) \rightleftharpoons 2NH_3(g) + CO_2(g),$$
if equilibrium pressure is 3X bar then $\Delta_r G°$ would be
(a) $-RT \ln 9 - 3RT \ln X$
(b) $RT \ln 4 - 3RT \ln X$
(c) $-3RT \ln X$
(d) None of these

6. The heat of combustion of ethane gas is 368 kcal/mol. Assuming that 60% of the heat is useful, how many m^3 of ethane measured at STP must be burnt to supply enough heat to convert 50 kg of water at 10ºC to steam at 100ºC? (Specific heat of water is 1 cal/g, heat of vaporisation of H_2O is 540 cal/g)
(a) 2.196 m^3 (b) 1.196 m^3
(c) 4.196 m^3 (d) 3.196 m^3

7. If bond enthalpies of $N \equiv N$, $H - H$ and $N - H$ bonds are x_1, x_2 and x_3 respectively, ΔH_f° for NH_3 will be

(a) $x_1 + 3x_2 - 6x_3$ (b) $\frac{1}{2}x_1 + 3/2x_2 - 3x_3$

(c) $3x_3 - \frac{1}{2}x_1 - 3/2x_2$ (d) $6x_3 - x_1 - 3x_2$

8. If the ratio of molar heat capacities of a gas at constant pressure and constant volume *i.e.*, $\frac{C_P}{C_V} = \gamma$, the respective values of C_P and C_V are

(a) $\frac{R}{\gamma - 1}, \frac{\gamma R}{\gamma - 1}$ (b) $\frac{\gamma R}{\gamma - 1}, \frac{R}{\gamma - 1}$

(c) $\frac{\gamma - 1}{\gamma R}, \frac{\gamma - 1}{R}$ (d) $\frac{\gamma - 1}{R}, \frac{\gamma - 1}{\gamma R}$

9. The bond dissociation energies of CH_4 and C_2H_6 respectively are 360 and 620 k cal mol^{-1}. The C – C bond energy would be

(a) 260 k cal/mol (b) 180 k cal/mol

(c) 130 k cal/mol (d) 80 k cal/mol

10. Given that:

(i) $\Delta_f H^\circ$ of N_2O is 82 kJ mol^{-1}

(ii) Bond energies of $N \equiv N$, $N=N$, $O = O$ and $N = O$ are 946, 418, 498 and 607 kJ mol^{-1} respectively,

The resonance energy of N_2O is :

(a) – 88 kJ (b) – 66 kJ (c) –62 kJ (d) –44 kJ

11. Calculate enthalpy change for the change $8S(g) \longrightarrow S_8(g)$, given that

$H_2S_2(g) \longrightarrow 2H(g) + 2S(g),\ \Delta H = 239.0$ k cal mol^{-1} ;

$H_2S(g) \longrightarrow 2H(g) + S(g),\ \Delta H = 175.0$ k cal mol^{-1}

(a) + 512.0 k cal (b) – 512.0 k cal

(c) 508.0 k cal (d) – 508.0 k cal

12. Fixed mass of an ideal gas contained in a 24.63 L sealed rigid vessel at 1 atm is heated from – 73°C to 27°C. Calculate change in Gibb's energy if entropy of gas is a function of temperature as $S = 2 + 10^{-2}\,T$ (J/K): (Use 1 atm L = 0.1 kJ)

(a) 1231.5 J (b) 1281.5 J

(c) 781.5 J (d) 0

13. The densities of graphite and diamond at 298 K are 2.25 and 3.31 g cm^{-3}, respectively. If the standard free energy difference (ΔG°) is equal to 1895 J mol^{-1}, the pressure at which graphite will be transformed into diamond at 298 K is

(a) 9.92×10^5 Pa (b) 11.094×10^8 Pa

(c) 10.952×10^7 Pa (d) 9.92×10^6 Pa

14. If H is considered as the function of P and T, then which of the following relations is /are correct?

(a) $dH = \left(\frac{dH}{dT}\right)_P dT + \left(\frac{dH}{dP}\right)_T dP$

(b) $dH = C_p dT + \left(\frac{dH}{dP}\right)_T dP$

(c) $\left(\frac{dH}{dP}\right)_T = 0$

(d) all

Exercise 5 : Numeric Value Answer Questions

1. A gas present in a cylinder fitted with a frictionless piston expands against a constant pressure of 1 atm from a volume of 2 litre to a volume of 6 litre. In doing so, it absorbs 800 J heat from surroundings. Determine increase in internal energy of process.

2. For the reaction

$H_2F_2(g) \rightarrow H_2(g) + F_2(g)$

$\Delta U = -59.6$ kJ mol^{-1} at 27 °C.

The enthalpy change for the above reaction is (–) ______ kJ mol^{-1} [nearest integer]

Given : R = 8.314 JK^{-1} mol^{-1}.

3. Given

Reaction	Energy Change (in kJ)
$Li(s) \rightarrow Li(g)$	161
$Li(g) \rightarrow Li^+(g)$	520
$\frac{1}{2}F_2(g) \rightarrow F(g)$	77
$F(g) + e^- \rightarrow F^-(g)$	(Electron gain enthalpy)
$Li^+(g) + F^-(g) \rightarrow LiF(s)$	– 1047
$Li(s) + \frac{1}{2}F_2(g) \rightarrow LiF(s)$	– 617

Based on data provided, find the value of electron gain enthalpy of fluorine.

4. The standard enthalpy of formation of NH_3 is – 46.0 kJ/mol. If the enthalpy of formation of H_2 from its atoms is – 436 kJ/mol and that of N_2 is – 712 kJ/mol, find the average bond enthalpy of N – H bond in NH_3.

5. The enthalpy of neutralization of a weak acid in 1 M solution with a strong base is –56.1 kJ mol^{-1}. If enthalpy of ionization of the acid is 1.5 kJ mol^{-1} and enthalpy of neutralization of the strong acid with a strong base is –57.3 kJ equiv^{-1}, what is the % ionization of the weak acid in molar solution (assume the acid to be monobasic)?

6. When 0.2 mole of anhydrous $CuSO_4$ is dissolved in water, the heat evolved is 1.451 kcal. If 0.2 mole of $CuSO_4.5H_2O$ is dissolved in water, the heat absorbed is 0.264 kcal. Calculate the molar heat of hydration of $CuSO_4$.

7. The specific heat of a monoatomic gas at constant pressure is 248.2 J kg^{-1} K^{-1} and at constant volume it is 149.0 J kg^{-1} K^{-1}. Find the mean molar mass of the gas.

8. The standard entropies of $CO_2(g), C(s)$ and $O_2(g)$ are 213.5, 5.740 and 205 JK^{-1} respectively. Calculate the standard entropy of formation of $CO_2(g)$.

9. Titanium metal is extensively used in aerospace industry because the metal imparts strength to structures but does not unduly add to their masses. The metal is produced by the reduction of $TiCl_4(l)$ which in turn is produced from mineral rutile $TiO_2(s)$. Calculate the Gibb's free energy for the following reaction

$$TiO_2(s) + 2Cl_2(g) \rightarrow TiCl_4(l) + O_2(g)$$

Given that: H_f° for $TiO_2(s)$, $TiCl_4(l)$, $Cl_2(g)$ and $O_2(g)$ are $-944.7, -804.2, 0.0,$ 0.0 kJ mol^{-1}

Also S° for $TiO_2(g)$, $TiCl_4(l)$, $Cl_2(g)$ and $O_2(g)$ are 50.3, 252.3, 233.0, 205.1 J mol^{-1} K^{-1} respectively.

10. For combustion of one mole of magnesium in an open container at 300 K and 1 bar pressure, $\Delta_C H^\circ = -601.70$ kJ mol^{-1}, the magnitude of change in internal energy for the reaction is ______ kJ. (Nearest integer)
(Given : R = 8.3 J K^{-1} mol^{-1})

Answer Keys

Exercise - 1 : (NCERT Based Topic-wise MCQs)																			
1	(b)	**8**	(d)	**15**	(d)	**22**	(b)	**29**	(a)	**36**	(b)	**43**	(a)	**50**	(c)	**57**	(b)		
2	(c)	**9**	(d)	**16**	(b)	**23**	(c)	**30**	(d)	**37**	(b)	**44**	(d)	**51**	(b)	**58**	(b)		
3	(b)	**10**	(a)	**17**	(c)	**24**	(b)	**31**	(a)	**38**	(a)	**45**	(a)	**52**	(a)	**59**	(c)		
4	(c)	**11**	(b)	**18**	(a)	**25**	(a)	**32**	(a)	**39**	(a)	**46**	(d)	**53**	(a)	**60**	(a)		
5	(d)	**12**	(c)	**19**	(d)	**26**	(d)	**33**	(c)	**40**	(b)	**47**	(b)	**54**	(d)	**61**	(a)		
6	(a)	**13**	(c)	**20**	(b)	**27**	(a)	**34**	(a)	**41**	(b)	**48**	(b)	**55**	(d)	**62**	(c)		
7	(c)	**14**	(d)	**21**	(d)	**28**	(c)	**35**	(d)	**42**	(c)	**49**	(a)	**56**	(a)	**63**	(a)		
Exercise - 2 : (NCERT Exemplar & Past Years NEET & JEE Main)																			
1	(c)	**4**	(c)	**7**	(c)	**10**	(c)	**13**	(d)	**16**	(a)	**19**	(a)	**22**	(c)	**25**	(b)	**28**	(d)
2	(c)	**5**	(c)	**8**	(b)	**11**	(c)	**14**	(d)	**17**	(d)	**20**	(b)	**23**	(336)	**26**	(a)	**29**	(c)
3	(d)	**6**	(b)	**9**	(c)	**12**	(a)	**15**	(c)	**18**	(d)	**21**	(c)	**24**	(–2.70)	**27**	(a)	**30**	(b)
Exercise - 3 : (Matching, Statement & Assertion-Reason Type)																			
1	(b)	**3**	(b)	**5**	(b)	**7**	(a)	**9**	(c)	**11**	(a)	**13**	(b)	**15**	(c)	**17**	(a)	**19**	(c)
2	(a)	**4**	(c)	**6**	(d)	**8**	(c)	**10**	(d)	**12**	(b)	**14**	(a)	**16**	(b)	**18**	(b)	**20**	(b)
Exercise - 4 : (Skill Enhancer MCQs)																			
1	(c)	**3**	(c)	**5**	(d)	**7**	(b)	**9**	(d)	**11**	(b)	**13**	(b)						
2	(c)	**4**	(c)	**6**	(d)	**8**	(b)	**10**	(a)	**12**	(c)	**14**	(d)						
Exercise - 5 : (Numeric Value Answer Questions)																			
1	(395)	**2**	(57)	**3**	(–328)	**4**	(–964)	**5**	(20)	**6**	(–8.575)	**7**	(83.8)	**8**	(2.76)	**9**	(158)	**10**	(600)

Chapter 06

Thermodynamics

EXERCISE - 1

1. **(b)** The laws of thermodynamics deal with energy changes of macroscopic systems involving a large number of molecules rather than microscopic systems containing a few molecules.
2. **(c)** Closed system can exchange energy but not matter with surroundings. Pressure cooker provides closed system.
3. **(b)** We can describe the state of a gas by quoting its pressure (P), volume (V), temperature (T), amount (n) etc.
4. **(c)** Enthalpy is a state function which depends on the initial and final state.
5. **(d)** The factor which affects the internal energy is:
   (i) Heat passes into or out.
   (ii) Work is done on or by the system.
   (iii) Matter enters or leaves the system.
6. **(a)** $\Delta E = \Delta Q - W$
   For adiabatic expansion, $\Delta Q = 0$
   $\Rightarrow \Delta E = -W$
   The negative sign shows decrease in internal energy, which is equal to the work done by the system on the surroundings.
7. **(c)** Internal energy and molar enthalpy are state functions. Work (reversible or irreversible) is a path function.
8. **(d)** Mathematical expression of first law of thermodynamics
   $\Delta E = q + w$, ΔE is a state function, where ΔE = Internal energy
9. **(d)** When work is done by the system, $\Delta U = q - W$
10. **(a)** The shaded area shows work done on an ideal gas in a cylinder when it is compressed by a constant external pressure.
11. **(b)** As volume is constant hence, work done in this process is zero. Hence, heat supplied is equal to change in internal energy.
12. **(c)** For isothermal reversible expansion.
   $w = -nRT \ln \dfrac{V_2}{V_1}$
13. **(c)** $W = -P\Delta V = -10^5(1\times10^{-2} - 1\times10^{-3}) = -900\text{J}$
14. **(d)** The difference between ΔH and ΔU is not usually significant for systems consisting of only solids or liquids. Solids and liquids do not suffer any significant volume changes upon heating. The difference, however, becomes significant when gases are involved.
15. **(d)** We know that
   $\Delta H = \Delta E + P\Delta V$
   In the reactions, $H_2(g) + Br_2(g) \rightarrow 2HBr(g)$ there is no change in volume or $\Delta V = 0$.
   So, $\Delta H = \Delta E$ for this reaction.
16. **(b)** $\Delta n = -\dfrac{1}{2}$; $\Delta H = \Delta E - \dfrac{1}{2}RT$; $\Rightarrow \Delta E > \Delta H$
17. **(c)** $\Delta H = \Delta E + \Delta nRT$
   $\Delta n = 3 - (1 + 5) = 3 - 6 = -3$
   $\Delta H - \Delta E = (-3RT)$
18. **(a)** Volume depends upon mass. Hence, it is an extensive property.
19. **(d)** As $\Delta H = \Delta E + \Delta n_g RT$
   if $n_p < n_r$; $\Delta n_g = n_p - n_r = -$ ve.
   Hence $\Delta H < \Delta E$.
20. **(b)** 1 Calorie = 4.184 Joule
21. **(d)** $\dfrac{C_P}{C_V} = \dfrac{\frac{5}{2}R}{\frac{3}{2}R} = \dfrac{5}{3} = 1.67$
22. **(b)** $\Delta H = \Delta E + P\Delta V$, for solid and liquid,
   $\Delta V = 0$ or $\Delta H = \Delta E + \Delta n\, RT$, for solids and liquids $\Delta n = 0$.
23. **(c)** During isothermal expansion of an ideal gas,
   $\Delta T = 0$. Now $H = U + PV$
   $\because \Delta H = \Delta U + \Delta(PV)$
   $\therefore \Delta H = \Delta U + \Delta(nRT)$;
   Thus if $\Delta T = 0$, $\Delta H = \Delta U$
   i.e., remain unaffected
24. **(b)** $\Delta H = \Delta U + \Delta nRT$; for $N_2 + 3H_2 \longrightarrow 2NH_3$
   $\Delta n_g = 2 - 4 = -2$
   $\therefore \Delta H = \Delta U - 2RT$ or $\Delta U = \Delta H + 2RT$ $\therefore \Delta U > \Delta H$
25. **(a)** Mass independent properties (molar conductivity and electromotive force) are intensive properties. Resistance and heat capacity are mass dependent, hence extensive properties.
26. **(d)** The magnitude of the heat capacity depends on the size, composition and nature of the system.
27. **(a)** H = U + PV (By definition)
   $\Delta H = \Delta U + \Delta(PV)$ at constant pressure
   $\Delta H = \Delta U + P\Delta V$
28. **(c)** For a cyclic process the net change in the internal energy is zero because the change in internal energy does not depend on the path.
29. **(a)** $-W_{\text{irreversible}} = P_{ext}(V_2 - V_1)$
   $= 10\text{ atm }(2\text{L} - 1\text{L}) = 10\text{ atm} - \text{L}$

$$-W_{\text{reversible}} = 2.303\, nRT \log \frac{V_2}{V_1}$$

$$= 1 \times 2.303 \times 0.0821 \times 298 \text{ atm–L/K/mol} \times \log \frac{2}{1}$$

$= 16.96$ atm–L

$$\frac{W_{\text{reversible}}}{W_{\text{irreversible}}} = \frac{16.96}{10.00} = 1.69 \approx 1.7$$

30. **(d)** In expansion against vacuum,
$P_{\text{ext}} = 0$
$w = -P_{\text{ext}}\, \Delta V = 0$

31. **(a)** $q_p = \Delta H = C_p dT$

$$\Rightarrow q_p = 75.32 \frac{\text{J}}{\text{K mol}} \times (299 - 298)\text{K}$$

$$\Rightarrow q_p = 75.32 \frac{\text{J}}{\text{K mol}}$$

For 180 kg of water, no. of moles of water

$$= \frac{180 \times 10^3 \text{g}}{18 \text{g/mol}} = 10^4 \text{ moles}$$

$$q_p = 75.32 \frac{\text{J}}{\text{mol}} \times 10^4 \text{ moles}$$

$= 753.2 \times 10^3$ J $= 753.2$ kJ

ΔH for ATP = 7 kcal / mol

$= 7 \times 4.184$ kJ/mol $= 29.2$ kJ/mol

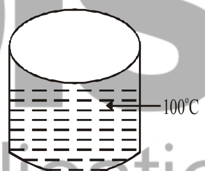
29.2 kJ produced from 6.022×10^{23} molecules

753.2 kJ produced from $6.022 \times 10^{23} \times \dfrac{753.2}{29.2}$

$= 1.5 \times 10^{25}$ molecules

32. **(a)** 18 g of water at 100°C

10 g of Cu at 25°C is added.



$q_p = C_{p,m}$ dT

$$= 75.32 \times \frac{\text{J}}{\text{K mol}} \times \frac{18\text{g}}{18\text{g/mol}} (373 - 298)\text{K}$$

$$= 75.32 \frac{\text{J}}{\text{K}} \times 75 \text{ K} = 5649 \text{ J}$$

If now 10g of copper is added $C_{p,m} = 24.47$ J/ mol K

Amount of heat gained by Cu

$$= 24.47 \frac{\text{J}}{\text{K mol}} \times \frac{10\text{g}}{63\text{g/mol}} (373 - 298)\text{ K} = 291.3 \text{ J}$$

Heat lost by water = 291.30 J

$$-291.30 \text{ J} = 75.32 \frac{\text{J}}{\text{K}} \times (T_2 - 373 \text{K})$$

$\Rightarrow -3.947 \text{ K} = T_2 - 373 \text{ K}$

$\Rightarrow T_2 = 369.05$ K

33. **(c)** Given $C_p = 75 \text{ JK}^{-1} \text{ mol}^{-1}$

$n = \dfrac{100}{18}$ mole, $\quad Q = 1000$ J $\quad \Delta T = ?$

$$Q = nC_p\Delta T \Rightarrow \Delta T = \frac{1000 \times 18}{100 \times 75} = 2.4 \text{ K}$$

34. **(a)** For reactions involving gases, there is no work done as $\Delta V = 0$.

35. **(d)** As we know that, $q = -C_V \times \Delta T$

$= -20.7 \times (300 - 298) = -41.4$ kJ

For combustion of 1 mol of graphite

$$= \frac{12.0 \text{ g/mol} \times (-41.4)}{1}$$

$= -4.96 \times 10^2$ kJ/mol, since $\Delta n_g = 0$

$\Delta H = \Delta E = -4.96 \times 10^2$ kJ/mol

36. **(b)** The coefficients in a balanced thermo-chemical equation refer to the number of moles (not to molecules) of reactants and products involved in the reaction.

37. **(b)** Enthalpy of formation of C_2H_4, CO_2 and H_2O are 52, – 394 and – 286 kJ/ mol respectively. (Given)

The reaction is

$C_2H_4 + 3O_2 \rightarrow 2CO_2 + 2H_2O$.

change in enthalpy,

$(\Delta H) = \Delta H_{\text{products}} - \Delta H_{\text{reactants}}$

$= 2 \times (-394) + 2 \times (-286) - (52 + 0) = -1412$ kJ/ mol.

38. **(a)** $Fe_2O_{3(s)} + CO_{(g)} \longrightarrow 2FeO_{(s)} + CO_{2(g)}$ [(i) – 2 × (ii)]

$\Delta H = -26.8 + 33.0 = +6.2$ kJ

39. **(a)** Hess's law is used for calculating enthalpy of reaction.

40. **(b)** $\frac{1}{2}H_2 + \frac{1}{2}Cl_2 \longrightarrow HCl$

$$\Delta H_{HCl} = \sum \text{B.E. of reactant} - \sum \text{B.E. of products}$$

$$-90 = \frac{1}{2} \times 430 + \frac{1}{2} \times 240 - \text{B.E. of HCl}$$

$\therefore$ B.E. of HCl $= 215 + 120 + 90 = 425 \text{ kJ mol}^{-1}$

41. **(b)** Enthalpy of reaction

$= \text{B.E.}_{(\text{Reactant})} - \text{B.E.}_{(\text{Product})}$

$$= \left[\text{B.E.}_{(C=C)} + 4\,\text{B.E.}_{(C-H)} + \text{B.E.}_{(H-H)}\right] - \left[\text{B.E.}_{(C-C)} + 6\,\text{B.E.}_{(C-H)}\right]$$

$= [606.1 + (4 \times 410.5) + 431.37)] - [336.49 + (6 \times 410.5)]$

$= -120.0 \text{ kJ mol}^{-1}$

42. **(c)** $\Delta_r H = \Sigma\Delta_c H\,(\text{Reactant}) - \Sigma\Delta_c H\,(\text{Product})$

$= 3 \times (-1300) - (-3268) = -632 \text{ kJ mol}^{-1}$

43. **(a)** $H_2O\,(l) \rightarrow H_2O\,(g)$; $\Delta H_{\text{vap}} = 40.79$ kJ/mol

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

$\Rightarrow 40.79 \text{ kJ/mol} = \Delta U + (1)\,(8.314 \text{ JK}^{-1} \text{ mol}^{-1})\,(373 \text{ K})$

$$\Rightarrow \Delta U^o = \left(40.79 \text{ kJ/mol} - \frac{8.314 \times 373}{1000} \text{kJ/mol}\right)$$

$$= (40.79 - 3.10) \text{ kJ/mol} = 37.69 \frac{\text{kJ}}{\text{mol}}$$

Internal energy change for 36 g of water

$$= 37.69 \frac{\text{kJ}}{\text{mol}} \times \frac{36\text{g}}{18\text{ g/mol}}$$

$\Delta U = 75.98$ kJ

44. (d) $4NO_2(g) + O_2(g) \rightarrow 2N_2O_5(g), \Delta_r H = -111$ kJ

$$\begin{array}{ccc} 4NO_2(g)+O_2(g) & \rightarrow & 2N_2O_5(g) \\ & \searrow^{\Delta H'} & \downarrow{-54\text{ kJ}} \\ & & 2N_2O_5(s) \end{array}$$

$-111 - 54 = \Delta H'$

$\Delta H' = -165$ kJ

45. (a) $H_2O\ (l) \rightleftharpoons H_2O\ (g) + Q\ ;\ \Delta n_g = 1$

$\Delta H = \Delta E + \Delta n_g RT \Rightarrow 40660 = \Delta E + 8.314 \times 373$

$\Delta E = 37558\ J/mol = 37.56\ kJ\ mol^{-1}$

46. (d) This reaction shows the formation of H_2O, and the X_2 represents the enthalpy of formation of H_2O because as the definition suggests that the enthalpy of formation is the heat evolved or absorbed when one mole of substance is formed from its constituent atoms.

47. (b) Metallic bonding breaks in this reaction.

48. (b) For the equation

$B_2H_6(g) + 3O_2(g) \longrightarrow B_2O_3(g) + 3H_2O(g)$

Eqs. (i) + 3 (ii) + 3 (iii) – (iv)

$\Delta H = -1273 + 3(-286) + 3(44) - 36$

$= -1273 - 858 + 132 - 36 = -2035$ kJ/mol

49. (a) Crystallization of sucrose solution. Entropy is a measure of randomness during the crystallisation of sucrose solution liquid state is changing into solid state hence entropy decreases.

50. (c) ΔS has negative value if number of gaseous moles decreases during a reaction, $\Delta n_g = -$ve

For the reaction

$2SO_2 + O_2 \longrightarrow 2SO_3;\ \Delta n_g = 2 - 3 = -1$

51. (b) For the reaction

$PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$

The reaction given is an example of decomposition reaction and we know that decomposition reactions are endothermic in nature, *i.e*, $\Delta H > 0$.

Further, $\Delta n = (1 + 1) - 1 = +1$

Hence, more number of molecules are present in products which shows more randomness *i.e.* $\Delta S > 0$

52. (a) $\Delta S = \frac{q}{T}$, Unit of entropy is $JK^{-1}\ mol^{-1}$

53. (a) For a spontaneous process, ΔS_{total} is always positive.

54. (d) We know that $\Delta G = \Delta H - T\Delta S$

When $\Delta H < 0$ and $\Delta S < 0$ then ΔG will be negative at low temperatures (positive at high temperature) and the reaction will be spontaneous.

55. (d) Since the process is at equilibrium $\Delta G = 0$, for $\Delta G = 0$, there should be $\Delta H > 0$, $\Delta S > 0$.

56. (a) $\Delta G = -RT \ln K_{eq}$: Normal body temperature = 37°C

$\Rightarrow\ -50\frac{kJ}{mol} = 8.314\frac{J}{K\,mol} \times 310\ \ln K_{eq}$

$\Rightarrow\ 19.39 = \ln K_{eq}\ \Rightarrow\ K_{eq} = 2.6 \times 10^8$

57. (b) $\Delta G = \Delta H - T\Delta S$

$\Delta G = -T\Delta S$ (when $\Delta H = 0$ and $\Delta S = +$ve)

$\Rightarrow \Delta G = -$ve

58. (b) $\Delta G = \Delta H - T\Delta S$

$\Delta G = -57.8 - 298 \times (-176 \times 10^{-3}) = -5\ kJ\ mol^{-1}$

59. (c) For a spontaneous reaction

ΔG(–ve), which is possible if $\Delta S = +$ve, $\Delta H = +$ve

and $T\Delta S > \Delta H$ [As $\Delta G = \Delta H - T\Delta S$]

60. (a) If $\Delta G_{system} = 0$, the system has attained equilibrium, is right choice.

In it, alternative (d) is most confusing as when $\Delta G > 0$, the process may be spontaneous when it is coupled with a reaction which has $\Delta G < 0$ and total ΔG is negative, so right answer is (a).

61. (a) For spontaneous reaction, $dS > 0$ and dG should be negative *i.e.* < 0.

62. (c) $\Delta H = 200\ J\ mol^{-1}$, $\Delta S = 40\ JK^{-1}\ mol^{-1}$

For spontaneous reaction,

$\Delta G < 0$

$\Delta H - T\Delta S < 0;\ \Delta H < T\Delta S$

$\frac{\Delta H}{\Delta S} < T;\ \frac{200}{40} < T \Rightarrow 5 < T$

So, minimum temperature is 5 K

63. (a) $\Delta G° = \Delta H° - T\Delta S°$

For a spontaneous reaction $\Delta G° < 0$

or $\Delta H° - T\Delta S° < 0\ \Rightarrow\ T > \frac{\Delta H°}{\Delta S°}$

$\Rightarrow\ T > \frac{179.3 \times 10^3}{160.2} > 1117.9K \approx 1118K$

EXERCISE - 2

1. (c) Thermodynamics deals with the energy change, feasibility and extent of a reaction, but not with the rate and mechanism of a process.

2. (c) For a closed vessel made of copper, there will be no exchange of matter between the system and the surroundings but energy exchange can occur through its walls.

3. (d) The state of a gas can be described by quoting the relationship between pressure, volume, temperature and amount. The ideal gas equation is

$PV = nRT$

4. (c) Specific heat is an intensive property which depends only on the nature of the gas. Hence, if the volume of gas is reduced to half from its original volume the specific heat will remain constant.

5. (c) The complete combustion of one mole of butane is represented by

$$C_4H_{10}(g) + \frac{13}{2}O_2(g) \rightarrow 4CO_2(g) + 5H_2O(l)$$

$\Delta_c H$ should be negative and have a value of $2658\ kJ\ mol^{-1}$.

6. **(b)** $\Delta_f H^\circ = \Delta_f U^\circ + \Delta n_g RT$
For the reaction, $C(s) + 2H_2(g) \rightarrow CH_4(g)$
$\Delta n_g = 1 - 2 = -1$
$\therefore \quad \Delta_f H^\circ = \Delta U - 1 \times RT \quad \therefore \quad \Delta_f H^\circ < \Delta_f U^\circ$

7. **(c)** For free expansion, $W = 0$; and
For Adiabatic process, $q = 0$
According to first law of thermodynamics, $\Delta U = q + W = 0$
Since, there is no change in ΔU hence, temperature change will be zero *i.e.*, $\Delta T = 0$

8. **(b)** Area under the curve is always greater in irreversible compression than that in reversible compression.

9. **(c)** During the process of freezing, energy is released which is absorbed by the surroundings.

$\therefore \quad \Delta S_{sys} = -\dfrac{q_{rev}}{T}$

$\Delta S_{surr} = \dfrac{q_{rev}}{T}$ *i.e.*, on freezing, entropy of the system decreases and of surrounding increases.

10. **(c)**
(a) C (graphite) + $O_2(g) \rightarrow CO_2(g)$; $\Delta_r H = x$ kJ mol^{-1} … (i)
(b) C (graphite) + $\frac{1}{2}O_2(g) \rightarrow CO(g)$; $\Delta_r H = y$ kJ mol^{-1} … (ii)
On subtracting eqn (i) & (ii) we get
$CO(g) + \frac{1}{2}O_2(g) \rightarrow CO_2(g); \Delta_r H = z$ kJ mol^{-1}
Hence, $x - y = z$ or $x = y + z$

11. **(c)** x > y because same bonds are formed in reaction (1) and (2) but no bonds are broken in reaction (1) whereas in reaction (2) bonds in the reactant molecules are broken. As energy is absorbed when bonds are broken, energy released in reaction (1) is greater than that in reaction (2).

12. **(a)** Area under the p-V curve is maximum in the first option, which is equal to work done.

13. **(d)** For a spontaneous process, $\Delta S_{total} > 0$ and since irreversible process is always spontaneous therefore $\Delta S_{total} > 0$.
Since $\Delta U = nC_V\Delta T$ and $\Delta T = 0$ for isothermal process therefore $\Delta U = 0$.

14. **(d)** Free expansion of ideal gas
$P_{ex} = 0$
$\therefore w = -P_{ex}\Delta V = 0$
$\because$ Adiabatic process $\Rightarrow q = 0$
$\Delta E = q + w$ (first law of thermodynamics)
$\therefore \Delta E = 0$
$\Delta E = nC_v dT \Rightarrow \Delta E = 0$
So, $q = 0, \Delta T = 0, w = 0$.

15. **(c)** We know that, $Cl_2(g) \longrightarrow 2Cl(g)$ is endothermic reaction because it required energy to break bond.
So reverse reaction, $2Cl(g) \longrightarrow Cl_2(g)$ will be exothermic, $\Delta_r H < 0$.
Also, two gaseous atom combine together to form 1 gaseous molecule.
So, randomness decreases i.e., $\Delta_r S < 0$.

16. **(a)** $W = -P_{ext}(V_2 - V_1)$ (Irreversible isothermal expansion)
$= -2\,(0.25 - 0.1) = -2\,(0.15) = -0.3$ L Bar
$= -0.3 \times 100$ J $= -30$ J

17. **(d)** In $2H(g) \longrightarrow H_2(g)$, no. of species decreases, therefore entropy decreases.

18. **(d)** Let B.E of X_2, Y_2 and XY are x kJ mol^{-1}, $0.5\,x$ kJ mol^{-1} and x kJ mol^{-1} respectively.

$\frac{1}{2}X_2 + \frac{1}{2}Y_2 \rightarrow XY; \ \Delta H = -200$ kJ mol^{-1}

$\Delta H = -200 = \Sigma\,(B.E)_{Reactants} - \Sigma(B.E)_{Product}$

$= \left[\frac{1}{2}\times(x) + \frac{1}{2}\times(0.5x)\right] - [1\times(x)]$

On solving, $x = 800$ kJ mol^{-1}

19. **(a)** Given $\Delta H = 35.5$ kJ mol^{-1}
$\Delta S = 83.6$ JK^{-1} mol^{-1}
$\because \Delta G = \Delta H - T\Delta S$
For a reaction to be spontaneous, ΔG = –ve
i.e., $\Delta H < T\Delta S$

$\therefore \quad T > \dfrac{\Delta H}{\Delta S} = \dfrac{35.5\times10^3 \text{ Jmol}^{-1}}{83.6 \text{ JK}^{-1}}$

So, the given reaction will be spontaneous at $T > 425$ K

20. **(b)** The system is in isolated state.
$\because$ For an adiabatic process, $q = 0$
$\Delta U = q + w$
$\therefore \quad \Delta U = w = -P\Delta V = -2.5$ atm $\times (4.5 - 2.5)$ L
$= -2.5 \times 2$ L-atm $= -5 \times 101.3$ J $= -506.5$ J ≈ -505J
[1 lit - atm = 101.3 J]

21. **(c)** $\Delta G = \Delta H - T\Delta S$
For a spontaneous reaction ΔG = –ve (always)
which is possible only if
$\Delta H < 0$ and $\Delta S > 0$
$\therefore$ spontaneous at all temperatures.

22. **(c)** $C_2H_6(g) + \frac{7}{2}O_2(g) \longrightarrow 2CO_2(g) + 3H_2O(l)$
Heat of combustion
$= \Sigma\Delta_f H_{(\text{products})} - \Sigma\Delta_f H_{(\text{reactants})}$
$\Delta_c H(C_2H_6, g) = 2\Delta H_c(C, s) + 3\Delta_c H(H_2, g) - \Delta_f H(O_2, g) - \Delta_f H(C_2H_6, g)$
$\Rightarrow \quad -1560 = 2(-394) + 3(-286) - 0 - \Delta_f H(C_2H_6, g)$
$\Rightarrow \quad \Delta_f H(C_2H_6, g) = -86$ kJ mol^{-1}

23. **(336)** Given chemical reaction:

$A \xrightarrow[T\ 300K]{} B \ \Delta G = -49.4$ kJ / mol

$\Delta H = 51.4$ kJ/mol
$\Delta S = ?$

$\Rightarrow$ From the relation $\Delta G = \Delta H - T\Delta S$

$$\Rightarrow \Delta S = \frac{\Delta H - \Delta G}{T}$$

$$= \frac{[51.4-(-49.4)]\times 1000}{300}\frac{J}{mol\ K}$$

$\Rightarrow$ $\Delta S = 336\ JK^{-1}\ mol^{-1}$.

24. **(–2.70)** $\Delta U = 2.1$ kcal $= 2.1 \times 10^3$ cal

$\Delta n_g = 2$

$\Delta H = \Delta U + \Delta n_g RT = 2.1 \times 10^3 + 2 \times 2 \times 300$

$= 2100 + 1200 = 3300$ cal

$\Delta G = \Delta H - T\Delta S = 3300 - 300 \times 20$

$= 3300 - 6000 = -2700$ cals $= -2.7$ kcal

25. **(b)** For reversible isothermal expansion,

$$w = -nRT \ln \frac{V_2}{V_1}$$

$$|w| = nRT \ln \frac{V_2}{V_1}$$

$|w| = nRT(\ln V_2 - \ln V_1)$

$|w| = nRT \ln V_2 - nRT\ V_1$

$y = mx + c$

So, slope of curve 2 is more than curve 1 and intercept of curve 2 is more negative than curve 1.

26. **(a)** We know that heat and work are not state functions but $q + w = \Delta U$ is a state function. $H - TS$ (i.e. G) is also a state function.

27. **(a)** $\Delta G = -RT \ln K \Rightarrow \Delta H - T\Delta S = -RT \ln K$

$$\Rightarrow \ln K = \frac{-\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R}$$

$\Delta H = -$ve exothermic reaction

$$\text{slope} = \frac{-\Delta H^\circ}{R} = +\text{ve}$$

So from graph, line should be A and B.

28. **(d)** $C_6H_6(l) + \frac{15}{2}O_2(g) \rightarrow 6CO_2(g) + 3H_2O(l)$

$\Delta n_g = 6 - 7.5 = -1.5$

ΔU or $\Delta E = -3263.9$ kJ

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

So, $\Delta H = -3263.9 + -1.5 \times 8.314 \times 10^{-3} \times 298$

$= -3267.6$ kJ

29. **(c)** From 1st law of thermodynamics

$\Delta U = q + w$

For adiabatic process,

$q = 0 \Rightarrow \Delta U = w$

30. **(b)** Given

$C(s) + O_2(g) \rightarrow CO_2(g);\quad \Delta H = -393.5\ kJ\ mol^{-1}$ ...(i)

$CO(g) + \frac{1}{2}O_2(g) \rightarrow CO_2(g);\ \Delta H = -283.5\ kJ\ mol^{-1}$ ...(ii)

$\therefore$ Heat of formation of CO = eq^n(i) – eq^n(ii)

$= -393.5 - (-283.5) = -110$ kJ

EXERCISE - 3

1. **(b)** A – (q), B – (s), C – (p), D – (r)

2. **(a)** A – (p), B – (s), C – (r), D – (q)

3. **(b)**

4. **(c)** A – (r), B – (p), C – (q), D – (s)

5. **(b)** A – (r), B – (p), C – (q), D – (s)

For spontaneity, $\Delta H - T\Delta S < 0$

6. **(d)** The positive sign expresses when work is done on the system. Similarly, negative sign expresses when work is done by the system.

7. **(a)** In case of isothermal expansion, maximum work done is obtained in reversible process rather than irreversible process and work done is positive in case of isothermal compression.

8. **(c)** All the statements regarding spontaneity of a reaction are correct.

9. **(c)** Standard state of solid iron at 298 K is pure iron at 1 bar. The standard conditions are denoted by adding the superscript $\ominus$ to the symbol ΔH *e.g.*, $-\Delta H^\ominus$.

10. **(d)** A process is spontaneous only when there is decrease in the value of free energy, *i.e.*, ΔG is –ve.

11. **(a)** Third law of Thermodynamics.

12. **(b)** Spontaneity of reaction depends on tendency to acquire minimum energy state and maximum randomness. For a spontaneous process in an isolated system, the change in entropy is positive.

13. **(b)** For adsorption $\Delta S < 0$ and for a spontaneous change $\Delta G = -$ ve

hence, ΔH should be highly negative which is clear from the equation

$\Delta G = \Delta H - T\Delta S = -\Delta H - T(-\Delta S) = -\Delta H + T\Delta S$

So, if ΔH is highly negative ΔG will be (– ve)

14. **(a)** It is fact that absolute values of internal energy of substances cannot be determined. It is also true that it is not possible to determine exact values of constitutent energies of a substance.

15. **(c)** It may involve increase or decrease in temperature of the system. Systems in which such processes occur, are thermally insulated from the surroundings.

16. **(b)** The mass and volume depend upon the quantity of matter so these are extensive properties while ratio of mass to its volume does not depend upon the quantity of matter so this ratio is an intensive property.

17. **(a)** In case of electric fan, electrical energy is converted into mechanical energy and in case of heater, electrical energy is converted into heat energy. Therefore, these follow the first law of thermodynamics.

18. **(b)** In an isothermal process change in internal energy (ΔE) is zero (as it is a function of temperature).
$\therefore$ According to first law of thermodynamics
$\because$ $Q + W = \Delta E$. Hence $Q = -W$ (if $\Delta E = 0$)
If a system undergoes a change in which internal energy of the system remains constant (i.e. $\Delta E = 0$) then $-W = Q$. This means that work done by the system equals the heat absorbed by the system.

19. **(c)** The value of enthalpy of neutralisation of weak acid by strong base is less than 57.1 kJ. This is due to the reason that the part of energy liberated during combination of H^+ and OH^- ions is utilised in the ionisation of weak acid.

20. **(b)** The factor $T\Delta S$ increases with increase in temperature.

EXERCISE - 4

1. **(c)** $I_2(s) \longrightarrow I_2(g)$
Heat of reaction depend upon temperature i.e., it varies with temperature, as given by Kirchoff's equation,

$$\Delta H_{T_2} = \Delta H_{T_1} + \int_{T_1}^{T_2} \Delta C_p dT$$

where $\Delta C_p = C_p$ of product $- C_p$ of reactant

$\therefore\quad \Delta C_p = 0.031 - 0.055 = -0.024$ cal/g

Now, $\Delta H_{T_2} - \Delta H_{T_1} = \Delta C_p(T_2 - T_1)$

$\Delta H_{(250)} - \Delta H_{(200)} = -0.024\,(523 - 473)$

$\Delta H_{(250)} = 24 - 50 \times 0.024 = 22.8$ cal/g

2. **(c)** (a) From charle's law : $V \propto T$

$\Rightarrow\quad V = k_1 T \qquad$ (at cons. P)

$$\Rightarrow \left(\frac{dV}{dT}\right)_P = k_1 \neq 0$$

(b) From Gay Lussac's law :
$P \propto T \qquad$ (at cons. V)

$\Rightarrow\quad P = K_2 T$

$$\Rightarrow \left(\frac{dP}{dT}\right)_V = k_2 \neq 0$$

(c) For an ideal gas, change in internal energy is zero at constant temperature. $(dU)_T = 0$

$$\Rightarrow \left(\frac{dU}{dV}\right)_T = 0$$

(d) $\Delta U = nC_V \Delta T \qquad$ (at cons. V)

$$\Rightarrow \left(\frac{dU}{dT}\right)_V = nC_V \neq 0$$

3. **(c)** $\Delta H = (n_1 C_{p,m_1} + n_2 C_{p,m_2})\,\Delta T$

$$= \left(0.5 \times \frac{7}{2}R + 0.5 \times 4\,R\right)(-100)$$

$= -375\,R \qquad$ (ΔH is defined at cons. P)

4. **(c)** $w = -P_{ext}(V_f - V_i)$

$$= -10^5 \left(\frac{60 \times 10^{-3}}{0.60} + \frac{40 \times 10^{-3}}{1000} - \frac{100 \times 10^{-3}}{1000}\right)$$

$= -10^5\,(100 \times 10^{-3} + 0.04 \times 10^{-3} - 0.1 \times 10^{-3})$

$|w| = 9994$ J

5. **(d)** $\Delta G° = -RT \ln K_P$; initial mole
mole at e.g. Mole fraction partial pressure

$$NH_2COONH_4(s) \rightleftharpoons 2NH_3(g) + CO_2(g)$$

1	0	0
$1 - z$	$2z$	z
	$\frac{2}{3} \times 3X$	$\frac{1}{3} \times 3X$

$K_p = (2X)^2 \times X \Rightarrow K_p = 4X^3$

$\Delta G° = RT \ln K_p \Rightarrow \Delta G° = -RT \ln (4X^3)$

$\Delta G° = -RT \ln 4 - 3RT \ln X$

6. **(d)** ΔH needed for change $= \Delta H_{heating} + \Delta H_{vaporisation}$

$= 50 \times 10^3 \times 1 \times (100 - 10)°C + 540 \times 50 \times 10^3$

$= 31500 \times 10^3$ cal

ΔH actually needed $= \dfrac{31500 \times 10^3 \times 100}{60}$

(Since only 60% of heat is used to do so)

Now 368×10^3 cal heat is given on combustion by 22.4 litre C_2H_6

$\therefore\quad \dfrac{31500 \times 10^3 \times 100}{60}$ heat is given by

$$= \frac{22.4 \times 31500 \times 10^3 \times 100}{60 \times 368 \times 10^3}$$

$= 3.196 \times 10^3$ litre $= 3.196\,m^3$

7. **(b)** $\frac{1}{2}N_2(g) + \frac{3}{2}H_2(g) \longrightarrow NH_3(g)$

$$\frac{1}{2}(N \equiv N) + \frac{3}{2}(H\text{–}H) \longrightarrow \underset{\substack{|\\ H}}{H - N - H}$$

$$\Delta H_f^\circ = \frac{1}{2}\Delta H_{N\equiv N} + \frac{3}{2}\Delta H_{H-H} - 3\Delta H_{N-H}$$

$$\Delta H_f^\circ = \frac{1}{2}x_1 + \frac{3}{2}x_2 - 3x_3$$

8. **(b)** $\dfrac{C_P}{C_V} = \gamma$ and $C_P - C_V = R$

$$C_P - \frac{C_P}{\gamma} = R$$

$$\Rightarrow\quad C_P\left(\frac{\gamma - 1}{\gamma}\right) = R \;\Rightarrow\; C_P = \frac{\gamma R}{\gamma - 1}$$

$$\gamma C_V - C_V = R$$

$$\Rightarrow\quad C_V(\gamma - 1) = R \;\Rightarrow\; C_V = \frac{R}{\gamma - 1}$$

9. **(d)** In case of dissociation of CH_4, the dissociation energy is equal to the energy required to break four C – H bonds.

$\therefore$ C – H bond energy $= \frac{360}{4} = 90$

In case of dissociation of C_2H_6
6 C – H bonds and one C – C bond break
$\therefore$ C – C bond energy = 620 – 6 × 90
= 620 – 540 = 80 k cal/mol

10. **(a)** $N_2(g) + \frac{1}{2}O_2 \to N_2O(g)$

$N \equiv N(g) + \frac{1}{2}(O = O) \to \ddot{N} = \overset{+}{N} = \ddot{O}$ (g)

ΔH_f° = [Energy required for breaking of bonds] −[Energy released for forming of bonds]

$= (\Delta H_{(N\equiv N)} + \frac{1}{2}\Delta H_{(O=O)}) - (\Delta H_{N=N} + \Delta H_{(N=O)})$

$= (946 + \frac{1}{2} \times 498) - (418 + 607) = 170 \text{ kJ mol}^{-1}$

Resonance energy = Observed $\Delta_f H^\circ$ – Calculated $\Delta_f H^\circ$
= 87 – 170 = –88 kJ mol^{-1}

11. **(b)** $\Delta H_{S-S} + 2\Delta H_{H-S} = 239$, $2\Delta H_{H-S} = 175$

Hence, $\Delta H_{S-S} = 239 - 175 = 64 \text{ kcal mol}^{-1}$

Then, ΔH for $8S(g) \to S_8(g)$ is 8 × (–64) = –512k cal

12. **(c)** At constant volume, $\frac{P_1}{T_1} = \frac{P_2}{T_2}$

$\Rightarrow P_2 = 1 \times \frac{300}{200} = \frac{3}{2}$ atm = 1.5 atm

and $V_1 = 24.63$ L

$\because$ $dG = Vdp - SdT$

$$\int_1^2 dG = V\int_1^2 dP - \int_{200}^{300} \left(2 + 10^{-2}T\right) dT$$

$$G_2 - G_1 = V(P_2 - P_1) - \left[2T + \frac{10^{-2}}{2}T^2\right]_{200}^{300}$$

$$\Delta G = V\Delta P - 2(300 - 200) - \frac{10^{-2}}{2}(300^2 - 200^2)$$

$$\Delta G = 24.63(1.5 - 1) - 200 - \frac{10^{-2}}{2}(5 \times 10^4)$$

$$\Delta G = 12.315 \times 100 \text{ J} - 450 \text{ J}$$

ΔG = 781.5 J [1L-atm = 100 J]

13. **(b)** $\Delta G = -P\Delta V$ = Work done

ΔV is the change in molar volume in the conversion of graphite to diamond.

$$\Delta V = \left(\frac{12}{3.31} - \frac{12}{2.25}\right) \times 10^{-6} m^3 = -1.708 \times 10^{-6} m^3$$

Work done = –(–1.708 × 10^{-6}) × P J
1895 Jmol^{-1} = – (– 1.708 × 10^{-6}) × P J

$$\therefore P = \frac{1895 \text{J mol}^{-1}}{1.708 \times 10^{-3}} = 1109.4 \times 10^6 \text{ Pa}$$

= 11.094 × 10^8 Pa

14. **(d)** Given : H = $f(P, T)$

$$dH = \left(\frac{\partial H}{\partial T}\right)_P \cdot dT + \left(\frac{\partial H}{\partial P}\right)_T \cdot dP$$

At constant pressure $\frac{\Delta H}{\Delta T} = C_P$,

Thus, $dH = C_P \cdot dT + \left(\frac{\partial H}{\partial P}\right)_T \cdot dp$

We know that $H = U + PV$

$$\left(\frac{\partial H}{\partial P}\right)_T = \left(\frac{\partial H}{\partial P}\right)_T + P\left(\frac{\partial V}{\partial P}\right)_T + V\left(\frac{\partial P}{\partial P}\right)_T$$

$$\left(\frac{\partial H}{\partial P}\right)_T = 0 + P\left[\frac{\partial}{\partial P}\left(\frac{RT}{P}\right)\right]_T + V$$

[At constant temperature $\Delta U = 0$ and $PV = RT$]

$$\left(\frac{\partial H}{\partial P}\right)_T = PRT\left(-\frac{1}{P^2}\right) + V$$

$$\left(\frac{\partial H}{\partial P}\right)_T = -\frac{RT}{P} + V = -V + V = 0$$

EXERCISE - 5

1. **(395)** Since, work is done against constant pressure and thus, irreversible.

Given, ΔV = (6 – 2) = 4 L; P = 1 atm

$\therefore$ W = – 1 × 4 L-atm = $-\frac{1 \times 4 \times 1.987}{0.0821}$ cal

(since 0.0821 L-atm = 1.987 cal)

= – 96.81 cal = – 96.81 × 4.184 J ($\because$ 1 cal = 4.184 J)

= – 405.05 J

Now from Ist law of thermodynamics
q = ΔU – W ⇒ 800 = ΔU + 405.05 $\therefore$ ΔU = 395 J

2. **(57)** $\Delta H = \Delta U + \Delta n_g RT$

$\Delta n_g = n_R(g) - n_p(g) = 2 - 1 = 1$

$\Delta H = -59.6 + 1 \times 8.314 \times 300 \times 10^{-3} = -57.10$

3. **(–328)** Applying Hess's Law

$$\Delta_f H^\circ = \Delta_{sub}H + \frac{1}{2}\Delta_{diss}H + \text{I.E.} + \text{E.A} + \Delta_{lattice}H$$

$$-617 = 161 + 520 + 77 + \text{E.A.} + (-1047)$$

$\text{E.A.} = -617 + 289 = -328 \text{ kJ mol}^{-1}$

$\therefore$ electron affinity of fluorine

$= -328 \text{ kJ mol}^{-1}$

4. **(–964)** Given $\frac{1}{2}N_2 + \frac{3}{2}H_2 \rightleftharpoons NH_3$;

$$\Delta H_f = -46.0 \text{ kJ / mol}$$

$$H + H \rightleftharpoons H_2;\ \Delta H_f = -436 \text{ kJ / mol}$$

$$N + N \rightleftharpoons N_2;\ \Delta H_f = -712 \text{ kJ / mol}$$

$$\Delta H_f(NH_3) = \frac{1}{2}\Delta H_{N-N} + \frac{3}{2}\Delta H_{H-H} - \Delta H_{N-H}$$

$$-46 = \frac{1}{2}(-712) + \frac{3}{2}(-436) - \Delta H_{N-H}$$

On calculation

$$\Delta H_{N-H} = -964 \text{ kJ / mol}$$

5. **(20)** $HA + aq \rightarrow H^+_{(aq)} + A^-_{(aq)}, \Delta H = x \text{ kJ mol}^{-1}$

$$H^+_{(aq)} + OH^-_{(aq)} \rightarrow H_2O_{(\ell)}\ \ \Delta H = -57.3 \text{ kJ mol}^{-1}$$

Hence, $HA + OH^-_{(aq)} \rightarrow H_2O_{(\ell)} + A^-_{(aq)},$

$\Delta H = x - 57.3$

But $\Delta H = x - 57.3 = -56.1$ (given),

$x = 1.2 \text{ kJ mol}^{-1}$

if no self ionization of HA occurs at all,

$\Delta H(\text{ionization}) = 1.5 \text{ kJ mol}^{-1}$

Hence, % ionization in 1 M solution

$$= \frac{(1.5 - 1.2)}{1.5} \times 100 = 20$$

6. **(–8.575)** (i) $CuSO_4(s) + H_2O \longrightarrow CuSO_4(aq)$

$$\Delta H = \frac{-1.451}{0.2} = -7.255 \text{ k cal mol}^{-1}$$

(ii) $CuSO_4.5H_2O(s) \longrightarrow CuSO_4(aq) + 5H_2O$

$$\Delta H = \frac{0.264}{0.2} = 1.32 \text{ k cal mol}^{-1}$$

From (i) – (ii),

$$CuSO_4(s) + 5H_2O(l) \longrightarrow CuSO_4.5H_2O(s);$$

$$\Delta H = -8.575 \text{ k cal mol}^{-1}$$

7. **(83.8)** Molar heat capacity at constant pressure,

$C_p = 248.2 \times M \text{ J kg}^{-1}$

where M is the molar mass of the gas.

Similarly, $C_v = 149 \times M \text{ J kg}^{-1}$

$C_p - C_v = R$

$\therefore 248.2 \times M - 149M = 8.314$

$$M = \frac{8.314}{248.2 - 149} = 0.0838 \text{ kg/mol}$$

Molar mass of the gas = 83.8 g/mol

8. **(2.76)** Given :

$\Delta S^\circ_{CO_2} = 213.5 \text{ JK}^{-1}$; $\Delta S^\circ_{C(s)} = 5.74 \text{ JK}^{-1}$;

$\Delta S^\circ_{O_2} = 205 \text{ JK}^{-1}$

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

Standard entropy of formation of $CO_2(g)$

$$= \Delta S^\circ_{CO_2} - [\Delta S^\circ_{C(s)} + \Delta S^\circ_{O_2}]$$

$$= 213.5 - [5.740 + 205] = 2.76 \text{ JK}^{-1}$$

9. **(158)** ΔH° for reaction

$$= \left[H^\circ_{TiCl_4}(l) + H^\circ_{O_2}(g) - H^\circ_{TiO_2} - H^\circ_{Cl_2} \times 2\right]$$

$$= \left[-804.2 + 0.0 - (-944.7) - 0.0\right] = 140.5 \text{ kJ}$$

Also, ΔS° for reaction

$$= \left[S^\circ_{TiCl_4}(l) + S^\circ_{O_2}(g) - S^\circ_{TiO_2}(s) - S^\circ_{Cl_2}(g) \times 2\right]$$

$$= [252.3 + 205.1 - 50.3 - 2 \times 233.0]$$

$$= -58.9 \text{ J} = -0.0589 \text{ kJ K}^{-1}$$

Now, $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ = 140.5 - 298 \times (-0.0589) = 158 \text{ kJ}$

10. **(600)** $Mg(s) + \frac{1}{2}O_2(g) \longrightarrow MgO(s)$

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

$$\Delta n_g = \Sigma n_P - \Sigma n_R = 0 - \frac{1}{2} = -\frac{1}{2}$$

$$-601.70 \times 10^3 = \Delta U - \frac{1}{2} \times 8.3 \times 300$$

$$-601.70 \text{ kJ} = \Delta U - 1.245 \text{ kJ}$$

$$\Delta U = -600.455 \text{ kJ} \approx -600 \text{ kJ}$$