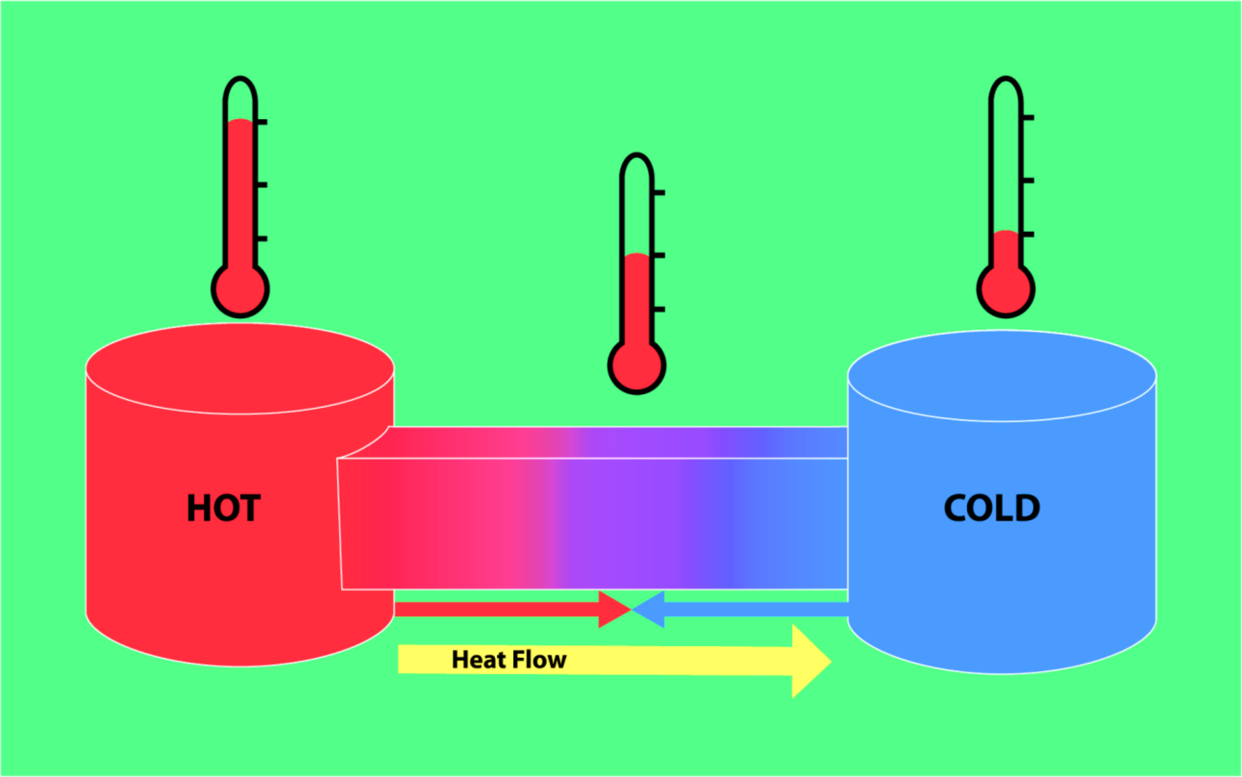
6. THERMODYNAMICS



Chemistry Smart Booklet

Theory + NCERT MCQs + Topicwise Practice
MCQs+NEET PYQs

THERMODYNAMICS

THERMODYNAMICS PROCESSES

- Isothermal Process
  $dt = -, \Delta U = 0$
- Isochoric Process
  $\Delta V = 0$
- Adiabatic Process
  $\Delta q = 0$
- Cyclic Process
  $\Delta U_{cyclic} = 0$

THERMODYNAMICS PROPERTIES

INTENSIVE PROPERTIES

P, T, N

Properties of the system which only depend on the nature of matter

STATE FUNCTION

$\Delta U, \Delta H, \Delta G$

Properties of the system which only depend on the nature of matter

EXTENSIVE PROPERTIES

V, U, H

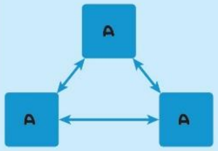
Properties of the system which depend on the path of the system

PATH FUNCTION

HEAT WORK

Properties of the system which depend on the path of the system

ZEROTH LAW OF THERMODYNAMICS



If two thermodynamics states are in thermal equilibrium with a third one, then they are in thermal equilibrium with each other.

GIBB'S FREE ENERGY

The net energy available to do useful work and is a measure of 'free energy'.

Standard free energy of a reaction: $\Delta rG^\circ = \Sigma\Delta_f G^\circ_{products} - \Sigma\Delta_f G^\circ_{reactants}$

Gibb's – Helmholtz equation $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \Delta G^\circ = NFE^\circ_{cell}$

GIBB'S ENERGY CHANGE & EQUILIBRIUM

$\Delta rG^\circ = -2.303RT \log K$

$\Delta G^\circ = 0$	$\log K = 0$	Equilibrium reached
$\Delta G^\circ < 0$	$\log K > 0$ $\log K < 0$	Mixture contains products
$\Delta G^\circ > 0$		Mixture contains reactants

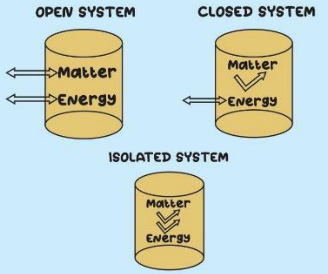
DG < 0, rocess is spontaneous

DG > 0, rocess is non-spontaneous

DG < 0, rocess is equilibrium

Sign of ΔH	Sign of ΔS	$\Delta G = \Delta H - T\Delta S$	Equilibrium reached
Negative	Positive	Always Negative	Spontaneous at all temp
Positive	Negative	Always Negative	Non-spontaneous at all temperature
Postive	Postive	+ve @ low temp. -ve @ low temp.	Non-spontaneous at all temperature Spontaneous at high temperature
Negative	Negative	-ve @ low temp. +ve @ low temp.	Spontaneous at low temperature Spontaneous at low temperature

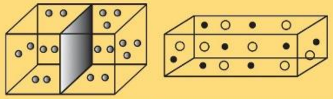
TYPES OF SYSTEM



EXPANSION: $V_i > V_f$
COMPRESSION: $V_f < V_i$

$w_{pv} = -P_{ext}\Delta V$ ISOTHERMAL IRREVERSIBLE WORK	ISOTHERMAL REVERSIBLE $w_{rev} = -2.303nRT \log\left(\frac{V_2}{V_1}\right)$
$w_{rev} = \frac{nR}{r-1}(T_2 - T_1)$ ADIABATIC REVERSIBLE	ADIABATIC IRREVERSIBLE $w_{irrev} = -P_{ext}R\left(\frac{P_1T_1 - P_2T_2}{P_1P_2}\right)$

SPONTANEITY



ENTHALPY

$\Delta H = \Delta U + \Delta(PV)$
$\Delta H = \Delta U + \Delta n_g RT$

Enthalpy of reaction ($\Delta n_r H$)

Reactants → Products

$\Delta_r H = e\sum_i a_i H \text{ products} - \sum_i b_i H \text{ reactants}$

STANDARD ENTHALPY OF REACTIONS (ΔH°)

Standard enthalpy of fusion $=\Delta_{fus}H^\circ$

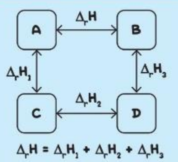
Standard enthalpy of phase change
$\Delta_{fus}H^\circ, \Delta_{vap}H^\circ, \Delta_{sub}H^\circ$

Standard enthalpy of combustion $\Delta_c H^\circ$

Standard enthalpy $= \Delta_{bond}H^\circ$

Lattice enthalpy $= \Delta_{lattice}H^\circ$

HESS' LAW CONSTANT HEAT SUMMATION



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

HEAT CAPACITY

Amount of heat required to raise the temperature of a system by 1°C.
Molar heat capacity 1°C.

Molar heat capacity $\Rightarrow q = nC\Delta T$

Specific heat capacity $\Rightarrow q = mC\Delta T$

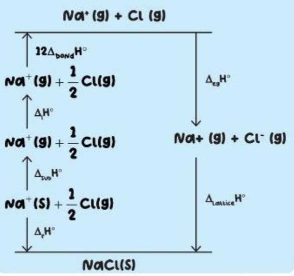
MEYERS'S FORMULA

$C_p - C_v = R$

POISSON'S RATIO

$\frac{C_p}{C_v} = r$

EORN HABER CYCLE



HEAT (Q)

Exchange of energy due to temperature differnece.

INTERNAL ENERGY

Total energy within the substance

WORK (W)

When there is difference between presence of the system and surroundings, the work done is known as $w_p V$

FIRST LAW OF THERMODYNAMICS

Law of conservation of energy total energy of an isolated system is constant.

Mathematically, $\Delta U = q + w$

SIGN CONVENTION

Heat absorbed by the system = +ve

Heat evolved by the system = -ve

work done by the system = -ve

work done on the system = +ve

At constant volume
$\Delta U = q_v$

At constant pressure
$\Delta H = q_p$

CALORIMETRY

$(\Delta U) = CV \times \Delta T \times M$

$(\Delta U) = CV \times \Delta T \times M$

FREE EXPANSION

When an ideal gas expands in vacuum then, $P_{ext} = 0$.

$\therefore w = 0$

SECOND LAW OF THERMODYNAMICS

The entropy of the universe is always increasing in the course of every s pontaneous or natural change.

THIRD LAW OF THERMODYNAMICS

The Entropy of a perfectly crystalline substance at 0K or absolute zero is taken to be zero.

$\Delta S = \int_0^T C_p d \ln T$

ENTROPY

This is the measure of the degree of randomness or disorder of the system.

$\Delta S = \frac{q_{rev}}{T(\text{Reversible Process})}$

$\Delta S_{Total} = \Delta S_{syestem} + \Delta S_{surroundings}$

Entropy changes during phase transformation

$\Delta_{fusion}S = \frac{\Delta_{fusion}H}{T_m}, \Delta_{vap}S = \Delta_{vap}S = \frac{\Delta_{vap}H}{T_m}$

$\Delta_{sub}S = \frac{\Delta_{subs}H}{T_m}$

$\Delta_r S^\circ = \Sigma S^\circ_{products} - \Sigma S^\circ_{reactants}$

THERMODYNAMICS

Introduction

Chemical thermodynamics deals with the relationship between various form of energy in a process. Thermodynamics deals with macroscopic properties. This chapter introduces a major subsidiary thermodynamic property, the Gibbs free energy which lets us express the spontaneity of a process in terms of the properties of the system. This chapter helps to explain why gases expand or diffuse.

System and Surrounding

1. **System:** A specific portion of universe under study which is seperated from rest of the universe with a boundary is called system.
2. **Surroundings:** Rest of the universe which might be in a position to exchange energy and matter with the system is known as surrounding.

Types of System:

1. **Open system:** System can be open if it can exchange both energy and matter with surroundings.
2. **Closed system:** System can be closed if it can exchange energy but not matter with surroundings.
3. **Isolated system:** System can be isolated if it can neither exchange energy nor matter with surroundings.

Extensive Properties

The properties which depend upon mass of the substance is known as extensive properties i.e., mass, volume, internal energy, enthalpy etc.

Intensive Properties

The properties which are independent of mass of the substance is known as intensive properties i.e., temperature, pressure, density, refractive index.

Thermodynamic State of a System

A state is the condition of a system as specified by its physical properties. We can describe the state of a gas by quoting its pressure (p), volume (V), temperature (T), amount (n) etc. Variables like p, V, T are called state variables or state functions because their values depend only on the state of the system and not on how it is reached.

State Functions

The thermodynamic parameters which depends only on initial and final states of system is known as state function. i.e., internal energy(E), Enthalpy (H), entropy (S), Gibb's free energy (G).

Path Functions

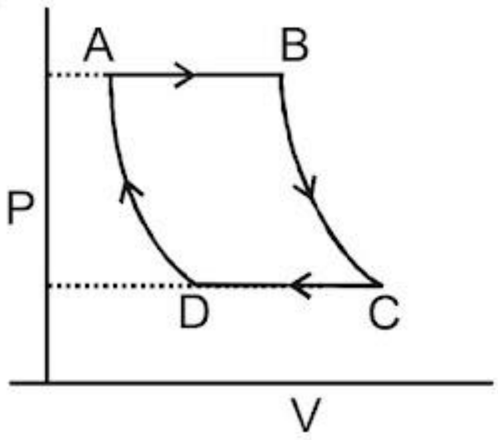
The thermodynamic parameters where value does not depend merely on initial and final state but depends upon the path followed is known as path function. i.e., heat (q), work done (W).

Thermodynamic Process

The sequence followed to change one thermodynamic state of a system into another is called thermodynamic process. The types of thermodynamic processes are:

1. **Isothermal process:** It is the process in which temperature is kept constant means temperature of initial and final state of system along with entire path of process is same.
2. **Isobaric process:** It is the process in which pressure is kept constant for entire process.
3. **Isochoric process:** It is the process in which volume is kept constant.
4. **Adiabatic process:** The process in which heat transaction across boundary is not allowed.
5. **Reversible process and Irreversible process:** In thermodynamics, a process is said to be reversible when energy change in each step of the process can be reversed by changing the variables such as pressure, volume or temperature acting on them. In such a process, the driving and opposing forces differ infinitesimally and the process can be reversed completely by increasing the opposing force by an infinitesimally small amount.

   Any process which does not take place in the above mentioned manner is said to be an irreversible process. In an irreversible process the driving and opposing force differ by a large amount.
6. **Cyclic process:** It is the process which run in close loop means process in which initial and final states are identical.

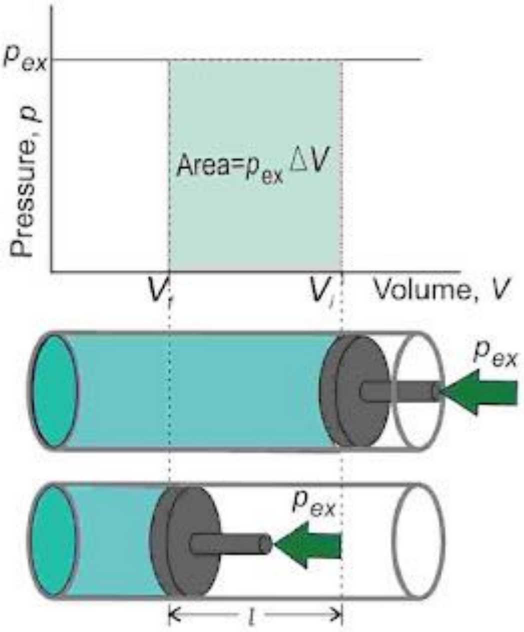


Internal Energy

Every substance is associated with definite amount of energy that is called internal energy. It is an extensive property and a state function. Internal energy of ideal gases is a function of temperature only.

Pressure-Volume Work

It is the work done when the gas expands or contracts against the external pressure. Consider a cylinder containing one mole of an ideal gas fitted with a frictionless and weightless piston having an area of cross-section A. The total volume of the gas is Vi and the initial pressure of the gas inside P.



Let the external pressure acting on the piston is Pex. If the external pressure Pex is slightly greater than P piston moves downward till the pressure inside the cylinder becomes equal to Pex. Let this change be achieved in a single step and the final volume be Vf. During this compression, suppose the piston moves a very small distance Δl. Thus, the work done on the gas is given by,

$$\omega = -\int_{V_i}^{V_f} P_{ex} dv$$

Heat

The change in internal energy of a system can be brought about by the transfer of heat from the surroundings to the system or vice-versa. This exchange of energy between the system and surroundings is possible as a result of the temperature difference between them. This energy called heat is represented by Q.

First Law of Thermodynamics

First law of thermodynamics states the law of conservation of energy in a different manner. According to this law, whenever a quantity of one kind of energy disappears an equivalent amount of energy appears in some other form.

According to first law of thermodynamics,

$\Delta U = q + W$

Where, Q = Heat change

W = Work done

ΔU = Change in internal energy

Enthalpy (H)

The total heat content of a system at constant pressure is known as its enthalpy. Mathematically it is the sum of internal energy and pressure-volume energy

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

It is an extensive property and a state function. Increase in enthalpy H is equal to heat absorbed at constant pressure.

Heat Capacity

Heat capacity is amount of heat require to raise the temperature of a system by unity. It is represented as "C". It is an extensive property and temperature dependent.

Types of heat capacity

1. Specific heat: For 1 gram system the heat loose or gained by system to bring one unit change in temperature is called specific heat denoted by 's'. specific heat is the intensive property.

$$S = \frac{C}{m}$$

2. Molar heat capacity: It is heat capacity for a system having 1 mole of material. It is represented as Cm. It is an intensive property.

$$C_m = \frac{C}{m}$$

3. Heat capacity at constant volume: Heat capacity of a system in isochoric condition is called heat capacity at constant volume, it is represented as C_v means molar heat capacity at constant volume.

$$C_v = \frac{dU}{dT}$$

4. Heat capacity at constant pressure: Heat capacity of a system in isobaric condition. It is represented by C_p means molar heat capacity at constant pressure.

$$C_p = \frac{dH}{dT}$$

Relation between Cp and Cv

We know that,

$\Delta H = \Delta U + P\Delta V$ .....(i)

As per ideal gas equation

$P\Delta V = R\Delta T$ .....(ii)

From (i) and (ii)

$\Delta H = \Delta U + R\Delta T$

$$\frac{\Delta H}{\Delta T} = \frac{\Delta U}{\Delta T} + R$$

$C_p = C_v + R$

$C_p - C_v = R$

Hess's Law

According to Hess's law, 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.

1st method: $C(s) + O_2(g) \rightarrow CO_2(g) = \Delta H$

2nd method: $C(s) + \frac{1}{2}O_2(g) \rightarrow CO(g) = \Delta H_1$

$\mathrm{CO(s)} + \frac{1}{2}\mathrm{O_2(g)} \rightarrow \mathrm{CO_2(g)} = \Delta H_2$

According to Hess's law,

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

Application of Hess's Law

1. Calculation of enthalpy of formation.
2. Determination of standard enthalpies of reactions.

Bond Dissociation Energy

The energy required to break one mole bond of a particular type in gaseous molecule is known as bond dissociation energy. For example, we consider the dissociation of water,

$\mathrm{H - OH(g)} \rightarrow \mathrm{H(g)} + \mathrm{OH(g)} = \Delta H \ = 498\ \mathrm{kJ/mol}$

Entropy

Entropy is a measure of degree of randomness or disorder in a system. Entropy is an extensive property and a state function.. Its value depends upon the amount of substance present in the system.

Second Law of Thermodynamics

This states that the entropy of the universe always increases in every spontaneous (natural) change.

Free Energy (G)

Gibb's free energy is defined as,

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

H is enthalpy, S is entropy and T is the temperature on Kelvin scale.

Summary

1. **System:** A part of universe which is under investigation.
2. **Surroundings:** The rest of the universe which is not a part of the system.
3. **State of the system:** The conditions of existence of a system when its macroscopic properties have definite values.
4. **State functions:** The thermodynamic quantities which depend only on the initial and final state of the system.
5. **Energy:** Energy is exchanged between the system and the surroundings as heat if they are at different temperatures.

6. The properties of the system whose value is independent of the amount of substance are called intensive properties. e.g., temperature, pressure, viscosity, surface tension, dielectric constant, specific heat capacity.

7. The properties of the system whose value depends upon the amount of substance present in the system are called extensive properties. e.g., mass, volume, surface area, energy, enthalpy, entropy, free energy, heat capacity.

8. Work is also a mode of transference of energy between system and the surroundings. Work done by the system on the surroundings is given by $p\Delta V$.

9. **Internal energy (U):** The energy associated with the system at a particular conditions of temperature and pressure.

10. **Enthalpy (H):** It is sum of internal energy and pressure-volume energy of the system at a particular temperature and pressure. It is also called heat content ($H = E + pV$).

11. **Hess's law:** The enthalpy change in a particular reaction is the same whether the reaction takes place in one step or in a number of steps.

12. **Bond enthalpy:** The average amount of energy required to break one mole of the bonds of a particular type in gaseous molecules.

13. **Entropy (S):** It is a measure of randomness or disorder of the system. Thus, the order is Gas > Liquid > Solid.

NCERT LINE BY LINE QUESTIONS

(1.) An adiabatic process occurs in

(a.) Open system
(b.) Closed system
(c.) Isolated system
(d.) In all the given system

(2.) When two moles of hydrogen expands isothermally against a constant pressure of 1 atm, at 25°C from 15 L to 50 L, the work done (in litre atm) will be

(a.) 17.5
(b.) 35
(c.) 51.5
(d.) 70

(3.) The enthalpy of combustion of H_2, cyclohexane (C_6H_{10}) and cyclohexane (C_6H_{12}) are $-241, -3800$ and -3920 kJ per mol respectively. Heat of hydrogenation of cyclohexane is

(a.) 121 kJ/mol
(b.) −121 kJ/mol
(c.) +242 kJ/mol
(d.) −242 kJ/mol

(4.) To calculate the amount of work done in joules during reversible isothermal expansion of an ideal gas, the volume must be expressed in

(a.) m^3 only
(b.) dm^3 only
(c.) cm^3 only
(d.) Any of these

(5.) Which one of the following is not a state function?

(a.) Enthalpy
(b.) Entropy
(c.) Work
(d.) Free energy

(6.) When one mole of monoatomic ideal gas at T K undergoes adiabatic change under a constant external pressure of 1 atm changes volume from 1 L to 2 L. The final temperature in Kelvin would be

(a.) $\frac{T}{2^{2/3}}$
(b.) $T+\frac{2}{3\times0.0821}$
(c.) T
(d.) $T-\frac{2}{3\times0.0821}$

(7.) For a reaction at 25°C, enthalpy and entropy changes are $-11.7\times10^3\text{J mol}^{-1}$ and $-105\text{ J mol}^{-1}\text{K}^{-1}$ respectively. What is the Gibbs free energy?

(a.) 15.05 kJ
(b.) 19.59 kJ
(c.) 2.55 kJ
(d.) 22.55 kJ

(8.) For the reaction of one mole of zinc dust with one mole of sulphuric acid in a bomb calorimeter, ΔU and W correspond to

(a.) $\Delta U<0, W=0$
(b.) $\Delta U=0, W<0$
(c.) $\Delta U>0, W=0$
(d.) $\Delta U=0, W>0$

(9.) A heat engine absorbs heat Q_1 at temperature T_1 and heat Q_2 at temperature T_2, work done by the engine is $(Q_1 + Q_2)$ this data

(a.) Violates 1st law of thermodynamics

(b.) Violates 1st law of thermodynamics if a_1 is –ve

(c.) Violates 1st law of thermodynamics if a_2 is −ve

(d.) Does not violates 1st law of thermodynamics

(10.) In the combustion of 2.0 g of methane, 25 kcal heat is liberated. Heat of combustion of methane would be

(a.) 150 kcal

(b.) 200 kcal

(c.) 250 kcal

(d.) 350 kcal

(11.) The resultant heat change in a reaction is the same whether it takes place in one or several stages. This statement is called

(a.) Lavoisier and Laplace law

(b.) Hess's law

(c.) Joule's law

(d.) Le-Chatelier's principle

(12.) For the isothermal expansion of an ideal gas

(a.) E and H increases

(b.) E increases but H decreases

(c.) H increases but E decreases

(d.) E and H are unaltered

(13.) A gas expands isothermally against a constant external pressure of 1 atm from a volume of 10 dm^3 to a volume of 20 dm^3. It absorbs 800 J of thermal energy from its surroundings. The ΔU is

(a.) −312 J

(b.) +123 J

(c.) −213 J

(d.) +231 J

(14.) Mark the correct statement

(a.) For a chemical reaction to be feasible, ΔG should be zero

(b.) Entropy is a measure of order in a system

(c.) For a chemical reaction to be feasible, ΔG should be positive

(d.) The total energy of an isolated system is constant

(15.) The amount of heat measured for a reaction in a bomb calorimeter is

(a.) ΔG

(b.) ΔH

(c.) ΔE

(d.) p.ΔV

(16.) Equal volumes of monoatomic and diatomic gases at same initial temperature and pressure are mixed. The ratio of specific heats of the mixture (C_p/C_v) will be

(a.) 1

(b.) 2

(c.) 1.67

(d.) 1.2

(17.) ΔS^o will be highest for the reaction

(a.) $Ca(s)+\frac{1}{2}O_2(g) \rightarrow CaO(s)$

(b.) $CaCO_3(g) \rightarrow CaO(s)+CO_2(g)$

(c.) $C(g)+O_2(g) \rightarrow CO_2(g)$

(d.) $N_2(g)+O_2(g) \rightarrow 2NO(g)$

(18.) The quantity of heat measured for a reaction in a bomb calorimeter is equal to

(a.) ΔG

(b.) ΔH

(c.) $p\Delta V$

(d.) ΔE

(19.) Two moles of helium gas expanded isothermally and irreversible at 27°C from volume 1 dm^3 to 1 m^3 at constant pressure of 100 k Pa. Calculate the work done.

(a.) 99900 kJ

(b.) 99900 J

(c.) 34464.65 kJ

(d.) 34464.65 J

(20.) $\Delta E°$of combustion of isobutylene is $-x$ kJ mol^{-1}. The value of $\Delta H°$ is

(a.) $=\Delta E°$

(b.) $>\Delta E°$

(c.) $=0$

(d.) $<\Delta E°$

(21.) Molar heat of vaporisation of a liquid is 6 $kJmol^{-1}$. If the entropy change is 16 J $mol^{-1}K^{-1}$, the boiling point of the liquid is

(a.) 273 K

(b.) 375°C

(c.) 375 K

(d.) 102°C

(22.) The molar heat capacity of water at constant pressure is 75 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.) 2.4 K

(b.) 3.6 K

(c.) 4.8 K

(d.) 1.2 K

(23.) Which is correct for an endothermic reaction?

(a.) ΔH is positive

(b.) ΔH is negative

(c.) ΔE is negative

(d.) $\Delta H=0$

(24.) Hess's law is based on

(a.) Law of conservation of mass

(b.) Law of conservation of energy

(c.) First law of thermodynamics

(d.) None of the above

(25.) An ideal gas is allowed to expand both reversibly and irreversibly in an isolated system. If T_i is the initial temperature and $T_f$is the final temperature, which of the following statements is correct?

(a.) $(T_f)_{\text{irrev}} > (T_f)_{\text{rev}}$

(b.) $T_f > T_i$ for reversible process but $T_f = T_i$ for irreversible process

(c.) $(T_f)_{\text{rev}} = (T_f)_{\text{irrev}}$

(d.) $T_f = T_i$ for both reversible and irreversible processes

(26.) The correct relationship between free energy change in a reaction and the corresponding equilibrium constant K_c is

(a.) $\Delta G = RT\ \text{In}K_c$

(b.) $-\Delta G = RT\ \text{In}K_c$

(c.) $\Delta G° = RT\ \text{In}K_c$

(d.) $-\Delta G° = RT\ \text{In}K_c$

(27.) Combustion of glucose takes place according to the equation
$C_6H_{12}O_6 + CO_2 \rightarrow 6CO_2 + 6H_2O; \Delta H = -72$kcal. How much energy will be required for the production of 1.6 g of glucose (Molecular mass of glucose = 180)?

(a.) 0.064 kcal

(b.) 0.64 kcal

(c.) 6.4 kcal

(d.) 64 kcal

(28.) Based on the first law of thermodynamics, which one of the following is correct?

(a.) For an isochoric process=$\Delta E = -Q$

(b.) For an adiabatic process=$\Delta E = -W$

(c.) For an isothermal process=$Q = +W$

(d.) For a cyclic process=$Q = -W$

(29.) In an adiabatic process

(a.) $p.\Delta V = 0$

(b.) $q = +W$

(c.) $\Delta E = q$

(d.) $q = 0$

(30.) In which of the following condition a chemical reaction can not occur?

(a.) ΔH and ΔS increase and $T\Delta S > \Delta H$

(b.) ΔH and ΔS decrease and $\Delta H > T\Delta S$

(c.) ΔH increase and ΔS decreases

(d.) ΔH decreases and ΔS increases

(31.) Identify the intensive quantity from the following

(a.) Enthalpy and temperature

(b.) Volume and temperature

(c.) Enthalpy and volume

(d.) Temperature and refractive index

(32.) A hypothetical reaction $A \rightarrow 2B$, proceeds through following sequence of steps
(i) $A \rightarrow C; \Delta H = q$ (ii)$C \rightarrow D; \Delta H = v$
(iii)$\frac{1}{2}D \rightarrow B;\ \Delta H = x$
Then the heat of reaction i

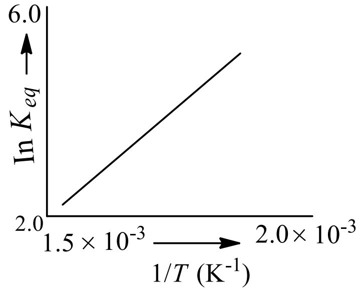
(a.) $q - v + 2x$

(b.) $q + v - 2x$

(c.) $q + v + 2x$

(d.) $q + 2v - 2x$

(33.) A schematic plot of In K_{eq} *versus* inverse of temperature for a reaction is shown below



The reaction must be

(a.) Exothermic

(b.) Endothermic

(c.) One with negligible enthalpy change

(d.) Highly spontaneous at ordinary temperature

(34.) In an isochoric process, the increase in internal energy is

(a.) Equal to the heat absorbed

(b.) Equal to the heat evolved

(c.) Equal to the work done

(d.) Equal to the sum of the heat adsorbed and work done

(35.) Heat of combustion of a substance:

(a.) Is always positive

(b.) Is always negative

(c.) Is equal to heat of formation

(d.) Nothing can be said without reaction

(36.) The free energy change for a reversible reaction at equilibrium is

(a.) Large, positive

(b.) Small, negative

(c.) Small, positive

(d.) 0

(37.) If gas at constant temperature and pressure expands then its

(a.) Internal energy increases and then decreases

(b.) Internal energy increases

(c.) Internal energy remains the same

(d.) Internal energy decreases

(38.) For the following two reactions,

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

$\Delta H = -890.4$ kJ

(ii)$2HgO(s) \rightarrow 2Hg(l) + O_2(g) - 181.6$ kJ

Which one of the following statements is correct?

(a.) Both of them are exothermic

(b.) Both of them are endothermic

(c.) (i) is exothermic and (ii) is endothermic

(d.) (i) is endothermic and (ii) is exothermic

(39.) Internal energy is sum of

(a.) Kinetic energy and potential energy

(b.) All types of energy of the system

(c.) Energy of internal system
(d.) None of the above

(40.) What is ΔE for system that does 500 cal of work on surrounding and 300 cal of heat is absorbed by the system?

(a.) -200 cal
(b.) -300 cal
(c.) +200 cal
(d.) +300 cal

(41.) 50 mL of water takes 5 min to evaporate from a vessel on a heater connected to an electric source which delivers 400 W. The enthalpy of vaporisation of water is

(a.) 40.3 kJ per mol
(b.) 43.2 kJ per mol
(c.) 16.7 kJ per mol
(d.) 180.4 kJ per mol

(42.) Which of the following taking place in the blast furnace is endothermic?

(a.) $CaCO_3 \rightarrow CaO + CO_2$
(b.) $2C + O_2 \rightarrow 2CO$
(c.) $C + O_2 \rightarrow CO_2$
(d.) $Fe_2O_3 + 3CO \rightarrow 2Fe + 3CO_2$

(43.) An ideal gas expands in volume from 1×10^{-3} m^3 to 1×10^{-2} m^3 at 300 K against a constant pressure of 1×10^5 Nm^{-2}. The work done is

(a.) -900 J
(b.) -900 kJ
(c.) 270 kJ
(d.) 900 kJ

(44.) If a refrigerator's door is opened then, we get

(a.) Room heated
(b.) Room cooled
(c.) More amount of heat is passed out
(d.) No effect on room

(45.) Which of the following equations correctly represents the standard heat of formation (ΔH_f^o) of methane?

(a.) C(diamond)+ $2H_2(g) \rightarrow CH_4(g)$
(b.) C(graphite) + $2H_2(g) \rightarrow CH_4(l)$
(c.) C(graphite) + $2H(g) \rightarrow CH_4(g)$
(d.) C(graphite) + $4H \rightarrow CH_4(g)$

(46.) The heat of neutralisation of a strong acid and a strong alkali is 57.0 kJ mol^{-1}. The heat released when 0.5 mole of HNO_3 solution is mixed with 0.2 mole of KOH is

(a.) 57.0 kJ
(b.) 11.4 kJ
(c.) 28.5 kJ
(d.) 34.9 kJ

(47.) A system absorbs 10 kJ of heat and does 4 kJ of work. The internal energy of the system

(a.) Increases by 6 kJ
(b.) Decreases by 6 kJ
(c.) Decreases by 14 kJ
(d.) Increases by 14 kJ

(48.) A process is taking place at constant temperature and pressure. Then

(a.) $\Delta H = \Delta E$ (b.) $\Delta H = T\Delta S$

(c.) $\Delta H = 0$ (d.) $\Delta S = 0$

(49.) Enthalpy change for a reaction does not depend upon

(a.) The physical states of reactants and products (b.) Use of different reactants for the same products

(c.) The nature of intermediate reaction steps (d.) The differences in initial and final temperature of involved substances

(50.) Which of the following conditions will always lead to a non spontaneous change?

(a.) Positive ΔH and positive ΔS (b.) Negative ΔH and negative ΔS

(c.) Positive ΔH and negative ΔS (d.) Negative ΔS and positive ΔS

TOPIC WISE PRACTICE QUESTIONS

TOPIC 1: First Law and Basic Fundamentals of Thermodynamics

1. Which has maximum internal energy at 290 K?
(1) Neon gas (2) Nitrogen gas (3) Ozone gas (4) Equal for all

2. One mole of a non-ideal gas undergoes a change of state from (1.0 atm, 3.0 L, 200 K) to (4.0 atm, 5.0 L, 250 K) with a change in internal energy (ΔU) = 40 L-atm. The change in enthalpy of the process in L–atm :
(1) 43 (2) 57 (3) 42 (4) None of these

3. Which of the following is closed system?
(1) Jet engine (2) Tea placed in a steel kettle
(3) Pressure cooker (4) Rocket engine during propulsion

4. The state of a thermodynamic system is described by its measurable or macroscopic (bulk) properties. These are
(1) Pressure and volume (2) Pressure, volume, temperature and amount
(3) Volume, temperature and amount (4) Pressure and temperature

5. Enthalpy change (ΔH) of a system depends upon its
(1) Initial state (2) Final state (3) Both on initial and final state (4) None of these

6. One mole of an ideal gas at 300 K is expanded isothermally from an initial volume of 1 L to 10 L. The ΔE for this process is (R =2 cal. mol^{-1} K^{-1})
(1) 163.7 cal (2) zero (3) 1381.1 cal (4) 9 lit. atm

7. When 1 mol of a gas is heated at constant volume, temperature is raised from 298 to 308 K. If heat supplied to the gas is 500 J, then which statement is correct ?
(1) $q = w = 500$ J, $\Delta U = 0$ (2) $q = \Delta U = 500$ J, $w = 0$
(3) $q = -w = 500$ J, $\Delta U = 0$ (4) $\Delta U = 0$, $q = w = -500$ J

8. In a closed insulated container, a liquid is stirred with a paddle to increase the temperature, which of the following is true?
(1) $\Delta E = W \neq 0, q = 0$ (2) $\Delta E = W = q \neq 0$ (3) $\Delta E = 0, W = q \neq 0$ (4) $W = 0$, $\Delta E = q \neq 0$

9. Which of the following factors affect the internal energy of the system ?
(1) Heat passes into or out of the system. (2) Work is done on or by the system.

(3) Matter enters or leaves the system. (4) All of the above

10. Adiabatic expansions of an ideal gas is accompanied by

(1) decrease in ΔE (2) increase in temperature

(3) decrease in ΔS (4) no change in any one of the above properties

11. During isothermal expansion of an ideal gas, its

(1) internal energy increases (2) enthalpy decreases

(3) enthalpy remains unaffected (4) enthalpy reduces to zero.

12. Which of the following are *not* state functions ?

(I) q + w (II) q (III) w (IV) H - TS

(1) (I) and (IV) (2) (II), (III) and (IV) (3) (I), (II) and (III) (4) (II) and (III)

13. For a cyclic process, which of the following is not true?

(1) $\Delta H = 0$ (2) $\Delta E = 0$ (3) $\Delta G = 0$ (4) Total W = 0

14. Work out the heat change (cal) when 40 g of He gas at 27 ºC undergoes isothermal and reversible compression from initial pressure of 1 atm to 10 atm ($R = 2$ cal K^{-1} mol^{-1}).

(1) 13.818 k cal (2) –13.818 k cal (3) 55.272 k cal (4) –55.272 k cal

15. If an ideal gas does the work of expansion solely at the cost of its internal energy, the process is

(1) reversible (2) irrerversible (3) isothermal (4) adiabatic

16. In order to maintain constant temperature of a system involving an ideal gas, heat has to be removed. Then what is true?

(1) The gas is being compressed (2) The gas is undergoing expansion

(3) The gas is performing the work (4) There is neither expansion nor contraction of the gas

17. Temperature of 5 moles of a gas is decreased by 2K at constant pressure. Indicate the correct statement.

(1) work done by the gas = 5 R (2) work done by the gas = 10 R

(3) work done over the gas = 10R (4) work done = 0

18. According to the first law of thermodynamics, $\Delta U = q + W$. In special cases the statement can be expressed in different ways. Which of the following is not a correct expression?

(1) At constant temperature $q = -W$ (2) When no work is done $\Delta U = q$

(3) In gaseous system $\Delta U = q + P\Delta V$ (4) When work is done by the system : $\Delta U = q + W$

19. The maximum work done when pressure on 10 g of hydrogen is reduced from 20 to 1 atm at a constant temperature of 273 K will be

(1) 8170 cal (2) 8180 cal (3) 8200 cal (4) 8350 cal

20. Which of the following statements/relationships is **not** correct in thermodynamic changes?

(1) $\Delta U = 0$ (isothermal reversible expansion of a gas)

(2) $w = -nRT\ln\frac{V_2}{V_1}$ (isothermal reversible expansion of an ideal gas)

(3) $w = -nRT\ln\frac{V_2}{V_1}$ (isothermal reversible expansion of an ideal gas)

(4) For a system of constant volume heat involved directly changes to internal energy.

21. An ideal gas expands in volume from 1×10^{-3} to 1×10^{-2} m^3 at 300 K against a constant pressure of 1×10^5 Nm^{-2}. The work done is

(1) 270 kJ (2) – 900 kJ (3) – 900 J (4) 900 kJ

TOPIC 2: Laws of Thermochemistry

22. The difference between ΔH and ΔU is usually significant for systems consisting of

(1) only solids (2) only liquids (3) both solids and liquids (4) only gases

23. The molar heat capacity of water at constant pressure is 75 JK^{-1} mol^{-1}. When 1kJ of heat is supplied to 100 g of water, which is free to expand, the increase in temperature of water is

(1) 6.6 K (2) 1.2 K (3) 2.4 K (4) 4.8 K

24. If a reaction involves only solids and liquids which of the following is true ?

(1) $\Delta H < \Delta E$ (2) $\Delta H = \Delta E$ (3) $\Delta H > \Delta E$ (4) $\Delta H = \Delta E + RT\Delta n$

25. Consider the reaction : $N_2 + 3H_2 \rightarrow 2NH_3$ carried out at constant temperature and pressure. If ΔH and Δ U are the enthalpy and internal energy changes for the reaction, which of the following expressions is true ?

(1) $\Delta H > \Delta U$ (2) $\Delta H < \Delta U$ (3) $\Delta H = \Delta U$ (4) $\Delta H = 0$

26. The $\Delta_f H^o$ of O_3, CO_2, NH_3 and HI are 142.2, –393.3, –46.2 and + 25.9 kJ per mol respectively. The order of their increasing stabilities will be

(1) O_3, CO_2, NH_3, HI (2) CO_2, NH_3, HI, O_3 (3) O_3, HI, NH_3, CO_2 (4) NH_3, HI, CO_2, O_3

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

(1) + 315 kJ (2) – 31.5 kJ (3) – 315 kJ (4) + 31.5 kJ

28. Assume each reaction is carried out in an open container. For which reaction will $\Delta H = \Delta E$?

(1) $C(s) + 2H_2O(g) \rightarrow 2H_2(g) + CO_2(g)$ (2) $PCl_5(g) \rightarrow PCl_3(g) + Cl_2(g)$

(3) $2CO(g) + O_2(g) \rightarrow 2CO_2(g)$ (4) $H_2(g) + Br_2(g) \rightarrow 2HBr(g)$

29. The enthalpies of formation of Al_2O_3 and Cr_2O_3 are –1596 kJ and –1134 kJ respectively. ΔH for the reaction $2Al + Cr_2O_3 \rightarrow 2Cr + Al_2O_3$ is

(1) –2730 kJ (2) –462 kJ (3) –1365 kJ (4) +2730 kJ

30. Equal volumes of molar hydrochloric acid and sulphuric acid are neutralized by dil. NaOH solution and x kcal and y kcal of heat are liberated respectively. Which of the following is true?

(1) $x = y$ (2) $x = \frac{1}{2}y$ (3) $x = 2y$ (4) None of these

31. For the reaction $A \rightarrow B$; $\Delta H = +\ 24$ kJ/mol and $B \rightarrow C$; $\Delta H = -\ 18$ kJ/mol, the decreasing order of enthalpy of A, B and C follows the order

(1) A, B, C (2) B, C, A (3) C, B, A (4) C, A, B

32. Energy required to dissociate 4 g of gaseous hydrogen into free gaseous atoms is 208 kcal at 25 °C. The bond energy of H–H will be :

(1) 104 kcal (2) 52 kcal (3) 10.4 kcal (4) 1040 kcal

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

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

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

(1) + 512.0 k cal (2) – 512.0 k cal (3) 508.0 k cal (4) – 508.0 k cal

34. An ideal gas is allowed to expand both reversibly and irreversibly in an isolated system. If T_i is the initial temperature and T_f is the final temperature, which of the following statements is correct?

(1) $(T_f)_{rev} = (T_f)_{irrev}$ (2) $T_f = T_i$ for both reversible and irreversible processes

(3) $(T_f)_{irrev} > (T_f)_{rev}$ (4) $T_f > T_i$ for reversible process but $T_f = T_i$ for irreversible process

35. On the basis of thermochemical equations (I), (II) and (III) find out which of the algebraic relationships given in options (i) to (iv) is correct.

(I) $C\,(\text{graphite}) + O_2(g) \rightarrow CO_2(g); \Delta_r H = x\ \text{kJ mol}^{-1}$

(II) $C(\text{graphite}) + \frac{1}{2} O_2(g) \rightarrow CO(g); \Delta_r H = y\ \text{kJ mol}^{-1}$

(III) $CO\,(g) + \frac{1}{2} O_2(g) \rightarrow CO_2(g);\ \Delta_r H = z\ \text{kJ mol}^{-1}$

(1) $z = x + y$ (2) $x = y - z$ (3) $x = y + z$ (4) $y = 2z - x$

36. Consider the following reaction occurring in an automobile

$2C_8H_{18}(g) + 25O_2(g) \longrightarrow 16CO_2(g) + 18H_2O(g)$ the sign of ΔH, ΔS and ΔG would be

(1) +, –, + (2) –, +, – (3) –, +, + (4) +, +, –

37. Enthalpy of $CH_4 + \frac{1}{2}O_2 \rightarrow CH_3OH$ is negative. If enthalpy of combustion of CH_4 and CH_3OH are x and y respectively, then which relation is correct

(1) $x > y$ (2) $x < y$ (3) $x = y$ (4) $x \geq y$

38. If the bond energies of H-H, Br- Br, and H-Br are 433, 192 and 364 kJ mol^{-1} respectively, the $\Delta H°$ for the reaction $H_2(g) + Br_2(g) \rightarrow 2HBr(g)$ is

(1) – 261 kJ (2) + 103 kJ (3) + 261kJ (4) – 103 kJ

39. Calculate the standard enthalpy change (in kJ mol^{-1}) for the reaction $H_2(g) + O_2(g) \rightarrow H_2O_2(g)$, given that bond enthalpy of H–H, O=O, O–H and O–O (in kJ mol^{-1}) are respectively 438, 498, 464 and 138.

(1) – 130 (2) – 65 (3) + 130 (4) – 334

40. Four grams of graphite is burnt in a bomb calorimeter of heat capacity 30 kJ K^{-1} in excess of oxygen at 1 atmospheric pressure. The temperature rises from 300 to 304 K. What is the enthalpy of combustion of graphite (in kJ mol^{-1})?

(1) 360 (2) 1440 (3) –360 (4) –1440

41. The standard enthalpy of formation (ΔfH^{o}_{298}) for methane, CH_4 is – 74.9 kJ mol^{-1}. In order to calculate the average energy given out in the formation of a C – H bond from this it is necessary to know which one of the following?

(1) The dissociation energy of the hydrogen molecule, H_2.

(2) The first four ionisation energies of carbon.

(3) The dissociation energy of H_2 and enthalpy and sublimation of carbon (graphite).

(4) The first four ionisation energies of carbon and electron affinity of hydrogen.

42. At 25ºC and 1 bar which one of the following has a non-zero of ΔH^{o}_{f} ?

(1) Br_2 (l) (2) C (graphite) (3) I_2 (s) (4) O_3 (g)

43. If enthalpy of formation of $C_2H_4(g)$, $CO_2(g)$ and $H_2O(l)$ at 25°C and 1atm pressure are 52, – 394 and – 286 kJ/mol respectively, the change in enthalpy is equal to

(1) – 141.2 kJ/mol (2) – 1412 kJ/mol (3) + 14.2 kJ/mol (4) + 1412 kJ/mol

44. 250 mL of 0.1 M HCl and 250 mL of 0.1 M KOH, both being at the same temperature, are mixed thoroughly and the temperature rise is found to be ΔT_1. If the experiment is repeated using 500 mL each of the two solutions and ΔT_2 is the temperature rise, then which is true?

(1) $\Delta T_2 > 2\Delta T_1$ (2) $\Delta T_1 = 2\Delta T_2$ (3) $\Delta T_1 = \Delta T_2$ (4) none of these

45. From the following bond energies:

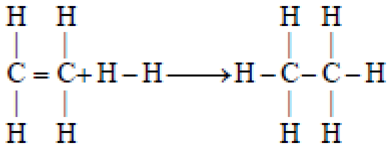
H – H bond energy: 431.37 kJ mol^{-1}

C = C bond energy: 606.10 kJ mol^{-1}

C – C bond energy: 336.49 kJ mol^{-1}

C – H bond energy: 410.50 kJ mol^{-1}

Enthalpy for the reaction,



$\mathrm{H_2C{=}CH_2 + H{-}H \longrightarrow H{-}CH_2{-}CH_2{-}H}$

will be:

(1) – 243.6 kJ mol^{-1} (2) –120.0 kJ mol^{-1} (3) 553.0 kJ mol^{-1} (4) 1523.6 kJ mol^{-1}

46. The values of standard enthalpy of formation of $SF_6(g)$, S(g)and F(g) are : – 1100, 275 and 80 kJ mol^{-1} respectively. The average S–F bond energy in SF_6 will be

(1) 309 kJ (2) 315 kJ (3) 320 kJ (4) 300 kJ

47. The following two reactions are known :

$Fe_2O_3(s) + 3CO(g) \longrightarrow 2Fe(s) + 3CO_2(g)$; $\Delta H = –26.8$ kJ

$FeO(s) + CO(g) \longrightarrow Fe(s) + CO_2(g)$; $\Delta H = –16.5$ kJ

The value of ΔH for the following reaction

$Fe_2O_3(s) + CO(g) \longrightarrow 2FeO(s) + CO_2(g)$ is;

(1) + 6.2 kJ (2) + 10.3 kJ (3) – 43.3 kJ (4) –10.3 kJ

48. The fat, $C_{57}H_{104}O_6(s)$, is metabolized via the following reaction $C_{57}H_{104}O_6(s) + 80\ O_2(g) \rightarrow 57CO_2(g) + 52H_2O(l)$ the energy (kJ) liberated when 1.0 g of this fat reacts will be Given the enthalpies of formation,

$\Delta_f H^o$ ($C_{57}H_{104}O_6$,s) = –70870 kJ/mol;

$\Delta_f H^o$ (H_2O, l) = – 285.8 kJ/mol;

$\Delta_f H^o$ (CO_2, g) = – 393.5 kJ/mol

(1) – 37.98 (2) – 40.4 (3) – 33.4 (4) – 30.2

49. Hess's law is used to calculate :

(1) enthalpy of reaction. (2) entropy of reaction

(3) work done in reaction (4) All of the above

50. An imaginary reaction $X \longrightarrow Y$ takes place in three steps

$X \longrightarrow A, \Delta H = -q_1$; $B \longrightarrow A, \Delta H = -q_2$; $B \longrightarrow Y, \Delta H = -q_3$
If Hess' law applicable, then the heat of the reaction ($X \rightarrow Y$) is :
(1) $q_1 - q_2 + q_3$ (2) $q_2 - q_3 - q_1$ (3) $q_1 - q_2 - q_3$ (4) $q_3 - q_2 - q_1$

51. What amount of energy (kJ) is released in the combustion of 5.8 g of $C_4H_{10}(g)$?
$2C_4H_{10}(g) + 13O_2(g) \longrightarrow 8CO_2(g) + 10H_2O(l)$; $\Delta H^\circ = -5756$ kJ
(1) 575.6 (2) 287.8 (3) 182 (4) 57.56

52. What is the internal energy (kJ) change occurs when 36 g of $H_2O(l)$ converted to $H_2O(g)$?
ΔH°(vapourisation) = 40.79kJ/mol
(1) 75.38 (2) 80.98 (3) 70.98 (4) 45.89

53. If bond energies are denoted by E, the enthalpy of the reaction**:**
$CH \equiv CH(g) + 2H_2(g) \longrightarrow C_2H_6(g)$, is
(1) $E_{C\equiv C} + 2E_{H-H} - E_{C-C} - 4E_{C-H}$ (2) $E_{C\equiv C} + 2E_{H-H} - E_{C-C} - 6E_{C-H}$
(3) $E_{C\equiv C} - 2E_{H-H} - E_{C-C} - 4E_{C-H}$ (4) $E_{C\equiv C} + 2E_{H-H} - E_{C=C} - 4E_{C-H}$

TOPIC 3: Entropy and Second Law of Thermodynamics

54. Identify the correct statement regarding entropy:
(1) At absolute zero temperature, the entropy of perfectly crystalline substances is positive.
(2) At absolute zero temperature, entropy of perfectly crystalline substance is taken to be zero.
(3) At 0°C the entropy of a perfectly crystalline substance is taken to be zero.
(4) At absolute zero temperature, the entropy of all crystalline substances is taken to be zero.

55. Unit of entropy is
(1) $JK^{-1}\ mol^{-1}$ (2) $J\ mol^{-1}$ (3) $J^{-1}\ K^{-1}\ mol^{-1}$ (4) $JK\ mol^{-1}$

56. ΔS° will be highest for the reaction
(1) $Ca(s) + \frac{1}{2}O_2(g) \longrightarrow CaO(s)$ (2) $CaCO_3(s) \longrightarrow CaO(s) + CO_2(g)$
(3) $C(s) + O_2(s) \longrightarrow CO_2(g)$ (4) $N_2(g) + O_2(s) \longrightarrow 2NO(g)$

57. In which of the following entropy decreases?
(1) Crystallization of sucrose from solution (2) Rusting of iron
(3) Melting of ice (4) Vaporization of camphor

58. Given the following entropy values (in $J\ K^{-1}mol^{-1}$) at 298 K and 1 atm :$H_2(g)$, $Cl_2(g)$ and $HCl(g)$ are 130.6, 223 and 186.7 respectively. The entropy change (in $J\ K^{-1}\ mol^{-1}$) for the reaction $H_2(g) + Cl_2(g) \longrightarrow 2HCl(g)$ is
(1) +540.3 (2) +727.0 (3) –166.9 (4) +19.8

59. Which one of the following demonstrates a decrease in entropy?
(1) Dissolving a solid into solution (2) An expanding universe
(3) Burning a log in a fireplace (4) Raking up leaves into a trash bag

60. Considering entropy (S) as a thermodynamic parameter, the criterion for the spontaneity of any process is
(1) $\Delta S_{system} + \Delta S_{surroundings} > 0$ (2) $\Delta S_{system} - \Delta S_{surroundings} > 0$
(3) $\Delta S_{system} > 0$ only (4) $\Delta S_{surroundings} > 0$ only

TOPIC 4: Spontaneity, Gibb's Free Energy and Equilibrium Constant

61. A reaction with $\Delta H = 0$, is found to be spontaneous. This is due to
(1) ΔS is negative (2) ΔS is positive (3) $T\Delta S$ is positive (4) Both (2) and (3)

62. If for the reaction at 300 K : $2Mg(g) + O_2(g) \rightarrow 2MgO(s)$; $\Delta_r H = -1202\ kJ\ mol^{-1}$ and $\Delta_r S = -217.0\ JK^{-1}\ mol^{-1}$. The total entropy change $(\Delta S)_T$ and gibbs energy change during the course of reaction ($\Delta_r G$) are respectively :
(1) $3.79 \times 10^3 Jk^{-1}mol^{-1}$, – 1136.9 Kj (2) $3.79 \times 10^3 Jk^{-1}mol^{-1}$, + 1000 J
(3) + 1000 $Jk^{-1}mol^{-1}$, 3.79×10^3 J (4) – 1136.9 kJ, 3.79×10^3 J

63. Which of the following pairs of processes is certain to occur in a spontaneous chemical reaction?
(1) Exothermic and increasing disorder (2) Exothermic and decreasing disorder
(3) Endothermic and increasing disorder (4) Endothermic and decreasing disorder

64. The enthalpy and entropy change for the reaction
$Br_2(l) + Cl_2(g) \rightarrow 2\ BrCl(g)$

are 30kJ mol^{-1} and 10^5 JK^{-1} mol^{-1} respectively. The temperature at which the reaction will be in equilibrium is

(1) 273 K (2) 450 K (3) 300 K (4) 285.7 K

65. ΔG in $Ag_2O \rightarrow 2Ag + 1/2O_2$ at a certain temperature is –10 kJ mol^{-1}. Pick the correct statement.

(1) Ag_2O decomposes to Ag and O_2 (2) Ag and O_2 combines to form Ag_2O

(3) Reaction is in equilibrium (4) Reaction does not take place

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

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

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

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

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

67. A spontaneous reaction is impossible if

(1) both ΔH and ΔS are negative. (2) both ΔH and ΔS are positive.

(3) ΔH is negative and ΔS is positive. (4) ΔH is positive and ΔS is negative.

68. Pick out the wrong statement:

(1) The standard free energy of formation of all elements is zero

(2) A process accompanied by decrease in entropy is spontaneous under certain conditions

(3) The entropy of a perfectly crystalline substance at absolute zero is zero

(4) A process that leads to increase in free energy will be Spontaneous

69. The dissolution of KCl in water is endothermic yet it dissolves in water spontaneously. Which one of the following best explains this behaviour ?

(1) Endothermic processes are energetically favoured.

(2) The electrostatic bonds between the ions are not too strong.

(3) Energy changes have nothing to do with the dissolution processes.

(4) The entropy driving force causes the dissolution.

70. Which of the following thermodynamic condition at constant pressure and temperature is necessary for the spontaneity of a process?

(1) $d(U - TS + PV) > 0$ (2) $d(U - TS + PV) < 0$

(3) $d(U - TS + PV) = 0$ (4) $d(U + TS + PV) < 0$

NEET PREVIOUS YEARS QUESTIONS

1. 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 **[2018]**

(1) 200 kJ mol^{-1} (2) 100 kJ mol^{-1} (3) 400 kJ mol^{-1} (4) 800 kJ mol^{-1}

2. 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) **[2017]**

(1) T > 425 K (2) All temperatures (3) T > 298 K (4) T < 425 K

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

(1) – 500J (2) – 505J (3) + 505J (4) 1136.25J

4. The correct thermodynamic conditions for the spontaneous reaction at all temperatures is **[2016]**

(1) $\Delta H < 0$ and $\Delta S = 0$ (2) $\Delta H > 0$ and $\Delta S < 0$

(3) $\Delta H < 0$ and $\Delta S > 0$ (4) $\Delta H < 0$ and $\Delta S < 0$

5. The heat of combustion of carbon to CO_2 is –393.5 kJ/mol. The heat released upon formation of 35.2 g of CO_2 from carbon and oxygen gas is **[2015]**

(1) –315 kJ (2) +315kJ (3) –630 kJ (4) –3.15 kJ

6. For the reaction :

$$X_2O_4(l) \rightarrow 2XO_2(g)$$

$\Delta U = 2.1$ Kcal, $\Delta S = 20$ cal K^{-1} at 300 K

Hence ΔG is:- **[2014]**

(1) 2.7 Kcal (2) – 2.7 Kcal (3) 9.3 Kcal (4) – 9.3 Kcal

7. Under isothermal condition, a gas at 300 K expands from 0.1L to 0.25L against a constant external pressure of 2 bar. The work done by the gas is:-
[Given that 1L bar = 100 J] **[NEET-2019]**

(1) -30 J (2) 5kJ (3) 25 J (4) 30 J

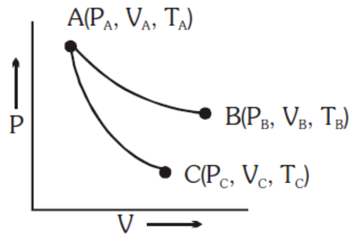
8. In which case change in entropy is negative? **[NEET-2019]**

(1) Evaporation of water (2) Expansion of a gas at constant temperature
(3) Sublimation of solid to gas (4) $2H(g) \rightarrow H_2(g)$

9. 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-2019(ODISSA)]**

(1) +270 kJ (2) .900 J (3) +900 kJ (4) -900 kJ

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



AB $\rightarrow$ Isothermal expansion
AC $\rightarrow$ Adiabatic expansion

Which of the following options is not correct? **[NEET-2019(ODISSA)]**

(1) $\Delta S_{isothermal} > \Delta S_{adiabatic}$ (2) $T_A = T_B$ (3) $W_{isothermal} > W_{adiabatic}$ (4) $T_C > T_A$

11. If for a certain reaction $\Delta_r H$ is 30 kJ mol^{-1} at 450 K, the value of $\Delta_r S$ (in JK^{-1}mol^{-1}) for which the same Reaction will be spontaneous at the same temperature is **[NEET-2020(COVID)]**

(1) 70 (2) -33 (3) 33 (4) -70

12. At standard conditions, if the change in the enthalpy for the following reaction is -109 kJ mol^{-1}.

$H_{2(g)} + Br_{2(g)} \rightarrow 2HBr_{(g)}$

Given that bond energy of H_2 and Br_2 is 435 kJ mol^{-1} and 192 kJ mol^{-1}, respectively, what is the bond energy (in kJ mol^{-1}) of HBr? **[NEET-2020(COVID)]**

(1) 368 (2) 736 (3) 518 (4) 259

13. The correct option for free expansion of an ideal gas under adiabatic condition is : **[NEET-2020]**

1. $q > 0,\ \Delta T > 0\ and\ w > 0$ 2. $q = 0,\ \Delta T = 0\ and\ w = 0$
3. $q = 0,\ \Delta T < 0\ and\ w > 0$ 4. $q < 0,\ \Delta T = 0\ and\ w = 0$

14. For the reaction $2Cl(g) \rightarrow Cl_2(g)$, the correct option is : **[NEET-2020]**

1. $\Delta_r H < 0\ and\ \Delta_r S < 0$ 2. $\Delta_r H > 0\ and\ \Delta_r S > 0$
3. $\Delta_r H > 0\ and\ \Delta_r S < 0$ 4. $\Delta_r H < 0\ and\ \Delta_r S > 0$

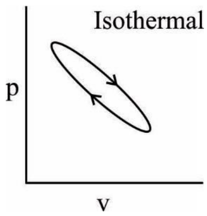
15. Which one among the following is the correct option for right relationship between C_P and C_V for one mole of ideal gas? **[NEET-2021]**

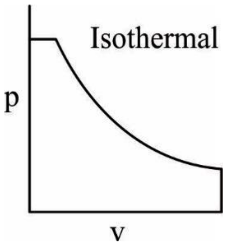
1. $C_P - C_V = R$ **2.** $C_P = RC_V$ **3.** $C_V = RC_P$ **4.** $C_P + C_V = R$

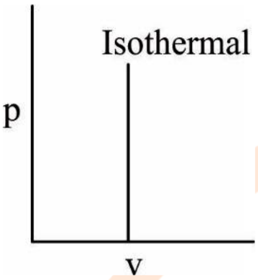
16. For irreversible expansion of an ideal gas under isothermal condition, the correct option is: **[NEET-2021]**

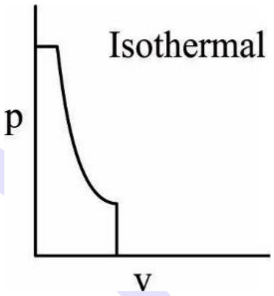
1) $\Delta U \neq 0, \Delta S_{total} \neq 0$ 2) $\Delta U = 0, \Delta S_{total} \neq 0$
3) $\Delta U \neq 0, \Delta S_{total} = 0$ 4) $\Delta U = 0, \Delta S_{total} = 0$

17. Which of the following p – V curve represents maximum work done? **[NEET-2022]**

1) 

2) 

3) 

4) 

NCERT LINE BY LINE QUESTIONS – ANSWERS

(1.)	c	(2.)	b	(3.)	b	(4.)	d	(5.)	c
(6.)	a	(7.)	b	(8.)	a	(9.)	d	(10.)	b
(11.)	b	(12.)	d	(13.)	c	(14.)	d	(15.)	c
(16.)	d	(17.)	b	(18.)	d	(19.)	b	(20.)	d
(21.)	c	(22.)	a	(23.)	a	(24.)	b	(25.)	a
(26.)	d	(27.)	b	(28.)	d	(29.)	d	(30.)	c
(31.)	d	(32.)	c	(33.)	a	(34.)	a	(35.)	b
(36.)	d	(37.)	c	(38.)	c	(39.)	b	(40.)	a
(41.)	b	(42.)	a	(43.)	a	(44.)	a	(45.)	c
(46.)	b	(47.)	a	(48.)	a	(49.)	c	(50.)	c

TOPIC WISE PRACTICE QUESTIONS - ANSWERS

1) 3	2) 2	3) 3	4) 2	5) 3	6) 2	7) 2	8) 1	9) 4	10) 1
11) 3	12) 4	13) 4	14) 2	15) 4	16) 1	17) 3	18) 4	19) 2	20) 3
21) 3	22) 4	23) 3	24) 2	25) 2	26) 3	27) 3	28) 4	29) 2	30) 2
31) 2	32) 1	33) 2	34) 3	35) 3	36) 2	37) 2	38) 4	39) 1	40) 3
41) 1	42) 4	43) 2	44) 3	45) 2	46) 1	47) 1	48) 1	49) 2	50) 2
51) 2	52) 1	53) 1	54) 2	55) 1	56) 2	57) 1	58) 4	59) 4	60) 4
61) 1	62) 2	63) 1	64) 4	65) 1	66) 1	67) 4	68) 4	69) 4	70) 2

NEET PREVIOUS YEARS QUESTIONS-ANSWERS

1) 4	2) 1	3) 2	4) 3	5) 1	6) 2	7) 1	8) 4	9) 2
10) 4	11) 1	12) 1	13) 2	14) 1	15) 1	16) 2	17) 2	

NCERT LINE BY LINE QUESTIONS – SOLUTIONS

(1.) **(c)**

In an adiabatic process, no exchange of heat takes place between the system and surroundings, *i.e.*, $dQ = 0$. Such a condition exists when the system is thermally isolated.

(2.) **(b)**

p=1 atm

$$\Delta V = (50 - 15) = 35\ \text{L}$$

$$\therefore \quad W = -p.\Delta V = -1 \times 35$$

$= -35$ Latm

Hence, work done by the system on the surroundings is equal to 35 L-atm.

(3.) **(b)**

Given: (i)$H_2 + \frac{1}{2}O_2 \rightarrow H_2O$; $\Delta H = -241$ kJ

(ii)$C_6H_{10} + \frac{17}{2}O_2 \rightarrow 6CO_2 + 5H_2O$; $\Delta H = -3800$ kJ

(iii)$C_6H_{12} + 9O_2 \rightarrow 6CO_2 + 6H_2O$; $\Delta H = -3920$ kJ for the reaction

$C_6H_{10} + H_2 \rightarrow C_6H_{12}$

[It is infact Eq.(i)+Eq.(ii)−Eq.(iii)]

Thus, $\Delta H = -241 - 3800 - (-3920) = -121$ kJ

(4.) **(d)**

As we know that,

$$\text{Work done}(W) = 2.303\, nRT \log\frac{V_2}{V_1}.$$

Hence, $V_1$and V_2 are in ratio in the relation. So, unit may be expressed in any one of m^3, dm^3 or cm^3.

(5.) **(c)**

Macroscopic properties which determine the state of a system are referred as state functions. The change in the state properties depends only upon the initial and final state of the system. All thermodynamic functions are state functions except work and heat.

(6.) **(a)**

$TV^{\gamma-1}$ =constant

$$\frac{T}{T_{\text{final}}}=\left(\frac{V_2}{V_1}\right)^{\gamma-1}$$

$$\frac{T}{T_{\text{final}}}=\left(\frac{2}{1}\right)^{(5/3-1)}=2^{(2/3)}$$

$$\frac{T}{T_{\text{final}}}=\frac{T}{2^{(2/3)}}$$

(7.) **(b)**

$\Delta G=\Delta H-T\Delta S, T=25+273=298\ \mathrm{K}$

$=-11.7\times10^3-298\times(-105)=19590\ \mathrm{J}=19.59\ \mathrm{kJ}$

(8.) **(a)**

Bomb calorimeter is commonly used to find the heat of combustion of organic substance which consists of a sealed combustion chamber called a bomb, if a process is run in a sealed container then no expansion or compression is allowed, so $W=0$ and $\Delta U=q$. Thus it has $\Delta U<0, W=0$

(9.) **(d)**

It does not violate the first law of thermodynamics but violates the II law of thermodynamics

(10.) **(b)**

$\mathrm{CH_4+2O_2\rightarrow CO_2+2H_2O}$

Molecular weight of $\mathrm{CH_4}=12+4=16$

∴ On the combustion of 2.0 g of methane = 25.0 kcal

∴ On the combustion of 16.0 g methane $=\frac{25\times16}{2}=200$ kcal

(12.) **(d)**

In isothermal reversible process, ideal gas has constant volume and so, $\Delta E=0$ and $\Delta H=\Delta E=0$

(13.) **(c)**

$$W=\int_{1/1}^{1/2}pdV=-p(V_2-V_1)$$

$W=-1(20-10)=-10\ \mathrm{dm^3\ atm}$

$=-10\ \mathrm{dm^3}\times\frac{8.314\ \mathrm{JK^{-1}mol^{-1}}}{0.0821\ \mathrm{dm^3K^{-1}mol^{-1}}}=-1013\ \mathrm{J}$

From, 1st law of thermodynamics

$\Delta U=q+W$

$=800\ \mathrm{J}+(-1013\ \mathrm{J})=-213\ \mathrm{J}$

(15.) **(c)**

Bomb calorimeter measures q_v which is equal to ΔE.

(16.) **(d)**

For monoatomic gas, $\gamma_2=\frac{C_p}{C_v}=1.67$

For diatomic gas, $\gamma_2=\frac{C_p}{C_v}=1.40$

$$\therefore\ \gamma_1:\gamma_2=\frac{1.67}{1.40}=1.19:1$$

(17.) **(b)**

Eq.(b) shows largest phase change *ie*,gas → solid

(18.) (d)

Heat of combustion is usually measured by placing a known mass of a compound in a steel container called a constant volume bomb calorimeter.

$$\Delta E = C \times \Delta t \times \frac{M}{m}$$

Where, C=heat capacity of calorimeter, $\Delta t = (t_2 - t_1)$ m=mass of substance taken and M=molar mass of substance

(19.) (b)

$W = -p\Delta V$

Given, $p + 100\text{kPa} = 10^5$ Pa,

$V_1 = 1\text{dm}^3 = 10^{-3}\text{m}^3, V_2 = 1\text{m}^3$

$W = 10^5 \times (1 - 10^{-3})$ J

∴ $W = 99900$ J

(20.) (d)

$(\text{CH}_3)_2\text{C} = \text{CH}_2(\text{g}) + 6\text{O}_2(\text{g}) \rightarrow 4\text{CO}_2(\text{g}) + 4\text{H}_2\text{O}(l)$

$\Delta ng = 4 - 7 = -3$(*ie*, negative)

We know that $\Delta H = \Delta E + \Delta n_g RT$

$= \Delta E - (\Delta m)RT \quad (\because \Delta n_g = -\text{ve})$

$\therefore \Delta H < \Delta E$

(21.) (c)

$\Delta S = 16 \text{ J mol}^{-1}\text{K}^{-1}$

$$T_{\text{b.p}} = \frac{\Delta H_{\text{vapour}}}{\Delta S_{\text{vapour}}} = \frac{6 \times 1000}{16}$$

$= 375\text{K}$

(22.) (a)

Heat capacity of water per gram $= \frac{75}{18} = 4.17$ J

$Q = mst = 100 \times 4.17 \times t = 1000$

$$t = \frac{1000}{100 \times 4.17} = 2.4 \text{ K}$$

(23.) (a)

For an endothermic reactions ΔH is positive because in endothermic reaction heat is always absorbed.

(24.) (b)

Hess's law is based upon law of conservation of energy *i.e.*, first law of thermodynamics.

(25.) (a)

$T_{f_{irreversible}} > T_{f_{reversible}}$ it is an adiabatic expansion and W(rev) is maximum.

(27.) (b)

ΔH per 1.6 g $= \frac{72 \times 1.6}{180} = 0.64$ kcal

(28.) (d)

(a) For isochoric process, $\Delta V = 0$

$W = p\Delta V = 0$

∴ $\Delta E = Q$

(b) For adiabatic process, $Q = 0$

$\Delta E = W$

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

and $\Delta E = 0$

$Q = -W$

(d) For cyclic process, state functions like

$\Delta E = 0$

$Q = -W$

(29.) **(d)**

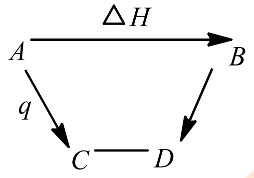
In the adiabatic process no heat enters or leaves the system $i.e.$, $q = 0$.

(30.) **(c)**

If $\Delta H = +$ ve and $\Delta S = -$ ve then the reaction is spontaneous

(32.) **(c)**

According to Hess's law, the total heat changes occurring during a chemical reaction are independent of path.



$\Delta H = q + V + 2x$

(33.) **(a)**

For exothermic reactions, K_{eq} varies inversely with T while in case of endothermic reactions, K_{eq} varies directly with T

(34.) **(a)**

For isochoric process, $\Delta V = 0$ so, $q_v = \Delta E$ ie, heat given to a system under constant volume is used up in increasing ΔE

(37.) **(c)**

We know that internal energy of a gas depends upon its pressure and temperature. Thus, if a gas expands at constant temperature and pressure, than its internal energy remains same

(38.) **(c)**

For exothermic reaction, $\Delta H = (-)$ for endothermic reaction, $\Delta H = (+)$.

(39.) **(b)**

Every system having some quantity of matter, is associated with a definite amount of energy. This energy is known as internal energy. It is sum of many type of energies, such as translation energy, rotational energy, vibrational energy, electronic energy and bonding energy of the molecule.

$E = E_{\text{trans}} + E_{\text{rot}} + E_{\text{vib}} + E_{\text{bonding}} + E_{\text{electronic}}$

(40.) **(a)**

From first law of thermodynamic.

$\Delta E = q + W$ Given, $q = +300$ cal (∵Heat is absorbed)

$W = -500$ cal

(∵Work is done on surroundings)

$\therefore \quad \Delta E = q + W = 300 + (-500)$

$= -200$ cal

(41.) **(b)**

Work done in 1 s = 400 J

Hence, work in 5 min (300 s)

$= 400 \times 300 = 120$ kJ

$\Delta H^{\text{o}}_{\text{vap.}} = \frac{120\text{ kJ}}{50/18} = 43.2$ kJ/mol

(42.) **(a)**

Bond breaking process or decomposition processes are endothermic process.

(43.) **(a)**

Work done due to change in volume against constant pressure,

$W = -p(V_2 - V_1)$

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

$= -900\ \text{Nm} = -900\ \text{J}$ (1 Nm=1 J)

(44.) **(a)**

The compressor has to run for longer time releasing more heat to the surroundings

(45.) (c)

Standard heat of formation of methane is represented by C(graphite)+2H(g) = $CH_4(g)$ because the elements taken are in their standard state

(46.) (b)

0.2 mole will neutralize 0.2 mole of HNO_3 heat evolved = $51 \times 0.2 = 11.4$ kJ

(47.) (a)

$q = +10 \text{ kJ}, W = -4 \text{ kJ}$

$\because\ \Delta E = q + W$

$= 10 - 4 = 6 \text{ kJ}$

So, energy increases by 6 kJ

(48.) (a)

For an isothermal process, $\Delta E = 0$

As the process is taking place at constant T and p hence, from equation,

$\Delta H = \Delta E + \Delta p.V$

We have, $\Delta H = 0 + 0 \times V = 0$

Hence, for the process, $\Delta H = \Delta E = 0$

TOPIC WISE PRACTICE QUESTIONS - SOLUTIONS

1. **(3)** Ozone gas have maximum internal energy.
For non-linear molecule,
$$E = \frac{3RT}{2} + \frac{2RT}{2} + (3N-6)RT$$
For linear molecule,
$$E = \frac{3RT}{2} + \frac{2RT}{2} + (3N-5)RT$$

2. **(2)** When both P and V are changing
$\Delta H = \Delta U + \Delta(PV)$
$= \Delta U + (P_2V_2 - P_1V_1)$
$\Delta H = 40 + (20 - 3)$
$= 57$ L atm

3. **(3)** Closed system can exchange energy and not matter with surroundings. Pressure cooker provides closed system.

4. **(2)** We can describe the state of a gas by quoting its pressure (P), volume (V), temperature (T), amount (n) etc.

5. **(3)**

6. **(2)** For an isothermal process $\Delta E = 0$

7. **(2)** As volume is constant hence work done in this process is zero therefore heat supplied is equal to change in internal energy.

8. **(1)** Internal energy is dependent upon temperature and according to first law of thermodynamics total energy of an isolated system remains same, i.e., in a system of constant mass, energy can neither be created nor destroyed by any physical or chemical change but can be transformed from one form to another $\Delta E = q + W$
For closed insulated container, $q = 0$, so, $\Delta E = +W$, as work is done by the system.

9. **(4)**

10. **(1)** $\Delta E = \Delta Q - W$
For adiabatic expansion, $\Delta Q = 0$
$\Rightarrow \Delta E = -W$
The negative sign shows decrease in Internal energy, which is equal to the work done on the system by the surroundings.

11. **(3)** During isothermal expansion of ideal gas,

$\Delta T = 0$. Now $H = E + PV$
$\because \Delta H = \Delta E + \Delta(PV)$; $\therefore \Delta H = \Delta E + \Delta(nRT)$; Thus if $\Delta T = 0.$, $\Delta H = \Delta E$
i.e., enthalpy remains unaffected

12. **(4)** We know that heat (q) and work (w) are not state functions but (q + w) is a state function. H – TS (i.e. G) is also a state function.

13. **(4)** For a cyclic process
$\Delta E = 0$, $\Delta H = 0$ and $\Delta G = 0$. As all depend upon final state and initial state, 'W' doesn't depend on path followed.

14. **(2)** $q = -w_{rev} = -\left(-2.303nRT\log\frac{P_1}{P_2}\right) = 2.303\times\frac{40}{4}\times 2\times 300\log\frac{1}{10} = -13.82\,\text{kcal}$

15. **(4)**

16. **(1)** Heat is generated on compression of a gas.

17. **(3)** For 5 moles of gas at T, $PV_1 = 5\,RT$
For 5 moles of gas at T-2, $PV_2 = 5R(T-2)$
Hence, $PV2 - PV_1 = P(V_2 - V_1) = PDV$
$= 5R[T-2-T] = -10R$
or, $-P\Delta V = 10R$ (ΔV is negative , W is positive)

18. **(4)** When work is done by the system, $\Delta U = q - W$

19. **(2)** $W = 2.303\ nRT\ \log\frac{P_1}{P_2}$

$= 2.303\times\frac{10}{2}\times 2\times 273\log\frac{20}{1} = 8180$ calories

20. **(3)** For isothermal reversible expansion.

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

21. **(3)** $W = -P\Delta V = -10^5\left(1\times10^{-2} - 1\times10^{-3}\right) = -900J$

22. **(4)** The difference between ΔH and ΔU is not usually significant for systems consisting of only solids or liquids. Solids and liquids do not suffer any significant volume changes upon heating. The difference, however, becomes significant when gases are involved.

23. **(3)** Given $C_p = 75\ JK^{-1}\ mol^{-1}$.

$n = \frac{100}{18}$ moles, $Q = 1000$ J, $\Delta T = ?$

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

24. **(2)** $\Delta H = \Delta E + P\Delta V$, for solid and liquid,
$\Delta V =$ or $\Delta H = \Delta E + \Delta n\ RT$, for solids and liquids $\Delta n = 0$.

25. **(2)** For $N_2 + 3H_2 \longrightarrow 2NH_3$; $\Delta n_g = 2 - 4 = -2$
$\Delta H = \Delta U + \Delta nRT$
Now, $\Delta H = \Delta U - 2RT$ or $\Delta U = \Delta H + 2RT$; $\therefore \Delta U > \Delta H$

26. **(3)** Energy absorbed $\propto \frac{1}{\text{stability of compound}}$

Energy released μ stability of compound
Thus, the order of stability is
142.2 > 25.9 > – 46.2 > – 393.2 i.e. $O_3 > HI > NH_3 > CO_2$

27. **(3)** $C + O_2 \longrightarrow CO_2$, $\Delta H = -393.5$ kJ /mol
It means heat of formation of 1 mole (44 g) of CO_2
$= -393.5$ kJ/mol

$\therefore$ Heat of formation of 1 g of $CO_2 = = \frac{-393.5}{44}$ kJ / mol

Heat of formation of 35.2 g of CO_2 $= \frac{-393.5}{44} \times 35.2 = -314.8$ kJ ; – 315 kJ

28. **(4)** We know that

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

In the reactions, $H_2 + Br_2 \rightarrow 2HBr$ there is no change in volume or $\Delta V = 0$

So, $\Delta H = \Delta E$ for this reaction

29. **(2)** $2Al + \frac{3}{2}O_2 \rightarrow Al_2O_3, \Delta H = -1596kJ$ -------(i)

$2Cr + \frac{3}{2}O_2 \rightarrow Cr_2O_3, \Delta H = -1134kJ$ --------(ii)

By (i) – (ii) ; $2Al + Cr_2O_3 \rightarrow 2Cr + Al_2O_3$, $\Delta H = -462$ kJ.

30. **(2)** 1 M H_2SO_4 = 2g eq. of H_2SO_4.

Hence $y = 2x$ or $x = \frac{1}{2}y$

31. **(2)** $A \longrightarrow B$, $\Delta H = +24$ kJ / mol

$\Rightarrow H_B - H_A = +24$ ...(i)

$B \longrightarrow C$, $\Delta H = -18$ kJ/mol

$\Rightarrow H_C - H_B = -18$ ...(ii)

From Eqs. (i) and (ii), we have

$H_C - H_A = 6$

$\therefore H_B > H_C > H_A$

32. **(1)** No. of moles of hydrogen

$= \frac{\text{Mass}}{\text{Molecular mass}} = \frac{4}{2} = 2\,\text{moles}$

Given $2H_2(g) \rightarrow 4H(g), \Delta H = 208\,\text{kcal}$

$\therefore \underset{1\text{mol}}{H_2(g)} \rightarrow 2H(g)\,\Delta H = 104\,\text{kcal}$

$\therefore$ Bond energy of H–H bond is 104 kcal

33. **(2)** $\Delta H_{S\text{-}S} + 2\Delta H_{H\text{-}S} = 239$ $2\Delta H_{H\text{-}S} = 175$

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

Then, ΔH for $8S(g) \rightarrow S_8(g)$ is $8 \times (-64) = -512$ kcal

34. **(3)** In a reversible process the work done is greater than in irreversible process. Hence the heat absorbed in reversible process would be greater than in the latter case. So,

$T_f(\text{rev}) < T_f(\text{irrev})$

35. **(3)**

36. **(2)** This is combustion reaction, which is always exothermic

hence $\Delta H = -ve$

As the no. of gaseous molecules are increasing hence entropy increases

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

For a spontaneous reaction

$\Delta G = -ve$

Which is possible in this case as $\Delta H = -ve$ and $\Delta S = +ve$.

37. **(2)** $CH_4(g) + \frac{1}{2}O_2(g) \rightarrow CH_3OH(l); \Delta H = ?$

$\therefore \Delta H$ =[(ΔH of combustion of CH_3OH) – (ΔH of combustion of CH_4)]

$= [(-y) - (-x)] = [-y + x] = x - y$

Given, $\Delta H = -ve$

$\therefore x - y < 0$

hence $x < y$

38. **(4)** $H_2(g) + Br_2(g) \rightarrow 2HBr(g)$

$\Delta H^\circ = (BE)_{reactant} - (BE)_{product}$
$= (433 + 192) - (2 \times 364)$
$= 625 - 728 = -103$ kJ

39. **(1)** $H_2(g) + O_2(g) \longrightarrow H_2O_2(g)$
$\Delta H_{reaction} = B.E._{Reactants} - B.E._{Products}$
$= [B.E.(H - H) + B.E.(O = O)] - [2B.E.(O - H) + B.E.(O - O)]$
$= [438 + 498] - [2 \times 464 + 138] = 936 - 1066 = -130$ kJ mol^{-1}

40. **(3)** $\Delta E = C \times \Delta t \times \frac{M}{m} = 30 \times 4 \times \frac{12}{4} = 360$
$\Delta E = -360$ kJ mol^{-1}

41. **(1)** To calculate average enthalpy of C – H bond in methane following information's are needed
(i) dissociation energy of H_2 i.e.
$\frac{1}{2} H_2(g) \longrightarrow H(g);\ \Delta H = x$ (suppose)
(ii) Sublimation energy of C(graphite) to C(g)
$C(graphite) \longrightarrow C(g);\ \Delta H = y$ (suppose)
Given
$C(graphite) + 2H_2(g) \longrightarrow CH_4(g);\ \Delta H = 75$ kJ mol^{-1}

42. **(4)** Ozone (O_3), the allotropic form of oxygen is of higher energy (by 68 kcal mol^{-1}) than O_2. Hence, O_3 can not be taken as the reference or standard state.

43. **(2)** Enthalpy of formation of C_2H_4,CO_2 and H_2O are 52, – 394 and – 286 kJ/ mol respectively. (Given)
The reaction is
$C_2H_4 + 3O_2 \rightarrow 2CO_2 + 2H_2O$.
change in enthalpy,
$(\Delta H) = \Delta H_{products} - \Delta H_{reactants}$
$= 2 \times (-394) + 2 \times (-286) - (52 + 0)$
$= -1412$ kJ/ mol.

44. **(3)** In the second experiment , the heat produced is twice that in first case but at the same time thermal capacity of the resulting solution (twice as that in first case) is doubled. Hence, temperature rise will be the same.

45. **(2)** Enthalpy of reaction
$= B.E_{(Reactant)} - B.E_{(Product)}$
$$= \left[B.E_{(C=C)} + 4B.E_{(C-H)} + B.E_{(H-H)}\right] - \left[B.E_{(C-C)} + 6B.E_{(C-H)}\right]$$
$= [606.1 + (4 \times 410.5) + 431.37)] - [336.49 + (6 \times 410.5)]$
$= -120.0$ kJ mol^{-1}

46. **(1)** Given $S(s) + 3F_2(g) \rightarrow SF_6(g)$; $\Delta H = -1100$ kJ ...(i)
$S(s) \rightarrow S(g);\ \Delta H = 275$ kJ .....(ii)
$1/2\ F_2(g)\ F(g);\ \Delta H = 80$ kJ .....(iii)
To get $SF_6(g) \rightarrow S(g) + 6F(g)$ we can proceed as
(ii) + 6$\times$ (iii) – (i)
$\therefore SF_6(g) \rightarrow S(g) + 6F(g);\ \Delta H = 1855$ kJ
Thus average bond energy for S-F bond $= \frac{1855}{6} = 309.16$ kJ

47. **(1)** $Fe_2O_3(s) + CO(g) \longrightarrow 2FeO(s) + CO_2(g)$
$\Delta H = -26.8 + 33.0 = +6.2$ kJ

48. **(1)**

49. **(1)** Hess's law is used for calculating enthalpy of reaction.

50. **(2)** $X \rightarrow A + q_1$
$q_2 + A \rightarrow B$
$B \rightarrow Y + q_3$
$q_2 + X \rightarrow Y + q_1 + q_3,\ \Delta H = q_2 - q_1 - q_3$

51. **(2)** $Q = \frac{5.8}{58} \times \frac{5756}{2} = 287.8\,kJ$

52. **(1)** $H_2O\ (l) \rightarrow H_2O\ (g)$

$\Delta H_{vap} = 40.79$ kJ/mol

$\Delta H = \Delta U + \Delta ngRT$

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

$$\Rightarrow \Delta U^o == \left(40.79\,kJ/mol - \frac{8.314 \times 373}{1000}\,kJ/mol\right) = (40.79 - 3.10)\,kJ/mol = 37.69\,\frac{kJ}{mol}$$

Internal energy change for 36 g of water $= 37.69\,\frac{kJ}{mol} \times \frac{36g}{18g/mol}$

$\Delta U = 75.98$ kJ

53. **(1)**

54. **(2)** According to 3rd law of thermodynamics at absolute zero temperature entropy of perfectly crystalline substance is taken to be zero.

55. **(1)** $\Delta S = \frac{q}{T}$

$q \longrightarrow$ required heat per mole

$T \longrightarrow$ constant absolute temperature

Unit of entropy is $JK^{-1}\ mol^{-1}$

56. **(2)** Eq. (2) shows largest phase change i.e., solid $\longrightarrow$ gas

57. **(1)** Because randomness is decreased.

58. **(4)**

59. **(4)** Raking up leaves into a thrash bag results in decrease in randomness i.e. decrease in entropy.

60. **(1)** For a spontaneous process, ΔS_{total} is always positive.

61. **(2)** $\Delta G = \Delta H - T\Delta S$

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

$\Delta G = -ve$

62. **(1)** $\Delta G = \Delta H - T\Delta S$

$= -1202 - (-217 \times 10^{-3} \times 300) = -1136.9$ kJ

Heat released will be absorbed by the surroundings to increase the entropy of surroundings.

$$\Delta S_{surr.} = +\frac{1202 \times 10^3}{300} = +4.01 \times 10^3\,JK^{-1}mol^{-1}$$

$\Delta S_{total} = -217 + 4.01 \times 10^3 = +3793\ JK^{-1}mol^{-1}$

63. **(1)**

64. **(4)** We know that, $\Delta G = \Delta H - T\Delta S$

When the reaction is in equilibrium, $\Delta G = 0$

$$0 = \Delta H - T\Delta S \Rightarrow T = \frac{\Delta H}{\Delta S}$$

$$T = \frac{30 \times 1000}{105} = 285.7K$$

65. **(1)** $\Delta G = -ve$ means the reaction is spontaneous.

66. **(1)** If $\Delta G_{system} = 0$ the system has attained equilibrium is right. In it alternative (4) is most confusing as when $\Delta G > 0$, the process may be spontaneous when it is coupled with a reaction which has $\Delta G < 0$ and total ΔG is negative, so right answer is (1).

67. **(4)** $\Delta G = \Delta H - T\Delta S$; ΔG is positive for a reaction to be non-spontaneous when ΔH is positive and ΔS is negative.

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

69. **(4)**

70. **(2)**

NEET PREVIOUS YEARS QUESTIONS-EXPLANATIONS

1. **(4)** Let B.E of x_2, y_2 and xy are x kJ mol^{-1}, 0.5 x kJ mol^{-1} and x kJ mol^{-1} respectively

$$\frac{1}{2}x_2+\frac{1}{2}y_2 \rightarrow xy;\ \Delta H -200 \text{ kJ mol}^{-1}$$

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

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

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

2. **(1)** Given ΔH 35.5 kJ mol^{-1}

$\Delta S = 83.6$ JK^{-1} mol^{-1} ; $\because \Delta G = \Delta H - T\Delta S$

For a reaction to be spontaneous, $\Delta G = -ve$

i.e., $\Delta H < T\Delta S$

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

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

3. **(2)** The system is in isolated state.

$\because$ For an adiabatic process, q = 0

$\Delta U = q + w$

$\therefore \Delta U = w = -p\Delta V = -2.5$ atm × (4.5 – 2.5) L

$= -2.5 \times 2$ L-atm $= -5 \times 101.3$ J $= -506.5$ J ≈ -505J

4. **(3)** $\Delta G = \Delta H - T\cdot\Delta S$

For a spontaneous reaction $\Delta G = -ve$ (always)

which is possible only if

$\Delta H < 0$ and $\Delta S > 0$

$\therefore$ spontaneous at all temperatures.

5. **(1)** $C + O_2 \rightarrow CO_2 + 393.5$ kJ/mol

12g $\quad$ 44g

44g is formed from 12g of carbon

35.2g is formed from $\frac{12\times35.2}{44}$ g of C

= 9.6 g of C = 9.6/12 = 0.8 mole

1 mole release heat 393.5 kJ

0.8 mole release heat = 393.5 × 0.8

= 314.8 kJ $\approx$ 315 kg

6. **(2)** Given $\Delta U = 2.1$ k cal., $\Delta S = 20$ cal. K^{-1}

T = 300 K

$\because \Delta H = \Delta U + \Delta ngRT$

Putting the values given in the equation

$$\Delta H = 2.1 + 2\times\frac{2}{1000}\times300$$

= 2.1 + 1.2 = 3.3 Kcal.

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

$$= 3.3 - 300\times\frac{20}{1000} = -2.7 \text{Kcal}.$$

7. $W = -P_{ext}(V_2 - V_1)$

$P_{ext} = 2$ bar

$V_1 = 0.1$ L

$V_2 = 0.25$ L

W = –2 bar[0.25 – 0.1] L

W = –2 × 0.15 bar L

W = –0.30 bar L

W = (–0.30) × 100 = –30 J

8. $2H(g) \rightarrow H_2(g)$

Due to bond formation, entropy decreases.

9.

$w_{PV} = -P_{ext}(V_f - V_i)$

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

$= -10^5\ Nm^{-2} \times 10^{-3}\ [10 - 1]m^3$

$\mathbf{= -900\ J}$

10.

In adiabatic expansion cooling effect will take place, T_C will be less then T_A.

in adiabatic expansion $q = 0$

$\Delta U = w$

$w_{PV} < 0$

$\Delta U < 0$

$nC_{vm}\,\Delta T < 0$

$\Delta T < 0$

$T_C - T_A < 0$

$\mathbf{T_C < T_A}$

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

For spontaneous,

$\Delta G < 0$

$\Delta H - T\Delta S < O$

$$\Delta S > \frac{\Delta H}{T}$$

$$\Delta S > \frac{30 \times 10^3\,J\,mol^{-1}}{450K}$$

$\Delta S > 66.6\,J\,mol^{-1}K^{-1}$ (Check by options)

12.

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

$-109 = [B.E_{(H-H)} + B.E_{(Br-Br)}] - [2 \times B.E_{(H-Br)}]$

$-109 = 435 + 192 - 2 \times B.E_{(H-Br)}$

$$B.E_{(H-Br)} = \frac{435 + 192 + 109}{2} = 368\ KJ/mol$$

13. For free expansion of an ideal gas under adiabatic conditions w = 0, q = 0 and $\Delta T=0$

14. $2Cl \rightarrow Cl_2(g)$; $\Delta_r H < 0$ and $\Delta_r S < 0$

15. Cp – Cv =R

16. Isothermal condition $dT = 0 \Rightarrow du = 0 (or) \Delta u = 0$

Irreversible isothermal expansion $\Delta S_{total} \neq 0$

17. Work can be calculated as area under the curve