CHAPTER > 06

Thermodynamics

KEY NOTES

- **Thermodynamics** deals with the study of different energy transformations and the quantitative relationship between them.
- The laws of thermodynamics deals with change in energy of the macroscopic systems involving a large number of molecules rather than microscopic systems which contains small number of molecules.

Thermodynamic Terms

- A **system** in thermodynamics refers to that part of universe in which observations are made and remaining universe constitutes the **surroundings**.
- For all practical purposes, the surroundings are that portion of the remaining universe which can interact with system.
- The wall that separate the system from the surroundings is called **boundary**.
- Depending upon the movement of matter or energy in or out of the system, the system can be classified as :
  - **Open system** In which energy and matter both can be exchanged with surroundings, e.g. presence of reactants in an open beaker.
  - **Closed system** In which only energy can be exchanged with surroundings, e.g. hot water kept in closed container.
  - **Isolated system** In which neither matter nor energy can be exchanged with surroundings, e.g. thermos flask.
- **Extensive properties** are those properties which depend upon the quantity or size of matter, e.g. mass, volume, internal energy, enthalpy, heat capacity, etc.
- **Intensive properties** are those which do not depend upon the quantity or size of matter, e.g. pressure, temperature, concentration, viscosity, etc.

Note : *Ratio of two extensive properties become intensive in nature.*

- The state of a system is described by its measurable properties such as T, V, p etc., of the system.
- These properties of the system are called **state variables** or **state functions** as their values depends upon the state of the system and not on the path followed.
- The variables, values of which is affected by the path followed are called **path functions,** e.g. work (W), heat (q), etc.

Thermodynamic Process

The state of a system can be changed *via* thermodynamic process. These processes are of the following types :

- **Adiabatic process** The process in which system does not exchange heat with its surrounding is called **adiabatic process.** For adiabatic process, $dq = 0$ and $\Delta U = U_2 - U_1 = W_{ad}$.
- **Isothermal process** This process is carried out at constant temperature, i.e. $dT = 0$ and thus, $dE = 0$.
- **Isobaric process** In this process, change of state is brought about at constant pressure, i.e. $dp = 0$
- **Isochoric process** In this process, volume of the system remains constant, i.e. $dV = 0$
- **Cyclic process** When a system has undergone a number of different states and finally returns to its initial state the process is called cyclic process.

$$dE \text{ or } dU = 0 \text{ and } dH = 0$$

- **Reversible process** A system where change takes place infinitesimally slow and the direction of which at any point can be reversed by infinitesimal change in the state of the system.
- **Irreversible process** An irreversible process is one in which direction of that process cannot be reversed by small change in variables.

Internal Energy

In thermodynamics, energy of the system is called internal energy (E or U). It is a state function.

Heat and Work

- Heat is defined as the quantity of energy which flows between system and surroundings on account of temperature difference.

  It is also a path function. It is given as,

  $$q = mc\Delta t$$

  where, c is specific heat capacity, m is mass of substance and Δt is rise in temperature.
- Work of the system involves gaseous substances and there is a difference of pressure between system and surroundings, work is referred as pressure-volume work.
- If mechanical work is done in a single step, i.e. W is the work done on the system by movement of pistol, then

  $$W = -p_{\text{ext}}\ \Delta V$$

  or $$W = -p_{\text{ext}}(V_f - V_i)$$

Note *The negative sign (–ve) represents the work is done by the system in case of expansion. In case of compression, the sign should be positive (+ve).*

- If the pressure-volume work is done in a number of steps, i.e.

  (i) If the pressure changes in number of steps, then work done on the gas will be given as :

  $$W = -\Sigma p\Delta V$$

  (ii) If pressure is not constant at each stage of compression and the process is reversible isothermal, then work done is given as :

  $$W_{\text{rev}} = -\int_{V_i}^{V_f} p_{\text{int}}\ dV$$

  or $$W_{\text{rev}} = -2.303\ nRT\log\frac{V_f}{V_i}$$

  or $$W_{\text{rev}} = -2.303\ nRT\ \log\frac{p_i}{p_f}$$

  where, n = number of moles of gas

  R = gas constant, T = temperature (in K)

  V_i = initial volume, V_f = final volume

  p_i = initial pressure, p_f = final pressure
- Work done is maximum in case of **reversible isothermal expansion of a gas.**
- In case of **free expansion,** a gas expands under vacuum ($p_{\text{ext}} = 0$). In this case, W is also zero, i.e. no work is done.

First Law of Thermodynamics

- According to first law of thermodynamics, the energy can neither be created nor be destroyed but can be converted into one form to another.

  That's why, it is also called **law of conservation of energy**.
- The mathematical expression of first law of thermodynamics is given as,

  $$\Delta U = q + W$$

  where, ΔU = change in internal energy

  q = heat consumed

  W = work done on the system
- If there is no heat transfer or work done (i.e. in a isolated system), ΔU will be zero.
- If a process is carried out at constant volume, then $\Delta U = qV$. (Here, V denotes that heat is supplied at constant volume).
- For isothermal irreversible charge, $q = -W = p_{\text{ext}}(V_f - V_i)$ and for isothermal reversible change.

  $$q = -W = 2.303\ nRT\log\frac{V_f}{V_i}$$

Sign Convention

- q is +ve = heat is supplied to the system.
- q is – ve = heat is lost by the system.
- W is +ve= work done on the system.
- W is – ve = work done by the system
- ΔU is – ve = energy transfer from system to surrounding.
- ΔU is +ve = energy transfer from surrounding to system.

Enthalpy

The total heat content of a system at constant pressure is called **enthalpy of the system**.
It is a state function and is given by the expression
$\Delta H = \Delta U + p\Delta V$.

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

- At constant volume; $\Delta U = q_V$, i.e. heat supplied at constant volume.
- $\Delta H = -$ ve for an exothermic reaction and $\Delta H = +$ ve for an endothermic reaction.
- For solids and liquids, ΔH and ΔU is insignificant but for gases, if pressure and temperature remains constant, then

  $$p\Delta V = \Delta n_g RT$$

  Here, $$\Delta n_g = n_P - n_R$$

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

Heat Capacity

- Heat capacity (C) of a system is defined as the amount of heat required to raise the temperature of the system by 1°C, i.e., $q = C\Delta T$.
- The **molar heat capacity** of the system is defined as the quantity of heat required to raise the temperature of one mole of the substance by one degree Celsius.

  i.e. $$C_m = \frac{C}{n}$$

  where, C_m = molar heat capacity

  n = amount of substance

- **Specific heat capacity** of the system is defined as the quantity of heat needed to raise the temperature of one unit mass of a substance by 1°C.

  It is given as,

$$q = m \times C \times \Delta T$$

where, m = mass of the substance.

C = specific heat of the substance

Note *Specific heat capacity of water* $= 1\ \text{cal g}^{-1}\ \text{K}^{-1}$ *or* $4.18\ \text{J g}^{-1}\ \text{K}^{-1}$

- At constant volume, $q = q_V = C_V \Delta T = \Delta U$ and at constant pressure, $q = q_p = C_p \Delta T = \Delta H$.
- For a n moles of an ideal gas, $C_p - C_V = nR$
- Poisson ratio, $\dfrac{C_p}{C_V} = \gamma$; For monoatomic gas, $\gamma = 1.66$, For diatomic gas, $\gamma = 1.40$; For triatomic gas, $\gamma = 1.33$.
- Heat change occurring at constant volume are measured by using bomb-calorimeter and the heat change occurring at constant pressure is measured by coffee cup calorimeter.
- From the temperature change, ΔU calculated by the expression

$$\Delta U = \frac{C \cdot \Delta T \cdot M}{m_i} \quad (M = \text{molar mass},\ m_i = \text{mass})$$

Thermochemical Equation

A thermochemical equation is a balanced chemical equation in which the value of $\Delta_r H^\circ$ is also mentioned.

e.g. $C_2H_5OH(l) + 3O_2(g) \longrightarrow 2CO_2(g) + 3H_2O(l)$; $\Delta_r H^\circ = -1367\ \text{kJ / mol}$

Note *Negative (–ve) sign indicates, it is an exothermic reaction.*

- Some conventions related to thermochemical equations are as follows :
  - (i) The coefficients of different substances in a balanced thermochemical equation show only their number of moles (never molecules) involved in that reaction.
  - (ii) On reversing a reaction, the sign of ΔH is also reversed but its magnitude remain the same.
  - (iii) Enthalpy is an extensive property, thus if a thermochemical equation is multipled or divided by an integer, n, the value of $\Delta_r H^s$ is also multiplied or divided by the integer, n.

Enthalpy Change of a Reaction, $\Delta_r H$

- It is the heat change that accommpanies a chemical reaction represented by a balanced chemical equation.

$$\Delta_r H = \sum_i x_i H_P - \sum_i y_i H_R$$

where, x_i and y_i = stoichiometric coefficients of products and reactants respectively in a balanced equation.

H_P = enthalpy of formation of products

H_R = enthalpy of formation of reactants

Note *Enthalpy change of reaction can also be calculated by bond enthalpy as :*

$$\Delta_r H^\circ = \Sigma_{\text{bond enthalphies of reactants}} - \Sigma_{\text{bond enthalpies of products}}$$

$$\text{or } \Delta_r H^\circ = \Sigma\, \Delta_f H^\circ_{\text{bonds of products}} - \Sigma \Delta_f H^\circ_{\text{bonds of reactants}}.$$

- **Molar enthalpy change** (H_m) is the enthalpy change when quantities (moles) of reactants have reacted completely as indicated by the balanced chemical equation.

  e.g. $CH_4(g) + 2O_2(g) \longrightarrow CO_2(g) + 2H_2O(l)$

$$\Delta_r H = [H_m(CO_2\ (g)) + 2H_m(H_2O\,(l))] - [H_m(CH_4\,(g)) + 2H_m(CO_2\ (g))]$$

- The enthalpy change occurring during a reaction when all the involved substances are in their **standard states**, is called the **standard enthalpy of the reaction**.
- The purest and most stable form of a substance at 1 bar and at a specified temperature is called its **standard state**, e.g. the standard state of solid iron at 500 K is pure iron at 1 bar.

Standard Enthalpy Changes for Different Types of Processes (Based on IUPAC Recommendations)

Transition Enthalpy	Examples	Definition	Symbol
Enthalpy of fusion	$H_2O(s) \longrightarrow H_2O(l)$	One mole of the liquid is formed from the solid in its standard state. In case of freezing, $\Delta_{\text{freezing}} H^\circ$ is negative.	$\Delta_{\text{fus}} H^\circ$ or $\Delta H^\circ_{\text{fus}}$
Enthalpy of vaporisation	$H_2O(l) \longrightarrow H_2O(g)$	One mole of the vapour formed from the liquid at its boiling temperature and under standard pressure.	$\Delta_{\text{vap}} H^\circ$ or $\Delta H^\circ_{\text{vap}}$
Enthalpy of sublimation	$H_2O(s) \longrightarrow H_2O(g)$	One mole of solid is converted into vapours without melting at a temperature below its melting point (and at 1 bar pressure).	$\Delta_{\text{sub}} H^\circ$ or $\Delta H^\circ_{\text{sub}}$
Enthalpy of formation	$H_2(g) + \frac{1}{2}O_2(g) \longrightarrow H_2O(l)$	One mole of the compound formed from its constituent elements, when they are in their most stable states or reference states.	$\Delta_f H^\circ$ or ΔH°_f

Transition Enthalpy	Examples	Definition	Symbol
Enthalpy of combustion	$CH_4(g) + \frac{13}{2} O_2(g) \longrightarrow 4CO_2(g) + 5H_2O(l)$	One mole of the compound (fuel) is burnt completely in oxygen (oxidation) and all the reactants and products are in their standard states. $\Delta_c H^\circ$ is always negative.	$\Delta_c H^\circ$ or ΔH_c°
Enthalpy of atomisation	$H_2(g) \longrightarrow 2H(g)$ (In this case enthalpy of atomisation is same as the bond dissociation enthalpy) $Na(s) \longrightarrow Na(g)$ (Here, enthalpy of atomisation is same as that of sublimation enthalpy.)	One mole of the substance broken into isolated atoms in the gas phase.	$\Delta_a H^\circ$ or ΔH_a°
Bond dissociation enthalpy (bond A—B)	$HX(g) \longrightarrow H(g) + X(g)$	One mole of covalent bond broken when species are in the gaseous phase. In case of polyatomic molecules, instead of bond dissociation enthalpy, mean dissociation enthalpy of all the bonds present in the compound is taken.	ΔH_{A-B}°
Lattice enthalpy	$KCl(s) \longrightarrow K^+(g) + Cl^-(g)$	One mole of an ionic compound dissociates completely into its constituent ions in the gaseous phase.	$\Delta_{\text{lattice}} H^\circ$ or $\Delta H_{\text{lattice}}^\circ$
Enthalpy of solution	$A(s) + H_2O(\text{excess}) \longrightarrow A(aq)$	One mole of the solute dissolved completely in specified amount of solvent. If a large excess of solvent is taken then the interaction between the ions are negligible and the enthalpy change is called enthalpy of solution at infinite dilution.	$\Delta_{\text{sol}} H^\circ$ or $\Delta H_{\text{sol}}^\circ$ $\Delta_{\text{sol}} H^\circ = \Delta_{\text{lattice}} H^\circ + \Delta_{\text{hyd}} H^\circ$
Enthlalpy of dilution	$HCl.25aq + 40aq \longrightarrow HCl.40aq$	Solution containing one mole of a substance is diluted from one concentration to another.	$\Delta_{\text{dil}} H^\circ$ or $\Delta H_{\text{dil}}^\circ$

Note *The most stable state of aggregation of an element at 25°C and 1 bar pressure is called its reference state, e.g.* H_2 *gas is the reference state for dihydrogen and* O_2 *gas is the reference state for dioxygen etc.*

Hess's Law of Constant Heat Summation

According to this law, "the total heat change (ΔH) accompanying a chemical reaction is the same, whether the reaction takes place in one or more steps."

It can be represented as,

$$\Delta H = \Delta H_1 + \Delta H_2 + \Delta H_3 + \ldots$$

$$\begin{tikzcd}
A \arrow[r, "\Delta H"] \arrow[d, "\Delta H_1"'] & B \\
C \arrow[r, "\Delta H_2"'] & D \arrow[u, "\Delta H_3"']
\end{tikzcd}$$

Born-Haber Cycle

- It is an approach to calculate energy involved during a process and is based on the Hess's Law of constant heat summation.
- Lattice enthalpy can be indirectly calculated by Born-Haber cycle as shown below :

$$\begin{tikzcd}
\mathrm{Na}(s) \arrow[dd, "\Delta_{\text{sub}} H^\circ"'] & + \ 1/2\ \mathrm{Cl_2}(g) \arrow[rr, "\Delta_f H^\circ"] \arrow[d, "1/2\ \Delta_{\text{bond}} H^\circ"] & & \mathrm{Na^+Cl^-}(s) \\
 & \mathrm{Cl}(g) \arrow[rr, "\Delta_{eg} H"] & & \boxed{\mathrm{Cl^-}(g) + \mathrm{Na^+}(g)} \arrow[u, "\Delta_{\text{lattice}} H^\circ"'] \\
\mathrm{Na}(g) \arrow[rrru, "\Delta_i H^\circ"'] & & &
\end{tikzcd}$$

Expression for Ionisation Enthalpy and Electron Affinity Using Heat Capacities

Ionisation enthalpy and electron affinity are defined at absolute zero. At any other temperature, heat capacities are considered.

$$\Delta_r H^\circ(T) = \Delta_r H^\circ(0) + \int_0^T \Delta_r C_p^\circ dT$$

and $\Delta_r C_p^\circ = +\frac{5}{2}R$ (for ionisation)

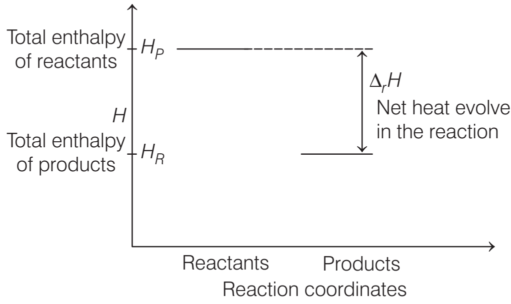
$\Delta_r C_p^\circ = -(5/2)R$ (for electron gain enthalpy)

$\therefore \Delta_r H^\circ$(ionisation enthalpy) $= 1E + (5/2)RT$ and

$\Delta_r H^\circ$(electron gain enthalpy) $= -EA \cdot (5/2)RT$

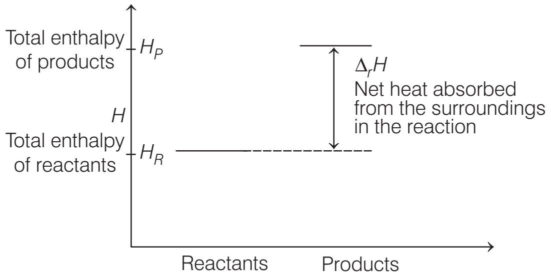
Spontaneity

- A spontaneous process is an irreversible process and may only be reversed by some external agency, e.g. burning of carbon on dioxygen giving CO_2, heat flow, rolling ball, gas flow etc.
- A tendency to attain the minimum energy, i.e. decrease in energy is responsible for the spontaneity or feasibility of a reaction. The enthalpy diagram for an exothermic reaction, showing the decrease in enthalpy when reactants are converted into products is shown below :



Enthalpy diagram for exothermic reactions

- Decrease in energy, the criteria for spontaneity has the following limitation. In case of endothermic reactions, ΔH is positive, i.e. enthalpy of the system increases but there are several endothermic reactions that are spontaneous.
- The enthalpy diagram for such reactions is shown below :



Enthalpy diagram for endothermic reactions

Entropy

- The another thermodynamic function, entropy is introduced for determining spontaneous reaction. It is the measure of degree of randomness or disorderness in an isolated system and is represented by the symbol (S). The greater the degree of randomness, higher is the entropy. It is also a state function.
- For a given substance, the crystalline solid state is the most ordered state and, therefore has the lowest entropy, while gaseous state is the most disordered and has a state of highest entropy.
- Entropy change is inversely proportional to the temperature. For an isothermal reversible process,

$$\Delta S_{\text{system}} = \frac{q_{\text{rev, sys}}}{T}$$

$$\Delta S_{\text{surroundings}} = -\frac{q_{\text{rev, surroundings}}}{T}$$

Total change in entropy of process = Entropy of system + Entropy of surroundings

- The total entropy change for the spontaneous process is given as,

$$\Delta S_{\text{Total}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}} > 0$$

- The change in entropy at equilibrium, i.e. $\Delta S = 0$

Gibbs Energy

- Gibbs function or Gibbs energy is introduced as decrease in enthalpy and increase in entropy cannot determined the spontaneity of the reaction.

It is given as,

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

where, ΔG = change in Gibbs energy
ΔH = change in enthalpy
ΔS = change in entropy

It is an extensive property and a state function.

- The criteria of spontaneity through Gibbs free energies is as follows :

At a given temperature and pressure.

(i) If ΔG is negative, (< 0) the process is spontaneous.
(ii) If ΔG is positive (> 0), the process is non-spontaneous.
(iii) If ΔG is zero, the process is in equilibrium state.

- The various conditions in which a reaction occur spontaneously are tabulated below :

Effect of Temperature on Spontaneity of Reactions

$\Delta_r H^S$	$\Delta_r S^S$	$\Delta_r G^S$	Description
−	+	− (at all T)	Reaction is spontaneous at all temperature.
−	−	− (at low T)	Reaction is spontaneous at low temperature.
−	−	+ (at high T)	Reaction is non-spontaneous at high temperature.
+	+	+ (at low T)	Reaction is non-spontaneous at low temperature.
+	+	− (at high T)	Reaction is spontaneous at high temperature.
+	−	+ (at all T)	Reaction is non-spontaneous at all temperature.

Second Law of Thermodynamics

According to second law of thermodynamics, whenever a spontaneous process takes place, it is always accompanied by increase in total entropy of universe.

Third Law of Thermodynamics

According to third law of thermodynamics, ''the entropy of a perfectly crystalline substance approaches zero as the absolute zero of temperature is approached''.

It forms the basis from which entropies at other temperatures can be measured.

$$\lim_{T \to 0} S = 0$$

Note *In case of* CO *and* NO *molecules in solid state, there is randomness even at* 0 K *due to their dipole moment, hence entropy in such cases is not zero even at* 0 K.

Standard Free Energy Change

The free energy change for a process at 298 K and 1 atm pressure in which the reactants in their standard state are converted into products in their standard state is called standard free energy change.

It is denoted by ΔG°.

$$\Delta_r G^\circ = \begin{bmatrix}\text{Sum of the standard free energy}\\ \text{of formation of products}\end{bmatrix} - \begin{bmatrix}\text{Sum of the standard free energy of}\\ \text{formation of reactants}\end{bmatrix}$$

$$= \Sigma_f G^\circ_{(\text{products})} - \Sigma \Delta_f G^\circ_{(\text{reactants})}$$

- The ΔG° is related to equilibrium constant of the reaction by the following equation,

$$\Delta G = \Delta G^\circ + RT \ln k$$

$\because$ $\Delta G = 0$ at equilibrium

$\therefore$ $\Delta G^\circ = -RT \ln K$ or $-2.303 RT \log K$

Also, $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ - RT \ln K$

- In case of strongly endothermic reactions, ΔH° is large and positive. Therefore, $K <<< 1$ and, thus reaction does not takes place.
- In case of endothermic reaction, ΔH° is large and negative and, therefore $K >>>> 1$.

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MULTIPLE CHOICE QUESTIONS

TOPIC 1 ~ *Thermodynamics Terms*

1 Thermodynamics is based on
(a) initial and final states of a system undergoing to change
(b) rate of reaction
(c) physical and chemical properties of the system
(d) All of the above

2 Thermodynamics, a process is called reversible when
(a) surroundings and system change into each other
(b) there is no boundary between system and surroundings
(c) the surroundings are always in equilibrium with the system
(d) the system changes into the surroundings spontaneously

3 The value of ΔE for an open and isolated system respectively is
(a) zero; non-zero (b) zero
(c) non-zero; zero (d) non-zero

4 Which of the following is an extensive property?
(a) Temperature (b) Density
(c) Gibbs free energy (d) Molar volume

5 Among the following the set of parameters that represents path functions, is ***JEE Main 2019***
(A) $q + W$ (B) q
(C) W (D) $H - TS$
(a) (A) and (D) (b) (A), (B) and (C)
(c) (B), (C) and (D) (d) (B) and (C)

6 On which of the following factor(s) does the internal energy of the system depend?
(a) Matter enters or leaves the system
(b) Work is done on or by the system
(c) Heat passes into or out of the system
(d) All of the above

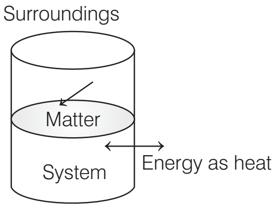
7 A system containing some quantity of water in a thermos flask or in an insulated beaker. This would not allow exchange of heat between the system and surrounding through its boundary. The process applied on the system is called
(a) isothermal process
(b) adiabatic process
(c) isochoric process
(d) isobaric process

8 The scientist who showed that a given amount of work done on the system produced the same change of state as measured by the change in temperature of the system was
(a) J.P. Joule
(b) Maxwell
(c) Rutherford
(d) Newton

9 Which of the following property of a system can be changed by transfer of heat from the surrounding to the system or *vice-versa* without expenditure of work?

(a) Enthalpy (b) Internal energy
(c) Both (a) and (b) (d) None of these

10



Name the type of wall used in the above figure.

(a) Adiabatic walls
(b) Thermally insulating walls
(c) Thermally conducting walls
(d) None of the above

11 If we take water at temperature T_A in a container having thermally conducting walls and enclosed in a huge heat reservoir at temperature T_B. What is the correct expression of change in internal energy if no work is done at constant volume?

(a) $\Delta U = U_B - U_A$ (b) $\Delta U = q$
(c) $\Delta U = W_{\text{ad}}$ (d) All of these

12 The mathematical expression of first law of thermodynamics is

(a) $\Delta U = q$ (b) $\Delta U = W$
(c) $\Delta U = q + W$ (d) $\Delta U = W_{\text{ad}}$

13 W is the amount of work done by the system and q is the amount of heat supplied to the system. Choose the correct option for the change in internal energy and type of a system from the given options respectively.

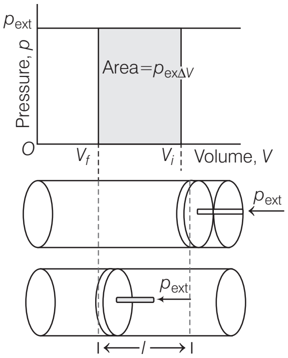
(a) $\Delta U = W_{\text{ad}}$, adiabatic system
(b) $\Delta U = -q$, open system
(c) $\Delta U = q - W$, closed system
(d) None of the above

14 The change in the energy of system if 500 cal of heat energy are added to a system and system does 350 cal of work on the surroundings will be

(a) –150 cal (b) +150 cal
(c) + 850 cal (d) –850 cal

TOPIC 2 ~ *Applications of Thermodynamics Terms*

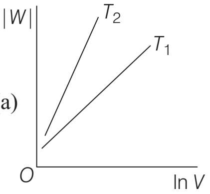
15 What will be the work done on an ideal gas enclosed in a cylinder, when it is compressed by a constant external pressure, p_{ext} in a single step as shown in figure?



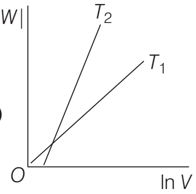
(a) Work done $= -p_{\text{ext}}(V_f - V_i)$
(b) Work done $= -p_{\text{ext}}(V_i - V_f)$
(c) Work done $= +p_{\text{ext}}(V_f - V_i)$
(d) Work done $= -p(V_f - V_i)$

16 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 **JEE Main 2019**

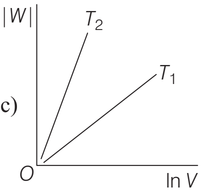
(a)



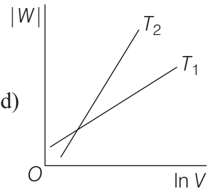
(b)



(c)



(d)



17 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) < 40 kJ (d) Zero

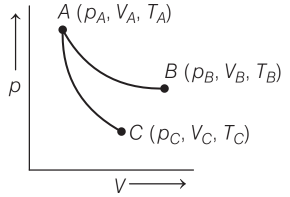
18 An ideal gas expands isothermally from 10^{-3} m^3 to 10^{-2} m^3 at 300 K against a constant pressure of 10^5 Nm^{-2}. The work done on the gas is **NEET (Odisha) 2019**

(a) + 270 kJ (b) − 900 J (c) + 900 kJ (d) − 900 kJ

19 Under isothermal condition, a gas at 300 K expands from 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)

(a) 5 kJ (b) 25 J (c) 30 J (d) -30 J

20 Reversible expansion of an ideal gas under isothermal and adiabatic conditions are as shown in the figure.



$AB \longrightarrow$ Isothermal expansion

$AC \longrightarrow$ Adiabatic expansion

Which of the following option is not correct? ***NEET (Odisha) 2019***

(a) $\Delta S_{\text{isothermal}} > \Delta S_{\text{adiabatic}}$ (b) $T_A = T_B$
(c) $W_{\text{isothermal}} > W_{\text{adiabatic}}$ (d) $T_C > T_A$

21 No work is done on the system, but q amount of heat is taken out from the system and given to the surrounding. The change in internal energy of a system is

(a) $\Delta U = -q$ (b) $\Delta U = +q$
(c) $\Delta U = W_{\text{ad}}$ (d) $\Delta U = q - W$

22 A piston filled with 0.04 mole of an ideal gas expands reversibly from 50.0 mL to 375 mL at a constant temperature of 37.0°C. As it does so, it absorbs 208 J of heat. The values of q and W for the process will be ($R = 8.314 \text{J} / \text{mol K}, \ln 7.5 = 2.01$) ***JEE Main 2013***

(a) $q = +208$ J, $W = -208$ J
(b) $q = -208$ J, $W = -208$ J
(c) $q = -208$ J, $W = +208$ J
(d) $q = +208$ J, $W = +208$ J

23 When heat is absorbed by the system at constant pressure then

(a) $\Delta H = qV$ (b) $\Delta U = qP$ (c) $\Delta H = qP$ (d) $\Delta U = qV$

24 When the expansion of a gas occurs in vaccum and at constant volume, then

(a) $\Delta U = qV$ (b) $\Delta U = qp$ (c) $\Delta H = qV$ (d) $\Delta H = qp$

25 A gas is allowed to expand in a well insulated container against a constant external pressure of 2.5 atm from an initial volume of 2.50 L to a final volume of 4.50 L. The change in internal energy ΔU of the gas in joules will be ***NEET 2017***

(a) 1136.25 J (b) -500 J (c) -505 J (d) $+505$ J

26 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 ($R = 8.314 \text{ JK}^{-1} \text{ mol}^{-1}$) ***JEE Main 2018***

(a) 4152.6 (b) -452.46 (c) 3260 (d) -3267.6

27 When 1 mole of ice melts at 0°C and at a constant pressure of 1 atm, 1440 cal of heat is absorbed by the system. If the molar volume of ice and water are 0.0196 and 0.0180L, then the value of ΔH and ΔU will be

(a) 1440 cal, 1440.039 cal (b) 1440 cal, 1438 cal
(c) 1440.039 cal, 1440 cal (d) 1438 cal, 1440 cal

28 Argon (10 g) is compressed isothermally and reversibly at a temperature of 27°C from 10 L to 5 L. Choose the correct option for ΔH, ΔE, q and W

	ΔH	ΔE	q	W
(a)	0	0	0	0
(b)	+103.980	0	–103.980 cal	0
(c)	0	–103.980	+103.980 cal	0
(d)	0	0	–103.980 cal	+103.980 cal

29 ΔH and ΔE for the reaction,

$$Fe_2O_3(s) + 3H_2(g) \longrightarrow 2Fe(s) + H_2O(l)$$

at constant temperature are related as ***AIIMS 2018***

(a) $\Delta H = \Delta E$ (b) $\Delta H = \Delta E + RT$
(c) $\Delta H = \Delta E + 3RT$ (d) $\Delta H = \Delta E - 3RT$

30 At 25°C, 1 mole of butane is heated then CO_2 and H_2O liquid is formed. The work done for the given process is ***AIIMS 2019***

(a) 75.6 L atm (b) 85.6 L atm
(c) 50.3 L atm (d) None of these

31 Consider the following equation,

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

The magnitude of the coefficient depends on

(a) size (b) composition
(c) nature of the system (d) All of these

32 The quantity of heat needed to raise the temperature of one mole of the substance by one degree celsius and heat required to raise the temperature of one unit mass of a substance by one degree celsius, respectively are

(a) specific heat capacity and molar heat capacity
(b) molar heat capacity and specific heat capacity
(c) specific heat and molar enthalpy
(d) molar heat and molar entropy

33 Calculate the difference between C_p and C_V for 10 moles of an ideal gas.

(a) 83.14 J/K (b) 8.314 J/K
(c) 831.4 J/K (d) 0.831 J/K

34 Choose the correct equation.

(a) $C_m = \frac{C}{n}$ (b) $q = c \times m \times \Delta T$
(c) $C_p - C_V = R$ (d) All of these

35 What is the value of γ for monoatomic gas (ideal gas)? ***JIPMER 2019***

(a) $\frac{7}{5}$ (b) $\frac{4}{3}$

(c) $\frac{5}{2}$ (d) None of these

36 In adiabatic conditions, 2 mole of CO_2 gas at 300 K is expanded such that its volume becomes 27 times. Then, the work done is ($C_V = 6$ cal mol^{-1} and $\gamma = 1.33$)

(a) 1400 cal (b) 1000 cal

(c) 900 cal (d) 1200 cal

TOPIC 3 ~ *Measurement of ΔU and ΔH : Calorimetry*

37 Which of the following conditions is/are applied for the measurement made in calorimeter?

(a) Constant volume, q_V (b) Constant pressure, q_p

(c) Constant temperature, q_T (d) Both (a) or (b)

38 Heat absorbed at constant volume is measured in a calorimeter in which steel vessel is immersed to ensure that

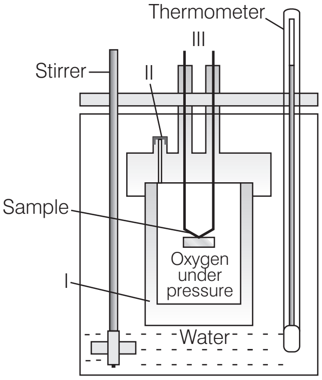
(a) no work is done by the system

(b) no work is done on the system

(c) no heat is lost to the surrounding

(d) no heat is lost by the surrounding

39 The bomb calorimeter diagram is given below.



Choose the correct term for I, II, III in the above figure from the following.

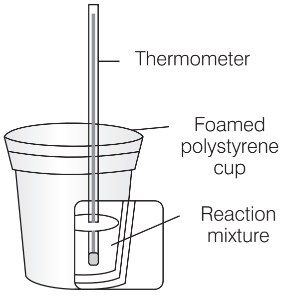
(a) I. Bomb II. Nitrogen inlet III. Firing leads

(b) I. Bomb II. Oxygen inlet III. Firing leads

(c) I. Steel II. Hydrogen inlet III. Graphite rods

(d) I. Plastic II. Oxygen inlet III. Graphite rods

40 The figure given below represents



(a) Calorimeter for measuring heat changes at constant temperature.

(b) Bomb calorimeter for measuring heat changes at constant volume

(c) Calorimeter for measuring heat changes at constant pressure

(d) None of the above

41 For the complete combustion of ethanol,

$$C_2H_5OH(l) + 3O_2(g) \longrightarrow 2CO_2(g) + 3H_2O(l),$$

the amount of heat produced as measured in bomb calorimeter, is 1364.47 kJ mol^{-1} at 25°C. Assuming ideality the enthalpy of combustion, $\Delta_C H$, for the reaction will be ($R = 8.314\,JK^{-1}mol^{-1}$) ***JEE Main 2014***

(a) -1366.95 kJ mol^{-1}

(b) -1361.95 kJ mol^{-1}

(c) -1460.50 kJ mol^{-1}

(d) -1350.50 kJ mol^{-1}

42 In a constant volume calorimeter, 3.5 g of gas with molecular weight = 28 was burnt in excess of oxygen at 298.0 K. The temperature of the calorimeter was found to increase from 298.0 K to 298.45 K due to the combustion process.

Given, that the heat capacity of the calorimeter is 2.5 kJ K^{-1}, the numerical value for the enthalpy of combustion of the gas in kJ mol^{-1} is

(a) 7 (b) 9

(c) 0 (d) 8

43 CCl_2F_2 cooled 1.25 g sample at constant atmospheric pressure of 1 atm from 320 K to 293 K. During cooling the sample volume decreased from 274 to 248 mL. Calculate ΔH for the CCl_2F_2 for this process. ($C_p = 80.7$ J mol^{-1} K^{-1}).

(a) 22.51 J (b) –19.83 J

(c) 19.88 J (d) –22.51 J

44 The molar heat capacity of water at constant pressure is 84 JK^{-1} mol^{-1}. When 1.0 kJ of heat is supplied to 100 g of water which is free to expand; the increase in temperature of water is

(a) 3.8 K (b) 2.1 K

(c) 4.8 K (d) 1.5 K

TOPIC 4~ Enthalpy Change, $\Delta_r H$ of a Reaction-Reaction Enthalpy

45 For the given reaction,

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

The correct expression for $\Delta_r H$ is

(a) $[H_m(CO_2, g) + 2H_m(O_2, g)] - [2H_m(H_2O, l) + H_m(CH_4, g)]$

(b) $[2H_m(O_2, g) + H_m(CH_4, g)] - [H_m(CO_2, g) + 2H_m(H_2O, l)]$

(c) $[H_m(CO_2, g) + 2H_m(H_2O, l)] - [H_m(CH_4, g) + 2H_m(O_2, g)]$

(d) $[H_m(CO_2, g) + H_m(H_2O, l)] - [H_m(CH_4, g) + 2H_m(O_2, g)]$

46 The melting of ice

(a) is the phase transformation
(b) takes place at constant pressure and temperature
(c) take place at 373 K
(d) Both (a) and (b)

47 Standard enthalpy of vaporisation $\Delta_{vap}H^\circ$ for water at 100ºC is 40.66 kJ mol^{-1}. The internal energy of vaporisation of water at 100°C (in kJ mol^{-1}) is (Assume water vapour to behave like an ideal gas).

CBSE AIPMT 2012

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

48 If the sublimation energy and enthalpy of fusion of I_2 are 57.3 kJ mol^{-1} and 15.5 kJ mol^{-1}, respectively then, the enthalpy of vaporisation of I_2 will be

(a) –72.8 kJ mol^{-1} (b) 72.8 kJ mol^{-1}
(c) – 41.8 kJ mol^{-1} (d) +41.8 kJ mol^{-1}

49 The standard enthalpy of formation of $NH_3(g)$ is – 81.9 kJ mol^{-1}. The amount of heat required to decompose 26 g of NH_3 (g) into its elements, is

(a) 122.9 (b) 143.8 (c) 164.7 (d) 105.6

50 How much of heat is required by the chemical reaction in order to decompose $CaCO_3$ to lime and CO_2? (Standard molar enthalpies of formation is given in the table).

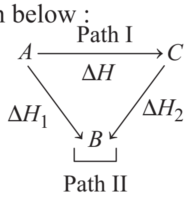
Substance	$\Delta_f H^\circ$/(kJ mol^{-1})
$CaCO_3(s)$	–1206.92
CaO (s)	– 635.09
$CO_2(g)$	–393.51

(a) 187 kJ mol^{-1} (b) 170.0 kJ mol^{-1}
(c) 178.3 kJ mol^{-1} (d) Cannot be determined

51 Hess's law is based on

(a) law of conservation of mass
(b) law of conservation of energy
(c) law of active mass
(d) Both (a) and (b)

52 The reaction $A \longrightarrow C$ proceeds through two paths I and II as shown below :



The correct relationship between ΔH, ΔH_1 and ΔH_2 will be

(a) $\Delta H = \Delta H_2 - \Delta H_1$ (b) $\Delta H = \Delta H_1 / \Delta H_2$
(c) $\Delta H = \Delta H_1 + \Delta H_2$ (d) $\Delta H = \Delta H_1 \times \Delta H_2$

53 A reaction takes place in a several sequential steps *A*, *B*, *C* and *D*. The value of enthalpy change for sequential steps are *p*, *q*, *r* and *s*, respectively. If *B* and *C* have equal values of enthalpy change with total enthalpy change *t*, then choose the incorrect symbolic equation among the following.

(a) $q = r$ (b) $q + r = t - (s + p)$
(c) $2q = t - (s + p)$ (d) $q + r = p + s$

TOPIC 5~ Enthalpies for Different Types of Reactions

54 The heat of combustion of carbon to CO_2 is –393.5 kJ/mol. The heat released upon the formation of 35.2 g of CO_2 from carbon and oxygen gas is

CBSE AIPMT 2015

(a) –315 kJ (b) +315 kJ (c) –630 kJ (d) –3.15 kJ

55 The heat of formations of CO(g) and $CO_2(g)$ are – 26.4 K cal and – 94.0 kcal respectively. The heat of combustion of carbon monoxide will be

(a) – 46.5 kcal (b) 36.5 kcal
(c) – 36.5 kcal (d) – 67.6 kcal

56 Given,

$$C_{\text{diamond}} + O_2 \longrightarrow CO_2;\ \Delta H = -395.3\ \text{kJ/mol}$$
$$C_{\text{graphite}} + O_2 \longrightarrow CO_2; \Delta H = -393.4\ \text{kJ/mol}$$

The enthalpy change (ΔH) for the reaction,

$$C_{\text{graphite}} \longrightarrow C_{\text{diamond}}\ \text{in kJ/mol is}$$

(a) + 1.9 (b) – 1.9
(c) + 3.8 (d) – 3.8

57 In the given reaction,

$$H_2(g) \longrightarrow 2H(g);\ \Delta H = 435.0\ \text{kJ mol}^{-1}$$

The enthalpy change is known as

(a) enthalpy of formation (b) enthalpy of atomisation
(c) bond dissociation enthalpy (d) Both (b) and (c)

58 The bond dissociation energies of H_2, Cl_2 and HCl are 104, 58 and 103 kcal mol^{-1} respectively. The enthalpy of formation of HCl would be

(a) –22 kcal mol^{-1} (b) – 44 kcal mol^{-1}
(c) +44 kcal mol^{-1} (d) +22 kcal mol^{-1}

59 Calculate the bond enthalpy of Xe—F bond as given in the equation

$$XeF_4(g) \longrightarrow Xe^+(g) + F^-(g) + F_2(g) + F(g);$$

[Given, $\Delta_r H = 292$ kcal mol^{-1}

Ionisation energy of Xe = 279 kcal/mol

Bond energy (F—F) = 38 kcal/mol

Electron affinity of F = 85 kcal/mol]

(a) 8.5 kcal/mol (b) 34 kcal/mol
(c) 24 kcal/mol (d) None of these

60 Enthalpy change for the reaction,

$$4H\ (g) \longrightarrow 2H_2(g)\ \text{is} -869.6\ \text{kJ}$$

The dissociation energy of H—H bond is **CBSE AIPMT 2011**

(a) –869.6 kJ (b) +434.8 kJ
(c) +217.4 kJ (d) –434.8 kJ

61 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 **NEET 2018**

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

62 Find the multiple bond energy (kJ mol^{-1}) of a C ≡ C bond in C_2H_2 molecule from the following data. (Take the bond energy of a C—H bond as 350 kJ mol^{-1}) **JEE Main 2012**

$$2C(s) + H_2(g) \longrightarrow C_2H_2(g);\ \Delta H = 225\ \text{kJ mol}^{-1}$$
$$2C(s) \longrightarrow 2C(g); \Delta H = 1410\ \text{kJ mol}^{-1}$$
$$H_2\ (g) \longrightarrow 2H(g); \Delta H = 330\ \text{kJ mol}^{-1}$$

(a) 1165 (b) 837 (c) 865 (d) 815

63 Given that, for the reaction,

$$\frac{1}{2}H_2 + \frac{1}{2}Cl_2 \longrightarrow HCl$$

ΔH_f (HCl) = –93 kJ/mol

BE (H_2) = 434 kJ/mol

BE (Cl_2) = 242 kJ/mol

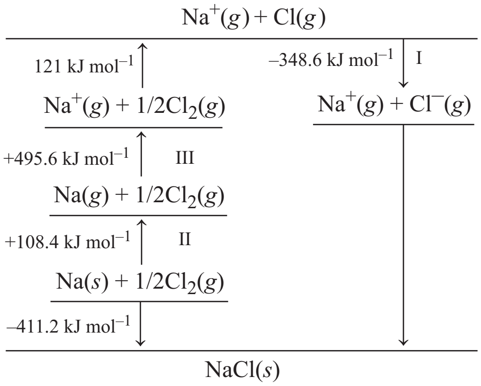
The bond dissociation energy of HCl is **JIPMER 2018**

(a) 232 kJ/mol (b) 331 kJ/mol
(c) 431 kJ/mol (d) 530 kJ/mol

64 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 **JEE Main 2019**

(a) 2.85 (b) 5.7 (c) 22.8 (d) 11.4

65 Consider the Born-Haber cycle,



Identify I, II, III in the above Born-Haber cycle.

	I	II	III
(a)	Electron gain enthalpy	Sublimation enthalpy	Ionisation enthalpy
(b)	Enthalpy of formation	Bond dissociation enthalpy	Enthalpy of transformation
(c)	Lattice enthalpy	Bond dissociation enthalpy	Enthalpy of formation
(d)	Electron gain enthalpy	Bond dissociation enthalpy	Sublimation enthalpy

66

$$\begin{tikzcd} AB(s) \arrow[r, "\text{I}"] \arrow[d, "\text{II}"'] & A^+(aq) + B^-(aq) \\ A^+(g) + B^-(g) \arrow[ur, "\text{III}"'] & \end{tikzcd}$$

Identify I, II, III in the above diagram.

	I	II	II
(a)	$\Delta_{\text{lattice}}H^\circ$	$\Delta_{\text{hyd}}H^\circ$	$\Delta_{\text{sol}}H^\circ$
(b)	$\Delta_{\text{lattice}}H^\circ$	$\Delta_{\text{sol}}H^\circ$	$\Delta_{\text{hyd}}H^\circ$
(c)	$\Delta_{\text{sol}}H^\circ$	$\Delta_{\text{lattice}}H^\circ$	$\Delta_{\text{hyd}}H^\circ$
(d)	$\Delta_{\text{sol}}H^\circ$	$\Delta_{\text{hyd}}H^\circ$	$\Delta_{\text{lattice}}H^\circ$

67 Consider the chemical equation,

$$Na^+(g) + Cl^-(g) \longrightarrow Na^+Cl^-(s)$$

For 1 mole of NaCl(s),

Lattice enthalpy $= +788$ kJ mol^{-1},

$$\Delta_{hyd} H^\circ = -784 \text{ kJ mol}^{-1}$$

The enthalpy of solution is calculated as

(a) -4 kJ mol^{-1} (b) -8 kJ mol^{-1}
(c) $+4$ kJ mol^{-1} (d) -6 kJ mol^{-1}

68 On which of the following factors does enthalpy of dilution depends?

I. Amount of solute added
II. Concentration of the solution
III. Amount of solvent added
IV. Amount of solution

(a) II and III
(b) Only I
(c) I and IV
(d) Only III

TOPIC 6 ~ *Spontaneity*

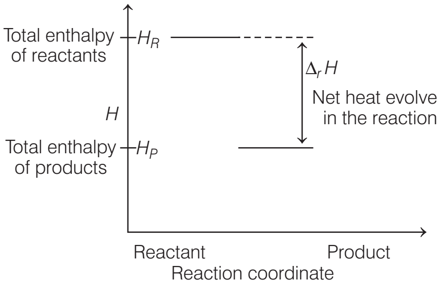
69 Which of the following process is an irreversible process and may only be reversed by some external agency?

(a) Spontaneous (b) Non-spontaneous
(c) Atomisation (d) None of these

70 The exothermic reaction is spontaneous, because

(a) increase in energy has taken place
(b) decrease in energy has taken place
(c) energy remains same during reaction
(d) Both (a) and (c)

71



The above diagram represents

(a) enthalpy for exothermic reactions
(b) enthalpy for endothermic reactions
(c) entropy for exothermic reactions
(d) entropy for endothermic reactions

72 C (graphite, s) + 2S(l) $\longrightarrow$ CS$_2$(l);

$$\Delta_r H^\circ = +\ 128.5 \text{ kJ mol}^{-1}$$

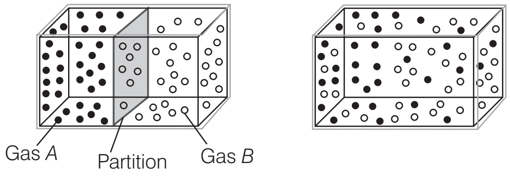
The above reaction is

(a) exothermic and spontaneous
(b) exothermic and non-spontaneous
(c) endothermic and spontaneous
(d) endothermic and non-spontaneous

73 Which of the following pair(s) of conditions are certain to result in a spontaneous reaction?

(a) Endothermic and decreasing order
(b) Exothermic and increasing disorder
(c) Endothermic and increasing disorder
(d) Exothermic and decreasing disorder

74



Identify the process which occur in the above diagram?

(a) Osmosis of two gases (b) Diffusion of two gases
(c) Movement of two gases (d) None of these

75 Entropy is

(a) a thermodynamic concept (b) a state function
(c) independent of path (d) All of these

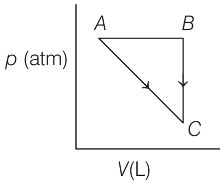
76 Which of the following reactions will have the value of ΔS with a negative sign?

(a) $H_2O(l) \longrightarrow H_2O(g)$
(b) $2SO_2(g) + O_2(g) \longrightarrow 2SO_3(g)$
(c) $Cl_2(g) \longrightarrow 2Cl(g)$
(d) $CaCO_3(s) \longrightarrow CaO(s) + CO_2(g)$

77 For both reversible and irreversible expansion for an ideal gas, under isothermal condition,

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

78 For an ideal gas, consider only $(p - V)$ work on going from initial state A to final state C. The final state C can be reached by either of two paths as shown below. Which of the option is correct? (Take ΔS as change in entropy and was work done.)



(a) $\Delta S_{A \to C} = \Delta S_{A \to B} + \Delta S_{A \to C}$
(b) $W_{A \to B \to C} = W_{A \to B}$
(c) $W_{A \to B \to C} = W_{A \to B} + W_{B \to C}$
(d) Both (a) and (b)

79 In the given equation,

$$4\text{Fe}(s) + 3\text{O}_2(g) \longrightarrow 2\text{Fe}_2\text{O}_3(s)$$

The entropy change is -549.4 JK^{-1} mol^{-1} at 298 K. ($\Delta_r H° = -1648 \times 10^3$ J mol^{-1}). The above reaction is

(a) spontaneous
(b) non-spontaneous
(c) non-spontaneous at 500 K
(d) None of these

80 In which of the following reactions, standard reaction entropy changes ($\Delta S°$) is positive and standard Gibbs energy change ($\Delta G°$) decreases sharply with increasing temperature? ***CBSE AIPMT 2012***

(a) $\text{C (graphite)} + \frac{1}{2}\text{O}_2(g) \longrightarrow \text{CO}(g)$

(b) $\text{CO}(g) + \frac{1}{2}\text{O}_2(g) \longrightarrow \text{CO}_2(g)$

(c) $\text{Mg}(s) + \frac{1}{2}\text{O}_2(g) \longrightarrow \text{MgO}(s)$

(d) $\frac{1}{2}\text{C(graphite)} + \frac{1}{2}\text{O}_2(g) \longrightarrow \frac{1}{2}\text{CO}_2(g)$

81 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 temperature) ***NEET 2017***

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

82 If the enthalpy change for the transition of liquid water to steam is 30 kJ mol^{-1} at 27°C, the entropy change for the process would be ***CBSE AIPMT 2011***

(a) 1.0 J mol^{-1} K^{-1}
(b) 0.1 J mol^{-1} K^{-1}
(c) 100 J mol^{-1} K^{-1}
(d) 10 J mol^{-1} K^{-1}

83 The enthalpy of fusion of water is 1.435 kcal/mol. The molar entropy change for the melting of ice at 0°C is ***CBSE AIPMT 2012***

(a) 10.52 cal/mol K
(b) 21.04 cal/mol K
(c) 5.260 cal/mol K
(d) 0.526 cal/mol K

84 A process will be spontaneous at all temperature if ***JEE Main 2019***

(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 $\Delta S > 0$

85 The entropy change for

$$\text{CH}_4(g) + \text{H}_2\text{O}(g) \longrightarrow 3\text{H}_2(g) + \text{CO}(g)$$

using the following data is

Substance	$\text{CH}_4(g)$	$\text{H}_2\text{O}(g)$	$\text{H}_2(g)$	$\text{CO}(g)$
$S°$/JK^{-1}mol^{-1}	186.2	188.7	130.6	197.6

(a) -46 JK^{-1} mol^{-1}
(b) $+46$ JK^{-1} mol^{-1}
(c) -214.5 JK^{-1} mol^{-1}
(d) 214.5 JK^{-1} mol^{-1}

86 Effect of temperature on spontaneity of reactions is given in the table below.

$\Delta_r H°$	**$\Delta_r S°$**	**$\Delta_r G°$**	**Description**
–	+	–	Reaction is spontaneous at all temperature
–	–	(II)	Reaction is spontaneous at low temperature
–	–	+ (at high T)	Reaction is non-spontaneous at high temperature
+	+	+ (at low T)	(III)
(I)	+	– (at high T)	Reaction is spontaneous at high temperature
+	–	+ (at all T)	Reaction is non-spontaneous at all temperatures

Identify I, II, III in the above table.

	I	II	III
(a)	+ve	–ve (at low T)	Reaction is non-spontaneous at low temperature
(b)	–ve	+ve (at low T)	Reaction is non-spontaneous at low temperature
(c)	+ve	–ve (at low T)	Reaction is spontaneous at low temperature
(d)	–ve	+ve (at low T)	Reaction is spontaneous at low temperature

87 Select the incorrect expression from the following.

(a) $\Delta S_{\text{total}} = \Delta S_{\text{system}} + \Delta S_{\text{surr}}$

(b) $\Delta S_{\text{surr}} = \dfrac{\Delta H_{\text{surr}}}{T} = -\dfrac{\Delta H_{\text{sys}}}{T}$

(c) $\Delta S_{\text{total}} < 0$ (spontaneous process)

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

88 The entropy change associated with the conversion of 1 kg of ice at 273 K to water vapours at 383 K is (Specific heat of water liquid and water vapour are 4.2 kJK^{-1}kg^{-1} and 2.0 kJK^{-1} kg^{-1}; heat of liquid fusion and vapourisation of water are 334 kJ kg^{-1} and 2491 kJkg^{-1} respectively). ***JEE Main 2019***
($\log 273 = 2.436$, $\log 373 = 2.572$, $\log 383 = 2.583$)

(a) 9.26 kJ kg^{-1} K^{-1}
(b) 8.49 kJ kg^{-1}K^{-1}
(c) 7.90 kJ kg^{-1}K^{-1}
(d) 2.64 kJ kg^{-1}K^{-1}

TOPIC 7 ~ *Gibbs Energy Change and Equilibrium*

89 For the reaction,

$$CO(g) + \frac{1}{2}O_2\ (g) \longrightarrow CO_2\ (g)$$

If the standard entropy change at 298 K is $-0.082\ \text{kJ mol}^{-1}\ \text{K}^{-1}$ and standard Gibb's energies of for formation of CO_2 and CO are – 298.4 and – 114.6 kJ/mol respectively, then the enthalpy change for the given reaction will be

(a) 314.5 kJ/mol
(b) 159.8 kJ/mol
(c) 208.24 kJ/mol
(d) 418.3 kJ/mol

90 The equilibrium constant (K) of a reaction may be written as,

(a) $K = e^{-\Delta H^\circ/RT}$
(b) $K = e^{-\Delta G/RT}$
(c) $K = e^{-\Delta H/RT}$
(d) $K = e^{-\Delta G^\circ/RT}$

91 The value of $\Delta_r G^\circ$ is equal to

(a) $-2.303\ RT \log K$
(b) $+2.303\ RT \log K$
(c) $\Delta_r H^\circ - T\Delta_r S^\circ$
(d) Both (a) and (c)

92 Which of the following expression is correct for a reversible process in a state of equilibrium? ***CBSE AIPMT 2015***

(a) $\Delta G = -2.30RT \log K$
(b) $\Delta G = 2.30RT \log K$
(c) $\Delta G^\circ = -2.303RT \log K$
(d) $\Delta G^\circ = 2.303RT \log K$

93 For the reaction, $X_2O_4(l) \longrightarrow 2XO_2(g)$,
$\Delta U = 2.1\ \text{kcal}$, $\Delta S = 20\ \text{cal K}^{-1}$ at 300 K.
Hence, ΔG is ***CBSE AIPMT 2014***

(a) 2.7 kcal
(b) –2.7 kcal
(c) 9.3 kcal
(d) –9.3 kcal

94 A process has $\Delta H = 200\ \text{J mol}^{-1}$ and $\Delta S = 40\ \text{JK}^{-1}\ \text{mol}^{-1}$. Out of the values given below, choose the minimum temperature above which the process will be spontaneous ***JEE Main 2019***

(a) 20 K (b) 4 K (c) 5 K (d) 12 K

95 The value of logarithm of equilibrium constant K_p if the standard free energy change of a reaction is $\Delta G^\circ = -115$ kJ at 298 K will be

(a) 2.303 (b) 13.83 (c) 2.015 (d) 20.15

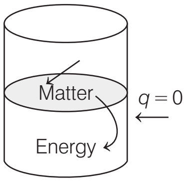
SPECIAL TYPES QUESTIONS

Statement Based Questions

96 Select the correct statement about the system.

(a) Reactants in an open beaker is an example of open system
(b) Reactants in closed insulated vessel is an example of closed system
(c) Reactants in closed conducting vessel is an example of open system
(d) Reactants in closed conducting vessel is an example of isolated system

97



Select the correct statements for the above figure.

(a) It is the process in which there is the transfer of heat between the system and surroundings
(b) Wall separating the system and the surrounding is called isolated wall
(c) It is the process which does not permit the transfer of heat through the boundary called the adiabatic wall.
(d) All of the above

98 Which of the following statements/expressions is/are correct ?

(a) Internal energy change is equal to the adiabatic work done
(b) W_{ad} = + ve, when work is done on the system
(c) W_{ad} = – ve, when work is done by the system
(d) All of the above

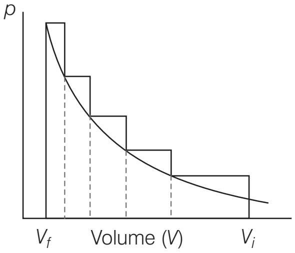
99 Select the correct statements.

(a) q = +ve means heat is transferred from the system to the surroundings
(b) q = –ve means heat is transferred from the surroundings to the system

(c) q = +ve means heat is transferred from the surroundings to the system
(d) All of the above

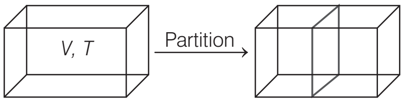
100 Which of the following statements is correct ?
(a) The energy can be created
(b) According to first law of thermodynamics, the energy of an isolated system is not constant
(c) In the isolated system, $W = 0, q = 0, \Delta U \neq 0$
(d) $\Delta U = q + W$, will depend only on initial and final state

101 Select the correct statement about the graph.



(a) It is an irreversible compression
(b) Pressure is not constant and changes finite steps during compression from initial volume, V_i to final volume, V_f
(c) Work done on gas will be equal to $-\sum p\Delta V$
(d) All of the above

102 The correct inference that can be observed from the given figure is



(a) Each part has double the temperature of the gas
(b) Each part has the same temperature of the gas
(c) Each part only have half the temperature of the gas
(d) Each part has one-fourth the temperature of the gas

103 Which of the following statement is correct?
(a) The heat transferred to the system is directly related to increase in temperature.
(b) $q = C\Delta T$, the coefficient C is called the heat capacity
(c) Water has a large heat capacity
(d) All of the above

104 Which of the following statements is/are correct?
(a) Unit of $\Delta_r H°$ is kJ mol^{-1}
(b) Enthalpy is an intensive quantity
(c) When a chemical equation is reversed the value of $\Delta_r H°$ remain same in sign
(d) All of the above

105 Which of the following statements correctly represents the uses of the enthalpy change?
(a) The enthalpy change is required to maintain an industrial chemical reaction at constant temperature
(b) It is also required to calculate temperature dependence of equilibrium constant
(c) Both (a) and (b)
(d) None of the above

106 Which of the following statements is incorrect?
(a) The standard enthalpy of reaction is the enthalpy change for a reaction when all the participating substances are in their standard states
(b) The standard state of a substance at a specified temperature is its pure form at 1 bar
(c) The standard state of solid iron at 298 K is equal to pure iron at 1 bar
(d) Standard conditions are denoted by adding the superscript 'o' to the symbol ΔH

107 Which of the following statement is correct for the reaction?

$$\text{CaO}(s) + \text{CO}_2(g) \longrightarrow \text{CaCO}_3(s); \quad \Delta_r H° = -178.3 \text{ kJ mol}^{-1}$$

(a) $\Delta_r H°$ is the enthalpy of formation of $CaCO_3$
(b) $\Delta_r H°$ is not the enthalpy of formation of $CaCO_3$
(c) $\Delta_r H°$ is the enthalpy of combustion of $CaCO_3$
(d) None of the above

108 Which of the following statement is incorrect for the reaction?

$$\text{H}_2(g) + \text{Br}_2(l) \longrightarrow 2\text{HBr}(g); \quad \Delta_r H^{°} = -178.3 \text{ kJ mol}^{-1}$$

(a) The enthalpy change given is equal to $\Delta_f H°$ HBr.
(b) $\Delta_r H° = 2\Delta_f H°$ HBr
(c) $\Delta_f H°$ of an element in refrence state is taken as zero
(d) None of the above

109 Which of the following statements is incorrect about the equation?

$$\text{C}_2\text{H}_5\text{OH}(l) + 3\text{O}_2(g) \longrightarrow 2\text{CO}_2(g) + 3\text{H}_2\text{O}(l); \quad \Delta_r H° = -1367 \text{ kJ mol}^{-1}$$

(a) The reaction is an endothermic
(b) The numerical value of $\Delta_r H°$ refers to the number of moles of substances specified by an equation.
(c) The coefficients in a balanced thermochemical equations refer to the number of moles (never molecules) of reactants and product involved in the reaction
(d) The equation describes the combustion of liquid ethanol at constant temperature and pressure

110 Which of the following statements are incorrect?
(a) The subscript in $\Delta_f H^{°}$ indicates that one mole of the compound is formed in its standard state
(b) The refrence state of an element is its most stable state of aggregation at 273K
(c) The refrence state for dihydrogen is H_2 gas and for sulphur is S rhombic
(d) None of the above

111 Which of the following statements is correct?

(a) Combustion reactions are endothermic in nature
(b) During complete combustion of 1 mole of butane, 2658 kJ of heat is released
(c) Our body generates energy from food by the process of atomisation
(d) All of the above

112 Which of the following statements is correct?

(a) Mean C—H bond enthalpies differ slightly from compound to compound, as in CH_3, CH_2Cl, CH_3NO_2 etc., but it does not differ in a great deal
(b) The reaction enthalpies are very important quantities as these arise from the changes that accompany the breaking of old bonds and formation of the new bonds
(c) $\Delta_r H^\circ = \Sigma_{bond\ enthalpies\ of\ reactants} - \Sigma_{bond\ enthalpies\ of\ products}$
(d) All of the above

113 Find out the incorrect expression.

(a) $\Delta_r H^\circ(T) = \Delta_r H^\circ(0) + \int_0^T \Delta_r C_p^\circ dT$
(b) $\Delta_r C_p^\circ = -\frac{5}{2} R$ (for ionisation)
(c) $\Delta_r H^\circ$ (electron gain enthalpy) $= -$ A (electron affinity) $- \frac{5}{2} RT$
(d) $\Delta_r H^\circ$ (ionisation enthalpy) $= E_0$ (ionisation energy) $+ \frac{5}{2} RT$

114 Which of the following statements correctly represents the enthalpy of dilution?

(a) The heat withdrawn from the system when additional solvent is added to solution
(b) The heat withdrawn from the surroundings when additional solvent is added to solution
(c) The heat withdrawn from the system when additional solute is added to solution
(d) The heat withdrawn from the surroundings when additional solute is added to solution

115 Which of the following statement is correct?

(a) In case of chemical reactions, entropy change shows the rearrangement of atoms or ions from one pattern in the reactants to another
(b) The greater the degree of randomness, higher is the entropy
(c) The crystalline solid state is most ordered, while gaseous state is most disordered
(d) All of the above

116 Which of the following statement is incorrect?

(a) Heat (q) has randomising influence on the system.
(b) Entropy change varies directly with temperature.
(c) Entropy change is a state function.
(d) Temperature is the measure of average chaotic motion of the particle in the system.

117 Which of the following statement is incorrect regarding spontaneity of a reaction?

(a) The flow of heat is undirectional from higher temperature to lower temperature
(b) All naturally occuring processes tend to proceed spontaneously in any direction
(c) The gas in a container will not spontaneously contract into one corner
(d) Spontaneous reactions occurs immediately when contact is made between the reactants

118 Which of the following statement is incorrect regarding entropy?

(a) The greater the disorder in an isolated system, the lower is the entropy
(b) The entropy change can be attributed to rearrangement of atoms or ions from one pattern in the reactants to another in the product
(c) The gaseous state is the state of highest entropy
(d) None of the above

119 Which of the following statement is incorrect regarding third law of thermodynamics.

(a) The statement of third law is confined to pure crystalline solids
(b) There is imperfect order in a crystal at absolute zero
(c) The calculation of absolute values of entropy of pure substances is done from thermal data alone
(d) For pure substances, the calculation of absolute value of entropy of pure substance can be done by summing $\frac{q_{rev}}{T}$ increments from 0K to 298K

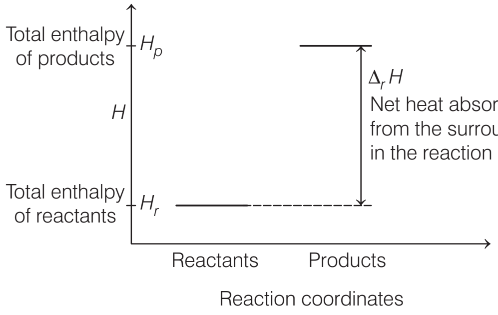
120 Consider the following statements

I. The entire universe other than system is affected by the changes taking place in the universe.
II. The wall separating the system from the surroundings is called boundary.
III. The region of space in the neighbourhood of the system constitutes its surroundings.

Select the incorrect statement and choose the correct option

(a) only I	(b) only II
(c) Both I and III	(d) only III

121 Consider the following statements about the diagram given below :



I. This graph represents the enthalpy diagram for endothermic reactions.

II. In case of endothermic reactions, ΔH is positive and thus increase in enthalpy is observed.

Select the correct statement and choose the correct option.

(a) Only I (b) Only II
(c) Both I and II (d) None of these

122 Consider the following statements about the Hess's law of constant heat summation.

I. 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.

II. The enthalpy of an overall reaction $A \rightarrow B$ along one route is $\Delta_r H$ and $\Delta_r H_1, \Delta_r H_2, \Delta_r H_3$ ... representing enthalpies of reactions leading to the same product, B along another route, then we have
$\Delta_r H = \Delta_r H_1 + \Delta_r H_2 + \Delta_r H_3 \ldots$

Select the correct statement and choose the correct option.

(a) Only I (b) Only II
(c) Both I and II (d) None of these

123 Consider the following statements for the reaction between zinc and oxygen.

$$2\text{Zn}(s) + \text{O}_2(g) \longrightarrow 2\text{ZnO}(s); \quad \Delta H = -693.8 \text{ kJmol}^{-1}$$

I. The enthalpy of two moles of ZnO is less than the total enthalpy of two moles of Zn and one mole of oxygen by 693.8 kJ

II. The enthalpy of two moles of ZnO is more than the total enthalpy of two moles of Zn and one mole of oxygen by 693.8 kJ

III. 693.8 kJ mol^{-1} energy is evolved in the reaction

IV. 693.8 kJ mol^{-1} energy is absorbed in the reaction

Select the correct statements and choose the correct option.

(a) Only I (b) I and III
(c) II and IV (d) II and III

124 Consider the following conventions related to thermochemical equations.

I. The coefficients of different substances in a balanced thermochemical equation show only number of moles involved in the reaction.

II. Enthalpy is an extensive property thus if a thermochemical equation is multiplied or divided by an integer n, the value of $\Delta_r H^\circ$ is also multiplied or divided by the integer, n.

III. On reversed a reaction, the sign of ΔH is also reversed but its magnitude also changes.

Select the correct statement and choose the correct option.

(a) Only I (b) Only III
(c) Both I and II (d) All of these

125 Consider the following statements about ways choosen for the change in state of the system.

I. When some mechanical work of 1 kJ is done by rotating a small set of paddles and there by churning water, then the final state temperature is found to be greater than initial state temperature.

II. In case of electric work done of 1 kJ with the help of immersion rod, the change in temperature will same as that of the case I, i.e. mechanical work done.

Select the correct statement and choose the correct option.

(a) Only I (b) Only II
(c) Both I and II (d) Neither I nor II

126 The process which occur spontaneously are

I. flow of heat from colder to warmer body

II. gas expanding to fill the available volume

III. gas in a container contracting into one corner

Select the correct statements and choose the correct option.

(a) Only I (b) Only II
(c) Only III (d) All of these

127 Consider the following statements for the given reactions :

(i) $\frac{1}{2}\text{N}_2(g) + \frac{1}{2}\text{O}_2(g) \longrightarrow \text{NO}(g); \quad \Delta_r H^\circ = 90 \text{ kJ mol}^{-1}$

(ii) $\text{NO}(g) + \frac{1}{2}\text{O}_2(g) \longrightarrow \text{NO}_2(g); \quad \Delta_r H^\circ = -74 \text{ kJ mol}^{-1}$

I. In (i) reaction, NO(g) is unstable because the energy is released and unstable NO(g) changes into the stable $\text{NO}_2(g)$.

II. The energy is absorbed in (i) reaction, NO(g) is unstable and unstable NO(g) changes into the stable $\text{NO}_2(g)$.

Select the correct statements and choose the correct option.

(a) Only I (b) Only II
(c) Both I and II (d) None of these

II. Assertion and Reason

■ **Directions** (Q.Nos. 128-140) *In the following questions, a statement of Assertion* (A) *is followed by a corresponding statement of Reason* (R). *Of the following statements, choose the correct one.*

(a) Both A and R are correct; R is the correct explanation of A.
(b) Both A and R are correct; R is not the correct explanation of A.
(c) A is correct; R is incorrect.
(d) A is incorrect; R is correct.

128 **Assertion** (A) The variables like p, V, T are called state functions.

Reason (R) Their values depend only on the state of the system

129 **Assertion** (A) Volume of water in a pond is not a state function.

Reason (R) Volume of water is independent of the route by which water is filled in the pond either by rain or by tubewell or by both.

130 **Assertion** (A) First law of thermodynamics is applicable to an electric fan or a heater.

Reason (R) 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.

131 **Assertion** (A) In the equation, $H = U + pV$, H is a state function and independent of path.

Reason (R) U, p, V all are state functions.

132 **Assertion** (A) The difference between ΔH and ΔU is not significant for systems consisting of only solids or liquids.

Reason (R) Solids and liquids do not suffer any significant volume changes upon heating.

133 **Assertion** (A) 1 mole of acetone requires more heat to vaporise than the 1 mole of water to vaporise.

Reason (R) There is strong hydrogen bonds between water molecules but weaker intermolecular dipole-dipole interactions in acetone.

134 **Assertion** (A) U is a state function.

Reason (R) T is an intensive property. ***AIIMS 2019***

135 **Assertion** (A) The solubility of most salts in water increases with rise in temperature.

Reason (R) For most of the ionic compounds, $\Delta_{\text{sol}} H^\circ$ is positive and the dissociation process is endothermic.

136 **Assertion** (A) The mean bond energy of all the four C—H bonds in CH_4 molecule is not equal.

Reason (R) After breaking of C—H bonds one by one, the electronic environments changes.

137 **Assertion** (A) The phenomenon like flow of water down hill or fall of a stone on to the ground is an example of a spontaneous process.

Reason (R) There is a net increase in potential energy in the direction of change.

138 **Assertion** (A) The dissolution of NH_4Cl in water is endothermic but it dissolves in water.

Reason (R) On dissolution of NH_4Cl, entropy increases.

139 **Assertion** (A) ΔG has the unit of energy.

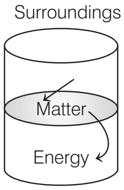
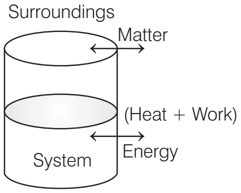
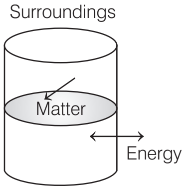
Reason (R) ΔH and $T\Delta S$ are the energy dependent terms.

140 **Assertion** (A) The entropy decreases when the temperature of a crystalline solid is raised from 0 K to 115 K.

Reason (R) On raising temperature from 0 K to 115 K, the constituent particles begin to move.

III. Matching Type Questions

141 Match the following diagram given in Column I with their system given in Column II and choose the correct option from the codes given below.

	Column I		Column II
A.		1.	Open system
B.		2.	Isolated system
C.		3.	Closed system

Codes

	A	B	C		A	B	C
(a)	2	1	3	(b)	3	2	1
(c)	2	3	1	(d)	1	2	3

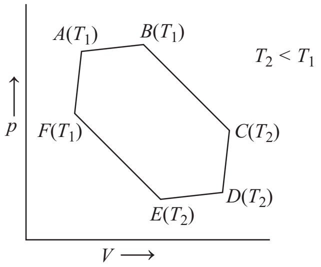
142 Match the following Column I with Column II and choose the correct codes given below.

	Column I		Column II
A.	$p_{\text{ext}} = 0$	1.	Free expansion of an ideal gas
B.	$q = p_{\text{ext}} (V_f - V_i)$	2.	Adiabatic change
C.	$q = 2.303 \, nRT \log (V_f/V_i)$	3.	Isothermal reversible change
D.	$\Delta U = W_{\text{ad}}$	4.	Isothermal irreversible change

Codes

	A	B	C	D		A	B	C	D
(a)	1	4	3	2	(b)	1	3	3	4
(c)	1	3	4	2	(d)	1	3	2	4

143 The following cyclic process is represented by the graph given below.



Match the following process given in Column I with changes take place given in Column II and choose the correct codes given below.

	Column I (Process)		Column II (Type)
A.	$A \to B$	1.	Adiabatic contraction, temperature increases to T_1.
B.	$C \to D$	2.	Isothermal and isobaric expansion at T_1.
C.	$E \to F$	3.	Isochoric and isothermal (pressure falls).
D.	$F \to A$	4.	Isochoric and isothermal (pressure increases).

Codes

	A	B	C	D		A	B	C	D
(a)	1	2	3	4	(b)	2	3	1	4
(c)	2	4	1	3	(d)	4	2	3	1

144 Match the following Column I with Column II and choose the correct codes given below.

	Column I		Column II
A.	q	1.	ΔH
B.	$C_p - C_V$	2.	$C\,\Delta T$
C.	q_v	3.	ΔU
D.	q_p	4.	R

Codes

	A	B	C	D		A	B	C	D
(a)	1	4	3	2	(b)	1	2	3	4
(c)	2	4	3	1	(d)	2	4	1	3

145 Match the Column I with Column II and mark the option given in the codes below.

	Column I		Column II
A.	$CH_4(g) + 2O_2(g) \longrightarrow CO_2(g) + 2H_2O$	1.	$\Delta_{sol}H°$
B.	$H_2(g) \longrightarrow 2H(g)$	2.	$\Delta_{lattice}H°$
C.	$NaCl(s) \longrightarrow Na^+(g) + Cl^-(g)$	3.	$\Delta_c H°$
D.	$NaCl(s) \longrightarrow Na^+(aq) + Cl^-(aq)$	4.	$\Delta_{bond}H°$

Codes

	A	B	C	D		A	B	C	D
(a)	4	3	1	2	(b)	2	1	4	3
(c)	1	2	3	4	(d)	3	4	2	1

NCERT & NCERT Exemplar

MULTIPLE CHOICE QUESTIONS

NCERT

146 For the process to occur under adiabatic conditions, the correct condition is

(a) $\Delta T = 0$ (b) $\Delta p = 0$ (c) $q = 0$ (d) $W = 0$

147 The enthalpies of all the elements in their standard states are

(a) unity (b) zero
(c) < 0 (d) different for each element

148 $\Delta U°$ of combustion of ethane is $-X$ kJ mol^{-1}. The value of $\Delta H°$ is

(a) $= \Delta U°$ (b) $> \Delta U°$ (c) $< \Delta U°$ (d) $= 0$

149 The enthalpy of combustion of methane, graphite and dihydrogen at 298 K are, – 890.3 kJ mol^{-1}, – 393.5 kJ mol^{-1} and –285.8 kJ mol^{-1} respectively. Enthalpy of formation of $CH_4(g)$ will be

(a) – 74.8 kJ mol^{-1} (b) – 52.27 kJ mol^{-1}
(c) + 74.8 kJ mol^{-1} (d) + 52.26 kJ mol^{-1}

150 A reaction, $A + B \longrightarrow C + D + q$ is found to have a positive entropy change. The reaction will be

(a) possible at high temperature
(b) possible only at low temperature
(c) not possible at any temperature
(d) possible at any temperature

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

(a) Increases by 307 J
(b) Decreases by 307 J
(c) Increases by 400 J
(d) Decreases by 400 J

152 The reaction of cyanamide, $NH_2CN\,(s)$, with dioxygen was carried out in a bomb calorimeter and ΔU was found to be – 742.7 kJ mol^{-1} at 298 K.

Calculate the enthalpy change for the reaction at 298 K ($R = 8.314 \times 10^{-3}$ kJ K^{-1} mol^{-1})

$$NH_2CN(s)+\frac{3}{2}O_2(g)\longrightarrow N_2(g)+CO_2(g)+H_2O(l)$$

(a) 741.4 $kJmol^{-1}$ (b) – 741.4 $kJmol^{-1}$
(c) 741.4 $Jmol^{-1}$ (d) – 741.4 $Jmol^{-1}$

153 The number of kJ of heat necessary to raise the temperature of 60.0 g of aluminium from 35°C to 55°C will be (Given molar heat capacity of Al is 24 J mol^{-1} K^{-1}. Molar mass of Al = 27 g mol^{-1}.)

(a) 1.067 (b) 2.0181 (c) 3.214 (d) 0

154 The enthalpy change on freezing of 1.0 mole of water at 10.0°C to ice at – 10.0°C will be,

Given : $\Delta_{fus}H = 6.03$ kJ mol^{-1} at 0°C

$$C_p[H_2O(l)] = 75.3 \text{ J mol}^{-1}\ K^{-1}$$

$$C_p[H_2O(s)] = 36.8 \text{ J mol}^{-1}\ K^{-1}$$

(a) 7.920 kJ mol^{-1} (b) 9.281 J mol^{-1}
(c) –7.151 kJ mol^{-1} (d) –9.281 J mol^{-1}

155 For the process :

$$CCl_4(g) \longrightarrow C(g) + 4Cl(g)$$

The enthalpy change and the bond enthalpy of C — Cl in $CCl_4(g)$ will be

Given : $\Delta_{vap}H°(CCl_4) = 30.5$ kJ mol^{-1}.

$$\Delta_f H°(CCl_4) = -135.5 \text{ kJ mol}^{-1}.$$

$$\Delta_a H°(C) = 715.0 \text{ kJ mol}^{-1},$$

$$\Delta_a H°(Cl_2) = 242 \text{ kJ mol}^{-1}$$

where, $\Delta_a H°$ is enthalpy of atomisation.

(a) 1214 kJ mol^{-1}, 426 kJ mol^{-1}
(b) 1081 kJ mol^{-1}, 310 kJ mol^{-1}
(c) 1304 kJ mol^{-1}, 326 kJ mol^{-1}
(d) None of the above

156 For the reaction at 298 K,

$$2A + B \longrightarrow C$$

$\Delta H = 400$ kJ mol^{-1} and $\Delta S = 0.2$ kJ K^{-1} mol^{-1}

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

(a) below 2000 K (b) above 2000 K
(c) below 1000 K (d) above 1000 K

157 For the reaction,

$$2A(g) + B(g) \longrightarrow 2D(g);$$

$\Delta U° = -\ 10.5$ kJ and $\Delta S° = -\ 44.1$ JK^{-1}.

The $\Delta G°$ for the reaction will be, also predict whether the reaction may occur spontaneously.

($R = 8.314 \times 10^{-3}$ kJ K^{-1} mol^{-1} and $T = 298$ K)

(a) 0.165 kJ mol^{-1}, No (b) –0.182 kJ mol^{-1}, Yes
(c) 2.142 kJ mol^{-1}, No (d) –4.68 kJ mol^{-1}, Yes

158 The entropy change in surroundings, when 1.00 mole of $H_2O(l)$ is formed under standard conditions will be, Given : $\Delta_f H° = -286$ kJ mol^{-1}.

(a) 959·7 JK^{-1} mol^{-1} (b) 1000 JK^{-1} mol^{-1}
(c) 821 JK^{-1} mol^{-1} (d) None of these

NCERT Exemplar

159 Thermodynamics is not concerned about

(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

160 Which of the following statements is correct?

(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

161 The state of a gas can be described by quoting the relationship between

(a) pressure, volume and temperature
(b) temperature, amount and pressure
(c) amount, volume and temperature
(d) pressure, volume, temperature and amount

162 The volume of gas is reduced to half from its original volume. The specific heat will

(a) reduce to half (b) be doubled
(c) remain constant (d) increase four times

163 During complete combustion of one mole of butane, 2658 kJ of heat is released. The thermochemical reaction for above change is

(a) $2C_4H_{10}(g) + 13O_2(g) \rightarrow 8CO_2(g) + 10H_2O(l)$; $\Delta_C H = -2658.0$ kJ mol^{-1}

(b) $C_4H_{10}(g) + \frac{13}{2}O_2(g) \rightarrow 4CO_2(g) + 5H_2O(l)$; $\Delta_C H = -1329.0$ kJ mol^{-1}

(c) $C_4H_{10}(g) + \frac{13}{2}O_2(g) \rightarrow 4CO_2(g) + 5H_2O(l)$; $\Delta_C H = -2658.0$ kJ mol^{-1}

(d) $C_4H_{10}(g) + \frac{13}{2}O_2(g) \rightarrow 4CO_2(g) + 5H_2O(l)$; $\Delta_C H = +\ 2658.0$ kJ mol^{-1}

164 $\Delta_f U°$ of combustion of $CH_4(g)$ at certain temperature is –393 kJ mol^{-1}. The value of $\Delta_f H°$ is

(a) zero (b) $< \Delta_f U°$
(c) $> \Delta_f U°$ (d) equal to $\Delta_f U°$

165 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) $q = 0, \Delta T \neq 0$ and $W = 0$
(b) $q \neq 0, \Delta T = 0$ and $W = 0$
(c) $q = 0, \Delta T = 0$ and $W = 0$
(d) $q = 0, \Delta T < 0$ and $W \neq 0$

166 The pressure-volume work for an ideal gas can be calculated by using the expression $W = -\int_{V_i}^{V_f} p_{\text{ext}}\, dV$.

The work done 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.

(a) W (= reversible) = W (= irreversible)
(b) W (= reversible) < W (= irreversible)
(c) W (= reversible) = W (= irreversible)
(d) W (= reversible) = W (= irreversible) $+ p_{\text{ext}}.\Delta V$

167 The enthalpies of elements in their standard states are taken as zero. The enthalpy of formation of a compound

(a) is always negative
(b) is always positive
(c) may be positive or negative
(d) is never negative

168 On the basis of thermochemical equations (1), (2) and (3), find out which of the algebraic relationships given in options (a) to (d) is correct.

1. $\text{C(graphite)} + \text{O}_2(g) \rightarrow \text{CO}_2(g); \Delta_r H = x \text{ kJmol}^{-1}$
2. $\text{C(graphite)} + \frac{1}{2}\text{O}_2(g) \rightarrow \text{CO}(g); \Delta_r H = y \text{ kJmol}^{-1}$
3. $\text{CO}(g) + \frac{1}{2}\text{O}_2(g) \rightarrow \text{CO}_2(g); \Delta_r H = z \text{ kJmol}^{-1}$

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

169 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?

1. $\text{C}(g) + 4\text{H}(g) \longrightarrow \text{CH}_4(g); \Delta_r H = x \text{ kJmol}^{-1}$
2. $\text{C (graphite}, s) + 2\text{H}_2(g) \longrightarrow \text{CH}_4(g); \Delta_r H = y \text{ kJmol}^{-1}$

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

170 Enthalpy of sublimation of a substance is equal to

(a) enthalpy of fusion + enthalpy of vaporisation
(b) enthalpy of fusion
(c) enthalpy of vaporisation
(d) twice the enthalpy of vaporisation

■ **Directions** (Q.Nos. 171-173) *In the following questions, a statement of Assertion* (A) *is followed by a corresponding statement of Reason* (R). *Of the following statements, choose the correct one.*

(a) Both A and R are correct; R is the correct explanation of A.
(b) Both A and R are correct; R is not the correct explanation of A.
(c) A is correct; R is incorrect.
(d) A is incorrect; R is correct.

171 **Assertion** (A) Combustion of all organic compound is an exothermic reaction.

Reason (R) The enthalpies of all elements in their standard state are zero.

172 **Assertion** (A) A liquid crystallises into a solid and is accompanied by decrease in entropy.

Reason (R) In crystals, molecules arrange in an ordered manner.

173 **Assertion** (A) Spontaneous process is an irreversible process and may be reversed by some external agency.

Reason (R) Decrease in enthalpy is a contributory factor for spontaneity.

174 Match the following processes with entropy change and choose the correct codes given below.

	Reaction		Entropy change
A.	A liquid vaporises	1.	$\Delta S = 0$
B.	Reaction is non-spontaneous at all temperatures with positive ΔH	2.	ΔS = positive
C.	Reversible expansion of an ideal gas	3.	ΔS = negative

Codes

	A	B	C		A	B	C
(a)	2	1	3	(b)	3	2	1
(c)	1	2	3	(d)	2	3	1

175 Match the following parameters with description for spontaneity and choose the correct codes given below.

	(Parameters $\Delta_r H°$	$\Delta_r S°$	$\Delta_r G°$)		Description
A.	+	–	+	1.	Non-spontaneous at high temperature
B.	–	–	+ at high T	2.	Spontaneous at all temperatures
C.	–	+	–	3.	Non-spontaneous at all temperatures

Codes

	A	B	C		A	B	C
(a)	1	3	2	(b)	3	2	1
(c)	1	2	3	(d)	3	1	2

Answers

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1	(a)	2	(c)	3	(c)	4	(c)	5	(d)	6	(d)	7	(b)	8	(a)	9	(b)	10	(c)
11	(b)	12	(c)	13	(c)	14	(b)	15	(a)	16	(c)	17	(d)	18	(b)	19	(d)	20	(d)
21	(a)	22	(a)	23	(c)	24	(a)	25	(c)	26	(a)	27	(a)	28	(d)	29	(d)	30	(b)
31	(d)	32	(b)	33	(a)	34	(d)	35	(d)	36	(d)	37	(d)	38	(c)	39	(b)	40	(c)
41	(a)	42	(b)	43	(a)	44	(b)	45	(c)	46	(d)	47	(a)	48	(d)	49	(a)	50	(c)
51	(b)	52	(c)	53	(d)	54	(a)	55	(d)	56	(a)	57	(d)	58	(a)	59	(b)	60	(b)
61	(a)	62	(d)	63	(c)	64	(c)	65	(a)	66	(c)	67	(c)	68	(a)	69	(a)	70	(b)
71	(a)	72	(c)	73	(b)	74	(b)	75	(d)	76	(b)	77	(a)	78	(d)	79	(a)	80	(a)
81	(b)	82	(c)	83	(c)	84	(b)	85	(d)	86	(a)	87	(c)	88	(a)	89	(c)	90	(d)
91	(d)	92	(c)	93	(b)	94	(c)	95	(d)										

Special Types Questions

96	(a)	97	(c)	98	(d)	99	(c)	100	(d)	101	(d)	102	(b)	103	(d)	104	(a)	105	(c)
106	(c)	107	(b)	108	(a)	109	(a)	110	(b)	111	(b)	112	(d)	113	(b)	114	(b)	115	(d)
116	(b)	117	(b)	118	(a)	119	(b)	120	(a)	121	(c)	122	(c)	123	(b)	124	(c)	125	(c)
126	(b)	127	(b)	128	(a)	129	(d)	130	(a)	131	(a)	132	(a)	133	(d)	134	(b)	135	(a)
136	(a)	137	(c)	138	(b)	139	(a)	140	(d)	141	(a)	142	(a)	143	(b)	144	(c)	145	(d)

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146	(c)	147	(b)	148	(c)	149	(a)	150	(d)	151	(a)	152	(b)	153	(a)	154	(c)	155	(c)
156	(b)	157	(a)	158	(a)	159	(c)	160	(c)	161	(d)	162	(c)	163	(c)	164	(b)	165	(c)
166	(b)	167	(c)	168	(c)	169	(c)	170	(a)	171	(b)	172	(a)	173	(c)	174	(d)	175	(d)

2 (*c*) In thermodynamics, process is called reversible when the surroundings are always in equilibrium with the system.

3 (*c*) For an open system; exchange of matter as well as energy with its surroundings can takes place.

Thus, $\Delta E \neq 0$, whereas an isolated system exchanges neither matter nor energy with the surroundings and, therefore $\Delta E = 0$.

5 (*d*) q (heat) and W (work) represents path functions. These variables are path dependent and their values depends upon the path followed by the system in attaining that state. They are inexact differentials whose integration gives a total quantity depending upon the path.

Option (a), i.e. $q + W$ and option (d), i.e. $H–TS$ are state functions. The value of state functions is independent to the way in which the state is attained. All the state functions are exact differentials and cyclic integration involving a state functions is zero.

6 (*c*) No exchange of heat takes place between the system and surroundings, i.e. $dq = 0$ in an adiabatic process. This condition exists when the system is thermally isolated.

7 (*b*) A thermoflask or an insulated beaker does not allow exchange of heat between the system and surroundings through its boundary. This type of system is called adiabatic system. The manner in which the state of such a system may be changed is called adiabatic process.

9 (*b*) The internal energy of a system can be changed by transfer of heat from the surroundings to the system or *vice-versa* without expenditure of work. This exchange of energy which is a result of temperature difference is called heat, (q).

10 (*c*) There is transfer of heat through thermally conducting walls instead of adiabatic walls.

Thus, thermally conducting wall is used in the given figure.

11 (*b*) In the given case, change in internal energy, $\Delta U = q$, as no work is done at constant volume.

13 (*c*) From the given options; option (c) is correct as, W amount of work is done by the system and q amount of heat is supplied to the system.

i.e. $\Delta U = q - W$ (closed system)

14 (*b*) Heat absorbed, $q = 500$ cal

Work done by the system, $W = -350$ cal

According to the first law of thermodynamics,

$$\Delta E = q + W = 500 + (-350) = +150 \text{ cal}$$

15 (*a*) Since, W is the work done on the system by movement of the piston, therefore

$$\begin{aligned} W &= \text{force} \times \text{distance} \\ &= p_{\text{ext}} \cdot A \cdot l \\ &= p_{\text{ext}} (-\Delta V) \\ &= -p_{\text{ext}} (V_f - V_i) \end{aligned}$$

16 (*c*) For isothermal reversible expansion,

$$|W| = nRT \ln \frac{V_f}{V_i} = nRT \ln \frac{V}{V_i}$$

where, V = final volume, V_i = initial final.

or $\quad |W| = nRT \ln V - nRT \ln V_i$

On comparing with equation of straight line, $y = mx + c$, we get

$$\text{slope} = m = +\, nRT$$

$$\text{intercept} = -\, nRT \ln V_i$$

Thus, plot of $|W|$ with $\ln V$ will give straight line in which slope of $2(T_2)$ is greater than slope of $1(T_1)$ which is given in all options.

Now, if $V_i < 1$ then y intercept $(-\, nRT\, V_i)$ becomes positive and if it is positive for one case then it is positive for other case also. Thus, it is not possible that one y-intercept goes above and other y-intercept goes below. Thus, option (b) and (d) are incorrect.

If we extent plot given in option (a) it seems to be merging which is not possible because if they are merging they give same +ve y-intercept. But they cannot give same y-intercept because value of T is different.

Now, if we extent the line of T_1 and T_2 given in option (c) it seems to be touching the origin. If they touch the origin then y-intercept becomes zero which is not possible. Thus, it is not the exactly correct answer but among the given options it is the most appropriate one.

17 (*d*) The net change in internal energy, i.e. $\Delta E = 0$ as it is a cyclic process.

18 (*b*) For an isothermal irreversible expansion,

Work done $(W) = -p_{\text{ext}} (V_2 - V_1)$ …(i)

where, V_1 = initial volume

V_2 = final volume

Given, $\quad p_{\text{ext}} = 10^5 \text{ Nm}^{-2}$

$V_1 = 10^{-3} \text{m}^3$

$V_2 = 10^{-2} \text{ m}^3$

On substituting the given values in Eq. (i),

We get, $\quad W = -10^5 \text{Nm}^{-2} (10^{-2} \text{m}^3 - 10^{-3} \text{m}^3)$

$$= -10^5 \text{Nm}^{-2} \times 10^{-3} \ (10 - 1) \text{m}^3$$

$$= -900 \text{ Nm} = -900 \text{ J}$$

19 (*d*) Given,

$$V_1 = 0.1 \text{ L}, V_2 = 0.25 \text{ L}, \ p_{\text{ext}} = 2 \text{ bar}$$

We know that, $W_{\text{irrev}} = -\, p_{\text{ext}} (V_2 - V_1)$

On substituting the given values in the above equation, we get

$$\begin{aligned} W_{\text{irrev}} &= -\, 2 \text{ bar } (0.25 - 0.1) \text{ L} \\ &= -\, 2 \times 0.15 \text{ L bar} = -\, 0.3 \text{ L bar} \\ &= -\, 0.3 \times 100 \text{ J} = -\, 30 \text{ J} \qquad [\because 1 \text{ L bar} = 100 \text{ J}] \end{aligned}$$

20 (*d*) Option (d) is incorrect. It's correct form is as follows :

From first law of thermodynamics,

$$\Delta U = q + W$$

In adiabatic expansion, $q = 0$

$\therefore \qquad \Delta U = W$

During expansion of a gas, W is negative, i.e $W < 0$ or $\Delta U < 0$.

We know that, $\Delta U = nC_V \Delta T$

$\therefore \qquad nC_V \Delta T < 0 \quad \text{or} \quad \Delta T < 0$

$\therefore \qquad T_C - T_A < 0 \quad \text{or} \quad T_C < T_A$

Rest other options are correct.

22 (*a*) Given,

$$V_2 = 375 \text{ mL}, \quad V_1 = 50 \text{ mL}, \quad n = 0.04 \text{ mol}$$

$$T = 310 \text{ K}, \qquad q = 208 \text{ J}$$

$\because$ The process is isothermal expansion, hence

$$q = -\, W \ \text{ and } \Delta E = 0$$

Now, $\quad W = -2.303 nRT \log \dfrac{V_2}{V_1}$

$$= -2.303 \times 0.04 \times 8.314 \times 310 \times \log \frac{375}{50}$$

$$= -208 \text{ J}$$

$\Rightarrow \qquad q = +208 \text{ J},$

$W = -208 \text{ J}$ (expansion work)

24 (*a*) As we know that,

$$\Delta U = q - \, p_{\text{ext}} \Delta V$$

Now, if a process of expansion of a gas occurs in vacuum and at constant volume, then

$$\Delta U = qV \qquad (\because \Delta V = 0, \ p_{\text{ext}} = 0)$$

25 (*c*) According to first law of thermodynamics,

$$\Delta U = q + W$$

where, ΔU = internal energy

q = heat absorbed or evolved

W = work done

Also, work done against constant external pressure (irreversible process)

$$\begin{aligned} W &= -\, p_{\text{ext}} \Delta V = -p_{\text{ext}} (V_2 - V_1) \\ &= -\, 2.5 \text{ atm } (4.5 \text{ L} - 2.5 \text{ L}) \\ &= -\, 5 \text{ L atm} = -\, 5 \times 101.3 \text{ J} \\ &= -\, 505 \text{ J} \end{aligned}$$

Since, the system is well insulated, $q = 0$

$\therefore \quad \Delta U = W = -505\,\text{J}$

Hence, change in internal energy, ΔU of the gas is $-505\,\text{J}$.

26 (*d*) From the equation,

$$C_6H_6(l) + \frac{15}{2}O_2(g) \longrightarrow 6CO_2(g) + 3H_2O(l)$$

Change in the number of gaseous moles i.e.

$$\Delta n_g = 6 - \frac{15}{2} = -\frac{3}{2} \text{ or } -1.5$$

Now we have Δn_g and other values given in the question are

$$\Delta U = -3263.9\,\text{kJ/mol}$$

$$T = 25°\,\text{C} = 273 + 25 = 298\,\text{K}$$

$$R = 8.314\,\text{JK}^{-1}\text{mol}^{-1}$$

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

$$= -3267.6\,\text{kJ mol}^{-1}$$

27 (*a*) Since, heat absorbed at constant pressure, is $q = 1440\,\text{cal}$

$\therefore \quad \Delta H = 1440\,\text{cal}$

Given : $H_2O(s) \rightleftharpoons H_2O(l)$

$$\Delta V = (0.0180 - 0.0196)$$
$$= -0.0016\,\text{L}$$

$\therefore \quad p\Delta V = -1\,\text{atm} \times 0.0016\,\text{L}$

$$= -0.0016\,\text{L atm}$$
$$= -0.039\,\text{cal} \qquad (\because 1\text{ L atm} = 24.20\text{ cal})$$

Using, $\Delta H = \Delta U + p\Delta V$

$$\Delta U = \Delta H - P\Delta V$$
$$= 1440 - (-0.039)$$
$$= 1440.039\,\text{cal}$$

28 (*d*) Given, $w = 10\,\text{g}, \quad T = 300\,\text{K}$

$$V_1 = 10;\ V_2 = 5\,\text{L}$$

$\because \quad q = 2.303\, nRT \log\,(V_2/V_1)$

$\therefore \quad q = 2.303 \times \frac{10}{40} \times 2 \times 300 \times \log\left(\frac{5}{10}\right)$

$$= -103.980\text{ cal}$$

For isothermal expansion, $\Delta U = 0$

$$W = \Delta U - q = 0 - (-103.980)$$
$$= +103.980\text{ cal}$$

When the temperature is constant,

$$p_1V_1 = p_2V_2$$
$$\Delta H = \Delta U + \Delta(pV) = 0 + 0 = 0$$

29 (*d*) For any chemical reaction,

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

where,

Δn_g = total number of moles of gaseous products − total number of moles of gaseous reactants

For the given reaction,

$$Fe_2O_3(s) + 3H_2(g) \longrightarrow 2Fe(s) + H_2O(l)$$

$$\Delta n_g = 0 - 3 = -3$$

$\therefore \quad \Delta H = \Delta E + (-3)RT$

$$\Delta H = \Delta E - 3RT$$

30 (*b*) Using gas equation, $p\Delta V = \Delta n_g RT$

where, $p\Delta V$ = work done (W)

Thus, work done (W) = $\Delta n_g RT$

where, Δn_g = number of moles of gaseous products − number of moles of gaseous reactants.

Temperature, $T = 25 + 273 = 298\,\text{K}$

For the reaction,

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

$$\Delta n_g = 4 - \left(1 + \frac{13}{2}\right) = -\frac{7}{2}$$

Thus,

$$W = -\left[-\frac{7}{2}\text{mol} \times 0.0821\,\text{L atm K}^{-1}\ \text{mol}^{-1} \times 298\,\text{K}\right]$$
$$= 85.6\,\text{L atm}$$

33 (*a*) As we know that,

$$C_p - C_V = nR$$

where, n = no. of moles of gas

$$R = 8.314\ \text{J/K/mol}$$

$$C_p - C_V = 10 \times 8.314 = 83.14\ \text{J/K}$$

35 (*d*) For monoatomic gas,

$$C_p = 5\,\text{cal}, C_V = 3\,\text{cal}$$

$$\gamma = \frac{C_p}{C_V} = \frac{5}{3} = 1.67$$

36 (*d*) Given, $T_2 = ?, T_1 = 300\,\text{K}, V_2 = 27V_1, n = 1\,\text{mol}$

$$C_V = 6\,\text{cal mol}^{-1}, \gamma = 1.33.$$

In adiabatic conditions,

$$\frac{T_2}{T_1} = \left(\frac{V_1}{V_2}\right)^{\gamma - 1}$$

or, $\quad \frac{T_2}{T_1} = \left(\frac{1}{27}\right)^{1.33 - 1}$

$$= \left(\frac{1}{27}\right)^{0.33} = \left(\frac{1}{27}\right)^{1/3} = \frac{1}{3}$$

or, $\quad T_2 = 300 \times \frac{1}{3} = 100\,\text{K}$

Thus, $T_2 < T_1$ and, therefore cooling takes place due to expansion under adiabatic condition.

$$\Delta E = q + W$$

$$\Delta E = W \qquad (q = 0 \text{ for adiabatic change})$$

$\because \quad \Delta E = -$ ve because gas expands.

$$\therefore \quad W = -\Delta E = -C_V(T_2 - T_1)$$
$$= -6(100 - 300) = 1200 \text{ cal}$$

38 (*c*) Heat absorbed at constant volume is measured in a bomb calorimeter. Here a steel vessel (the bomb) is immersed in a water bath to ensure that, no heat is lost to the surroundings.

41 (*a*) For the reaction,

$$C_2H_5OH(l) + 3O_2(g) \longrightarrow 2CO_2(g) + 3H_2O(l);$$
$$\Delta U = -1364.47 \text{kJ / mol}$$
$$\Delta H = \Delta U + \Delta n_g RT \Rightarrow \Delta n_g = -1$$
$$\therefore \quad \Delta H = -1364.47 + \frac{-1 \times 8.314 \times 298}{1000}$$

[Here, value of R in unit of J must be converted into kJ]

$$= -1364.47 - 2.4776 = -1366.9476 \text{ kJ / mol}$$

or $\quad \Delta H = -1366.95 \text{ kJ / mol}$

42 (*b*) Since, volume is constant, therefore the heat involved in internal energy, i.e. ΔU.

We know that, $\Delta U = q_V = C_V \Delta T$.

Since, heat is lost by the system,

$$\therefore \quad q_V = -C_V \Delta T = -2.5 \text{ kJ K}^{-1} \times (298.45 - 298) \text{ K}$$
$$= -1.125 \text{ kJ}$$

(Here, – ve sign indicates the exothemic nature of the reaction.)

Thus, ΔU for the combustion of gas = – 1.125 kJ

For combustion of 1 mole of gas,

$$\Delta H = \frac{28 \text{g / mol} \times (-1.125 \text{ kJ})}{3.5 \text{ g}}$$
$$= -9 \text{kJ mol}^{-1}$$

43 (*a*) $\Delta H = q_p$ and C_p is the heat evolved or absorbed per mole for 1° fall or rise in temperature.

Here, fall in temperature is given,

$$= 320 - 293 = 27 \text{ K}$$

Molar mass of $CCl_2F_2 = 12 + 2 \times 35.5 + 2 \times 19$

$$= 121 \text{ g mol}^{-1}$$

Thus, heat evolved from 1.25 g of the sample on being cooled from 320 K to 293 K at constant pressure will be

$$= \frac{80.7}{121} \times 1.25 \times 27 = 22.51 \text{ J}$$

44 (*b*) Molar heat capacity of water per gram = 84/18 = 4.7J

As we know that; $q = 1 \text{ kJ} = 1000 \text{ J}$

molar heat capacity $(q) = m \times c \times \Delta T$

where m = mass, $\quad c$ = specific heat capacity

ΔT = temperature change

$$\therefore \quad q = 100 \times 4.7 \times \Delta T$$

or $\quad 1000 = 100 \times 4.7 \times \Delta T$

$$\Rightarrow \quad \Delta T = \frac{1000}{100 \times 4.7} = 2.1 \text{K}$$

Thus, the increase in temperature of water is 2.1 K.

45 (*c*) For the reaction,

$$CH_4(g) + 2O_2(g) \longrightarrow CO_2(g) + 2H_2O(l)$$
$$\Delta_r H = \sum_i a_i H_{(\text{products})} - \sum_i b_i H_{(\text{reactants})}$$
$$= [H_m(CO_2, g) + 2H_m(H_2O, l)] - [H_m(CH_4, g) + 2H_m(O_2, g)]$$

where, H_m is the molar enthalpy.

46 (*d*) Phase transformations involve the energy changes e.g. ice, requires heat for melting. Normally, this melting takes place at constant pressure and during phase change, temperature remains constant (at 273 K).

47 (*a*) Given, $\quad H_2O(l) \xrightarrow{100°\text{C}} H_2O(g)$

As we know that, $\Delta_{\text{vap}}H° = \Delta_{\text{vap}}U° + \Delta n_g RT$

$$\Delta_{\text{vap}}H° = \text{enthalpy of vaporisation}$$
$$= 40.66 \text{ kJ mol}^{-1}$$

For the above reaction,

$$\Delta n_g = n_p - n_r = 1 - 0 = 1$$
$$R = 8.314 \text{ J/mol K}$$
$$T = 100° \text{C} = 273 + 100 = 373 \text{K}$$
$$\therefore \quad 40.66 \text{ kJ mol}^{-1} = \Delta_{\text{vap}}U° + 1 \times 8.314 \times 10^{-3} \times 373$$
$$\Delta_{\text{vap}}U° = 40.66 - 3.1 = +37.56 \text{ kJ mol}^{-1}$$

48 (*d*) (i) $I_2(s) \longrightarrow I_2(g); \; \Delta H_1 = +57.3 \text{ kJ mol}^{-1}$

(ii) $I_2(s) \longrightarrow I_2(l); \Delta H_2 = +15.5 \text{ kJ mol}^{-1}$

(iii) $I_2(l) \longrightarrow I_2(g); \Delta H = ?$

Eq (iii) will be obtained, if we substract Eq (ii) from (i), i.e (iii) = (i) – (ii)

Now, $\Delta H = 57.3 - 15.5 = +41.8 \text{ kJ mol}^{-1}$

49 (*a*) Given, $\Delta H_f^{\circ} (NH_3(g)) = 8.19 \text{ kJ mol}^{-1}$;

Mass of $NH_3 = 26$ g

$$\because \text{ Number of moles of } NH_3 = \frac{\text{Mass}}{\text{Molecular mass}}$$
$$= \frac{26}{17} = 1.53$$

Now, heat of decomposition for 1.5 moles of NH_3

$$= \text{number of moles} \times \text{standard enthalpy}$$
$$= 1.5 \times 81.9 = 122.9 \text{ kJ}$$

50 (*c*) $CaCO_3(s) \longrightarrow CaO(s) + CO_2(g)$

$$\Delta_r H° = \sum_i a_i \Delta_f H^{\circ}_{(\text{products})} - \sum_i b_i \Delta_f H^{\circ}_{(\text{reactants})}$$

where, a and b are represent the coefficients of the products and reactants in the balanced equation.

$$\begin{aligned}\Delta_r H^\circ &= \Delta_f H^\circ[\mathrm{CaO}(s)] + \Delta_f H^\circ[\mathrm{CO_2}(g)] - \Delta_f H^\circ[\mathrm{CaCO_3}(s)]\\ &= 1\,(-635.1\ \mathrm{kJ\ mol^{-1}}) + (1)\,(-393.5\ \mathrm{kJ\ mol^{-1}}) - 1\,(-1206.9\ \mathrm{kJ\ mol^{-1}})\\ &= 178.3\ \mathrm{kJ\ mol^{-1}}\end{aligned}$$

52 (*c*) According to Hess's law; the total heat change (ΔH) accompanying a chemical reaction is the same, whether the reaction takes place in one or more steps or follows one or more paths.

Therefore, the correct relation between ΔH and $\Delta H_1, \Delta H_2$ will be

$$\Delta H = \Delta H_1 + \Delta H_2$$

53 (*d*) According to the question, the diagrammatic representation of given reaction can be

$$\begin{tikzcd}
\mathrm{I} \arrow[rr, "\Delta_r H_{\mathrm{I-V}} = t"] \arrow[d, "\Delta_r H_{\mathrm{I-II}} = p"', "A"] & & \mathrm{V} \\
\mathrm{II} \arrow[r, "B", "\Delta_r H_{\mathrm{II-III}} = q"'] & \mathrm{III} \arrow[r, "C", "\Delta_r H_{\mathrm{III-IV}} = r"'] & \mathrm{IV} \arrow[u, "D", "\Delta_r H_{\mathrm{IV-V}} = s"']
\end{tikzcd}$$

As given, $q = r$ [Hence, (a) is correct]

Using concept of Hess's law, $t = p + q + r + s$

$\therefore \quad q + r = t - (s + p)$ [Hence, (b) is correct]

$2q = t - (s + p)$ [Hence, (c) is correct]

$[\because q = r]$

but $q + r = p + s$ is incorrect because exact amount of enthalpy change for each step is not given.

54 (*a*) Given,

$\mathrm{C}(s) + \mathrm{O_2}(g) \longrightarrow \mathrm{CO_2}(g);\ \Delta_f H = -393.5\ \mathrm{kJ\ mol^{-1}}$

$\because$ Heat released on formation of 44 g or 1 mole $\mathrm{CO_2}$

$= -393.5\ \mathrm{kJ\ mol^{-1}}$

$\therefore$ Heat released on formation of 35.2 g of $\mathrm{CO_2}$

$$= \frac{-393.5\ \mathrm{kJ\ mol^{-1}}}{44\ \mathrm{g}} \times 35.2\ \mathrm{g} = -315\ \mathrm{kJ\ mol^{-1}}$$

55 (*d*) Given,

$\mathrm{C}(s) + \frac{1}{2}\mathrm{O_2}(g) \longrightarrow \mathrm{CO}(g);\ \Delta H_1 = -26.4\ \mathrm{kcal}$ ...(i)

$\mathrm{C}(s) + \mathrm{O_2}(g) \longrightarrow \mathrm{CO_2}(g);\ \Delta H_2 = -94.0\ \mathrm{kcal}$

$\because$ We have to find ΔH for the reaction ...(ii)

$$\mathrm{CO} + \frac{1}{2}\mathrm{O_2} \longrightarrow \mathrm{CO_2}; \quad \Delta H = ?$$

$\therefore$ On subtracting Eq. (i) from Eq. (ii), we get

$$\Delta H = -94 - (-26.4) = -67.6\ \mathrm{kcal}$$

56 (*a*) Given,

$\mathrm{C(diamond)} + \mathrm{O_2} \longrightarrow \mathrm{CO_2};\ \Delta H = -395.3\ \mathrm{kJ/mol}$ ...(i)

$\mathrm{C(graphite)} + \mathrm{O_2} \longrightarrow \mathrm{CO_2};\ \Delta H = -393.4\ \mathrm{kJ/mol}$

Thus, on subtracting Eq. (i) from Eq. (ii), we get

$$\mathrm{C(graphite)} \longrightarrow \mathrm{C(diamond)}$$

i.e. $\Delta H = [-393.4 - (-395.3)]\ \mathrm{kJ/mol}$

$= +1.9\ \mathrm{kJ/mol}$

57 (*d*) In the reaction,

$$\mathrm{H_2}(g) \longrightarrow 2\mathrm{H}(g);\ \Delta_a H^\circ = 435\ \mathrm{kJ\ mol^{-1}}$$

H-atoms are formed by breaking H—H bond in dihydrogen. The enthalpy change in this process is known as enthalpy of atomisation, $\Delta_a H^\circ$.

In case of diatomic molecules like dihydrogen, the enthalpy of atomisation is also known as bond dissociation enthalpy.

58 (*a*) For the reaction,

$$\mathrm{H_2} + \mathrm{Cl_2} \longrightarrow 2\mathrm{HCl}$$

Given, B.E of $\mathrm{H_2} = 104\ \mathrm{kcal\ mol^{-1}}$

B.E of $\mathrm{Cl_2} = 58\ \mathrm{kcal\ mol^{-1}}$

B.E of $\mathrm{HCl} = 103\ \mathrm{kcal\ mol^{-1}}$

$\therefore$ Enthalpy of formation of HCl

$$= \frac{(104 + 58) - (2 \times 103)}{2}$$

$$= \frac{162 - 206}{2} = -\frac{44}{2} = -22\ \mathrm{kcal\ mol^{-1}}$$

59 (*b*) Given, I.E. of Xe = 279 kcal/mol

B.E. (F—F) = 38 kcal/mol

Electron affinity of F = 85 kcal/mol

$\because \quad \Delta_r H =$ Heat supplied − Heat evolved

$\therefore \quad 292 = (4x + 279) - (38 + 85)$

$\Rightarrow \quad x = 34\ \mathrm{kcal\ mol^{-1}}$

60 (*b*) Given,

$4\mathrm{H}(g) \longrightarrow 2\mathrm{H_2}(g);\ \Delta H = -869.6\ \mathrm{kJ}$

$\therefore\ 2\mathrm{H_2}(g) \longrightarrow 4\mathrm{H}(g);\ \Delta H = 869.6\ \mathrm{kJ}$

Thus, dissociation energy of H—H bond

$$= \frac{869.6}{2} = +434.8\ \mathrm{kJ}$$

61 (*a*) **Key concept** Relation between heat of reaction ($\Delta_r H$) and bond energies (BE) of reactions and products is given by,

$$\Delta_r H = \Sigma \mathrm{BE_{Reactants}} - \Sigma \mathrm{BE_{Products}}$$

The reaction of formation for XY is given as,

$$\frac{1}{2}X_2(g) + \frac{1}{2}Y_2(g) \longrightarrow XY(g);\ \Delta H = -200\ \mathrm{kJ\ mol^{-1}}$$

Given, the bond dissociation energies of X_2, Y_2 and XY are in the ratio 1 : 0.5 : 1. Let the bond dissociation energies of X_2, Y_2 and XY are a kJ mol^{-1}, $0.5a$ kJ mol^{-1} and a kJ mol^{-1}, respectively.

$$\therefore \quad \Delta_r H = \Sigma \text{BE}_{\text{Reactants}} - \Delta\ \text{BE}_{\text{Products}}$$

$$-200 = \left[\frac{1}{2} \times a + \frac{1}{2} \times 0.5a\right] - [1 \times a]$$

$$= \frac{a}{2} + \frac{a}{4} - a$$

$$-200 = \frac{2a + a - 4a}{4} = \frac{-a}{4}$$

$$a = 800 \text{ kJ mol}^{-1}$$

∴ The bond dissociation energy of X_2 will be

$$X_2 = a \text{ kJ mol}^{-1}$$

$$= 800 \text{ kJ mol}^{-1}$$

62 (*d*) For calculation of $\text{C} \equiv \text{C}$ bond energy, we must first calculate dissociation energy of C_2H_2 as,

$$C_2H_2(g) \longrightarrow 2C(g) + 2H(g) \qquad \text{...(i)}$$

Using the given bond energies and enthalpies :

$$C_2H_2(g) \longrightarrow 2C(s) + H_2(g);\ \Delta H = -225 \text{ kJ/mol} \quad \text{...(ii)}$$

$$2C(s) \longrightarrow 2C(g);\ \Delta H = 1410 \text{ kJ/mol} \quad \text{...(iii)}$$

$$H_2(g) \longrightarrow 2H(g);\ \Delta H = 330 \text{ kJ/mol} \quad \text{...(iv)}$$

Adding Eq. (ii), (iii) and (iv) gives Eq. (i).

$$\Rightarrow C_2H_2(g) \longrightarrow 2C(g) + 2H(g);\ \Delta H = 1515 \text{ kJ}$$

Since, $\Delta_r H = \Sigma \text{BE}_{(\text{reactants})} - \Sigma \text{BE}_{(\text{products})}$

$$\Rightarrow 1515 \text{ kJ / mol} = 2 \times (\text{C—H})\text{BE} + (\text{C} \equiv \text{C}) \text{ BE}$$

$$\Rightarrow 1515 \text{ kJ / mol} = 2 \times 350 + (\text{C} \equiv \text{C}) \text{ BE}$$

$$\Rightarrow (\text{C} \equiv \text{C}) \text{ BE} = 1515 - 700 = 815 \text{ kJ/mol}$$

63 (*c*) Given,

$$\frac{1}{2} H_2 + \frac{1}{2} Cl_2 \longrightarrow HCl,\ \Delta H_f = -93 \text{ kJ / mol}$$

∵ In this reaction, one mole of HCl is formed.

∴ ΔH_f of the reaction will remain same, i.e. – 93 kJ / mol.

Let the bond dissociation energy of H — Cl bond be *x*.

For the given reaction,

$$\Delta H_f = \Sigma \text{B.E}_{(\text{reactants})} - \Sigma \text{B.E}_{(\text{products})}$$

$$-93 = \frac{1}{2}(434) + \frac{1}{2}(242) - x$$

$$-93 = +338 - x \Rightarrow x = 431 \text{ kJ / mol}$$

64 (*c*) Given reaction :

$$I_2(s) \longrightarrow I_2(g)$$

Specific heat of $I_2(s) = 0.055 \text{ cal g}^{-1} \text{ K}^{-1}$.

Specific heat of $I_2(\text{vap}) = 0.031 \text{ cal g}^{-1}\text{K}^{-1}$.

Enthalpy (H_1) of sublimation of iodine = 24 cal g^{-1}

If *q* is the amount of heat involved in a system then at constant pressure $q = q_p$ and $\Delta H = C_p \Delta T$

$$H_2 - H_1 = C_p(T_2 - T_1)$$

$$H_2 = H_1 + \Delta C_p(T_2 - T_1)$$

$$H_2 = 24 + (0.031 - 0.055)(250 - 200)$$

$$H_2 = 24 + (-0.024)(50) = 24 - 1.2 = 22.8 \text{ cal/g}$$

Thus, the enthalpy of sublimation of iodine at 250 is 22.8 cal/g.

65 (*a*) In the given Born-Haber cycle, I, II and III represents respectively as follows :

I. Electron gain enthalpy as one mole of anion being formed from gaseous atoms in its ground state;

i.e. $\quad Cl(g) + e^- \longrightarrow Cl^-(g)$

II. Enthalpy of sublimation as one mole of vapour formed from the solid,

i.e. $\quad Na(s) \longrightarrow Na(g)$

III. Ionisation enthalpy as one mole of an electrolyte completely dissociates into ions,

i.e. $\quad Na(g) \longrightarrow Na^+(g) + e^-$

66 (*c*)

$$\begin{tikzcd} AB(s) \arrow[r, "\Delta_{\text{sol}} H^\circ"] \arrow[d, "\Delta_{\text{lattice}} H^\circ"'] & A^+(aq) + B^-(aq) \\ A^+(g) + B^-(g) \arrow[ur, "\Delta_{\text{hyd}} H^\circ"'] & \end{tikzcd}$$

The enthalpy of solution $AB(s), \Delta_{\text{sol}} H^\circ$ in water is determined by the selective values of the lattice enthalpy, $(\Delta_{\text{lattice}} H^\circ)$ and enthalpy of hydration of ions $(\Delta_{\text{hyd}} H^\circ)$ as $\Delta_{\text{sol}} H^\circ = \Delta_{\text{lattice}} H^\circ + \Delta_{\text{hyd}} H^\circ$

67 (*c*) Given : $\Delta_{\text{lattice}} H^\circ = +788 \text{ kJ/mol}$

$$\Delta_{\text{hyd}} H^\circ = -784 \text{ kJ/mol}$$

$$\because \quad \Delta_{\text{sol}} H^\circ = \Delta_{\text{lattice}} H^\circ + \Delta_{\text{hyd}} H^\circ$$

$$\therefore \quad \Delta_{\text{sol}} H^\circ = +788 \text{ kJ mol}^{-1} - 784 \text{ kJ mol}^{-1}$$

$$= +4 \text{ kJ mol}^{-1}$$

71 (*a*) In an exothermic reaction, there is the decrease in enthalpy when reactants are converted into products. Therefore, the given diagram represents the enthalpy diagram for exothermic reactions.

73 (*b*) In exothermic process, heat released increases the disorderness of the surroundings and overall entropy change is positive which makes the reaction spontaneous.

74 (*b*) When the partition is withdrawn between two gases they begin to diffuse into each other and after a period of time diffusion will be completed.

Thus, diffusion of two gases occurs in the given diagram.

76 (*b*) The entropy (ΔS) of a reaction is negative, if the reactants are in more random state as compared to the products.

Order of randomness is

(gas > liquid > solid)

Among the given reactions, in the reaction (b)

$$2SO_2(g) + O_2(g) \longrightarrow 2SO_3(g);$$

there is decrease in number of moles of the gas and, therefore is accompanied by decrease in entropy, i.e. ΔS will be negative.

77 (*a*) For both reversible and irreversible expansion for an ideal gas, under isothermal conditions, $\Delta U = 0$, but ΔS_{total}, i.e. $\Delta S_{\text{sys}} + \Delta S_{\text{surr}}$ is not zero for irreversible process.

78 (*d*) Since, entropy is a state function and work done (W) is a path function and, therefore

$$\Delta S_{A \to C} = \Delta S_{A \to B} + \Delta S_{A \to C} \text{ is true but}$$

$$\Delta W_{A \to B \to C} = W_{A \to B} + W_{B \to C} \text{ is not true.}$$

Moreover, $\quad W_{B \to C} = p\Delta V = 0$

as change in $B \to C$ is isochoric.

Therefore, $\quad W_{A \to B \to C} = W_{A \to B}$ is true

79 (*a*) As we know that,

$$\Delta S_{\text{total}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}}$$

For ΔS_{surr}, we have to consider the heat absorbed by the surroundings which is equal to $-\Delta_r H°$. At temperature (T), entropy change of the surroundings is

$$\Delta S_{\text{surr}} = -\frac{\Delta_r H°}{T} \qquad \text{(at constant pressure)}$$

$$= \frac{-(-1648 \times 10^3 \text{ J mol}^{-1})}{298 \text{ K}}$$

$$= 5530 \text{ JK}^{-1} \text{ mol}^{-1}$$

$$\Delta_r S_{\text{total}} = 5530 + (-549.4)$$

$$= 4980.6 \text{ JK}^{-1} \text{ mol}^{-1}$$

Hence, the above reaction is spontaneous.

80 (*a*) Among the given reactions, only in the case of

$$\text{C(graphite)} + \frac{1}{2}\text{O}_2(g) \longrightarrow \text{CO}(g)$$

entropy increases because randomness (disorder) increases. Thus, standard entropy change ($\Delta S°$) is positive.

Moreover, it is a combustion reaction and all the combustion reactions are generally exothermic, i.e. $\Delta H° = -\text{ve}$

We know that,

$$\Delta G° = \Delta H° - T\Delta S° = -\text{ve} - T(+\text{ve})$$

Thus, as the temperature increases, the value of $\Delta G°$ decreases.

81 (*b*) According to Gibbs-Helmholtz equation,

Gibbs energy $(\Delta G) = \Delta H - T\Delta S$

where, ΔH = Enthalpy change

ΔS = Entropy change

T = Temperature

For a reaction to be spontaneous,

$$\Delta G < 0.$$

∴ Gibbs -Helmholtz equation becomes,

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

or, $\quad \Delta H < T\Delta S$

or, $\quad T > \dfrac{\Delta H}{\Delta S} = \dfrac{35.5 \text{ kJ mol}^{-1}}{83.6 \text{ JK}^{-1}\text{mol}^{-1}}$

$$= \frac{35.5 \times 1000 \text{ J mol}^{-1}}{83.6 \text{ J K}^{-1} \text{ mol}^{-1}} = 425 \text{ K}$$

Thus, the reaction is spontaneous at

$$T > 425 \text{ K}$$

82 (*c*) As we know that,

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

Given, $\Delta H_{\text{vap}} = 30 \text{ kJ mol}^{-1}$

∵ $\quad \Delta G° = 0$ at equilibrium,

∴ $\quad \Delta S_{\text{vap}} = \dfrac{\Delta H_{\text{vap}}}{T}$

$$= \frac{30 \times 10^3 \text{ J mol}^{-1}}{300 \text{ K}}$$

$$= 100 \text{ J mol}^{-1} \text{ K}^{-1}$$

83 (*c*) Molar entropy change for the melting of ice,

$$\Delta S_{\text{melt}} = \frac{\Delta H_{\text{fusion}}}{T} = \frac{1.435 \text{ kcal/mol}}{(0 + 273)\text{K}}$$

$$= 5.26 \times 10^{-3} \text{ kcal / mol K}$$

$$= 5.260 \text{ cal/mol K}$$

84 (*b*) A process will be spontaneous when its free energy (Gibb's energy) change will be negative, i.e. $\Delta G < 0$.

Spontaneity of a process is decided by the value of ΔG, which can be predicted from the Gibb's equation, $\Delta G = \Delta H - T\Delta S$ for positive/negative signs of ΔH and ΔS at any/higher/lower temperature as:

ΔH	ΔS	Comment on temperature (T)	ΔG	Comment on the process
< 0	> 0	at any temp.	< 0	spontaneous
> 0	< 0	at any temp.	> 0	non-spontaneous
< 0	< 0	at lower temp.	< 0	spontaneous
> 0	> 0	at higher temp.	< 0	spontaneous

85 (*d*) ∵ $\Delta S^{\circ}_{\text{reaction}} = \Delta S^{\circ}_{\text{Products}} - \Delta S^{\circ}_{\text{Reactants}}$

For the reaction,

$$\text{CH}_4(g) + \text{H}_2\text{O}(g) \longrightarrow 3\text{H}_2(g) + \text{CO}(g)$$

$$\Delta S^{\circ}_{\text{reaction}} = [3 \times S^{\circ}_{\text{H}_2} + S^{\circ}_{\text{CO}}] - [S^{\circ}_{\text{CH}_4} + S^{\circ}_{\text{H}_2\text{O}}]$$

$$= [3 \times 130.6 + 197.6] - [186.2 + 188.7]$$

$$= 589.4 - 374.9$$

$$= 214.5 \text{ JK}^{-1} \text{ mol}^{-1}$$

87 (*c*) Option (c) is incorrect.

It's correct form is as follows :

For a spontaneous process, $\Delta S > 0$.

Rest other expressions are correct.

88 (*a*) The conversion of 1 kg of ice at 273 K into water vapours at 383 K takes place as follows:

$$\begin{tikzcd}
\underset{273\text{K}}{H_2O(s)} \arrow[r, "\Delta S_1"] & \underset{273\text{K}}{H_2O(l)} \arrow[r, "\Delta S_2"] & \underset{373\text{K}}{H_2O(l)} \arrow[d, "\Delta S_3"] \\
 & \underset{383\text{K}}{H_2O(g)} & \underset{373\text{K}}{H_2O(g)} \arrow[l, "\Delta S_4"']
\end{tikzcd}$$

$$\Delta S_1 = \frac{\Delta H_{\text{Fusion}}}{\Delta T_{\text{Fusion}}} = \frac{334 \text{ kJ kg}^{-1}}{273 \text{ K}} = 1.22 \text{ kJ kg}^{-1}\text{K}^{-1}$$

$$\Delta S_2 = C \ln \frac{T_2}{T_1} = 4.2 \text{ kJ K}^{-1}\text{kg}^{-1} \ln\left(\frac{373 \text{ K}}{273 \text{ K}}\right)$$

$$= 4.2 \times 2.303 \, (\log 373 - \log 273) \text{ kJ K}^{-1}\text{kg}^{-1}$$

$$= 4.2 \times 2.303 \, (2.572 - 2.436) = 1.31 \text{ kJ K}^{-1}\text{kg}^{-1}$$

$$\Delta S_3 = \frac{\Delta H_{\text{vap.}}}{\Delta T_{\text{vap.}}} = \frac{2491 \text{ kJ kg}^{-1}}{373 \text{ K}} = 6.67 \text{ kJ kg}^{-1}\text{K}^{-1}$$

$$\Delta S_4 = \text{C} \ln \frac{T_2}{T_1} = 2 \text{ kJ K}^{-1}\text{kg}^{-1} \ln\left(\frac{383 \text{ K}}{373 \text{ K}}\right)$$

$$= 2 \times 2.303 \, (\log 383 - \log 373) \text{ kJ K}^{-1}\text{kg}^{-1}$$

$$= 2 \times 2.303 \, (2.583 - 2.572) \text{ kJ K}^{-1}\text{kg}^{-1}$$

$$= 0.05 \text{ kJ K}^{-1}\text{kg}^{-1}$$

$$\Delta S_{\text{Total}} = \Delta S_1 + \Delta S_2 + \Delta S_3 + \Delta S_4$$

$$= 1.22 + 1.31 + 6.67 + 0.05$$

$$= 9.26 \text{ kJ kg}^{-1}\text{K}^{-1}$$

89 (*c*) As we know that,

$$\Delta G^\circ_{(\text{reaction})} = \Sigma_f G^\circ_{(\text{products})} - \Sigma_f G^\circ_{(\text{reactants})}$$

∴ For the reaction,

$$\text{CO}(g) + \frac{1}{2}\text{O}_2(g) \longrightarrow \text{CO}_2(g)$$

$$\Delta G^\circ_{(\text{reaction})} = \Sigma G^\circ_f(\text{CO}_2) - [G^\circ_f(\text{CO}) + \frac{1}{2}G^\circ_f(\text{O}_2)]$$

$$\Rightarrow -298.4 - [-114.6 + 0] \qquad [\because G^\circ_f(\text{CO}_2) = 0]$$

$$\Rightarrow -183.8 \text{ kJ/mol}$$

Also, $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$

$\Rightarrow$ $-183.8 = \Delta H^\circ - [298 \times (-0.082)]$

$\Rightarrow$ $\Delta H^\circ = 208.24 \text{ kJ/mol}$

91 (*d*) $\Delta_r G^\circ$ is related to the equilibrium constant of the reaction as follows :

$$0 = \Delta_r G^\circ + RT \ln K$$

$$\Delta_r G^\circ = -RT \ln K$$

$$\Delta_r G^\circ = -2.303 RT \log K$$

$$\Delta_r G^\circ = \Delta_r H^\circ - T\Delta_r S^\circ$$

$$= -RT \ln K$$

92 (*c*) Mathematical expression for the thermodynamic equilibrium is,

$$\Delta G = \Delta G^\circ + 2.303 RT \log Q$$

At equilibrium when $\Delta G = 0$ and $Q = K$

then, $\Delta G = \Delta G^\circ + 2.303 RT \log K = 0$

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

93 (*b*) As we know that,

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

where, ΔU = change in internal energy

Δn_g = number of moles of gaseous products − number of moles of gaseous reactants = 2 − 0 = 2

R = gas constant = 2 cal

But, $\Delta U = 2.1 \text{ kcal}$

$$= 2.1 \times 10^3 \text{ cal} \qquad [\because 1 \text{ kcal} = 10^3 \text{ cal}]$$

$$\therefore \Delta H = (2.1 \times 10^3) + (2 \times 2 \times 300) = 3300 \text{ cal}$$

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

$\Rightarrow$ $\Delta G = (3300) - (300 \times 20)$

$\Rightarrow$ $\Delta G = -2700 \text{ cal}$

$\therefore$ $\Delta G = -2.7 \text{ kcal}$

94 (*c*) $\Delta G = \Delta H - T\Delta S$

The process will be spontaneous, when

$\Delta G = -$ ve, i.e. $|T\Delta S| > |\Delta H|$

Given : $\Delta H = 200 \text{ J mol}^{-1}$

and $\Delta S = 40 \text{ JK}^{-1} \text{ mol}^{-1}$

$$\Rightarrow \qquad T > \frac{|\Delta H|}{|\Delta S|} = \frac{200}{40} = 5 \text{ K}$$

So, the minimum temperature for spontaneity of the process is 5 K.

95 (*d*) Given,

$$\Delta G^\circ = -115 \times 10^3 \text{ J}$$

$$T = 298 \text{ K}, R = 8.314 \text{ JK}^{-1} \text{ mol}^{-1}$$

$$\because \qquad -\Delta G^\circ = 2.303 RT \log_{10} K_p$$

$$\therefore \qquad -(-115 \times 10^3) = 2.303 \times 8.314 \times 298 \log_{10} K_p$$

$$\log_{10} K_p = \frac{115000}{2.303 \times 8.314 \times 298} = 20.15$$

96 (*a*) Statement (a) is correct, while the other statements are incorrect. Corrected form are as follows :

Reactants in a closed vessel made up of conducting material is an example of closed system and reactants in a thermosflask or any other closed insulated vessel is an example of an isolated system.

97 (*c*) Adiabatic process is a process in which there is no transfer of heat between the system and surroundings. The wall separating the system and the surroundings is called the adiabatic wall.

Thus, statement (c) is correct.

99 (*c*) The q is positive, when heat is transferred from the surroundings to the system and q is negative when heat is transferred from system to the surroundings.
Thus, statement (c) is correct.

100 (*d*) Statement (d) is correct, while the other statements are incorrect. Corrected form are as follows :

$\Delta U = q + W$ is the mathematical expression of the first law of thermodynamics which states that the energy of an isolated system is constant.

i.e. energy can neither be created nor destroyed but can be converted into one form to another.

Moreover, in an isolated system,

$$W = 0, q = 0 \text{ and, therefore } \Delta U = 0.$$

102 (*b*) Temperature (T) will still remain the same, because volume is an extensive property and temperature is an intensive property.

Thus, statement (b) is correct.

104 (*a*) Statement (a) is correct, while the other statements are incorrect. Corrected form are as follows :
(b) Enthalpy is an extensive property.
(c) When a chemical equation is reversed, the value of $\Delta_r H°$ is also reversed in sign.

106 (*c*) Statement (c) is incorrect.
It's correct form is as follows :
Standard state of solid iron at 500 K is equal to pure iron at 1 bar.
Rest other statements are correct.

107 (*b*) Statement (b) is correct, while other statements are incorrect. Corrected form are as follows :
In the given reaction,

$$\mathrm{CaO}(s) + \mathrm{CO}_2(g) \longrightarrow \mathrm{CaCO}_3(s); \quad \Delta_r H° = -178.3 \text{ kJ mol}^{-1}$$

$\Delta_r H°$ is not the enthalpy of formation of CaCO_3, since CaCO_3 has been formed from other compounds and not from its constituent elements.

Moreover, the given reaction is not the example of combustion reaction.

108 (*a*) Statement (a) is incorrect.
It's correct form is as follows :

The enthalpy change given, i.e. $\Delta_r H^{\circ} = -\ 178.3$ kJ / mol is not equal to $\Delta_f H^{\circ}$ HBr as here two moles, instead of one mole of the product is formed.
Rest other statements are correct.

109 (*a*) Statement (a) is incorrect.
It's correct form is as follows :

$$\mathrm{C_2H_5OH}(l) + 3\mathrm{O}_2(g) \longrightarrow 2\mathrm{CO}_2(g) + 3\ \mathrm{H_2O}(l); \quad \Delta_r H = -1367 \text{ kJ mol}^{-1}$$

The negative sign (–ve) of enthalpy change in the above reaction indicates that this is an exothermic reaction.

Rest other statements are correct.

110 (*b*) Statement (b) is incorrect.
It's correct form is as follows :

The reference state of an element is most stable state of aggregation at 25°C and 1 bar pressure.

Rest other statements are correct.

111 (*b*) Statement (b) is correct, while the other statements are incorrect. Corrected form are as follows :
(a) Combustion reactions are exothermic in nature.
(c) Our body generates energy from food by the same overall process as combustion, although, the final products are produced after a series of complex biochemical reaction involving enzymes.

113 (*b*) Statement (b) is incorrect.
It's correct form is as follows :

$$\Delta_r C_p^{\circ} = +\frac{5}{2}R \qquad \text{(for ionisation)}$$

and

$$\Delta_r C_p^{\circ} = -\frac{5}{2}R \qquad \text{(for electron gain)}$$

Rest other statements are correct.

116 (*b*) Statement (b) is incorrect.
It's correct form is as follows :

Entropy changes varies inversely with temperature as, if similar amount of heat is given to a system at lower temperature than to a system at higher temperature, the randomness will be more for the former than the latter.
Rest other statements are correct.

117 (*b*) Statement (b) is incorrect.
It's correct form is as follows :
All naturally occurring processes, whether physical or chemical tend to proceed spontaneously only in one direction.
Rest other statements are correct.

118 (*a*) Statement (a) is incorrect. It's correct form is as follows :
The greater the disorder in an isolated system, the higher is the entropy.
Rest other statements are correct.

119 (*b*) Statement (b) is incorrect.
It's correct form is as follows :
There is perfect order in a crystal due to which the entropy of a pure crystalline solid approaches zero which is in accordance with third law of thermodynamics.
Rest other statements are correct.

120 (*a*) Statement I is incorrect.
It's correct form is as follows :

The entire universe other than system is not effected by the changes taking place in the universe. Therefore, for all partical purposes, surroundings are considered as the portion of the remaining universe which interacts with the system.

Rest other statements are correct.

123 (*b*) Statements I and III are correct, while the statement II and IV are incorrect. Corrected form are as follows :

For the reaction,

$$2\text{Zn}(s) + \text{O}_2(g) \longrightarrow 2\text{ZnO}(s); \Delta H = -693.8 \text{ kJmol}^{-1}$$

As we know that, $\Delta H = H_p - H_R$

A negative value of ΔH shows that $H_R > H_P$, i.e. enthalpy of two moles of ZnO is less than the enthalpy of two moles of zinc and one mole of oxygen by 693.8 kJ.

As $H_R > H_p$, 693.8 kJ mol^{-1} of energy is evolved in the reaction.

124 (*c*) Statement I and II are correct, while the statement III is incorrect.

It's correct form is as follows :

"On reversing a reaction, the sign of ΔH is also reversed but its magnitude remains the same.

126 (*b*) Statement II is correct, while the other statements are incorrect.

Corrected form are as follows :

Flowing of heat from warmer to colder body, expanding of gas and burining of carbon to give carbon dioxide, all are spontaneous processes.

127 (*b*) Statement II is correct, while the other statements are incorrect.

Corrected form are as follows :

In reaction (i) energy is absorbed, hence NO become unstable.

So, in reaction (ii) transform to stable NO_2 by releasing energy.

129 (*d*) Volume of water in a pond is a state function because change in volume of its water is independent of the route by which water is filled in the pond, either by rain or by tubewell or by both.

Thus, A is incorrect but R is correct.

133 (*d*) The magnitude of the enthalpy change depends on the strength of the intermolecular interactions in the substance undergoing the phase transformations.

The strong hydrogen bonds between water molecules hold them tightly in liquid phase. For an organic liquid such as acetone the intermolecular dipole-dipole interactions are significantly weaker.

Thus, it requires less heat to vaporise 1 mole of acetone then it does to vaporise 1 mole of water.

Thus, A is incorrect but R is correct.

134 (*b*) External energy (*U*) is a state function as it depends only upon the state of the system (i.e. initial and final states) and does not depend on path.

Moreover, temperature (T) is an intensive property as it does not depend on the quantity.

Thus, both A and R are correct but R is not the correct explanation of A.

137 (*c*) The phenomenon like flow of water down hill or fall of a stone on to the ground is an example of spontaneous process because there is a net decrease in potential energy in the direction of change.

Thus, A is correct but R is incorrect.

138 (*b*) The dissolution of NH_4Cl in water is endothermic but it dissolves in water because on dissolution, entropy increases $\Delta S = +$ ve and ΔH is +ve but if $T\Delta S > \Delta H$, then according to the equation,

$\Delta G = \Delta H - T\Delta S$, $\Delta G = -$ ve and the process is spontaneous.

Thus, both A and R are correct but R is not the correct explanation of A.

140 (*d*) At 0 K, the constitutent particles are static and entropy is minimum. If temperature is raised to 115 K, these begin to move and oscillate about their equilibrium positions in the lattice and system becomes more disordered, therefore entropy increases.

Thus, A is incorrect but R is correct.

144 (*c*) The correct match is :

$$\text{A} \rightarrow 2, \text{B} \rightarrow 4, \text{C} \rightarrow 3, \text{D} \rightarrow 1$$

At constant volume,

$$q_V = C_V \Delta T = \Delta U$$

At constant pressure,

$$q_p = C_p \Delta T = \Delta H$$

For a mole of an ideal gas,

$$\begin{aligned} \Delta H &= \Delta U + \Delta(pV) \\ &= \Delta U + \Delta(RT) \\ \Delta H &= \Delta U + R\Delta T \qquad \text{...(i)} \end{aligned}$$

Putting the value of ΔH and ΔU in Eq. (i)

We get, $\quad C_p \Delta T = C_V \Delta T + R\Delta T$

$$C_p = C_V + R$$

$$C_p - C_V = R$$

148 (*c*) $C_2H_6(g) + 7O_2(g) \longrightarrow 4CO_2(g) + 6H_2O(l)$

$$\Delta n_g = (n_p - n_r) = 4 - 8 = -4$$

$$\Delta H° = \Delta U° + \Delta n_g RT = -X - 4RT$$

Hence, $\quad \Delta H° < \Delta U°$

149 (*a*) Required equation for the formation of 1 mole of methane, (CH_4) is given by :

Given,

$$C(g) + 2H_2(g) \longrightarrow CH_4(g); \Delta_f H° = ?$$

(i) The enthalpy of combustion of 1 mole of methane is

$$CH_4(g) + 2O_2(g) \longrightarrow CO_2(g) + 2H_2O(l); \quad \Delta H = -890.3 \text{ kJ mol}^{-1}$$

(ii) The enthalpy of combustion of 1 mole of graphite is

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

(iii) The enthalpy of combustion of 1 mole of dihydrogen is

$$H_2(g) + \frac{1}{2}O_2(g) \longrightarrow H_2O\ (l); \quad \Delta H = -285.8 \text{ kJ mol}^{-1}$$

Multiplying Eq. (iii) by 2, we get

(iv) $2H_2(g) + O_2(g) \longrightarrow 2\,H_2O\ (l); \quad \Delta H = -571.6 \text{ kJ mol}^{-1}$

Adding Eqs. (ii) and (iv), we get

(v) $C\,(s) + 2H_2\,(g) + 2O_2(g) \longrightarrow CO_2\,(g) + 2H_2O\,(l); \Delta H = -965.1 \text{ kJ mol}^{-1}$

Reversing Eq. (i) we get,

(vi) $CO_2\,(g) + 2H_2O\,(l) \longrightarrow CH_4\,(g) + 2O_2\,(g); \quad \Delta H = +890.3 \text{ kJ mol}^{-1}$

Adding Eq. (v) and (vi), we get required equation

$$C\,(s) + 2H_2(g) \longrightarrow CH_4(g); \quad \Delta H = -74.8 \text{ kJ mol}^{-1}$$

150 (*d*) $\Delta G = \Delta H - T\Delta S$

For the given reaction, $\Delta H = -\text{ve}$ as it is exothermic, $\Delta S = +\text{ve}$, therefore $\Delta G = -\text{ve}$.

So, the reaction will be spontaneous at all temperatures.

151 (*a*) Given, $q = +701$ J (heat is absorbed, hence q is positive.)

$W = -394$ J (work is done by the system, hence W is negative.)

By first law of thermodynamics;

Internal energy change, $\Delta U = q + W$

$$= +701\text{J} + (-394 \text{ J}) = +307 \text{ J}$$

Hence, internal energy of the system increases by 307 J.

152 (*b*) $NH_2CN(s) + \frac{3}{2}O_2(g) \rightarrow N_2(g) + CO_2(g) + H_2O(l)$

Difference of moles of gaseous products and reactants,

$$\Delta n_g = n_p - n_r = 2 - \frac{3}{2} = \frac{1}{2} = 0.5 \text{ mol}$$

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

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

$$\Delta H = (-742.7 \text{ kJ} + 1238.786 \times 10^{-3} \text{ kJ}) \text{ mol}^{-1}$$

$$= -741.4 \text{ kJ mol}^{-1}$$

153 (*a*) Given, mass of Al = 60.0 g

Molar mass of Al = 27 g mol^{-1}

Molar heat capacity, $C = 24 \text{ J mol}^{-1}\text{K}^{-1}$

$$\Delta T = 55°\text{C} - 35°\text{C} = 20°\text{C or } 20 \text{ K}$$

$\because$ Heat, $q = n\,.\,C.\,\Delta T$

$$\therefore \quad q = \frac{60}{27} \times 24 \text{ J mol}^{-1} \text{ K}^{-1} \times 20\text{K} \quad \left(n = \frac{60}{27} \text{ mol}\right)$$

$$= 1066.66 \text{ J} = 1.067 \text{ kJ}$$

154 (*c*) Enthalpy change for the conversion of 1 mole liquid water at 10°C into 1 mole liquid water at 0°C is given as,

$$\Delta H_1 = C_p\ H_2O(l) \times \Delta T$$
$$= -75.3 \text{ J mol}^{-1} \text{ K}^{-1} \times 10 \text{ K}$$
$$= -753 \text{ J mol}^{-1}$$

Enthalpy of fusion,

$$\Delta H_2 = \Delta H_{\text{freezing}} = -\Delta H_{\text{fusion}} = -6.03 \text{ kJ mol}^{-1}$$

Enthalpy change for the conversion of 1 mole of ice at 0°C to 1 mole of ice at − 10°C is given as,

$$\Delta H_3 = C_p H_2O\ (s) \times \Delta T$$
$$= -36.8 \text{ J mol}^{-1} \text{ K}^{-1} \times 10\text{K}$$
$$= -368 \text{ J mol}^{-1}$$
$$\Delta H_{\text{total}} = -(0.753 + 6 \cdot 03 + 0.368) \text{ kJ mol}^{-1}$$
$$= -7.151 \text{ kJ mol}^{-1}$$

155 (*c*) Given,

(i) $CCl_4(l) \longrightarrow CCl_4(g); \quad \Delta_{\text{vap}}H° = +30.5 \text{ kJ mol}^{-1}$

(ii) $C(s) + 2Cl_2(g) \longrightarrow CCl_4(l); \quad \Delta_f H° = -135.5 \text{ kJ mol}^{-1}$

(iii) $C(s) \longrightarrow C(g); \Delta_a H° = 715.0 \text{ kJ mol}^{-1}$

(iv) $Cl_2(g) \longrightarrow 2Cl(g); \quad \Delta_a H° = 242 \text{ kJ mol}^{-1}$

Multiplying Eq. (iv) by 2, we get

(v) $2Cl_2(g) \longrightarrow 4Cl(g); \quad \Delta_a H° = 484.0 \text{ kJ mol}^{-1}$

Adding Eq. (iii) and (v), we get

(vi) $C(s) + 2Cl_2(g) \longrightarrow C(g) + 4Cl(g); \quad \Delta H = 1199 \text{ kJ mol}^{-1}$

Reversing Eq. (i) and (ii), we get

(vii) $CCl_4(g) \longrightarrow CCl_4(l); \quad \Delta H = -30.5 \text{ kJ mol}^{-1}$

(viii) $CCl_4(l) \longrightarrow C(s) + 2Cl_2(g); \Delta H = +135.5 \text{ kJmol}^{-1}$

Adding Eq. (vi), (vii) and (viii), we get

$$CCl_4(g) \longrightarrow C(g) + 4Cl(g); \quad \Delta H = 1304 \text{ kJ mol}^{-1}$$

Bond enthalpy of C — Cl bond in CCl_4

$$= \frac{1304}{4} = 326 \text{ kJ mol}^{-1}.$$

($\because$ There are four C — Cl bonds in CCl_4)

156 (b) Given, $\Delta H = 400$ kJ mol^{-1},

$\Delta S = 0.2$ kJ K^{-1}mol^{-1},

$\because$ Gibbs free energy, $\Delta G = \Delta H - T\Delta S$

$\Rightarrow 0 = 400 \text{ kJ mol}^{-1} - T \times 0.2 \text{ kJ K}^{-1} \text{ mol}^{-1}$

$$\text{Temperature, } T = \frac{400 \text{ kJ mol}^{-1}}{0.2 \text{ kJ K}^{-1} \text{ mol}^{-1}} = 2000 \text{ K}$$

Therefore, above 2000 K, the reaction will become spontaneous.

157 (a) For the reaction,

$$2A(g) + B(g) \longrightarrow 2D(g)$$

$$\Delta n_g = n_p - n_r = 2 - 3 = -1$$

$$\because \quad \Delta H^\circ = \Delta U^\circ + \Delta n_g RT$$

$$\therefore \; \Delta H^\circ = -10.5 \text{kJ}$$
$$+(-1 \times 8.314 \times 10^{-3} \text{ kJ K}^{-1}\text{mol}^{-1} \times 298 \text{ K})$$

$$\Delta H^\circ = -10.5 + (-2.477) \text{ kJ mol}^{-1}$$
$$= -12.977 \text{ kJ mol}^{-1}$$

Now, $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$

$$\Rightarrow \quad \Delta G^\circ = -12.977 \text{ kJ mol}^{-1}$$

$$-(298 \text{ K} \times -44.1 \times 10^{-3} \text{ kJ K}^{-1} \text{ mol}^{-1})$$

$$\Delta G^\circ = -12.977 + 13.14 = +0.165 \text{ kJ mol}^{-1}$$

The reaction will not occur spontaneously because ΔG° is positive.

158 (a) Enthalpy change for the formation of 1 mole of H_2O **(**l**)** is given as,

$$H_2(g) + \frac{1}{2} O_2(g) \longrightarrow H_2O(l); \Delta_f H^\circ = -286 \text{kJ}$$
mol^{-1}

Energy released in the above reaction is absorbed by the surroundings. It means $q_{\text{surr}} = +286$ kJ mol^{-1}.

$$\Delta S = \frac{q_{\text{surr}}}{T} = \frac{+286 \text{ kJ mol}^{-1}}{298 \text{ K}}$$
$$= 0.9597 \text{ kJ K}^{-1}\text{mol}^{-1}$$
$$= 959.7 \text{ JK}^{-1}\text{mol}^{-1}$$

159 (c) Thermodynamics deals with the energy changes, feasibility and extent of a reactions, but not with the rate and mechanism of a process.

160 (c) Statement (c) is incorrect, while other statements are incorrect.

Corrected form are as follows :

- (a) Presence of reactive species in a covered beaker is an example of closed system.
- (b) Exchange of matter as well as energy occurs in open system.
- (d) Presence of reactant in a closed vessel is an example of closed system and presence of reactant in thermos flask is an example of isolated system.

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

Thus, p, V, T and n describe the state of the system.

162 (c) The specific heat will remains constant even when the volume of gas is reduced to half from its original volume.

This is because, specific heat is an intensive property which depends only on the nature of the gas.

163 (c) Given that, there is complete combustion of one mole of butane and, thus is represented by thermochemical reaction as,

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

We have to take the combustion of one mole of C_4H_{10} and $\Delta_C H$ should be negative and have a value of 2658 kJ mol^{-1}.

Therefore, option (c) is correct.

164 (b) The reaction for the combustion of $CH_4(g)$ is given as,

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

$$\Delta n_g = (n_p - n_r) = 1 - 3 = -2$$

$$\because \quad \Delta_f H^\circ = \Delta_f U^\circ + \Delta n_g RT$$

$$\text{As} \quad \Delta n_g = -2$$

$$\therefore \quad \Delta_f H^\circ < \Delta_f U^\circ$$

165 (c) For free expansion, $W = 0$

For adiabatic process, $q = 0$

Thus, $\Delta U = q + W = 0$, this means that, internal energy remains constant. Therefore, $\Delta T = 0$.

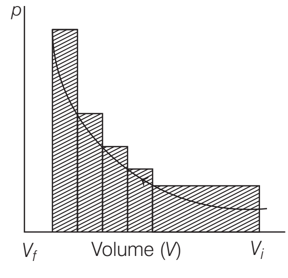
Moreover, in ideal gas there is no intermolecular attraction.

Hence, when such a gas expands under adiabatic conditions into a vacuum, no heat is absorbed or evolved since no external work is done to separate the molecules.

166 (b) The correct option is

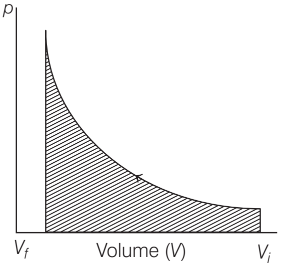
$$W(= \text{reversible}) < W(= \text{irreversible}).$$

This is because area under the curve is always more in irreversible compression as can be seen from given figure.



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.

(Irreversible compression)



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.

(Reversible compression)

167 (*c*) Combustion of elements to form a compound can be exothermic or endothermic. e.g. $\mathrm{C} + \mathrm{O}_2 \longrightarrow \mathrm{CO}_2$ is exothermic.

Whereas, $\mathrm{C} + 2S \longrightarrow \mathrm{CS}_2$ is endothermic.

Hence, enthalpy of formation may be positive or negative.

168 (*c*) The algebraic relationships of the given reaction is

equation (1) − equation (2) = equation (3)

$$\mathrm{C\ (graphite)} + \mathrm{O}_2\ (g) \longrightarrow \mathrm{CO}_2\ (g)\ ;\Delta_r H = x \text{ kJ mol}^{-1}$$

$$\underset{(-)}{\mathrm{C}}\,\mathrm{(graphite)} + \frac{1}{(-)2}\,\mathrm{O}_2(g) \longrightarrow \underset{(-)}{\mathrm{CO}}\,(g);\Delta_r H = y \text{ kJ mol}^{-1}$$

$$\mathrm{CO}\ (g) + \frac{1}{2}\,\mathrm{O}_2\ (g) \longrightarrow \mathrm{CO}_2\ (g)\ ;\Delta_r H = z \text{ kJ mol}^{-1}$$

Hence, $x - y = z$ or $x = y + z$

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

171 (*b*) In a combustion reaction, sum of enthalpies of reactants is greater than the sum of the enthalpies of products and therefore is an exothermic reaction. Moreover, enthalpies of the elements in the standard state are zero.

Thus, both A and R are correct but R is not the correct explanation of A.

172 (*a*) When a liquid crystallises, entropy decreases because in crystalline form, the molecules here are more in ordered manner as compared to the liquid.

Thus, both A and R are correct and R is the correct explanation of A.

173 (*c*) Spontaneous processes are accompanied by decrease in energy and increase in randomness and, thus is an irreversible process and may be reversed by some external energy.

Thus, A is correct but R is incorrect.