Chapter 10

Thermodynamics and Thermochemistry

Thermodynamics

Thermodynamics (Greek word thermo means heat and dynamics means motion) is the branch of science which deals with the study of different forms of energy and the quantitative relationships between them.

The complete study of thermodynamics is based upon three generalizations called first, second and third law of thermodynamics. These laws have been arrived purely on the basis of human experience and there is no theoretical proof for any of these laws.

Basic concepts

(1) **System, surroundings and Boundary :** A specified part of the universe which is under observation is called the *system* and the remaining portion of the universe which is not a part of the system is called the *surroundings*.

The system and the surroundings are separated by *real or imaginary boundaries*. The boundary also defines the limits of the system. The system and the surroundings can interact across the boundary.

(2) **Types of systems**

(i) ***Isolated system*** **:** This type of system has no interaction with its surroundings. The boundary is sealed and insulated. Neither matter nor energy can be exchanged with surrounding. A substance contained in an ideal thermos flask is an example of an isolated system.

(ii) ***Closed system*** **:** This type of system can exchange energy in the form of heat, work or radiations but not matter with its surroundings. The boundary between system and surroundings is sealed but not insulated. For example, liquid in contact with vapour in a sealed tube and pressure cooker.

(iii) ***Open system*** **:** This type of system can exchange matter as well as energy with its surroundings. The boundary is neither sealed nor insulated. Sodium reacting with water in an open beaker is an example of open system.

(iv) ***Homogeneous system*** **:** A system is said to be homogeneous when it is completely uniform throughout. A homogeneous system is made of one phase only. Examples: a pure single solid, liquid or gas, mixture of gases and a true solution.

(v) ***Heterogeneous system*** **:** A system is said to be heterogeneous when it is not uniform throughout, *i.e.*, it consist of two or more phases. Examples : ice in contact with water, two or more immiscible liquids, insoluble solid in contact with a liquid, a liquid in contact with vapour, etc.

(vi) ***Macroscopic system*** **:** A macroscopic system is one in which there are a large number of particles (may be molecules, atoms, ions etc.)

(3) **Macroscopic properties of the system**

Thermodynamics deals with matter in terms of bulk (large number of chemical species) behaviour. The properties of the system which arise from the bulk behaviour of matter are called *macroscopic properties*. The common examples of macroscopic properties are pressure, volume, temperature, surface tension, viscosity, density, refractive index, etc.

The macroscopic properties can be subdivided into two types,

(i) ***Intensive properties*** : The properties which do not depend upon the quantity of matter present in the system or size of the system are called *intensive properties.* Its examples are pressure, temperature, density, specific heat, surface tension, refractive index, viscosity, melting point, boiling point, volume per mole, concentration etc.

(ii) ***Extensive properties*** **:** The properties whose magnitude depends upon the quantity of matter present in the system are called *extensive properties*. Its examples are total mass, volume, internal energy, enthalpy, entropy etc. These properties are additive in nature.

Any extensive property if expressed as per mole or per gram becomes an intensive property.

(4) **State of a system and State Variables**

Macroscopic properties which determine the state of a system are referred to as *state variables* or *state functions* or *thermodynamic parameters*. The change in the state properties depends only upon the *initial and final states of the system*, but it is independent of the manner in which the change has been brought about. In other words, the state properties do not depend upon a path followed.

(5) **Thermodynamic equilibrium :** *"A system is said to have attained a state of thermodynamic equilibrium when it shows no further tendency to change its property with time".*

The criterion for thermodynamic equilibrium requires that the following three types of equilibrium exist simultaneously in a system,

(i) ***Chemical Equilibrium*** **:** A system in which the composition of the system remains fixed and definite.

(ii) ***Mechanical Equilibrium*** **:** No chemical work is done between different parts of the system or between the system and surrounding. It can be achieved by keeping pressure constant.

(iii) ***Thermal Equilibrium*** **:** Temperature remains constant *i.e.* no flow of heat between system and surrounding.

(6) **Thermodynamic process :** When the thermodynamic system changes from one state to another, the operation is called a **process**. The various types of the processes are

(i) ***Isothermal process*** **:** In this process operation is done at constant temperature. $dT = 0$ thus $\Delta E = 0$.

(ii) ***Adiabatic process*** **:** In this a process there is no exchange of heat takes place between the system and surroundings. The system is thermally isolated, i.e., $dQ = 0$ and its boundaries are insulated.

(iii) ***Isobaric process*** **:** In this process the pressure remains constant throughout the change i.e., $dP = 0$.

(iv) ***Isochoric process*** **:** In this process volume remains constant throughout the change, *i.e.,* $dV = 0$.

(v) ***Cyclic process*** **:** When a system undergoes a number of different processes and finally return to its initial state, it is termed *cyclic process*. For a cyclic process $dE = 0$ and $dH = 0$.

(vi) ***Reversible process*** **:** A process which occurs infinitesimally slowly, i.e. opposing force is infinitesimally smaller than driving force and when infinitesimal increase in the opposing force can reverse the process, it is said to be *reversible process*.

(vii) ***Irreversible process*** **:** When the process occurs from initial to final state in single step in finite time and cannot be reversed, it is termed an *irreversible process*. Amount of entropy increases in irreversible process.

Irreversible processes are spontaneous in nature. All natural processes are irreversible in nature

Internal energy, heat and Work

(1) **Internal energy** (E) : *"Every system having some quantity of matter is associated with a definite amount of energy. This energy is known as internal energy."*

$$E = E_{\text{translational}} + E_{\text{rotational}} + E_{\text{vibrational}} + E_{\text{bonding}} + E_{\text{electronic}} + ...$$

(i) ***Characteristics of internal energy***

(a) Internal energy of a system is an extensive property.

(b) Internal energy is a state property.

(c) The change in the internal energy does not depend on the path by which the final state is reached.

(d) There is no change in internal energy in a cyclic process.

(e) The internal energy of an ideal gas is a function of temperature only.

(f) Internal energy of a system depends upon the quantity of substance, its chemical nature, temperature, pressure and volume.

(g) The unit of E is ergs in *CGS* or joules in *SI*

1 *Joule* = 10^7 *ergs.*

(ii) ***Change in internal energy*** (ΔE) **:** It is neither possible nor necessary to calculate the absolute value of internal energy of a system then, $\Delta E = E_f - E_{in}$; ΔE is positive if $E_f > E_{in}$ and negative if $E_f < E_{in}$.

(2) **Heat** (q) **and work** (w) **:** The energy of a system may increase or decrease in several ways but two common ways are *heat and work*.

Heat is a form of energy. It flows from one system to another because of the difference in temperature between them. Heat flows from higher temperature to lower temperature. Therefore, it is regarded as *energy on the move*.

Work is said to be performed if the point of application of force is displaced in the direction of the force. It is equal to the force multiplied by the displacement (distance through which the force acts).

There are three main types of work which we generally come across. These are, Gravitational work, electrical work and mechanical work.

Mechanical work = Force × displacement = F.d

Electrical work = potential difference × charge = V.q

Gravitational work = *mgh*

(i) ***Units of heat and work*** **:** The heat changes are measured in calories (cal), Kilo calories (kcal), joules (*J*) or kilo joules (*kJ*)**.** These are related as, 1 *cal* = 4.184 *J;* 1*kcal* = 4.184*kJ*

The *S.I.* unit of heat is joule (*J*) or *kilojoule*. The Joule (*J*) is equal to *Newton – metre* (1 *J= 1 Nm*).

Work is measured in terms of ergs or joules. The *S.I.* unit of work is Joule.

1 *Joule* = 10^7 *ergs* = 0.2390 *cal.*

1 *cal* > 1 *joule* > 1 *erg*

(ii) ***Sign conventions for heat and work***

Heat absorbed by the system = *q* positive

Heat evolved by the system = *q* negative

Work done on the system = *w* positive

Work done by the system = *w* negative.

Zeroth law of thermodynamics

This law forms the basis of concept of temperature. This law can be stated as follows,

"*If a system A is in thermal equilibrium with a system C and if B is also in thermal equilibrium with system C, then A and B are in thermal equilibrium with each other whatever the composition of the system.*"

$$\boxed{A} \rightleftharpoons \boxed{C} \qquad \boxed{B} \rightleftharpoons \boxed{C}$$

$$\boxed{A} \rightleftharpoons \boxed{B}$$

First law of thermodynamics

Helmholtz and Robert Mayer proposed first law of thermodynamics. This law is also known as *law of conservation of energy*. It states that,

"Energy can neither be created nor destroyed although it can be converted from one form into another."

$$E_2 - E_1 = \Delta E = q + w$$

i.e. (Change in internal energy) = (Heat added to the system) +(Work done on the system)

If a system does work (*w*) on the surroundings, its internal energy decreases. In this case, $\Delta E = q + (-w) = q - w$

i.e.(Change in internal energy)=(Heat added to the system) – (work done by the system)

The relationship between internal energy, work and heat is a mathematical *statement of first law of thermodynamics.*

Enthalpy and Enthalpy change

Heat content of a system at constant pressure is called *enthalpy* denoted by '*H*'.

From first law of thermodynamics, $q = E + PV$ ....(i)

Heat change at constant pressure can be given as

$\Delta q = \Delta E + P\Delta V$ ....(ii)

At constant pressure heat can be replaced at enthalpy.

$\Delta H = \Delta E + P\Delta V$ ....(iii)

$\therefore \Delta H =$ Heat change or heat of reaction (in chemical process) at constant pressure

$\Delta E =$ Heat change or heat of reaction at constant volume.

In case of solids and liquids participating in a reaction,

$$\Delta H = \Delta E (P\Delta V \approx 0)$$

Difference between ΔH and ΔE is significant when gases are involved in chemical reaction.

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

$$\Delta H = \Delta E + \Delta nRT$$

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

Here, $\Delta n = n_P - n_R$

Specific and Molar heat capacity

(1) **Specific heat** (or specific heat capacity) of a substance is the quantity of heat (in *calories*, *joules*, *kcal*, or *kilo joules*) required to raise the temperature of 1*g* of that substance through 1^oC. It can be measured at constant pressure (c_p) and at constant volume (c_v).

(2) **Molar heat capacity** of a substance is the quantity of heat required to raise the temperature of 1 *mole* of the substance by 1^oC.

∴ Molar heat capacity = Specific heat capacity × Molecular weight, *i.e.*, $C_v = c_v \times M$ and $C_p = c_p \times M$.

(3) Since gases on heating show considerable tendency towards expansion if heated under constant pressure conditions, an additional energy has to be supplied for raising its temperature by 1^oC relative to that required under constant volume conditions, *i.e.*,

$$C_p > C_v \text{ or } C_p = C_v + \text{Work done in expansion, } P\Delta V (= R)$$

where, $C_p =$ molar heat capacity at constant pressure

$C_v =$ molar heat capacity at constant volume.

(4) **Some useful relations of C_p and C_v**

(i) $C_p - C_v = R = 2\,calories = 8.314\,J$

(ii) $C_v = \frac{3}{2}R$ (for monoatomic gas) and $C_v = \frac{3}{2} + x$ (for *di* and polyatomic gas), where *x* varies from gas to gas.

(iii) $\frac{C_p}{C_v} = \gamma$ (Ratio of molar capacities)

(iv) For monoatomic gas, $C_v = 3\,calories$ whereas, $C_p = C_v + R = 5\,calories$

(v) For monoatomic gas, $(\gamma) = \frac{C_p}{C_v} = \frac{\frac{5}{2}R}{\frac{3}{2}R} = 1.66$

(vi) For diatomic gas $(\gamma) = \frac{C_p}{C_v} = \frac{\frac{7}{2}R}{\frac{5}{2}R} = 1.40$

(vii) For triatomic gas $(\gamma) = \frac{C_p}{C_v} = \frac{8R}{6R} = 1.33$

Expansion of an ideal gas

(1) **Isothermal Expansion** : For an isothermal expansion, $\Delta T = 0$; $\Delta E = 0$.

According to first law of thermodynamics,

$$\Delta E = q + w \qquad \therefore q = -w$$

This shows that in isothermal expansion, the work is done by the system at the expense of heat absorbed.

Since for isothermal process, ΔE and ΔT are zero respectively, hence, $\Delta H = 0$

(i) ***Work done in reversible isothermal expansion*** : Consider an ideal gas enclosed in a cylinder fitted with a weightless and frictionless piston. The cylinder is not insulated. The external pressure, P_{ext} is equal to pressure of the gas, P_{gas}.

$$P_{ext} = P_{gas} = P$$

If the external pressure is decreased by an infinitesimal amount *dP,* the gas will expand by an infinitesimal volume, *dV*. As a result of expansion, the pressure of the gas within the cylinder falls to $P_{gas} - dP$, *i.e.,* it becomes again equal to the external pressure and, thus, the piston comes to rest. Such a process is repeated for a number of times, *i.e.,* in each step the gas expa *dV*.

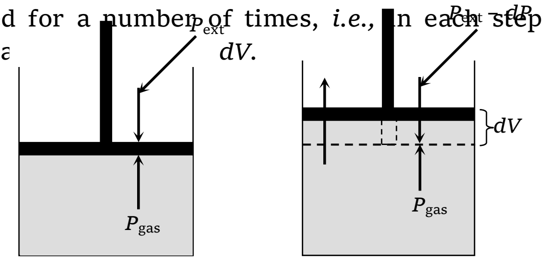


Fig. 10.1

Since the system is in thermal equilibrium with the surroundings, the infinitesimally small cooling produced due to expansion is balanced by the absorption of heat from the surroundings and the temperature remains constant throughout the expansion.

The work done by the gas in each step of expansion can be given as,

$$d_w = -(P_{ext} - dP)dV = -P_{ext}.dV - dP\,.\,dV$$

$dP.dV$, the product of two infinitesimal quantities, is negligible.

The total amount of work done by the isothermal reversible expansion of the ideal gas from volume V_1 to volume V_2 is, given as, $w = -nRT\log_e \frac{V_2}{V_1}$ or

$$w = -2.303\,nRT\log_{10}\frac{V_2}{V_1}$$

At constant temperature, according to Boyle's law,

$$P_1V_1 = P_2V_2 \text{ or } \frac{V_2}{V_1} = \frac{P_1}{P_2} \text{ So, } w = -2.303\,nRT\log_{10}\frac{P_1}{P_2}$$

Isothermal compression work of an ideal gas may be derived similarly and it has exactly the same value with positive sign.

$$w_{compression} = 2.303\,nRT\log\frac{V_1}{V_2} = 2.303\,nRT\log\frac{P_2}{P_1}$$

(ii) ***Work done in irreversible isothermal expansion*** : Two types of irreversible isothermal expansions are observed, *i.e.,* (a) Free expansion and (b) Intermediate expansion. In free expansion, the external pressure is zero, *i.e.,* work done is zero when gas expands in vacuum. In intermediate expansion, the external pressure is less than gas pressure. So, the work done when volume changes from V_1 to V_2 is given by

$$w = -\int_{V_1}^{V_2} P_{ext} \times dV = -P_{ext}(V_2 - V_1)$$

Since P_{ext} is less than the pressure of the gas, the work done during intermediate expansion is numerically less than the work done during reversible isothermal expansion in which P_{ext} is almost equal to P_{gas}.

(2) **Adiabatic Expansion :** In adiabatic expansion, no heat is allowed to enter or leave the system, hence, $q = 0$.

According to first law of thermodynamics,

$$\Delta E = q + w \quad \therefore \quad \Delta E = w$$

work is done by the gas during expansion at the expense of internal energy. In expansion, ΔE decreases while in compression ΔE increases.

The molar specific heat capacity at constant volume of an ideal gas is given by

$$C_v = \left(\frac{dE}{dT}\right)_v \text{ or } dE = C_v.dT$$

and for finite change $\Delta E = C_v \Delta T$ So, $w = \Delta E = C_v \Delta T$

The value of ΔT depends upon the process whether it is reversible or irreversible.

(i) ***Reversible adiabatic expansion*** : The following relationships are followed by an ideal gas under reversible adiabatic expansion.

$$PV^{\gamma} = \text{constant}$$

where, P = External pressure, V = Volume

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

where, $C_p =$ molar specific heat capacity at constant pressure, $C_v =$ molar specific heat capacity at constant volume.

$$\left(\frac{T_1}{T_2}\right)^{\gamma} = \left(\frac{P_1}{P_2}\right)^{\gamma - 1} = \left(\frac{P_2}{P_1}\right)^{1-\gamma}$$

knowing γ, P_1, P_2 and initial temperature T_1, the final temperature T_2 can be evaluated.

(ii) ***Irreversible adiabatic expansion*** **:** In free expansion, the external pressure is zero, *i.e,* work done is zero. Accordingly, ΔE which is equal to w is also zero. If ΔE is zero, ΔT should be zero. Thus, in free expansion (adiabatically), $\Delta T = 0$, $\Delta E = 0$, $w = 0$ and $\Delta H = 0$.

In intermediate expansion, the volume changes from V_1 to V_2 against external pressure, P_{ext}.

$$w = -P_{ext}(V_2 - V_1) = -P_{ext}\left(\frac{RT_2}{P_2} - \frac{RT_1}{P_1}\right)$$

$$= -P_{ext}\left(\frac{T_2P_1 - T_1P_2}{P_1P_2}\right) \times R$$

or $w = C_v(T_2 - T_1) = -RP_{ext}\left(\frac{T_2P_1 - T_1P_2}{P_1P_2}\right)$

Spontaneous and Non-spontaneous processes

A process which can take place by itself under the given set of conditions once it has been initiated if necessary, is said to be a *spontaneous process*. In other words, a spontaneous process is a process that can occur without work being done on it. The spontaneous processes are also called *feasible* or *probable processes*.

On the other hand, the processes which are forbidden and are made to take place only by supplying energy continuously from outside the system are called *non-spontaneous processes*. In other words, non spontaneous processes can be brought about by doing work.

Examples of Spontaneous and Non-spontaneous processes

(1) The diffusion of the solute from a concentrated solution to a dilute solution occurs when these are brought into contact is spontaneous process.

(2) Mixing of different gases is spontaneous process.

(3) Heat flows from a hot reservoir to a cold reservoir is spontaneous process.

(4) Electricity flows from high potential to low potential is spontaneous process.

(5) Expansion of an ideal gas into vacuum through a pinhole is spontaneous process.

All the above spontaneous processes becomes non-spontaneous when we reverse them by doing work.

Spontaneous process and Enthalpy change : A spontaneous process is accompanied by decrease in internal energy or enthalpy, *i.e.,* work can be obtained by the spontaneous process. It indicates that only exothermic reactions are spontaneous. But the melting of ice and evaporation of water are endothermic processes which also proceeds spontaneously. It means, there is some other factor in addition to enthalpy change (ΔH) which explains the spontaneous nature of the system. This factor is entropy.

Second law of thermodynamics

All the limitations of the first law of thermodynamics can be remove by the second law of thermodynamics. This law is generalisation of certain experiences about heat engines and refrigerators. It has been stated in a number of ways, but all the statements are logically equivalent to one another.

(1) **Statements of the law**

(i) ***Kelvin statement*** **:** *"It is impossible to derive a continuous supply of work by cooling a body to a* *temperature lower than that of the coldest of its surroundings."*

(ii) ***Clausius statement*** **:** *"It is impossible for a self acting machine, unaided by any external agency, to transfer heat from one body to another at a higher temperature or Heat cannot itself pass from a colder body to a hotter body, but tends invariably towards a lower thermal level."*

(iii) ***Ostwald statement*** **:** *"It is impossible to construct a machine functioning in cycle which can convert heat completely into equivalent amount of work without producing changes elsewhere, i.e., perpetual motions are not allowed."*

(iv) ***Carnot statement*** **:** *"It is impossible to take heat from a hot reservoir and convert it completely into work by a cyclic process without transferring a part of it to a cold reservoir."*

(2) **Proof of the law :** No rigorous proof is available for the second law. The formulation of the second law is based upon the observations and has yet to be disproved. No deviations of this law have so far been reported. However, the law is applicable to cyclic processes only.

The Carnot cycle

Carnot, a *French engineer*, in 1824 employed merely theoretical and an imaginary reversible cycle known as carnot cycle to demonstrate the maximum convertibility of heat into work.

The system consists of one mole of an ideal gas enclosed in a cylinder fitted with a piston, which is subjected to a series of four successive operations.

For cyclic process, the essential condition is that net work done is equal to heat absorbed. This condition is satisfied in a carnot cycle.

$$\frac{w}{q_2} = \frac{T_2 - T_1}{T_2} = \text{Thermodynamic efficiency}$$

Thus, the larger the temperature difference between high and low temperature reservoirs, the more the heat converted into work by the heat engine.

Since $\frac{T_2 - T_1}{T_2} < 1$, it follows that $w < q_2$. This means that only a part of heat absorbed by the system at the higher temperature is transformed into work. The rest of the heat is given out to surroundings. The efficiency of the heat engine is always less then 1. This has led to the following enunciation of the second law of thermodynamics.

It is impossible to convert heat into work without compensation.

Entropy and Entropy change

(1) **Definition :** Entropy is a thermodynamic state quantity which is a measure of randomness or disorder of the molecules of the system.

Entropy is represented by the symbol "S". It is difficult to define the actual entropy of a system. It is more convenient to define the change of entropy during a change of state.

The entropy change of a system may be defined as the integral of all the terms involving heat exchanged (q) divided by the absolute temperature (T) during each infinitesimally small change of the process carried out reversibly at constant temperature.

$$\Delta S = S_{final} - S_{initial} = \frac{q_{rev}}{T}$$

If heat is absorbed, then $\Delta S = +ve$ and if heat is evolved, then $\Delta S = -ve$.

(2) **Units of entropy :** Since entropy change is expressed by a heat term divided by temperature, it is expressed in terms of *calorie per degree*, *i.e.,*cal deg^{-1}. In *SI* units, the entropy is expressed in terms of joule per degree Kelvin, i.e., JK^{-1}.

(3) **Characteristics of entropy :** The important characteristics of entropy are summed up below

(i) Entropy is an extensive property. Its value depends upon the amount of the substance present in the system.

(ii) Entropy of a system is a state function. It depends upon the state variables (T, p, V, n).

(iii) The change in entropy in going from one state to another is independent of the path.

(iv) The change in entropy for a cyclic process is always zero.

(v) The total entropy change of an isolated system is equal to the entropy change of system and entropy change of the surroundings. The sum is called *entropy change of universe*.

$$\Delta S_{\text{universe}} = \Delta S_{sys} + \Delta S_{Surr}$$

(a) In a reversible process, $\Delta S_{universe} = 0$ and, therefore

$$\Delta S_{sys} = -\Delta S_{Surr}$$

(b) In an irreversible process, $\Delta S_{universe} > 0$. This means that there is increase in entropy of universe is spontaneous changes.

(vi) Entropy is a measure of unavailable energy for useful work.

Unavailable energy = Entropy × Temperature

(vii) Entropy, S is related to thermodynamic probability (W) by the relation,

$$S = k \log_e W \text{ and } S = 2.303\, k \log_{10} W$$

where, k is Boltzmann's constant

(4) **Entropy changes in system & surroundings and total entropy change for Exothermic and Endothermic reactions :** Heat increases the thermal motion of the atoms or molecules and increases their disorder and hence their entropy. In case of an exothermic process, the heat escapes into the surroundings and therefore, entropy of the surroundings increases on the other hand in case of endothermic process, the heat enters the system from the surroundings and therefore. The entropy of the surroundings decreases.

In general, there will be an overall increase of the total entropy (or disorder) whenever the disorder of the surroundings is greater than the decrease in disorder of the system. The process will be *spontaneous only when the total entropy increases*.

(5) **Entropy change during phase transition :** The change of matter from one state (solid, liquid or gas) to another is called *phase transition*. Such changes occur at definite temperature such as melting point (solid to liquid). boiling point (liquid to vapours) etc, and are accompanied by absorption or evolution of heat.

When a solid changes into a liquid at its fusion temperature, there is absorption of heat (latent heat). Let ΔH_f be the molar heat of fusion. The entropy change will be

$$\Delta S_f = \frac{\Delta H_f}{T_f}$$

Similarly, if the latent heat of vaporisation and sublimation are denoted by ΔH_{vap} and ΔH_{sub}, respectively, the entropy of vaporisation and sublimation are given by

$$\Delta S_{vap} = \frac{\Delta H_{vap}}{T_b} \quad \text{and} \quad \Delta S_{sub} = \frac{\Delta H_{sub}}{T_s}$$

Since $\Delta H_f, \Delta H_{vap}$ and ΔH_{Sub} are all positive, these processes are accompanied by increase of entropy and the reverse processes are accompanied by decrease in entropy.

(6) **Entropy change for an ideal gas :** In going from initial to final state, the entropy change, ΔS for an ideal gas is given by the following relations,

(i) When T and V are two variables,

$\Delta S = nC_v \ \ln\frac{T_2}{T_1} + nR\ \ln\frac{V_2}{V_1}$. Assuming C_v is constant

(ii) When T and p are two variables,

$\Delta S = nC_P \ \ln\frac{T_2}{T_1} - nR\ \ln\frac{p_2}{p_1}$. Assuming C_p, is constant

(a) Thus, for an *isothermal process* (T constant),

$$\Delta S = nR\ \ln\frac{V_2}{V_1}\ or = -nR\ \ln\frac{p_2}{p_1}$$

(b) For *isobaric process* (p constant), $\Delta S = n\,C_p \ln\frac{T_2}{T_1}$

(c) For *isochoric process* (V constant), $\Delta S = n\,C_v \ln\frac{T_2}{T_1}$

(d) *Entropy change during adiabatic expansion* : In such process $q=0$ at all stages. Hence $\Delta S = 0$. Thus, reversible adiabatic processes are called *isoentropic process*.

Free energy and Free energy change

Gibb's free energy (G) is a *state function* and is a measure of maximum work done or useful work done from a reversible reaction at constant temperature and pressure.

(1) **Characteristics of free energy**

(i) The free energy of a system is the enthalpy of the system minus the product of absolute temperature and entropy *i.e.,* $G = H - TS$

(ii) Like other state functions *E, H* and *S*, it is also expressed as ΔG. Also $\Delta G = \Delta H - T\Delta S_{system}$ where ΔS is entropy change for system only. This is *Gibb's Helmholtz equation*.

(iii) At equilibrium $\Delta G = 0$

(iv) For a spontaneous process decrease in free energy is noticed *i.e.,* $\Delta G = -ve$.

(v) At absolute zero, $T\Delta S$ is zero. Therefore if ΔG is – *ve*, ΔH should be – *ve* or only exothermic reactions proceed spontaneously at absolute zero.

(vi) $\Delta G_{system} = T\Delta S_{universe}$, where $\Delta H = 0$

(vii) The standard free energy change,

$\Delta G^o = -2.303\,RT\log_{10} K,$ where K is equilibrium constant.

(a) Thus if $K > 1,$ then $\Delta G^o = -ve$ thus reactions with equilibrium constant $K>1$ are thermodynamically spontaneous.

(b) If $K<1$, then $\Delta G^o = +ve$ and thus reactions with equilibrium constant $K<1$ are thermodynamically spontaneous in reverse direction.

(2) **Criteria for spontaneity of reaction** : For a spontaneous change $\Delta G = -ve$ and therefore use of

$\Delta G = \Delta H - T\Delta S,$ provides the following conditions for a change to be spontaneous.

Table :10.1 Criteria for spontaneity of reaction

ΔH	**ΔS**	**ΔG**	**Reaction characteristics**	**Example**
–	+	Always negative	Reaction is spontaneous at all temperatures	$2O_{3(g)} \rightarrow 3O_{2(g)}$
+	–	Always positive	Reaction is non spontaneous at all temperatures	$3O_{2(g)} \rightarrow 2O_{3(g)}$
–	–	Negative at low temperature but positive at high temperature	Reaction is spontaneous at low temperature but becomes non spontaneous at high temperature	$CaO_{(s)} + CO_{2(g)} \rightarrow CaCO_{3(s)}$
+	+	Positive at low temperature but negative at high temperature	Reaction is non spontaneous at low temperature but becomes spontaneous at high temperature	$CaCO_{3(s)} \rightarrow CaO_{(s)} + CO_{2(g)}$

Third law of thermodynamics

This law was first formulated by German chemist *Walther Nernst* in 1906. According to this law,

"The entropy of all perfectly crystalline solids is zero at the absolute zero temperature. Since entropy is a measure of disorder, it can be interpretated that at absolute zero, a perfectly crystalline solid has a perfect order of its constituent particles."

The most important application of the third law of thermodynamics is that it helps in the calculation of absolute entropies of the substance at any temperature *T*.

$$S = 2.303\, C_p \log T$$

Where C_P is the heat capacity of the substance at constant pressure and is supposed to remain constant in the range of 0 to *T*.

Limitations of the law

(1) Glassy solids even at 0^oK has entropy *greater than zero*.

(2) Solids having mixtures of *isotopes* do not have zero entropy at 0^oK. For example, entropy of solid chlorine is not zero at 0^oK.

(3) Crystals of CO, N_2O, NO, H_2O, etc. do not have perfect order even at 0^oK thus their entropy is not *equal to zero*.

Thermochemistry

"Thermochemistry is a branch of physical chemistry which is concerned with energy changes accompanying chemical transformation. It is also termed as chemical energetics. It is based on the first law of thermodynamics."

Exothermic and Endothermic reactions

(1) **Exothermic reactions :** The chemical reactions which proceed with the ***evolution of heat*** energy are called exothermic reactions. The heat energy produced during the reactions is indicated by writing $+q$ or more precisely by giving the actual numerical value on the products side. In general exothermic reactions may be represented as, $A + B \rightarrow C + D + q$ (heat energy)

In the exothermic reactions the *enthalpy of the products will be less than the enthalpy of the reactants*, so that the enthalpy change is negative as shown below

$$\Delta H = H_p - H_r \;;\; H_p < H_r \;;\; \Delta H = -ve$$

Examples : (i) $C(s) + O_2(g) \rightarrow CO_2(g) + 393.5kJ$

(at constant temperature and pressure)

or $C(s) + O_2(g) \rightarrow CO_2(g); \quad \Delta H = -393.5kJ$

(ii) $H_2(g) + \frac{1}{2}O_2(g) \rightarrow H_2O(l); \quad \Delta H = -285.8kJ$

(iii) Fermentation is also an example of exothermic reaction.

(2) **Endothermic reactions :** The chemical reactions which proceed with the absorption of heat energy are called endothermic reactions. Since the heat is added to the reactants in these reactions, the heat absorbed is indicated by either putting (–) or by writing the actual numerical value of heat on the reactant side

$A + B \rightarrow C + D - q$ (heat energy)

The heat absorbed at constant temperature and constant pressure measures enthalpy change. Because of the absorption of heat, the enthalpy of products will be more than the enthalpy of the reactants. Consequently, ΔH will be positive $(+ve)$ for the endothermic reactions.

$$\Delta H = H_p - H_r \;;\; H_p > H_r \;; \quad \Delta H = +ve$$

Example : (i) $N_2(g) + O_2(g) \rightarrow 2NO(g); \Delta H = +180.5kJ$

(ii) $C(s) + 2S(s) \rightarrow CS_2(l) \Delta H = +92.0kJ$

(iii) Preparation of ozone by passing silent electric discharged through oxygen is the example of endothermic reaction.

(iv) Evaporation of water is also the example of endothermic reaction.

For exothermic reaction : ΔH or $\Delta E = -ve$

For endothermic reaction : ΔH or $\Delta E = +ve$

Heat of reaction or Enthalpy of reaction

Heat of reaction is defined as the amount of heat evolved or absorbed when quantities of the substances indicated by the chemical equation have completely reacted. The heat of reaction (or enthalpy of reaction) is actually the difference between the enthalpies of the products and the reactants when the quantities of the reactants indicated by the chemical equation have completely reacted. Mathematically,

Enthalpy of reaction (heat of reaction) $= \Delta H = \Sigma H_P - \Sigma H_R$

(1) **Factors which influence the heat of reaction** : There are a number of factors which affect the magnitude of heat of reaction.

(i) ***Physical state of reactants and products*** **:** Heat energy is involved for changing the physical state of a chemical substance. For example in the conversion of water into steam, heat is absorbed and heat is evolved when steam is condensed. Considering the following two reactions

$$H_2(g) + \frac{1}{2}O_2(g) = H_2O(g); \quad \Delta H = -57.8\,kcal$$

$$H_2(g) + \frac{1}{2}O_2(g) = H_2O(l); \quad \Delta H = -68.32\,kcal$$

It is observed that there is difference in the value of ΔH if water is obtained in gaseous or liquid state. ΔH value in second case is higher because heat is evolved when steam condenses. Hence, physical sate always affects the heat of reaction.

(ii) ***Allotropic forms of the element*** **:** Heat energy is also involved when one allotropic form of an element is converted into another. Thus, the value of ΔH depends on the allotropic form used in the reaction. For example, the value of ΔH is different when carbon in the form of diamond or in amorphous form is used.

C (diamond) $+ O_2(g) \rightarrow CO_2(g); \quad \Delta H = -94.3\,kcal$

C (amorphous) $+ O_2(g) \rightarrow CO_2(g); \quad \Delta H = -97.6\,kcal$

The difference between the two values is equal to the heat absorbed when 12*g* of diamond is converted into 12*g* of amorphous carbon. This is termed as *heat of transition.*

(iii) ***Temperature*** **:** Heat of reaction has been found to depend upon the temperature at which reaction is occurring. The variation of the heat of reaction with temperature can be ascertained by using *Kirchhoff's equation.*

$$\frac{\Delta H_{T_2} - \Delta H_{T_1}}{T_2 - T_1} = \Delta C_P$$

Kirchhoff's equation at constant volume may be given as,

$$\frac{\Delta E_{T_2} - \Delta E_{T_1}}{T_2 - T_1} = \Delta C_V$$

(iv) ***Reaction carried out at constant pressure or constant volume*** **:** When a chemical reaction occurs at constant volume, the heat change is called the internal energy of reaction at constant volume. However, most of the reactions are carried out at constant pressure; the enthalpy change is then termed as the enthalpy of reaction at constant pressure. The difference in the values is negligible when solids and liquids are involved in a chemical change. But, in reactions which involve gases, the difference in two values is considerable.

$\Delta E + \Delta nRT = \Delta H$ or $q_v + \Delta nRT = q_p$

$\Delta E = q_v =$ heat change at constant volume;

$\Delta E \quad \Delta H = q_p =$ heat change at constant pressure,

$\Delta n =$ total number of moles of gaseous product

- total number of moles of gaseous reactants.

(2) **Types of heat of reaction**

(i) ***Heat of formation*** **:** It is the quantity of heat evolved or absorbed (*i.e.* the change in enthalpy) when one mole of the substance is formed from its constituent elements under given conditions of temperature and pressure. It is represented by ΔH_f. When the temperature and pressure are as 25°*C* and 1 atmospheric pressure. The heat of formation under these conditions is *called standard heat of formation*. It is usually represented by ΔH_f^0.

The standard heat of formation of 1 mole of $NH_3(g)$ and 1 mole of $HCl(g)$.

$$\frac{1}{2}N_2(g) + \frac{3}{2}H_2(g) \rightarrow NH_3(g); \quad \Delta H_{(g)} = -11\,kcal$$

$$\frac{1}{2}H_2(g) + \frac{1}{2}Cl_2(g) \rightarrow HCl\,; \quad \Delta H_f = -22\,kcal$$

It may be calculated by

$$\Delta H^0 = [\Sigma \Delta H^0_{(\text{products})} - \Sigma \Delta H^0_{(\text{Reactants})}]$$

(ii) ***Heat of combustion*** **:** It is the amount of heat evolved or absorbed (*i.e.* change in enthalpy) when one mole of the substance is completely burnt in air or oxygen. For example

$$CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(l); \Delta H = -192\ kcal$$

$$C_2H_6(g) + 3.5\ O_2(g) \rightarrow 2CO_2(g) + 3H_2O(l); \ \Delta H = -372.8\ kcal$$

It may be calculated by

$$\Delta H^0 = [\Sigma \Delta H^0_{f\,(\text{Products})} - \Sigma H^0_{f\,(\text{Reactants})}]$$

The enthalpy or heat of combustion have a number of applications. Some of these are described below,

(a) *Calorific value of foods and fuels* : Energy is needed for the working of all machines. Even human body is no exception. Coal, petroleum, natural gas etc. serve as the principal sources of energy for man-made machines, the food which we eat serves as a source of energy to our body.

The energy released by the combustion of foods or fuels is usually compared in terms of their combustion energies per gram. It is known as *calorific value*. The amount of heat produced in calories or Joules when one gram of a substance (food or fuel) is completely burnt or oxidised.

When methane burns, 890.3 $kJ\ mol^{-1}$ of energy is released.

$$\underset{\text{1 mole (16g)}}{CH_4(g)} + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(l);\ \Delta H_{CH_4} = -890.3\,kJ$$

So, the calorific value of methane =

$$-\frac{890.3}{16} = -55.6\,kJ/g$$

(b) *Enthalpies of formation* : Enthalpies of formation of various compounds, which are not directly obtained, can be calculated from the data of enthalpies of combustions easily by the application of Hess's law.

$$\text{Heat of reaction} = \Sigma\,\text{Heat of combustion of reactants}$$
$$-\ \Sigma\,\text{Heat of combustion of products.}$$

(iii) ***Heat of neutralisation*** **:** It is the amount of heat evolved (i.e., change in enthalpy) when one equivalent of an acid is neutralised by one equivalent of a base in fairly dilute solution, e.g., *Neutralisation reactions are always exothermic reaction and the value of* ΔH *is* $(-ve)$.

$$HCl(aq.) + NaOH\ (aq.) \rightarrow NaCl(aq.) + H_2O$$

$$\Delta H = -13.7\ kcal$$

The heat of neutralisation of a strong acid against a strong base is always constant $(13.7\ kcal$ or $57\ kJ\ mole^{-1})$. It is because in dilute solutions all strong acids and bases ionise completely and thus the heat of neutralisation in such cases is actually the heat of formation of water from H^+ and OH^- ions, *i.e.,*

$$H^+ + OH^- \rightarrow H_2O; \Delta H = -13.7\ kcal$$

In case of neutralisation of a weak acid or a weak base against a strong base or acid respectively, since a part of the evolved heat is used up in ionising the weak acid or base, it is always less than $13.7\ kcal\ mole^{-1}$ $(57\ kJ\ mole^{-1})$. For example,

$$HCN\ (aq.) + NaOH\ (aq.) \rightarrow NaCN(aq.) + H_2O$$

$$\Delta H = -2.9\ kcal$$

$$HCN\ (aq.) \rightleftharpoons H^+ + CN^-;\ \Delta H = 10.8\ Kcal$$

$10.8\,KCal$ of heat is absorbed for ionisation of HCN it is heat of dissociation or ionisation

(iv) ***Heat of solution*** **:** *It is the amount of heat evolved or absorbed (i.e., change in enthalpy) when one mole of the solute is dissolved completely in excess of the solvent (usually water)*. For example,

$$NH_4Cl(s) + H_2O(l) \rightarrow NH_4Cl(aq.);\quad \Delta H = +3.90\ kcal$$

$$BaCl_2(s) + H_2O(l) \rightarrow BaCl_2(aq.);\ \Delta H = -2.70\ kcal$$

(v) ***Heat of hydration*** **:** *It is the amount of heat evolved or absorbed (i.e change in enthalpy) when* 1 *mole of an anhydrous or a partially hydrated salt combines with the required number of moles of water to form a specific hydrate*. For example, $CuSO_4(s) + 5H_2O(l) \rightarrow CuSO_4.\,5H_2O(s);\ \Delta H = -18.69$

(vi) ***Heat of vapourisation*** **:** When a liquid is allowed to evaporate, it absorbs heat from the surroundings and evaporation is accompanied by increase in enthalpy. For example: $10.5\,k$ *cals* is the increase in enthalpy when one mole of water is allowed to evaporate at 25^oC. When the vapours are allowed to condense to liquid state, the heat is evolved and condensation of vapour is accompanied by decrease in enthalpy.

The evaporation and condensation can be represented as,

$$H_2O(l) \rightarrow H_2O(g);\ \Delta H = +10.5\ kcals\ \ (+43.93\ kJ)$$

$$H_2O(g) \rightarrow H_2O(l);\quad \Delta H = -10.5\ kcals\quad (-43.93\ kJ)$$

Thus the change in enthalpy when a liquid changes into vapour state or when vapour changes into liquid state is called *heat of vapourisation*.

(vii) ***Heat of fusion*** **:** When a solid is allowed to melt, it changes into liquid state with the absorption of heat (increase in enthalpy) and when a liquid is allowed to freeze, it changes into solid with the evolution of heat (decrease in enthalpy). The change in enthalpy of such type of transformations is called *enthalpy of fusion*. For example,

$$H_2O(ice) \rightarrow H_2O(liquid);\quad \Delta H = +1.44\ kcals\ \ (+6.02\ kJ)$$

$$H_2O\ (liquid) \rightarrow H_2O\ (ice);\quad \Delta H = -1.44\ kcals\ (-6.02\ kJ)$$

(viii) ***Heat of precipitation* :** It is defined as the amount of heat liberated in the precipitation of one mole of a sparingly soluble substance when solutions of suitable electrolytes are mixed, for example

$$Ba^{2+} + SO_4^{2-}(aq) \rightarrow BaSO_4(s): \ \Delta H = -4.66\, kcal$$

(ix) ***Heat of sublimation* :** Sublimation is a process in which a solid on heating changes directly into gaseous state below its melting point.

Heat of sublimation of a substance is the amount of heat absorbed in the conversion of 1 mole of a solid directly into vapour phase at a given temperature below its melting point.

$$I_2(s) \rightarrow I_2(g)\ ; \quad \Delta H = +62.39\, kJ$$

Most solids that sublime are molecular in nature e.g. iodine and naphthalene etc.

$$\Delta H_{sub.} = \Delta H_{\text{fusion}} + \Delta H_{vaporisation}$$

(3) **Experimental determination of the heat of reaction :** The heat evolved or absorbed in a chemical reaction is measured by carrying out the reaction in an apparatus called *calorimeter*. The principle of measurement is that heat given out is equal to heat taken, *i.e.*, $Q = (W+m) \times s \times (T_2 - T_1)$,

Where *Q* is the heat of the reaction (given out), *W* is the water equivalent of the calorimeter and *m* is the mass of liquid in the calorimeter and *s* its specific heat, T_2 is the final temperature and T_1 the initial temperature of the system. Different types of calorimeters are used but two of the common types are,

(i) Water calorimeter and (ii) Bomb calorimeter

***Bomb calorimeter* :** This is commonly used to find the heat of combustion of organic substances.

Since the reaction in a bomb calorimeter proceeds at constant volume, the heat of combustion measured is ΔE

$$\Delta E = \frac{(W+m)(t_2 - t_1) \times s}{w_1} \times M\, kcal$$

Where *M* is the molecular mass of the substance, w_1 is the weight of substance taken, *W* is the water equivalent of calorimeter, *m* is the mass of liquid in the calorimeter and *s* is the specific heat of liquid.

ΔH can be calculated from the relation, $\Delta H = \Delta E + \Delta nRT$

Laws of thermochemistry

(1) **Levoisier and Laplace law :** According to this law enthalpy of decomposition of a compound is numerically equal to the enthalpy of formation of that compound with opposite sign, For example,

$$C(s) + O_2 \rightarrow CO_2(g); \Delta H = -94.3\, kcal$$

$$CO_2(g) \rightarrow C(s) + O_2(g); \Delta H = +94.3 kcal$$

(2) **Hess's law** (the law of constant heat summation) **:** This law was presented by Hess in 1840. According to this law "*If a chemical reaction can be made to take place in a number of ways in one or in several steps, the total enthalpy change (total heat change) is always the same, i.e. the total enthalpy change is independent of intermediate steps involved in the change*." The enthalpy change of a chemical reaction depends on the initial and final stages only. Let a substance A be changed in three steps to *D* with enthalpy change from *A* to *B*, ΔH_1 calorie, from *B* to $C, \Delta H_2$ calorie and from *C* to $D, \Delta H_3$ calorie. Total enthalpy change from *A* to *D* will be equal to the sum of enthalpies involved in various steps, Total enthalpy change $\Delta H_{\text{steps}} = \Delta H_1 + \Delta H_2 + \Delta H_3$

Now if *D* is directly converted into A, let the enthalpy change be ΔH_{direct}. According to Hess's law $\Delta H_{\text{steps}} + \Delta H_{\text{direct}} = 0$, i.e. ΔH_{steps} must be equal to ΔH_{direct} numerically but with opposite sign. In case it is not so, say ΔH_{steps} (which is negative) is more that ΔH_{direct} (which is positive), then in one cycle, some energy will be created which is not possible on the basis of first law of thermodynamics. Thus, ΔH_{steps} must be equal to ΔH_{direct} numerically.

(i) ***Experimental verification of Hess's law***

(a) *Formation of carbon dioxide from carbon*

First method : carbon is directly converted into $CO_2(g)$.

$$C(s) + O_2(g) = CO_2(g);\ \Delta H = -94.0\, kcal$$

Second method : Carbon is first converted into $CO(g)$ and then $CO(g)$ into $CO_2(g)$, i.e. conversion has been carried in two steps,

$$C(s) + \frac{1}{2}O_2 = CO(g)\ ;\ \Delta H = -26.0\, kcal$$

$$CO(g) + \frac{1}{2}O_2 = CO_2(g); \quad \Delta H = -68.0\, kcal$$

Total enthalpy change $C(s)$ to $CO_2(g)$; $\Delta H = -94.0\, kcal$

(b) *Formation of ammonium chloride from ammonia and hydrochloric acid:*

First method

$$NH_3(g)+HCl=NH_4Cl(g);\ \Delta H=-42.2\,kcal$$

$$NH_4Cl(g)+aq=NH_4Cl(aq);\ \Delta H=+4.0\ kcal$$

$$NH_3(g)+HCl(g)+aq=NH_4Cl(aq);\quad \Delta H=-38.2\,kcal$$

Second method

$$NH_3(g)+aq=NH_3(aq);\ \Delta H=-8.4\,kcal$$

$$HCl(g)+aq=HCl(aq);\Delta H\ =-17.3\,kcal$$

$$NH_3(aq)+HCl(aq)=NH_4Cl(aq);\quad \Delta H=-12.3\,kcal$$

$$NH_3(g)+HCl(g)+aq=NH_4Cl(aq);\quad \Delta H=-38.0\,kcal$$

(ii) ***Applications of Hess's law***

(a) For the determination of enthalpies of formation of those compounds which cannot be prepared directly from the elements easily using enthalpies of combustion of compounds.

(b) For the determination of enthalpies of extremely slow reactions.

(c) For the determination of enthalpies of transformation of one allotropic form into another.

(d) For the determination of bond energies.

$\Delta H_{\text{reaction}}=\Sigma$ Bond energies of reactants – Σ Bond energies of products.

(e) For the determination of resonance energy.

(f) For the determination of lattice energy.

Bond energy or Bond enthalpies

When a bond is formed between atoms, energy is released. Obviously same amount of energy will be required to break the bond. The energy required to break the bond is termed *bond dissociation energy*. The more precise definition is,

"*The amount of energy required to break one mole of bond of a particular type between the atoms in the gaseous state, i.e., to separate the atoms in the gaseous state under 1 atmospheric pressure and the specified temperature is called bond dissociation energy*."

For example, $H-H(g)\rightarrow 2H(g);\ \Delta H=+433\ kJ\,mol^{-1}$

$$Cl-Cl(g)\rightarrow 2Cl(g);\ \Delta H=+242.5\,kJ\,mol^{-1}$$

$$H-Cl(g)\rightarrow H(g)+Cl(g);\ \Delta H=+431\ kJ\,mol^{-1}$$

The bond dissociation energy of a diatomic molecule is also called *bond energy*. However, the bond dissociation energy depends upon the nature of bond and also the molecule in which the bond is present. When a molecule of a compound contains more than one bond of the same kind, the average value of the dissociation energies of a given bond is taken. *This average bond dissociation energy required to break each bond in a compound is called bond energy.*

Bond energy is also called, the heat of formation of the bond from gaseous atoms constituting the bond with reverse sign.

$$H(g)+Cl(g)\rightarrow H-Cl(g);\ \Delta H=-431\,kJ\,mol^{-1}$$

Bond energy of $H-Cl=-$(enthalpy of formation) $=-(-431)=+431\ kJ\ mol^{-1}$

Consider the dissociation of water molecule which consists of two $O-H$ bonds. The dissociation occurs in two stages.

$$H_2O(g)\rightarrow H(g)+OH(g);\ \Delta H=497.89\,kJ\,mol^{-1}$$

$$OH(g)\rightarrow H(g)+O(g);\ \Delta H=428.5\,kJ\,mol^{-1}$$

The average of these two bond dissociation energies gives the value of bond energy of $O-H$.

Bond energy of $O-H$ bond

$$=\frac{497.8+428.5}{2}=463.15\,kJ\,mol^{-1}$$

Similarly, the bond energy of $N-H$ bond in NH_3 is equal to one – third of the energy of dissociation of NH_3 and those of $C-H$ bond in CH_4 is equal to one – fourth of the energy of dissociation of CH_4.

Bond energy of $C-H=\frac{1664}{4}=416\,kJ\,mol^{-1}$

$$[CH_4(g)\rightarrow C(g)+4H(g);\ \Delta H=1664\ kJ\,mol^{-1}]$$

Applications of bond energy

(1) Heat of a reaction $=\Sigma$ Bond energy of reactants – Σ Bond energy of products.

(2) **Determination of resonance energy :** When a compound shows resonance, there is considerable difference between the heat of formation as calculated from bond energies and that determined experimentally.

Resonance energy = Experimental or actual heat of formation – Calculated heat of formation.

Tips & Tricks

- Joule thomson coeffient $\mu = \left(\frac{\partial T}{\partial p}\right)_H$

  For cooling $\mu = +ve$

  For Heating $\mu = -ve$

  Neither cooling nor heating $\mu = 0$
- The temperature at which a real gas shows neither cooling nor heating effect on adiabatic expansion (*i.e.*, $\mu = 0$) is called inversion temperature.
- Hydrogen has highest calorific value.
- $13.7\,Kcal/mol = 57\,KJ/mol$ (be cause of $1\,cal$ =4.2 Joule)
- Enthalpy of fusion of ice per mole is $6KJ$.
- Order of bond energy in halogen $Cl_2 > Br_2 > F_2 > I_2$.
- Heat of vapourisation of water per mole is 10.5 *KCal*.
- The heat of reaction is independent of the time consumed in the process.

Ordinary Thinking

Objective Questions

Basic concepts

1. Internal energy of an ideal gas depends on

(a) Volume (b) Temperature

(c) Pressure (d) None of these

2. Any series of operations so carried out that at the end, the system is back to its initial state is called

(a) Boyle's cycle (b) Reversible process

(c) Adiabatic process (d) Cyclic process

3. One calorie is equal to **[CPMT 1988]**

(a) 0.4184 *Joule* (b) 4.184 *Joule*

(c) 41.84 *Joule* (d) 418.4 *Joule*

4. The total internal energy change for a reversible isothermal cycles is

(a) Always 100 calories per degree

(b) Always negative

(c) 0

(d) Always positive

5. A well stoppered thermos flask contains some ice cubes. This is an example of a **[AIIMS 1992]**

(a) Closed system

(b) Open system

(c) Isolated system

(d) Non-thermodynamic system

6. Identify the intensive quantity from the following **[IIT JEE 1993]**

(a) Enthalpy and temperature

(b) Volume and temperature

(c) Enthalpy and volume

(d) Temperature and refractive index

7. Which of the following units represents the largest amount of energy **[CPMT 1989; MP PET 2000]**

(a) Electron volt (b) Erg

(c) Joule (d) Calorie

8. Energy equivalent to one erg, one joule and one calorie is in the order **[NCERT 1980; CPMT 1997]**

(a) $1\,erg > 1\,joule > 1\,calorie$ (b) $1\,erg > 1\,calorie > 1\,joule$

(c) $1\,calorie > 1\,joule > 1\,erg$ (d) $1\,joule > 1\,calorie > 1\,erg$

9. Heat produced in calories by the combustion of one gram of carbon is called
(a) Heat of combustion of carbon
(b) Heat of formation of carbon
(c) Calorific value of carbon
(d) Heat of production of carbon

10. Conditions of standard state used in thermochemistry is
(a) $0^o C$ and 1 atm (b) $20^o C$ and 1 atm
(c) $25^o C$ and 1 atm (d) $0 K$ and 1 atm

11. The temperature of the system decreases in an **[KCET 2005]**
(a) Adiabatic compression (b) Isothermal compression
(c) Isothermal expansion (d) Adiabatic expansion

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. If a refrigerator's door is opened, then we get **[CPMT 1980]**
(a) Room heated
(b) Room cooled
(c) More amount of heat is passed out
(d) No effect on room

14. The cooling in refrigerator is due to **[KCET 2005]**
(a) Reaction of the refrigerator gas
(b) Expansion of ice
(c) The expansion of the gas in the refrigerator
(d) The work of the compressor

15. Point out the wrong statement in relation to enthalpy
(a) It is a state function
(b) It is an intensive property
(c) It is independent of the path followed for the change
(d) Its value depends upon the amount of substance in the system

16. Which of the following is zero for an isochoric process
(a) dP (b) dV
(c) dT (d) dE

17. Mark the *correct* statement **[MP PET 1997]**
(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

18. In an isochoric process the increase in internal energy is **[MP PMT 1997]**
(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 absorbed and work done

19. It is general principle that the less energy a system contains, it is **[MH CET 1999]**
(a) Less stable (b) More stable
(c) Unstable (d) More unstable

20. Internal energy is an example of **[Pb. PMT 2000]**
(a) Path function (b) State function
(c) Both (a) and (b) (d) None of these

21. The process, in which no heat enters or leaves the system, is termed as **[Pb. PMT 1999; Kerala (Med.) 2002; J & K 2005]**
(a) Isochoric (b) Isobaric
(c) Isothermal (d) Adiabatic

22. The intensive property among these quantities is **[KCET 2002]**
(a) Enthalpy (b) Mass/volume
(c) Mass (d) Volume

23. In thermodynamics which one of the following is not an intensive property **[Kerala (Med.) 2002]**
(a) Pressure (b) Density
(c) Volume (d) Temperature

24. If in a container neither mass and nor heat exchange occurs then it constitutes a **[MP PMT 1993; AFMC 2003]**
(a) Closed system (b) Open system
(c) Isolated system (d) Imaginary system

25. Which of the following is not a state function **[DCE 2002]**
(a) ΔS (b) ΔG
(c) ΔH (d) ΔQ

26. Which of the following is true for an adiabatic process **[DCE 2002; MP PET 1995, 98, 2004; CPMT 1990; MP PMT 1998, 2002]**
(a) $\Delta H = 0$ (b) $\Delta W = 0$
(c) $\Delta Q = 0$ (d) $\Delta V = 0$

27. Which of the following is not a state function **[MH CET 2004; AIIMS 2001]**
(a) Internal energy (b) Enthalpy
(c) Work (d) Entropy

28. Among them intensive property is **[AFMC 2004]**
(a) Mass (b) Volume
(c) Surface tension (d) Enthalpy

First law of thermodynamics and Hess law

1. The first law of thermodynamics is only
(a) The law of conservation of energy
(b) The law of conservation of mass
(c) The law of conservation of momentum
(d) Both (a) and (b)

2. A mixture of two moles of carbon monoxide and one mole of oxygen, in a closed vessel is ignited to convert the carbon monoxide to carbon dioxide. If ΔH is the enthalpy change and ΔE is the change in internal energy, then **[KCET 2005]**
(a) $\Delta H > \Delta E$
(b) $\Delta H < \Delta E$
(c) $\Delta H = \Delta E$
(d) The relationship depends on the capacity of the vessel

3. Which of the following is always negative for exothermic reaction? **[BCECE 2005]**
(a) ΔH (b) ΔS
(c) ΔG (d) None of these

4. The relation between ΔE and ΔH is

[MP PET 1992; MP PMT 1996; MP PET/PMT 1998]

(a) $\Delta H = \Delta E - P\,\Delta V$ (b) $\Delta H = \Delta E + P\,\Delta V$

(c) $\Delta E = \Delta V + \Delta H$ (d) $\Delta E = \Delta H + P\,\Delta V$

5. At constant T and P, which one of the following statements is correct for the reaction, $CO(g) + \frac{1}{2}O_2(g) \rightarrow CO_2(g)$

[AIIMS 1982, 83; KCET 1988; BHU 1995; MP PET 1997, 99]

(a) ΔH is independent of the physical state of the reactants of that compound

(b) $\Delta H > \Delta E$

(c) $\Delta H < \Delta E$

(d) $\Delta H = \Delta E$

6. For the reaction of one mole of zinc dust with one mole of sulphuric acid in a bomb calorimeter, ΔU and w correspond to **[AIIMS 2005]**

(a) $\Delta U < 0, w = 0$ (b) $\Delta U = 0, w < 0$

(c) $\Delta U > 0, w = 0$ (d) $\Delta U < 0, w > 0$

7. Which is not the correct relation between enthalpy (ΔH) and intrinsic energy (ΔE) **[EAMCET 1992]**

(a) $\Delta H = \Delta E + P\,\Delta V$ (b) $\Delta H = \Delta E + nRT$

(c) $\Delta H = \Delta E - P\,\Delta V$ (d) $\Delta E = \Delta H - P\,\Delta V$

8. The law of Lavoisier and Laplace illustrates

[KCET 1989]

(a) The principle of conservation of energy

(b) Equivalence of mechanical and thermal energy

(c) The principle of conservation of matter

(d) Equivalence of mechanical and chemical energy

9. For the reaction $N_2 + 3H_2 \rightleftharpoons 2NH_3; \Delta H =$

[Roorkee 2000; CBSE PMT 1991, 2002]

(a) $\Delta E - RT$ (b) $\Delta E - 2RT$

(c) $\Delta E + RT$ (d) $\Delta E + 2RT$

10. If ΔH is the change in enthalpy and ΔE the change in internal energy accompanying a gaseous reaction

[KCET 1989; CBSE PMT 1990]

(a) ΔH is always greater than ΔE

(b) $\Delta H < \Delta E$ only if the number of moles of the products is greater than the number of the reactants

(c) ΔH is always less than ΔE

(d) $\Delta H < \Delta E$ only if the number of moles of the products is less than the number of moles of the reactants

11. "The resultant heat change in a reaction is the same whether it takes place in one or several stages." This statement is called **[MP PMT/PET 1988; MP PMT 1989]**

(a) Lavoisier and Laplace law

(b) Hess's law

(c) Joule's law

(d) Le–chatelier's principle

12. Hess's law of constant heat summation in based on

[MP PET 2001]

(a) $E = mc^2$

(b) Conservation of mass

(c) First law of thermodynamics

(d) None of the above

13. Consider the reaction : $N_2 + 3H_2 \rightarrow 2NH_3$ carried out at constant temperature and pressure. If ΔH and ΔU are the enthalpy and internal energy changes for the reaction, which of the following expression is true **[AIEEE 2005]**

(a) $\Delta H = 0$ (b) $\Delta H = \Delta U$

(c) $\Delta H < \Delta U$ (d) $\Delta H > \Delta U$

14. Which of the following is the correct equation

[CBSE PMT 1996]

(a) $\Delta U = \Delta Q - W$ (b) $\Delta W = \Delta U + \Delta Q$

(c) $\Delta U = \Delta W + \Delta Q$ (d) None of these

15. Hess law is applicable for the determination of heat of

[AIIMS 1998; Pb. PET/PMT 1999]

(a) Reaction (b) Formation

(c) Transition (d) All of these

16. Enthalpy for the reaction $C + O_2 \rightarrow CO_2$ is

[DPMT 1987, 91]

(a) Positive (b) Negative

(c) Zero (d) None

17. During an isothermal expansion of an ideal gas its

[CBSE PMT 1991]

(a) Internal energy increases

(b) Enthalpy decreases

(c) Enthalpy remains unaffected

(d) Enthalpy reduces to zero

18. The work done in ergs for the reversible expansion of one mole of an ideal gas from a volume of 10 litres to 20 litres at 25^oC is **[CMC Vellore 1991]**

(a) $2.303 \times 298 \times 0.082 \log 2$

(b) $298 \times 10^7 \times 8.31 \times 2.303 \log 2$

(c) $2.303 \times 298 \times 0.082 \log 0.5$

(d) $8.31 \times 10^7 \times 298 - 2.303 \log 0.5$

(e) $2.303 \times 298 \times 2 \log 2$

19. The law of conservation of energy states that

[NCERT 1984]

(a) The internal energy of a system is constant

(b) The heat content of a system is constant

(c) Energy is neither created nor destroyed

(d) There is an equivalence between energy and mass

20. The enthalpies of the elements in their standard states are assumed to be

(a) Zero at 298 K
(b) Unit at 298 K
(c) Zero at all temperatures
(d) Zero at 273 K

21. The heat Q for a reaction at constant volume is equal to

(a) $H_P - H_R$ (b) $H_R - H_P$
(c) $E_P - E_R$ (d) None of these

22. Which of the following expressions represents the first law of thermodynamics

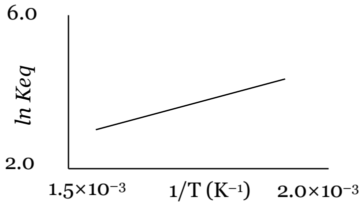
[MP PET 1996, 2000; AFMC 1997; BHU 1999; AMU 2000; KCET (Med.) 2000, 01; CBSE PMT 2000; MP PMT 2002]

(a) $\Delta E = -q + W$ (b) $\Delta E = q - W$
(c) $\Delta E = q + W$ (d) $\Delta E = -q - W$

23. In a reversible isothermal process, the change in internal energy is

(a) Zero (b) Positive
(c) Negative (d) None of these

24. A schematic plot of lnK_{eq} versus inverse of temperature for a reaction is shown below



The reaction must be **[AIEEE 2005]**

(a) Exothermic
(b) Endothermic
(c) One with negligible enthalpy change
(d) Highly spontaneous at ordinary temperature

25. Hess law of heat summation includes **[AFMC 1992]**

(a) Initial reactants only
(b) Initial reactants and final products
(c) Final products only
(d) Intermediates only

26. An ideal gas at constant temperature and pressure expands, then its **[BHU 1998]**

(a) Internal energy remains same
(b) Internal energy decreases
(c) Internal energy increases
(d) Entropy first increases and then decreases

27. The internal energy of a substance

[KCET 1998; AFMC 2001; AIIMS 2001]

(a) Increases with increase in temperature
(b) Decreases with increase in temperature
(c) Can be calculated by the relation $E = mc^2$
(d) Remains unaffected with change in temperature

28. The relation between change in internal energy (ΔE), change in enthalpy (ΔH) and work done (W) is represented as **[AFMC 1999]**

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

29. The enthalpy of neutralization of which of the following acids and bases is nearly $-13.6\,Kcal$ **[Roorkee 1999]**

(a) HCN and $NaOH$ (b) HCl and KOH
(c) HCl and $NaOH$ (d) HCl and NH_4OH

30. Work done during isothermal expansion of one mole of an ideal gas from 10 *atm* to 1 *atm* at 300 *K* is (Gas constant = 2) **[AIIMS 2000]**

(a) 938.8 *cal.* (b) 1138.8 *cal.*
(c) 1381.8 *cal.* (d) 1581.8 *cal.*

31. Joule-Thomson expansion is **[JIPMER 2000]**

(a) Isobaric (b) Isoenthalpic
(c) Isothermal (d) None of these

32. In which of the following $\Delta E = \Delta H$ **[MP PMT 2001]**

(a) $N_2O_4(g) \rightleftharpoons 2NO_2(g)$
(b) $2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$
(c) $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$
(d) $H_2(g) + \frac{1}{2}O_2(g) \rightleftharpoons H_2O(l)$

33. In an adiabatic expansion of an ideal gas

[KCET (Med.) 2001; MH CET 2000]

(a) $W = -\Delta E$ (b) $W = \Delta E$
(c) $\Delta E = 0$ (d) $W = 0$

34. For the reaction

$CH_3COOH(l) + 2O_2(g) \rightleftharpoons 2CO_2(g) + 2H_2O(l)$ at 25^oC and 1 *atm.* pressure, $\Delta H = -874\,kJ$. Then the change in internal energy (ΔE) is .... **[Orissa JEE 2002]**

(a) – 874 *kJ* (b) – 871.53 *kJ*
(c) – 876.47 *kJ* (d) + 874 *kJ*

35. In a closed insulated container, a liquid is stirred with a paddle to increase its temperature. In this process, which of the following is true **[CBSE PMT 2002]**

(a) $\Delta E = W = Q = 0$ (b) $\Delta E \neq 0, Q = W = 0$
(c) $\Delta E = W \neq 0, Q = 0$ (d) $\Delta E = Q \neq 0, W = 0$

36. Hess law is based on **[MH CET 2002]**

(a) Law of conservation of mass
(b) Law of conservation of energy
(c) Enthalpy is a state function
(d) None of these

37. For the reaction,

$C_3H_8(g) + 5O_2(g) \rightarrow 3CO_2(g) + 4H_2O(l)$

at constant temperature, $\Delta H - \Delta E$ is **[CBSE PMT 2003]**

(a) – *RT* (b) + *RT*
(c) – 3*RT* (d) + 3*RT*

38. According to Hess's law, the heat of reaction depends upon

[MP PMT 2003]

(a) Initial condition of reactants
(b) Initial and final conditions of reactants
(c) Intermediate path of the reaction
(d) End conditions of reactants

39. The value of $\Delta H - \Delta E$ for the following reaction at $27^o C$ will be $2NH_3(g) \rightarrow N_2(g) + 3H_2(g)$ **[Kerala (Med.) 2002]**

(a) $8.314 \times 273 \times (-2)$ (b) $8.314 \times 300 \times (-2)$
(c) $8.314 \times 27 \times (-2)$ (d) $8.314 \times 300 \times (2)$

40. For which of the following $\Delta E = \Delta H$ **[MP PET 2003]**

(a) $N_2O_4(g) \rightleftharpoons 2NO_2(g)$
(b) $2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$
(c) $H_2(g) + Cl_2(g) \rightleftharpoons 2HCl(g)$
(d) $H_2(g) + \frac{1}{2}O_2(g) \rightleftharpoons H_2O(l)$

41. One mole of an ideal gas is allowed to expand freely and adiabatically into vacuum until its volume has doubled. A statement which is not true concerning this expression is **[Pb. PMT 1998]**

(a) $\Delta H = 0$ (b) $\Delta S = 0$
(c) $\Delta E = 0$ (d) $W = 0$

42. At $27^o C,$ one mole of an ideal gas is compressed isothermally and reversibly from a pressure of 2 *atm* to 10 *atm*. The values of ΔE and q are $(R = 2)$ **[BHU 2001]**

(a) 0, – 965.84 *cal*
(b) – 965.84 *cal*, + 965.84 *cal*
(c) + 865.58 *cal*, – 865.58 *cal*
(d) – 865.58 *cal*, – 865.58 *cal*

43. The work done by a system is 8 *joule*, when 40 *joule* heat is supplied to it. What is the increase in internal energy of system **[BHU 2001]**

(a) 25 J (b) 30 J
(c) 32 J (d) 28 J

44. A system absorb 600J of heat and work equivalent to 300J on its surroundings. The change in internal energy is **[Pb. PMT 2004]**

(a) 300 J (b) 400 J
(c) 500 J (d) 600 J

45. Work done during isothermal expansion of one mole of an ideal gas from 10 atom. to 1 atm at 300K is **[BHU 2004]**

(a) 4938.8 J (b) 4138.8 J
(c) 5744.1 J (d) 6257.2 J

46. If gas, at constant temperature and pressure expands then its **[MH CET 2003]**

(a) Entropy increases and then decreases
(b) Internal energy increases
(c) Internal energy remains the same
(d) Internal energy decreases

47. For the reaction
$PCl_5(g) \rightarrow PCl_3(g) + Cl_2(g)$ **[MH CET 2004]**

(a) $\Delta H = \Delta E$ (b) $\Delta H > \Delta E$
(c) $\Delta H < \Delta E$ (d) None of these

48. Enthalpy (H) is equal to **[MH CET 2004]**

(a) Internal energy (E)
(b) Product of pressure (P) and volume (V) of gas
(c) Internal energy (E)+PV
(d) Work (W) done by a system

49. ΔE^o of combustion of isobutylene is $-X\, kJ\, mol^{-1}$. The value of ΔH^o is **[DCE 2004]**

(a) $= \Delta E^o$ (b) $> \Delta E^o$
(c) $= 0$ (d) $< \Delta E^o$

50. One mole of an ideal gas is allowed to expand reversibly and adibatically from a temperature of $27^o C$. If the work done during the process is $3\, kJ$, then final temperature of the gas is $(C_V = 20\, J/K)$ **[Pb. CET 2002]**

(a) 100 K (b) 150 K
(c) 195 K (d) 255 K

51. Which of the following is correct regarding the internal energy of a substance **[Pb. CET 2002]**

(a) It is a state function
(b) It increases with increase in temperature
(c) It can be calculated by experiment
(d) It remains unaffected with change in temperature

52. For the gaseous reaction,
$N_2O_4 \rightarrow 2NO_2$ **[Pb. CET 2003]**

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

53. $2C + O_2 \rightarrow 2CO; \Delta H = -220\, kJ$

Which of the following statement is correct for this reaction **[BVP 2004]**

(a) Heat of combustion of carbon is 110 *kJ*
(b) Reaction is exothermic
(c) Reaction needs no initiation
(d) All of these are correct

54. An ideal gas expands in volume from $1 \times 10^{-3} m^3$ to $1 \times 10^{-2} m^3$ at 300 K against a constant pressure of $1 \times 10^5\, Nm^{-2}$. The work done is **[AIEEE 2004]**

(a) 270 *kJ* (b) –900 *kJ*
(c) –900 J (d) 900 *kJ*

55. Internal energy is **[AFMC 2004]**

(a) Partly potential and partly kinetic
(b) Totally kinetic
(c) Totally potential
(d) None of these

56. For which of the reaction $\Delta H = \Delta E$ **[MP PET 2004]**

(a) $N_2 + 3H_2 \rightleftharpoons 2NH_3$ (b) $N_2 + O_2 \rightarrow 2NO$

(c) $2Na + Cl_2 \rightarrow 2NaCl$ (d) $PCl_5 \rightarrow PCl_3 + Cl_2$

57. The work done during the expansion of a gas from a volume of $4dm^3$ to $6dm^3$ against a constant external pressure of $3atm$ is ($1 L\, atm = 101.32\ J$) **[CBSE PMT 2004]**

(a) $+304\,J$ (b) $-304\,J$

(c) $-6\,J$ (d) $-608\,J$

58. For the reaction, $A_{(s)} + 2B_{(g)} \rightarrow 4C_{(s)} + D_{(l)}$. ΔH and ΔU are related as .... **[Orissa JEE 2004]**

(a) $\Delta H = \Delta U$ (b) $\Delta H = \Delta U + 3RT$

(c) $\Delta H = \Delta U + RT$ (d) $\Delta H = \Delta U - 3RT$

II^nd^ & III^rd^ Law of thermodynamics and Entropy

1. For a reversible spontaneous change ΔS is

(a) $\frac{\Delta E}{T}$ (b) $\frac{P\,\Delta V}{T}$

(c) $\frac{q}{T}$ (d) $RT \log K$

2. When disorder of a system increases, the change is said to be

(a) Exothermic (b) Non-spontaneous

(c) Endothermic (d) Spontaneous

3. The spontaneous flow of heat is always

(a) From low to high pressure

(b) From high to high pressure

(c) Unidirectional from lower temperature to higher temperature

(d) Unidirectional from the higher to lower temperature

4. Mixing of non-reacting gases is generally accompanied by

(a) Decrease in entropy

(b) Increase in entropy

(c) Change in enthalpy

(d) Change in free energy

5. An irreversible process occuring isothermally in an isolated system leads to

(a) Zero entropy

(b) An increase in the total entropy of the system

(c) A decrease in the total entropy of the system

(d) None of these

6. The entropy values (in $JK^{-1}\,mol^{-1}$) of $H_{2(g)}$ = 130.6, $Cl_{2(g)}$ = 223.0 and $HCl_{(g)}$ = 186.7 at 298 K and 1 atm pressure. Then entropy change for the reaction

$H_{2(g)} + Cl_{2(g)} \rightarrow 2HCl_{(g)}$ is **[BHU 2005]**

(a) + 540.3 (b) + 727.3

(c) – 166.9 (d) + 19.8

7. Which of the following is the least random state of water

(a) Ice

(b) Liquid water

(c) Steam

(d) All present same random state

8. Which one of the following process is non-spontaneous

(a) Dissolution of $CuSO_4$ in water

(b) Reaction between H_2 and O_2 to form water

(c) Water flowing down hill

(d) Flow of electric current from low potential to high potential

9. Which of the following is zero during adiabatic expansion of the gas

(a) ΔT (b) ΔS

(c) ΔE (d) None of these

10. The entropy of crystalline substances at absolute zero going by the third law of thermodynamics should be taken as

[J & K 2005]

(a) 100

(b) 50

(c) Zero

(d) Different for different substances

11. In which state, the matter have highest entropy

(a) Solid (b) Liquid

(c) Gas (d) Equal in all

12. Which of the following pairs of a chemical reaction is certain to result in spontaneous reaction ? **[CBSE PMT 2005]**

(a) Exothermic and decreasing disorder

(b) Endothermic and increasing disorder

(c) Exothermic and increasing disorder

(d) Endothermic and decreasing disorder

13. 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 litre to 2 litre. The final temperature in Kelvin would be **[IIT 2005]**

(a) $\frac{T}{2^{(2/3)}}$ (b) $T + \frac{2}{3 \times 0.0821}$

(c) T (d) $T - \frac{2}{3 \times 0.0821}$

14. 9.0 gm of H_2O is vaporised at $100\,^oC$ and 1 atm pressure. If the latent heat of vaporisation of water is $x\,J/gm$, then ΔS is given by

(a) $\frac{x}{373}$ (b) $\frac{18\,x}{100}$

(c) $\frac{18\,x}{373}$ (d) $\frac{1}{2} \times \frac{18\,x}{373}$

15. The ΔS for the vaporisation of 1 mol of water is 88.3 $J/mole\ K$. The value of ΔS for the condensation of 1 mol of vapour will be

(a) $88.3\,J/mol\,K$ (b) $(88.3)^2\ J/mol\,K$

(c) $-88.3\,J/mol\,K$ (d) $\frac{1}{88.3}\ J/mol\,K$

16. For which reaction from the following, ΔS will be maximum

[AIIMS 1982, 83, 94; AMU 2000]

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

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

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

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

17. The occurrence of a reaction is impossible if **[AIIMS 1982, 91; MP PET 1997; MP PMT 1999; DPMT 2002]**

(a) ΔH is +ve ; ΔS is also + ve but $\Delta H < T\Delta S$

(b) ΔH is – ve ; ΔS is also – ve but $\Delta H > T\Delta S$

(c) ΔH is – ve ; ΔS is + ve

(d) ΔH is + ve ; ΔS is – ve

18. If the enthalpy of vaporization for water is 186.5 $kJ\ mol^{-1}$, the entropy of its vaporization will be **[CPMT 1988; DCE 2000]**

(a) $0.5\ JK^{-1}mol^{-1}$
(b) $1.0\ JK^{-1}mol^{-1}$
(c) $1.5\ JK^{-1}mol^{-1}$
(d) $2.0\ JK^{-1}mol^{-1}$

19. Which of the following statement is true. The entropy of the universe **[MP PMT 1993; CET Pune 1998]**

(a) Increases and tends towards maximum value
(b) Decreases and tends to be zero
(c) Remains constant
(d) Decreases and increases with a periodic rate

20. When enthalpy and entropy change for a chemical reaction are $-2.5 \times 10^3\ cal$ and $7.4\ cal\ \deg^{-1}$ respectively. Predict the reaction at $298\ K$ is **[AFMC 1998; MH CET 1999; CBSE PMT 2000]**

(a) Spontaneous
(b) Reversible
(c) Irreversible
(d) Non-spontaneous

21. The total entropy change for a system and its surroundings increases, if the process is

(a) Reversible
(b) Irreversible
(c) Exothermic
(d) Endothermic

22. For chemical reactions, the calculation of change in entropy is normally done

(a) At constant pressure
(b) At constant temperature
(c) At constant temperature and pressure both
(d) At constant volume

23. When the value of entropy is greater, then the ability of work

(a) Is maximum
(b) Is minimum
(c) Is medium
(d) None of these

24. Which of the following is true for the reaction $H_2O(l) \rightleftharpoons H_2O(g)$ at 100^oC and 1 atmosphere **[KCET 1991; AIIMS 1996]**

(a) $\Delta E = 0$
(b) $\Delta H = 0$
(c) $\Delta H = \Delta E$
(d) $\Delta H = T\Delta S$

25. The enthalpy change for the transition of liquid water to steam, $\Delta H_{vap} = 37.3\, kJ\, mol^{-1}$ at $373\ K$. The entropy change for the process is **[MP PET 1994]**

(a) $111.9\ J\,mol^{-1}K^{-1}$
(b) $37.3\ J\,mol^{-1}K^{-1}$
(c) $100\ J\,mol^{-1}K^{-1}$
(d) $74.6\ J\,mol^{-1}K^{-1}$

26. When a solid is converted into liquid, entropy **[MP PET 1993, 95; MP PMT 1996]**

(a) Becomes zero
(b) Remains the same
(c) Decreases
(d) Increases

27. In a spontaneous process, the entropy of the system and its surroundings **[MP PET 1996; NCERT 1975]**

(a) Equals zero
(b) Decreases
(c) Increases
(d) Remains constant

28. The positive value of ΔS indicates that **[MP PMT 1997]**

(a) The system becomes less disordered
(b) The system becomes more disordered
(c) The system is in equilibrium position
(d) The system tends to reach at equilibrium position

29. For reaction $2Cl(s) \rightarrow Cl_2(s)$, the signs of ΔH and ΔS respectively are **[KCET 1996]**

(a) +, –
(b) +, +
(c) –, –
(d) –, +

30. The enthalpy of water is $386\ kJ$. What is entropy of water **[BHU 1997]**

(a) 0.5 kJ
(b) 1.03 kJ
(c) 1.5 kJ
(d) 22.05 kJ

31. For which of the processes is ΔS negative **[Pb. PMT 1998]**

(a) $H_2(g) \rightarrow 2H(g)$
(b) $N_2(g) 1 atm \rightarrow N_2(g) 8\ atm$
(c) $2SO_3(g) \rightarrow 2SO_2(g) + O_2(g)$
(d) $C_{(diamond)} \rightarrow C_{(graphite)}$

32. Identify the correct statement regarding entropy **[CBSE PMT 1998; BHU 2001]**

(a) At 0^oC, the entropy of a perfectly crystalline substance is taken to be zero
(b) At absolute zero of temperature, the entropy of a perfectly crystalline substance is *+ve*
(c) At absolute zero of temperature, the entropy of all crystalline substances is taken to be zero
(d) At absolute zero of temperature, the entropy of a perfectly crystalline substance is taken to be zero

33. One mole of an ideal gas at $300\,K$ is expanded isothermally from an initial volume of 1 litre to 10 litres. The change in energy for this process is $(R = 2\ cal\,mol^{-1}K^{-1})$ **[CBSE PMT 1998]**

(a) 163.7 *cal*
(b) 850.2 *cal*
(c) 1381.1 *cal*
(d) Zero

34. If $900\ J/g$ of heat is exchanged at boiling point of water, then what is increase in entropy **[BHU 1998]**

(a) 43.4 *J/mole*
(b) 87.2 *J/mole*
(c) 900 *J/mole*
(d) Zero

35. A container has hydrogen and oxygen mixture in ratio of 4 : 1 by weight, then **[BHU 1998]**

(a) Internal energy of the mixture decreases
(b) Internal energy of the mixture increases
(c) Entropy of the mixture increases
(d) Entropy of the mixture decreases

36. If 0.75 *mole* of an ideal gas expands isothermally at 27^oC from 15 *litres* to 25 *litres,* the maximum work obtained is **[AFMC 1999]**

(a) 8.40 J
(b) 9.34 J
(c) 10.86 J
(d) 10.43 J

37. In which of the following conditions a chemical reaction can not occur **[AMU 1999]**

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

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

(c) ΔH increases and ΔS decreases

(d) ΔH decreases and ΔS increases

38. An engine operating between $150^o C$ and $25^o C$ takes 500 J heat from a higher temperature reservoir if there are no frictional losses, then work done by engine is **[MH CET 1999]**

(a) 147.7 J (b) 157.75 J

(c) 165.85 J (d) 169.95 J

39. The entropy of a perfectly crystalline solid at absolute zero is **[AMU 2000]**

(a) Positive (b) Negative

(c) Zero (d) Not definite

40. Which of the following conditions will always lead to a non-spontaneous change **[AMU 2000; KCET (Med.) 2000]**

(a) Positive ΔH and positive ΔS

(b) Negative ΔH and negative ΔS

(c) Positive ΔH and negative ΔS

(d) Negative ΔH and positive ΔS

41. Following data is known about melting of a compound AB. $\Delta H = 9.2\, kJ\, mol^{-1}$, $\Delta S = 0.008\ kJ\, K^{-1} mol^{-1}$. Its melting point is **[Pb. PMT 2000; AIIMS 2000]**

(a) 736 K (b) 1050 K

(c) 1150 K (d) $1150\ ^o C$

42. The volume of a gas decreases from $500\, cc$ to $300\, cc$ when a sample of gas is compressed by an average pressure of 0.6 *atm*. During this process 10 J of heat is liberated. The change in internal energy is **[Pb. PMT 2000]**

(a) – 2.16 J (b) 12.156 J

(c) 2.16 J (d) 101.3 J

43. The standard entropies of $CO_2(g), C(s)$ and $O_2(g)$ are 213.5, 5.690 and $205\ JK^{-1}$ respectively. The standard entropy of formation of $CO_2(g)$ is **[CPMT 2001]**

(a) $1.86\ JK^{-1}$ (b) $1.96\ JK^{-1}$

(c) $2.81\ JK^{-1}$ (d) $2.86\ JK^{-1}$

44. Which of the following endothermic processes are spontaneous **[CBSE PMT 2001]**

(a) Melting of ice (b) Evaporation of water

(c) Heat of combustion (d) Both (a) and (b)

45. For the reaction $H_2O(s) \rightleftharpoons H_2O(l)$ at $0^o C$ and normal pressure **[KCET 2001]**

(a) $\Delta H > T\Delta S$ (b) $\Delta H = T\Delta S$

(c) $\Delta H = \Delta G$ (d) $\Delta H < T\Delta S$

46. One mole of an ideal gas is allowed to expand reversibly and adiabatically from a temperature of $27^o C$. If the work done during the process is 3 *kJ*, the final temperature will be equal to $(C_v = 20\ JK^{-1})$

[KCET 2000; AFMC 2000; AIIMS 2001]

(a) 150 K (b) 100 K

(c) $26.85\, ^o C$ (d) 295 K

47. The entropy change, in the conversion of one mole of liquid water at 373 K to vapour at the same temperature is (Latent heat of vaporization of water, $\Delta H_{vap} = 2.257\ kJ / g$)

[AFMC 2002; KCET 2002]

(a) $105.9\ Jk^{-1}$ (b) $107.9\ Jk^{-1}$

(c) $108.9\ Jk^{-1}$ (d) $109.9\ Jk^{-1}$

48. 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 **[AIEEE 2002]**

(a) Violates Ist law of thermodynamics

(b) Violates Ist law of thermodynamics if Q_1 is $-ve$

(c) Violates Ist law of thermodynamics if Q_2 is $-ve$

(d) Does not violate Ist law of thermodynamics

49. 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

[AFMC 2002]

(a) 1 (b) 2

(c) 1.67 (d) 1.5

50. The law formulated by Dr. Nernst is **[Kerala (Med.) 2002]**

(a) First law of thermodynamics

(b) Second law of thermodynamics

(c) Third law of thermodynamics

(d) Both (a) and (b)

51. The unit of entropy is **[CBSE PMT 2002]**

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

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

52. The entropy changed involved in the conversion of 1 *mole* of liquid water at 373 K to vapour at the same temperature will be

$[\Delta H_{\text{vap}} = 2.257\, kJ / gm]$ **[MP PET 2002]**

(a) 0.119 *kJ* (b) 0.109 *kJ*

(c) 0.129 *kJ* (d) 0.120 *kJ*

53. When a liquid boils, there is **[JIPMER 2002]**

(a) An increase in entropy

(b) A decrease in entropy

(c) An increase in heat of vaporization

(d) An increase in free energy

54. Which one of the following has ΔS^o greater than zero

[AIIMS 2003]

(a) $CaO + CO_2(g) \rightleftharpoons CaCO_3(s)$

(b) $NaCl\,(aq) \rightleftharpoons NaCl(s)$

(c) $NaNO_3(s) \rightleftharpoons Na^+(aq) + NO_3^-(aq)$

(d) $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$

55. 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 **[CBSE PMT 2003]**

(a) 6.6 K (b) 1.2 K

(c) 2.4 K (d) 4.8 K

56. The work done to contract a gas in a cylinder, is 462 *joules*. 128 *joule* energy is evolved in the process. What will be the internal energy change in the process **[MP PMT 2003]**

(a) + 590 *joules* (b) – 334 *joules*

(c) + 334 *joules* (d) – 590 *joules*

57. Highest entropy is in **[BVP 2003]**

(a) Hydrogen (b) Water

(c) Graphite (d) Mercury

58. $\underset{S^o(298\,K)K^{-1}mol^{-1}}{H^+(aq)} + \underset{-10.7}{OH^-(aq)} \longrightarrow \underset{+70}{H_2O(l)}$

Standard entropy change for the above reaction is **[DPMT 2004]**

(a) $60.3\ JK^{-1}mol^{-1}$ (b) $80.7\ JK^{-1}mol^{-1}$

(c) $-70\ JK^{-1}mol^{-1}$ (d) $+10.7\ JK^{-1}mol^{-1}$

59. One mole of water at 100^oC is converted into steam at 100^oC at a constant pressure of 1 atm. The change in entropy is [heat of vaporisation of water at $100^oC = 540\ cal/gm$] **[Pb. PMT 2004]**

(a) 8.74 (b) 18.76

(c) 24.06 (d) 26.06

60. For a carnot engine, the source is at $500\,K$ and the sink at $300\,K$. What is efficiency of this engine **[BHU 2004]**

(a) 0.2 (b) 0.4

(c) 0.6 (d) 0.3

61. Heat require to raise the temperature of 1 mol of a substance by 1^oC is called **[DCE 2002]**

(a) Specific heat (b) Molar heat capacity

(c) Water equivalent (d) Specific gravity

62. Maximum entropy will be in which of the following **[DCE 2004]**

(a) Ice (b) Liquid water

(c) Snow (d) Water vapours

63. The standard entropies of $CO_2(g), C(s)$ and $O_2(g)$ are 213.5, 5.740 and 205 JK^{-1} respectively. The standard entropy of formation of CO_2 is **[Pb. CET 2001]**

(a) $2.76\ JK^{-1}$ (b) $2.12\ JK^{-1}$

(c) $1.12\ JK^{-1}$ (d) $1.40\ JK^{-1}$

64. Which law of thermodyanamics help in calculating entropy at different temperatures **[Pb. CET 2003]**

(a) First law (b) Second law

(c) Third law (d) Zeroth law

65. Entropy is maximum in case of **[BVP 2004]**

(a) Steam (b) Water at 0^oC

(c) Water at 4^oC (d) Ice

66. Considering entropy (S) as a thermodynamic parameter, the criterion for the spontaneity of any process is **[CBSE PMT 2004]**

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

(b) $\Delta S_{surroundin\,gs} > 0$ only

(c) $\Delta S_{system} + \Delta S_{surroundin\,gs} > 0$

(d) $\Delta S_{system} - \Delta S_{surroundin\,gs} > 0$

67. A process is taking place at constant temperature and pressure. Then **[KCET 2004]**

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

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

68. The enthalpy of vapourization of a liquid is $30\ kJ\ mol^{-1}$ and entropy of vapourization is $75\ J\ mol^{-1}K$. The boiling point of the liquid at 1 *atm* is **[IIT JEE (Screening) 2004]**

(a) 250*K* (b) 400*K*

(c) 450*K* (d) 600*K*

Heat of reaction

1. If $C + O_2 \rightarrow CO_2 + 94.2\,kcal$

$H_2 + \frac{1}{2}O_2 \rightarrow H_2O + 68.3\,kcal$

$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O + 210.8\,kcal$

then the possible heat of methane will be **[MP PET 1990]**

(a) 47.3 *kcal* (b) 20.0 *kcal*

(c) 45.9 *kcal* (d) – 47.3 *kcal*

2. Molar heat of vaporisation of a liquid is $6\,kJ\ mol^{-1}$. If the entropy change is $16\,J\ mol^{-1}\ K^{-1}$, the boiling point of the liquid is **[KCET 2005]**

(a) 375^oC (b) $375\,K$

(c) $273\,K$ (d) 102^oC

3. The enthalpy of fusion of ice per mole

(a) 18 *kJ* (b) 8 *kJ*

(c) 80 *kJ* (d) 6 *kJ*

4. In which of the following neutralisation reactions, the heat of neutralisation will be highest **[MP PMT 1989, 91; AIIMS 1999]**

(a) NH_4OH and CH_3COOH

(b) NH_4OH and HCl

(c) $NaOH$ and CH_3COOH

(d) $NaOH$ and HCl

5. If $S + O_2 \rightarrow SO_2; (\Delta H = -298.2)$

$SO_2 + \frac{1}{2}O_2 \rightarrow SO_3; (\Delta H = -98.2)$

$SO_3 + H_2O \rightarrow H_2SO_4; (\Delta H = -130.2)$

$H_2 + \frac{1}{2}O_2 \rightarrow H_2O; (\Delta H = -287.3)$

then the enthalpy of formation of H_2SO_4 at 298K will be **[DPMT 1983; Orissa JEE 2005]**

(a) $-433.7\,kJ$ (b) $-650.3\,kJ$

(c) $+320.5\,kJ$ (d) $-813.9\,kJ$

6. From Kirchhoff's equation which factor affects the heat of reaction **[MP PMT 1990]**

(a) Pressure (b) Temperature

(c) Volume (d) Molecularity

7. The molar neutralization heat for KOH and HNO_3 as compared to molar neutralization heat of $NaOH$ and HCl **[MP PMT 1989]**

(a) Less (b) More

(c) Equal (d) Depends on pressure

8. An exothermic reaction is one in which the reacting substances **[CPMT 1974, 79; Bihar MEE 1982; KCET 1992; JIPMER 2001]**

(a) Have more energy than the products

(b) Have less energy than the products

(c) Are at a higher temperature than the product

(d) None of the above

9. The heat evolved in the combustion of benzene is given by

$$C_6H_6 + 7\frac{1}{2}O_2 \rightarrow 6CO_2(g) + 3H_2O(l); \Delta H = -3264.6\,kJ$$

Which of the following quantities of heat energy will be evolved when $39\,g\,C_6H_6$ are burnt

[NCERT 1978; MP PET 1990; JIPMER 2001]

(a) 816.15 kJ (b) 1632.3 kJ

(c) 6528.2 kJ (d) 2448.45 kJ

10. Thermochemical reactions

$$C(\text{graphite}) + \frac{1}{2}O_2(g) \rightarrow CO(g); \Delta H = -110.5\,kJ$$

$$CO(g) + \frac{1}{2}O_2(g) \rightarrow CO_2(g); \Delta H = -283.2\,kJ$$

From the above reaction, the heat of reaction for $C(\text{graphite}) + O_2(g) \rightarrow CO_2(g)$ will be

[CPMT 1988; MP PMT 1989]

(a) − 393.7 kJ (b) + 393.7 kJ

(c) − 172.7 kJ (d) + 172.7 kJ

11. The following is (are) endothermic reaction **[IIT JEE 1999]**

(a) Combustion of methane

(b) Decomposition of water

(c) Dehydrogenation of ethane to ethylene

(d) Conversion of graphite to diamond

12. Evaporation of water is

[CPMT 1973; DPMT 1982; MP PMT 1989; MP PET 1999]

(a) An endothermic change

(b) An exothermic change

(c) A process where no heat change occurs

(d) A process accompanied by chemical reaction

13. An exothermic reaction is one which

[NCERT 1977; MP PMT 1990]

(a) Takes place only on heating

(b) Is accompanied by a flame

(c) Is accompanied by a absorption of heat

(d) Is accompanied by evolution of heat

14. An endothermic reaction is one in which

[MNR 1980; NCERT 1976]

(a) Heat is converted into electricity

(b) Heat is absorbed

(c) Heat is evolved

(d) Heat is converted into mechanical work

15. Which of the following statement is correct

[NCERT 1978]

(a) ΔH is positive for exothermic reaction

(b) ΔH is negative for endothermic reaction

(c) The heat of neutralization of strong acid and strong base is always the same

(d) The enthalpy of fusion is negative

16. The absolute enthalphy of neutralisation of the reaction $MgO(s) + 2HCl(aq) \rightarrow MgCl_2(aq) + H_2O(l)$ will be

[CBSE PMT 2005]

(a) Less than $-57.33\,kJ\,mol^{-1}$

(b) $-57.33\,kJ\,mol^{-1}$

(c) Greater than $-57.33\,kJ\,mol^{-1}$

(d) $57.33\,kJ\,mol^{-1}$

17. $\Delta H°_f$ (298 K) of methanol is given by the chemical equation **[AIIMS 2005]**

(a) $CH_4(g) + 1/2O_2(g) \rightarrow CH_3OH(g)$

(b) C (graphite) $+1/2O_2(g) + 2H_2(g) \rightarrow CH_3OH(l)$

(c) C (diamond) $+1/2O_2(g) + 2H_2(g) \rightarrow CH_3OH(l)$

(d) $CO(g) + 2H_2(g) \rightarrow CH_3OH(l)$

18. If ΔH_f^o for H_2O_2 and H_2O are $-188\,kJ/mole$ and $-286\,kJ/mole$. What will be the enthalpy change of the reaction $2H_2O_2(l) \rightarrow 2H_2O(l) + O_2(g)$ **[MP PMT 1992]**

(a) $-196\,kJ/mole$ (b) $146\,kJ/mole$

(c) $-494\,kJ/mole$ (d) $-98\,kJ/mole$

19. The heat of transition (ΔH_t) of graphite into diamond would be, where

$C(\text{graphite}) + O_2(g) \rightarrow CO_2(g);\ \Delta H = x\,kJ$

$C(\text{diamond}) + C_2(g) \rightarrow CO_2(g);\ \Delta H = y\,kJ$ **[Pb. PET 1985]**

(a) $(x+y)kJ\,mol^{-1}$ (b) $(x-y)kJ\,mol^{-1}$

(c) $(y-x)kJ\,mol^{-1}$ (d) None of these

20. Correct relationship between heat of fusion (ΔH_{fus}), heat of vaporization (ΔH_{vap}) and heat of sublimation (ΔH_{sub}) is

(a) $\Delta H_{fus} = \Delta H_{vap} + \Delta H_{sub}$

(b) $\Delta H_{vap} = \Delta H_{fus} + \Delta H_{sub}$

(c) $\Delta H_{sub} = \Delta H_{vap} + \Delta H_{fus}$

(d) $\Delta H_{sub} = \Delta H_{vap} - \Delta H_{fus}$

21. Which of the following is an example of endothermic reaction **[MP PMT 1980]**

(a) $C_2H_2 + 2H_2 \rightarrow C_2H_6;\ \Delta E = -314.0\,kJ$

(b) $C + O_2 \rightarrow CO_2;\ \Delta E = -393.5\,kJ$

(c) $N_2 + O_2 \rightarrow 2NO;\ \Delta E - 180.5\,kJ$

(d) $2H_2 + O_2 \rightarrow 2H_2O;\ \Delta E + 571.8\,kJ$

22. If the enthalpy of B is greater than of A, the reaction $A \rightarrow B$ is **[MP PMT 1997]**

(a) Endothermic (b) Exothermic

(c) Instantaneous (d) Spontaneous

23. Given that

$$2C(s) + 2O_2(g) \rightarrow 2CO_2(g);\ \Delta H = -787\,kJ$$

$$H_2(g) + \frac{1}{2}O_2(g) \rightarrow H_2O(l);\ \Delta H = -286\,kJ$$

$$C_2H_2(g)+2\frac{1}{2}O_2(g)\rightarrow 2CO_2(g)+H_2O(l);\Delta H=-1301\,kJ$$

Heat of formation of acetylene is **[KCET 1989; Orissa JEE 2005]**

(a) $-1802\,kJ$ (b) $+1802\,kJ$

(c) $-800\,kJ$ (d) $+228\,kJ$

24. Enthalpy change for reaction, $\frac{1}{2}H_2+\frac{1}{2}Cl_2\rightarrow HCl$, is called

(a) Enthalpy of combination (b) Enthalpy of reaction

(c) Enthalpy of formation (d) Enthalpy of fusion

25. The enthalpy of neutralization is about 57.3 *kJ* for the pair

(a) HCl and NH_4OH

(b) NH_4OH and HNO_3

(c) HCl and $NaOH$

(d) CH_3COOH and $NaOH$

26. Conversion of oxygen to ozone represented by the equation $3O_2\rightarrow 2O_3$ is an endothermic reaction. Enthalpy change ΔH accompanying the reaction **[KCET 1988, 92]**

(a) Is negative (b) Is positive

(c) Is zero (d) Depends on temperature

27. The mutual heat of neutralisation of 40 *gm* of $NaOH$ and 60 *gm* CH_3COOH will be **[MP PET/PMT 1988]**

(a) 56.1 *kcal* (b) Less than 56.1 *kcal*

(c) More than 56.1 *kcal* (d) 13.7 *kcal*

28. The heat of formations of $CO(g)$ and $CO_2(g)$ are –26.4 *kcal* and –94.0 *kcal* respectively. The heat of combustion of carbon monoxide will be **[MP PET/PMT 1988; EAMCET 1993]**

(a) $+26.4\,kcal$ (b) $-67.6\,kcal$

(c) $-120.6\,kcal$ (d) $+52.8\,kcal$

29. The enthalpy of combustion at 25°*C* of H_2, cyclohexane (C_6H_{12}) and cyclohexene (C_6H_{10}) are –241, –3920 and –800 *KJ / mole* respectively. The heat of hydrogenation of cyclohexene is **[BHU 2005]**

(a) – 121 *KJ / mole* (b) + 121 *KJ / mole*

(c) – 242 *KJ / mole* (d) + 242 *KJ / mole*

30. Heat of neutralisation of NH_4OH and HCl is **[EAMCET 1980; Roorkee 1990; MP PMT 1994]**

(a) $13.7\,kcal$ (b) $>13.7\,kcal$

(c) $<13.7\,kcal$ (d) None of the above

31. Heat of combustion ΔH of CH_4, C_2H_6, C_2H_4 and C_2H_2 gases are – 212.8, – 373.0, – 337.0 and – 310.5 *kcal* respectively at the same temperature. The best fuel among these gases is

(a) CH_4 (b) C_2H_6

(c) C_2H_4 (d) C_2H_2

32. Heat of formation of $CO_2(g)$, $H_2O(l)$ and $CH_4(g)$ are – 94.0, – 68.4 and – 17.9 *kcal* respectively. The heat of combustion of methane is

(a) – 212.9 *kcal* (b) – 136.8 *kcal*

(c) – 304.3 *kcal* (d) – 105.2 *kcal*

33. The heat of reaction does not depend upon

(a) Temperature of the reaction

(b) Physical state of reactants and products

(c) Whether the reaction is carried out at constant pressure or at constant volume

(d) The method by which the final products are obtained from the reactants

34. Heat of neutralisation of a strong acid by a strong base is a constant value because **[KCET 1984]**

(a) Salt formed does not hydrolyse

(b) Only H^+ and OH^- ions react in every case

(c) The strong base and strong acid react completely

(d) The strong base and strong acid react in aqueous solution

35. Heat of neutralisation of an acid by a base is highest when **[KCET 1985]**

(a) Both the acid and base are weak

(b) Both the acid and base are strong

(c) The acid is strong and the base is weak

(d) The acid is weak and the base is strong

36. The standard molar heat of formation of ethane, CO_2 and water (*l*) are respectively – 21.1, – 94.1 and – 68.3 *kcal*. The standard molar heat of combustion of ethane will be **[IIT JEE 1986; DPMT 2005]**

(a) – 372 *kcal* (b) 162 *kcal*

(c) –240 *kcal* (d) 183.5 *kcal*

37. Which of the following reaction is endothermic **[AFMC 1988]**

(a) $CaCO_3\rightarrow CaO+CO_2$

(b) $Fe+S\rightarrow FeS$

(c) $NaOH+HCl\rightarrow NaCl+H_2O$

(d) $CH_4+2O_2\rightarrow CO_2+2H_2O$

38. In the reaction

$CO_2(g)+H_2(g)\rightarrow CO(g)+H_2O(g);\Delta H=80\,kJ$

ΔH is known as **[CPMT 1987; KCET 1993; Bihar CEE 1995]**

(a) Heat of formation (b) Heat of combustion

(c) Heat of neutralization (d) Heat of reaction

39. Heat of combustion of a substance **[CPMT 1987, 96; AFMC 1992]**

(a) Is always positive

(b) Is always negative

(c) Is equal to heat of formation

(d) Nothing can be said without reaction

40. The heat change for the reaction $H_2+\frac{1}{2}O_2\rightarrow H_2O$ is called

(a) Heat of reaction (b) Heat of formation

(c) Heat of vaporisation (d) None of the above

41. The heat change ΔH for the reaction

$2CO+O_2\rightarrow 2CO_2;\Delta H=-135\,kcal$ is called

(a) Heat of formation (b) Heat of reaction

(c) Heat of combustion (d) Heat of solution

42. The heats of combustion of rhombic and monoclinic sulphur are respectively 70960 and 71030 calories. What will be the heat of conversion of rhombic sulphur to monoclinic **[MP PMT/PET 1988]**

(a) 70960 calories (b) 71030 calories
(c) – 70 calories (d) + 70 calories

43. The heat of formation of $H_2O(l)$ is – 68.0 *kcal*, the heat of formation of $H_2O(g)$ is likely to be

(a) – 68.0 *kcal* (b) – 67.4 *kcal*
(c) 80.0 *kcal* (d) – 58.3 *kcal*

44. Which of the following fuels will have the highest calorific value (*kJ/kg*) **[MP PMT 1990]**

(a) Charcoal (b) Kerosene
(c) Wood (d) Dung

45. The heat of combustion of carbon is –94 *kcal* at 1 *atm* pressure. The intrinsic energy of CO_2 is

(a) $+94\,kcal$ (b) $-94\,kcal$
(c) $+47\,kcal$ (d) $-47\,kcal$

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 **[KCET 1991; AIIMS 2002; AMU (Engg.) 2002]**

(a) $57.0\,kJ$ (b) $11.4\,kJ$
(c) $28.5\,kJ$ (d) $34.9\,kJ$

47. A solution of $500\,ml$ of $0.2\,M\,KOH$ and $500\,ml$ of $0.2\,M\,HCl$ is mixed and stirred; the rise in temperature is T_1. The experiment is repeated using $250\,ml$ each of solution, the temperature raised is T_2. Which of the following is true **[EAMCET 1987; MP PET 1994]**

(a) $T_1 = T_2$ (b) $T_1 = 2T_2$
(c) $T_1 = 4T_2$ (d) $T_2 = 9T_1$

48. Enthalpy of a compound is equal to its **[CMC Vellore 1991]**

(a) Heat of combustion (b) Heat of formation
(c) Heat of reaction (d) Heat of solution
(e) Heat of dilution

49. Which is the best definition of "heat of neutralization" **[CMC Vellore 1991]**

(a) The heat set free when one gram molecule of a base is neutralized by one gram molecule of an acid in dilute solution at a stated temperature
(b) The heat absorbed when one gram molecule of an acid is neutralized by one gram molecule of a base in dilute solution at a stated temperature
(c) The heat set free or absorbed when one gram atom of an acid is neutralized by one gram atom of a base at a stated temperature
(d) The heat set free or absorbed when a normal solution containing one gram equivalent of an acid is neutralized by a normal solution containing one gram equivalent of a base at a stated temperature
(e) The heat set free when one gram equivalent of an acid is neutralized by one gram equivalent of a base in dilute solution at a stated temperature

50. The compound with negative heat of formation are known as **[DPMT 1981]**

(a) Endothermic compound
(b) Exothermic compound
(c) Heat of formation compound
(d) None of the above

51. If $H^+ + OH^- \rightarrow H_2O + 13.7\,kcal$, then the heat of neutralization for complete neutralization of one mole of H_2SO_4 by base will be **[MP PMT 1990]**

(a) 13.7 *kcal* (b) 27.4 *kcal*
(c) 6.85 *kcal* (d) 3.425 *kcal*

52. The lowest value of heat of neutralization is obtained for **[KCET 1988; MP PMT 1990]**

(a) $HCl + NaOH$
(b) $CH_3COOH + NH_4OH$
(c) $NH_4OH + HCl$
(d) $NaOH + CH_3COOH$

53. Heat of neutralisation for the given reaction $NaOH + HCl \rightarrow NaCl + H_2O$ is $57.1\,kJ\,mol^{-1}$. What will be the heat released when $0.25\,mole$ of $NaOH$ is titrated against $0.25\,mole$ of HCl **[CPMT 1990]**

(a) $22.5\,kJ\,mol^{-1}$ (b) $57.1\,kJ\,mol^{-1}$
(c) $14.3\,kJ\,mol^{-1}$ (d) $28.6\,kJ\,mol^{-1}$

54. Reaction, $H_2(g) + I_2(g) \rightarrow 2HI(g)$ $\Delta H = -12.40\,kcal$. According to this, the heat of formation of *HI* will be **[MP PET 1990]**

(a) 12.4 *kcal* (b) – 12.4 *kcal*
(c) – 6.20 *kcal* (d) 6.20 *kcal*

55. All reactions with chemical dissociation are **[MP PMT 1990]**

(a) Reversible
(b) Reversible and endothermic
(c) Exothermic
(d) Reversible or irriversible and endothermic or exothermic

56. The heat of formation is the change in enthalpy accompanying the formation of a substance from its elements at 298 *K* and 1 atm pressure. Since the enthalpies of elements are taken to be zero, the heat of formation (ΔH) of compounds **[NCERT 1978; KCET 1993]**

(a) Is always negative
(b) Is always positive
(c) May be negative or positive
(d) Is zero

57. The heat of combustion of $CH_{4(g)}, C_{(\text{graphite})}$ and $H_{2(g)}$ are $20\,kcal, -40\,kcal$ and $-10\,kcal$ respectively. The heat of formation of methane is **[EAMCET 1998]**

(a) $-4.0\,kcal$ (b) $+40\,kcal$
(c) $-80\,kcal$ (d) $+80\,kcal$

58. If a chemical reaction is accompanied by the evolution of heat, it is **[BHU 1979]**

(a) Catalytic (b) Photochemical
(c) Endothermic (d) Exothermic

59. A reaction that takes place with the absorption of energy is **[EAMCET 1977]**

(a) Burning of a candle (b) Rusting of iron

(c) Electrolysis of water (d) Digestion of food

60. Which of the following is an endothermic reaction **[EAMCET 1980; MP PMT 1980; IIT JEE 1989; JIPMER 2002]**

(a) $2H_2 + O_2 \rightarrow 2H_2O$

(b) $N_2 + O_2 \rightarrow 2NO$

(c) $2NaOH + H_2SO_4 \rightarrow Na_2SO_4 + 2H_2O$

(d) $3O_2 + C_2H_5OH \rightarrow 2CO_2 + 3H_2O$

61. One of the phenomena which cannot be described as combustion is **[EAMCET 1979]**

(a) Oxidation of coal in air

(b) Burning of magnesium in nitrogen

(c) Reaction of antimony in chlorine

(d) Lighting of an electric lamp

62. Which of the following statements is correct about heat of combustion **[MADT Bihar 1982]**

(a) It may be exothermic in some cases and endothermic in other cases

(b) It is applicable to gaseous substances only

(c) It is always an exothermic reaction

(d) Its value does not change with temperature

63. $H_2 + \frac{1}{2}O_2 \rightarrow H_2O; \Delta H = -68.39\, kcal$

$K + H_2O + \text{Water} \rightarrow KOH(aq) + \frac{1}{2}H_2; \Delta H = -48\, kcal$

$KOH + \text{Water} \rightarrow KOH(aq); \Delta H = -14\, kcal$

The heat of formation of KOH is (in $kcal$) **[CPMT 1988]**

(a) $-68.39 + 48 - 14$ (b) $-68.39 - 48 + 14$

(c) $68.39 - 48 + 14$ (d) $68.39 + 48 + 14$

64. Which of the following reaction can be used to define the heat of formation of $CO_2(g)$ **[MP PMT 1989; MH CET 2001]**

(a) $C(\text{graphite}) + O_2(g) = CO_2(g)$

(b) $CH_4(g) + 2O_2(g) = CO_2(g) + 2H_2O(l)$

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

(d) $C_6H_6(l) + 7\frac{1}{2}O_2(g) = 6CO_2 + 3H_2O(l)$

65. The enthalpy of formation of ammonia is $-46.0\, kJ\, mol^{-1}$. The enthalpy change for the reaction $2NH_3(g) \rightarrow 2N_2(g) + 3H_2(g)$ is

(a) $46.0\, kJ\ mol^{-1}$ (b) $92.0\, kJ\ mol^{-1}$

(c) $-23.0\, kJ\ mol^{-1}$ (d) $-92.0\, kJ\ mol^{-1}$

66. The heat of combustion of benzene determined in a bomb calorimeter is $-870\, kcal\, mol^{-1}$ at $25^o C$. The value of ΔE for the reaction is

(a) $-1740\, kcal$ (b) $-870\, kcal$

(c) $-872\, kcal$ (d) $-874\, kcal$

67. The formation of water from $H_2(g)$ and $O_2(g)$ is an exothermic reaction because **[MP PMT/PET 1988]**

(a) The chemical energy of $H_2(g)$ and $O_2(g)$ is more than that of water

(b) The chemical energy of $H_2(g)$ and $O_2(g)$ is less than that of water

(c) Not dependent on energy

(d) The temperature of $H_2(g)$ and $O_2(g)$ is more than that of water

68. In the reaction for the transition of carbon in the diamond form to carbon in the graphite form, ΔH is $-453.5\, cal$. This points out that **[BHU 1981; KCET 1986, 89]**

(a) Graphite is chemically different from diamond

(b) Graphite is as stable as diamond

(c) Graphite is more stable than diamond

(d) Diamond is more stable than graphite

69. In the combustion of hydrocarbons, ΔH is **[BHU 1981]**

(a) Negative (b) Zero

(c) Positive (d) Undeterminate

70. The standard heats of formation in $kcal\ mol^{-1}$ of $NO_2(g)$ and $N_2O_4(g)$ are 8.0 and 2.0 respectively. The heat of dimerization of NO_2 in $kcal$ is

$2NO_2(g) = N_2O_4(g)$ **[NCERT 1983]**

(a) 10.0 (b) – 6.0

(c) – 12.0 (d) – 14.0

71. The difference between heats of reaction at constant pressure and at constant volume for the reaction $2C_6H_6(l) + 15O_2(g) \rightarrow 12CO_2(g) + 6H_2O(l)$ at $25^o C$ in kJ is **[IIT JEE 1991; Kerala PMT 2004]**

(a) –7.43 (b) + 3.72

(c) –3.72 (d) + 7.43

72. C (diamond) $+ C_2(g) \rightarrow CO_2(g); \Delta H = -395\ kJ$

C (graphite) $+ O_2(g) \rightarrow CO_2(g); \Delta H = -393.5\ kJ$

From the data, the ΔH when diamond is formed from graphite, is **[CBSE PMT 1989; BHU 1987]**

(a) $-1.5\, kJ$ (b) $+1.5\, kJ$

(c) $+3.0\, kJ$ (d) $-3.0\, kJ$

73. Which of the following values of heat of formation indicates that the product is least stable **[MP PMT 1991]**

(a) $-94\, kcal$ (b) $-231.6\, kcal$

(c) $+21.4\, kcal$ (d) $+64.8\, kcal$

74. Which of the following equations correctly represents the standard heat of formation (ΔH_f^o) of methane **[IIT JEE (Screening) 1992]**

(a) $C(diamond) + 2H_2(g) = CH_4(g)$

(b) $C(graphite) + 2H_2(g) = CH_4(l)$

(c) $C(graphite) + 2H_2(g) = CH_4(g)$

(d) $C(graphite)+4H=CH_4(g)$

75. In which of the following reactions does the heat change represent the heat of formation of water **[EAMCET 1991]**

(a) $2H_2(g)+O_2(g)\rightarrow 2H_2O(l);\Delta H=-116\,kcal$

(b) $H_2(g)+\frac{1}{2}O_2(g)\rightarrow H_2O(l);\Delta H=-58\,kcal$

(c) $H^+(aq.)+OH^-(aq.)\rightarrow 2H_2O(l);\Delta H=-13.7\,kcal$

(d) $C_2H_2(g)+2\frac{1}{2}O_2(g)\rightarrow 2CO_2(g)+H_2O(l)$;

$\Delta H=-310\,kcal$

76. Values of heats of formation for SiO_2 and MgO are -48.4 and $-34.7\,kJ$ respectively. The heat of the reaction $2Mg+SiO_2\rightarrow 2MgO+Si$ is **[KCET 1990]**

(a) $21.16\,kJ$ (b) $-21.10\,kJ$

(c) $-13.62\,kJ$ (d) $13.6\,kJ$

77. Based on the following thermochemical equations

$H_2O(g)+C(s)\rightarrow CO(g)+H_2(g);\Delta H=131\,kJ$

$CO(g)+\frac{1}{2}O_2(g)\rightarrow CO_2(g);\Delta H=-282\,kJ$

$H_2(g)+\frac{1}{2}O_2(g)\rightarrow H_2O(g);\Delta H=-242\,kJ$

$C(s)+O_2(g)\rightarrow CO_2(g);\Delta H=X\,kJ$

The value of X is **[CBSE PMT 1992]**

(a) $-393\,kJ$ (b) $-655\,kJ$

(c) $+393\,kJ$ (d) $+655\,kJ$

78. Heat of transition is the heat evolved or absorbed when a substance is converted from **[KCET 1984]**

(a) Solid to liquid

(b) Solid to vapour

(c) Liquid to vapour

(d) One allotropic form to another allotropic form

79. For the allotropic change represented by equation $C(diamond)\rightarrow C(graphite)$; the enthalpy change is $\Delta H=-1.89\,kJ$. If $6\,g$ of diamond and $6\,g$ of graphite are separately burnt to yield carbon dioxide, the heat liberated in the first case is **[KCET 1988; DPMT 2000]**

(a) Less than in the second case by $1.89\,kJ$

(b) More than in the second case by $1.89\,kJ$

(c) Less than in the second case by $11.34\,kJ$

(d) More than in the second case by $0.945\,kJ$

80. For an exothermic reaction

[MP PET 1994; Manipal MEE 1995]

(a) H of the products is less than H of the reactants

(b) H of the products is more than H of the reactants

(c) H of the products is equal to H of the reactants

(d) ΔH is always positive

81. The energy evolved is highest for which of the following reactions **[MP PET 1994]**

(a) $F+e^-\rightarrow F^{-1}$ (b) $Cl+e^-\rightarrow Cl^-$

(c) $S+2e^-\rightarrow S^{2-}$ (d) $O+2e^-\rightarrow O^{2-}$

82. In the combustion of $2.0\,gm$ of methane $25\,kcal$ heat is liberated, heat of combustion of methane would be

[MP PMT 1994]

(a) $100\,kcal$ (b) $200\,kcal$

(c) $300\,kcal$ (d) $400\,kcal$

83. Complete combustion of CH_4 gives **[BHU 1995]**

(a) CO_2+H_2O (b) CO_2+H_2

(c) $COCl_2$ (d) $CO+CO_2+H_2O$

84. If enthalpies of formation of $C_2H_4(g), CO_2(g)$ and $H_2O(l)$ at 25^oC and $1\,atm$ pressure be 52, – 394 and $-286\,kJ\,mol^{-1}$ respectively, the enthalpy of combustion of $C_2H_4(g)$ will be

[CBSE PMT 1995; AIIMS 1998; Pb. PMT 1999]

(a) $+1412\,kJ\,mol^{-1}$ (b) $-1412\,kJ\,mol^{-1}$

(c) $+141.2\,kJ\,mol^{-1}$ (d) $-141.2\,kJ\,mol^{-1}$

85. Carbon and carbon monoxide burn in oxygen to form carbon dioxide according to the following reactions

$C+O_2\rightarrow CO_2;\Delta H=-394\,kJ\,mol^{-1}$

$2CO+O_2\rightarrow 2CO_2;\Delta H=-569\,kJ\,mol^{-1}$

The heat of formation of $1\,mol$ of carbon monoxide is thus

[MP PET 1995]

(a) $-219.0\,kJ\,mol^{-1}$ (b) $-109.5\,kJ\,mol^{-1}$

(c) $-175.0\,kJ\,mol^{-1}$ (d) $-87.5\,kJ\,mol^{-1}$

86. Heat of formation in the reaction

$H_2+Cl_2\rightarrow 2HCl+44\,kcal$ is **[MP PMT 1995]**

(a) 44 kcal (b) 44000 kcal

(c) 22 kcal (d) 11 kcal

87. When water is added to quick lime, the reaction is

[MP PMT 1995]

(a) Exothermic (b) Endothermic

(c) Explosive (d) None of these

88. In an exothermic reaction ΔH is

[MP PMT 1995; CPMT 1999]

(a) Positive (b) Negative

(c) Zero (d) Both positive or negative

89. The heat change for the following reaction $C(s)+2S(s)\rightarrow CS_2(l)$ is known as **[MP PMT 1996]**

(a) Heat of vaporization (b) Heat of solution

(c) Heat of fusion (d) Heat of formation

90. The enthalpy of combustion of benzene from the following data will be

(i) $6C(s)+3H_2(g)\rightarrow C_6H_6(l);\Delta H=+45.9\,kJ$

(ii) $H_2(g)+\frac{1}{2}O_2(g)\rightarrow H_2O(l);\Delta H=-285.9\,kJ$

(iii) $C(s)+O_2(g)\rightarrow CO_2(g);\Delta H=-393.5\,kJ$

(a) + 3172.8 kJ (b) – 1549.2 kJ
(c) – 3172.8 kJ (d) – 3264.6 kJ

91. Enthalpy of formation of HF and HCl are $-161\,kJ$ and $-92\,kJ$ respectively. Which of the following statements is incorrect **[KCET 2003]**
(a) HCl is more stable than HF
(b) HF and HCl are exothermic compounds
(c) The affinity of fluorine to hydrogen is greater than the affinity of chlorine to hydrogen
(d) HF is more stable than HCl

92. The heat of reaction at constant pressure is given by **[MP PMT 1997]**
(a) $E_P - E_R$ (b) $E_R - E_P$
(c) $H_P - H_R$ (d) $H_R - H_P$

93. In an endothermic reaction, the value of ΔH is **[CBSE PMT 1999; AIIMS 1998; BHU 2000; MP PMT 2000]**
(a) Zero (b) Positive
(c) Negative (d) Constant

94. 2.2016 gm of acetaldehyde produced $13.95\,kcal$ of heat on combustion in O_2. Calculate the heat of combustion of CH_3CHO **[Bihar CEE 1995]**
(a) 279 $kcal$ (b) 972 $kcal$
(c) 27.9 $kcal$ (d) 2.79 $kcal$

95. $C + \frac{1}{2}O_2 \to CO; \Delta H = -42\,kJ$

$CO + \frac{1}{2}O_2 \to CO_2; \Delta H = -24\,kJ$

The heat of formation of CO_2 is **[CPMT 1996]**
(a) – 16 kJ (b) + 66 kJ
(c) + 16 kJ (d) – 66 kJ

96. Standard molar enthalpy of formation of CO_2 is equal to **[IIT JEE 1997; BHU 2001]**
(a) Zero
(b) The standard molar enthalpy of combustion of gaseous carbon
(c) The sum of standard molar enthalpies of formation of CO and O_2
(d) The standard molar enthalpy of combustion of carbon (graphite)

97. In the complete combustion of butanol $C_4H_9OH(l)$, if ΔH is enthalpy of combustion and ΔE is the heat of combustion at constant volume, then **[EAMCET 1997]**
(a) $\Delta H < \Delta E$
(b) $\Delta H = \Delta E$
(c) $\Delta H > \Delta E$
(d) $\Delta H, \Delta E$ relation cannot be predicted

98. $C + O_2 \to CO_2; \Delta H = X$

$CO + \frac{1}{2}O_2 \to CO_2; \Delta H = Y$

Then the heat of formation of CO is **[BHU 1997; DPMT 2002]**
(a) $X - Y$ (b) $Y - 2X$
(c) $X + Y$ (d) $2X - Y$

99. The values of heat of formation of SO_2 and SO_3 are $-298.2\,kJ$ and $-98.2\,kJ$. The heat of reaction of the following reaction will be

$SO_2 + \frac{1}{2}O_2 \to SO_3$ **[BHU 1997; CBSE PMT 2000]**
(a) $-200\,kJ$ (b) $-356.2\,kJ$
(c) $+200\,kJ$ (d) $-396.2\,kJ$

100. Calculate the standard heat of formation of carbon disulphide (l), given that the standard heat of combustion of carbon (s), sulphur (s) and carbon disulphide (l) are $-393.3, -293.72$ and $-1108.76\,kJ\,mol^{-1}$ respectively **[Roorkee 1989; BHU 1997]**
(a) $-128.02\,kJ\,mol^{-1}$ (b) $+12.802\,kJ\,mol^{-1}$
(c) $+128.02\,kJ\,mol^{-1}$ (d) $-12.802\,kJ\,mol^{-1}$

101. Fermentation is a reaction called **[RPMT 1997]**
(a) Endothermic (b) Exothermic
(c) Isotemperature (d) Reversible

102. $8\,gm$ of CH_4 is completely burnt in air. The number of moles of water produced are **[Orissa JEE 1997]**
(a) 0.5 (b) 1
(c) 2 (d) 18

103. For the reaction $A(g) + 2B(g) \to 2C(g) + 3D(g)$, the value of ΔE at 27^oC is 19.0 $kcal$. The value of ΔH for the reaction would be $(R = 2.0\,cal\,K^{-1}mol^{-1})$ **[Roorkee Qualifying 1998]**
(a) 20.8 $kcal$ (b) 19.8 $kcal$
(c) 18.8 $kcal$ (d) 20.2 $kcal$

104. The enthalpy of solution of $BaCl_2(s)$ and $BaCl_2.2H_2O(s)$ are -20.6 and $8.8\,kJ\,mol^{-1}$ respectively. The enthalpy change for the reaction $BaCl_2(s) + 2H_2O \to$ is **[Roorkee Qualifying 1998]**
(a) 29.4 kJ (b) – 11.8 kJ
(c) – 20.6 kJ (d) – 29.4 kJ

105. The enthalpy change of a reaction does not depend on **[AIIMS 1997]**
(a) The state of reactants and products
(b) Nature of reactants and products
(c) Different intermediate reaction
(d) Initial and final enthalpy change of a reaction

106. $S + \frac{3}{2}O_2 \to SO_3 + 2x\,kcal$

$SO_2 + \frac{1}{2}O_2 \to SO_3 + y\,kcal$

Find out the heat of formation of SO_2 **[AIIMS 1997; CBSE PMT 1999; KCET 1999]**
(a) $2x - y$ (b) $2x + y$
(c) $x + y$ (d) $2x / y$

107. The combustion enthalpies of carbon, hydrogen and methane are $-395.5\, kJ\, mol^{-1}$, $-285.8\, kJ\, mol^{-1}$ and $-890.4\, kJ\, mol^{-1}$ respectively at 25^oC. The value of standard formation enthalpies of methane at that temperature is **[Pb. PMT 1998]**

(a) $890.4\, kJ\, mol^{-1}$ (b) $-298.8\, kJ\, mol^{-1}$

(c) $-74.7\, kJ\, mol^{-1}$ (d) $-107.7\, kJ\, mol^{-1}$

108. Equal volumes of methanoic acid and sodium hydroxide are mixed. If x is the heat of formation of water, then heat evolved on neutralisation is **[BHU 1998]**

(a) More than x (b) Equal to x

(c) Twice of x (d) Less than x

109. The neutralisation of a strong acid by a strong base liberates an amount of energy per mole of H^+ that **[BHU 1998]**

(a) Depends upon which acid and base are involved

(b) Depends upon the temperature at which the reaction takes place

(c) Depends upon which catalyst is used

(d) Is always the same

110. When $0.5 g$ of sulphur is burnt to $SO_2, 4.6 kJ$ of heat is liberated. What is the enthalpy of formation of sulphur dioxide **[KCET 1998; AFMC 2001]**

(a) + 147.2 *kJ* (b) – 147.2 *kJ*

(c) – 294.4 *kJ* (d) + 294.4 *kJ*

111. Ozone is prepared by passing silent electric discharge through oxygen. In this reaction **[AFMC 1998]**

(a) Energy is given out

(b) Energy is absorbed

(c) Oxygen is loaded with energy

(d) Oxygen is dissociated into atoms

112. Combustion of glucose takes place according to the equation,

$C_6H_{12}O_6 + 6O_2 \rightarrow 6CO_2 + 6H_2O, \Delta H = -72\, kcal$. How much energy will be required for the production of 1.6 *g* of glucose (Molecular mass of glucose = 180 *g*) **[AFMC 1999]**

(a) 0.064 *kcal* (b) 0.64 *kcal*

(c) 6.4 *kcal* (d) 64 *kcal*

113. Given that

$C(s) + O_2(g) \rightarrow CO_2(g), \Delta H = -394\, kJ$

$2H_2(g) + O_2(g) \rightarrow 2H_2O(l), \Delta H = 568\, kJ$

$CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(l)\ \ \Delta H = -892\, kJ$

Heat of formation of CH_4 is

(a) – 70 *kJ* (b) 71.8 *kJ*

(c) – 244 *kJ* (d) + 782 *kJ*

114. Calculate the heat of formation of $PCl_5(s)$ from the following data

$2P(s) + 3Cl_2(g) \rightarrow 2PCl_3(l); \Delta H = -151.8\, kcal$

$PCl_3(l) + Cl_2(g) \rightarrow PCl_5(s);\ \Delta H = -32.8\, kcal$

[JIPMER 1999]

(a) – 108.7 *kcal* (b) + 108.7 *kcal*

(c) – 184.6 *kcal* (d) + 184.6 *kcal*

115. When $50\, cm^3$ of a strong acid is added to $50\, cm^3$ of an alkali, the temperature rises by 5^oC. If $250\, cm^3$ of each liquid are mixed, the temperature rise would be **[KCET 1999]**

(a) 5^oC (b) 10^oC

(c) 25^oC (d) 20^oC

116. $H_2(g) + \frac{1}{2}O_2(g) \rightarrow H_2O(l)$;

ΔH at 298 K = – 285.8 *kJ*

The molar enthalpy of vaporisation of water at 1 *atm* and 25^oC is 44 *kJ*. The standard enthalpy of formation of 1 *mole* of water vapour at 25^oC is **[KCET 1999]**

(a) – 241.8 *kJ* (b) 241.8 *kJ*

(c) 329.8 *kJ* (d) –329.8 *kJ*

117. When 4 *g* of iron is burnt to ferric oxide at constant pressure, 29.28 *kJ* of heat is evolved. What is the enthalpy of formation of ferric oxide (At. Wt. of *Fe* = 56) **[AIIMS 1999]**

(a) – 81.98 *kJ* (b) – 819.8 *kJ*

(c) – 40.99 *kJ* (d) + 819.8 *kJ*

118. When a strong acid, strong base or their salt are dissolved in water, they are completely ionised. If a strong acid is added to a strong base, H^+ ions from the former combine with OH^- ions of the latter forming water. The formation of each water molecule liberates a certain quantity of energy and the reaction is exothermic. The heat liberated when one mole of water is formed by combining hydrochloric acid and sodium hydroxide is 13.7 *kcal*. The heat liberated when one mole of water is formed by combining sulphuric acid and sodium hydroxide is **[AMU (Engg.) 1**

(a) 25.5 *kcal* (b) 8.5 *kcal*

(c) 13.7 *kcal* (d) 34 *kcal*

119. 2.1 *g* of *Fe* combines with *S* evolving 3.77 *kJ*. The heat of formation of *FeS* in *kJ/mol* is **[AMU (Engg.) 1999]**

(a) – 1.79 (b) – 100.5

(c) – 3.77 (d) None of these

120. In the reaction: $H_2 + Cl_2 \rightarrow 2HCl, \Delta H = 194\, kJ$. Heat of formation of HCl is **[KCET 2000; AFMC 2000; CPMT 2000]**

(a) + 97 *kJ* (b) + 194 *kJ*

(c) – 194 *kJ* (d) – 97 *kJ*

121. Enthalpy of neutralisation of acetic acid by $NaOH$ is $-50.6\, kJ/mol$. and the heat of neutralisation of a strong acid with a strong base is – 55.9 *kJ/mol*. What is the value **[DCE 1999]** of ΔH for the ionisation of CH_3COOH **[AIIMS 2000]**

(a) + 5.3 *kJ/mol* (b) + 6.2 *kJ/mol*

(c) + 8.2 *kJ/mol* (d) + 9.3 *kJ/mol*

122. Heat of neutralization of the acid-base reaction is 57.32 *kJ* for **[JIPMER 2000]**

(a) $HNO_3 + LiOH$ (b) $HCOOH + KOH$

(c) $HCl + NH_4OH$ (d) $CH_3COOH + NaOH$

123. The heat change for the following reaction at 298^oK and at constant pressure is $+7.3\, kcal$

$A_2B(s) \rightarrow 2A(s) + 1/2\, B_2(g)$, $\Delta H = +7.3\, kcal$

The heat change at constant volume would be **[DCE 2000]**

(a) 7.3 *kcal*
(b) More than 7.3
(c) Zero
(d) None of these

124. The heat evolved in the combustion of benzene is given by the equation

$$C_6H_6(l) + 7\frac{1}{2}O_2(g) \rightarrow 3H_2O(l) + 6CO_2(g)$$

$$\Delta H = 781.0\,kcal\ mol^{-1}$$

Which of the following quantities of heat energy will be evolved when 39 *g* of benzene is burnt in an open container **[MP PET 2000]**

(a) 122.25 $kcal\ mol^{-1}$
(b) 390.5 $kcal\ mol^{-1}$
(c) 1562.0 $kcal\ mol^{-1}$
(d) 586.75 $kcal\ mol^{-1}$

125. $H_2(g) + Cl_2(g) \rightarrow 2HCl(g). \Delta H = -44\,kcal$

$2Na(s) + 2HCl(g) \rightarrow 2NaCl(s) + H_2(g),\ \Delta H = -152\,kcal$

For the reaction $Na(s) + \frac{1}{2}Cl_2(g) \rightarrow NaCl(s), \Delta H =$ **[KCET 2000]**

(a) – 108 *kcal*
(b) – 196 *kcal*
(c) – 98 *kcal*
(d) 54 *kcal*

126. The ΔH_f^o for $CO_2(g), CO(g)$ and $H_2O(g)$ are – 393.5, –110.5 and – 241.8$kJmol^{-1}$ respectively. The standard enthalpy change (in *kJ*) for the reaction $CO_2(g) + H_2(g) \rightarrow CO(g) + H_2O(g)$ is **[IIT JEE (Screening) 2000]**

(a) 524.1
(b) 41.2
(c) – 262.5
(d) – 41.2

127. Which of the following compounds will absorb the maximum quantity of heat when dissolved in the same amount of water ? The heats of solution of these compounds at 25^oC in *kJ/mole* of each solute is given in brackets **[AMU (Engg.) 2000]**

(a) $HNO_3 (\Delta H = -33)$
(b) $KCl (\Delta H = +17.64)$
(c) $NH_4NO_3 (\Delta H = +25.5)$
(d) $HCl (\Delta H = -74.1)$

128. In the reaction $C + 2S \rightarrow CS_2 + \Delta H, \Delta H$ is the **[AMU (Engg.) 2000]**

(a) Heat of combustion
(b) Heat of neutralisation
(c) Heat of solution
(d) None of these

129. The heat of formation of methane $C(s) + 2H_2(g) \rightarrow CH_4(g)$ at constant pressure is 18500 *cal* at 25^oC. The heat of reaction at constant volume would be **[MH CET 2000]**

(a) 17904 *cal*
(b) 18202 *cal*
(c) 18798 *cal*
(d) 19096 *cal*

130. The enthalpy of combustion of $C_6H_{6(l)}$ is – 3250 *kJ*. When 0.39 *g* of benzene is burnt excess of oxygen in an open vessel, the amount of heat evolved is **[KCET 2000; AFMC 2000; DCE 2000]**

(a) 16.25 *J*
(b) 16.25 *kJ*
(c) 32.5 *J*
(d) 32.5 *kJ*

131. $C(s) + O_2(g) \rightarrow CO_2;\ \Delta H = -94\,kcal$

$CO(g) + \frac{1}{2}O_2(g) \rightarrow CO_2;\ \Delta H = 135.2\,kcal$

Then heat of formation of $CO(g)$ is **[DCE 2001]**

(a) – 26.4 *kcal*
(b) 41.2 *kcal*
(c) 26.4 *kcal*
(d) – 229.2 *kcal*

132. The heat of neutralization of HCl and $NaOH$ is **[MP PET 2001]**

(a) Zero
(b) – 57.3 *kJ*
(c) + 57.3 *kJ*
(d) None of these

133. The following thermochemical reactions are given

$$M + \frac{1}{2}O_2 \rightarrow MO + 351.4\,kJ$$

$$X + \frac{1}{2}O_2 \rightarrow XO + 90.8\,kJ$$

It follows that the heat of reaction for the following process $M + XO \rightleftharpoons MO + X$ is given by

(a) 422.2 *kJ*
(b) 268.7 *kJ*
(c) – 442.2 *kJ*
(d) 260.6 *kJ*

134. If the heat of combustion of carbon monoxide at constant volume and at 17^oC is – 283.3 *kJ*, then its heat of combustion at constant pressure $(R = 8.314\ J\ \text{degree}^{-1} mol^{-1})$ **[CPMT 2001]**

(a) – 284.5 *kJ*
(b) 284.5 *kJ*
(c) 384.5 *kJ*
(d) – 384.5 *kJ*

135. Heat of formation of H_2O is $-188\,kJ/mole$ and H_2O_2 is $-286\,kJ/mole$. The enthalpy change for the reaction $2H_2O_2 \rightarrow 2H_2O + O_2$ is **[BHU 2001]**

(a) 196 *kJ*
(b) – 196 *kJ*
(c) 984 *kJ*
(d) – 984 *kJ*

136. The values of ΔH for the combustion of ethene and ethyne are – 341.1 and – 310.0*kcal* respectively. Which of the following is a better fuel **[BHU 2001]**

(a) C_2H_2
(b) C_2H_4
(c) Both of these
(d) None of these

137. For exothermic reaction, the equilibrium constant **[JIPMER 2001]**

(a) Increases with increase of *P*
(b) Decreases with increase of *P*
(c) Increases with increase of temperature
(d) Decreases with increase of temperature

138. In order to decompose 9 *g* water 142.5 *kJ* heat is required. Hence the enthalpy of formation of water is **[KCET 2001]**

(a) – 142.5 *kJ*
(b) + 142.5 *kJ*
(c) – 285 *kJ*
(d) + 285 *kJ*

139. What is Δn for combustion of 1 mole of benzene, when both the reactants and the products are gas at 298 *K* **[Pb. PMT 2001]**

(a) 0
(b) 3/2
(c) – 3/2
(d) 1/2

140. If $C + O_2 \rightarrow CO_2 + 94.2\,kcal$

$$H_2 + \frac{1}{2}O_2 \rightarrow H_2O + 68.3\,kcal$$

$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O + 210.8\,kcal$

Then the possible heat of methane will be **[UPSEAT 2001]**

(a) 47.3 *kcal* (b) 20.0 *kcal*
(c) 45.9 *kcal* (d) – 47.3 *kcal*

141. Heat of neutralization of strong acid and weak base is **[UPSEAT 2001]**

(a) $57.1\,kJ\,mol^{-1}$
(b) $13.7\,kJ\,mol^{-1}$
(c) Less than $13.7\,kcal\,mol^{-1}$
(d) More than $13.7\,kcal\,mol^{-1}$

142. A system is changed from state *A* to state *B* by one path and from *B* to *A* another path. If E_1 and E_2 are the corresponding changes in internal energy, then **[Pb. PMT 2001]**

(a) $E_1 + E_2 = -ve$ (b) $E_1 + E_2 = +ve$
(c) $E_1 + E_2 = 0$ (d) None of these

143. The heat evolved during the combination of 24 *g C* and 128 *g S* following the change is

$C + S_2 \rightarrow CS_2; \Delta H = 22.0\,kcal$ **[MH CET 2001]**

(a) 11 *kcal* (b) 32 *kcal*
(c) 44 *kcal* (d) 22 *kcal*

144. When the aqueous solution of 0.5 mole HNO_3 is mixed with the 0.3 mole of OH^- solution, then what will be the liberated heat (Enthalpy of neutralization is = 57.1 *kJ*) **[Kerala CET 2005]**

(a) 28.5 *kJ* (b) 17.1 *kJ*
(c) 45.7 *kJ* (d) 1.7 *kJ*
(e) 2.85 *kJ*

145. A cylinder of gas is assumed to contain 11.2 *kg* of butane (C_4H_{10}). If a normal family needs 20000 *kJ* of energy per day. The cylinder will last: (Given that ΔH for combustion of butane is – 2658 *kJ*) **[AMU (Engg.) 2002]**

(a) 20 days (b) 25 days
(c) 26 days (d) 24 days

146. Compounds with high heat of formation are less stable because **[KCET 2002]**

(a) High temperature is required to synthesise them
(b) Molecules of such compounds are distorted
(c) It is difficult to synthesis them
(d) Energy rich state leads to instability

147. The heat evolved in the combustion of methane is given by the following equations:

$CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + H_2O(l);\ \Delta H = -890.3\,kJ$

How many grams of methane would be required to produce 445.15 *kJ* of heat of combustion

(a) 4 *g* (b) 8 *g*
(c) 12 *g* (d) 16 *g*

148. Heats of combustion (ΔH^o) for $C(s), H_2(g)$ and $CH_4(g)$ are $-94, -68$ and $-213\,kcal/mol$. respectively. The value of ΔH^o for the reaction,

$C(s) + 2H_2(g) \rightarrow CH_4(g)$ is **[CBSE PMT 2002]**

(a) – 85 *kcal* (b) – 111 *kcal*
(c) – 17 *kcal* (d) – 170 *kcal*

149. If the value of ΔH in a reaction is positive, then the reaction is called **[BHU 2002]**

(a) Exothermic (b) Endothermic
(c) Polymorphic (d) Polytropic

150. Enthalpy of neutralisation of NH_4OH and HCl, is numerically **[JIPMER 2002; Kurukshetra CEE 2002]**

(a) $57.1\,kJ\,mol^{-1}$ (b) $< 57.1\,kJ\,mol^{-1}$
(c) $> 57.1\,kJ\,mol^{-1}$ (d) Zero

151. The heat of neutralisation will be highest in **[MP PMT 2002]**

(a) NH_4OH and CH_3COOH
(b) NH_4OH and HCl
(c) KOH and CH_3COOH
(d) KOH and HCl

152. If a mole of H_2 molecule is heated to high temperature the following reaction takes place **[Kerala (Med.) 2002]**

(a) $H_2(g) + 436\,kJ = H(g) + H(g)$
(b) $H_2(g) + 820\,kJ = 2H_2(g)$
(c) $2H_2(g) + 436\,J = 2H_2$
(d) $H_2 + H_2 = H^+ + H^+$

153. Which of the following reactions is not exothermic **[MP PET 2002]**

(a) $C(s) + O_2(g) \rightarrow CO_2(g)$
(b) $C(s) + 2S(s) \rightarrow CS_2(g)$
(c) $CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(l)$
(d) $CO(g) + \frac{1}{2}O_2(g) \rightarrow CO_2(g)$

154. On combustion, carbon forms two oxides *CO* and CO_2, Heat of formation of CO_2 gas is 94.3 *kcal* and that of *CO* is 26.0 *kcal*. Heat of combustion of carbon is **[JIPMER 2002]**

(a) 26.0 *kcal* (b) – 94.3 *kcal*
(c) 68.3 *kcal* (d) – 120.3 *kcal*

155. 1 *mole* of conc. *HCl* requires *X* moles of dilute *NaOH* for neutralisation and 1 *mole* of concentrate H_2SO_4 requires *Y moles* of small dilute *NaOH* then which of the following reaction is true **[MH CET 2002]**

(a) $Y = \frac{1}{2}X$ (b) $X = \frac{1}{2}Y$
(c) $X = 2Y$ (d) None of these

156. Which of the reaction defines ΔH_f^o **[IIT -JEE (Screening) 2003]**

[AMU 2002]

(a) $C_{(\text{diamond})} + O_2(g) \rightarrow CO_2(g)$
(b) $\frac{1}{2}H_2(g) + \frac{1}{2}F_2(g) \rightarrow HF(g)$
(c) $N_2(g) + 3H_2(g) \rightarrow 2NH_3(g)$
(d) $CO(g) + \frac{1}{2}O_2(g) \rightarrow CO_2(g)$

157. One gram sample of NH_4NO_3 is decomposed in a bomb calorimeter. The temperature of the calorimeter increases by 6.12 K the heat capacity of the system is 1.23 $kJ/g/deg$. What is the molar heat of decomposition for NH_4NO_3 **[AIIMS 2003]**

(a) $-7.53\ kJ/mol$ (b) $-398.1\ kJ/mol$

(c) $-16.1\ kJ/mol$ (d) $-602\ kJ/mol$

158. For which one of the following equations is $\Delta H^o_{\text{react}}$ equal to ΔH^o_f for the product **[CBSE PMT 2003]**

(a) $2CO(g)+O_2(g)\rightarrow 2CO_2(g)$

(b) $N_2(g)+O_3(g)\rightarrow N_2O_3(g)$

(c) $CH_4(g)+2Cl_2(g)\rightarrow CH_2Cl_2(l)+2HCl(g)$

(d) $Xe(g)+2F_2(g)\rightarrow XeF_4(g)$

159. Enthalpy change for a reaction does not depend upon **[AIEEE 2003]**

(a) The physical states of reactants and products

(b) Use of different reactants for the same product

(c) The nature of intermediate reaction steps

(d) The differences in initial or final temperatures of involved substances

160. $C_{\text{dia}} + O_2 \rightarrow CO_2;\ \Delta H = -395.3\, kJ/mole$

$C_{gr} + O_2 \rightarrow CO_2; \Delta H = -393.4\, kJ/mole$

$C_{gr} \rightarrow C_{\text{dia}}; \Delta H =$ **[BHU 2003]**

(a) -3.8 (b) -1.9

(c) $+3.8$ (d) $+1.9$

161. What is the weight of oxygen that is required for the complete combustion of 2.8 kg of ethylene? **[BVP 2003]**

(a) 9.6 kg (b) 96.0 kg

(c) 6.4 kg (d) 2.8 kg

162. For complete neutralization of HCl with $NaOH$, the heat of neutralization is **[MP PET 2003]**

(a) $+13.70\, kJ\, mol^{-1}$ (b) $-13.70\, kJ\, mol^{-1}$

(c) $-57.32\, kJ\, mol^{-1}$ (d) $+57.32\, kJ\, mol^{-1}$

163. 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 **[UPSEAT 2004]**

(a) $+315\ kJ$ (b) $-31.5\, kJ$

(c) $-315\ kJ$ (d) $+31.5\, kJ$

164. Which of the following equations correctly represents the standard heat of formation (ΔH^o_f) of methane **[UPSEAT 2004]**

(a) C (diamond) $+4H_{(g)} \rightarrow CH_{4(g)}$

(b) C (diamond) $+2H_{2(g)} \rightarrow CH_{4(g)}$

(c) C (graphite) $+2H_{2(g)} \rightarrow CH_{4(g)}$

(d) C (graphite) $+4H_{(g)} \rightarrow CH_{4(g)}$

165. If the heat of formation of CO_2 is $-393\ kJ$. The amount of heat evolved in the formation of 0.156 kg of CO_2 is **[MH CET 2004]**

(a) $-1357.9\ kJ$ (b) $-1275.9\, kJ$

(c) $-1572.0\, kJ$ (d) $-1165.5\, kJ$

166. Which of the following pairs has heat of neutralisation equal to 13.7 Kcals **[DCE 2003]**

(a) HCl, NH_4OH (b) HNO_3, KOH

(c) $NaOH, CH_3COOH$ (d) H_2SO_4, NH_4OH

167. The enthalpies of combustion of carbon and carbon monodie are -393.5 and -283 $kJ\ mol^{-1}$ respectivley. The enthalpy of formation of carbon monoxide per mole is **[AIEEE 2004]**

(a) $-676.5\, kJ$ (b) $676.5\, kJ$

(c) $110.5\, kJ$ (d) $-110.5\, kJ$

168. The enthalpy of combustion of methane at 25^oC is $890\ kJ$. The heat liberated when $3.2\, g$ of methane is burnt in air is **[KCET 2004]**

(a) $445\ kJ$ (b) $278\ kJ$

(c) $-890\ kJ$ (d) $178\ kJ$

169. If (i) $C+O_2 \rightarrow CO_2$, (ii) $C+1/2O_2 \rightarrow CO$, (iii) $CO+1/2O_2 \rightarrow CO_2$, the heats of reaction are $Q, -12, -10$ respectively. Then $Q =$ **[Orissa JEE 2004]**

(a) -2 (b) 2

(c) -22 (d) -16

170. How much energy is released when 6 mole of octane is burnt in air ? Given ΔH^o_f for $CO_2(g), H_2O(g)$ and $C_8H_{18}(l)$ respectively are – 490,– 240 and + 160 kJ/mol **[AIIMS 2004]**

(a) $-6.2\ kJ$ (b) $-37.4\ kJ$

(c) $-35.5\ kJ$ (d) $-20.0\ kJ$

171. Given : $2Fe + \frac{3}{2}O_2 \rightarrow Fe_2O_3, \Delta H = -193.4\, kJ$;

$Mg + \frac{1}{2}O_2 \rightarrow MgO, \Delta H = -140.2\, kJ$

What is the ΔH of the reaction

$Mg + Fe_2O_3 \rightarrow 3MgO + 2Fe$ **[Orissa JEE 2005]**

(a) $-1802\ kJ$ (b) $+1802\ kJ$

(c) $-800\ kJ$ (d) $+228\ kJ$

172. The enthalpy change (ΔH) for the neutralisation of $1M\ HCl$ by caustic potash in dilute solution at $298\, K$ is **[DPMT 2005]**

(a) 68 kJ (b) 65 kJ

(c) 57.3 kJ (d) 50 kJ

Bond energy

1. If the bond dissociation energies of XY, X_2 and Y_2 (all diatomic molecules) are in the ratio of 1 : 1 : 0.5 and $\Delta_f H$ for the formation of XY is $-200\ kJ\ mole^{-1}$. The bond dissociation energy of X_2 will be **[AIEEE 2005]**

(a) $100\ kJ\ mol^{-1}$ (b) $800\ kJ\ mol^{-1}$
(c) $300\ kJ\ mol^{-1}$ (d) $400\ kJ\ mol^{-1}$

2. Energy required to dissociate 4 *gm* of gaseous hydrogen into free gaseous atoms is 208 kcal at $25^o C$. The bond energy of $H-H$ bond will be
[CPMT 1989; MP PET 2000; J & K 2005]

(a) 104 *kcal* (b) 10.4 *kcal*
(c) 1040 *kcal* (d) 104 *cal*

3. The bond dissociation energy needed to form benzyl radical from toluene is ..... than the formation of the methyl radical from methane **[IIT 1994]**

(a) Less (b) Much
(c) Equal (d) None of the above

4. Which one of the following bonds has the highest average bond energy (*kcal/mol*) **[CPMT 1994]**

(a) $S=O$ (b) $C\equiv C$
(c) $C\equiv N$ (d) $N\equiv N$

5. The bond dissociation energies of gaseous H_2, Cl_2 and HCl are 104, 58 and 103 *kcal* respectively. The enthalpy of formation of HCl gas would be
[MP PET 1997; MP PMT 1999, 2001]

(a) – 44 *kcal* (b) 44 *kcal*
(c) – 22 *kcal* (d) 22 *kcal*

6. The first ionization energy for *Li* is 5.4 *eV* and electron affinity of *Cl* is 3.61*eV*. The ΔH (in *kJ/mol*) for the reaction $Li(g)+Cl(g)\rightarrow Li^+ + Cl^-$ is (if resulting ions do not combine with each other) $(1\,eV = 1.6\times10^{-19}\ J)$ **[MP PMT 2000, 03]**

(a) 70 (b) 100
(c) 170 (d) 270

7. Given that $C(g)+4H(g)\rightarrow CH_4(g); \Delta H = -166\ kJ$
The bond energy $C-H$ will be **[AMU 2002]**

(a) 208 *kJ/mole*
(b) – 41.6 *kJ/mole*
(c) 832 *kJ/mole*
(d) None of these

8. The $H-H$ bond energy is 430 *kJ mol* and $Cl-Cl$ bond energy is $240\ kJ\ mol^{-1}$. ΔH for HCl is $-90\ kJ$. The $H-Cl$ bond energy is about **[BVP 2003]**

(a) $180\ kJ\ mol^{-1}$ (b) $360\ kJ\ mol^{-1}$
(c) $213\ kJ\ mol^{-1}$ (d) $425\ kJ\ mol^{-1}$

9. If enthalpies of methane and ethane are respectively 320 and 360 calories then the bond energy of $C-C$ bond is
[UPSEAT 2003]

(a) 80 *calories* (b) 40 *calories*
(c) 60 *calories* (d) 120 *calories*

10. If the bond energies of $H-H$, $Br-Br$ and HBr are 433, 192 and 364 $kJ\ mol^{-1}$ respectively, the ΔH^o for the reaction, $H_2(g)+Br_2(g)\rightarrow 2HBr(g)$ is **[CBSE PMT 2004]**

(a) + 261 *kJ* (b) – 103 *kJ*
(c) – 261 *kJ* (d) + 103 *kJ*

Free energy and Work function

1. The free energy change for a reversible reaction at equilibrium is
[NCERT 1984; Kurukshetra CEE 1998; AMU 1999]

(a) Large positive (b) Small negative
(c) Small positive (d) 0

2. For a spontaneous change, free energy change ΔG is
[MNR 1983; BHU 1981, 95; AMU 1999; DCE 2000, 01; BHU 2000; MP PMT 2003]

(a) Positive
(b) Negative
(c) Zero
(d) Can be positive or negative

3. A minus sign of the free energy change denotes that

(a) The reaction tends to proceed spontaneously
(b) The reaction is non-spontaneous
(c) The system is in equilibrium
(d) The reaction is very much unlikely

4. The relation between ΔG and ΔH is
[MP PMT 1994, 95, 97; AFMC 1997; Kurukshetra CEE 1998]

(a) $\Delta H = \Delta G - T\Delta S$ (b) $\Delta G = \Delta H - T\Delta S$
(c) $T\Delta S - \Delta G = \Delta H$ (d) $\Delta H = T\Delta G + \Delta S$

5. At 300 *K*, the reactions which have following values of thermodynamic parameters occur spontaneously
[Roorkee 1999]

(a) $\Delta G^o = -400\ kJ\ mol^{-1}$
(b) $\Delta H^o = 200\ kJ\ mol^{-1},\ \Delta S^o = -4\ JK^{-1}mol^{-1}$
(c) $\Delta H^o = -200\ kJ\ mol^{-1},\ \Delta S^o = 4\ JK^{-1}mol^{-1}$
(d) $\Delta H^o = 200\ J\ mol^{-1},\ \Delta S^o = 40\ JK^{-1}mol^{-1}$

6. The relation $\Delta G = \Delta H - T\Delta S$ was given by
[MP PMT 2000; KCET 2002]

(a) Boltzmann (b) Faraday
(c) Gibbs–Helmholtz (d) Thomson

7. For precipitation reaction of Ag^+ ions with $NaCl$, which of the following statements is correct **[CPMT 1988]**

(a) ΔH for the reaction is zero
(b) ΔG for the reaction is zero
(c) ΔG for the reaction is negative
(d) $[\Delta G]=[\Delta H]$

8. At constant pressure and temperature, the direction to the result of any chemical reaction is where, there is less amount of

(a) Entropy (b) Enthalpy
(c) Gibb's free energy (d) None of the above

9. The dependence of Gibbs free energy on pressure for an isothermal process of an ideal gas is given by **[MP PET 1996]**

(a) $\Delta G_T = nRT \ln \frac{P_2}{P_1}$ (b) $\Delta G_T = nRT \ln \frac{V_2}{V_1}$

(c) $\Delta G_T = nRT \log \frac{P_1}{P_2}$ (d) $\Delta G_T = nRT \log \frac{V_2}{V_1}$

10. For the change $H_2O(l) \rightarrow H_2O(g); P = 1\,atm$, $T = 373\,K$, the free energy change $\Delta G = 0$. This indicates that

(a) $H_2O(l)$ is in equilibrium with $H_2O(g)$

(b) Water boils spontaneously at $373\,K$

(c) Water does not boil spontaneously at $373\,K$

(d) Condensation of water vapour occurs spontaneously at $373\,K$

11. What is the free energy change ΔG when $1.0\,mole$ of water at $100\,^oC$ and $1\,atm$ pressure is converted into steam at $100\,^oC$ and $1\,atm$ pressure **[MP PET/PMT 1998]**

(a) $540\,cal$ (b) $-9800\,cal$

(c) $9800\,cal$ (d) $0\,cal$

12. ΔG^o for the reaction $X + Y \rightleftharpoons Z$ is $-4.606\,kcal$. The value of equilibrium constant of the reaction at $227\,^oC$ is $(R = 2.0\,cal.mol^{-1}K^{-1})$ **[Roorkee 1999]**

(a) 100 (b) 10

(c) 2 (d) 0.01

13. The standard enthalpy of the decomposition of N_2O_4 to NO_2 is 58.04 kJ and standard entropy of this reaction is 176.7 J/K. The standard free energy change for this reaction at $25\,^oC$ is **[AIIMS 1999]**

(a) 539 kJ (b) – 539 kJ

(c) – 5.39 kJ (d) 5.39 kJ

14. Spontaneity of a chemical reaction is decided by the negative change in **[MP PET 2001]**

(a) Internal energy (b) Enthalpy

(c) Entropy (d) Free energy

15. For a reaction at $25\,^oC$ enthalpy change and entropy changes are $-11.7 \times 10^3\,J\,mol^{-1}$ and $-105\,J\,mol^{-1}K^{-1}$ respectively. What is the Gibbs free energy **[BHU 2001]**

(a) 15.05 kJ (b) 19.59 kJ

(c) 2.55 kJ (d) 22.55 kJ

16. Born-Haber cycle is used to determine **[UPSEAT 2001]**

(a) Crystal energy (b) Electron affinity

(c) Lattice energy (d) All of these

17. Gibbs free energy G, enthalpy H and entropy S are interrelated as in **[MP PMT 2002]**

(a) $G = H + TS$ (b) $G = H - TS$

(c) $G - TS = H$ (d) $G = S = H$

18. The essential condition for the feasibility of a reaction is that **[JIPMER 2002]**

(a) The reaction should be exothermic

(b) The entropy of products must be larger than that of reactants

(c) The reaction is to be accompanied with free energy decrease

(d) The reaction has to possess high activation energy

19. The correct relationship between free energy change in a reaction and the corresponding equilibrium constant K_c is **[AIEEE 2003]**

(a) $\Delta G = RT \ln K_c$ (b) $-\Delta G = RT \ln K_c$

(c) $\Delta G^o = RT \ln K_c$ (d) $-\Delta G^o = RT \ln K_c$

20. In an irreversible process taking place at constant T and P and in which only pressure-volume work is being done, the change in Gibbs free energy (dG) and change in entropy (dS), satisfy the criteria **[AIEEE 2003]**

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

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

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

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

21. The densities of graphite and diamond at 298 K are 2.25 and 3.31 $g\ cm^{-3}$, respectively. If the standard free energy difference (ΔG^o) is equal to 1895 $J\ mol^{-1}$, the pressure at which graphite will be transformed diamond at 298 K is **[CBSE PMT 2003]**

(a) $9.92 \times 10^5\,Pa$ (b) $9.92 \times 10^8\,Pa$

(c) $9.92 \times 10^7\,Pa$ (d) $9.92 \times 10^6\,Pa$

22. The free energy change for the following reactions are given below,

$$C_2H_2(g) + \frac{5}{2}O_2(g) \rightarrow 2CO_2(g) + H_2O(l); \Delta G^o = -1234\,kJ$$

$$C(s) + O_2(g) \rightarrow CO_2(g)\ \Delta G^o = -394\,kJ$$

$$H_2(g) + \frac{1}{2}O_2(g) \rightarrow H_2O(l)\ \Delta G^o = -237\,kJ$$

What is the standard free energy change for the reaction $H_2(g) + 2C(s) \rightarrow C_2H_2(g)$ **[Kerala (Med.) 2002]**

(a) – 209 kJ (b) – 2259 kJ

(c) + 2259 kJ (d) 209 kJ

23. The equilibrium concentration of the species in the reaction $A + B \equiv C + D$ are 3, 5, 10 and 15 $mole\ L^{-1}$ respectively at $300\,K$ the ΔG for the reaction is **[Pb. PMT 2004]**

(a) 13.81 (b) – 1381.8

(c) – 138.18 (d) 1391.6

24. Gibb's free enrgy (G) is defined as **[Pb. CET 2001]**

(a) $\Delta G = \Delta H - T\Delta S$ (b) $\Delta G = \Delta H + \frac{T}{\Delta S}$

(c) $\Delta H = \Delta G - T\Delta S$ (d) $\Delta G = \Delta H + T.C_p$

25. Standard enthalpy and standard entropy changes for the oxidation of ammonia at $298\,K$ are $-382.64\,kJ\,mol^{-1}$

and $-145.6\ JK^{-1}mol^{-1}$, respectively. Standard Gibbs energy change for the same reaction at $298\ K$ is **[CBSE PMT 2004]**

(a) – 439.3 kJ mol^{-1} (b) – 523.2 $kJ\ mol^{-1}$

(c) – 221.1 $kJ\ mol^{-1}$ (d) – 339.3 $kJ\ mol^{-1}$

26. For spontaneity of a cell, which is correct **[Orissa JEE 2004]**

(a) $\Delta G = 0, \Delta E = 0$

(b) $\Delta G = -ve, \Delta E = 0$

(c) $\Delta G = +ve, \Delta E = +ve$

(d) $\Delta G = -ve, \Delta E = +ve$

27. The free energy for a reaction having $\Delta H = 31400\ ca;$. $\Delta S = 32\ cal\ K^{-1}\ mol^{-1}$ at $1000\,^{\circ}C$ is **[Orissa JEE 2005]**

(a) – 9336 *cal* (b) – 7386 *cal*

(c) –1936 *cal* (d) + 9336 *cal*

28. The ΔH and ΔS for a reaction at one atmospheric pressure are +30.558 *kJ* and $0.066\ kJk^{-1}$ respectively. The temperature at which the free energy change will be zero and below of this temperature the nature of reaction would be **[Kerala CET 2005]**

(a) 483 *K*, spontaneous

(b) 443 *K*, non-spontaneous

(c) 443 *K*, spontaneous

(d) 463 *K*, non-spontaneous

(e) 463 *K*, spontaneous

CT Critical Thinking

Objective Questions

1. Adsorption of gases on solid surface is generally exothermic because **[IIT JEE (Screening) 2004]**

(a) Enthalpy is positive (b) Entropy decreases

(c) Entropy increases (d) Free energy increase

2. Two mole of an ideal gas is expanded isothermally and reversibly from 1 litre ot 10 litre at $300\,K$. The enthalpy change (in kJ) for the process is **[IIT JEE (Screening) 2004]**

(a) 11.4 *kJ* (b) –11.4 *kJ*

(c) 0 *kJ* (d) 4.8 *kJ*

3. Heat of neutralization of strong acid against strong base is constant and is equal to **[EAMCET 1980; AFMC 1989; DPMT 1991; MP PET 1999; BHU 1999; MP PMT 1995]**

(a) 13.7 *kcal* (b) 57 *kJ*

(c) $5.7 \times 10^4\ J$ (d) All of the above

4. The value of heat generated when 36.5 *gm* HCl and 40 *gm* of $NaOH$ reacts during neutralization **[NCERT 1984; CPMT 1993]**

(a) 76.5 *kcal* (b) 13.7 *kcal*

(c) More than 13.7 *kcal* (d) 108 kcal

5. When a gas undergoes adiabatic expansion, it gets cooled due to **[DCE 2002]**

(a) Loos of kinetic energy

(b) Fall in temperature

(c) Decrease in velocity

(d) Energy used in doing work

6. The heat content of a system is called

(a) Internal energy (b) Entropy

(c) Free energy (d) Enthalpy

7. To calculate the amount of work done in joules during reversible isothermal expansion of an ideal gas, the volume must be expressed in **[KCET (Med.) 2001]**

(a) m^3 only (b) dm^3 only

(c) cm^3 only (d) Any one of them

8. In an isobaric process, the ratio of heat supplied to the system (dQ) and work done by the system (dW) for diatomic gas is **[AFMC 2002]**

(a) 1 : 1 (b) 7 : 2

(c) 7 : 5 (d) 5 : 7

9. The enthalpy change for the reaction of 50.00 ml of ethylene with 50.00 ml of H_2 at 1.5 atm pressure is $\Delta H = -0.31\ kJ$. The value of ΔE will be **[DPMT 2004]**

(a) –0.3024 *kJ* (b) 0.3024 *kJ*

(c) 2.567 *kJ* (d) –0.0076 *kJ*

10. Enthalpy of solution of $NaOH$ (solid) in water is $-41.6\ kJ\ mol^{-1}$. When $NaOH$ is dissolved in water, the temperature of water **[UPSEAT 2004]**

(a) Increase (b) Decreases

(c) Does not change (d) Fluctuates indefinitely

11. In which of the following entropy decreases ? **[CPMT 1988, 94; MP PMT 2000]**

(a) Crystallization of sucrose from solution

(b) Rusting of iron

(c) Melting of ice

(d) Vaporization of camphor

12. For conversion C (graphite) $\rightarrow C$ (diamond) the ΔS is **[MP PMT 2001; MP PET 2003]**

(a) Zero (b) Positive

(c) Negative (d) Unknown

13. For a reaction $\Delta H = 9.08\ kJ\ mol^{-1}$ and

$\Delta S = 35.7\ JK^{-1}mol^{-1}$

Which of the following statements is correct for the reaction **[AMU (Engg.) 2000]**

(a) Reversible and Isothermal

(b) Reversible and Exothermic

(c) Spontaneous and Endothermic

(d) Spontaneous and Exothermic

14. For a reaction to occur spontaneously **[CBSE PMT 1995]**

(a) $(\Delta H - T\Delta S)$ must be negative

(b) $(\Delta H + T\Delta S)$ must be negative

(c) ΔH must be negative

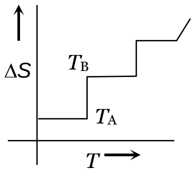
(d) ΔS must be negative

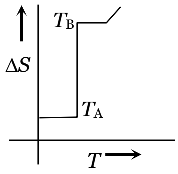
15. The total amount of energy in the universe is fixed, but **[AMU (Engg.) 1999]**

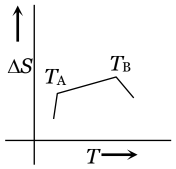
(a) Disorder is increasing (b) Lightning is increasing

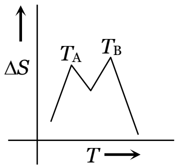
(c) Matter is increasing (d) Gravitation is decreasing

16. If for a given substance melting point is T_B and freezing point is T_A, then correct variation shown by graph between entropy change and temperature is **[DCE 2001]**

(a)


(b)


(c)


(d)


17. In endothermic reaction, the value of change in enthalpy (ΔH) is **[Pb. CET 2001]**

(a) Positive (b) Negative

(c) Zero (d) None of these

18. Which of the following would be expected to have the largest antropy per mole **[MP PMT 2004]**

(a) $SO_2Cl_2(s)$ (b) $SO_2Cl_2(g)$

(c) $SO_2Cl_2(l)$ (d) $SO_2(g)$

19. 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 **[KCET 2003]**

(a) $-2730\,kJ$ (b) $-462\,kJ$

(c) $-1365\,kJ$ (d) $+2730\,kJ$

20. Heat of reaction at constant volume is measured in the apparatus

(a) Bomb calorimeter (b) Calorimeter

(c) Pyknometer (d) Pyrometer

21. Which of the following gas has the highest heat of combustion

(a) Methane (b) Ethane

(c) Ethylene (d) Acetylene

22. The amount of heat measured for a reaction in a bomb calorimeter is **[AIIMS 1991]**

(a) ΔG (b) ΔH

(c) ΔE (d) $P\Delta V$

23. For an endothermic reaction where ΔH represents the enthalpy of the reaction in *kJ/mole*, the minimum value for the energy of activation will be

[IIT JEE 1992; MP PET 1993]

(a) Less than ΔH (b) Zero

(c) More than ΔH (d) Equal to ΔH

24. The heat of neutralization of a strong acid by a strong base is nearly equal to **[MP PET 1993; BCECE 2005]**

(a) $+57.32\,J$ (b) $-57.32\,kJ$

(c) $+13.7\,J$ (d) $-13.7\,kJ$

25. A Beckmann thermometer is used to measure

[Kurukshetra CEE 2002]

(a) High temperature (b) Low temperature

(c) Normal temperature (d) All temperature

26. The heat required to raise the temperature of a body by 1 *K* is called **[AIEEE 2002]**

(a) Specific heat (b) Thermal capacity

(c) Water equivalent (d) None of these

27. Mechanical work is specially important in system that contain **[Kerala (Med.) 2002]**

(a) Solid-liquid (b) Liquid-liquid

(c) Solid-solid (d) Amalgam

(e) Gases

28. "The quantity of heat which must be supplied to decompose a compound into its element is equal to the heat evolved during the formation of that compound from the elements." This statement is known as

(a) Hess's law

(b) Joule's law

(c) Le–chatelier's principle

(d) Lavoiser and Laplace law

29. Hess law deals with **[BHU 1979]**

(a) Changes in heat of reaction

(b) Rate of reaction

(c) Equilibrium constant

(d) Influence of pressure on volume of a gas

30. For which one of the following reactions, ΔH is not equal to ΔE **[IIT JEE 1995]**

(a) $H_{2(g)} + I_{2(g)} \rightleftharpoons 2HI_{(g)}$

(b) $C_{(s)} + O_{2(g)} \rightleftharpoons CO_{2(g)}$

(c) $N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)}$

(d) $HCl_{(aq)} + NaOH_{(aq)} \rightleftharpoons NaCl_{(aq)} + H_2O$

31. The heat liberated when 1.89 *g* of benzoic acid is burnt in a bomb calorimeter at $25\,^oC$ increases the temperature of 18.94 *kg* of water by $0.632\,^oC$. If the specific heat of water at $25\,^oC$ is 0.998 *cal/g-deg*, the value of the heat combustion of benzoic acid is **[CPMT 1999; BHU 2000]**

(a) 771.1 *kcal* (b) 871.2 *kcal*

(c) 881.1 *kcal* (d) 981.1 *kcal*

32. For a hypothetical reaction $A \rightarrow B$, the activation energies for forward and backward reactions are 19 *kJ/mole* and 9 *kJ/mole* respectively. The heat of reaction is

[CBSE PMT 2000]

(a) 28 *kJ* (b) 19 *kJ*

(c) 10 *kJ* (d) 9 *kJ*

33. The enthalpy of neutralization of HCN by $NaOH$ is $-12.13\,kJ\,mol^{-1}$. The enthalpy of ionisation of HCN will be **[BHU 1997]**

(a) 4.519 *kJ* (b) 45.10 *kJ*
(c) 451.9 *kJ* (d) 45.19 *kJ*

34. In thermodynamics, a process is called reversible when **[AIIMS 2001]**

(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

35. Which of the following unit represents largest amount of energy **[AMU 2001]**

(a) *Calorie* (b) *Joule*
(c) *Erg* (d) *Electron volt*

36. Which of the following will have the highest bond energy **[MP PMT 1990]**

(a) F_2 (b) Cl_2
(c) Br_2 (d) I_2

37. $C_{(\text{graphite})} + O_2(g) \rightarrow CO_2(g)$

$\Delta H = -94.05\ kcal\,mol^{-1}$

$C_{(\text{diamond})} + O_2(g) \rightarrow CO_2(g);\ \Delta H = -94.50\ kcal\,mol^{-1}$

therefore **[DPMT 2001]**

(a) $C_{(\text{graphite})} \rightarrow C_{(\text{diamond})}$; $\Delta H^o_{298\,K} = -450\ cal\,mol^{-1}$
(b) $C_{(\text{diamond})} \rightarrow C_{(\text{graphite})}$; $\Delta H^o_{298\,K} = +450\ cal\,mol^{-1}$
(c) Graphite is the stabler allotrope
(d) Diamond is harder than graphite

38. Enthalpy of formation of two compounds *x* and *y* are – 84 *kJ* and – 156 *kJ* respectively. Which of the following statements is correct **[CBSE PMT 2001]**

(a) *x* is more stable than *y*
(b) *x* is less stable than *y*
(c) Both *x* and *y* are unstable
(d) *x* and *y* are endothermic compounds

39. For the process dry ice $\longrightarrow CO_2(g)$ **[KCET 2000]**

(a) ΔH is positive while $\Delta\rho$ is negative
(b) Both ΔH and $\Delta\rho$ are negative
(c) Both ΔH and $\Delta\rho$ are positive
(d) ΔH is negative while $\Delta\rho$ is positive

40. For melting of 3 moles of water at $0^o C$ the ΔG^o is **[MP PMT 2001]**

(a) Zero (b) + *ve*
(c) – *ve* (d) Unpredictable

41. The equilibrium constant of a reaction at $298\,K$ is 5×10^{-3} and at $1000\,K$ is 2×10^{-5}. What is the sign of ΔH for the reaction **[Pb. CET 1998]**

(a) $\Delta H = 0$ (b) ΔH is negative
(c) ΔH is positive (d) None of these

42. Which of the following has lowest fusion temperature **[MP PET 2003]**

(a) Naphthalene (b) Diamond
(c) *NaCl* (d) *Mn*

43. Consider the reactions

$C(s) + 2H_2(g) \rightarrow CH_4(g), \Delta H = -x\ kcal$

$C(g) + 4H(g) \rightarrow CH_4(g), \Delta H = -x_1\ kcal$

$CH_4(g) \rightarrow CH_3(g) + H(g), \Delta H = +y\ kcal$

The bond energy of $C-H$ bond is **[JIPMER 1997]**

(a) $y\ kcal\,mol^{-1}$ (b) $x_1\ kcal\,mol^{-1}$
(c) $x/4\ kcal\,mol^{-1}$ (d) $x_1/4\ kcal\,mol^{-1}$

44. Given the bond energies $N\equiv N$, $H-H$ and $N-H$ bonds are $945, 436$ and $391\ kJ\,mole^{-1}$ respectively, the enthalpy of the following reaction $N_2(g) + 3H_2(g) \rightarrow 2NH_3(g)$ is **[EAMCET 1992; JIPMER 1997]**

(a) $-93\ kJ$ (b) $102\ kJ$
(c) $90\ kJ$ (d) $105\ kJ$

45. The relation between ΔG and E for a cell is $\Delta G = -nFE$; the cell reaction will be spontaneous if **[MP PET 1995]**

(a) G is negative (b) G is positive
(c) E is negative (d) E is positive

46. Which of the following is not a correct statement? **[AMU (Engg.) 2002]**

(a) When ΔG is negative, the process is spontaneous
(b) When ΔG is zero, the process is in a state of equilibrium
(c) When ΔG is positive, the process is non-spontaneous
(d) None of these

47. If at 298 *K* the bond energies of $C-H, C-C$, $C=C$ and $H-H$ bonds are respectively 414, 347, 615 and 435 *kJ* mol^{-1}, the value of enthalpy change for the reaction $H_2C=CH_2(g) + H_2(g) \rightarrow H_3C-CH_3(g)$ at 298 *K* will be **[AIEEE 2003]**

(a) + 250 *kJ* (b) – 250 *kJ*
(c) + 125 *kJ* (d) – 125 *kJ*

48. The equation

$\frac{1}{2}H_2 + \frac{1}{2}Cl_2 \rightarrow HCl$ ($\Delta H_{298} = -22060\ kcal$) means **[CMC Vellore 1991]**

(a) The heat absorbed when one gram molecule of HCl is formed from its elements at $25^o C$ is 22.060 *kcal*
(b) The heat given out when one gram molecule of HCl is formed from its elements at 298 *K* is 22.060 *kcal*
(c) The heat absorbed when one atom of hydrogen reacts with one atom of chlorine to form one molecule of HCl at $25^o C$ and one atmospheric pressure is 22.060 *kcal*

(d) The heat absorbed when one gram equivalent of HCl is formed from its elements at 298 K is 22.060 $kcal$

(e) The intrinsic heat of one molecule of HCl is 22.060 $kcal$ more than the intrinsic heats of one atom of hydrogen and one atom of chlorine

49. The $H_2O(g)$ molecule dissociates as

(i) $H_2O(g) \rightarrow H(g) + OH(g); \Delta H = 490\ kJ$

(ii) $OH(g) \rightarrow H(g) + O(g); \Delta H = 424\ kJ$

The average bond energy (in kJ) for water is

(a) 490 (b) 424
(c) 914 (d) 914/2

50. When $50\,cm^3$ of $0.2\,N\,H_2SO_4$ is mixed with $50\,cm^3$ of $1\,N\,KOH$, the heat liberated is **[KCET 2004]**

(a) 11.46 kJ (b) 57.3 kJ
(c) 573 kJ (d) 573 J

51. Following reaction occurring in an automobile $2C_8H_{18}(g) + 25O_2(g) \rightarrow 16CO_2(g) + 18H_2O(g)$. The sign of $\Delta H, \Delta S$ and ΔG would be **[CBSE PMT 1994; KCET 1999]**

(a) +, –, + (b) –, +, –
(c) –, +, + (d) +, +, –

52. For the reaction

$$H_2(g) + \frac{1}{2}O_2(g) \rightarrow H_2O(l), \Delta H = -285.8\ kJ\ mol^{-1}$$

$\Delta S = -0.163\,kJ\,mol^{-1}K^{-1}$. What is the value of free energy change at $27^\circ C$ for the reaction **[KCET 1999]**

(a) $-236.9\,kJ\,mol^{-1}$ (b) $-281.4\,kJ\,mol^{-1}$
(c) $-334.7\,kJ\,mol^{-1}$ (d) $+334.7\,kJ\,mol^{-1}$

AR Assertion & Reason

For AIIMS Aspirants

Read the assertion and reason carefully to mark the correct option out of the options given below :

(a) If both assertion and reason are true and the reason is the correct explanation of the assertion.
(b) If both assertion and reason are true but reason is not the correct explanation of the assertion.
(c) If assertion is true but reason is false.
(d) If the assertion and reason both are false.
(e) If assertion is false but reason is true.

1. Assertion : The enthalpy of formation of gaseous oxygen molecules at $298\,K$ and under pressure of $1\,atm$ is zero.
Reason : The entropy of formation of gaseous oxygen molecules under the same condition is zero. **[AIIMS 1996]**

2. Assertion : We feel cold on touching the ice.
Reason : Ice is a solid form of water. **[AIIMS 1999]**

3. Assertion : Entropy of ice is less than water.
Reason : Ice have cage like structure. **[AIIMS 2000]**

4. Assertion : The heat absored during the isothermal expansion of an ideal gas against vacuum is zero.
Reason : The volume occupied by the molecules of an ideal gas is zero. **[AIIMS 2002]**

5. Assertion : Absolute values of internal energy of substance can not be determined.
Reason : It is impossible to determine exact values of constituent energies of the substances. **[AIIMS 2002]**

6. Assertion : Mass and volume are extensive properties.
Reason : Mass / volume is also an extensive parameter. **[AIIMS 2002]**

7. Assertion : Molar entropy of vaporization of water is different from ethanol.
Reason : Water is more polar than ethanol.

8. Assertion : The increase in internal energy (ΔE) for the vaporiation of one mole of water at 1 atm and 373K is zero.
Reason : For all isothermal processes $\Delta E = 0$. **[AIIMS 2003]**

9. Assertion : ΔH and ΔE are almost the same for the reaction. $N_2(g) + O_2(g) \rightleftharpoons 2NO(g)$.
Reason : All reactants and products are gases. **[AIIMS 2003]**

10. Assertion : The enthalpies of neutralisation of strong acids and strong bases are always same.
Reason : Neutralisation is heat of formation of water. **[AIIMS 1996]**

11. Assertion : Zeroth law can also be termed as law of thermal equilibirum.
Reason : Two objects in thermal equilibrium with the third one, are in thermal equilibrium with each other.

12. Assertion : There is no reaction known for which ΔG is positive, yet it is spontaneous.
Reason : For photochemical reactions ΔG is negative.

13. Assertion : Heat of neutralisation of perchloric acid, $HClO_4$ with $NaOH$ is same as is that of HCl with $NaOH$.
Reason : Both HCl and $HClO_4$ are strong acids.

14. Assertion : Heat absorbed in a reaction at constant temperature and constant volume is $-\Delta G$.
Reason : ΔG should be negative for the reaction to be spontaneous.

15. Assertion : T, P and V are state variables or state functions.
Reason : Their values depends on the state of the system and how it is reached.

16. Assertion : Internal energy is an extensive property.
Reason : Internal energy depends upon the amount of the system.

17. Assertion : For the combustion reactions, the value of ΔH is always negative.

Reason : The combustions reactions are always endothermic.

18. Assertion : For an isothermal reversible process $Q = -w$ i.e. work done by the system equals the heat absorbed by the system.

Reason : Enthalpy change (ΔH) is zero for isothermal process.

19. Assertion : Enthalpy of formation of graphite is zero but of diamond is not zero.

Reason : Enthalpy of formation of most stable allotrope is taken as zero.

20. Assertion : If a refrigerator's door is kept open room gets cooled.

Reason : Material kept inside the refrigerator reamins cool.

21. Assertion : Enthalpy and entropy of any elementary substance in the standard state are taken as zero.

Reason : At zero degree absolute, the constituent particles become completely motionless.

22. Assertion : A process is called adiabatic if the system does not exchange heat with the surroundings.

Reason : It does not involve increase or decreae in temperature of the system.

Answers

Basic concepts

1	b	2	d	3	b	4	c	5	c
6	d	7	d	8	c	9	c	10	c
11	d	12	d	13	a	14	c	15	b
16	b	17	d	18	a	19	b	20	b
21	d	22	b	23	c	24	c	25	d
26	c	27	c	28	c				

First law of thermodynamics and Hess law

1	d	2	b	3	a	4	b	5	c
6	a	7	c	8	a	9	b	10	d
11	b	12	c	13	c	14	c	15	b
16	b	17	c	18	b	19	c	20	a
21	c	22	c	23	a	24	a	25	b
26	a	27	a	28	a	29	bc	30	c
31	b	32	c	33	b	34	a	35	c
36	b	37	c	38	b	39	d	40	c
41	d	42	a	43	c	44	a	45	c
46	c	47	b	48	c	49	d	50	b
51	a	52	d	53	b	54	c	55	a
56	b	57	d	58	d				

IInd & IIIrd Law of thermodynamics and Entropy

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

Heat of reaction

1	b	2	b	3	d	4	d	5	d
6	b	7	c	8	a	9	b	10	a
11	bcd	12	a	13	d	14	b	15	c
16	a	17	b	18	a	19	b	20	c
21	c	22	a	23	d	24	c	25	c
26	b	27	b	28	b	29	a	30	c
31	a	32	a	33	d	34	b	35	b
36	a	37	a	38	d	39	b	40	b
41	c	42	c	43	b	44	b	45	b
46	b	47	a	48	c	49	e	50	b
51	a	52	b	53	c	54	c	55	b
56	c	57	c	58	d	59	c	60	b
61	d	62	c	63	b	64	a	65	b
66	b	67	a	68	c	69	a	70	d
71	a	72	b	73	d	74	c	75	b
76	b	77	a	78	d	79	d	80	a
81	b	82	b	83	a	84	b	85	b
86	c	87	a	88	b	89	d	90	d
91	a	92	c	93	b	94	a	95	d
96	d	97	c	98	a	99	c	100	c
101	b	102	c	103	d	104	d	105	c
106	a	107	c	108	d	109	d	110	c
111	a	112	b	113	a	114	a	115	a
116	a	117	b	118	c	119	b	120	a
121	a	122	a	123	d	124	b	125	b
126	b	127	c	128	d	129	d	130	b
131	d	132	b	133	d	134	a	135	a
136	a	137	d	138	c	139	d	140	b
141	c	142	d	143	c	144	b	145	c
146	d	147	b	148	c	149	b	150	b
151	d	152	a	153	b	154	b	155	b
156	b	157	a	158	d	159	c	160	d
161	a	162	c	163	c	164	c	165	c
166	b	167	d	168	d	169	c	170	b
171	a	172	c						

Bond energy

1	b	2	a	3	a	4	d	5	c
6	c	7	b	8	d	9	b	10	b

Free energy and Work function

1	d	2	b	3	a	4	b	5	acd
6	c	7	c	8	c	9	a	10	a
11	d	12	a	13	d	14	d	15	b
16	d	17	b	18	c	19	d	20	b
21	b	22	d	23	b	24	a	25	d
26	d	27	a	28	d				

Critical Thinking Questions

1	b	2	c	3	d	4	b	5	b
6	d	7	d	8	b	9	a	10	a
11	a	12	c	13	c	14	a	15	a
16	a	17	a	18	d	19	b	20	a
21	b	22	c	23	c	24	b	25	b
26	b	27	e	28	d	29	a	30	c
31	a	32	c	33	d	34	ac	35	a
36	b	37	c	38	b	39	c	40	a
41	b	42	a	43	a	44	a	45	d
46	d	47	d	48	b	49	d	50	d
51	b	52	a						

Assertion & Reason

1	b	2	b	3	b	4	c	5	a
6	b	7	b	8	a	9	b	10	a
11	a	12	d	13	a	14	e	15	c
16	a	17	c	18	b	19	a	20	e
21	c	22	c						

AS Answers and Solutions

Basic concepts

1. (b) Internal energy of an ideal gas is a function of temperature only.

2. (d) In cyclic process, a system in a given state goes through a series of different processes, but in the end returns to its initial state.

4. (c) $\Delta E = 0$ for isothermal reversible cycle.

5. (c) In isolated system neither exchange of matter nor exchange of energy is possible with surroundings.

9. (c) It is the definition of calorific value.

11. (d) When a real gas is forced through a porous plug into a region of low pressure, it is found that due to expansion, the gas on the side of low pressure gets cooled.

The phenomenon of producing lowering of temperature when a gas is made to expand adiabatically from a region of high pressure into a region of low pressure is known as Joule-Thomson effect.

12. (d) In isothermal reversible process ideal gas has constant volume and so $\Delta E = 0$ and $\Delta H = \Delta E = 0$.

13. (a) The compressor has to run for longer time releasing more heat to the surroundings.

14. (c) This is based on Joule-Thomson effect.

15. (b) Enthalpy is an extensive property.

16. (b) $dV = 0$ for an isochoric process.

17. (d) Total energy of an isolated system is constant.

18. (a) For isochoric process $\Delta V = 0$ so $q_V = \Delta E$ i.e. heat given to a system under constant volume is used up in increasing ΔE.

19. (b) The less energy of a system and more is its stability.

20. (b) The functions whose value depends only on the state of a system are known as state functions.

21. (d) For adiabatic process $q = 0$.

22. (b) The intensive property is mass/volume.

23. (c) Volume is not an intensive property.

24. (c) An isolated system neither shows exchange of heat nor matter with surroundings.

25. (d) ΔQ is not a state function.

26. (c) For adiabatic process $\Delta Q = 0$.

27. (c) Work is not a state function as during a process its value depends on the path followed. The value of enthalpy, internal energy and entropy depends on the state and not on the path followed to get that state, hence these are state functions.

28. (c) Surface tension is an intensive property which do not depend upon the quantity of matter present in the system.

First law of thermodynamics and Hess law

1. (d) First low of thermodynamics is also known as Law of conservation of mass and energy.

2. (b) Formation of CO_2 from CO is an exothermic reaction; heat is evolved from the system, *i.e.*, energy is lowered. Thus, exothermic reactions occur spontaneously on account of decrease in enthapy of system. Thus, $\Delta E > \Delta H$.

4. (b) $\Delta H = \Delta E + P\Delta V$.

5. (c) $\Delta n_g = 1 - \frac{3}{2} = \frac{-1}{2}$, As Δn_g is negative, thus $\Delta H < \Delta E$.

6. (a) Bomb calorimeter is commonly used to find the heat of combustion of organic substances 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 $\Delta U = q$.

$\Delta U < 0$, $w = 0$

9. (b) $\Delta H = \Delta E + \Delta nRT$

Since $\Delta n = -2$

Than $\Delta H = \Delta E - 2RT$.

10. (d) If $\Delta n = -ve$ than $\Delta H < \Delta E$.

12. (c) Hess's law is an application of first law of thermodynamics .

13. (c) At constant P or T

$\Delta H = \Delta U + \Delta nRT \Rightarrow \Delta n = n_P - n_R = 2 - 4 = -2$

$\therefore \Delta H < \Delta U$.

16. (b) It is a combustion reaction, $\Delta H = -ve$.

17. (c) During isothermal expansion of ideal gas, $\Delta T = 0$

$\Delta H = \Delta E + P\Delta V = \Delta E + nR\Delta T = 0 + 0 = 0$.

18. (b) $W = 2.303\ nRT \log \frac{V_2}{V_1}$

$= 2.303 \times 1 \times 8.314 \times 10^7 \times 298 \log \frac{20}{10}$

$= 298 \times 10^7 \times 8.314 \times 2.303 \log 2$.

20. (a) The enthalpies of all elements in their standard state at $25^o C$ or $298K$ are zero.

21. (c) $\Delta E_V = E_P - E_R$.

22. (c) $\Delta E = q + w$.

23. (a) $\Delta E = 0$ for reversible isothermal process.

25. (b) Hess law includes initial reactants and final products.

26. (a) At constant T and P internal energy of ideal gas remains unaffected.

27. (a) ΔE increases with temperature.

28. (a) $\Delta H = \Delta E + W$ or $\Delta H = \Delta E + P\Delta V$.

29. (bc) Heat of neutralisation of a strong acid and strong base is equal to $-13.7\,kcal$.

30. (c) $-W = +2.303\,nRT \log \frac{p_1}{p_2}$

$-W = 2.303 \times 1 \times 2 \times 300 \log \frac{10}{1} = 1381.8\,cal.$

31. (b) Joule-Thomson expansion is isoenthalpic.

32. (c) Here $\Delta n = 0$ so, $\Delta E = \Delta H$.

33. (b) $q = \Delta E - W$ if $q = 0$ for adiabatic process, than $\Delta E = W$.

34. (a) For this reaction $\Delta n = 0$ than $\Delta E = \Delta H$.

35. (c) As the system is closed and insulated no heat enter or leave the system, *i.e.* $q = 0$; $\therefore \Delta E = Q + W = W$.

37. (c) $\Delta H - \Delta E = \Delta nRT$; $\Delta n = -3$

so, $\Delta H - \Delta E = -3RT$.

38. (b) According to Hess's law. The heat of reaction depends upon initial and final conditions of reactants.

39. (d) $\Delta H - \Delta E = \Delta nRT$

also, $2NH_{3(g)} \rightarrow N_{2(g)} + 3H_{2(g)}$

$\Delta n = 2$.

40. (c) $\Delta n = 0$ for this reaction so, $\Delta E = \Delta H$.

41. (d) $W = 0$ is not true.

42. (a) $W = 2.303\, nRT \log \frac{P_2}{P_1}$

$= 2.303 \times 1 \times 2 \times 300 \log \frac{10}{2} = 965.84$

at constant temperature, $\Delta E = 0$.

$\Delta E = q + w$; $q = -w = -965.84\, cal$.

43. (c) $q = 40\, J$

$w = -8\, J$ (work done by the system)

$\Delta E = q + w = 40 - 8 = 32\, J$.

44. (a) We know that $\Delta E = Q + W = 600 + (-300) = 300\, J$

$W = 300$, because the work done by the system.

45. (c) Given that

$P_1 = 10\, atm$, $P_2 = 1\, atm$, $T = 300\, K$, $n = 1$

$R = 8.314\, J/K/mol$

Now, by using

$W = 2.303\, nRT \log_{10} \frac{P_2}{P_1}$

$= 2.303 \times 1 \times 8.314 \times 300 \log_{10} \frac{1}{10}$

$W = 5744.1\, Joule$

46. (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, then its internal energy remains same.

47. (b) $PCl_5(g) \rightarrow PCl_3(g) + Cl_2(g)$

For this reaction $\Delta ng = 2 - 1 = 1$

Δng is positive, *i.e.*, there is an increase in the number of gaseous moles then $\Delta H > \Delta E$

48. (c) Enthalpy (H) is defined as the sum of internal energy $E + PV$, $H = E + PV$.

49. (d) $(CH_3)_2C = CH_2(g) + 6O_2(g) \rightarrow 4CO_2(g) + 4H_2O(l)$

$\Delta ng = 4 - 6 = -2$ (i.e., negative)

we know that $\Delta H = \Delta E + \Delta ngRT$

$= \Delta E - (\Delta ng)RT$ $(\because \Delta ng = -ve)$

$\therefore \Delta H < \Delta E$

50. (b) Given number of moles =1

Initial temperature $= 27^o C = 300\, K$

Work done by the system $= 3\, KJ = 3000\, K$

It will be $(-)$ because work is done by the system.

Heat capacity at constant volume $(Cv) = 20\, J/k$

We know that work done

$W = -nC_V(T_2 - T_1)$; $3000 = -1 \times 20\,(T_2 - 300)$

$3000 = -20T_2 + 6000$

$20T_2 = 3000$; $T_2 = \frac{3000}{20} = 150\, K$

51. (a) Internal energy of a system is a state function and extensive property and is independent of the path by which it is obtained.

52. (d) $N_2O_4(g) \rightarrow 2NO_2(g)$

For this reaction $\Delta ng = 2 - 1 = 1$

Δng is positive *i.e.*, there is an increase in the number of gaseous moles then $\Delta H > \Delta E$

53. (b) $2C + O_2 \rightarrow 2CO$; $\Delta H = -220\, KJ$

This reaction does not represent complete combustion of carbon, hence heat of combustion of carbon will not be equal to $110\, kJ$. The negative sign of ΔH indicates that this reaction is exothermic. Also, despite being spontaneous reaction, it requires initiation.

54. (c) $W = -P\Delta V = -1 \times 10^5 (1 \times 10^{-2} - 1 \times 10^{-3})$

$= -1 \times 10^5 \times 9 \times 10^{-3} = -900\, J$

55. (a) The exact value of internal energy is not known as it includes all type of energies of molecules constituting the given mass of matter such as translational, vibrational, rotational. The kinetic & potential energy of the nuclei & electron with in the individual molecules and the manner in which the molecule are linked together etc.

$E = E_{translational} + E_{rotational} + E_{vibrational}$

Thus, we can say that internal energy is partly potential and partly kinetic.

56. (b) $N_2(g) + O_2(g) \rightarrow 2NO(g)$; $\Delta n_g = 2 - 2 = 0$

$\Delta H = \Delta E + \Delta n_g RT$; $\Delta H = \Delta E + 0$; $\Delta H = \Delta E$

57. (d) $W = -p\Delta V$; $W = -3 \times (6 - 4)$

$W = -6 \times 101.32$ $(\therefore 1\, L\, atm = 101.32\, J)$

$W = -608\, J$

58. (d) $A(s) + 3B(g) \rightarrow 4C(s) + D(l)$

$\Delta ng = 0 - 3 = -3$; $\Delta H = \Delta E + \Delta ngRT$ $[\because \Delta E = \Delta U]$

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

$\Delta H = \Delta U - 3(RT)$; $\Delta H = \Delta U - 3RT$

IInd & IIIrd Law of thermodynamics and Entropy

2. (d) When $\Delta S = +ve$ the change is spontaneous.

3. (d) Heat is always flow from the higher to lower temperature.

4. (b) Mixing of non-reacting gases increases randomness and so increase entropy .

5. (b) Entropy of the system increases as the process occur irreversibly and isothermally in an isolated system.

6. (d) $\Delta S^o = 2S^o_{HCl} - (S^o_{H_2} + S^o_{Cl_2})$

$= 2 \times 186.7 - (130.6 + 223.0) = 19.8\ JK^{-1} mol^{-1}$

9. (b) For adiabatic expansion $q = 0$ than according to following relation $\Delta S = \frac{q}{T}, \Delta S = 0$.

10. (c) It is the third law of thermodynamics.

11. (c) Entropy of gases is highest.

12. (c) $\Delta G = \Delta H - T\Delta S$

for spontaneous process ΔG *should be negative in option (3)* $\Delta H = -ve$ and $\Delta S = +ve$ *than*

$\Delta G = (-ve) - T(+ve) \ = -ve$

15. (c) For reverse reaction sign will be change.

16. (b) Solid $\longrightarrow$ Gas, ΔS is maximum.

17. (d) $+ve\ \Delta H$ and $-ve\ \Delta S$ both oppose the reaction.

18. (a) $\Delta S_{vap} = 186.5/373 = 0.5\ JK^{-1}\ mol^{-1}$.

20. (a) When ΔH = –*ve*, ΔS = +*ve* and ΔG = –*ve* than reaction is spontaneous .

21. (d) For endothermic process ΔS increases.

22. (c) Calculation of change in entropy is done at constant temperature and pressure both.

23. (a) When the value of entropy is greater, then ability of work is maximum.

24. (d) At equilibrium, ΔG = 0

Hence 0 = $\Delta H - T\Delta S$ or $\Delta H = T\Delta S$.

25. (c) $\Delta S_{vap} = \frac{\Delta H_{vap}}{T} = \frac{37.3\ KJ\ mol^{-1}}{373\ K}$

$= 0.1\ kJ\ mol^{-1}\ K^{-1} = 100\ \ J\ mol^{-1}\ K^{-1}$.

26. (d) Solid $\rightarrow$ Liquid, ΔS increases .

27. (c) $\Delta S = +ve$ than process is spontaneous.

28. (b) $\Delta S = +ve$ than the system is more disordered.

29. (c) Because solid $\rightarrow$ solid, ΔS is same and ΔH is –*ve*.

30. (b) $\Delta S_{vap} = \frac{\Delta H_{vap}}{T} = \frac{386}{298} = 1.2\ kJ$.

31. (b) Processes (a) and (c) take place with the increase of no. of moles of gaseous species and hence the disorder or entropy increases. (b) on increasing pressure, disorder or randomness decreases and so also the entropy (d) is endothermic process and ΔS is positive.

32. (d) This is the statement of third law of thermodynamics.

33. (d) For isothermal expansion of ideal gas, $\Delta E = 0$.

34. (a) $\Delta S_{vap} = \frac{(900 \times 18)}{373} = 43.4\ \ JK^{-1}\ mol^{-1}$.

35. (c) Entropy of the mixture increases due to increase in impurity.

37. (c) If $\Delta H = +ve$ and $\Delta S = -ve$ than the reaction is non-spontaneous *i.e.* can not occur.

38. (a) $T_2 = 150 + 273 = 423\ K$

$T_1 = 25 + 273 = 298\ K$

$Q = 500\ K$

$\frac{W}{Q} = \frac{T_2 - T_1}{T_2}$; $W = 500\left(\frac{423 - 298}{423}\right) = 147.7\ J$.

39. (c) According to III law of thermodynamics.

40. (c) When $\Delta H = +ve$ and $\Delta S = -ve$ reaction is non-spontaneous.

41. (c) $T_m = \frac{\Delta H_{\text{fusion}}}{\Delta S_{\text{fusion}}} = \frac{9.2}{0.008} = 1150\ K$.

42. (c) Here: Change in

Volume $(V) = 500 - 300 = 200\,cc = 0.2\,litre,$

Pressure $(P) = 0.6\,atm$ and heat liberated (q) = 10*J*

Work done $(W) = P\Delta V = (0.2 \times 0.6) = 0.12\,litre - atm$

But $1\,litre - atm = 101.3\,J$.

hence $W = 0.12 \times 101.3 = 12.156\ J$. We also know that heat is liberated, therefore it would be negative. Thus change in $\Delta E = q + W = -10 + 12.16 = 2.16\ J$.

43. (c) Formation of CO_2 is,

$C_{(s)} + O_{2(g)} \rightarrow CO_{2(g)}$

$\Delta S^o = 213.5 - 5.690 - 205 = 2.81\ JK^{-1}$.

45. (b) $H_2O_{(g)} \rightleftharpoons H_2O_{(l)}$

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

at equilibrium $\Delta G = 0$

Therefore $\Delta H = T\Delta S$.

46. (a) We know that work done, $W = C_v(T_1 - T_2)$

$3 \times 1000 = 20\,(300 - T_2)$; $\therefore 3000 = 6000 - 20\,T_2$

$\therefore T_2 = \frac{3000}{20} = 150\ K$.

48. (d) It does not violates the first law of thermodynamics but violates the II law of thermodynamics.

49. (d) $C_v = \frac{3}{2}RT;\ C_p = \frac{5}{2}RT$ for monoatomic gas

$C_v = \frac{5}{2}\text{RT}; C_p = \frac{7}{2}RT$ for diatomic gas

Thus for mixture of 1 *mole* each,

$C_v = \frac{\frac{3}{2}RT + \frac{5}{2}RT}{2}$ and $C_p = \frac{\frac{5}{2}RT + \frac{7}{2}RT}{2}$

Therefore, $C_p / C_v = \frac{3RT}{2RT} = 1.5$.

51. (c) $\Delta S = \frac{q_{rev}}{T}$ $\therefore$ unit of S is $JK^{-1}mol^{-1}$.

52. (b) $H_2O_{(l)} \rightleftharpoons H_2O_{(g)}$, $\Delta S = \frac{\Delta H_{vap}}{T}$,

$\Delta H_{vap.} = 2.257\ KJ/g$

or $\Delta H_{vap} = 2.257 \times 18\ kJ/mol. = 40.7\ KJ/mol$

hence, $\Delta S = \frac{40.7}{373} = 0.109\ kJ/mol/K.$

53. (a) Liquid $\longrightarrow$ Vapour, entropy increases.

54. (c) $NaNO_3$ is a solid, which is converted to liquid ions.

55. (c) Heat capacity of water per gram $= \frac{75}{18} = 4.17\,J$

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

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

56. (c) As the work is done on system, it will be positive *i.e.* $W = +462$ *joule*, $E = -128$ *joule* (heat is evolving)

From the Ist law of thermodynamics

$\Delta E = q + w = (-128) + (+462) = +334$ *Joules*.

57. (a) Gases show highest entropy.

58. (b)

$$\underset{S^o(298\,K)K^{-}mol^{-1}}{} \quad H^+{}_{(aq)} + \underset{-10.7}{OH^-{}_{(aq)}} \rightarrow \underset{+70}{H_2O_{(l)}}$$

$\Delta S^o(298\,K) = \Delta S_P - \Delta S_R = 70 - (-10.7 + 0)$

$80.7\ JK^{-1}\ mol^{-1}$

59. (d) The entropy change $= \frac{\text{heat of vaporisation}}{\text{temperature}}$

Here, heat of vaporisation $= 540\ cal/gm$

$= 540 \times 18\ cal\,mol^{-1}$

Temperature of water $= 100 + 273 = 373\,K$

$\therefore$ entropy change $= \frac{540 \times 18}{373} = 26.06\ cal\,mol^{-1}K^{-1}$

60. (b) Given that, $T_1 = 500\,K$, $T_2 = 300\,K$

By using, $\eta = \frac{T_1 - T_2}{T_1} = \frac{500 - 300}{500} = \frac{200}{500} = 0.4$.

61. (b) It is molar heat capacity.

62. (d) Entropy is the measure of randomness in the molecules. Randomness is maximum in case of gases. Hence, entropy is maximum for water vapours.

63. (a) Standard entropy of formation of $CO_2(g) =$ standard entropy of $CO_2(g) -$ [Standard entropy of $C(s) -$ standard entropy of $O_2(g)$]

$= 213.5 - [5.740 + 205] = 2.76\ J/K$.

64. (c) Third law of thermodynamics help in calculating entropy of different temperatures.

65. (a) In case of gas randomness is maximum therefore entropy is maximum in case of steam.

66. (c) $\Delta S_{system} + \Delta S_{surroundings} > O$ (for spontaneity)

Because of $\Delta S = R \ln \frac{V_2}{V_1}$

Here the volume of gas increase from V_1 to V_2 at constant temperature T.

The total increase in entropy of the system and its surrounding during the spontaneous process of expansion considered above is, thus $R \ln\left(\frac{V_2}{V_1}\right)$ since $V_2 > V_1$ it is obvious that the spontaneous (irreversible) isothermal expansion of a gas is accompanied by an increase in the entropy of the system and its surrounding considered together.

$\Delta S_{system} + \Delta S_{surroundings} > 0$.

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

at constant temperature and pressure $\Delta G = 0$

$0 = \Delta T - T\Delta S$ so $\Delta H = T\Delta S$

68. (b) $dS = \frac{dQ_{rev.}}{T}$; $T = \frac{30 \times 10^3}{75}$; $T = 400\,K$

Heat of reaction

1. (b) $C + O_2 \rightarrow CO_2 + 94.2\ Kcal.$ .....(i)

$H_2 + \frac{1}{2}O_2 \rightarrow H_2O + 68.3\ Kcal.$ ....(ii)

On multiplication of *eq*. (ii) by 2 and than adding in *eq*. (i)

$C + 2H_2 + 2O_2 \rightarrow CO_2 + 2H_2O + 230.8\ Kcal$ ...(iii)

On subtracting *eq*. (iii) by following *eq*.

$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O + 210.8\ Kcal.$ we get,

$C + 2H_2 \rightarrow CH_4\ \ \Delta H = 20\ Kcal.$

2. (b) $\Delta S = 16\,J\,mole^{-1}K^{-1}$

$T_{b.p.} = \frac{\Delta H_{\text{vapour}}}{\Delta S_{\text{vapour}}} = \frac{6 \times 1000}{16} = 375\,K$

4. (d) Heat of neutralisation between strong acid and a strong base is about $-13.7\,Kcal.$

6. (b) Effect of temperature in heat of reaction is given by Kirchoff's equation.

7. (c) Heat of neutralisation between strong acid and a strong base is about $-13.7\,Kcal.$

8. (a) For exothermic reactions $H_p < H_R$.

For endothermic reactions $H_p > H_R$.

9. (b) 78*g* of benzene on combustion produces heat = – 3264.6 *kJ*

$\therefore 39\,g$ will produce $= \frac{-3264.6}{2} = -1632.3\,kJ$.

10. (a) *eq*. (i) + *eq*. (ii) gives the required result.

11. (bcd) (b,c,d) are endothermic reactions because they proceeds by the absorption of heat.

12. (a) Change of liquid to vapour takes energy in the form of heat so it is endothermic reaction.

13. (d) In exothermic reactions heat is evolute.

15. (c) $\Delta H = -ve$ for exothermic reaction.

$\Delta H = +ve$ for endothermic reaction

Enthalpy of fusion is + *ve*.

16. (a) Heat of neutralisation will be less than $-57.33\ kJ/mole$ because some amount of this energy will be required for the dissociation of weak base (MgO)

18. (a) $H_2 + O_2 \to H_2O_2 \quad \Delta H_f^o = -188\ kJ/mole$ ....(i)

$H_2 + \frac{1}{2}O_2 \to H_2O \quad \Delta H_f^o = -286\ kJ/mole$ ....(ii)

eq. (i) – eq. (ii) × 2 gives the required result.

19. (b) Graphite $\longrightarrow$ diamond $\Delta H_t = (x-y) kJ\ mol^{-1}$.

21. (c) Heats of combustions are always exothermic except oxidation of N as,

$N_2 + \frac{1}{2}O_2 \to N_2O \quad \Delta H = +ve$

$N_2 + O_2 \to 2NO \quad \Delta H = +ve$

22. (a) For exothermic reactions $H_p < H_R$.

For endothermic reactions $H_p > H_R$.

23. (d) Aim: $2C + H_{2(g)} \to C_2H_{2(g)}$.

eq. (ii) + eq. (iii) → eq. (iv) – eq. (i)

find the required result.

24. (c) Enthalpy of formation of *HCl*.

25. (c) Heat of neutralisation between strong acid and a strong base is about $-13.7\ Kcal$.

26. (b) For endothermic reaction, $\Delta H = +ve$.

27. (b) Heat of neutralisation is less than 56.1 *Kcal* when a strong base and a weak acid reacts.

28. (b) Aim: $CO + \frac{1}{2}O_2 \to CO_2$

$$\Delta H = \Delta H_f^0(CO_2) - \left[\Delta H_f^0(CO) + \frac{1}{2}\Delta H_f^0(O_2)\right]$$

$= -94.0 - (-26.4) = -67.6\ kcal.$

29. (a)

(i) $H_2 + \frac{1}{2}O_2 \to H_2O, \Delta H = -241\ kJ$

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

(iii) $C_6H_{12} + 9O_2 \to 6CO_2 + 6H_2O, \Delta H = -3920\ kJ$

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

Eq. (i) + Eq. (ii) – Eq. (iii)

$\Delta H = -241 - 3800 - (-3920)$

$= -4041 + 3920 = -121\ kJ$

30. (c) NH_4OH is a weak base. Heat of neutralisation < 13.7*kcal*.

31. (a) CH_4 is the best fuel because its calorific value $= \frac{-212.8}{16} = -13.3\ kcal/g$ is higher among the other gases.

32. (a) Find ΔH for $CH_4 + 2O_2 \to CO_2 + 2H_2O_{(g)}$.

34. (b) In neutralisation of a strong acid and base only H^+ and OH^- ions react.

35. (b) When both acid and base are strong than heat of neutralisation is $57.1\ kJ\ mol^{-1}$.

36. (a) $C_2H_6 + \frac{7}{2}O_2 \to 2CO_2 + 3H_2O$ substitute the values.

37. (a) Decomposition is an endothermic process.

38. (d) ΔH for this reaction is Heat of reaction.

40. (b) One mole of H_2O is formed from its initial components.

41. (c) One mole of a substance is completely oxidized in air.

42. (c) *S* (rhombic) $+O_2 \to SO_2$, $\Delta H = 70960\ cal.$ ...(i)

S (monoclinic) $+O_2 \to SO_2 \quad \Delta H = 71030\ cal$ ...(ii)

Aim: S (rhombic) → *S* (monoclinic)

eq. (i) – *eq*. (ii) gives the required result.

43. (b) When $H_2O_{(l)}$ is convert to form $H_2O_{(g)}$, heat is absorbed hence $\Delta H_1 > \Delta H_2$.

44. (b) Out of given substances, kerosene oil has maximum calorific value.

45. (b) $C_{(S)} + O_{2(g)} \to CO_{2(g)}$, $\Delta n_g = 1 - 1 = 0$

$\therefore \Delta E = \Delta H = -94\ kcal$

$\Delta E = E_{CO_2} - (E_C + E_{O_2}) = E_{CO_2} - (0+0)$

or $E_{CO_2} = \Delta E = -94\ kcal.$

46. (b) 0.2 *mole* will neutralize 0.2 mole of HNO_3, heat evolved $= 57 \times 0.2 = 11.4\ kJ.$

47. (a) Suppose heat evolved in Ist case is Q_1 and that in the IInd case it is Q_2. Then $Q_2 = \frac{1}{2}Q_1$.

But $Q_1 = 1000\ T_1$ and $Q_2 = 500\ T_2$

$\therefore 500\ T_2 = \frac{1}{2} \times 1000\ T_1$ *i.e.* $T_2 = T_1$.

48. (c) Enthalpy of a compound = Heat of reaction of that compound.

49. (e) It is the definition of heat of neutralization.

50. (b) $\Delta H = -ve$ for exothermic compound.

51. (a) If acid or base or both are strong, heat of neutralization $= 13.7\ kcal.$

52. (b) Both NH_4OH and CH_3COOH are weak.

53. (c) $57.1 \times 0.25 = 14.3\ kJ\ mol^{-1}$.

54. (c) Heat of formation is for 1 *mole*.
Hence $\Delta H_f^0(HI) = -12.40/2 = -6.20\,kcal.$

55. (b) Chemical dissociations are reversible and endothermic.

57. (c) Given,
(i) $CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$, $\Delta H = +20\ kcal$
(ii) $C + O_2 \rightarrow CO_2$, $\Delta H = -40\ kcal.$
(iii) $H_2 + \frac{1}{2}O_2 \rightarrow H_2O$, $\Delta H = -10\ kcal.$
Aim: $C + 2H_2 \rightarrow CH_4$
(ii) + 2 × (iii) – (i) gives.
$\Delta H = -40 + 2(-10) - (+20) = -80\ kcal.$

58. (d) For exothermic reaction heat is evolved.

59. (c) $H_2O_{(l)} \xrightarrow{\text{electrolys is}} H_{2(g)} + \frac{1}{2}O_{2(g)}$.

61. (d) All other are combustion phenomena.

62. (c) $\Delta H_{\text{combustion}}$ = –*ve*, so exothermic process.

63. (b) Aim: $K_{(S)} + \frac{1}{2}O_{2(g)} + \frac{1}{2}H_{2(g)} \rightarrow KOH_{(S)}$
eq. (ii) + *eq*. (i) – *eq*. (iii) gives
$\Delta H = -48 + (-68.39) - (-14) = -68.39 - 48 + 14$.

64. (a) By definition of heat of formation.

68. (c) $C_D \rightarrow C_G, \Delta H = -453.5\ cal.$
i.e. energy of C_G is less and thus more stable.

69. (a) $\Delta H_{\text{combustion}}$ is always negative .

70. (d) $\Delta H_{\text{reaction}} = \Delta H_f^0(N_2O_4) - 2\Delta H_f^0(NO_2)$
$= 2 - 2(8) = -14\ kcal.$

71. (a) $\Delta H - \Delta E = \Delta nRT = 3 \times 8.314 \times 298$
$= -7432\ J = -7.43\,kJ.$

72. (b) Aim: $C_{(\text{graphite})} \rightarrow C_{(\text{diamond})}$; *eq*. (i) – (ii) gives the result.

73. (d) In the formation of a compound, more the heat absorbed, less stable is the compound.

74. (c) $C_{(\text{graphite})} + 2H_{2(g)} = CH_{4(g)}$.

75. (b) Heat of formation is the formation of one mole of the substance from its elements.

76. (b) $\Delta H_{(\text{reaction})} = 2\Delta H_f^0(MgO) = -\Delta H_f^0(SiO_2)$
$= 2(-34.7) - (-48.4) = -21\,kJ.$

77. (a) *eq*. (i) + *eq*. (ii) + *eq*. (iii) gives
$X = 131 - 282 - 242 = -393\,kJ$.

78. (d) It is the definition of heat of transition.

79. (d) $C_{(\text{graphite})} \rightarrow C_{(\text{diamond})}, \Delta H = 1.9\,kJ$
$C_{(\text{graphite})} + O_2 \rightarrow CO_2, \Delta H = -\Delta H_1$
$C_{(\text{diamond})} + O_2 \rightarrow CO_2, \Delta H = -\Delta H_2$
$(-\Delta H_1) - (-\Delta H_2) = 1.9\,kJ$ or $\Delta H_2 = \Delta H_1 + 1.9$
For combustion of $6g, \Delta H_2 > \Delta H_1$ by $1.9/2 = 0.95\,kJ.$

80. (a) $H_{\text{product}} \times H_{\text{reactant}}$ for exothermic reaction.

81. (b) Due to high electron affinity of *Cl* the highest energy is evolved.

82. (b) $CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$
Molecular weight of $CH_4 = 12 + 4 = 16$
∴ On the combustion of 2.0*gm* of methane= 25.0 *kcal*
∴ On the combustion of $16.0gm = \frac{25 \times 16}{2} = 200\ kcal.$

83. (a) $CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$.

84. (b) $C_2H_4 + 3O_2 \rightarrow 2CO_2 + 2H_2O$
$\Delta H_{\text{reaction}} = [2 \times \Delta H_f^o(CO_2) + 2 \times \Delta H_f^o(H_2O)]$
$-[\Delta H_f^o(C_2H_4) + 3 \times \Delta H_f^o(O_2)]$
$= [2(-394) + 2(-286)] - [52 + 0] = -1412\ kJ$.

85. (b) $C + O_2 \rightarrow CO_2 + 394\ kJ$.
$2C + 2O_2 \rightarrow 2CO_2 + 788\ kJ$ ....(i)
$2CO + O_2 \rightarrow 2CO_2 + 569\ kJ$ ....(ii)
$2CO_2 \rightarrow 2CO + O_2 - 569\ kJ$ .....(iii)
eq. (i) + *eq*. (iii) = –109.5 *kJ mol*$^{-1}$.

86. (c) $\Delta H_f = \frac{44}{2}kcal = 22\ kcal$.

87. (a) $CaO_{(s)} + H_2O_{(l)} \rightarrow Ca(OH)_2$ is exothermic.

88. (b) $\Delta H = -ve$ in exothermic reaction.

89. (d) According to the definition of heat of formation.

90. (d) Multiplying *eq*. (ii) by (iii) and *eq*. (iii) by (vi), and then add
$6C + 3H_2 + \frac{15}{2}O_2 \rightarrow 6CO_2 + 6H_2O; \Delta H = 3218.7$
Subtract *eq*. (i) from the above equation and find the required result.

91. (a) *HF* is more stable than *HCl.*

92. (c) $\Delta H(H_P - H_R) = q_p$.

93. (b) $\Delta H = +ve$ for endothermic reaction.

94. (a) $\Delta H = \frac{13.95 \times 44}{2.2016} = 278.7\ kcal$.

95. (d) *eq*. (i) + *eq*. (ii) gives the required result.

96. (d) Standard molar heat enthalpy (H^o) of a compound is equal to its standard heat of formation from most stable states of initial components.

97. (c) In the complete combustion of butanol $\Delta H > \Delta E$.

98. (a) *X* – *Y* and find the required result.

99. (c) $S + O_2 \rightarrow SO_2$ $\Delta H = -298.2\ kJ$ ....(i)
$SO_2 + \frac{1}{2}O_2 \rightarrow SO_3$ $\Delta H = -98.2\ kJ$ ....(ii)
eq. (i) – (ii) and find the required result.

100. (c) $C + 2S \rightarrow CS_2$ $\Delta H = ?$
$C + O_2 \rightarrow CO_2$ $\Delta H = -393.3\ kJ$ ....(i)
$S + O_2 \rightarrow SO_2$ $\Delta H = -293.72\ kJ$ .....(ii)

$CS_2 + 3O_2 \rightarrow CO_2 + 2SO_2 \quad \Delta H = -1108.76\,kJ$ .....(iii)

eq. (ii) × 2 + *eq*. (i) – (iv) *eq*. (iii) – *eq*. (iv) and find required result .

101. (b) Fermentation is exothermic reaction.

102. (c) $CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$.

103. (d) Use $\Delta H = \Delta E + \Delta n RT$

$\Delta H = 19 + 2 \times 2 \times 10^{-3} \times 300 = 20.2\,kcal$; $\Delta n = 2$.

104. (d) $-20.6 - 8.8\,KJ\,mol^{-1} = -29.4\ kJ$.

106. (a) Subtract equation (ii) from (i).

107. (c) $CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O, \Delta H = -890.4\,kJ$ ....(i)

$C + O_2 \rightarrow CO_2,\ \Delta H = -395.5\,kJ$ .....(ii)

$C + O_2 \rightarrow CO_2,\ \Delta H = -395.5\,kJ$ .....(ii)

$H_2 + \frac{1}{2}O_2 \rightarrow H_2O,\ \Delta H = -285.8\,kJ$ .....(iii)

from (i), (ii), (iii).

$\Delta H_{comb.}(CH_4)$

$= \Delta H_f(CO_2) + 2\Delta H_f(H_2O) - \Delta H_f(CH_4) - 2\Delta H_f(O_2)$

$= -890.4 = -395.5 + 2(-285.5) - \Delta H_f(CH_4) - 2 \times 0$

$\Delta H_f(CH_4) = -76.7\,kJ\,mol^{-1}$.

108. (d) As methanoic acid is weak acid, heat of neutralization < *x*.

109. (d) Neutralization of a strong acid by a strong base is always same.

110. (c) $S + O_2 \rightarrow SO_2,\ \Delta H_f = -4.6\,kJ$

∵ 0.5 *gm*. of sulphur on burning produce 1*gm* of SO_2

∴ 32 *gm* of sulphur on burning produce 64 *gm*.. of SO_2

$\therefore \Delta H = (-4.6\,kJ) \times 64 = -294.4\,kJ$.

111. (a) $3O_2 \rightleftharpoons 2O_3$ – energy is given out.

112. (b) $\Delta H\ per\ 1.6g = \frac{72 \times 1.6}{180} = 0.64\ kcal$.

113. (a) $C + O_2 \rightarrow CO_2,\ \Delta H = -394\ kJ$ .....(i)

$2H_2 + O_2 \rightarrow 2H_2O,\ \Delta H = -568\ kJ$ ....(ii)

$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O,\ \Delta H = -892\,kJ$ .....(iii)

(i) + (ii) – (iii) and find the required result.

115. (a) No doubt heat evolved during neutralisation of $250\ cm^3$ of each acid and base is five time the heat evolved during neutralisation of $50\ cm^3$ of each acid and base but the quantity if solution taking heat is also five time thus same temperature rise is noticed.

116. (a) $H_2 + \frac{1}{2}O_2 \rightarrow H_2O_{(l)};\ \Delta H = -285.8\,KJ$

$H_2O_{(l)} \rightarrow H_2O_{(g)};\ \Delta H = 44\ KJ$

$\therefore H_2 + \frac{1}{2}O_2 \rightarrow H_2O_{(g)};\ \Delta H^o = -241.8\,KJ$

117. (b) Given: Weight of iron burnt $= 4g$; Heat liberated $= 29.28\ KJ$ and atomic weight of iron $(Fe) = 56$. We know that in ferric oxide (Fe_2O_3), 2 *moles* of iron or $2 \times 56 = 112\ gram$ of iron are burnt. We also know that when 4*grams* of iron are burnt, then heat liberated = 29.28 *kJ*, therefore when 112 *grams* of the iron are burnt, then heat liberated $= \frac{29.28 \times 112}{4} = -819.8\,kJ$ (Minus sign due to liberation of heat).

118. (c) $H^+ + OH^- \rightarrow H_2O,\ \Delta H_{\text{neutralization}} = 13.7\,kcal$.

119. (b) $\Delta H / mole$ of $FeS = \frac{3.77 \times 56}{2.1} = 100.5$.

120. (a) Heat of formation $= \frac{194}{2} = 97\,kJ$.

121. (a) $\Delta H = \Delta H_{\text{ioniz}} + \Delta H_{neu} = -50.6 = \Delta H_{\text{ioniz}} + (-55.9)$

$\Delta H_{\text{ioniz}} = +5.3\,kJ/mol$.

122. (a) Strong acid (HNO_3) and strong base $(LiOH)$.

123. (d) $\Delta H = \Delta E + \Delta nRT$ or $\Delta E = \Delta H - \Delta nRT$

$\therefore \Delta E = +7.3 - \frac{1}{2} \times 0.002 \times 298 = 7.3 - 0.298 = 7\ kcal.$

124. (b) Heat evolved during burning of $39g$

$C_6H_6 = \frac{781.0 \times 39}{78} = 390.5\,kcal\,mol^{-1}$

125. (b) By (i) + (ii) ; $Na + \frac{1}{2}Cl_2 \rightarrow NaCl,\ \Delta H = -196\ kcal$.

126. (b) $C + O_2 \rightarrow CO_{2(g)},\ \Delta H_f^o = -393.5\,kJ\,mol^{-1}$ ....(i)

$C + \frac{1}{2}O_2 \rightarrow CO_{(g)},\ \Delta H_f^o = -110.5\,kJ\,mol^{-1}$ ....(ii)

$H_2 + \frac{1}{2}O_2 \rightarrow H_2O_{(g)},\ \Delta H_f^o = -241.8\,kJmol^{-1}$ ...(iii)

By (ii) + (iii) – (i)

$CO_{2(g)} + H_{2(g)} \rightarrow CO_{(g)} + H_2O_{(g)},\ \Delta H = +41.2$.

127. (c) More +*ve* is ΔH_s more is heat of solution.

128. (d) CS_2 is formed from its initial components carbon and sulphur so, ΔH is heat of formation of CS_2 .

129. (d) $\Delta H = 18500 = \Delta E + \Delta nRT$

or $18500 = \Delta E + (-1) \times 2 \times 298 = 19096\ cal$.

130. (b) Heat evolved during combustion of 0.39*g*

$C_6H_6 = \frac{3250 \times 0.39}{78} = 16.25\,kJ.$

131. (d) By (i) – (ii) : $C + \frac{1}{2}O_2 \rightarrow CO;\ \Delta H = -229.2.$

132. (b) Strong acid (HCl) and strong base $(NaOH)$ shows $\Delta H_{\text{neutralization}}$ = –57.3 *kJ*.

133. (d) By (i) – (ii) and find required result.

134. (a) $CO_{(g)} + \frac{1}{2}O_{2(g)} \to CO_{(g)}, \Delta n = 1 - 1 + \frac{1}{2} = -\frac{1}{2}$

$\Delta H = \Delta E + \Delta nRT$

$\Delta H = -283.3 - \frac{1}{2} \times \frac{8.314}{1000} \times 290 = -284.5 kJ$.

135. (a) $H_2 + \frac{1}{2}O_2 \to H_2O \quad \Delta H = -188\ kJ/mole$ ....(i)

$H_2 + O_2 \to H_2O_2; \ \Delta H = -286\ kJ/mole$ ......(ii)

By 2 × (i) and (ii)

$2H_2 + O_2 \to 2H_2O; \Delta H = -376\ kJ/mole$ .....(iii)

$2H_2 + 2O_2 \to 2H_2O_2 \quad \Delta H = -572\ kJ/mole$ .....(iv)

By (iii) – (iv)

$2H_2O_2 \to 2H_2O + O_2 \quad \Delta H = +196\ kJ$.

136. (a) ΔH for $C_2H_6 = -341.1 Kcal$

its calorific value $= \frac{-341.1}{30} = -11.37\ kcal / g$.

ΔH for $C_2H_2 = -310.0\, kcal$

its Calorific value $= \frac{-310.0}{26} = -11.92$,

hence C_2H_2 is a better fuel.

138. (c) For the decomposition of 9*gm* of water heat required $= 142.5 kJ$

we know $H_2O = 2 + 16 = 18$

Therefore heat required for decomposition of 18*gm* water $= \frac{18}{9} \times 142.5 = 285\ KJ$

Than, enthalpy of formation of water is reverse of heat required = – 285 *kJ*.

139. (d) $C_6H_{6(g)} + \frac{15}{2}O_{2(g)} \to 6CO_{2(g)} + 3H_2O_{(g)}$

$\Delta n = 6 + 3 - 1 - \frac{15}{2} = +\frac{1}{2}$.

140. (b) By 2 × (i) + (ii) – (iii)

ΔH of methane $= 20.0\, kcal$.

141. (c) Heat of neutralization of strong acid and weak base is less than $13.7\, kcal\, mol^{-1}$.

142. (d) $\Delta E = 0$ for a cyclic process.

143. (c) $22.0 \times 2 = 44\, kcal$.

144. (b) 0.3 mole OH^-, neutralize 0.3 mole of HNO_3

Evolved heat, $= 57.1 \times 0.3 = 17.13 kJ$

146. (d) Compounds with high heat of formation are less stable because energy rich state leads to instability.

147. (b) CH_4 required $= \frac{445.15 \times 16}{890.3} = 8\, gm$.

148. (c) $C_{(s)} + 2H_{2(g)} \to CH_{4(g)}$ .....(i)

$C_{(s)} + O_{2(g)} \to CO_{2(g)} \quad \Delta H = -94\ kcal\, mol^{-1}$ .....(ii)

$H_{2(g)} + \frac{1}{2}O_{2(g)} \to H_2O_{(l)} \quad \Delta H = -68\ kcal\, mol^{-1}$ ... (iii)

$CH_4 + 3/_2\, O_2 \to CO_2 + 2H_2O$

$\Delta H = -213\ kcal\, mol^{-1}$ ... (iv)

to obtain equation (i) operate-(ii) + 2 × (iii) – (iv).

149. (b) $\Delta H = +ve$ for endothermic reactions.

150. (b) It pertains to neutralization of strong acid weak base.

151. (d) Strong base (KOH) and strong acid (HCl)

153. (b) This reaction absorbed heat, so it is endothermic reaction.

154. (b) $C + O_2 \to CO_2, \ \Delta H = -94.3$

This is also heat of formation of CO_2

$C + \frac{1}{2}O_2 \to CO, \ \Delta H = -26.0$.

155. (b) $X = \frac{1}{2}Y$.

157. (a) Molecular weight of $NH_4NO_3 = 80$

Heat evolved $= 1.23 \times 6.12$

$\therefore$ Molar heat capacity $= 1.23 \times 6.12 \times C$.

158. (d) Both X_e and F_2 are gaseous elements at 25^oC and in their standard states and form $XeF_{4(g)}$

hence $\Delta H^\circ_{(f)} = \Delta H^\circ_{\text{react}}$.

159. (c) According to Hess low, enthalpy change for a reaction does not depend on the nature of inter mediate reaction steps.

160. (d) By (ii) – (i), $C_{gr} \to C_{dia}, \ \Delta H = +1.9$.

162. (c) Heat of neutralization of strong acid and strong base is equal to the $-57.32\ KJ\ mol^{-1}$

163. (c) $C + O_2 \to CO_2 \ \ \Delta H = -393.5\, KJ / mol$

$\because$ 44 *gm* of CO_2 form by which heat released

$= -393.5 kJ$

$\therefore$ 1*gm* of CO_2 form by which heat released

$= -\frac{393.5}{44}$

$\therefore$ 35.2 *gm* (given) of CO_2 form by which heat released

$= -\frac{393.5}{44} \times 35.2 = -315\, kJ$

164. (c) $C_{(graphite)} + 2H_2(g) \to CH_4(g)$

165. (c) Heat of formation of a substance is the heat exchanged when one mole of that substance is formed by its constituent elements.

$\because$ Heat evolved when 1 mole $(44g)CO_2$ is formed $= 393\,kJ$

$\therefore$ Heat evolved when $0.156\,Kg(156\,g)$ is formed $= \frac{393 \times 156}{44}$

$\therefore$ ΔH for the process $= 1572\,kJ = -1572.0\,kJ$

166. (b) It is heat of neutralisation $(13.7\,Kcal)$ for strong acid and strong base.

167. (d) $C(s) + O_2(g) \rightarrow CO_2(g)$

$\Delta H = -393.5\,KJ\,mol^{-1}$ .....(i)

$CO(g) + 1/2O_2(g) \rightarrow CO_2(g)$

$\Delta H = -283\,KJ\,mol^{-1}$ .....(ii)

On substracting equation (ii) from equation (i)

We get

$C(s) + O_2(g) \rightarrow CO(g);\ \Delta H = -110.5\,KJ\,mol^{-1}$

The enthalpy of formation of carbon monooxide per mole $= -110.5\,KJ\,mol^{-1}$

168. (d) 1 mole (i.e.,) $16\,gm$ of methane on combustion liberate $890\,kJ$

$\therefore$ $3.2\,gm$ will liberate $= \frac{890 \times 3.2}{16} = 178\,KJ$

169. (c) $C + O_2 \rightarrow CO_2;\ \Delta H = q$

$C + 1/2O_2 \rightarrow CO;\ \Delta H = -12$ .....(i)

$CO + 1/2O_2 \rightarrow CO_2;\ \Delta H = -10$ .....(ii)

adding equation (i) and (ii) we can get

$\Delta H = -12 + (-10) = -22$

170. (b) $C + O_2 \rightarrow CO_2;\ \Delta H_F = -490\,KJ/mol$ – (I)

$H_2 + 1/2O_2 \rightarrow H_2O;\ \Delta H_F = -240\,KJ/mol$ – (II)

$8C + 18H \rightarrow C_8H_{18};\ \Delta H_F = +160\,KJ/mol$ – (III)

applying

(I) $\times 8 +$ (II) $\times 9 +$ (III)

$C_8H_{18} + \frac{25}{2}O_2 \rightarrow 8CO_2 + 9H_2O$

$\Delta H^o = -3920 - 2160 - 160 = 6240\,KJ/mol$

$\Delta H^o =$ for 6 moles of octane $= 6240 \times 6$

$= 37440\,KJ/mol = -37.4\,KJ$

171. (d) $2Fe + \frac{3}{2}O_2 \rightarrow Fe_2O_3;\Delta H = -193.4\,kJ$ .....(i)

$Mg + \frac{1}{2}O_2 \rightarrow MgO;\ \Delta H = -140.2\,kJ$ .....(ii)

On multiplying eq. (ii) by 3

$3Mg + \frac{3}{2}O_2 \rightarrow 3MgO;\ \Delta H = -420.6\,kJ$ ......(iiii)

Resulting equation can be obtained by subtracting eq. (i) from (iii)

$3Mg + \frac{3}{2}O_2 \rightarrow 3MgO;\ \Delta H = -420.6\,kJ$

$2Fe + \frac{3}{2}O_2 \rightarrow Fe_2O_3;\ \Delta H = -193.4\,kJ$

Subtraction :

$3Mg + Fe_2O_3 \rightarrow 2Fe + 3MgO; \Delta H = -227.2\,kJ$

172. (c) HCl and KOH both are strong

Bond energy

1. **(b)** $XY \longrightarrow X_{(g)} + Y_{(g)};\ \Delta H = +a\ kJ/mole$ ....(i)

$X_2 \longrightarrow 2X;\ \Delta H = +a\ kJ/mole$ ....(ii)

$Y_2 \longrightarrow 2Y;$ $\Delta H = +0.5\,a\ kJ/mole$ ....(iii)

$\frac{1}{2} \times \text{(ii)} + \frac{1}{2} \times \text{(iii)} - \text{(i)},$ gives

$\frac{1}{2}X_2 + \frac{1}{2}Y_2 \longrightarrow XY;$

$\Delta H = \left(+ \frac{a}{2} + \frac{0.5}{2}a - a \right) kJ/mole$

$+\frac{a}{2} + \frac{0.5a}{2} - a = -200$

$a = 800$

2. (a) $4g\,H_2 = 2\,moles$. Bond energy for 1 *mole* of $H_2 = 208/2 = 104\ kcal.$

4. (d) By definition of Hess's law.

5. (c) Aim: $\frac{1}{2}H_2 + \frac{1}{2}Cl_2 \rightarrow HCl$

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

$= B.E.(HCl) - \left[\frac{1}{2}B.E.(H_2) + \frac{1}{2}B.E.(Cl_2)\right]$

$= -103 - \left[\frac{1}{2}(-104) + \frac{1}{2}(-58)\right]$

$= -103 - (-52 - 29) = -22\ kcal$.

6. (c) First ionization potential of $Li = 5.4eV$

Electron affinity of $Cl = 3.61eV$

We have $\Delta H = I.P. - E.A.$

$= 5.4 - 3.61 = 1.80\,eV = 1.80 \times 1.6 \times 10^{-22}\,kJ$

$\Delta H = 2.86\times 10^{-22}\,kJ,$

for 1mol Avogadro's number $= 6.02\times 10^{23}$.

$\Delta H = 2.86\times 10^{-22}\times 6.02\times 10^{23} = 170\,kJ/mole.$

7. (b) $\frac{-166}{4} = -41.5\,kJ/mole$.

8. (d) $\frac{1}{2}H_2 + \frac{1}{2}Cl_2 \to HCl,\ \Delta H = -90\,KJ$

$\therefore \Delta H = \frac{1}{2}E_{H-H} + \frac{1}{2}E_{Cl-Cl}$

or $-90 = \frac{1}{2}\times 430 + \frac{1}{2}\times 240 - E_{HCl}$

$\therefore E_{H-Cl} = 425\,kJ\,mol^{-1}$.

9. (b) $CH_4 \to C + 4H,\ \Delta H = 320$

$E_{C-H} = 90\,cal$

$C_2H_6 \to 2C + 6H,\ \Delta H = 360$

$\therefore 360 = E_{C-C} + 6E_{C-H}$

$\therefore E_{C-C} = 360 - 320 = 40\ cal$.

10. (b) $H-H + Br-Br \to 2H-Br$

$433 + 192 \qquad 2\times 364$

625 728

Energy absorbed = Energy released

Net energy released $= 728 - 625 = 103\,kJ$

i.e., $= \Delta H = -103\,KJ$

Free energy and Work function

1. (d) ΔG at equilibrium = 0.

2. (b) For spontaneous change $\Delta G = -ve$.

3. (a) When $\Delta G = -ve$ than the reaction is spontaneous in nature.

5. (acd)When $\Delta H = +ve$ and $\Delta S = -ve$ than the reaction is non-spontaneous.

7. (c) Because the reaction is spontaneous .

8. (c) $\Delta G = -ve.$

9. (a) $\Delta G_T = nRT\ln\frac{P_2}{P_1}$.

10. (a) $\Delta G = 0$ for equilibrium.

11. (d) At equilibrium $\Delta G = 0$.

12. (a) $\Delta G^o = -2.303\,RT\log K$

$-4.606 = -2.303\times 0.002\times 500\log K$

$\log K = 2,\ K = 100$.

14. (d) Spontaneous change shows $\Delta G = -ve$.

15. (b) $\Delta G = \Delta H - T\Delta S,\ T = 25 + 273 = 298\,K$

$= -11.7\times 10^3 - 298\times(-105) = 19590\,J = 19.59\,kJ$

18. (c) If $\Delta G = -ve$ reaction is spontaneous.

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

21. (b) Only high pressure favours the conversion.

22. (d) By 2× (ii) – (i) – (iii)

$H_{2(g)} + 2C_{(s)} \to C_2H_{2(g)},\ \Delta G^\circ = 209\,kJ$.

23. (b) $\Delta G = -2.303\,RT\log K'$, Here $R = 2\,cal,\ T = 300\,K$

$K' = \frac{10\times 15}{3\times 5} = 10$; $\Delta G = -2.303\times 2\times 300\times \log_{10}10$

$= -2.303\times 2\times 300\times 1 = -1381.8\,cal$

24. (a) $\Delta G = \Delta H - T\Delta S$ (Gibb's free energy equation)

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

$\Delta G = -382.64 - (-145.6)\times 10^{-3}\times 298$

$= -339.3\,KJ\,mol^{-1}$

26. (d) $\Delta G = \Delta H - T\Delta S$; $\Delta G = \Delta E + P\Delta V - T\Delta S$

For spontaneity $(\Delta G = -ve)$

$\because\ \Delta G = -ve$, $\Delta E = +ve$

27. (a) $\Delta G = \Delta H - T\Delta S = 31400 - 1273\times 32$

$= 31400 - 40736 = -9336\,cal$

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

$0 = +30.558 - T\times 0.066$

or $T = \frac{30.558}{0.066} = 463\,K$

If $(dG)_{T,P} = 0$ sign '=' mean. If is reversible process

Critical Thinking Questions

1. (b) Due to randomness of particles is reduced since entropy decreases.

2. (c) $\Delta H = nCp\,\Delta T$

The process is isothermal therefore

$\Delta G = 0$; $\therefore \Delta H = 0$

3. (d) $13.7\ kcal = 57\,kJ = 5.7\times 10^4\,J$.

4. (b) When strong acid and strong base neutralize each other than the value of heat generated is about 13.7 *kcal.*

5. (b) Due to fall in temperature.

6. (d) $q_p = \Delta H$.

7. (d) $w = 2.303\,RT\log\frac{V_2}{V_1}$. As it involves the ratio $\frac{V_2}{V_1}$, volume can be used in any units. (R should be in joules).

8. (b) $-\frac{dQ}{dW} = \frac{dQ}{dQ - dE}$; $dE = dW + dQ$; $-dW = dQ - dE$

$$= \frac{nc_p\,dT}{nc_p dT - nc_v dT} = \frac{c_p}{(c_p - c_v)}$$

$= \frac{7R}{2R}$ {for diatomic of gas $c_p = \frac{7R}{2}$ }

9. (a) $C_2H_2(g) + H_2(g) \rightarrow C_2H_4(g)$

$\Delta ng = 1 - 2 = -1$; $\Delta H = -0.31\, KJ\, mol^{-1}$

$P = 1.5\, atm$, $\Delta V = -50\, mL = -0.050\, L$

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

$-0.31 = \Delta E - 0.0076$; $\Delta E = -0.3024\, KJ$

10. (a) Since process is exothermic then heat is evolved due to this temperature of water increases.

11. (a) Because randomness is decreases.

12. (c) Conversion of graphite into diamond is an endothermic reaction. So, heat of diamond is higher than that of graphite. But ΔS would be negative for the conversion of graphite into diamond.

13. (c) ΔH and ΔS both are $+ve$ for spontaneous change, and $\Delta H = +ve$ for endothermic reaction.

14. (a) $\Delta G = \Delta H - T\Delta S$ is negative for spontaneity.

15. (a) Entropy (a measure of disorder) of universe is increasing toward maximum. This is II law of thermodynamics.

16. (a) For a pure substance T_A and T_B represent the same temperature. Hence A is a correct choice.

17. (a) For endothermic reaction enthalpy of products (H_P) > enthalpy of reactant (H_R)

Hence, change in enthalpy,

$\Delta H = H_P - H_R =$ Positive

18. (d) Suppose the no. of gm, 1gm for each case so the max. no of mole expected for $SO_2(g)$ which has to expected maximum entropy.

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

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

By (i) – (ii)

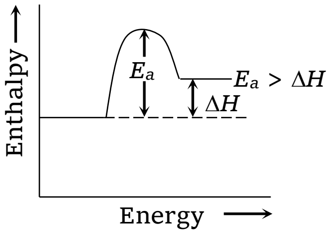
$2Al + Cr_2O_3 \rightarrow 2Cr + Al_2O_3,\ \Delta H = -462\, kJ$.

20. (a) Bomb calorimeter is used to measure heat of reaction.

21. (b) Larger the number of C and H atoms, greater is the heat of combustion.

22. (c) The bomb calorimeter is used to measure ΔE .

23. (c)



24. (b) $\Delta H_{\text{Neutralization}} = -57.1\, kJ = -13.7\, kcal$.

25. (b) Backmann thermometer is used to measure low temperature.

26. (b) Heat required to rise the temperature of a body by 1K called thermal capacity of the body.

27. (e) Mechanical work is important only in gases as they undergo appreciable change in volume.

28. (d) It is Lavoisier and Laplace law. This is another law of thermochemistry which was put forward before Hess's law.

29. (a) It is also known as "constant heat summation" law. It state that the total amount of heat evolved or absorbed in a reaction is same whether the reaction takes place in one step or in a number of steps.

30. (c) In this reaction $\Delta n = 2 - 4 = -2$ so $\Delta H \neq \Delta E$.

31. (a) $Q = \frac{18.94 \times 0.632 \times 0.998 \times 122}{1.89} =$ 771.1 $Kcal$

32. (c) $\Delta H = E_a$ for forward reaction $-E_a$ for backward reaction $= 19 - 9 = 10\, kJ$.

33. (d) $Q = 18.94 \times 0.632 \times 0.998 \times 1000$

$-57.4 + x = -12.13$

$x = 45.2$

34. (c) Thermodynamics is a reversible process in which surroundings are always equilibrium with system.

35. (a) $1\, cal = 4.18\, J = 4.18 \times 10^7\, erg = \frac{4.18}{1.602} \times 10^{19}\, eV$.

36. (b) Order of bond energy : $Cl_2 > Br_2 > F_2 > I_2$.

37. (c) Heat energy is also involved when one allotropic form of an element is converted in to another. graphite is the stabler allotrope because the heat of transformation of $C_{(diamond)} \rightarrow C_{(graphite)}$.

(i) $C_{(dia)} + O_{2(g)} = CO_{2(g)} \Delta H = -94.5 kcal$

(ii) $C_{(graphite)} + O_{2(g)} = CO_{2(g)} \Delta H = -94.0\, k\, cal$

$\Delta H_{transformation} = -94.5 - (-94.0)$

$= -0.5 k\, cal$.

38. (b) The compound Y possess less energy than the X and thus Y is more stable than X.

39. (c) Both ΔH and Δp are positive.

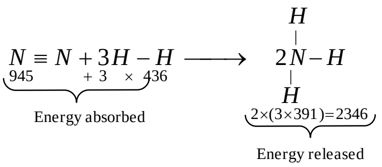
40. (a) For equilibrium $\Delta G^o = 0$.

41. (b) Equilibrium constant is decreases with temperature and ΔH is also decreases so it is $-ve$.

42. (a) The fusion temperature of napthalene is minimum, because it is non-polar covalent compound and has less fusion temperature.

43. (a) The bond energy of $C-H$ bond is $y\ kcal\ mol^{-1}$.

44. (a)



$$\underbrace{\underset{945}{N\equiv N}+\underset{+\,3\,\times\,436}{3H-H}}_{\text{Energy absorbed}} \longrightarrow \underbrace{2\,\underset{\substack{|\\ H}}{\overset{\substack{H\\ |}}{N}}-H}_{\substack{2\times(3\times391)=2346\\ \text{Energy released}}}$$

Net. energy released = 2346 – 2253 = 93 kJ

i.e. $\Delta H = -\,93\ kJ$.

45. (d) If $E=+ve$ than the cell reaction will be spontaneous.

46. (d) All are the correct statements.

47. (d) $CH_2=CH_{2(g)}+H_{2(g)}\rightarrow H_3C-CH_{3(g)}$

$$\begin{array}{ll} 414\times4=1656 & 414\times6=2484 \\ 615\times1=615 & 347\times1=\underline{347} \\ 435\times1=\underline{435} & \underline{\quad 2831} \\ \qquad\quad \underline{2706} & \end{array}$$

$\Delta H = 2706-2831=-125\ kJ$

48. (b) It means that the heat absorbed when one gram molecule of HCl is formed from its elements at $298\,K$ is

$=22.060\,k\,cal$.

49. (d) *eq.* (i) + *eq.* (ii) find the required result and divide by 2.

50. (d) For complete neutralization of strong acid and strong base energy released is $57.32\,KJ/mol$

No. of mole of $H_2SO_4=\frac{0.2\times50}{1000}=10^{-2}$

No. of mole of $KOH=\frac{1}{1000}\times50=5\times10^{-2}$

So $=57.32\times10^{-2}=0.5732\ KJ\ =573.2\ Joule$.

51. (b) For Combustion reaction, ΔH is negative, $\Delta n=(16+18)-(25+2)=+7$, so ΔS is $+ve$, reaction is spontaneous, hence ΔG is $-ve$.

52. (a) $\Delta G=\Delta H-T\Delta S$, $T=27+273=300\ K$

$\Delta G=(-285.8)-(300)(-0.163)=-236.9\,kJ\ mol^{-1}$

Assertion & Reason

1. (b) Assertion and reason show, reaction at equilibrium state in which $\Delta G=0$, $\Delta S=0$, $\Delta H=0$.

2. (b) It is correct that on touching the ice we feel cold because ice absorb heat from our hand.

3. (b) Entropy of ice is less than water because water molecules in solid state lose kinetic energy and hence their tendency of movement minimise. Hence entropy decrease in solid state. The reason that ice have cage like structure is also correct but reason is not or correct explanation for assertion.

4. (c) During isothermal expansion of an ideal gas against vacuum is zero because expansion is isothermal. The reason, that volume occupied by the molecules of an ideal gas is zero, is false.

5. (a) it is fact that absolute values of internal energy of substances can not be determined. It is also true that to determine exact values of constituent energies of the substance is impossible.

6. (b) Mass and volume are extensive properties. mass/volume is also an extensive parameter. Here, both assertion and reason are true.

7. (b) The molar entropy of vaporization of water it differ from ethanol due to hydrogen bonding according to VSEPR theory water molecule having two lone pair of electron by which it angular and show some polarity which is higher than that of ethanol so both assertion and reason are correct but reason is not explaination assertion.

8. (a) The assertion that the increase in internal energy for the vaporisation of one mole of water at 1 *atm* and 373 *K* is zero is true and this is because that for all isothermal process internal energy is zero.

9. (b) $N_2(g)+O_2(g)\rightleftharpoons 2NO(g)$

We know that $\Delta H=\Delta E+\Delta nRT$

$\Delta n=2-2=0$ hence, $\Delta nRT=0$

Therefore, $\Delta H=\Delta E$

10. (a) The enthalpies of neutralisation of strong acids and strong bases are same they are 13.7

Kcal. The reason is that it is heat of formation of water from H^+ and OH^- ions. $H^+ + OH^- \rightarrow H_2O, \Delta H = 13.7\, Kcal$. Thus, both assertion and reason are true.

11. (a) Zeroth (law of temperature) can also be summarized as two objects at different temperature in thermal contact with each other tend to move towards the same temperature.

12. (d) Photo chemical reactions have $+ve\ \Delta G$.

14. (e) Heat absorbed in a reaction at constant temperature and constant volume $(Qv) = E$.

15. (c) Values of state functions depend only on the state of the system and not on how it is reached.

16. (a) The properties whose magnitude depends upon the quantity of matter present in the system are called extensive properties.

17. (c) Combustion reactions are always accompanied by the evolution of heat therefore, for such reactions the value of ΔH is always negative.

18. (b) In an isothermal process change in internal energy (ΔE) is zero (as it is a fucntion of temperature). $\therefore$ According to first law of thermodynamics

$\because q + w = \Delta E$, hence $Q = -W$ (if $\Delta E = 0$)

If a system undergoes a change in which internal energy of the system remains constant (*i.e.,* $\Delta E = 0$), then $-W = Q$.

This means that work done by the system equals the heat absorbed by the system.

20. (e) If a refrigerator's door is kept open room gets heated as heat energy is released to the surroundings.

21. (c) Enthalpy is zero but entropy is not zero. Vibrational motion exists even at absolute zero.

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

Thermodynamics and Thermochemistry

SET Self Evaluation Test -10

1. The internal energy change when a system goes from state *A* to *B* is 40 *kJ/mole*. 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

[CBSE PMT 2003]

(a) 40 *kJ* (b) > 0 *kJ*

(c) < 40 *kJ* (d) Zero

2. The correct relationship is **[DPMT 2002]**

(a) $\Delta H + P\Delta V = \Delta V$ (b) $\Delta H - \Delta nRT = \Delta E$

(c) $\Delta E + \Delta nRT = \Delta P$ (d) None of these

3. For $CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$ at 977^oC; $\Delta H = 176$ *kJ mol*, then ΔE is **[BVP 2003]**

(a) 180 *kJ* (b) 186.4 *kJ*

(c) 165.6 *kJ* (d) 160 *kJ*

4. Values of ΔH and ΔS for five different reactions are given below.

Reaction	$\Delta H\, (kJ\, mol^{-1})$	$\Delta S\, (JK^{-1}\, mol^{-1})$
I	+98.0	+14.8
II	– 55.5	–84.6
III	+28.3	–17.0
IV	– 40.5	+24.6
V	+ 34.7	0.0

On the basis of these values predict which one of these will be spontaneous at all tempeature

[Kerala PMT 2004; KCET 1988,90]

(a) Reaction I (b) Reaction II

(c) Reaction III (d) Reaction IV

(e) Reaction V

5. Molar heat capacity of water in equilibrium with ice at constant pressure is **[IIT JEE 1997]**

(a) Zero (b) Infinity (∞)

(c) $40.45\, kJ\, K^{-1} mol^{-1}$ (d) $75.48\, J\, K^{-1}$

6. Internal energy does not include

[AIIMS 1999; CPMT 2000]

(a) Nuclear energy

(b) Rotational energy

(c) Vibrational energy

(d) Energy arising by gravitational pull

7. Two moles of an ideal gas expand spontaneously into a vacuum. The work done is **[AMU 2000]**

(a) 2 *Joule* (b) 4 *Joule*

(c) Zero (d) Infinite

8. Heat exchanged in a chemical reaction at constant temperature and constant pressure is called as

[BHU 1998; Pb. PET 2000; MP PET 2002]

(a) Internal energy (b) Enthalpy

(c) Entropy (d) Free energy

9. Which of the following statements is true**[KCET 2002]**

(a) ΔE is always greater than ΔH

(b) ΔE is always less than ΔH

(c) ΔE may be lesser or greater or equal to ΔH

(d) ΔE is always proportional to ΔH

10. Mass and energy are conserved is demonstrated by

[MH CET 2002]

(a) First law of thermodynamics

(b) Law of conservation of energy

(c) Law of conservation of mass

(d) Modified form of Ist law of thermodynamics

11. The enthalpy of the reaction,

$H_2(g) + \frac{1}{2}O_2(g) \rightarrow H_2O(g)$ is ΔH_1 and that of

$H_2(g) + \frac{1}{2}O_2(g) \rightarrow H_2O(l)$ is ΔH_2. Then **[KCET 2004]**

(a) $\Delta H_1 < \Delta H_2$ (b) $\Delta H_1 + \Delta H_2 = 0$

(c) $\Delta H_1 > \Delta H_2$ (d) $\Delta H_1 = \Delta H_2$

12. A reaction occurs spontaneously if

[MP PET 2002; CBSE PMT 2005]

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

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

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

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

13. Which expression is correct for the work done in adiabatic reversible expansion of an ideal gas**[AMU 2002]**

(a) $W = nRT \ln\frac{V_2}{V_1}$ (b) $W = n_e \ln\frac{T_2}{T_1}$

(c) $W = P\Delta V$ (d) $W = -\int_1^2 PdV$

14. If an endothermic reaction is non-spontaneous at freezing point of water and becomes feasible at its boiling point, then

[AIEEE 2002]

(a) ΔH is $-ve$, ΔS is $+ve$

(b) ΔH and ΔS both are $+ve$

(c) ΔH and ΔS both are $-ve$

(d) ΔH is $+ve$, ΔS is $-ve$

15. What is the entropy change (in $JK^{-1} mol^{-1}$) when one mole of ice is converted into water at $0^o C$ (The enthalpy change for the conversion of ice to liquid water is 6.0 $kJ\ mol^{-1}$ at $0^o C$)**[CBSE PMT 2003]**

(a) 21.98 (b) 20.13

(c) 2.013 (d) 2.198

16. One mole of $NaCl$ (s) on melting absorbed $30.5\, kJ$ of heat and its entropy is increased by $28.8\ JK^{-1}$. The melting point of $NaCl$ is **[DPMT 2004]**

(a) 1059 K (b) 30.5 K

(c) 28.8 K (d) 28800 K

17. The enthalpy change (ΔH) for the process $N_2H_4(g) \rightarrow 2N(g) + 4H(g)$ in $1724\ KJ\, mol^{-1}$. If the bond energy of $N-H$ bond in ammonia is $391\ KJ\, mol^{-1}$. What is the bond energy of $N-N$ bond is N_2H_4

[MP PMT 2004]

(a) $160\ KJ\, mol^{-1}$ (b) $391\ KJ\, mol^{-1}$

(c) $1173\ KJ\, mol^{-1}$ (d) $320\ KJ\, mol^{-1}$

18. Liquid ammonia is used in refrigeration because of its

[DCE 2003]

(a) High dipole moment

(b) High heat of vaporisation

(c) High basicity

(d) All of these

19. A cylinder of gas supplied by Bharat Petroleum is assumed to contain $14\, kg$ of butane. It a normal family requires $20{,}000\, kJ$ of energy per day for cooking, butane gas in the cylinder last for .... Days **[Kerala PMT 2004]**

(ΔH_c of $C_4H_{10} = -2658\ KJ\ per\ mole$)

(a) 15 days (b) 20 days

(c) 50 days (d) 40 days

(e) 32 days

20. The heat of neutralization of HCl by $NaOH$ under certain condition is – 55.9 kJ and that of HCN by $NaOH$ is –12.1 kJ. the heat of ionization of HCN is **[MP PET 2001]**

(a) $-68.0\, kJ\, mol^{-1}$ (b) $-43.8\, kJ\, mol^{-1}$

(c) $68.0\, kJ\, mol^{-1}$ (d) $43.8\, kJ\, mol^{-1}$

21. Equilibrium constant of a reaction is related to

[AIIMS 1991]

(a) Standard free energy change ΔG^o

(b) Free energy change ΔG

(c) Temperature T

(d) None

22. The standard Gibbs free energy change ΔG^o is related to equilibrium constant K_p as **[MP PET/PMT 1998]**

(a) $K_p = -RT \ln \Delta G^o$ (b) $K_p = \left(\frac{e}{RT}\right)^{\Delta G^o}$

(c) $K_p = -\frac{\Delta G^o}{RT}$ (d) $K_p = e^{-\frac{\Delta G^o}{RT}}$

23. The standard enthalpy or the decomposition of N_2O_5 to NO_2 is 58.04 kJ and standard entropy of this reaction is $176.7\, J/K$. The standard free energy change for this reaction at $25^o C$ is **[DCE 2004]**

(a) –5.38 kJ (b) 5.38 kJ

(c) 5.38 kJ (d) –538 kJ

24. For the equilibrium $H_2O(l) \rightleftharpoons H_2O(g)$ at 1 atm and 298 K

[AIIMS 2004]

(a) Standard free energy change is equal to zero $(G\Delta^o = 0)$

(b) Free energy change is less than zero $(\Delta G < 0)$

(c) Standard free energy change is less than zero $(\Delta G^o < 0)$

(d) Standard free energy change is greater than zero $(\Delta G^o > 0)$

25. For reaction $Ag_2O(s) \rightarrow 2Ag(s) + (1/2)O_2(g)$ the value of $\Delta H = 30.56\ kJ\ mol^{-1}$ and $\Delta S = 0.066\ kJK^{-1}\ mol^{-1}$. Temperature at which free energy change for reaction will be zero, is **[MH CET 1999]**

(a) 373 K (b) 413 K

(c) 463 K (d) 493 K

Answers and Solutions

(SET -10)

1. (d) $A \xrightarrow{40} B$

$A \xleftarrow{-40} B$

$\Delta H = 40 - 40 = 0$.

2. (b) $\Delta H = \Delta E + \Delta nRT$.

3. (c) $\Delta n = 1 - 0 = 1$

$\Delta E = \Delta H + \Delta nRT$

$\Delta E = +176 - 1 \times \frac{8.314}{1000} \times 1240 = 165.6\,kJ$.

4. (d) A spontaneous process is accompanied by decrease in enthalpy and increase in entropy means ΔH is negative and ΔS is positive.

5. (b) $C_P = \left(\frac{\delta H}{\delta T}\right)_P$, At equilibrium T is constant *i.e.* $\delta T = 0$, thus $C_P = \infty$.

6. (d) $E = E_{\text{ele.}} + E_{\text{nucl.}} + E_{\text{chemical}} + E_{\text{potential}} + E_{\text{kinetic}}(E_t + E_v + E_r)$.

7. (c) An ideal gas under going expansion in vacuum shows, $\Delta E = 0, W = 0$ and $q = 0$.

8. (b) $\Delta H = q_p$.

9. (c) ΔE may be greater or lesser or equal to ΔH.

$\because \Delta H = \Delta E + P\Delta V = \Delta E + \Delta nRT$.

10. (d) It is a modified form of Ist law of thermodynamics. It is a conservation law of mass and energy.

11. (a) for reaction (i) $\Delta n_1 = 0.5$

for reaction (ii) $\Delta n_2 = 1.5$

So, $\Delta H_1 < \Delta H_2$

12. (b) *For spontaneous reaction* ΔG *should be negative* $\Delta G = \Delta H - T\Delta S = (+ve) - T(+ve)$

If $T\Delta S > \Delta H$ *then* ΔG *will be negative and reaction will be spontaneous.*

13. (b) $W = P\Delta V$.

14. (b) ΔH and ΔS both are +*ve* than reaction is spontaneous.

15. (a) $\Delta S = \frac{q_{rev}}{T} = \frac{6000}{273} = 21.98\ JK^{-1}mol^{-1}$

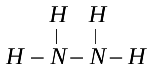
16. (a) $NaCl(s) \rightleftharpoons NaCl(l)$

Given that : $\Delta H = 30.5\,KJ\,mol^{-1}$

$\Delta S = 28.8\ JK^{-1} = 28.8 \times 10^{-3}\ KJ\,K^{-1}$

By using $\Delta S = \frac{\Delta H}{T}$

$= \frac{30.5}{28.8 \times 10^{-3}} = 1059\ K$

17. (a) 
$H-\overset{\overset{H}{|}}{N}-\overset{\overset{H}{|}}{N}-H$ (So, $4N-H$ bond present)

means their energy $= 391 \times 4 = 1564$

so the bond energy of $N-N$ in N_2H_4

$= 1724 - 1564 = 160\,KJ/mol$

18. (b) Ammonia has high heat of vaporisation hence is used in refrigeration.

19. (e) Calorific value of butane

$= \frac{\Delta H_c}{\text{mol. wt.}} = \frac{2658}{58} = 45.8\,KJ/gm$

Cylinder consist $14\,Kg$ of butane means $14000\ gm$ of butane

$\because 1gm$ gives $45.8\,KJ$

$\therefore 14000\ gm$ gives 14000×45.8

$= 641200\ KJ$

Family need $20{,}000\ KJ/day$

So gas full fill the requirement for

$\frac{641200}{20{,}000} = 32.06\ days$

20. (d)

21. (a) $\Delta G^o = -2.303\ \log k$.

22. (d) $K_p = e^{-\Delta G^o/RT}$.

23. (d)

24. (b) For reaction $H_2O(l) \rightleftharpoons H_2O(g)$

$\Delta n = 1$ means positive

so when Δn is positive then $\Delta G < 0$.

25. (c) $\Delta G = \Delta H - T\Delta S$

$\Delta G = 0$ at equilibrium

$\therefore \Delta H = T\Delta S$ or $30.56 = T \times 0.066$

$T = 463\ K$.

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