

CHEMICAL THERMODYNAMICS

1. Thermodynamics

The branch of science which deal with study of different forms of energy and the quantities relationship between them is known as Thermodynamics.

When the study of thermodynamics is confined to chemical changes and chemical substances only, it is known as chemical thermodynamics.

Energetics. It is that branch of chemistry which deals with energy changes taking place in a reaction.

Application in Chemistry :

Thermodynamics helps in

- (a) Determining feasibility of a particular process i.e., whether or not a particular process will occur under a given set of conditions.
- (b) Determining the extent to which a reaction would proceed before attainment of equilibrium.
- (c) Most important laws of physical chemistry such as Raoult's law, vant' Hoff law, distribution law, phase rule, law of equilibrium, laws of thermochemistry and expression for elevation in boiling point and depression in freezing point are in accordance with laws of thermodynamics.

2. Some fundamental Definitions

1. **System :** That part of the universe which is chosen for thermodynamics considerations is called system.
2. **Surrounding :** The remaining portion of the universe which is not chosen for thermodynamic consideration is called surrounding.
3. **Boundary :** The imaginary line which separates the system from the surrounding is called boundary.
4. **Types of system :**
 - (i) **Open system :** A system is said to be an open systems if it can exchange both matter and energy with the surroundings.
 - (ii) **Closed system :** If a system can exchange only energy with the surrounding but not matter is called closed systems.
 - (iii) **Isolated system :** If a system can neither exchange matter nor energy with the surrounding it is called an isolated systems.
5. **State of a System and state variable :**
 - (i) The existence of a system under a given set of conditions is called a state of systems.
 - (ii) The properties which change with change in the state of system are called as state variables e.g., pressure, volume and temperature etc.

The first and last state of a system are called initial state and final state respectively.

6. **State function and Path Function :** A physical quantity is said to be state function if its value depends only upon the state of the system and does not depend upon the path by which this state has been attained. For example, a person standing on the roof of a five storeyed building has a fixed potential energy, irrespective of the fact whether he reached there by stairs or by lift. Thus the potential energy of the person is a state function. On the other hand, the work done by the legs of the person to reach the same height, is not same in the two cases i.e., whether he went by lift or by stairs. Hence work is a 'path function'.

7. **Extensivity and Intensive properties :** An extensive property of a system is that which depends upon the amount of the substance or substances present in the system. e.g., mass, volume, energy etc.
An intensive property of a system is that which is independent of the amount of the substance present in the system e.g., temperature, pressure, density, velocity etc.

8. **Thermodynamics Processes :** The operation by which a thermodynamic system changes form one state to another is called is thermodynamic process.
 - (i) **Isothermal process :** A process in which although heat enters or leaves the system yet temperature of the system remains constant throughout the process is called an isothermal process. For an isothermal process, change in temperature (ΔT) = 0. Change of state (e.g., freezing, melting, evaporation and condensation) are all examples of isothermal process.
 - (ii) **Adiabatic process :** A process during which no heats enters or leaves the system during any step of the process is known as adiabatic process. A reaction carried out in an isolated system is an example of adiabatic process. For an adiabatic process, change in heat (Δq) = 0 or q remain constant.
 - (iii) **Isobaric process :** A process during which pressure of the system remains constant throughout the reaction is called as isobaric process. For example, heating of water to its boiling point, and its vaporisation taking place at the same atmospheric pressure. Expansion of a gas in an open system is an example of isobaric process. For an isobaric process $\Delta P = 0$.
 - (iv) **Isochoric process :** A process during which volume of the system remains constant throughout the reaction is known as isochoric processes. The heating of a substance in a non-expanding chamber or change taking place in a closed system are examples of isochoric process. For an isochoric process, $\Delta V = 0$.
 - (v) **Cyclic process :** A process during which system comes to its initial state through a number of different processes is called a cyclic process. For a cyclic process, $\Delta E = 0$, $\Delta H = 0$.

9. **Internal energy (E) :** The total energy stored in a substance by virtue of its chemical nature and state is called its internal energy, i.e., it is the sum of its translation, vibrational, rotational, chemical bond energy, electronic energy, nuclear energy of constituent atoms and potential energy due to interaction with neighbouring molecules. It is also called intrinsic energy.

$$E = E_t + E_r + E_v + E_e + E_n + E_{pe}$$
 Internal energy is a state property and its absolute value can't be determined. However, change in internal energy (difference between the internal energies of the products and that of reactants) can be determined experimentally using a bomb calorimeter.
 Internal energy of a system depends upon :
 - (a) the quantity of substance
 - (b) its chemical nature
 - (c) temperature, pressure and volume.

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- (i) For a given system, E is directly proportional to its absolute temperature. ($E \propto T$)
- (ii) At constant volume, the quantity of heat supplied to a system (isochoric process) is equal to the increase in its internal energy, i.e., $Q_v = \Delta E$
- (iii) In the adiabatic expansion of a gas, it gets cooled because of decrease in internal energy.
- (iv) In cyclic process the change in internal energy is zero ($\Delta E = 0$) since E is a state function.
- (v) For exothermic reactions, sign of ΔE is negative ($E_R > E_P$).
- (vi) For endothermic reactions, sign of ΔE is positive ($E_P > E_R$).

10. Work : Work is expressed as the product of two factors, i.e.,

$$W = \text{Intensity factor} \times \text{capacity factor}$$

where, intensity factor is a measure of force responsible for work and capacity factor is a measure extent to which the work is done. Thus,

- (a) Mechanical work = Force \times Displacement = $F \times d$
- (b) Electrical work = Potential difference \times Charge flown = $V \times Q = EnF$
- (c) Expansion work = Pressure \times change in volume = $P \times \Delta V$
- (d) Gravitation work = Gravitational force \times Height = $mg \times h$

(a) Pressure volume work (Irreversible)

It is a kind of mechanical work. The expression for such a work may be derived as follows
Consider a gas enclosed in a cylinder fitted with a weightless and frictionless piston.

Suppose area of cross section of a cylinder = a sq. cm.

Pressure on piston = P which is less than the internal pressure such that the gas expands.

Let dl be the distance covered by the piston when the gas expands. work done is given by

$$\begin{aligned} dW &= -Fdl \\ &= -\text{Force} \times \text{distance} \end{aligned}$$

$$\frac{\text{Force}}{\text{Area}} = \text{Pressure} \Rightarrow \text{Force} = \text{Pressure} \times \text{area}$$

$$\begin{aligned} dW &= -P \cdot a \cdot dl \\ &= -PdV \end{aligned}$$

Let the volume limits be V_1 and V_2 . Hence integrating the equation $dW = -PdV$

$$\int dW = \int PdV$$

$$W = -P\Delta V$$

$$W = -(V_2 - V_1)$$

\Rightarrow When expansion takes place

$$V_2 > V_1 \Rightarrow W = -ve$$

Hence work is done by the system

\Rightarrow When compression of gas takes place then $V_2 < V_1$, $W = +ve$. Hence work is done on the system.

(b) Work during isothermal Reversible Expansion of an Ideal Gas

We know that

$$dW = -PdV$$

$$\int dW = - \int_{V_1}^{V_2} Pdv$$

For an ideal gas $PV = nRT$

$$\Rightarrow P = \frac{nRT}{V}$$

$$\Rightarrow w = - \int_{V_2}^{V_1} \frac{nRT}{V} dV$$

$$\begin{aligned} \Rightarrow W &= -nRT - \int_{V_2}^{V_1} \frac{dV}{V} \\ &= -nRT - [\ln V]_{V_2}^{V_1} \\ &= -nRT \ln \frac{V_1}{V_2} \end{aligned}$$

$$W = -2.303 nRT \log \frac{V_1}{V_2}$$

Also as $V \propto \frac{1}{P}$

$$\Rightarrow W = -2.303 nRT \log \frac{P_2}{P_1}$$

$$W = 2.303 nRT \log \frac{P_1}{P_2}$$

- (i) Work is not a state function because amount of work performed depends upon the path followed.
- (ii) Positive value of work signifies that the work has been done on the system by the surroundings and it leads to an increase in the internal energy of the system. On the other hand, negative value of work indicates that work has been done by the system and it leads to decrease in the internal energy of the system.

3. Zeroth Law

It states that "Two system in thermal equilibrium separately with the third system are said to be in thermal equilibrium with each other" i.e., If system A and B separately are in thermal equilibrium with another system, then system A and B are also in thermal equilibrium.

4. Ist law of Thermodynamics

The first law of thermodynamics states that "Energy can neither be created nor be destroyed although it can be converted from one form to another".

Let a system be at state I with internal energy E_1 ,

Let it be change to State II with internal energy E_2

This can be achieve in the ways :

- (i) by heat transfer
- (ii) By doing work (either on system or by system)

Let the heat change taking place during the change of state of system from state I to state II be 'q' and work done be W.

$$E_2 = E_1 + q + W$$

$$E_2 - E_1 = q + W$$

$$\Delta E = q + W$$

or $\Delta E = q - P\Delta V$

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Illustration : 1.

A gas expands by 0.5 litre against a constant pressure one atmosphere. Calculate the work done in joule and calorie.

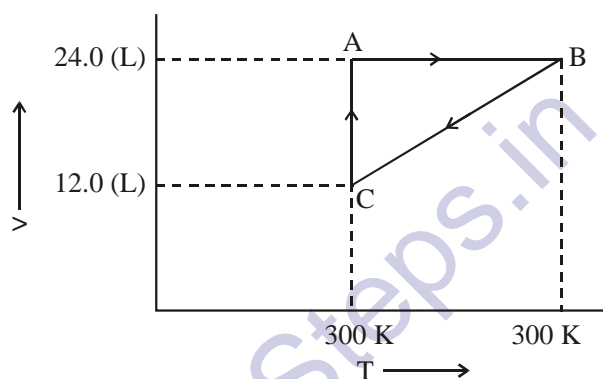
Solution :

$$\begin{aligned}
 \text{Work} &= -P_{\text{ext}} \times \text{volume change} \\
 &= -1 \times 0.5 = -0.5 \text{ litre-atm} \\
 &= -0.5 \times 101.328 \text{ J} = -50.644 \text{ J} \\
 0.5 \text{ lit-atm} &= -0.5 \times 24.20 \text{ cal} = -12.10 \text{ cal}
 \end{aligned}$$

Illustration : 2.

One mole of an ideal gas is put through a series of changes as shown in the graph in which A, B, C mark the three stages of the system. At each stage the variables are shown in the graph.

- (a) Calculate the pressure at three stages of the system.
 (b) Name the processes during the following changes:
 (i) A to B (ii) B to C (iii) C to A, and (iv) overall change.



Solution :

- (a) **At stage A;**
 $V = 24.0 \text{ L}$; $T = 300 \text{ K}$; $n = 1$; $R = 0.0821 \text{ lit-atm K}^{-1} \text{ mol}^{-1}$
 Substituting these values in the ideal gas equation,

$$P = \frac{1 \times 0.0821 \times 300}{24.0} = 1.026 \text{ atm}$$

At stage B : Volume remains the same but temperature change from 300 K to 600 K .
 Thus, according to pressure law, the pressure will be double at B with respect to A.

$$\text{Pressure at B} = 2 \times 1.026 = 2.052 \text{ atm}$$

At stage C : Temperature is 300 K and volume is half that of stage A. Thus, according to Boyle's law, the pressure at C will be double with respect to A.

$$\text{Pressure at C} = 2 \times 1.026 = 2.052 \text{ atm}$$

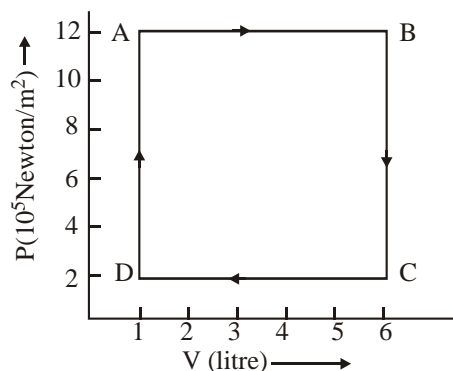
- (b) (i) During the change from A to B, volume remains constant, the process is isochoric.
 (ii) During the change from B to C the pressure remains constant, the process is isobaric.
 (iii) During the change from C to A, the temperature remains constant, the process is isothermal.
 (iv) Overall, the process is cyclic as it returns to initial state.

Illustration : 3.

The diagram shows a P - V graph of a thermodynamic behaviour of an ideal gas. Find out from this graph :

- (i) work done in the process $A \rightarrow B$, $B \rightarrow C$, $C \rightarrow D$ and $D \rightarrow A$
- (ii) work done in the complete cycle $A \rightarrow B \rightarrow C \rightarrow D \rightarrow A$.

Solution :



Work done in the process $A \rightarrow B$ (the process is expansion, hence work is done by the gas)

$$\begin{aligned}
 &= -P \times \Delta V = -12 \times 10^5 \times 5 \times 10^{-3} \\
 &= -6000 \text{ J}
 \end{aligned}$$

Work done in the process $B \rightarrow C$ is zero as volume remains constant.

Work done in the process $C \rightarrow D$ (The process is contraction, hence work is done on the gas)

$$\begin{aligned}
 &= P \times \Delta V = 2 \times 10^5 \times 5 \times 10^{-3} \\
 &= 1000 \text{ J}
 \end{aligned}$$

Work done in the process $D \rightarrow A$ is zero as volume remains constant.

Net work done in the whole cycle = $-6000 + 1000 = -5000 \text{ J}$

i.e. net work is done by the gas.

Illustration : 4.

Calculate the work done when 1.0 mole of water at 373K vaporizes against an atmospheric pressure of 1.0 atmosphere. Assume ideal gas behaviour.

Solution :

The volume occupied by water is very small and thus the volume change is equal to the volume occupied by one gram mole of water vapour.

$$V = \frac{nRT}{P} = \frac{1.0 \times 0.821 \times 373}{1.0} = 31.0 \text{ litre}$$

$$\begin{aligned}
 W &= -P_{\text{ext}} \times \Delta V \\
 &= -(1.0) \times (31.0) \text{ litre-atm} \\
 &= -(31.0) \times 101.3 \text{ J} \\
 &= -3140.3 \text{ J}
 \end{aligned}$$

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Illustration : 5.

Calculate w and ΔE for the conversion of 0.5 mole of water at 100°C to steam at 1 atm pressure. Heat of vaporisation of water at 100°C is 40670 J mol^{-1} .

Solution :

Volume of 0.5 mole of steam at 1 atm pressure

$$= \frac{nRT}{P} = \frac{0.5 \times 0.0821 \times 373}{1.0} = 15.3 \text{ L}$$

Change in volume = Vol. of steam – vol. of water

$$= 15.3 - \text{negligible} = 15.3 \text{ L}$$

Work done by the system,

$$\begin{aligned} w &= P_{\text{ext}} \times \text{volume change} \\ &= 1 \times 15.3 = 15.3 \text{ litre-atm} \\ &= 15.3 \times 101.3 \text{ J} = 1549.89 \text{ J} \end{aligned}$$

‘ w ’ should be negative as the work has been done by the system on the surroundings.

$$w = -1549.89 \text{ J}$$

Heat required to convert 0.5 mole of water in 100°C to steam

$$= 0.5 \times 40670 \text{ J} = 20335 \text{ J}$$

According to first law of thermodynamics,

$$\begin{aligned} \Delta E &= q + w \\ &= 20335 - 1549.89 \\ &= 18785.11 \text{ J} \end{aligned}$$

Illustration : 6.

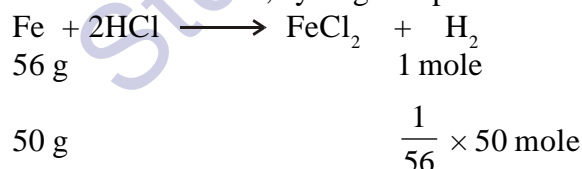
Calculate the work done when 50 g of iron is dissolved in HCl at 25°C in :

- (i) a closed vessel and
- (ii) an open beaker when the atmospheric pressure is 1 atm.

Solution :

- (i) When the reaction is carried in a closed vessel, the change in volume is zero. Hence, the work done by the system will be zero.

- (ii) When iron dissolves in HCl, hydrogen is produced.



Volume of hydrogen produced at 25°C

$$\begin{aligned} &= \frac{nRT}{P} = \frac{50}{56} \times \frac{0.0821 \times 298}{1} \\ &= 21.84 \text{ L} \end{aligned}$$

This is equal to volume change when the reaction is carried in open beaker.

$$\begin{aligned} \text{Work done by the system} &= -P\Delta V = -1.0 \times 21.84 \\ &= -21.84 \text{ litre-atm} \\ &= -2212.39 \text{ J} \end{aligned}$$

Illustration : 7.

Calculate the amount of work done by 2 mole of an ideal gas at 298 K in reversible isothermal expansion from 10 litre 20 litre.

Solution :

Amount of work done in reversible isothermal expansion

$$w = -2.303nRT \log \frac{V_2}{V_1}$$

Given $n = 2$, $R = 8.314 \text{ JK}^{-1} \text{ mol}^{-1}$, $T = 298 \text{ K}$, $V_2 = 20 \text{ L}$ and $V_1 = 10 \text{ L}$.

Substituting the values in above equation

$$\begin{aligned} w &= -2.303 \times 2 \times 8.314 \times 298 \log \frac{20}{10} \\ &= -2.303 \times 2 \times 8.314 \times 298 \times 0.3010 \\ &= -3434.9 \text{ J} \end{aligned}$$

i.e., work is done by the system.

Illustration : 8.

5 mole of an ideal gas expand isothermally and reversibly from a pressure of 10 atm to 2 atm at 300 K. What is the largest mass which can be lifted through a height of 1 metre in this expansion ?

Solution :

Work done by the system

$$\begin{aligned} &= -nRT \log_e \frac{P_1}{P_2} = -2.303 nRT \log_{10} \frac{P_1}{P_2} \\ &= -2.303 \times 5 \times 8.314 \times 300 \log \frac{10}{2} \\ &= -20.075 \times 10^3 \text{ J} \end{aligned}$$

Let M be the mass which can be lifted through a height of 1m.

Work done in lifting the mass

$$= M g h = M \times 9.8 \times 1 \text{ J}$$

$$\text{So } M \times 9.8 = 20.075 \times 10^3$$

$$M = 2048.469 \text{ kg}$$

5. Enthalpy

Internally energy changes are usually measured at constant volume. But in actual practice, most processes are carried out at constant pressure rather than constant volume. Hence volume changes which occurs cause changes in internal energy. To account for these changes, a new thermodynamic property is introduced called as Enthalpy.

It is defined as sum of internal energy and product of pressure volume work

It is donated by the letter H .

$$\mathbf{H = E + PV}$$

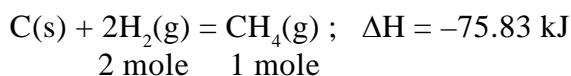
Enthalpy of a system is also called heat content of system, because it is the net energy available in a system which can be converted into heat.

Illustration : 10.

The enthalpy of formation of methane at constant pressure and 300 K -75.83 kJ.
What will be the heat of formation at constant volume ? [$R = 8.3 \text{ JK}^{-1} \text{ mol}^{-1}$]

Solution :

The equation for the formation of methane is



$$\Delta n = (1 - 2) = -1$$

Given $\Delta H = -75.83 \text{ kJ}, R = 8.3 \times 10^{-3} \text{ kJ K}^{-1} \text{ mol}^{-1}$

$$T = 300 \text{ K}$$

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

$$-75.83 = \Delta E + (-1) (8.3 \times 10^{-3}) (300)$$

$$\Delta E = -75.83 + 2.49$$

So $= -73.34 \text{ kJ}$

6. Heat capacity of a system

It is the amount of heat required to raise the temperature of a system through 1°C

If 'q' is the amount of heat supplied to a system and as a result let the temperature rise from T_1 to T_2 $^\circ\text{C}$.

$$\text{Then, heat capacity} = C = \frac{q}{T_2 - T_1} = \frac{q}{\Delta T}$$

When heat capacity varies with temperature then the value of C has to be considered over a narrow range of temperature.

$$\text{Then } C = \frac{q}{dT}$$

(a) Specific Heat and Molar Heat Capacity at Constant Volume

Specific Heat : It is the amount of heat required to raise the temperature of 1 gm of a gas through 1° at constant volume.

Molar heat capacity : It is the amount of heat required to raise the temperature of one mole of a gas through 1° at constant volume

$$dq = dE + PdV$$

$$\text{Molar heat Capacity : } C = \frac{dq}{dT} = \frac{dE + PdV}{dT}$$

At constant volume $dV = 0$

$$\Rightarrow C = \left(\frac{\partial E}{\partial T} \right)_V = \left(\frac{\partial E}{\partial T} \right)_V$$

$$\boxed{C_v = \frac{dE}{dT}}$$

$$\text{Hence } \frac{C_v}{\text{Molecular mass}} = S_v = \text{Specific heat at constant volume.}$$

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(b) **Heat Capacity at Constant Pressure :**

It is defined as the amount of heat required to raise the temperature of one mole of gas through 1° keeping pressure constant

$$C_P = \left(\frac{\partial E}{\partial T} \right)_P + P \left(\frac{\partial V}{\partial T} \right)_P \quad \dots\dots(a)$$

We know that $H = E + PV$

Differentiating w.r.t. temperature

$$\left(\frac{\partial H}{\partial T} \right)_P = \left(\frac{\partial E}{\partial T} \right)_P + P \left(\frac{\partial V}{\partial T} \right)_P$$

From (a) and (b)

$$C_P = \left(\frac{\partial H}{\partial T} \right)_P$$

$$\frac{C_P}{M_0} = S_P = \text{Specific heat at constant pressure}$$

C_P is always greater than C_V

When gas is heated at constant volume, the pressure of gas has to increase.

As the gas is not allowed to expand, therefore in case of C_V heat is required for raising the temperature of one mole of a gas through 1° . When gas is heated at constant P. It expands, the gas has done some work against external pressure. More heat is therefore supplied to raise its temperature through 1° .

\Rightarrow Thus C_P is heat required for the purpose of

(i) Increasing temperatures of one mole of gas through 1° .

(ii) For increasing the volume of the gas against external pressure.

$\Rightarrow C_P > C_V$

Relationship between C_P and C_V .

According to I law of thermodynamics.

$$dq_p = dq_v + PdV \quad \Rightarrow \quad C_P dT = C_V dT + PdV$$

For one mole of gas

$$PV = RT \quad PdV + VdP = RdT$$

\Rightarrow Since the gas is being heated at constant pressure $dP = 0$

$$\Rightarrow PdV = RdT \quad \Rightarrow \quad C_P dT = C_V dT + RdT$$

Dividing both sides by dT

$$\Rightarrow C_P = C_V + R \quad \Rightarrow \quad C_P - C_V = R \quad \Rightarrow \quad \boxed{C_P = C_V + R}$$

Calculation of W, E, H, for Isothermal Expansion of Ideal Gas

(A) (i) ΔE for an ideal gas E depends on temperatures. Since temperature is constant

$$\Rightarrow dE = 0 \quad \Rightarrow \quad \Delta E = 0$$

(ii) According to law

$$dE = dq + dW; \quad \text{since } dE = 0$$

$$\Rightarrow dq = -dW \quad \Rightarrow \quad q = -W$$

\Rightarrow Heat absorbed is equal to work done by the system during isothermal expansion of ideal gas

(iii) Enthalpy change $H = E + PV$

$$\Rightarrow \Delta H = \Delta E + P\Delta V = \Delta E + \Delta(nRT)$$

$$\Delta H = \Delta E + nR\Delta T \quad (\text{Because } \Delta T = 0)$$

$$\Delta H = 0 + 0 \quad \text{Hence, } \Delta H = 0$$

(B) Adiabatic Reversible Expansion of ideal Gas :

(a) Calculation of ΔE

$$= f(T, V)$$

$$dE = \left(\frac{\partial E}{\partial T} \right)_V dT + \left(\frac{\partial E}{\partial V} \right)_T dV$$

$$\text{But } \left(\frac{\partial E}{\partial T} \right)_T = 0 \quad \Rightarrow \quad dE = \left(\frac{\partial E}{\partial T} \right)_V dT$$

$$\begin{array}{ll} \text{Also } dE = nC_V dT & \text{for } n \text{ moles} \\ \text{and } dE = C_V dT & \text{for one moles} \end{array}$$

$$\Delta E = E_2 - E_1 = nC_V(T_2 - T_1)$$

$$= \boxed{\Delta E = nC_V \Delta T}$$

$$\Delta E \text{ or } E_2 - E_1 = nC_V(T_2 - T_1)$$

$$\text{Also } q = 0$$

$$\Rightarrow \Delta E = -W = C_V(T_2 - T_1) \text{ [Because expansion of gas takes place]}$$

$$\Rightarrow W = -C_V(T_2 - T_1)$$

$$W = -nC_V(T_2 - T_1) = -nC_V \Delta T$$

Illustration : 11.

A gas expands from a volume of 3.0 dm³ to 5.0 dm³ against a constant pressure of 3.0 atm. The work done during expansion is used to heat 10.0 mole of water of temperature 290.0 K. Calculate the final temperature of water .

[specific heat of water = 4.184 JK⁻¹g⁻¹]

Solution :

$$\text{Work done} = P \times dV = 3.0 \times (5.0 - 3.0) = 6.0 \text{ litre-atm} = 6.0 \times 101.3 \text{ J} = 607.8 \text{ J}$$

Let ΔT be the change in temperature.

$$\text{Heat absorbed} = m \times S \times \Delta T = 10.0 \times 18 \times 4.184 \times \Delta T$$

$$\text{Given } P \times dV = m \times S \times \Delta T$$

$$\text{or } \Delta T = \frac{P \times dV}{m \times S} = \frac{607.8}{10.0 \times 18.0 \times 4.184} = 0.807$$

$$\text{Final temperature} = 290 + 0.807 = 290.807 \text{ K}$$

Illustration : 12.

How much heat is required to change 10 g ice 0°C to steam at 100°C? Latent heat of fusion and vaporization for H₂O are 80cal/g and 540cal/g respectively. Specific heat of water is 1 cal/g.

Solution :

Total heat absorbed

$$= \Delta H_{\text{fusion}} + \Delta H_{\text{temp. rise}} + \Delta H_{\text{vap.}}$$

$$= 10 \times 80 + 10 \times 1 \times 100 + 10 \times 540 = 7200 \text{ cal.}$$

7. Corollary

(a) Adiabatic process

(i) Adiabatic compression

$$\Delta E = W, \quad \Rightarrow \quad \Delta E = + P\Delta V$$

(ii) Adiabatic expansion

$$\Delta E = -W \quad \Rightarrow \quad \Delta E = -P\Delta V$$

Hence during adiabatic compression of an ideal gas internal energy of system increases and during adiabatic energy of system decreases.

(b) Isochoric process $\Delta E = q_v$

(i) Isochoric absorption of heat

$$\Delta E = +q \Rightarrow \text{internal energy of system increase}$$

(ii) Isochoric liberation of heat

$$\Delta E = -q \Rightarrow \text{internal energy of system decreases}$$

(c) Heat absorbed by system and work done by system

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

(d) Heat liberation by system and work done on the system

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

(e) Isobatic process (expansion)

$$\Delta E = +q_p - P\Delta V$$

(i) when no gases are involved in reaction

$$\Delta E = +q_p$$

(ii) When gases are involved but initial and final volumes are not given

$$\Rightarrow \quad \Delta E = q - \Delta n_g RT \quad \text{where } \Delta n_g = n_{P(g)} - n_{R(g)}$$

1. Daily Practice Problem Sheet

I. Instructions : From Question (1 to 3) a single statement is made. Write *T* if the statement is true & *F* if the statement is false.

Q.1 A thermodynamic equilibrium is one when all the three thermal, mechanical and chemical equilibrium are attained by the system.

Q.2 Ice in contact with water constitutes a homogeneous system.

Q.3 The state properties are those which depends on the path followed by a system in bringing a particular change.

Q.4 The change in entropy in going from one state to another is independent of path.

II. Instructions : Questions (7 to 18) consist of a problem followed by several alternative answers, only one of which is correct. Mark the letter corresponding to the correct answer.

Q.5 For a hypothetical system, consider these conditions

(i) heat transferred to the surrounding

(ii) work done on the system

(iii) work done by the system.

State whether each of the following will increase or decrease the total energy content of the system

(A) decreases, increases, decreases

(B) increases, increases, decreases

(C) decreases, increases, increases

(D) decreases, decreases, increases

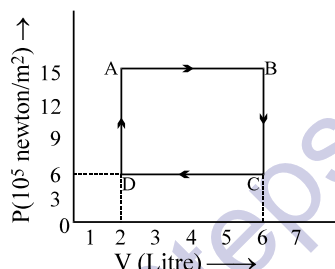
- Q.6** A well stoppered thermos flask contains some ice cubes. This is an example of :
 (A) closed system (B) open system
 (C) isolated system (D) non-thermodynamic system
- Q.7** Internal energy change when system goes from state A to state B is 40 kJ/mol. If the system goes from A to B by reversible path and returns to state A by irreversible path, what would be net change in internal energy ?
 (A) 40 kJ (B) > 40 kJ (C) < 40 kJ (D) zero
- Q.8** A system X undergoes following changes
 The overall process may be called

$$X \longrightarrow W \longrightarrow Z \longrightarrow X$$

$$(P_1V_1T_1) \quad (P_2V_2T_1) \quad (P_2V_2T_2) \quad (P_1V_1T_1)$$

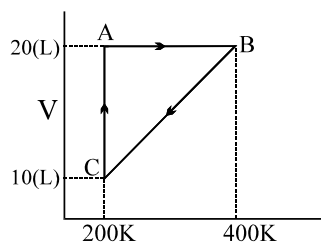
 (A) reversible process (B) cyclic process
 (C) cyclic as well as reversible (D) isochoric process

III. A In the adjoining diagram, the P-V graph of an ideal gas is shown. Answer the following question (11 to 13) from the graph.



- Q.9** Work done in taking the gas from the state A \longrightarrow B
 (A) 36×10^2 J (B) -36×10^2 J (C) 60×10^2 J (D) -60×10^2 J
- Q.10** Work done in taking the gas from B \longrightarrow C
 (A) zero (B) 1.5×10^2 J (C) 3.0×10^2 J (D) 3.0×10^{-2} J
- Q.11** Work done in a complete cycle (1 litre = 10^{-3} m³)
 (A) 36×10^2 J (B) -36×10^2 J (C) 60×10^2 J (D) -60×10^2 J

III. B For 1 mole of an ideal gas following V-T graph is given



Answer the following questions (14 to 18) from the graph

- Q.12** The pressure at A and B in atmosphere are respectively :
 (A) 0.821 & 1.642 (B) 1.642 & 0.821 (C) 1 & 2 (D) 0.082 & 0.164
- Q.13** The pressure at C is :
 (A) 3.284 atm (B) 1.642 atm (C) 0.0821 atm (D) 0.821 atm
- Q.14** The process which occurs in going from B \longrightarrow C is :
 (A) isothermal (B) adiabatic (C) isobaric (D) isochoric

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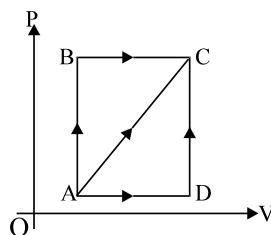
- Q.15** The work done in going from C to A is :
 (A) zero (B) -1.15 kJ (C) -2.3 kJ (D) unpredictable
- Q.16** The process $A \longrightarrow B$ refers to :
 (A) isentropic process (B) reversible process
 (C) isochoric process (D) isobaric process

2. Daily Practice Problem Sheet

- Q.1** Which one is not a state function ?
 (A) internal energy (E) (B) volume
 (C) heat (D) enthalpy
- Q.2** Which is the intensive property ?
 (A) temperature (B) viscosity (C) density (D) all
- Q.3** Warming ammonium chloride with sodium hydroxide in a test tube is an example of :
 (A) closed system (B) isolated system (C) open system (D) none of these
- Q.4** The work done by a system in an expansion against a constant external pressure is :
 (A) $P \cdot \Delta V$ (B) $-P \cdot \Delta V$ (C) Q (D) $V \cdot \Delta P$
- Q.5** An example of extensive property is :
 (A) temperature (B) internal energy (C) viscosity (D) surface tension
- Q.6** A gas expands isothermally and reversibly. The work done by the gas is :
 (A) zero (B) minimum (C) maximum (D) None
- Q.7** A system is changed from state A to state B by one path and from B to A by another path. If E_1 and E_2 are the corresponding changes in internal energy, then :
 (A) $E_1 + E_2 = +ve$ (B) $E_1 + E_2 = -ve$ (C) $E_1 + E_2 = 0$ (D) none
- Q.8** The maximum work done in expanding 16 g oxygen at 300 K and occupying a volume of 5 dm^3 isothermally until the volume becomes 25 dm^3 is :
 (A) $-2.01 \times 10^3 \text{ J}$ (B) $+2.81 \times 10^3 \text{ J}$ (C) $-2.01 \times 10^{-3} \text{ J}$ (D) $+2.01 \times 10^{-6} \text{ J}$
- Q.9** 1 mole of gas occupying 3 litre volume is expanded against a constant external pressure of 1 atm to a volume of 15 litre. The work done by the system is :
 (A) $-1.215 \times 10^3 \text{ J}$ (B) $-12.15 \times 10^3 \text{ J}$ (C) $-121.5 \times 10^3 \text{ J}$ (D) none
- Q.10** If 50 calorie are added to a system and system does work of 30 calorie on surroundings, the change in internal energy of system is :
 (A) 20 cal (B) 50 cal (C) 40 cal (D) 30 cal
- Q.11** One mole of an ideal gas at 300 K is expanded isothermally from an initial volume of 1 litre to 10 litre. The ΔE for this process is : [$R = 2 \text{ cal K}^{-1} \text{ mol}^{-1}$]
 (A) 163.7 cal (B) 1381.1 cal (C) 9 litre-atm (D) zero

- Q.12** A thermodynamic process is shown in the following figure. The pressure and volumes corresponding to some point in the figure are :

$$P_A = 3 \times 10^4 \text{ Pa}, \quad P_B = 8 \times 10^4 \text{ Pa}, \quad V_A = 2 \times 10^{-3} \text{ m}^3, \quad V_D = 5 \times 10^{-3} \text{ m}^3$$



In the process AB, 600 J of heat is added to the system and in BC, 200 J of heat is added to the system. The change in internal energy of the system in the process AC would be :

- (A) 560 J (B) 800 J (C) 600 J (D) 640 J

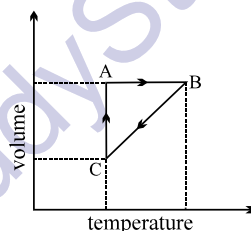
- Q.13** The 'q value' and work done in the isothermal reversible expansion of one mole of an ideal gas from an initial pressure of 1 bar to a final pressure of 0.1 bar at a constant temperature of 273 K are :

- (A) 5.22 kJ, - 5.22 kJ (B) - 5.22 kJ, 5.22 kJ
(C) 5.22 kJ, 5.22 kJ (D) - 5.22 kJ, - 5.22 kJ

- Q.14** In a given process of an ideal gas, $dW = 0$ and $dQ < 0$. Then for the gas :

- (A) the temperature will decrease (B) the volume will increase
(C) the pressure will remain constant (D) the temperature will increase

- Q.15** Five moles of a gas is put through a series of changes as shown graphically in a cyclic process. The process during $A \rightarrow B$, $B \rightarrow C$ and $C \rightarrow A$ respectively are :



- (A) isochoric, isobaric, isothermal (B) isobaric, isochoric, isothermal
(C) isochoric, isothermal, isobaric (D) isobaric, isothermal, isochoric

- Q.16** 20 gm of N_2 at 300 K is compressed reversibly and adiabatically from 20 dm^3 to 10 dm^3 . Change in internal energy for the process is :

- (A) 284.8 J (B) 142.46 J (C) 1424.69 J (D) 3462.89 J

8. Thermochemistry

Thermochemistry is the branch of physical chemistry which deals with the transfer of heat between a chemical system and its surrounding when a change of phase or a chemical reaction takes place within the system. It is also termed as chemical energetics.

Thermochemical equations : A chemical reaction which tells about the amount of heat evolved or absorbed during the reaction is called a thermochemical equation. A complete thermochemical equation supplies the following informations.

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- (i) It tells about the physical state of the reactants and products. This is done by inserting symbols (s), (l) and (g) for solid, liquid and gaseous state respectively with the chemical formulae.
- (ii) It tells about the allotropic form (if any) of the reactant.
- (iii) The aqueous solution of the substance is indicated by the word aq.
- (iv) It tells whether a reaction proceeds with the evolution of heat or with the absorption of heat, i.e. heat change involved in the system.

Exothermic Reactions :

Heat is evolved in these chemical reactions. It is possible when the bond energy of reactants is less at constant pressure

$$\Delta H = (H_p - H_R) = -ve \text{ i.e., } H_p < H_R$$

At constant volume

$$\Delta E = (E_p - E_R) = -ve \text{ i.e., } E_p < E_R$$

Endothermic Reactions :

Heat is absorbed in these chemical reactions. It is possible when bond energy of reactants is greater than the bond energy of products.

At constant pressure

$$\Delta H = [H_p - H_R] = +ve \quad \text{i.e., } H_p > H_R$$

At constant volume

$$\Delta E = [E_p - E_R] = +ve \quad \text{i.e., } E_p > E_R$$

Sign conventions :

	ΔH	ΔE
Exothermic	-ve	-ve
Endothermic	+ve	+ve

9. Heat of Reaction or Enthalpy of Reaction

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

From 1st Law of thermodynamics :

$$Q = E + PV$$

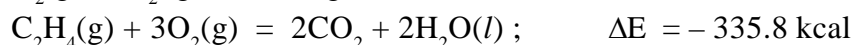
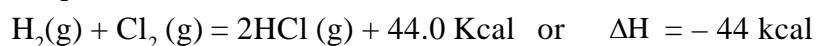
Heat change at constant pressure can be

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

Enthalpy of reaction is the difference between the enthalpies of the products and the reactants when the quantities of the reactants indicated by chemical reaction have completely reacted. Enthalpy of reaction (or heat of reaction)

$$\Delta H = H_p - H_R$$

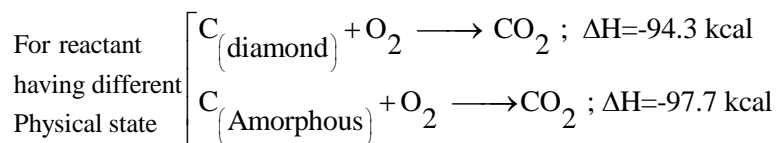
For example, the equation



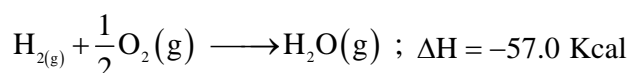
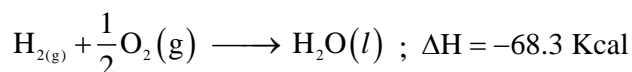
This equation indicates that reaction has been carried between 1 mole of C_2H_4 and 3 mole of oxygen at constant volume and $25^\circ C$. The heat evolved is 335.8 kcal or the internal energy of the system decreases by 335.8 kcal

10. Factors which affect the heat of reaction

- (a) **Physical State of Reactants and Products :** The heat of reaction varies for a given reaction with the change in physical nature of reactants or products e.g.,



For products having different physical state ;



- (b) **Reaction carried out a constant pressure or constant volume :**

From 1st Law of thermodynamics $q = \Delta E - \Delta W$

at constant volume $q_v = \Delta E$

and at constant pressure $q_p = \Delta H$

Two values are related as

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

where P : Pressure at which the reaction is carried out

ΔV : Change in volume during the course of reaction.

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

Δn = No. of moles of products – No. of moles of reactant (only gas phases)

- (c) **Temperature :** Heat of reaction also depends upon the temperature at which reaction is carried out. The variation in ΔH value with temperature are due to variation in heat capacities of system with temperature.

Kirchoff's equation

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

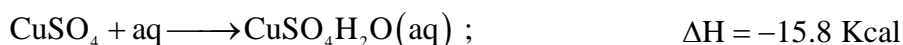
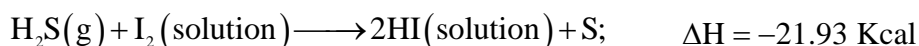
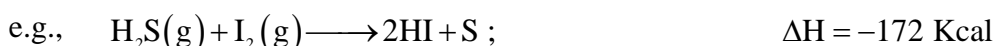
and $\Delta E_2 - \Delta E_1 = \Delta C_v (T_2 - T_1)$ where $\Delta C_p = (C_p \text{ of products} - C_p \text{ of reactants})$

$$\Delta C_v = (C_v \text{ of products} - C_v \text{ of reactants})$$

$\Delta H_2, \Delta H_1$ are change in heat enthalpies at temperature T_2 & T_1 respectively

$\Delta E_2, \Delta E_1$ are change in heat internal energy at temperature T_2 & T_1 respectively

- (d) **Enthalpies of Solution :** Enthalpies of reaction differ when in one case dry substances react and in another case when the same substance react in solution.

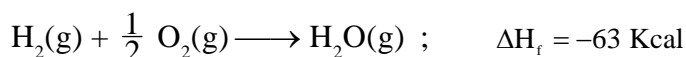
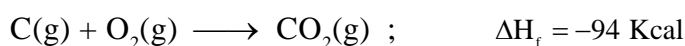


11. Terms used for Heat of Reactions

- (1) **Heat of Formation or enthalpy of Formation :** The amount of heat absorbed or evolved when 1 mole of the substance is directly obtained from its constituent elements is called “Heat of formation”.

Standard Heat Enthalpy : The heat enthalpy of a compound at 25° C and 1 atm pressure is known as standard heat enthalpy and represented by the symbol ΔH° .

Thus the standard heat of formation of 1 mole of $\text{CO}_2(\text{g})$ and 1 mole of $\text{H}_2\text{O}(\text{g})$ from their respective elements can be represented as below :



The compounds which have positive enthalpies of formation are called endothermic compounds and are less stable than the reactants. The compounds which have negative enthalpies of formation are known as exothermic compound are more stable than reactants.

Illustration 13 :

The standard enthalpies of formation at 298 K for $\text{CCl}_4(\text{g})$, $\text{H}_2\text{O}(\text{g})$, $\text{CO}_2(\text{g})$ and $\text{HCl}(\text{g})$ are -106.7 , -241.8 , -393.7 and $-92.5 \text{ kJ mol}^{-1}$, respectively. Calculate $\Delta H^\circ_{298\text{K}}$ for the reaction, $\text{CCl}_4(\text{g}) + 2\text{H}_2\text{O}(\text{g}) \rightleftharpoons \text{CO}_2(\text{g}) + 4\text{HCl}(\text{g})$

Solution :

The enthalpy change of the given reaction will be given as

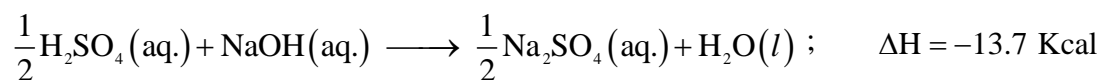
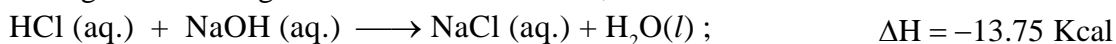
$$\begin{aligned} \Delta H^\circ &= \Delta H_f^\circ(\text{CO}_2, \text{g}) + 4\Delta H_f^\circ(\text{HCl}, \text{g}) - \Delta H_f^\circ(\text{CCl}_4, \text{g}) - 2\Delta H_f^\circ(\text{H}_2\text{O}, \text{g}) \\ &= (-393.7 - 4 \times 92.5 + 106.7 + 2 \times 241.8) \text{ kJ mol}^{-1} = -173.4 \text{ kJ mol}^{-1}. \end{aligned}$$

- (2) **Heat of Combustion or Enthalpy of combustion :** It is defined as the change in heat enthalpy when one mole of a substance is completely burnt in oxygen.

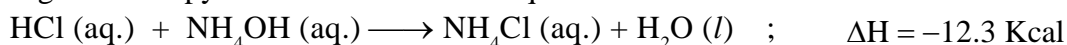


Calorific Value : The amount of heat produced in calorie or joule when one gram of a substance (food or fuel) is completely burnt or oxidised.

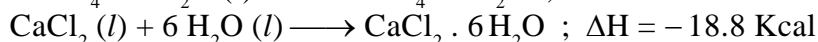
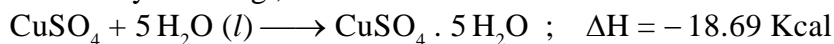
- (3) **Enthalpy of Neutralisation :** It is defined as the heat evolved or decrease in enthalpy when 1 gm equivalent of an acid is neutralised by 1 gm equivalent of a base-in solution.



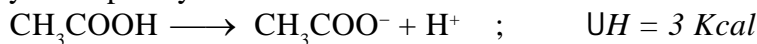
Thus heat of neutralisation of a strong acid and a strong base is merely the heat of formation of water from H^+ and OH^- ions. When strong acid and a weak base or a weak acid and a strong acid or weak acid and weak base are mixed in equivalent amounts, the heat evolved or change in enthalpy is less than 13.7 Kcal. eq.



- (4) **Enthalpy of Hydration** : It is the amount of heat evolved (i.e., change in enthalpy) when 1 mole of anhydrous or a partially hydrated salt combines with required number of moles of water to form a hydrate. e.g.,



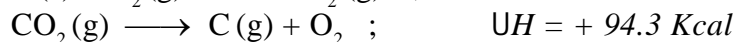
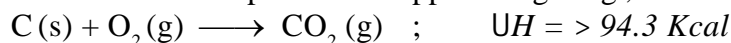
- (5) **Enthalpy of ionisation** : It is defined as the amount of heat absorbed when 1 mole of an electrolyte completely dissociates into ions.



12. Law of Thermochemistry

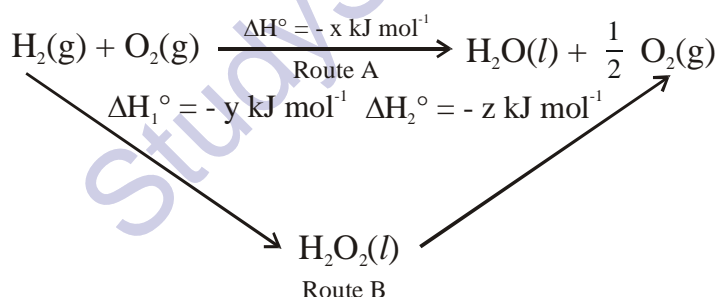
Levoisier and Laplace Law :

According to this “enthalpy of decomposition of a compound is numerically equal to enthalpy of formation of that compound with opposite sign. e.g.,



Hess's Law of Constant Heat Summation :

For a chemical equation that can be written as the sum of two or more steps, the enthalpy change for the overall equation is equal to the sum of the enthalpy changes for the individual steps. Thus, Hess's law enables us to break down a reaction into so many intermediate steps and passing to each step an individual enthalpy change. The sum of the individual changes must, of course, equal the overall enthalpy change provided the initial and final states are the same in each case.



For the above example

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

An energy level diagram for the above reaction cycle is shown in figure

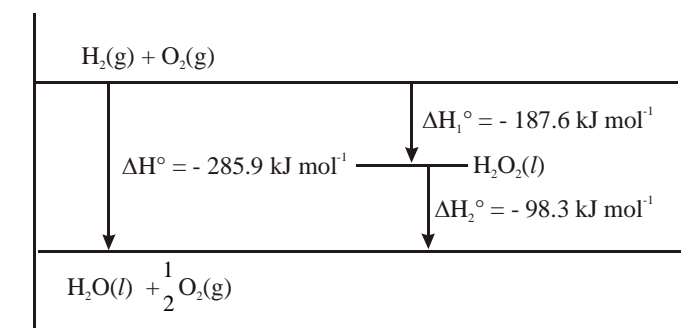


Fig. Energy level diagram to illustrate Hess's Law

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Illustration 14 :

Compute the resonance energy of gaseous benzene from the following data.

$$\nu(\text{C} - \text{H}) = 416.3 \text{ kJ mol}^{-1}$$

$$\nu(\text{C} - \text{C}) = 331.4 \text{ kJ mol}^{-1}$$

$$\nu(\text{C} = \text{C}) = 591.1 \text{ kJ mol}^{-1}$$

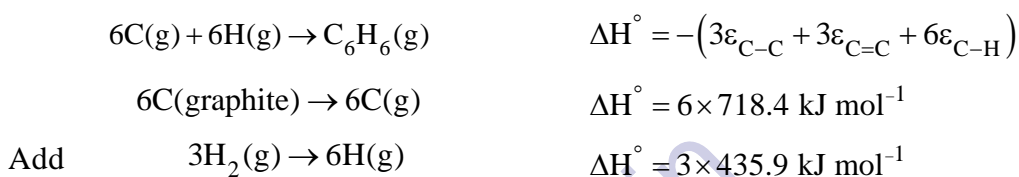
$$\Delta_{\text{sub}}^{\circ}(\text{C, graphite}) = 718.4 \text{ kJ mol}^{-1}$$

$$\Delta_{\text{diss}}^{\circ}(\text{H}_2, \text{g}) = 435.9 \text{ kJ mol}^{-1}$$

$$\Delta_{\text{f}}^{\circ}(\text{benzene, g}) = 82.9 \text{ kJ mol}^{-1}$$

Solution :

To compute resonance energy, we compare the calculated value of $\Delta_{\text{f}}^{\circ}(\text{benzene, g})$ with the given one. To calculate $\Delta_{\text{f}}^{\circ}(\text{benzene, g})$, we add the following reactions.



The corresponding enthalpy change is

$$\Delta_{\text{f}}^{\circ}H = -(3\varepsilon_{\text{C-C}} + 3\varepsilon_{\text{C=C}} + 6\varepsilon_{\text{C-H}}) + [6 \times 718.4 + 3 \times 435.9] \text{ kJ mol}^{-1}$$

$$= [- (3 \times 331.4 + 3 \times 591.1 + 6 \times 718.4 + 3 \times 435.9)] \text{ kJ mol}^{-1}$$

The given $\Delta_{\text{f}}^{\circ}H$ is $\Delta_{\text{f}}^{\circ}H(\text{benzene, g}) = 82.9 \text{ kJ mol}^{-1}$

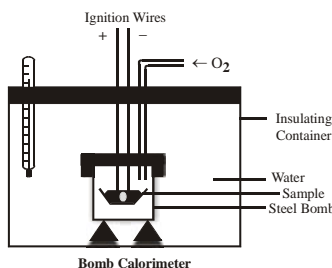
This means benzene becomes more stable by $(352.8 - 82.9) \text{ kJ mol}^{-1}$, i.e., $269.7 \text{ kJ mol}^{-1}$. This is its resonance energy.

❖ Experimental Determination of Heat of Reaction

The apparatus used is called calorimeter. There are two types of Calorimeters :

(a) Bomb Calorimeter (b) Water Calorimeter

Bomb Calorimeter : The calorimeter used for determining enthalpies of combustion known as the bomb calorimeter is shown in figure. This apparatus was devised by Berthelot (1881) to measure the heat of combustion of organic compounds. A modified form of the apparatus shown in figure consists of a sealed combustion chamber, called a bomb, containing a weighed quantity of the substance in a dish along with oxygen under about 20 atm pressure.



❖ Bond Energy

When bond is formed between the two free atoms in a gaseous state to form a molecular product in a gaseous state, some heat is always evolved which is known as the bond formation energy or the bond energy. The bond energy may be referred to as heat of formation of the bond.

Alternatively, bond energy may be defined as the average amount of energy required to dissociate (i.e. break bonds) of that type present in one molecule of the compound. Thus bond energy of C – H in methane (CH₄) is the average value of the dissociation energies of the four C – H bonds.

$$\Delta H_{\text{reaction}} =$$

$$\left[\begin{array}{l} \text{Bond energy data used for formation} \\ \text{of bond (to be taken as -ve)} \end{array} \right] + \left[\begin{array}{l} \text{Bond energy data used for dissociation} \\ \text{of bond (to be taken as +ve)} \end{array} \right]$$

$$\Delta H_{\text{reaction}} = BE_{(R)} - B.E._{(P)} \text{ taking Bond Energies as +ve values.}$$

❖ Bond Enthalpy :

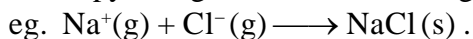
The average energy required to break a bond in gaseous molecule to produce gaseous species. Enthalpy of Reaction :

$$\Delta H = \Sigma (\text{bond energy of bonds broken}) - \Sigma (\text{bond energy of bonds formed})$$

Bond dissociation Energy. The energy required to break a particular bond in gaseous molecule to form gaseous species.

❖ Lattice energy :

Enthalpy change when one mole of gaseous ions condense to form a solid crystal lattice.



Born – Haber's cycle is useful in determination of lattice energy & related problems.

❖ Resonance energy :

(observed heat of formation) – (calculated heat of formation).

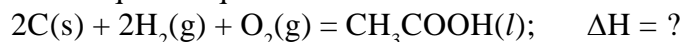
Illustration. 15 :

Calculate the heat of formation of acetic acid from the following data:

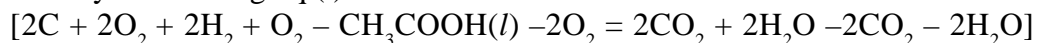


Solution :

First method : The required equation is



This equation can be obtained by multiplying Eq. (ii) by 2 and also Eq. (iii) by 2 and adding both and finally subtracting Eq. (i)



$$\Delta H_{\text{CH}_3\text{COOH}(\text{l})} = 2 \times (-94.48) + 2(-68.4) - (-207.9)$$

$$= -188.96 - 136.8 + 207.9$$

$$= -325.76 + 207.9 = -117.86 \text{ kcal}$$

Second method : From eq. (ii) and (iii)

$$\text{Enthalpy of CO}_2 = -94.48 \text{ kcal}$$

$$\text{Enthalpy of H}_2\text{O} = -68.4 \text{ kcal}$$

$$\text{Enthalpy of O}_2 = 0 \text{ (by convention)}$$

CHEMICAL THERMODYNAMICS

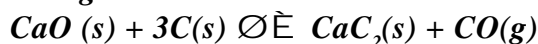
ΔH of Eq. (i) = Enthalpies of products = Enthalpies of reactants

$$-207.9 = 2 \times (-94.48) + 2(-68.4) - \Delta H_{\text{CH}_3\text{COOH}(l)}$$

$$\Delta H_{\text{CH}_3\text{COOH}(l)} = -188.96 - 136.8 + 207.9 = -235.76 + 207.9 = -117.86 \text{ kcal}$$

Illustration 16. :

.....) according to the following reaction ?



The heats of formation of $\text{CaO} (s)$, $\text{CaC}_2(s)$ and $\text{CO}(g)$ are -151.6 , -14.2 and -26.4 kcal respectively.

Solution :

$$\begin{aligned} \Delta H &= \sum \Delta H^\circ_{\text{f(products)}} - \sum \Delta H^\circ_{\text{f(reactants)}} \\ &= [\Delta H^\circ_{\text{f(CaC}_2)} + \Delta H^\circ_{\text{f(CO)}}] - [\Delta H^\circ_{\text{f(CaO)}} + 3\Delta H^\circ_{\text{f(C)}}] \\ &= [-14.2 - 26.4] - [-151.6 + 3 \times 0] \\ &= -40.6 + 151.6 = 111.0 \text{ kcal} \end{aligned}$$

For formation of 64 g of CaC_2 111.0 kcal of heat is required.

So, heat required for making 2000 g of

$$\text{CaC}_2 = \frac{111.0}{64} \times 2000 = 3468.75 \text{ kcal}$$

Example 17. :

Calculate heat of combustion of ethene:



From bond energy data :

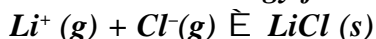
	C=C	C-H	O=O	C=O	O-H
K.E. KJ mol⁻¹	619	414	499	724	460

Solution :

$$\begin{aligned} \Delta H &= \text{sum of bond energies of reactants} - \text{Sum of bond energies of products} \\ &= [\Delta H(\text{C}=\text{C}) + 4\Delta H(\text{C}-\text{H}) + 3 \times \Delta H(\text{O}=\text{O})] - [4 \times \Delta H(\text{C}=\text{O}) + 4 \times \Delta H_{(\text{O}-\text{H})}] \\ &= [619 + 4 \times 414 + 3 \times 499] - [4 \times 724 + 4 \times 460] \\ &= -964 \text{ kJ mol}^{-1} \end{aligned}$$

Illustration 18. :

Calculate the lattice energy for the reaction



From the following data :

$$\text{U}H_{\text{sub(Li)}} = 160.67 \text{ kJ mol}^{-1}; \quad \frac{1}{2} \text{U}(\text{Cl}_2) = 122.17 \text{ kJ mol}^{-1}$$

$$\text{I.P.}_{(\text{Li})} = 520.07 \text{ kJ mol}^{-1}; \quad \text{E.A.}(\text{Cl}) = -365.26 \text{ kJ mol}^{-1}$$

and $\text{U}H_{\text{f(LiCl)}} = -401.66 \text{ kJ mol}^{-1}$

Solution :

Applying the equation

$$-Q = \Delta H + \frac{1}{2}D + \text{I.P.} - \text{E.A.} + U$$

And substituting the respective values,

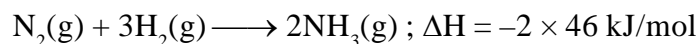
$$-401.66 = 160.67 + 122.17 + 520.07 - 365.26 + U$$

$$U = -839.31 \text{ kJ mol}^{-1}$$

Illustration 19. :

Bond dissociation enthalpies of $H_2(g)$ & $N_2(g)$ are $436.0 \text{ kJ mol}^{-1}$ and $941.8 \text{ kJ mol}^{-1}$ and enthalpy of formation of $NH_3(g)$ is -46 kJ mol^{-1} . What is enthalpy of atomization of $NH_3(g)$? What is the average bond enthalpy of N–H bond?

Solution :

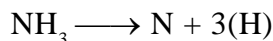


$$\Delta H = S(\text{B.E.})R - S(\text{B.e.})P$$

$$= (941.8 + 3 \times 436) - (6x) = -2 \times 46 \text{ kJ/mol}$$

(here x = B.E. of N–H bonds)

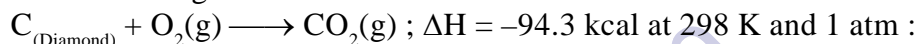
$$x = 380.3 \text{ kJ mol}^{-1}$$



$$\text{Heat of atomization} = 3 \times 380.3 = 1170.9 \text{ kJ mol}^{-1}$$

3. Daily Practice Problem Sheet

Q.1 Which of the following is incorrect about the reaction :



(A) heat of combustion of $C_D = -94.3 \text{ kcal}$

(B) heat of formation of $CO_2 = -94.3 \text{ kcal}$

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

(D) standard heat of formation of $CO_2 = -94.3 \text{ kcal}$

Q.2 At constant P and T which statement is correct for the reaction $CO(g) + \frac{1}{2} O_2(g) \longrightarrow CO_2(g)$

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

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

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

(D) ΔH is independent for physical state of reactant

Q.3 The formation of water from $H_2(g)$ and $O_2(g)$ is an exothermic reaction because :

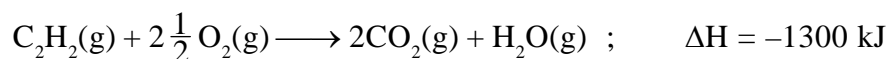
(A) the chemical energy of $H_2(g)$ and $O_2(g)$ is more than that of water

(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

Q.4 Equal volume of C_2H_2 and H_2 are combusted under identical condition. The ratio of their heat of combustion is :



(A) 5.37/1

(B) 1/5.37

(C) 1/1

(D) none of these

Q.5 Given $N_2(g) + 3H_2(g) \longrightarrow 2NH_3(g) ; \Delta H^\circ = -22 \text{ kcal}$. The standard enthalpy of formation of NH_3 gas is :

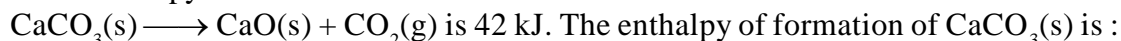
(A) -11 kcal/mol

(B) 11 kcal/mol

(C) -22 kcal/mol

(D) 22 kcal/mol

Q.6 Given enthalpy of formation of $CO_2(g)$ and $CaO(s)$ are -94.0 kJ and -152 kJ respectively and then enthalpy of the reaction :



(A) -42 kJ

(B) -202 kJ

(C) $+202 \text{ kJ}$

(D) -288 kJ

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- Q.7** The enthalpies of formation of N_2O and NO are 28 and 90 kJ mol^{-1} respectively. The enthalpy of the reaction, $2\text{N}_2\text{O(g)} + \text{O}_2\text{(g)} \longrightarrow 4\text{NO(g)}$ is equal to :
 (A) 8 kJ (B) 88 kJ (C) -16 kJ (D) 304 kJ
- Q.8** Give standard enthalpy of formation of CO (-110 kJ mol^{-1}) and CO_2 (-394 kJ mol^{-1}). The heat of combustion when one mole of graphite burns is :
 (A) -110 kJ (B) -284 kJ (C) -394 kJ (D) -504 kJ
- Q.9** The ΔH values for the reaction,

$$\text{C(s)} + \frac{1}{2} \text{O}_2\text{(g)} \longrightarrow \text{CO(g)} \quad ; \quad \Delta H = -100 \text{ kJ}$$

$$\text{CO(g)} + \frac{1}{2} \text{O}_2\text{(g)} \longrightarrow \text{CO}_2\text{(g)} \quad ; \quad \Delta H = -200 \text{ kJ}$$
 The heat of reaction for $\text{C(s)} + \text{O}_2\text{(g)} \longrightarrow \text{CO}_2\text{(g)}$ is :
 (A) -50 kJ (B) -100 kJ (C) -150 kJ (D) -300 kJ
- Q.10** If, $\text{S} + \text{O}_2 \longrightarrow \text{SO}_2 \quad ; \quad \Delta H = -298.2 \text{ kJ} \quad \dots\dots (i)$
 $\text{SO}_2 + \frac{1}{2} \text{O}_2 \longrightarrow \text{SO}_3 \quad ; \quad \Delta H = -98.7 \text{ kJ} \quad \dots\dots (ii)$
 $\text{SO}_3 + \text{H}_2\text{O} \longrightarrow \text{H}_2\text{SO}_4 \quad ; \quad \Delta H = -130.2 \text{ kJ} \quad \dots\dots (iii)$
 $\text{H}_2 + \frac{1}{2} \text{O}_2 \longrightarrow \text{H}_2\text{O} \quad ; \quad \Delta H = -227.3 \text{ kJ} \quad \dots\dots (iv)$
 The enthalpy of formation of H_2SO_4 at 298 K will be :
 (A) -754.4 kJ (B) $+320.5 \text{ kJ}$ (C) -650.3 kJ (D) -433.7 kJ
- Q.11** Standard heat of formation of $\text{CH}_4\text{(g)}$, $\text{CO}_2\text{(g)}$ and water at 25° are -17.9 , -94.1 and $-68.3 \text{ kcal mol}^{-1}$ respectively. The heat change (in kcal) in the following reaction at 25°C is :

$$\text{CH}_4\text{(g)} + 2\text{O}_2\text{(g)} \longrightarrow \text{CO}_2\text{(g)} + 2\text{H}_2\text{O(l)}$$
 (A) -144.5 (B) -180.3 (C) -248.6 (D) -212.8
- Q.12** According to the equation,

$$\text{C}_6\text{H}_6\text{(l)} + \frac{15}{2} \text{O}_2\text{(g)} \longrightarrow 3\text{H}_2\text{O(l)} + 6\text{CO}_2\text{(g)}$$
 $\Delta H = -3264.4 \text{ kJ/mol}$, the energy evolved when 7.8 g of benzene is burnt in air will be :
 (A) 163.22 kJ/mol (B) 326.4 kJ/mol (C) 32.64 kJ/mol (D) 3.264 kJ/mol
- Q.13** When a certain amount of ethylene was burnt 6226 kJ heat was evolved. If heat of combustion of ethylene is 1411 kJ, the volume of O_2 (at NTP) that entered into the reaction is
 (A) 296.5 mL (B) 296.5 litre (C) 6226×22.4 litre (D) 22.4 litre
- Q.14** For the reactions,

$$\text{H}_2\text{(g)} + \text{Cl}_2\text{(g)} \longrightarrow 2\text{HCl(g)} + x_1 \text{ kJ} \quad \dots\dots (i)$$

$$2\text{HCl(g)} \longrightarrow \text{H}_2\text{(g)} + \text{Cl}_2\text{(g)} - x_2 \text{ kJ} \quad \dots\dots (ii)$$
 Which of the following statements is correct :
 (A) x_1 and x_2 are numerically equal (B) x_1 and x_2 are numerically different
 (C) $x_1 - x_2 > 0$ (D) $x_1 - x_2 < 0$
- Q.15** If, $\text{H}_2\text{(g)} + \text{Cl}_2\text{(g)} \longrightarrow 2\text{HCl} ; \Delta H^\circ = -44 \text{ kcal}$
 $2\text{Na(s)} + 2\text{HCl(g)} \longrightarrow 2\text{NaCl(s)} + \text{H}_2\text{(g)} ; \Delta H = -152 \text{ kcal}$ then
 $\text{Na(s)} + 0.5 \text{Cl}_2\text{(g)} \longrightarrow \text{NaCl(s)} ; \Delta H^\circ = ?$
 (A) 108 kcal (B) -196 kcal (C) -98 kcal (D) 54 kcal

- Q.16** Combustion of carbon forms two oxides CO and CO₂. Heat of formation of CO₂ is 94.3 kcal and that of CO is 26.0 kcal. Heat of combustion of carbon is :
 (A) 26.0 kcal (B) -94.3 kcal (C) 68.3 kcal (D) -120.3 kcal
- Q.17** $S + \frac{3}{2} O_2 \longrightarrow SO_3 + 2x \text{ kcal}$
 $SO_2 + \frac{1}{2} O_2 \longrightarrow SO_3 + y \text{ kcal}$
 The heat of formation of SO₂ is :
 (A) $y - 2x$ (B) $(2x + y)$ (C) $x + y$ (D) $2x/y$
- Q.18** ΔH for $CaCO_3(s) \longrightarrow CaO(s) + CO_2(g)$ is 176 kJ mol⁻¹ at 1240 K. The ΔE for the change is equal to :
 (A) 160 kJ (B) 165.6 kJ (C) 186.3 kJ (D) 180.0 kJ
- Q.19** From the thermochemical reactions ,
 $C_{\text{graphite}} + \frac{1}{2} O_2 \longrightarrow CO ; \Delta H = -110.5 \text{ kJ}$
 $CO + \frac{1}{2} O_2 \longrightarrow CO_2 ; \Delta H = -283.2 \text{ kJ}$
 ΔH for the reaction, $C_{\text{graphite}} + O_2 \longrightarrow CO_2$ is :
 (A) -393.7 kJ (B) +393.7 kJ (C) -172.7 kJ (D) +172.7 kJ
- Q.20** $H_2(g) + \frac{1}{2} O_2(g) \longrightarrow H_2O(l) ; \Delta H_{298K} = -68.32 \text{ kcal}$. Heat of vapourisation of water at 1 atm and 25 °C is 10.52 kcal. The standard heat of formation (in kcal) of 1 mole of water vapour at 25 °C is :
 (A) -78.84 (B) 78.84 (C) +57.80 (D) -57.80
- Q.21** Given that standard heat enthalpy of CH₄, C₂H₄ and C₃H₈ are -17.9, 12.5, -24.8 kcal/mol. The ΔH for $CH_4 + C_2H_4 \longrightarrow C_3H_8$ is :
 (A) -55.2 kcal (B) -30.2 kcal (C) 55.2 kcal (D) -19.4 kcal
- Q.22** For the reaction ,
 $C_3H_8(g) + 5O_2(g) \longrightarrow 3CO_2(g) + 4H_2O(l)$
 at constant temperature, $\Delta H - \Delta E$ is :
 (A) +RT (B) -3RT (C) +3RT (D) -RT
- Q.23** The standard enthalpy change for a reaction ,
 $CO_2(g) + H_2(g) \longrightarrow CO(g) + H_2O(g)$ is -
 [Given that ΔH_f° for CO(g) and H₂O(g) as -110.5 and -241.8 kJ mol⁻¹ and heat of combustion of C(s) is -393.5 kJ/mole]
 (A) 41.2 kJ (B) -41.2 kJ (C) -393.5 kJ (D) +393.5 kJ
- Q.24** The standard internal energy change (ΔU°) for the reaction,
 $OF_2(g) + H_2O(g) \longrightarrow O_2(g) + 2HF(g)$ is -
 Given that standard enthalpies of formation ΔH_f° of OF₂(g), H₂O(g) and HF(g) as +23.0, -241.8, -268.6 kJ mol⁻¹ respectively.
 (A) -393.5 kJ (B) -318.4 kJ (C) -537.2 kJ (D) -320.8 kJ
- Q.25** The standard enthalpies of formation of NO₂(g) and N₂O₄(g) 8 and 2 kcal mol⁻¹ respectively. The heat of dimerisation of NO₂ in gaseous state is -
 (A) 10 kcal mol⁻¹ (B) 6.0 kcal mol⁻¹ (C) -14 kcal mol⁻¹ (D) -6.0 kcal mol⁻¹

CHEMICAL THERMODYNAMICS

- Q.26** Given that, $C + O_2 \longrightarrow CO_2$; $\Delta H^\circ = -x \text{ kJ}$ and $2CO + O_2 \longrightarrow 2CO_2$; $\Delta H^\circ = -y \text{ kJ}$.
The standard enthalpy of formation of carbon monoxide is :
- (A) $y - 2x$ (B) $\frac{2x - y}{2}$ (C) $\frac{y - 2x}{2}$ (D) $2x - y$
- Q.27** Given that ,
 $NH_3 + 3Cl_2(g) \longrightarrow NCl_3(g) + 3HCl(g)$; $\Delta H_1 = -x_1$
 $N_2(g) + 3H_2(g) \longrightarrow 2NH_3(g)$; $\Delta H_2 = -x_2$
 $H_2(g) + Cl_2(g) \longrightarrow 2HCl(g)$; $\Delta H_3 = +x_3$
 The heat of formation of $NCl_3(g)$ from the above data is -
- (A) $-x_1 + \frac{x_2}{3} - \frac{3}{2}x_3$ (B) $x_1 + \frac{x_2}{2} - \frac{3}{2}x_3$ (C) $x_1 - \frac{x_2}{2} - \frac{3}{2}x_3$ (D) $-x_1 - \frac{x_2}{2} - \frac{3}{2}x_3$
- Q.28** ΔH°_f of $CO_2(g)$, $CO(g)$, $N_2O(g)$ and $NO_2(g)$ in kJ/mol are respectively - 393, -110, 81 and 34. ΔH in kJ of the following reaction : $2NO_2(g) + 3CO(g) \longrightarrow N_2O(g) + 3CO_2(g)$
- (A) 836 (B) 1460 (C) -836 (D) -1460
- Q.29** If ΔE is the heat of reaction,
 $C_2H_5OH(l) + 3O_2(g) \longrightarrow 2CO_2(g) + 3H_2O(l)$
 at constant volume, the ΔH (heat of reaction at constant pressure) at constant temperature is -
- (A) $\Delta H = \Delta E - RT$ (B) $\Delta H = \Delta E - 2RT$
 (C) $\Delta H = \Delta E + 2RT$ (D) $\Delta H = \Delta E + RT$
- Q.30** Change in enthalpy for the reaction,
 $2H_2O_2(l) \longrightarrow 2H_2O(l) + O_2(g)$
 if heat of formation of $H_2O_2(l)$ and $H_2O(l)$ are -188 kJ mol^{-1} and -286 kJ mol^{-1} respectively is
- (A) -196 kJ mol^{-1} (B) $+196 \text{ kJ mol}^{-1}$ (C) $+948 \text{ kJ mol}^{-1}$ (D) -948 kJ mol^{-1}
- Q.31** Enthalpy of $CH_4 + \frac{1}{2}O_2 \longrightarrow CH_3OH$ is negative. If enthalpy of combustion of CH_4 and CH_3OH are x and y respectively, then which relation is correct :
- (A) $x > y$ (B) $x < y$ (C) $x = y$ (D) $x \geq y$
- Q.32** The heat of combustion of graphite and carbon monoxide respectively are $-393.5 \text{ kJ mol}^{-1}$ and -283 kJ mol^{-1} . Therefore the heat of formation of carbon monoxide in kJ mol^{-1} is :
- (A) $+172.5$ (B) -110.5 (C) -1070 (D) $+110.5$
- Q.33** In a reaction involving only solids and liquids, which of the following is true
- (A) $\Delta H < \Delta E$ (B) $\Delta H = \Delta E$ (C) $\Delta H > \Delta E$ (D) $\Delta H = \Delta E + RT \Delta n$
- Q.34** ΔH for the reaction,
 $CH_3COOC_2H_5(l) + H_2O(l) \longrightarrow CH_3COOH(l) + C_2H_5OH(l)$
 Given heat of formation of $CO_2(g)$, $H_2O(l)$, $C_2H_5OH(l)$ is a , b and $c \text{ kJ/mole}$ respectively and heat of combustion of $CH_3COOC_2H_5(l)$ and $CH_3COOH(l)$ is d and $e \text{ kJ/mole}$ respectively.
- Q.35** ΔH for the reaction,
 $C_3H_8(g) + \frac{9}{2}O_2(g) \longrightarrow CO(g) + 2CO_2(g) + 4H_2O(g)$
 Given heat of formation of $CO(g)$, $C_3H_8(g)$, $H_2O(l)$ is -110.5 kJ/mole , -104.16 kJ/mole and -286 kJ/mole respectively. Heat of combustion of $CO(g)$ is -283.2 kJ/mole and heat of vapourisation of water is 44.2 kJ/mole .

4. Daily Practice Problem Sheet

- Q.1** The amount of heat evolved when one mole of H_2SO_4 reacts with two mole of NaOH is :
(A) 13.7 kcal (B) less than 13.7 kcal (C) more than 13.7 kcal (D) none
- Q.2** Energy required to dissociate 4 g of gaseous hydrogen into free gaseous atom is 208 kcal at 25°C . The bond energy of $\text{H}-\text{H}$ bond will be :
(A) 104 kcal (B) 10.4 kcal (C) 1040 kcal (D) 104 cal
- Q.3** The heat of neutralisation of HCl by NaOH is -55.9 kJ/mol . If the heat of neutralisation of HCN by NaOH is -12.1 kJ/mol . The energy of dissociation of HCN is :
(A) -43.8 kJ (B) 43.8 kJ (C) 68 kJ (D) -68 kJ
- Q.4** Bond energies of $(\text{H}-\text{H})$, $(\text{O}=\text{O})$ and $(\text{O}-\text{H})$ are 105, 120 and 220 kcal/mol respectively then ΔH in the reaction,
$$2\text{H}_2(\text{g}) + \text{O}_2(\text{g}) \longrightarrow 2\text{H}_2\text{O}(\text{l})$$

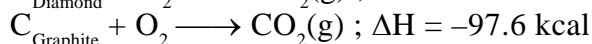
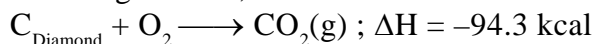
(A) -115 (B) -130 (C) -118 (D) -550
- Q.5** Heat evolved in the reaction, $\text{H}_2 + \text{Cl}_2 \longrightarrow 2\text{HCl}$ is 182 kJ. Bond energies of $\text{H}-\text{H}$ and $\text{Cl}-\text{Cl}$ are 430 and 242 kJ/mol respectively. The $\text{H}-\text{Cl}$ bond energy is :
(A) 245 kJ mol^{-1} (B) 427 kJ mol^{-1} (C) 336 kJ mol^{-1} (D) 154 kJ mol^{-1}
- Q.6** If the enthalpy change for the reaction
$$\text{CH}_4(\text{g}) + \text{Cl}_2(\text{g}) \longrightarrow \text{CH}_3\text{Cl}(\text{g}) + \text{HCl}(\text{g})$$

 $\Delta H = -25 \text{ kcal}$. bond energy of $\text{C}-\text{H}$ is 20 kcal mol^{-1} greater than the bond energy of $\text{C}-\text{Cl}$ and bond energies of $\text{H}-\text{H}$ and $\text{H}-\text{Cl}$ are same in magnitude, then for the reaction :
$$\frac{1}{2} \text{H}_2(\text{g}) + \frac{1}{2} \text{Cl}_2(\text{g}) \longrightarrow \text{HCl}(\text{g}) ; \Delta H = ?$$

(A) -22.5 kcal/mol (B) -20.5 kcal/mol (C) -32.5 kcal/mol (D) -12.5 kcal/mol
- Q.7** Enthalpy of neutralization of HCl with NaOH is x . The heat evolved when 500 ml of 2 N HCl are mixed with 250 ml of 4 N NaOH will be
(A) $500 x$ (B) $100 x$ (C) x (D) $10 x$
- Q.8** The bond energies of $\text{C}-\text{C}$, $\text{C}=\text{C}$, $\text{H}-\text{H}$ and $\text{C}-\text{H}$ linkages are 350, 600, 400 and 410 kJ per mole respectively. The heat of hydrogenation of ethylene is :
(A) -170 kJ mol^{-1} (B) -260 kJ mol^{-1} (C) -400 kJ mol^{-1} (D) -450 kJ mol^{-1}
- Q.9** The enthalpy change (ΔH_r) of the following reaction,
$$2\text{C}_2\text{H}_2(\text{g}) + 5\text{O}_2(\text{g}) \longrightarrow 4\text{CO}_2(\text{g}) + 2\text{H}_2\text{O}(\text{g})$$
 is –
Given average bond energies of various bonds, i.e., $\text{C}-\text{H}$, $\text{C}\equiv\text{C}$, $\text{O}=\text{O}$, $\text{C}=\text{O}$, $\text{O}-\text{H}$ as 414, 814, 499, 724 and 640 kJ mol^{-1} respectively
(A) -7632 kJ (B) -186.1 kJ (C) -2573 kJ (D) -763.2 kJ
- Q.10** The bond energy of $\text{C}-\text{H}$ bond in methane from the following data :
(a) $\text{C}(\text{s}) + 2\text{H}_2(\text{g}) \longrightarrow \text{CH}_4(\text{g}) ; \Delta H = -74.8 \text{ kJ}$
(b) $\text{H}_2(\text{g}) \longrightarrow 2\text{H}(\text{g}) ; \Delta H = 435.4 \text{ kJ}$
(c) $\text{C}(\text{s}) \longrightarrow \text{C}(\text{g}) ; \Delta H = 718.4 \text{ kJ}$
(A) 416 kJ mol^{-1} (B) 1664 kJ mol^{-1} (C) $217.7 \text{ kJ mol}^{-1}$ (D) 1741 kJ mol^{-1}

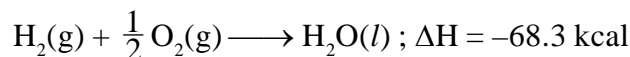
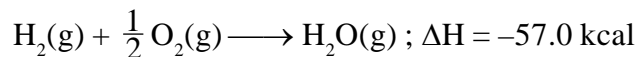
CHEMICAL THERMODYNAMICS

Q.11 For the following reaction,



- (i) The heat of transition for $\text{C}_{\text{Diamond}} \longrightarrow \text{C}_{\text{Graphite}}$
 (A) +3.3 kcal (B) -3.3 kcal (C) 19.19 kcal (D) 191.9 kcal
- (ii) The heat required to change 1g of $\text{C}_{\text{diamond}} \longrightarrow \text{C}_{\text{graphite}}$ is :
 (A) 1.59 kcal (B) 0.1375 kcal (C) 0.55 kcal (D) 0.275 kcal

Q.12 For the following reaction,



- (i) The enthalpy of vapourization for water is :
 (A) 11.3 kcal (B) -11.3 kcal (C) 125.3 kcal (D) -125.3 kcal
- (ii) The heat required to change 1 g of $\text{H}_2\text{O}(\text{l}) \longrightarrow \text{H}_2\text{O}(\text{g})$ is :
 (A) 1.56 kcal (B) 0.313 kcal (C) 1.25 kcal (D) 0.628 kcal

Q.13 The heat of reaction for $\text{N}_2 + 3\text{H}_2 \longrightarrow 2\text{NH}_3$ at 27°C is -91.94 kJ . What will be its value at 50°C ? The molar heat capacities at constant P and 27°C for N_2 , H_2 and NH_3 are 28.45, 28.32 and 37.07 joule respectively

- (A) +45.74 kJ (B) +92.84 kJ (C) -45.74 kJ (D) -92.84 kJ

Q.14 Enthalpy of neutralization of HCl by NaOH is $-57.32 \text{ kJ mol}^{-1}$ and by NH_4OH is $-51.34 \text{ kJ mol}^{-1}$. The enthalpy of dissociation of NH_4OH , is :

- (A) 4.98 kJ mol^{-1} (B) $108.66 \text{ kJ mol}^{-1}$ (C) $-108.66 \text{ kJ mol}^{-1}$ (D) $-5.98 \text{ kJ mol}^{-1}$

Q.15 The enthalpy of formation of $\text{H}_2\text{O}(\text{l})$ is $-285.83 \text{ kJ mol}^{-1}$ and enthalpy of neutralisation of a strong acid and a strong base is $-55.84 \text{ kJ mol}^{-1}$. The enthalpy of formation of OH^- ions is :

- (A) $341.67 \text{ kJ mol}^{-1}$ (B) $229.99 \text{ kJ mol}^{-1}$ (C) $-229.99 \text{ kJ mol}^{-1}$ (D) $-341.67 \text{ kJ mol}^{-1}$

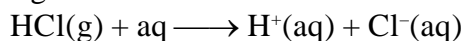
Q.16 ΔH_f° for the reaction,



at 25°C . Given $\Delta H_f^\circ(\text{Ag}^+, \text{aq}) = 105.58 \text{ kJ mol}^{-1}$, $\Delta H_f^\circ(\text{Cl}^-, \text{aq}) = -167.16 \text{ kJ mol}^{-1}$ and $\Delta H_f^\circ(\text{AgCl}, \text{s}) = -127.07 \text{ kJ mol}^{-1}$.

- (A) $-65.49 \text{ kJ mol}^{-1}$ (B) $65.49 \text{ kJ mol}^{-1}$ (C) $188.65 \text{ kJ mol}^{-1}$ (D) $-188.65 \text{ kJ mol}^{-1}$

Q.17 The change in state is



Given $\Delta H_f^\circ(\text{HCl}, \text{g}) = -92.31 \text{ kJ mol}^{-1}$ and $\Delta H_f^\circ(\text{Cl}^-, \text{aq}) = -167.16 \text{ kJ mol}^{-1}$, then

The enthalpy change when one mol of $\text{HCl}(\text{g})$ is dissolved in a very large amount of water at 25°C is :

- (A) $259.47 \text{ kJ mol}^{-1}$ (B) $74.85 \text{ kJ mol}^{-1}$ (C) $-259.47 \text{ kJ mol}^{-1}$ (D) $-74.85 \text{ kJ mol}^{-1}$

Q.18 Given :

Enthalpy of combustion of methane $\Delta_f H = -890.36 \text{ kJ mol}^{-1}$

Enthalpy of combustion of C (graphite) $\Delta_f H = -393.51 \text{ kJ mol}^{-1}$



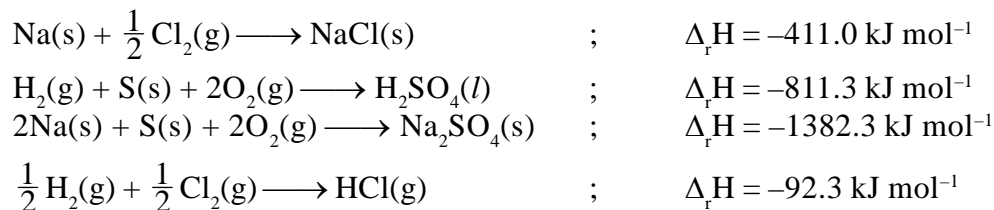
Enthalpy of dissociation of $\text{H}_2(\text{g})$ $\Delta_f H = -435.93 \text{ kJ mol}^{-1}$

Enthalpy of sublimation of C (graphite) $\Delta_f H = -716.68 \text{ kJ mol}^{-1}$

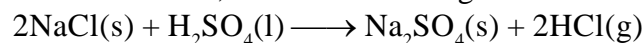
The bond enthalpy of C — H from the following data at 298 K is :

- (A) $-415.85 \text{ kJ mol}^{-1}$ (B) $415.85 \text{ kJ mol}^{-1}$ (C) $1663.39 \text{ kJ mol}^{-1}$ (D) $166.339 \text{ kJ mol}^{-1}$

Q.19 The enthalpy changes of the following reaction at 25°C are



From these data, find the heat change of reaction at constant volume at 25°C for the process

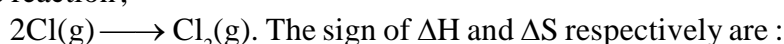


(A) 57.1 kJ mol⁻¹ (B) -60.92 kJ mol⁻¹ (C) 60.92 kJ mol⁻¹ (D) -57.1 kJ mol⁻¹

Q.20 Energy required to dissociate 4g of H₂(g) into free gaseous atoms is x kJ. The value of ΔH (H – H) will be :

(A) x kJ M⁻¹ (B) x/2 kJ M⁻¹ (C) x/3 kJ M⁻¹ (D) 0.25 x kJ M⁻¹

Q.21 For the reaction ,



(A) + and – (B) + and + (C) – and – (D) – and +

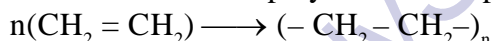
Q.22 The enthalpy of atomisation of CH₄ and C₂H₆ are 360 and 620 k cal mol⁻¹ respectively. The C – C bond energy is expected to be :

(A) 210 k cal mol⁻¹ (B) 130 k cal mol⁻¹ (C) 180 k cal mol⁻¹ (D) 80 k cal mol⁻¹

Q.23 The enthalpy of neutralization of NH₄OH and CH₃COOH is -10.5 k cal mol⁻¹ and enthalpy of neutralization of CH₃COOH with strong base is -12.5 kcal mol⁻¹. The enthalpy of ionization of NH₄OH will be :

(A) 4.0 k cal mol⁻¹ (B) 3.0 kcal mol⁻¹ (C) 2.0 kcal mol⁻¹ (D) 3.2 kcal mol⁻¹

Q.24 Polymerisation of ethene to poly-ethene is represented by the equation,



Given that average enthalpies of C = C & C – C bonds at 298 K are 590 and 331 k J mol⁻¹ respectively, predict the enthalpy change when 56 g of ethene changes to polyethylene.

(A) 72 kJ (B) -72 kJ (C) 144 kJ (D) -144 kJ

13. Limitations of First Law of Thermodynamics

Though the first law of thermodynamics gives us the exact equivalence of heat and work, whenever there is a change of heat into work or vice versa, but it suffers from the following two limitations :

- (i) No indication is available as regards the direction in which the change will proceed.
- (ii) It gives no idea about the extent to which the change takes place.
These limitations can be understood from the following examples :
- (iii) This law can easily explain the heating of a bullet when it strikes a block due to the conversion of kinetic energy into heat, but it fails to explain as to why heat in the block cannot be changed into kinetic energy of bullet and make it fly back from inside of the block.
- (iv) When a vessel of water is placed over fire, heat flows into the vessel. What prevents the heat from flowing from water into the fire, and thereby cooling the water and ultimately converting into ice. Thus direction of (flow) change is not known from first law.
- (v) It is practically found that whole of heat can never be converted into work. The first law has no answer to this observation. Thus, first law fails to tell extent to which the interchange of heat into work and vice versa is possible.

14. Spontaneous and Non-Spontaneous Processes

- 1. Spontaneous Process :** In our daily life, we come across a large number of physical and chemical processes which occur in a widely varying conditions. For example,
- (i) Some processes proceed on their own, e.g. Water always flows down a hill, heat flows from a body at higher temperature to a body at lower temperature.
 - (ii) Some processes require proper initiation but once properly initiated they continue on their own e.g. Kerosene oil once ignited continues to burn till whole of it has been consumed or exhausted.
 - (iii) Some processes proceed only so long as the external energy is available. e.g. Electrolysis of water continues so long as current is passed and stops as soon as current is cut off. “The process which can take place by itself or after proper initiation, under the given set of conditions, is called a spontaneous process.” the term “Spontaneous” simply means that given process is feasible or possible. Therefore, Spontaneous processes are also called as feasible or probable processes. Spontaneous process may or may not be instantaneous. But all instantaneous process are spontaneous.

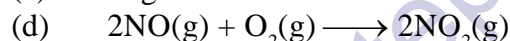
It may be pointed out that the term “Spontaneous” should not mean that the process occurs “instantaneously”. It simply implies that process has an urge to proceed or it is practically possible.

e.g. (i) Processes which occur on their own without proper initiation.



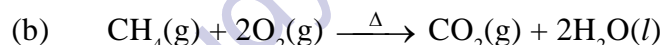
Water keeps on evaporating from ponds and rivers etc.

(c) Sugar dissolves in water and forms a solution.



(ii) Processes which require initiation

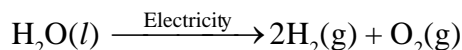
(a) In domestic oven, once coal (carbon) is ignited it keeps on burning



From the above discussion we conclude that spontaneous process is the one which has natural tendency to occur.

- 2. Non-Spontaneous Process :** A process which has no tendency to occur or which is made to occur only if energy from outside is continuously supplied e.g.

(i) Decomposition of water into H_2 and O_2 is non-spontaneous. However, water can be decomposed by passing an electric current through it, in a process called electrolysis.



The process will continue as long as electric current is supplied, and as soon as the supply of electricity is cut off the decomposition stops.

(ii) Water cannot be made to flow up the hill, without the help of a machine.

(iii) Gold ornaments do not get tarnished in air even after a number of years. This shows that gold does not combine with oxygen in the air.

Driving Force for a Spontaneous Process : the natural tendency of various processes to occur spontaneously indicated that there must be some driving force behind them.

15. Entropy

It may be defined as the measure of degree of randomness in the molecule. It is represented by the symbol S.

Characteristic of Entropy

- (i) It is a state of function
 - (ii) It is an extensive property
 - (iii) The exact value may be determined by applying the III law of thermodynamics
- The change in entropy during a process when a system undergoes change from one state to another is represented as ΔS .

Thus $\Delta S = S_{\text{final}} - S_{\text{initial}}$
 and for chemical reaction $\Delta S = S_{\text{product}} - S_{\text{Reactant}}$

Calculation of Changes in Entropy

(a) Reversible Process at Equilibrium

$$\Delta S = \frac{q_{\text{Rev}}}{T}$$

- (i) In a reversible reaction heat gained in the forward reaction is equal to heat lost in the reverse reaction.
 Hence in a reversible cyclic process the net change in entropy is zero. This is called Clausius Theorem

- (ii) $\Delta S_{\text{universe}} = \Delta S_{\text{system}} + \Delta S_{\text{Surrounding}}$
 $\Delta S_{\text{system}} = \frac{q_{\text{Rev(system)}}}{T}$ $\Delta S_{\text{surrounding}} = \frac{q_{\text{Rev(surrounding)}}}{T}$

Heat gained by system = heat lost by surrounding

$$\Rightarrow \Delta S_{\text{Rev(system)}} = Q_{\text{Rev(surrounding)}}$$

$$\Rightarrow \Delta S_{\text{universe}} = \frac{q_{\text{Rev(system)}}}{T} + \frac{q_{\text{Rev(surrounding)}}}{T}$$

$$= \frac{q_{\text{Rev(system)}}}{T} - \frac{q_{\text{Rev(system)}}}{T}$$

Hence $\Delta S_{\text{universe}}(\text{Rev})=0$

- (iii) $\Delta S_{\text{univ}} > 0$ for irreversible process
- (iv) Entropy change for an isothermal process

$$\Delta E = q + w$$

$$\Delta E = 0 \text{ (Isothermal process)} \quad \Rightarrow \quad q = -w$$

$$\text{But } w = -2.303 nRT \log \frac{V_2}{V_1} \quad \Rightarrow \quad q = 2.303 nRT \log \frac{V_2}{V_1}$$

$$\text{or for a reversible process} \quad q_{\text{rev}} = 2.303 nRT \log \frac{V_2}{V_1}$$

$$\Delta S = \frac{q_{\text{Rev}}}{T} = \frac{1}{T} (2.303 nRT \log \frac{V_2}{V_1}), \quad \Delta S = 2.303 nR \log \frac{V_2}{V_1}$$

$$\text{Also } V \propto \frac{1}{P} \quad \Rightarrow \quad \Delta S = 2.303 nR \log \frac{P_1}{P_2}$$

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- (v) Entropy change in an isobaric process

$$dS = \frac{dq_{\text{Rev}(P)}}{T} \text{ also } dq_{\text{Rev}(P)} = dH$$

But $dH = C_p dT \Rightarrow dS = C_p dT/T$
 Integrating both sides

$$\int_{S_1}^{S_2} dS = C_p \int_{T_1}^{T_2} \frac{dT}{T}, \quad \Delta S = C_p [\ln T]_{T_1}^{T_2} = C_p \ln \frac{T_2}{T_1}$$

$$\Delta S = 2.303 C_p \log \frac{T_2}{T_1}$$

- (vi) Entropy change for Isochoric process

$$dS = \frac{dq_{\text{Rev}(V)}}{T} \text{ Also } dq_{\text{Rev}(V)} = dE$$

But $dE = C_v dT \Rightarrow dq_v = C_v dT$
 Integrating both sides one get

$$\Delta S = \Delta V [\ln T]_{T_1}^{T_2} = C_v \ln \frac{T_2}{T_1}$$

$$\Delta S = 2.303 C_v \log \frac{T_2}{T_1}$$

- (vii) Entropy change during mixing of ideal gas

$$\begin{aligned} \Delta S_{\text{mix}} &= -R \sum n_i \ln x_i \\ &= -R [n_1 \ln x_1 + n_2 \ln x_2 + n_3 \ln x_3 \dots] \end{aligned}$$

$$\Delta S_{\text{mix}} = -R \sum n_i \ln x_i$$

$$n_i = m \sum n_i \ln x_i \text{ no. of moles of the gas}$$

$$n_i = \text{mole fraction of the gas}$$

- (viii) Entropy changes during phase transformation

$$\Delta S = \frac{q_{\text{Rev}}}{T}$$

- (a) **Entropy of fusion :** The entropy changes taking place when 1 mole of a solid substance change into liquid form, at the melting temperature.

$$\Delta S_{\text{fusion}} = \frac{\Delta H_{\text{fusion}}}{T_{\text{fusion}}}$$

- (b) Entropy of vaporization is the entropy change when one mole of a liquid changes into vapours at boiling point.

$$\Delta S_{\text{vap}} = S_{\text{vap}} - S_{\text{liquid}} = \frac{\Delta H_{\text{vapourisation}}}{T_{\text{boiling point}}}$$

- (c) Entropy of sublimation is the entropy change when one mole of a solid changes into vapours at sublimation temperature.

$$\Delta S_{\text{sub}} = \frac{\Delta H_{\text{sub}}}{T_{\text{sub}}}$$

(d) Hence for any physical transformation

$$\Delta S_{\text{transition}} = \frac{\Delta H_{\text{transition}}}{T_{\text{transition}}}$$

(ix) Let a given mass of a liquid be heated from temperature T_1 to T_2 . Assuming specific heat of liquid to be constant between T_1 and T_2 and that no change occurs the amount of heat required to raise the temperature by dT is given by $dq = mCdT$

$$\Delta S = mC \ln \frac{T_2}{T_1}$$

16. Second Law of Thermodynamics

It can be defined in number of ways as follows

1. All spontaneous processes (or naturally occurring processes) are thermodynamically irreversible.
2. Without the help of the an external agency, a spontaneous process cannot be reversed e.g., heat cannot by itself flow from a colder to hotter body.
3. The complete conversion of heat into work is impossible without leaving some effect elsewhere.
4. All spontaneous processes are accompanied by a net increase of entropy.
5. The entropy of the universe is increasing.
6. The entropy is a time arrow.

17. Gibb's Free energy

It is defined as, the energy available in the system for conversion into useful work.

It is that thermodynamic quantity of a system, the decrease in whose value during a process is equal to the useful work done by the system.

$$G = H - TS$$

where H is the enthalpy content, T is the absolute temperature and S is the entropy of the system. As before, for the isothermal processes, we have

$$\Delta G = \Delta H - T\Delta S \text{ (Gibb's Helmholtz equation)}$$

$$\Delta H = H_2 - H_1 \text{ is the enthalpy change of the system}$$

Deriving the criteria for spontaneity from Gibbs-Helmholtz equation. According to Gibbs-Helmholtz equation

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

The equation combines in itself both the factor which decide the spontaneity of a process, namely

- (i) the energy factor, ΔH (ii) the entropy factor, $T\Delta S$

Depending upon the signs of ΔH and $T\Delta S$ and their relative magnitudes, the following different possibilities arise.

1. When both ΔH and $T\Delta S$ are negative i.e., energy factor favours the process but randomness factor opposes it, Then
 - (i) If $\Delta H > T\Delta S$, the process is spontaneous and ΔG is negative.
 - (ii) If $\Delta H < T\Delta S$, the process is non-spontaneous and ΔG is positive.
 - (iii) If $\Delta H = T\Delta S$, the process is in equilibrium and ΔG is zero.

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2. When both ΔH and $T\Delta S$ are positive i.e., energy factor opposes the process but randomness factor favours it. Then
 - (i) If $\Delta H > T\Delta S$, the process is non-spontaneous and ΔG is positive.
 - (ii) If $\Delta H < T\Delta S$, the process is spontaneous and ΔG is negative.
 - (iii) If $\Delta H = T\Delta S$, the process is in equilibrium and ΔG is zero.
 3. When ΔH is negative but $T\Delta S$ is positive i.e., energy factor as well as the randomness factor favour the process. The process will be highly non-spontaneous and ΔG will be highly positive.
- An important advantage of free energy criteria over the entropy criteria lies in the fact that the former requires free energy change of the system only whereas the latter requires the total entropy change for the system and the surroundings.

Physical significance of Gibb's free energy :

$$\Delta S = q + w$$

$$\Delta E = q + w_{\text{expansion}} + w_{\text{nonexpansion}}$$

$$\Delta E = q - P\Delta V = + w_{\text{nonexpansion}} \quad (\text{because } w_{\text{expansion}} = -P\Delta V)$$

$$\Delta E + P\Delta V = q + w_{\text{nonexpansion}}$$

$$\Delta H = q_{\text{Rev}} + w_{\text{nonexpansion}}$$

(For a reversible process taking place at constant temperature. $\Delta S = \frac{q_{\text{Rev}}}{T} \Rightarrow q_{\text{Rev}} = T\Delta S$)

As $q_{\text{Rev}} = T\Delta S$ and $\Delta E + P\Delta V = \Delta H$ we get

$$\Delta H = T\Delta S + w_{\text{useful}} \quad [\because w_{\text{nonexpansion}} = w_{\text{useful}}]$$

$$\Delta H - T\Delta S = w_{\text{useful}}$$

$$\Rightarrow \Delta G = w_{\text{useful}}$$

- (i) When useful work is done by the system

$$w_{\text{useful}} = -\text{ve value}$$

$$\Rightarrow \Delta G = -\text{ve value and } \Delta G = w_{\text{useful}}$$

$$\Rightarrow G_{\text{product}} - G_{\text{reactant}} = -\text{ve}$$

$$\Rightarrow G_{\text{product}} < G_{\text{reactant}}$$

\Rightarrow Capacity to do useful work by product is less than the capacity to do useful work by reactant

\Rightarrow Product more stable than reactant.

Hence according to II law of thermodynamics the process is a spontaneous process as every substance wants to be in the state of maximum stability.

- (ii) When work is done on the system

$$\Rightarrow w_{\text{useful}} = +\text{ve} \quad \Rightarrow \Delta G = +\text{ve} \quad \Rightarrow G_{\text{P}} > G_{\text{R}}$$

\Rightarrow Capacity to do useful work by product is more than the capacity to do useful work by reactant

\Rightarrow Reactant more stable than product

\Rightarrow Process non-spontaneous according to II law of thermodynamics

Relationship between ΔG and Equilibrium constant

$$\Delta G = -2.303 RT \log K$$

where K = equilibrium constant

Relationship between ΔG and standard cell potential

$$\Delta G = -nFE^\circ$$

18. Third Law of Thermodynamics

It states that, "Entropy of all perfectly crystalline solids may be taken as zero as the absolute zero of temperature." Third law of thermodynamics may also be defined as

- (i) The entropy of a solid is zero at the absolute zero of temperature.
- (ii) It is impossible to reduce the temperature of any system to absolute zero by any process.
- (iii) At any pressure, the entropy of every crystalline solid in thermodynamic equilibrium at absolute zero is zero.
- (iv) At the absolute zero, increment in entropy for isothermal process in crystalline approaches zero as the limit.
- (v) At absolute zero, every crystal becomes ideal crystal.

5. Daily Practice Problem Sheet

- Q.1** In which case, a spontaneous reaction is possible at any temperature –
 (A) $\Delta H < 0, \Delta S > 0$ (B) $\Delta H < 0, \Delta S < 0$
 (C) $\Delta H > 0, \Delta S > 0$ (D) in none of the cases
- Q.2** In a chemical reaction $\Delta H = 150 \text{ kJ}$ and $\Delta S = 100 \text{ JK}^{-1}$ at 300 K. The ΔG for the reaction is
 (A) zero (B) 300 kJ (C) 330 kJ (D) 120 kJ
- Q.3** For reaction at 25 °C enthalpy change (ΔH) & entropy change (ΔS) are $-11.7 \times 10^3 \text{ J mol}^{-1}$ and $-105 \text{ J mol}^{-1} \text{ K}^{-1}$ respectively. The reaction is :
 (A) spontaneous (B) non-spontaneous (C) instantaneous (D) none
- Q.4** The temperature at which the reaction,
 $\text{Ag}_2\text{O(s)} \longrightarrow 2\text{Ag(s)} + 1/2 \text{ O}_2\text{(g)}$
 is at equilibrium is ; Given $\Delta H = 30.5 \text{ kJ mol}^{-1}$ and $\Delta S = 0.066 \text{ kJ K}^{-1} \text{ mol}^{-1}$
 (A) 462.12 K (B) 362.12 K (C) 262.12 K (D) 562.12 K
- Q.5** The enthalpy and entropy change for a chemical reaction are $-2.5 \times 10^3 \text{ cal}$ and 7.4 cal deg^{-1} respectively. Predict that nature of reaction at 298 K is –
 (A) spontaneous (B) reversible (C) irreversible (D) non-spontaneous
- Q.6** Which is not correct ?
 (A) in an exothermic reaction, the enthalpy of products is less than that of reactants
 (B) $\Delta H_{\text{fusion}} = \Delta H_{\text{sublimation}} - \Delta H_{\text{vaporisation}}$
 (C) a reaction for which $\Delta H^\circ < 0$ and $\Delta S^\circ > 0$ is possible at all temperature
 (D) ΔH is less than ΔE for the reaction $\text{C(s)} + (1/2) \text{ O}_2\text{(g)} \longrightarrow \text{CO}_2\text{(g)}$
- Q.7** For the reaction :
 $2\text{NO(g)} + \text{O}_2\text{(g)} \longrightarrow 2\text{NO}_2\text{(g)}$
 the enthalpy and entropy changes are $-113.0 \text{ kJ mol}^{-1}$ and $-145 \text{ J K}^{-1} \text{ mol}^{-1}$ respectively. Find the temperature above which the reaction is spontaneous
 (A) 432.3 K (B) 570.5 K (C) 1035.7 K (D) 779.3 K
- Q.8** The enthalpy change for a given reaction at 298 K is $-x \text{ cal/mol}$. If the reaction occurs spontaneously at 298 K, the entropy change at that temperature -
 (A) can be negative but numerically larger than $x/298 \text{ cal K}^{-1}$
 (B) can be negative, but numerically smaller than $x/298 \text{ cal K}^{-1}$
 (C) cannot be negative
 (D) cannot be positive

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- Q.9** The favorable condition for a process to be spontaneous is :
 (A) $T\Delta S > \Delta H$, $\Delta H = +\text{ive}$, $\Delta S = -\text{ive}$ (B) $T\Delta S > \Delta H$, $\Delta H = +\text{ive}$, $\Delta S = +\text{ive}$
 (C) $T\Delta S = \Delta H$, $\Delta H = -\text{ive}$, $\Delta S = -\text{ive}$ (D) $T\Delta S = \Delta H$, $\Delta H = +\text{ive}$, $\Delta S = +\text{ive}$
- Q.10** At 300 K, the reaction which have the following values of thermodynamic parameters, occur spontaneously
 (A) $\Delta G^\circ = -400 \text{ kJ mol}^{-1}$ (B) $\Delta H^\circ = 200 \text{ kJ mol}^{-1}$, $\Delta S^\circ = -4 \text{ JK}^{-1} \text{ mol}^{-1}$
 (C) $\Delta H^\circ = -200 \text{ kJ mol}^{-1}$, $\Delta S^\circ = 4 \text{ JK}^{-1} \text{ mol}^{-1}$ (D) $\Delta H^\circ = 200 \text{ kJ mol}^{-1}$, $\Delta S^\circ = 40 \text{ JK}^{-1} \text{ mol}^{-1}$
- Q.11** Which of the following statement(s) is/are correct ?
 (A) the system of constant entropy and constant volume will attain the equilibrium in a state of minimum energy
 (B) the entropy of the universe is on the increase
 (C) the process would be spontaneous when $(\Delta S)_{E,V} < 0$, $(\Delta E)_{S,V} > 0$
 (D) the process would be spontaneous when $(\Delta S)_{E,V} > 0$, $(\Delta E)_{S,V} < 0$
- Q.12** For melting of ice at 25°C the enthalpy of fusion is 6.97 kJ mol^{-1} , entropy of fusion is $25.4 \text{ J K}^{-1} \text{ mol}^{-1}$ and free energy change is -0.6 kJ mol^{-1} . Predict whether the melting of ice is
 (A) non spontaneous (B) spontaneous (C) at equilibrium (D) not predicted
- Q.13** For a process at ΔH and $T\Delta S$ both are positive in what condition, the process is spontaneous
 (A) $\Delta H > T\Delta S$ (B) $\Delta H < T\Delta S$ (C) $\Delta H = T\Delta S$ (D) not predicted
- Q.14** At 0°C , ice and water are in equilibrium and $\Delta H = 6.0 \text{ kJ mol}^{-1}$ for the process

$$\text{H}_2\text{O(s)} \rightleftharpoons \text{H}_2\text{O(l)}$$
 The value of ΔS and ΔG for the conversion of ice into liquid water are
 (A) $-21.8 \text{ J K}^{-1} \text{ mol}^{-1}$ and 0 (B) $0.219 \text{ J K}^{-1} \text{ mol}^{-1}$ and 0
 (C) $21.9 \text{ J K}^{-1} \text{ mol}^{-1}$ and 0 (D) $0.0219 \text{ J K}^{-1} \text{ mol}^{-1}$ and 0
- Q.15** The entropy change at 373 K for the transformation

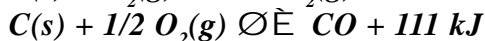
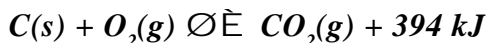
$$\text{H}_2\text{O(l)} \longrightarrow \text{H}_2\text{O(g)}$$
 is : [Given : $\Delta_{\text{vap}}H = 40.668 \text{ kJ mol}^{-1}$. Pressure = 1 bar]
 (A) $128.17 \text{ J K}^{-1} \text{ mol}^{-1}$ (B) $109.03 \text{ J K}^{-1} \text{ mol}^{-1}$
 (C) $19.15 \text{ J K}^{-1} \text{ mol}^{-1}$ (D) $98.35 \text{ J K}^{-1} \text{ mol}^{-1}$
- Q.16** The entropy change for the conversion of one gram of ice to water at 273 K and one atmospheric pressure is : [$\Delta H_{\text{fusion}} = 6.025 \text{ kJ mol}^{-1}$]
 (A) $7.30 \text{ J K}^{-1} \text{ mol}^{-1}$ (B) $1.226 \text{ J K}^{-1} \text{ g}^{-1}$ (C) $1.226 \text{ J K}^{-1} \text{ mol}^{-1}$ (D) $7.30 \text{ J K}^{-1} \text{ g}^{-1}$
- Q.17** In a reaction $A^+ + B \longrightarrow A + B^+$, there is no entropy change. If enthalpy change is 22 kJ for the reaction ΔG for the reaction is :
 (A) 22 kJ mol^{-1} (B) 11 kJ mol^{-1} (C) 33 kJ mol^{-1} (D) 44 kJ mol^{-1}
- Q.18** ΔH and ΔS for $\text{Br}_2(\text{l}) + \text{Cl}_2(\text{g}) \longrightarrow 2\text{BrCl}(\text{g})$ are 29.37 kJ and 104.0 J K^{-1} respectively. Above what temperature will this reaction become spontaneous ?
 (A) $T > 177.8 \text{ K}$ (B) $T > 354.1 \text{ K}$ (C) $T > 282.4 \text{ K}$ (D) $T > 141.2 \text{ K}$
- Q.19** ΔH and ΔS for the system $\text{H}_2\text{O(l)} \rightleftharpoons \text{H}_2\text{O(g)}$ at 1 atmospheric pressure are $40.63 \text{ kJ mol}^{-1}$ and $108.8 \text{ J K}^{-1} \text{ mol}^{-1}$ respectively. The temperature at which the rates of forward and backward reactions will be same, is :
 (A) 373.4 K (B) 256.2 K (C) 316.8 K (D) 278.5 K
- Q.20** The equilibrium constant K_c for the following reaction at 400 K

$$2\text{NOCl(g)} \rightleftharpoons 2\text{NO(g)} + \text{Cl}_2(\text{g})$$
 is : [Given : $\Delta H^\circ = 77.2 \text{ kJ}$ and $\Delta S^\circ = 122 \text{ J K}^{-1}$ at 400 K]
 (A) 2.577×10^{-4} (B) 1.958×10^{-4} (C) 28.4×10^{-3} (D) 1.466×10^{-2}

SOLVED PROBLEMS

SUBJECTIVE

Problem 1 :



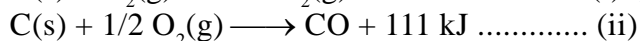
(a) In an oven using coal (assume the coal is 80% carbon in weight), insufficient oxygen is supplied such that 60% of carbon is converted to CO_2 and 40% carbon is converted to CO.

Find out the heat generated when 10 kg of coal is burnt in this fashion.

(b) Calculate the heat generated if a more efficient oven is used such that only CO_2 is formed.

(c) Calculate the percentage loss in heating value for the inefficient oven.

Solution :



Weight of C in 10 kg coal = $10000 \times 0.8 = 8000 \text{ g}$

Weight of C converted into CO_2 = $8000 \times 0.6 = 4800 \text{ g}$

weight of C converted into CO = $8000 \times 0.4 = 3200 \text{ g}$

12 g (1 mole) C on conversion into CO_2 liberates = 394 kJ

4800 g of c on conversion into CO_2 liberates = 153,600 kJ

12 g(1 mole) C on conversion into CO liberates = 111 kJ

$$3200 \text{ g of c on conversion into CO liberates} = \frac{111 \times 3200}{12} = 29600 \text{ kJ}$$

$$\text{Total heat liberated} = 153600 + 29600 \text{ kJ} = 183200 \text{ kJ}$$



12 g carbon liberates heat = 394 kJ

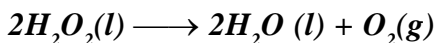
$$8000 \text{ g of carbon liberates heat} = \frac{394 \times 8000}{12} = 262666.67 \text{ kJ}$$

(c) Heat lost by oven = $262666.67 - 183200 = 79466.67 \text{ kJ}$

$$\% \text{ lost of heat} = \frac{79466.67 \times 100}{262666.67} = 32.25\%$$

Problem 2 :

Calculate the standard internal energy change for the following reaction at 25°C .



ΔH_f° at 25°C for $H_2O_2(l) = -188 \text{ kJ mol}^{-1}$, $H_2O(l) = -286 \text{ kJ mol}^{-1}$

Solution :

$$\begin{aligned} \Delta H^\circ &= \sum \Delta H^\circ_{(\text{product})} - \sum H^\circ_{(\text{reactants})} \\ &= 2(-286) + 0 - 2(-188) \\ &= -572 + 376 = -196 \text{ kJ} \end{aligned}$$

$$\Delta n(g) = 1 - 0 = 1$$

$$\begin{aligned} \Delta H^\circ &= \Delta E^\circ + \Delta n_{(g)} RT \\ &= -196 - 1 \times 8.314 \times 10^{-3} \times 298 = -198.4775 \text{ kJ} \end{aligned}$$

CHEMICAL THERMODYNAMICS

Problem 3 :

A sample of argon gas at 1 atm pressure and 27°C expands reversibly and adiabatically from 125 dm³ to 250 dm³. Calculate the enthalpy change in this process. C_v for argon is 12.48 JK⁻¹ mol⁻¹.

Solution :

For adiabatic expansion, we have

$$\frac{C_v}{R} \ln \frac{T_2}{T_1} = \ln \frac{V_2}{V_1}, \quad \frac{V_2}{V_1} = 2$$

$$\therefore \frac{12.48}{8.314} \ln \frac{T_2}{300} = \ln 2 \quad \frac{12.48}{8.314} \ln \frac{T_2}{300} = 0.3010$$

$$\ln \frac{T_2}{300} = \frac{0.3010 \times 8.314}{12.48} \quad \ln \frac{T_2}{300} = 0.200$$

$$T_2 = 300 \times 1.586 = 475.8 \text{ K or } 202.8^\circ\text{C}$$

$$\Delta T = T_2 - T_1 = 475.8 - 300 = 175.8 \text{ K}$$

$$C_p = C_v + R$$

$$C_p = 12.48 + 8.314 = 20.794 \text{ JK}^{-1}$$

Now, $PV = nRT$

$$1 \times 1.25 = n \times 0.0821 \times 300 \quad \Rightarrow \quad n = 0.05$$

We know

$$\Delta H = nC_p \Delta T = 0.05 \times 20.794 \times 175.8 = 182.77 \text{ J}$$

Problem 4 :

Calculate the heat of neutralization from the following data 200 ml of 1 M HCl is mixed with 400 ml of 0.5 M NaOH. The temperature rise in calorimeter was found to be 4.4°C. Water equivalent of calorimeter is 12 g and specific heat is 1 cal/ml/degree for solution.

Solution :

The heat produced (ΔH_1) during neutralization of 200 Meq. of NaOH and HCl each (Meq. = N × V) is taken up by calorimeter and solution in it.

$$\Delta H_1 = \text{Heat taken up by calorimeter} + \text{solution}$$

$$\therefore \Delta H_1 = m_1 S_1 \Delta T + m_2 S_2 \Delta T$$

$$= 12$$

$$[\Theta \text{ total solution} = (200 + 400) \text{ ml.}] = 2692.8 \text{ cal}$$

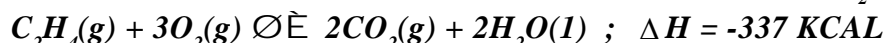
$$\Theta \quad \text{Neutralization of 200 Meq. gives heat} = -2692.8 \text{ cal}$$

$$\therefore \quad \text{Neutralization of 1000 Meq. gives heat} = -2692 \times 5 = -13464 \text{ cal}$$

$$= -13.464 \text{ k cal}$$

Problem 5 :

The thermochemical equation for the combustion of ethylene gas, C₂H₄, is



Assuming 70% efficiency, calculate the weight of water at 20°C that can be converted into steam at 100°C by burning 1 m³ of C₂H₄ gas measured at S.T.P. Heat of vaporization of water at 20°C and 100°C are 1.00 kcal/kg and 540 kcal/kg respectively.

Solution :

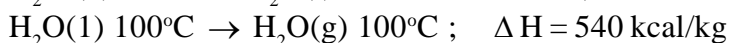
No. of moles in 1 m³ of ethylene = 44.6 mol

$$\Delta H \text{ for 1 m}^3 \text{ of ethylene (44.6 mol of ethylene)} = n(\text{C}_2\text{H}_4) \times \Delta H (1 \text{ mole})$$

$$= -1.50 \times 10^4 \text{ kcal}$$

$$\therefore \text{ The useful heat} = 1.05 \times 10^4 \text{ cal}$$

For the overall process, consider two stages :

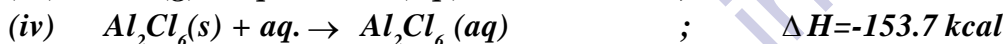
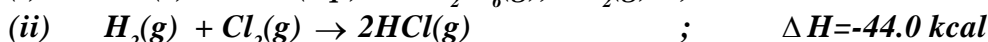
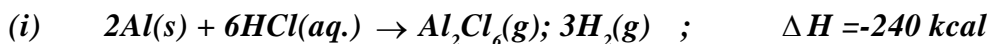


$$\therefore \Delta H (\text{total}) = 620 \text{ kcal/kg}$$

$$\therefore \text{ Wt. of water converted into steam} = \frac{\text{Amount of heat available}}{\text{Heat required / kg}} = \frac{1.05 \times 10^4}{620} = 16.9 \text{ kg}$$

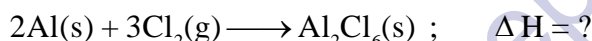
Problem 6 :

Calculate the heat of formation of anhydrous aluminium chloride, Al₂Cl₆, from the following data.



Solution :

The required equation is

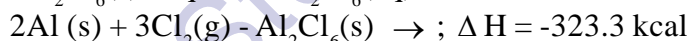
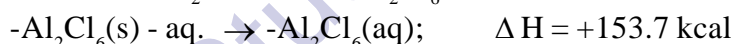


For obtaining this,

Multiply (ii) by 3, (iii) by 6 and add the resulting equations to (i)



Subtract (iv) from (v) and rearrange the product



Hence the heat of formation of anhydrous aluminium chloride = -323.3 kcal

Problem 7 :

10 g of argon gas is compressed isothermally and reversibly at a temperature of 27°C from 10L to 5 L. Calculate q, W and ΔE for this process. (At wt. of Ar =40)

Solution :

$$\text{No. of moles of argon} = \frac{10}{40} = 0.25 \text{ mole} \quad \text{and} \quad V_1 = 10 \text{ litre, } V_2 = 5 \text{ litres, } T = 300 \text{ K}$$

$$\text{For isothermal reversible compression} \quad W = -2.303 nRT \log \frac{V_2}{V_1}$$

$$= 2.302 \times 0.25 \times 2 \times 300 \times \log \frac{10}{5} = 103.6 \text{ cal}$$

Amount of heat absorbed = 103.6 cal

Now we know that during isothermal reversible process, internal energy remains constant throughout the process, hence the change in energy (ΔE) will be zero.

CHEMICAL THERMODYNAMICS

Problem 8 :

Calculate the maximum work done when pressure on 10 g of hydrogen is reduced from 20 to 1 atm at a constant temperature of 273 K. The gas behaves ideally. Will there be any change in internal energy. Also calculate Q.

Solution :

$$W = 2.303 nRT \log \frac{P_1}{P_2} = 2.303 \times \frac{10}{2} \times 2 \times 273 \log \frac{20}{1} = 8180 \text{ calories}$$

Since the change is taking place constant temperature, internal energy will not change, i.e.

$$\Delta E = 0 \Rightarrow Q = \Delta E + W = 0 + 8180 = 8180 \text{ calories}$$

Problem 9 :

The heat of combustion of glycogen is about 476 kJ/mol of carbon. Assume that average heat loss by an adult male is 150 watt. If we were to assume that all the heat comes from oxidation of glycogen, how many units of glycogen (1 mole carbon per unit) must be oxidised per day to provide for this heat loss ?

Solution :

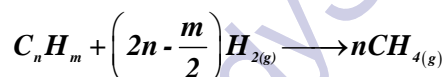
Total energy required in the day

$$= \frac{150 \times 24 \times 60 \times 60}{1000} \text{ kJ} \quad (1 \text{ watt} = \text{J sec}^{-1}) = 12960 \text{ kJ}$$

$$\text{Units of glycogen required} = \frac{12960}{476} = 27.22 \text{ units.}$$

Problem 10 :

The "heat of total cracking" of hydrocarbons H_{TC} is defined as H at 298.15 K and 101.325 kPa for the process below :

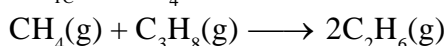


Given that H_{TC} is - 65.2 kJ for C_2H_6 and - 87.4 kJ for C_3H_8 , calculate ΔH for



Solution :

$$H_{TC} \text{ of } CH_4 = 0$$



$$\Delta H = 2\Delta H_{T.C.}(C_2H_6) - \Delta H_{T.C.}(C_3H_8)$$

$$= 2(-65.2) - (-87.4) = -43 \text{ kJ}$$

Problem 11 :

A constant pressure calorimeter consists of an insulated beaker of mass 92 g made up of glass with heat capacity $0.75 \text{ J K}^{-1} \text{ g}^{-1}$. The beaker contains 100 mL of 1 M HCl of 22.6°C to which 100 mL 1 M NaOH at 23.4°C is added. The final temperature after the reaction is complete is 29.3°C . What is ΔH per mole for this neutralization reaction ? Assume that the heat capacities of all solutions are equal to that of same volumes of water.

Solution :

Initial average temperature of the acid and base

$$= \frac{22.6 + 23.4}{2} = 23.0^{\circ}\text{C}$$

$$\text{Rise in temperature} = (29.3 - 23.0) = 6.3^{\circ}\text{C}$$

$$\begin{aligned} \text{Total heat produced} &= (92 \times 0.75 + 200 \times 4.184) \times 6.3 \\ &= (905.8) \times 6.3 = 5706.54 \text{ J} \end{aligned}$$

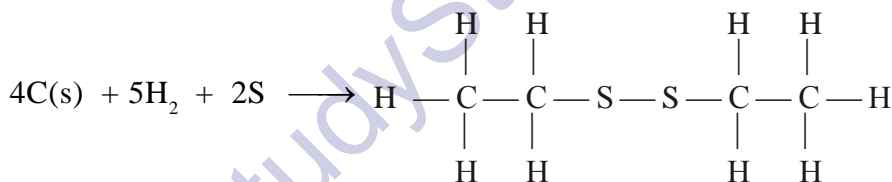
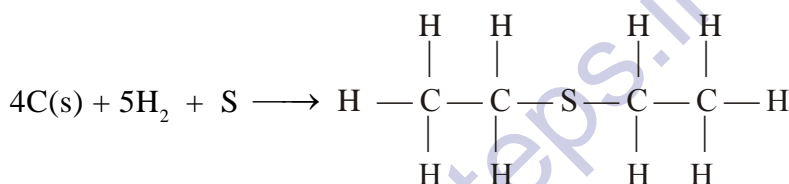
$$\begin{aligned} \text{Enthalpy of neutralisation} &= - \frac{5706.54}{100} \times 1000 \times 1 \\ &= - 57065.4 \text{ J} = - 57 \text{ kJ} \end{aligned}$$

Problem 12 :

Find bond enthalpy of S – S bond from the following data :



Solution :



$$\Delta H = \Sigma(\text{B.E.})_R - \Sigma(\text{B.E.})_P$$

(i) $- 147.2 = \text{Heat of atomization of } 4\text{C}, 10\text{H}, 1\text{S}$

$- \text{B.E. of } 10(\text{C} - \text{H}), 2(\text{C} - \text{S}), 2(\text{C} - \text{C})$

(ii) $- 201.9 = \text{Heat of atomization of } 4\text{C}, 10\text{H}, 2\text{S}$

$- \text{B.E. of } 10(\text{C} - \text{H}), 2(\text{C} - \text{S}), 2(\text{C} - \text{C}), (\text{S} - \text{S})$

Subtracting (i) from (ii)

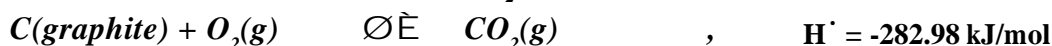
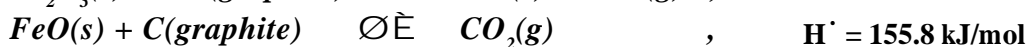
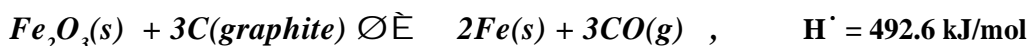
$- 201.9 + 147.2 = \text{Heat of formation of } 1\text{S} - \text{B.E. of } (\text{S} - \text{S})$

$= 222.8 \text{ kJ} - \text{B.E. of } (\text{S} - \text{S})$

$\text{B.E. of } (\text{S} - \text{S}) = 277.5 \text{ kJ}$

Problem 13 :

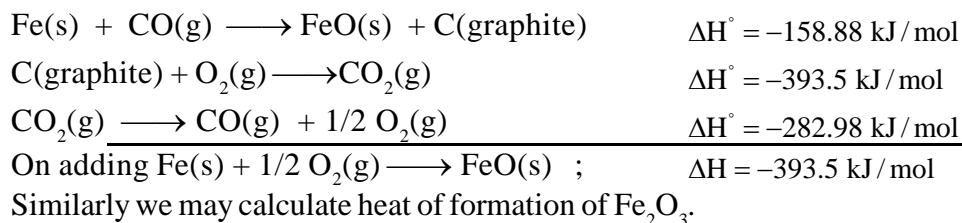
From the data at 25°C :



Calculate standard heat of formation of $\text{FeO}(\text{s})$ and $\text{Fe}_2\text{O}_3(\text{s})$.

CHEMICAL THERMODYNAMICS

Solution :

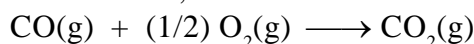


Problem 14 :

Show that the reaction, $\text{CO(g)} + (1/2) \text{O}_2\text{(g)} \rightleftharpoons \text{CO}_2\text{(g)}$ at 300 K is spontaneous and exothermic, when the standard entropy change is $-0.094 \text{ kJ mol}^{-1} \text{ K}^{-1}$. The standard Gibbs free energies of formation of CO_2 and CO are -394.4 and $-137.2 \text{ kJ mol}^{-1}$ respectively.

Solution :

The given reaction is,



$$\begin{aligned}
 \Delta G^\circ \text{ (for reaction)} &= G_{\text{CO}_2}^\circ - G_{\text{CO}}^\circ - \left(\frac{1}{2}\right) G_{\text{O}_2}^\circ \\
 &= -394.4 - (-137.2) - 0 \\
 &= -257.2 \text{ kJ mol}^{-1}
 \end{aligned}$$

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

$$-257.2 = \Delta H^\circ - 298 \times (0.094)$$

$$\text{or } \Delta H^\circ = -288.2 \text{ kJ}$$

ΔG° is $-ve$, hence the process is spontaneous, and ΔH° is also $-ve$, hence the process is also exothermic.

Problem 15 :

Assume that for a domestic hot water supply 150 kg of water per day must be heated from 10°C to 65°C and gaseous fuel propane C_3H_8 is used for this purpose. What moles & volume of propane (in litre at STP) would have to be used for heating domestic water. ΔH for combustion of propane is $-2050 \text{ kJ mol}^{-1}$ & specific heat of water is $4.184 \times 10^{-3} \text{ kJ/g}$.

Solution :

Heat taken up by water = $m S \Delta T$

$$= 150 \times 10^3 \times 4.184 \times 10^{-3} \times 55 = 34518 \text{ kJ}$$

Q 2050 kJ heat is provided by 1 mole C_3H_8

$$\therefore 34518 \text{ kJ heat is provided by} = 34518/2050$$

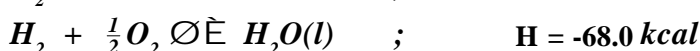
$$= 16.838 \text{ mole of } \text{C}_3\text{H}_8$$

$$\therefore \text{Volume of } \text{C}_3\text{H}_8 \text{ at NTP} = 16.838 \times 22.4 \text{ litre}$$

$$= 3.77 \times 10^2 \text{ litre}$$

Problem 16 :

Using the data (all values in kcal mol^{-1} at 25°C) given below, calculate bond energy of C – C & C – H bonds.



Solution : For C_3H_8 : $3C + 4H_2 \longrightarrow C_3H_8$; $\Delta H = ?$
 For C_2H_6 : $2C + 3H_2 \longrightarrow C_2H_6$; $\Delta H = ?$

$$\therefore \Delta H_1 = -[2(C-C) + 8(C-H)] + [3C_{s \rightarrow g} + 4(H-H)] \quad \dots\dots (1)$$

$$\Delta H_2 = -[1(C-C) + 6(C-H)] + [2C_{s \rightarrow g} + 3(H-H)] \quad \dots\dots (2)$$

$$\text{Also given } C + O_2 \longrightarrow CO_2 ; \Delta H = -94.0 \text{ k cal} \quad \dots\dots (5)$$

$$H_2 + \frac{1}{2} O_2 \longrightarrow H_2O ; \Delta H = -68.0 \text{ k cal} \quad \dots\dots (6)$$

$$C_2H_6 + (7/2)O_2 \longrightarrow 2CO_2 + 3H_2O ; \Delta H = -530 \text{ kcal} \quad \dots\dots (7)$$

$$C_3H_8 + 5O_2 \longrightarrow 3CO_2 + 4H_2O ; \Delta H = -530 \text{ kcal} \quad \dots\dots (8)$$

By inspection method : $2 \times (5) + 3 \times (6) - (7)$ gives

$$2C + 3H_2 \longrightarrow C_2H_6 ; \Delta H_2 = -20 \text{ k cal} \quad \dots\dots (9)$$

and $3 \times (5) + 4 \times (6) - (8)$ gives

$$3C + 4H_2 \longrightarrow C_3H_8 ; \Delta H_1 = -24 \text{ k cal} \quad \dots\dots (10)$$

\therefore By equation (3), (4), (9) and (10)

$$a + 6b = 676$$

$$2a + 8b = 956$$

\therefore $a = 82 \text{ k cal}$ and $b = 99 \text{ k cal}$

Bond energy of C – C bond = 82 k cal

and Bond energy of C – H bond = 99 k cal

Problem 17 :

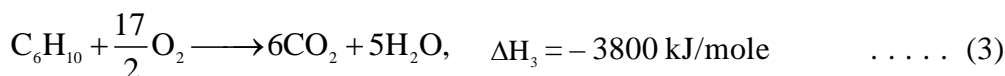
The standard enthalpy of combustion at 25°C of hydrogen, cyclohexene (C_6H_{10}) and cyclohexane (C_6H_{12}) are –241, –3800 and –3920 kJ/mole respectively. Calculate the heat of hydrogenation of cyclohexane.

Solution :

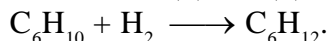
The required reaction is



Let us write the given facts



The required reaction (1) can be obtained by adding equations (2) and (3) and subtracting (4) from the sum of (2) and (3).



$$\begin{aligned} \Delta H_1 &= (\Delta H_2 + \Delta H_3) - \Delta H_4 \\ &= [-241 + (-3800)] - (-3920) \\ &= (-241 - 3800) - (-3920) \\ &= -4041 + 3920 = -121 \text{ kJ/mole} \end{aligned}$$

OBJECTIVE

Problem 1 :

If 1.00 kcal of heat is added to 1.2 L of oxygen in a cylinder at constant pressure of 1.000 atm, the volume increases to 1.5 L, Hence ΔE for this process is:

- (A) 0.993 kcal (B) 1.0073 kcal (C) 0.0993 kcal (D) 1.00073 kcal

Solution : (A)

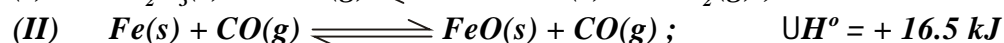
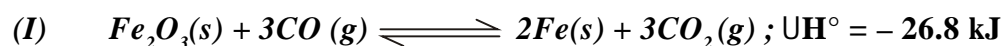
$$\Delta H = \Delta E + P\Delta V$$

$$1.00 = \Delta E + \frac{1(1.5 - 1.2)\text{L atm}}{0.082 \text{ L atm}} \times 2 \times 10^{-3} \text{ kcal}$$

$$\Delta E = 0.993 \text{ kcal}$$

Problem 2 :

Using only the following data:



the ΔH° value, in kilojoules, for the reaction $\text{Fe}_2\text{O}_3(\text{s}) + \text{CO}(\text{g}) \longrightarrow 2\text{FeO}(\text{s}) + \text{CO}_2(\text{g})$ is calculated to be:

- (A) -43.3 (B) -10.3 (C) +6.2 (D) +10.3

Solution : (C)

from equation (I) + (2 \times II) ; $\Delta H^\circ = 6.2 \text{ kJ}$

Problem 3 :

Enthalpy change when 1.00 g water is frozen at 0°C , is : ($\Delta H_{\text{fus}} = 1.435 \text{ kcal mol}^{-1}$)

- (A) 0.0797 kcal (B) -0.0797 kcal (C) 1.435 kcal (D) -1.435 kcal

Solution : (B)

$$\Delta H (\text{per g}) = \frac{-1.435}{18} \text{ kcal} = -0.0797 \text{ kcal g}^{-1}$$

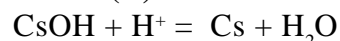
Problem 4 :

Heat of neutralisation of CsOH with all strong acids is $13.4 \text{ kcal mol}^{-1}$. the heat released on neutralization of CsOH with HF (weak acid) is $16.4 \text{ kcal mol}^{-1}$

ΔH° of ionisation of HF is:

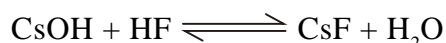
- (A) 3.0 kcal (B) -3.0 kcal (C) 6.0 kcal (D) 0.3 kcal

Solution : (B)



$$\Delta H = -13.4 \text{ kcal}$$

$$\text{Heat of ionisation of CsOH} = 13.7 - 13.4 = +0.3 \text{ kcal}$$



$$\Delta H = -16.4 \text{ kcal}$$

$$\text{Heat of ionisation of HF} = x \text{ kcal}$$

$$\text{Heat of ionisation of CsOH} = 0.3 \text{ kcal}$$

$$\text{Heat of neutralization} = -13.7$$

(of H^+ and OH^-)

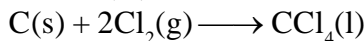
$$-13.9 + x + 0.3 = -16.4 \Rightarrow x = -3.0 \text{ kcal}$$

Problem 5 :

The C–Cl bond energy can be calculated from:

- (A) $\Delta H_f^\circ (CCl_4, l)$ only (B) $\Delta H_f^\circ (CCl_4, l)$ and $D(Cl_2)$
 (C) $\Delta H_f^\circ (CCl_4, l)$ and $D(Cl_2)$
 (D) $\Delta H_f^\circ (CCl_4, l)$, $\Delta H_f^\circ (C, g)$ and $\Delta H_{vap}^\circ (CCl_4)$

Solution : (D)



$$\Delta H_f^\circ (CCl_4, l) = \Delta H_f^\circ [C(s) \longrightarrow C(g)] + 2(BE)_{Cl-Cl} - [\Delta H_{vap}^\circ (CCl_4) + 4(BE)_{Cl-Cl}]$$

Problem 6 :

Enthalpy of fusion of a liquid is $1.435 \text{ kcal mol}^{-1}$ and molar entropy change is $5.26 \text{ cal mol}^{-1} \text{ K}^{-1}$. Hence melting point of liquid is :

- (A) 100°C (B) 0°C (C) 373 K (D) -273°

Solution : (B)

$$\Delta S = \frac{\Delta H}{T} \Rightarrow T = \frac{\Delta H}{\Delta S} \Rightarrow \frac{1435 \text{ cal}}{5.26} = 273 \text{ K} \Rightarrow 0^\circ\text{C}$$

Problem 7 :

For the reaction



$\Delta E = 2.1 \text{ kcal}$, $\Delta S = 20 \text{ cal/K}$ at 300 K

Hence ΔG is :

- (A) 2.7 kcal (B) -2.7 kcal (C) 9.3 kcal (D) -9.3 kcal

Solution : (B)

$$\Delta H = \Delta E + \Delta n_g RT = 2.1 + 2 \times 0.002 \times 300 = 3.03 \text{ kcal}$$

$$\Delta G = \Delta H - T\Delta S = 3.03 - 300 \times (0.02) = -2.7 \text{ kcal}$$

Problem 8 :

If $\Delta G = \Delta H - T\Delta S$ and $\Delta G = \Delta H + T \frac{d(\Delta G)}{dT}$ then variation of EMF of a cell E , with temperature T , is given by :

- (A) $\frac{\Delta H}{nF}$ (B) $\frac{\Delta G}{nF}$ (C) $\frac{\Delta S}{nF}$ (D) $-\frac{\Delta S}{nF}$

Solution : (C)

$$\text{On comparison : } \Delta S = \left[\frac{d(\Delta G)}{dT} \right]_P \quad \Delta S = \frac{d(-nFE)}{dT} = nF \left(\frac{dE}{dT} \right) \therefore \left(\frac{dE}{dT} \right) = \frac{\Delta S}{nF}$$

Problem 9 :

1 g H_2 gas at S.T.P. is expanded so that volume is doubled. Hence work done is:

- (A) 22.4 L atm (B) 5.6 L atm (C) 11.2 L atm (D) 44.8 L atm

Solution : (C)

$$V_1 (\text{volume of } 1 \text{ g } H_2) = 11.2 \text{ L at NTP}$$

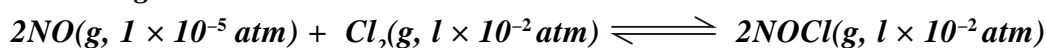
$$V_2 (\text{volume of } 1 \text{ g } H_2) = 22.4 \text{ L}$$

$$\therefore W = P\Delta V = 11.2 \text{ L atm}$$

CHEMICAL THERMODYNAMICS

Problem 10 :

Following reaction occurs at 25°C :



ΔG° is:

- (A) -45.65 kJ (B) -28.53 kJ (C) -22.82 kJ (D) -57.06 kJ

Solution : (A)

$$\Delta G^\circ = -2.303 RT \log K_{\text{eq}} \quad K_{\text{eq}} = \frac{P_{\text{NOCl}}^2}{P_{\text{NO}}^2 P_{\text{Cl}_2}} = 108 \quad \text{Hence } \Delta G^\circ = -45.65 \text{ kJ}$$

Problem 11 :

1 mol of NH₃ gas at 27°C is expanded under adiabatic condition to make volume 8 times ($\gamma = 1.33$). Final temperature and work done respectively are:

- (A) 160 K, 900 cal (B) 150K, 400 cal (c) 250 K, 1000 cal (D) 200 K, 800 cal

Solution : (A)

$$T_2 = T_1 \left(\frac{V_1}{V_2} \right)^{\gamma-1} = 300 \times \left(\frac{1}{8} \right)^{1.33-1} = 150 \text{ K}$$

$$w = -C_v \Delta T = -C_v (T_2 - T_1) \quad (\because \text{for adiabatic process } w = -q)$$

$$= -3 \times 2 \times (150 - 300) = 900 \text{ cal} \quad (\because \frac{C_v + R}{C_v} = 1.33 \Rightarrow C_v = 3 \times R)$$

Problem 12 :

Temperature of 1 mol of gas is increased by 1° at constant pressure. Work done is:

- (A) R (B) 2R (C) $\frac{R}{2}$ (D) 3R

Solution : (A)

$$W = P (\Delta V)$$

$$PV = RT$$

$$P(V + \Delta V) = R(T + 1) \quad \Rightarrow \quad PV + P\Delta V = RT + R$$

$$\therefore P\Delta V = R$$

Problem 13 :

The gas absorbs 100 J heat and is simultaneously compressed by a constant external pressure of 1.50 atm from 8 L to 2L in volume. Hence ΔE will be:

- (A) - 812 J (B) 812 J (C) 1011 J (D) 911 J

Solution : (C)

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

$$100 = \Delta E + \frac{1.5(-6)}{0.0821} \times 8.314$$

$$\Delta E = 1011.4 \text{ J}$$

Problem 14 :

The standard heat of combustion of solid boron is equal to:

- (A) $\Delta H_f^\circ(B_2O_3)$ (B) $\frac{1}{2} \Delta H_f^\circ(B_2O_3)$ (C) $2\Delta H_f^\circ(B_2O_3)$ (D) $-\frac{1}{2} \Delta H_f^\circ(B_2O_3)$

Solution : (B)

Problem 15 :

$C_p - C_v = R$. This R is :

- (A) Change in K.E. (B) Change in rotational energy
 (C) work done which system can do on expanding the gas per mol per degree increase in temperature
 (D) All correct

Solution : (C)

$PV = RT$ at temp T for one mol

$P(V + \Delta V) = R(T + 1)$ at temp. (T + 1) for one mol

$\therefore P\Delta V = R$

Problem 16 :

For A \rightleftharpoons B, $\Delta H = 4 \text{ kcal mol}^{-1}$, $\Delta S = 10 \text{ cal mol}^{-1}K^{-1}$.

Reaction is spontaneous when temperature can be :

- (A) 400K (B) 300K (C) 500K (D) none is correct

Solution : (C)

$\Delta G = -ve$ for spontaneous change

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

$$\therefore T\Delta S > \Delta H, T > \frac{\Delta H}{\Delta S} \Rightarrow T > \frac{4000}{10} \Rightarrow T > 400 \text{ K}$$

Problem 17 :

If a process is both endothermic and spontaneous, then :

- (A) $\Delta S > 0$ (B) $\Delta S < 0$ (C) $\Delta H < 0$ (D) $\Delta G > 0$

Solution : (A)

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

For spontaneous process, $\Delta G = \text{negative}$

For endothermic process, $\Delta H = \text{positive}$

Therefore $\Delta S > 0$

Problem 18 :

For which change $\Delta H \neq \Delta E$

- (A) $H_2 + I_2 \rightleftharpoons 2HI$ (B) $HCl + NaOH \longrightarrow NaCl + H_2O$
 (C) $C(s) + O_2(g) \rightleftharpoons CO_2(g)$ (D) $N_2 + 3H_2 \longrightarrow 2NH_3$

Solution : (D)

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

CHEMICAL THERMODYNAMICS

Problem 19 :

If a chemical change is brought about by one or more methods in one or more steps, then the amount of heat absorbed or evolved during the complete course of reaction is same, which ever method was followed. This law is known as

- (A) Le Chatelier's principle (B) Hess's law
(C) Joule Thomson effect (D) Trouton's law

Solution : (B)

The statement is definition of Hess's law

Problem 20 :

The Kirchhoff's equation gives the effect of on heat of reaction.

- (A) Pressure (B) Temperature (C) Volume (D) Molecularity

Solution : (B)

Kirchhoff's equation is : $\Delta H_2 - \Delta H_1 = \Delta C_p (T_2 - T_1)$

Problem 21 :

The heats of neutralisation of four acids A, B, C, D are - 13.7, - 9.4, - 11.2 and - 12.4 kcal respectively when they are neutralised by a common base. The acidic character obeys the order :

- (A) $A > B > C > D$ (B) $A > D > C > B$ (C) $D > C > B > A$ (D) $D > B > C > A$

Solution : (B)

Lower is heat of neutralisation, more is dissociation energy, weaker is acid

Problem 22 :

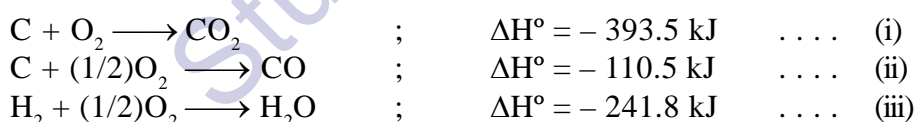
The ΔH_f° for $CO_2(g)$, $CO(g)$, and $H_2O(g)$ are - 393.5, -110.5 & - 241.8 kJ mol⁻¹ respectively. The standard enthalpy change (in kJ) for the reaction,

$CO_2(g) + H_2(g) \rightleftharpoons H_2O(g)$ is :

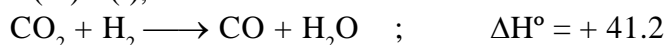
- (A) 524.21 (B) 41.2 (C) - 262.5 (D) - 41.2

Solution : (B)

Given



By (ii) + (iii) - (i),



ANSWERS

1. Daily Practice Problem Sheet

- | | | | | | | |
|-------|-------|-------|-------|-------|-------|-------|
| 1. T | 2. F | 3. F | 4. T | 5. A | 6. C | 7. D |
| 8. C | 9. D | 10. A | 11. B | 12. A | 13. B | 14. C |
| 15. B | 16. C | | | | | |

2. Daily Practice Problem Sheet

- | | | | | | | |
|-------|-------|-------|-------|-------|-------|-------|
| 1. C | 2. D | 3. C | 4. B | 5. B | 6. C | 7. C |
| 8. A | 9. A | 10. A | 11. D | 12. A | 13. A | 14. A |
| 15. A | 16. C | | | | | |

3. Daily Practice Problem Sheet

- | | | | | | | |
|---------------------------|------------------|-------|-------|-------|-------|-------|
| 1. D | 2. B | 3. A | 4. A | 5. A | 6. D | 7. D |
| 8. C | 9. D | 10. A | 11. D | 12. B | 13. B | 14. A |
| 15. C | 16. B | 17. A | 18. B | 19. A | 20. D | 21. D |
| 22. B | 23. A | 24. D | 25. C | 26. C | 27. D | 28. C |
| 29. A | 30. A | 31. B | 32. B | 33. B | | |
| 34. $d + c - e - 2a - 3b$ | 35. - 1539.94 kJ | | | | | |

4. Daily Practice Problem Sheet

- | | | | | | | |
|-------|-------|-------|-------|---------------------|-------|-------|
| 1. C | 2. A | 3. B | 4. D | 5. B | 6. A | 7. C |
| 8. A | 9. C | 10. A | 11. A | 12. (i) A, (ii) (D) | | 13. D |
| 14. A | 15. C | 16. A | 17. D | 18. B | 19. B | 20. B |
| 21. C | 22. D | 23. C | 24. B | | | |

5. Daily Practice Problem Sheet

- | | | | | | | |
|-------|-------|--------|---------|-------|-------|-------|
| 1. A | 2. D | 3. B | 4. A | 5. A | 6. D | 7. D |
| 8. B | 9. B | 10. AC | 11. ABD | 12. B | 13. B | 14. C |
| 15. B | 16. B | 17. A | 18. C | 19. A | 20. B | |

CHEMICAL THERMODYNAMICS

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