04

Chemical Thermodynamics

Syllabus

4.1 Introduction
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4.4 Expression for pressure- volume (*PV*)
4.5 Concept of maximum work
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4.7 First law of thermodynamics
4.8 Enthalpy (*H*)
4.9 Enthalpies of physical transformations
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Q.1 Can you recall?

i. How do you define energy?

Ans : The energy is the capacity to do work.

ii. What are the different forms of energy?

Ans: Electrical, mechanical, chemical, thermal, nuclear etc. are the different forms of energy.

4.1 Introduction

Q.2 Energy can be transformed from one form into another. Explain using an example.

Ans:

i. Transformation of liquid water into vapour, solid ice into liquid water or burning of carbon forming carbon dioxide, CO_2, are accompanied by a change in energy.

ii. In dry cell, the chemical energy is converted into electrical energy.

iii. On the other hand, in electroplating of metals electrical energy is converted into chemical energy.

iv. Thus it may be realized that the energy can be transformed from one form into another.

Do you know

At the top of dam, water is stored in a reservoir. It has certain potential energy due to its height from ground level and its kinetic energy is negligible as it is not in motion. As the water starts to fall down through an outlet its potential energy decreases and kinetic energy increases due to the downward velocity. It means that potential energy of falling water is converted into kinetic energy.

Q.3 What does thermodynamics deal with?

Ans:

i. Thermodynamics is concerned with the energy changes in physical and chemical transformations.

ii. Thermodynamics, however gives no information on the rates of physical or chemical processes or underlying mechanisms involved in these.

Q.4 Define the following.

i. System
ii. Surrounding
iii. Universe

Ans:

i. A part of the universe under thermodynamic investigation is called the system.

ii. All other parts of the universe outside the system such as cylinder, room and others, are surroundings.

iii. The universe is made of system plus surroundings.

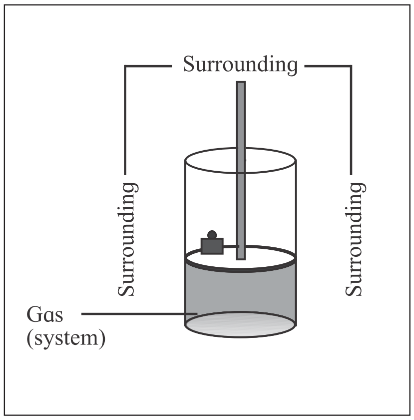
Q.5 Explain the terms system and surrounding with the help of a suitable diagram.

Ans:

i. Consider a gas enclosed in a cylinder equipped with a movable piston as shown in the thermodiagram.

ii. Suppose we undertake study of change in volume of a gas and the amount of energy released or gained by a gas when the pressure is varied by putting certain mass on the piston.

iii. In this case, a gas under study is called the system.



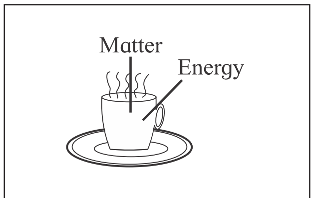
System and surroundings

Q.6 Observe and discuss

Observe the below figure and discuss with reference to transaction of energy and matter.

Ans:

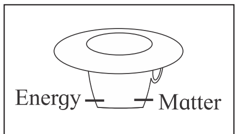
i. **Open system :**



Open system
(a)

a. An open cup containing hot coffee placed in a room.
b. You observe coffee cools down releasing heat to the surroundings.
c. The water vapour from coffee simultaneously passes into surrondings.
d. Such a system (coffee) which exchanges both energy and matter with the surroundings is called an open system.

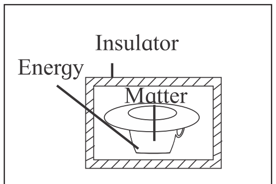
ii. **Closed system :**



Closed system
(b)

a. In a cup containing hot coffee is covered with a saucer.
b. Coffee cools down by giving away heat to the surroundings.
c. The water vapour from coffee now does not pass into surroundings.
d. Such a system that exchanges energy and not the matter with the surroundings is called a closed system.

iii. **Isolated system :**



Isolated system

a. A cup containing hot coffee covered with a saucer is insulated from the surroundings.
b. Coffee does not cool down. Moreover, there is no escape of water vapour into the surroundings.
c. Such a system that does not allow exchange of either energy or matter with the surroundings is an isolated system.

Q.7 What is extensive property? Give examples.

Ans:

i. A property which depends on the amount of matter present in a system is called an extensive property.

ii. Examples : Mass, volume, internal energy, heat capacity, number of moles.

Q.8 What is intensive property? Give examples.

Ans:

i. A property which is independent of the amount of matter in a system is called intensive property.

ii. Examples : Pressure, temperature, surface tension, viscosity, melting point, boiling point, specific heat.

Q.9 What is state function ? Give examples.

Ans: The property which depends on the state of a system and independent of a path followed to attain it, is called the state function.

Q.10 Explain state function.

Ans:

i. Consider certain amount of a gas is enclosed in a cylinder fitted with a movable piston.

ii. Suppose the pressure of the gas is 1 bar (P_1), volume is 1 dm^3 (V_1) and temperature is 300 K (T_1) in the beginning.

iii. This initial state of the system is fully defined by specifying the values of these properties.

iv Such properties defining the state of a system, are state functions.

v. Suppose the pressure of the system is increased to 2 bar, (P_2) volume changes to 0.5 dm^3 (V_2) and the temperature is maintained at 300 K (T_1).

vi. This is the final state of the system which is different from the initial state. A change in state functions of the system brings forth a change of its state.

vii. The final state of the system in Fig. 4.3. is described by pressure 2 bar (P_2), volume 0.5 dm^3(V_2) and temperature 300 K(T_1).

viii A system continues to be in such state as long as the state functions are unchanged.

xi. How the pressure 2 bar is attained whether by increasing from 1 bar to 2 bar or decreasing from 5 bar to 2 bar, would not matter.

x. The property which depends on the state of a system and independent of a path followed to attain it, is called the state function.

Q.11 Write a short note on process.

Ans:

i. The term process means a physical or chemical change in a system on going from one state to another.

ii. This can be achieved by a number of paths by some operation.

iii. A path here refers to a sequence of situations the system undergoes during the accomplishment of the change.

iv. In other words the process in general may not necessarily determine the change in unique way.

v. Only isothermal and adiabatic reversible processes follow the unique path to bring about the change of state of the system.

Q.12 What is path function? Give examples

Ans: The properties which depend on the path are called path functions. For example, work (*W*) and heat (*Q*).

Q.13 Explain the following : Thermodynamic equilibrium.

Ans:

i. A system is said to be in thermodynamic equilibrium when its state functions do not vary with time.

ii. Consider a gas enclosed in a cylinder fitted with a movable piston.

iii. The gas has temperature T_1, pressure P_1 and volume V_1.

iv. These state functions continue to be constant as long as piston is motionless, and no heat exchange takes place. This is an equilibrium state.

v. Now move the piston in upward direction so that the gas expands.

vi. It passes through states for which pressure, volume and temperature are not specified and vary continuously during the movement of the piston.

vii. The gas would then be in non equilibrium state.

viii. Stop the movement of the piston.

xi. Suppose at this stage the pressure and volume of the gas are respectively P_2 and V_2 and the temperature is constant at T_1.

x. The state functions are constant since the piston is motionless. The gas is then in another equilibrium state.

Note – Thermodynamics considered here is limited to equilibrium state.

Q.14 Define process.

Ans: A transition from one equilibrium state to another is called a process. They are of different types.

Q.15 Explain the following terms

- **i. Isothermal process**
- **ii. Isobaric process**
- **iii. Isochoric process**
- **iv. Adiabatic process**

Ans:

i. **Isothermal process** :

a. It is the process in which th temperature of the system remains constant throughout the transformation.

b. In such a process heat flows from the system to the surroundings and vice versa so as to keep the temperature constant.

c. For a given temperature the internal energy (U) of the system remains constant. Thus, $\Delta T = 0$ and $\Delta U = 0$.

ii. **Isobaric process :**

a. In isobaric process the pressure remains constant during the transformation.

b. In the laboratory chemical reactions are carried out in open containers at constant atmospheric pressure or $\Delta P = 0$

iii. **Isochoric process :**

a. It is a process during which the volume of the system remains constant during the transformation.

b. A chemical reaction carried out in a closed container is isochoric. For isochoric process $\Delta V = 0$.

iv. **Adiabatic process :**

a. A process in which there is no exchange of heat between system and surroundings is an adiabatic process. ($Q = 0$).

b. In adiabatic process the system is completely insulated from the surroundings.

c. For an exothermic process the heat is released which rises temperature of the system.

d. If the process is endothermic the temperature falls.

e. This results in either increase or decrease of internal energy.

Q.16 Distinguish between isothermal process and adiabatic process.

Ans:

Sr. No.	Parameter	Isothermal	Adiablatic
i.	Definition	It is defined on of thermodynamic process which occur at a constant temperature.	It is defined as one of the thermodynamic processes which occur without any heat transfer between the system and the surrounding.
ii.	Heat transfer	The pressure is more in comparison to volume.	The pressure is less in comparison to volume.
iii.	Temperature	The temperature remains constant in such a process.	Temperature changes due to variations in the internal system in such a process.
iv.	Heat	To maintain the temperature, heat can be added or released to the system.	No need to add or release the heat, constant temperture maunternance is not required here.
v.	Rate of transformation	The transformation is slow in such a process.	The transformation is fast in such a process.

Q.17 Explain reversible process.

Ans: A process conducted in such a way so that at every stage the driving force due to pressure (P) is infinitesimally greater than the opposing force due to external pressure (P_{ext}) and which can be reversed by a slight change of the opposing force is called reversible process.

Q.18 Explain thermodynamically reversible process.

Ans:

i. Consider a gas enclosed in a cylinder fitted with a movable piston.

ii. Let the external pressure be P_{ext} on the outer surface of the piston be set equal to pressure P of the gas.

iii. Neither expansion nor compression of the gas occurs. A system is then said to be in mechanical equilibrium with the surrounding.

iv. Consider P_{ext} is reduced by an infinitesimal amount.

v. Now it the P_{ext} is infinitesimally smaller than P the piston moves out slowly allowing gas to expand.

vi. If P_{ext} is slightly increased so that it becomes infinitesimally greater than P, the piston moves inward with a compression of the gas.

vii. For the system in mechanical equilibrium with its surroundings, infinitesimal change may cause the process to occur in the reverse direction.

viii. The process is then said to be thermodynamically reversible.

Q.19 Give the features of reversible process.

Ans:

i. The driving and opposing forces differ by an infinitesimal amount.

ii. The process can be reversed by an infinitesimal change in conditions.

iii. A reversible process proceeds infinitely slowly and takes place in infinite number of steps.

iv. At the end of every step of the process, the system attains mechanical equilibrium with the surrounding.

4.3 Nature of heat and work

Q.20 What is pressure - volume work or PV work.

Ans: Pressure - volume work or PV work is work done when the system (gas) expands or contracts aganist the external opposing force.

Q.21 Show that the product of pressure and volume is equal to the work.

Ans:

i. In mechanics the work is defined as the energy by which body is displaced through a distance d with an application of force.

ii. Thus, $W = f \times d$

iii. Pressure is defined as force per unit area.

iv. d is the distance, area $A = d^2$ and volume $V = d^3$.

v. Then $PV = \frac{f}{A} \times V = \frac{f}{d^2} \times d^3 = fd = W$

Q.22 Explain pressure - volume work (PV work) with the help of a diagram with respect to the following chemical reactions.

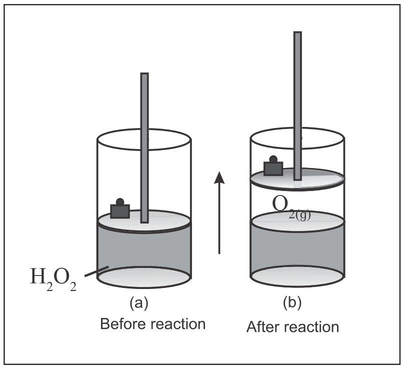
i. Decomposition of H_2O_2

ii. Reaction between NH_3 gas and HCl gas.

Ans:

i. **Decomposition of H_2:**

a. Consider $2H_2O_2(l) \rightarrow 2H_2O(l) + O_2(g)$



b. The gas produced in above reaction pushes the piston upwards so that the mass in the surroundings is raised as shown in the diagram.

c. In lifting the mass the system loses energy to the surroundings or it performs work on the surroundings.

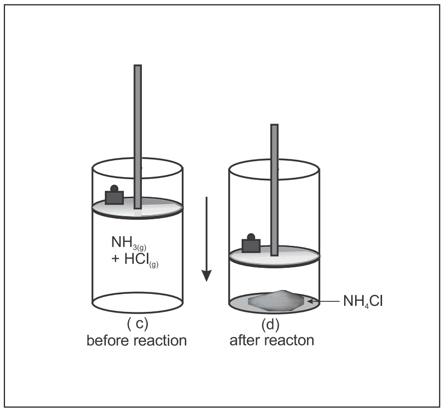
d. With no heat being transferred a loss of energy by the system is equal to work done by the system on the surroundings.

e. This is *PV* expansion.

ii. **Reaction between NH_3**

a. Now,Consider

$$NH_{3(g)} + HCl_{(g)} \rightarrow NH_4Cl_{(s)}$$



b. As the reaction progresses the gases are consumed resulting in a decrease of volume. The piston moves down.

c. A decrease in the height of the mass is shown in the diagram.

d. In the process the surroundings lose energy to the system and perform work on the system.

e. If no heat transfer occurs work done by the surroundings is equal to gain in energy by the system. This is *PV* work.

Q.23 What is heat?

Ans:

i. Heat is a form of energy by which the system exchanges energy with its surroundings.

ii. When the system and its surroundings are at different temperatures heat either flows in or let out of the system.

Q.24 Give the sign conventions for work (W) and heat (Q).

Ans:

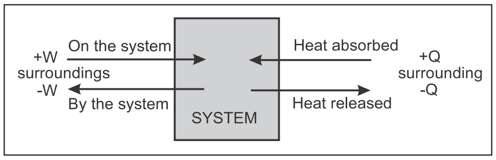
i. The energy entering the system from the surroundings has positive value. While the energy leaving the system and flowing into the surroundings is negative.

ii. $+Q$: Heat is absorbed by the system from the surroundings

iii. $-Q$: Heat is released by the system to the surroundings.

iv. $+W$: Work is done on the system by the surroundings.

v. $-W$: Work is done by the system on the surroundings.



Sign conventions

Note :

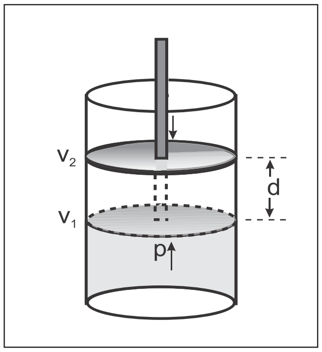
W and *Q* are path functions.

4.4 Expression for pressure-volume (*PV*) work

★ Q.25 Derive the expression for *PV* work.

Ans:

i. Consider a certain amount of gas at constant pressure *P* is enclosed in a cylinder fitted with frictionless, rigid movable piston of area A.Let volume of the gas be V_1at temperature T.This is shown in the diagram below.



Pressure-volume work

ii. On expansion the force exerted by a gas is equal to area of the piston multiplied by pressure with which the gas pushes against piston.

iii. This pressure is equal in magnitude and opposite in sign to the external atmospheric pressure that opposes the movement and has its value $-P_{ext}$.

iv. Thus, $f = -P_{ext} \times A$ .... (i)

v. where P_{ext} is the external atmospheric pressure. If the piston moves out a distance *d*, then the amount of work done is equal to the force multiplied by distance.

vi. $W = f \times d$ .... (ii)

vii. Substitution from Eq. gives

$W = - P_{ext} \times A \times d$ .... (iii)

viii. The product of area of the piston and distance it moves is the volume change (ΔV) in the system.

ix. $\Delta V = A \times d$ .... (iv)

x. Combining equations (iii) and (iv) we write

$W = - P_{ex} \Delta V$ ....(v)

$W = - P_{ex} (V_2 - V_1)$

xi. where V_2 is final volume of the gas.

xii. When the gas expands, work is done by the system on the surroundings.

xiii. Since $V_2 > V_1$, W is negative. When the gas is compressed, work is done on the system by surroundings. In this case $V_1 < V_2$, and $-P_{ext} \Delta V$ or W is positive

Note –

This shows the external pressure determines the work during expansion (or compression) of the gas. A volume change does no work unless the system is linked to the surroundings by external pressure.

Q.26 Comment on the statement : No work is involved in an expansion of gas in vacuum.

Ans:

i. A free expansion means expansion against zero opposing force. Such expansion occurs in vacuum.

ii. The work done by a system during such expansion is given by $W = - P_{ext} \Delta V$.

iii. When the gas expands in vacuum, there is no opposing force that is P_{ext} and hence, $W = 0$.

iv. Thus, no work is done when the gas expands freely in vacuum.

Q.27 Give the units of energy and work.

Ans:

i. $1\ J = 1\ kg\ m^2\ s^{-2} = 1\ Pa\ m^3$

ii. $1\ Pa = 1\ kg\ m^{-1}\ s^{-2}$

iii. From the equation, $W = - P_{ext} \Delta V$,

iv. If pressure is expressed in bar and ΔV in dm^3, then the work has the units of bar dm^3

v. $1\ bar = 10^5\ Pa = 10^5 kg\ m^{-1}\ s^{-2}$

vi. $1\ dm^3\ bar = dm^3 \times 10^5\ kg\ m^{-1}\ s^{-2}$

$= m^3 \times 10^{-3} \times 10^5\ kg\ m^{-1}\ s^{-2}$

vii. $= 100\ kg\ m^2 s^{-2} = 100\ J$

Type 1

Numericals based on pressure - Volume type of work

+1 Three moles of an ideal gas are expanded isothermally from 15 dm³ to 20 dm³ at constant external pressure of 1.2 bar. Estimate the amount of work in dm³ bar and J.

Solution:

$W = -P_{ext} \Delta V = P_{ext} (V_2 - V_1)$

$P_{ext} = 1.2$ bar, $V_1 = 15\ dm^3$, $V_2 = 20\ dm^3$

Substitution of these quantities into the equation gives.

$W = - 1.2$ bar $(20\ dm^3 - 15\ dm^3)$

$= - 1.2$ bar $\times 5\ dm^3 = - 6\ dm^3$ bar

$1 dm^3$ bar $= 100$ J

Hence, $W = - 6\ dm^3$ bar $\times 100\ J/dm^3$ bar $= - 600$ J

+2. Calculate the constant external pressure required to compress 2 moles of an ideal gas from volume of 25 dm³ to 13 dm³ when the work obtained is 4862.4 J.

Solution:

$W = -P_{ext} \Delta V - P_{ext} (V_2 - V_1)$

$V_1 = 25\ dm^3$, $V_2 = 13\ dm^3$, $W = 4862.4$ J

$$W = 4862.4\,J \times \frac{dm^3 bar}{100\,J} = 48.62 dm^3 bar$$

Substitution of these into the equation gives

$48.62\ dm^3$ bar $= -P_{ext} (13 dm^3 - 25\ dm^3)$

$= - P_{ext} \times 12\ dm^3$

$$\text{Hence, } P_{ext} = \frac{48.62\,dm^3 bar}{12\,dm^3} = 4.052\,bar$$

+3. 200 mL ethylene gas and 150 mL of HCl gas were allowed to react at l bar pressure according to the reaction

$C_2H_{4(g)} + HCl(g) \rightarrow C_2H_5Cl(g)$

Calculate the *PV* work in joules.

Solution:

$W = -P_{ext}\Delta V = -P_{ext}(V_2 - V_1)$

According to the equation of reaction 1 mole of C_2H_4 reacts with 1 mole of HCl to produce 1 mole of C_2H_5Cl. Hence, 150 mL of HCl would react with only 150 mL of C_2H_4 to produce 150 mL of C_2H_5Cl.

V_1 = 150 mL + 150 mL = 300 mL = 0.3 dm^3

V_2 = 150 mL = 0.15 L, P_{ext} = 1 bar

Substitution on these quantities in above

W = – 1 bar (0.15dm^3 bar)

= 0.15 dm3 bar

$$= 0.15 dm^3 bar \times 100 \frac{J}{dm^3 bar}$$

= 15.0 J

Problem for practice

1. One mole of an ideal monoatomic gas at 27°C expands adiabatically against constant external pressure at 1 atm from volume of 10 dm^3 to a volume of 20 dm^3. Estimate the amount of wourk in Joule and dm^3 bar.

Ans: W = 1013 Joule

W = – 1.013 dm^3 bar

2. Calculate the constant external pressure reuqired to compress one mole of an ideal gas from a volume of 20 L to 8 L from a volume of 20 L to 8 L when the work obtainedis 44.9 L atm.

Ans: P_{ex} = – 3.741 atm.

Q.3 What is the amount of work done when two moles of ideal gas is compressed from a volume of 1 m 3 to 10 dm^3 at 300 K aganist a pressure of 100 k Pa?

Ans: W = 99900 J

= 99.9 kJ

4.5 Concept of maximum work

Q.28 Explain the concept of maximum work.

Ans:

i. The equation $W = -P_{ex}\Delta V$ shows the amount of work performed by a system is governed by the opposing force (P_{ext}). Larger the opposing force more work is done by the system to overcome it.

ii. If the opposing force is zero no work is involved. With an increase of the opposing force from zero, more work will be needed by the system. When the opposing force reaches its maximum the system performs maximum work. With an opposing force being greatest more effort would be needed to overcome it.

iii. Thus when the opposing force (P_{ext})becomes greater than the driving force (P)the process gets reversed. Since the opposing force cannot be greater than the driving force it should be the maximum.

iv. If the pressure P of the gas differs from P_{ext} by a quantity ΔP then $P - P_{ext} = \Delta P$ and $P_{ext} = P - \Delta P$. The then becomes

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

v. The work (W) would be maximum when ΔP is smallest. This means the opposing force (P_{ex}) must be infinitesimally smaller than the driving force *(P)* for the work to be maximum.

vi. This is required for the process to be reversible. The maximum work is obtained from the change which is thermodynamically reversible.

Q.29 Derive the expression for the maximum work.

Ans:

i. Consider n moles of an ideal gas enclosed in a cylinder fitted with frictionless movable rigid piston. It expands isothermally and reversibly from the initial volume $V_1$to final volume V_2 at temperature T.

ii. The expansion takes place in a number of steps illustrated in

iii. During each step the external pressure P_{ext} is made infinitesimally smaller than the pressure P of the gas, with a gradual removal of masses from the piston. The gas expand slowly and its pressure P would decrease.

iv. The expansion continues until the pressure of the gas falls to P_{ext}. Beyond this no further expansion occurs and the system attains mechanical equilibrium with its surroundings.

v. The volume of a gas is increased by an infinitesimal quantity dv in each single step.

vi. When the volume of a gas increases by an infinitesimal amount dV in a single step, the small quantity of work done.

$dW = -P_{ext}\ dV$ .... (i)

vii. As the expansion is reversible, P is greater by a very small quantity dp than P_{ex}. Thus,

$P - P_{ext} = dP$ or $P_{ext} = P - dP$ .... (ii)

viii. Combining equations (i) and (ii),

$dW = -(P - dP)dV = -PdV + dP\ dV$

xi. Neglecting the product dpdV which is very small, we get

$dW = -PdV$ ....(iii)

x. The total amount of work done during entire expansion from volume V_1 to V_2 would be the sum of infinitesimal contributions of all the steps. The total work is obtained by integration of $dW = -PdV$ between the limits of initial and final states.

xi. This is the maximum work, the expansion being reversible. Thus,

$$\int_{\text{initial}}^{\text{final}} dW = \int_{V_1}^{V_2} PdV$$

Hence $W_{max} = -\int_{V_1}^{V_2} PdV$ .... (iv)

Using the ideal gas law

$PV = nRT$

$$W_{max} = -\int_{V_1}^{V_2} nRT\frac{dV}{V}$$

$= -nRT\int_{V_1}^{V_2}\frac{dV}{V}$ because T is consatant.

$= -nRT\ ln(V)_{V_1}^{V_2}$ [∴ in $x = 2.303\log_{10}x$]

$= -2.303\ nRT\log_{10}\frac{V_2}{V_1}$ .... (v)

Constant temperature, $P_1V_1 = P_2V_2$ or

$$\frac{V_2}{V_1} = \frac{P_1}{P_2}$$

xii. Replacing V_2/V_1 in by P_1/P_2, We have

$$W_{max} = -2.303\ nRT\log\frac{P_1}{P_2}$$

Type 2

Numericals based on work done in reversible isothermal process

+1. 2 moles of an ideal gas are expanded isothermally and reversibly from 20 L to 30 L at 300 K. Calculate the work done ($R = 8.314$ J K^{-1} mol $^{-1}$)

Solution:

$$W_{max} = -2.303nRT\log_{10}\frac{V_2}{V_1}$$

$n = 2$ mol, $T = 300$ K, $V_1 = 20$ L, $V_2 = 30$ L,
$R = 8.314$ J/K mol

Substitution of these quantities into the equation gives

$$W_{max} = -2.303 \times 2\text{ mol} \times 8.314\text{ J/K mol} \times 300\text{K} \times \log_{10}\frac{30\text{L}}{20\text{L}}$$

$= -2.303 \times 2 \times 8.314\text{ J} \times 300 \times \log_{10} 1.5$

$= -2.303 \times 2 \times 8.314\text{ J} \times 300 \times 0.1761$

$= -2023\text{ J} = -2.023\text{ kJ}$

+2. 22 g of CO_2 is compressed isothermally and reversibly at 298 K from initial pressure of 100 kPa when the final pressure.

Solution:

$$W = -2.303nRT\log_{10}\frac{P_1}{P_2}$$

$$n = \frac{22\text{g}}{44\text{g mol}^{-1}} = 0.5\text{mol}, T = 298\text{K},$$

P_l = 100 kPa, W = 1.2 kJ = 1200 J

Hence, 1200 J = – 2.303 × 0.5 mol × 8.314 J

$$\text{K}^{-1}\text{mol}^{-1} \times 298\text{K} \times \log_{10}\frac{100\text{kPa}}{P_2}$$

or $\log_{10}\frac{100\text{kPa}}{P_2} =$

$$\frac{-1200}{2.303\times0.5\times8.314\times298} = -\ 0.4206$$

$$\frac{100\text{kPa}}{P_2} = \text{antilog}\,(-\ 0.4206) = 0.3797$$

Therefore, $P_2 = \frac{100\text{kPa}}{0.3797} = 263.4\text{kPa}$

+3. 300 mmol of an ideal gas occupies 13.7 dm³ at 300 K. Calculate the work done when the gas is expanded until its volume has increased by 2.3 dm³ (a) isothermally against a constant external pressure of 0.3 bar (b) isothermally and reversibly (c) into vacuum.

Solution:

a. $W = -P_{ex}\Delta V = 2.3\text{dm}^3$

$P_{ext} = 0.3\text{bar}, \Delta V = 2.3\text{dm}^3$

$W = -\ 0.3\ \text{bar} \times 2.3\text{dm}^3$

$= -\ 0.69\ \text{dm}^3\ \text{bar}$

$$= -0.69\text{dm}^3\text{bar} \times \frac{100\text{J}}{\text{dm}^3\text{bar}}$$

$= -\ 69$ J

b. $W_{max} = -2.303 nRT \log_{10}\frac{V_2}{V_1}$

$n = 300\ \text{mmol} = 300 \times 10^{-3}\ \text{mol} = 0.3\ \text{mol}$,
$T = 300$ K

$W_{max} = -2.303 \times 0.3 \times 8.314\ \text{JK}^{-1}\ \text{mol}^{-1}$

$$= 300\text{K} \times \log_{10}\frac{16}{13.7}$$

$= -\ 2.303 \times 0.3 \times 8.314\ \text{J} \times 300 \times 0.0674$

$= -\ 116.1$ J

c. $W = -P_{ex}\Delta V$

When gas is expanded to vacuum, $P_{ext} = 0$ and $W = 0$

+4. Calculate the maximum work when 24 g of O_2 are expanded isothermally and reversibly from the pressure of 1.6 bar to 1 bar at 298 K.

Given : Mass of O_2 = 24 g
Initial pressure = P_1 = 1.6 bar
External pressure = P_2 = 1 bar
Temperature = T = 298 K

To find : Maximum work (W_{max})

Formulae : $W_{max} = -\ 2.303\ nRT\ \log_{10}\frac{P_1}{P_2}$

Solution: Number of moles of

$$O_2 = n = \frac{24\text{g}}{32\text{g mol}^{-1}} = 0.75\ \text{mol}$$

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

Now, using formula,

$$W_{max} = -\ 2.303\ nRT\ \log_{10}\frac{P_1}{P_2}$$

$$= -\ 2.303 \times 0.75\text{mol} \times 8.314\text{J}\,\text{K}^{-1}\ \text{mol}^{-1} \times 298\text{K} \times \log_{10}\frac{1.6}{1}$$

$= -\ 2.303 \times 0.75 \times 8.314 \times 298 \times \log_{10} 1.6$

$= 2.303 \times 0.75 \times 8.314 \times 298 \times 0.2041$

$= -1 \times 2.303 \times 0.75 \times 8.314 \times 298 \times 0.2041$

$= -\ 1 \times$ Antilog [log 2.303 + log 0.75 +
log 8.314+log 298 log 0.2041]

$= -\ 1 \times$ Antilog [0.3622 + (– 0.1249) +
(0.9198) + 2.4742 + (– 0.6901)

$= -\ 1 \times$ Antilog [(3.7561) – (0.815)]

$= -\ 1 \times$ Antilog [2.9411]

$= -\ 1 \times 873.1$ J

$= -873$ J

4.6 Internal energy (U)

Q.30 Define internal energy.

Ans: Every substance is associated with a definite amount of energy. This energy stored in a substance is internal energy it is denoted by U.

Q.31 Explain internal energy in brief.

Ans:

i. Every substance is associated with definite amount of internal energy. This energy in a substance is internal energy.

ii. The internal energy of a system is made up of kinetic and potential energies of individual particles of the system.

$\Delta U = U_2 - U_1$

iii. where U_1 and U_2 are internal energies of initial and final states, respectively. U is a state function and extensive property.

iv. A transfer of energy (as heat or work) from the system would change its internal energy.

v. To know (ΔU) the energy supplied to or removed from the system need to be monitored.

vi. The energy transferred to the system by heating it or performing work on it is added to the system.

vii. The energy transferred from the system by cooling or by performing work on the surroundings is removed from the system.

Q.32 Determine the change in internal energy of the system in the following condition.

Ans:

i. 30 kJ of heat supplied to the system. It would be added to internal energy of the system.

ii. Hence Δ U = +30 kJ.

iii. If 20 kJ of work is done on the system, it is added to internal energy of the system.

iv. Hence, Δ U = + 20 kJ.

v. Suppose a system releases 10 kJ of heat and performs 15 kJ of work on the surroundings. These quantities are removed from internal energy of the system

vi. Hence, Δ U = - 25 kJ

+Q.33 Try this

25 kJ of work is done on the system and if releases 10 kJ of heat. What is Δ U ?

Ans:

i. 25 kJ of work is done on the system. It is added to internal energy of the system.

ii. If system releases 10 kJ of heat. This quantity is removed from the internal energy is removed from the internal energy of the system.

Therefore Δ U = 25 – 10

= + 15 kJ.

4.7 first law of thermodynamics

Q.34 State the first law of thermodynamics.

Ans: According to this law the total energy of a system and surroundings remains constant when the system changes from an initial state to final state.

Q.35 State first law of thermodynamics in different ways.

Ans:

The first law of thermodynamics is stated in different ways as follows.

i. Energy of the universe remains constant

ii. The total internal energy of an isolated system is constant

iii. Energy is neither created nor destroyed and can only be converted from one form to another.

iv. All above statements are equivalent.

Q.36 Give the mathematical formulation of first law of thermodynamics.

Ans:

i. A system exchange energy with its surroundings either by transfer of heat or by doing work. An energy supplied to the system increases its internal energy.

ii. On the other hand, removal of heat or work from the system decreases its internal energy.

iii. Suppose (Q) is heat supplied to the system and W work done on the system by the surroundings.

iv. The internal energy of the system would increase.

v. Increase in internal energy of the system is equal to sum of the quantity of heat supplied to the system and amount of work done on the system i.e.

$\Delta U = Q + W$ .... (i)

vi. where 'U is an increase in internal energy of the system. Eq. (i) is the first law of thermodynamics. For infinitesimal changes.

$dU = dQ + dW$

Q.37 Explain first law of thermodynamics for the various processes given below.

i. Isothermal process

ii. Adiabatic process

iii. Isochoric process

iv. Isobaric process

Ans:

i. **Isothermal process**

a. According to the mathematical expression of the first law of thermodynamics

$\Delta U = Q + W$

b. Temperature is constant in such process, internal energy is constant. Hence, $\Delta U = 0$

c. For isothermal process

$0 = Q + W$ or $W = - Q$ .... (i)

d. The above equation implies that heat absorbed by the system is entirely used for doing work on the surroundings.

e. When work is done on the system by the surroundings it results in release of heat.

ii. **Adiabatic process**

a. According to the mathematical expression of the first law of thermodynamics.

$\Delta U = Q + W$

b. In adiabatic process, there is no exchange of heat between system and its surroundings that is, Q = 0. then

$- \Delta U = -W$

c. Thus an increase in internal energy of the system is the work done on it.

d. If the work is done by the system on the surroundings at the expense of its internal energy, the internal energy accompanying the adiabatic process would decrease.

iii. **Isochoric process**

a. According to the mathematical expression of the first law of thermodynamics

$\Delta U = Q + W$

b. since $W = - P_{ext}\ \Delta V$

$\Delta U = Q - P_{ext}\ \Delta V$

c. As the reaction is carried out in a closed container, volume of the system is constant or $\Delta V = 0$ and $\Delta U = Q_v$

d. Therefore the change in internal energy of the system is due to heat transfer at constant volume.

Note - The subscript 'V' indicates that heat is transferred at the constant volume. Further U being a state function, Q_v is also a state function.

iv. **Isobaric process:**

a. According to the mathematical expression of the first law of thermodynamics

$\Delta U = Q + W$

b. : Usually chemical reactions are carried out in the open containers under constant atmospheric pressure. In such reactions,

$\Delta V \neq 0$

Since $W = - P_{ext}\ \Delta V$

$\Delta U = Q - P_{ext}\ \Delta V$

Replacing Q by Q_p we get

$\Delta U = Q_p - P_{ext}\ \Delta V$

$Q_p = \Delta U + P_{ext}\ \Delta V$

Note –

The subscript 'P' in Q_p indicates. that the reaction occurs at constant pressure.

Remember –

Q is not a state function. Whereas Q_v and Q_p are state functions.

4.8 Enthalpy (H)

Q.38 Define enthalpy

Ans:

i. Enthalpy of a system is sum of internal energy of a system and the energy equivalent to PV work.

ii. It is denoted by H and its mathematical equation is given as $H = U + PV$.

Q.39 Show that at constant pressure

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

Ans:

$H = U + PV$ .... (i)

Change in enthalpy, ΔH, is also state function given by

$\Delta H = H_2 - H_1$ .... (ii)

where H_1 and H_2 are the enthalpies of initial and final states, respectively.,

From Eq. (i) we write

$H_1 = U_1 + P_1V_1$ and $H_2 = U_2 + P_2V_2$

From Eq (i) and Eq (ii)

$\Delta H = U_2 + P_2V_2 - U_1 + P_1V_1$

$= (U_2 - U_1) + (P_2V_2 - P_1V_1)$

$= \Delta U + \Delta (PV)$ .... (iii)

For constant pressure, $P_1 = P_2 = P$ and

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

If the pressure inside and outside is the same or $P_{ext} = P$,

$Q_p = \Delta U + P\ \Delta V$ ....(v)

From equations and

$\Delta H = Q_p$

Thus change in enthalpy of a system is equal to heat transferred from it at the constant pressure. H and Q_p are state functions.

Q.40 Explain : For the reactions involving solids and liquids. solids or liquids do not show volume change with change of pressure.

Ans: For reactions involving solids and liquids, ΔV usually is very small.

$$\Delta H = \Delta U + P\Delta V$$
$$\Delta H = \Delta U + 0$$
$$\Delta H = \Delta U$$

Therefore, for the reactions involving solids and liquids, $\Delta H = \Delta U$

⌈Q.41 Obtain the relationship between ΔH and ΔU for gas phase reactions.

Ans:

i. At constant pressure, ΔH and ΔU are related as $\Delta H = \Delta U + P\Delta V$

ii. For reactions involving solids and liquids, ΔV usually is very small (solids or liquids do not show volume change with change of pressure)and $\Delta H = \Delta U$

iii. For reactions involving gases, Δ V cannot be neglected Therefore

$$\Delta H = \Delta U + P\Delta V$$
$$= \Delta H + P(V_2 - V_1)$$
$$\Delta H = \Delta U + PV_2 - PV_1$$

iv. Where V_1 is the volume of gas phase reactants and V_2 that of the gaseous products.

v. We assume reactant and product behave ideally. Applying ideal gas equation $PV = nRT$.

vi. When $_1$ moles of gaseous reactants produce n_2 moles of gaseous products. The ideal gas equation give,

$$PV_1 = n_1RT \text{ and } PV_2 = n_2RT$$

vii. Substitution of Eq. (iii) into Eq. (ii) yields

$$\Delta H = \Delta U + n_2RT - n_1RT$$
$$= \Delta U + (n_2 - n_1)\ RT$$
$$= \Delta U + \Delta n_g\ RT$$

viii. where Δn_g is difference between the number of moles of products and those of reactants.

+Q.42 Under what conditions, ?

Ans:

i. For a reactions involving solids and liquids usually is very small and is negligible.

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

ii. For reactions occurring in gas phase in which the difference between the number of moles of products and those of reactants is zero i.e.

$$\Delta n_g = 0$$
$$\Delta H = \Delta U + \Delta n_g RT$$
$$\Delta H = \Delta U + 0$$
$$\Delta H = \Delta U$$

Q.43 Obtain the expression for work done in chemical reactions.

Ans:

i. The work done by a system at constant temperature and pressure is given by

$W = P_{ext}\ \Delta V$. Assuming $P_{ext} = P$,

$$W = -P\Delta V = -P\ (V_2 - V_1)$$
$$= -PV_2 + PV_1$$

ii. If the gases were ideal, using Eq.

$$PV_1 = n_1RT \text{ and } PV_2 = n_2RT$$

iii. At constant temperature and pressure.

$$W = -n_2RT + n_1RT = -(n_2 - n_1)\ RT$$
$$= -\Delta n_g\ RT$$

iv. The above equation gives the work done by the system in chemical reactions.

Q.44 **Give the sign conventions for work done in chemical reaction.**

Ans:

i. The sign of *W* depends on ΔV. We consider the following cases:

ii. If $n_2 > n_1$, Δn_g is positive and $W < 0$ or work is done by the system.

iii. If $n_1 > n_2$, Δn_g is negative and $W > 0$ or work is done on the system.

iv. If $n_1 = n_2$, $\Delta n_g = 0$ and $W = 0$, or

v. No *PV* work is done when number of moles of reactants and products are equal.

Type 3

Numricals based on work done in chemical reaction

1. **ΔH for the reaction,**

$2C_{(s)} + 3H_{2(g)} \rightarrow C_2H_{6(g)}$ is – 84.4 kJ at 25^0C. Calculate ΔU for the reaction at 25^0C. (R = 8.314 J K^{-1} mol^{-1})

Solution:

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

An_g = (moles of product gases) – (moles of reactant gases)

$$\Delta n_g = 1 - 3 = -2\,\text{mol}^{-1}$$

$\Delta H = -84.4$ kJ, $R = 8.314$ J K^{-1} mol^{-1}
$= 8.314 \times 10^{-3}$ kJ K^{-1} mol^{-1}

Substitution of these in above

-84.4 kJ $= \Delta U + 8.314 \times 10^{-3}$ kJ K^{-1} mol^{-1} $\times$ 298 K $\times$ (– 2 mol)

$= \Delta U - 4.96$ kJ

Hence, $\Delta U = -84.4$ kJ $+ 4.96$ kJ $= -79.44$kJ

2. **In a particular reaction 2 kJ of heat is released by the system and 6 kJ of work is done on the system. Determine of ΔH and ΔU?**

Solution: According to the first law of thermodynamics

$\Delta U = Q + W$

$Q = -2$ kJ, $W = +6$ kJ

$\Delta U = -2$ kJ $+ 6$ kJ $= 4$ kJ

$Q_p = \Delta H = -2$ kJ

3. **Calculate the work done in oxidation of 4 moles of SO_2 at 25^0C if**

$$2SO_{2(g)} + O_{2(g)} \rightarrow 2SO_{3(g)}$$

R = 8.314 J K^{-1} mol^{-1}

State whether work is done on the system or by the system.

Solution:

For oxidation of 4 moles of SO_2, the reaction is

$$4SO_{2(g)} + 2O_{2(g)} \rightarrow 4SO_{3(g)}$$

$W = -\Delta n_g RT$

$\Delta n_g = = 4 - 6 = -2$ mol, $T = 298$ K

Hence,

$W = -2$ mol $\times -8.314$ J K –1 mol –1 $\times$ 298 K

= 49955 J = 4.955 J

Work is done on the system (since $W > 0$).

4.9 Enthalpies of physical transformations

Q.45 **What is phase transition?**

Ans: In phase transition, one phase of a substance is converted into another at constant temperature and pressure without change in chemical composition.

Q.46 **What is enthalpy of fusion.**

Ans: Enthalpy change that occurs when one mole of a solid is converted into liquid without change in temperature at constant pressure is enthalpy of fusion.

Q.47 **Explain the follwing terms using an example.**

i. Enthalpy of fusion
ii. Enthalpy of vaporization
iii. Enthalpy of sublimation

Ans:

i. Enthalpy of fusion ($\Delta_{fus}H$) :

a. Enthalpy change that occurs when one mole of a solid is converted into liquid without change in temperature at constant pressure is enthalpy of fusion. For example,

b. $H_2O_{(s)} \rightarrow H_2O(l)$

$$\Delta_{fus}H = +6.01\,\text{kJ mol}^{-1}\text{at}0^{o}\text{C}$$

c. When 1 mole of solid ice melts at 0 ^{0}C and 1 atm pressure, change in enthalpy is

6.01 kJ. The same amount of heat is absorbed by ice during the melting.

d. A reverse of fusion is freezing of solid.

$$H_2O_{(l)} \rightarrow H_2O_{(s)}, \Delta_{freez} H = -6.1 \text{kJmol}^{-1} \text{at } 0^{o}C$$

e. Thus, when one mole of liquid water freezes at 0 ^{0}C, heat is evolved.

ii. **Enthalpy of vaporization (Δ_{vap}H) :**

a. It is the enthalpy change accompanying the vaporization of one mole of liquid without changing its temperature at constant pressure.

b. For example,

$$H_2O(l) \rightarrow H_2O_{(g)} \Delta_{vap} H = +40 \text{kJ mol}^{-1} \text{at } 100^{o}C$$

$$H_2O(l) \rightarrow H_2O_{(g)} \Delta_{vap} H = 44 \text{kJ mol}^{-1} \text{at } 25^{o}C$$

c. Thus, when one mole of water is vaporised at 1 atm presure, the enthalpy change is + 40 kJ at 100 ^{0}C and + 44 kJ at 25 ^{0}C.

d. On the other hand, the condensation to vapour is accompanied with a release of heat.

$$H_2O \rightarrow H_2O(l), \Delta_{con} H = -40.7 \text{ kJ mol}^{-1} \text{ at } 100\ ^{o}C$$

iii. **Enthalpy of sublimation (Δ_{sub}H) :**

a. It is the enthalpy change for the conversion of one mole of solid directly into vapour at constant temperature and pressure.

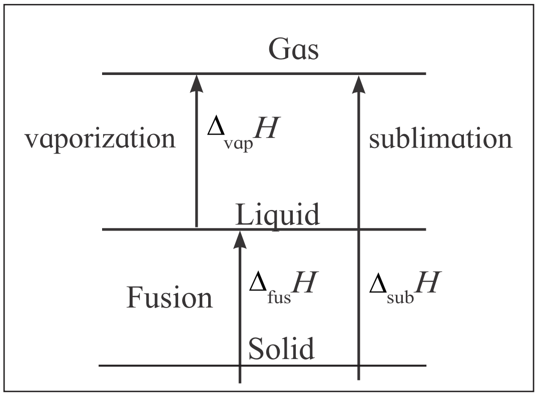
b. Consider

$$H_2O_{(s)} \rightarrow H_2O_{(g)}, \Delta_{sub} H = 51.08 \text{ kJ mol}^{-1} \text{at } 0\ ^{o}C$$

c. The conversion of solid to vapour occurs in one or two steps, first melting of solid into liquid and second its vaporization; the enthalpy change is the same since enthalpy is the state function. At 0 ^{0}C

$$\begin{array}{l} H_2O_{(s)} \rightarrow H_2O_{(l)} \Delta_{fus} H = 6.01 \text{kJ mol}^{-1} \\ H_2O_{(l)} \rightarrow H_2O_{(g)} \Delta_{vap} H = 45.07 \text{kJ mol}^{-1} \\ \hline H_2O_{(s)} \rightarrow H_2O_{(g)} \Delta_{sub} H = 51.08 \text{kJ mol}^{-1} \end{array}$$

$$\Delta_{sub} H = \Delta_{fus} H + \Delta_{vap} H.$$



Representing Δ_{fus} H, Δ_{fvap} H and Δ_{fsub} H

Q.48 State and explain enthalpy of ionization.

Ans:

i. It is the enthalpy change accompanying the removal of an electron from one mole of gaseous atom.

ii. For example,

$$Na_{(g)} \rightarrow Na^{+}_{(g)} + e^{-} \Delta_{ion} H = 494 \text{kJ mol}^{-1}$$

iii. The equation signifies when one mole of gas phase atomic sodium is ionized to gas phase Na$^+$ ions, the enthalpy change is 494 kJ.

Q.49 Define electron gain enthalpy and give an example.

Ans:

i. The electron gain enthalpy on the other hand, gives the enthalpy change when one mole of gas-phase atoms of an element accept electron to form gaseous anion.

ii. For example,

$$Cl_{(g)} + e^{+} \rightarrow Cl^{-}_{(g)} \Delta_{eg} H = -349 \text{kJ mol}^{-1}$$

iii. Electron gain enthalpy of Cl is –349 kJmol^{-1}.

Q.50 What is the enthalpy of atomization? Give an example.

Ans:

i. The enthalpy change accompanying the dissociation of one mole of gaseous substance into atoms is the enthalpy of atomization.

ii. Consider,

$$Cl_{2(g)} \rightarrow Cl_{(g)} + Cl_{(g)}; \Delta_{atom} H = 242 \text{kJ mol}^{-1}$$

Q.51 Name the enthalpy change involved in the reaction below.

$$CH_{4(g)} \rightarrow C_{(g)} + 2H_{2(g)} \Delta H = 1660\,kJ\,mol^{-1}$$

Ans: Energy of atomization. ($\Delta_{atom}H$)

$$CH_{4(g)} \rightarrow C_{(g)} + 4H_{(g)}; \Delta_{ato}H = 1660\,kJ\,mol^{-1}$$

Q.52 Define enthalpy of solution and give an example.

Ans:

i. Enthalpy of solution is the enthalpy change in a process when one mole of a substance is dissolved in specified amount of solvent.

ii. $NaCl_{(s)} + aq \rightleftharpoons NaCl(aq) \Delta_{soln}H = 4\,kJ\,mol^{-1}$

Note-

Enthalpy of solution at infinite dilution is the enthalpy change when one mole of substance is dissolved in infinite amount of solvent.

Q.53 Explain : The enthalpy of solution is the sum of crystal lattice enthalpy and enthalpy of hydration.

Ans:

i. An ionic compound dissolves in water in two steps:

ii. The ions are separated from the molecule

$$MX_{(s)} \rightarrow M^{+}{}_{(g)} + X^{-}{}_{(g)}$$

iii. Enthalpy change for this step is crystal lattice enthalpy, $\Delta_L H$ which is always positive.

iv. The ions are hydrated with water molecules surrounding them.

$$M^{+}{}_{(g)} + xH_2O \rightarrow [M(H_2O)_x]^{+}$$

$$X^{-}{}_{(g)} + yH_2O \rightarrow [x(H_2O)_y]^{-}$$

v. The enthalpy change for this step is always negative and called enthalpy of hydration, $\Delta_{hyd}H$.

vi. The enthalpy of solution is the sum of crystal lattice enthalpy and enthalpy of hydration.

Q.54 For NaCl, Δ_LH = +790 kJ / mol and Δ_{hyd} *H* = –786 kJ mol^{-1}. What will be its enthalpy of solution (Δ_{sdn}*H*).

Ans: $\Delta_{sol_n}H = \Delta H + \Delta_{hyd}H$

For NaCl, Δ LH = +790 kJ/mol and

$\Delta_{hyd}H$ = -786 kJ/mol-1

The enthalpy of solution of NaCl is

$\Delta_{sol_n}H$ (NaCl) = (+790 –786) kJ/mol^{-1}

= +4 kJ/mol^{-1}

+Q.55 Try this

For KCl, ΔH = 699 kJ mol^{-1} and Δ_{hyd}H = – 681.8 kJ mol^{-1}. what will be its enthalpy of solution?

Ans: $\Delta_{sol_n}H = \Delta_L H + \Delta_{hyd}H$

For KCl, Δ_LH = – 681.8 kJ mol^{-1}.

The enthalpy solution for KCl is

$\Delta_{sol_n}H$ (KCl) =

(+699 KJ mol^{-1}–68.8 kJ mol^{-1})

= + 17.2 kJ mol^{-1}

4.10 Thermochemistry

Q.56 What is thermochemistry?

Ans: Thermochemistry deals with enthalpy changes in chemical reactions.

Q.57 What is enthalpy of a chemical reaction.

Ans:

i. enthalpy of a chemical reaction is the difference between the sum of enthalpies of products and that of reactants with each substance in definite physical state and their amounts (moles) being represented by the coefficients in the balanced equation of the reaction.

Consider, $aA + bB \longrightarrow cC + dD$

The enthalpy change for the reaction is

$\Delta H = (cH_C + d\,H_D) - (a\,H_A + bH_B)$

where H_A, H_B, H_C and H_D are molar enthalpies of A, B, C and D, respectively. We write

$$\Delta_r H = \sum H_{products} - \sum H_{reac\tan ts}$$

The enthalpy of a reaction can be positive or negative depending on

$$\sum H_{products} \text{ and } \sum H_{reac\tan ts}$$

Q.58 What is an endothermic reaction? Give an example.

Ans:

i. The reaction in which enthalpy change is positive is called endothermic recation.

ii. For such reactions,

$\sum H_{products} > \sum H_{reac\tan ts}, \Delta_r H$ is positive signifies the reaction is endothermic

For example

$$N_2(g)+O_2(g)\rightarrow 2NO_2(g)$$

$\Delta_r H = 66.4\,kj$ (endothermic)

Q.59 What is an exothermic reaction? Give an example.

Ans:

i. The reaction in which enthalpy change is negative is called exothermic reaction

ii. For such reactions,

$\sum H_{product} < \sum H_{reactant}, \Delta_r H$ is negative which means that heat is released and the reaction is exothermic

$$2KC1O_3 \rightarrow 2KC1_5 + 3O_2$$

$\Delta_r H = -78\,KJ$ (Exothermic)

Q.60 What is standard state of a substance?

Ans:

i. The standard state of a substance is the form in which the substance is most stable at a pressure of 1 bar and at temperature 298 K.

ii. If the reaction involves species in solution its standard state refers to 1M concentration.

iii. Standard states of certain elements and compounds are H_2-(g), Hg(g), Na(s) or C(graphite) C_2H_5OH (*l*), $CaCO_3$(s),CO_2(g) refer to 1 bar and 25 ^{0}C.

Q.61 Define standard enthalpy of a reaction?

Ans: The standard enthalpy $\left(\Delta_r H^0\right)$ of reaction is the enthalpy change accompanying the reaction when the reactants and products involved are in their standard states

Q.62 What is thermochemical equation?

Ans: It is the balanced chemical equation in which the enthalpy change , physical states and the number of moles of reactants and products, have been specified.

Q.63 Give the guideline for writing thermochemical equations

Ans: Here follows the guidelines for writing thermochemical equations:

i. Consider the balanced equation for reactants and products.

ii. The values and appropriate sign of enthalpy change is given on the right hand side. This value is $\Delta_r H^0$

iii. The physical states of reactants and products are specified by letter, s (solid) *l* (liquid), g (gas) and aq (aqueous). $\Delta_r H^0$ value refers to physical states of substances those appear in the equation

iv. The given value of $\Delta_r H^0$ assumes that the reaction occurs in a given direction. $\Delta_r H^0$ for the reverse reaction equals in magnitude and opposite in the sign to that of the forward reaction. A exothermic reaction on reversal becomes endothermic and vice versa .

v. When the coefficients indicating the number of moles of all substances in thermochemical equation are multiplied or divided by a certain numerical factor, the corresponding $\Delta_r H^0$ need to be multiplied or divided by the same

Q.64 What does the following thermochemical equation signifies .

$$\mathbf{CH_{4(g)} + 2O_{2(g)} \rightarrow CO_{2(g)} + 2H_2O_{(\mathit{l})}\Delta_r H^o = -890KJ}$$

Ans: The equation signifies that when 1 mole of gaseous CH_4 and 2 moles of O_2 in their standard states produce 1 mole of CO_2 gas and 2 moles of liquid water also in their standard states the enthalpy change would be –890 KJ.

+65 Try this

Ans:

i. When the coefficients of substances are multiplied by 2, the enthalpy of a reaction $\left(\Delta_r H^0\right)$ is also multiplied by 2 Hence

$$2C_2H_{2(g)}+5O_{2(g)} \rightarrow 4CO_{2(g)}+2H_2O_{(2)}\Delta rH^o = -2600\,KJ$$

ii. When the equation is reverse the sign of enthalpy of a reaction $\left(\Delta_r H^0\right)$ is changed . Hence

$$2CO_{2(g)}+H_2O(1) \rightarrow C_2H_{2(g)} + \frac{5}{2}O_{2(g)}\Delta_r H^o = 2600\,KJ$$

Q.66 Explain : standard enthalpy of formation $\left(\Delta_r \boldsymbol{H^0}\right)$

Ans:

i. The standard enthalpy of formation of a compound is the enthalpy change that accompanies a reaction in which one mole of pure compound in its standard state is formed from its elements in their standard states

ii. Consider

$$H_{2(g)} + \frac{1}{2}O_{2(g)} \rightarrow H_2O_{(l)}, \Delta_r H^o = -286\,kJ$$

For the reaction where one mole of liquid water in standard state is formed H_2 and O_2 gases in their standard states, the enthalpy changes for the reaction would be the standard enthalpy of formation of water be the standard enthalpy of formation of water. $\Delta_f H$ of water is –286 KJmol^{-1}

iii. Similarly the formation of one mole of CH_4 in its standard state from the elements carbon and hydrogen in their standard states is represented by

$$C(\text{graphite})+2H_{2(g)} \rightarrow CH_{4(g)}, \Delta_r H^o = -74.8kJ$$

$$\text{or } \Delta_f H^o (CH_4) = -74.8\,kJ\,mol^{-1}$$

67. How standard enthalpies of formation of compounds are used to determine standards enthalpies of reaction?

Ans:

Calculations of $\Delta_r H^o$ from $\Delta_f H^o$ of compounds are based on the following.

i. Standard enthalpied of formation of an elements is Zero.

$$\Delta_f H^0 (H_2) = \Delta_f H^0 (Cl_2) = \Delta_f H^0 (C) = 0$$

ii. Standard enthalpy of fromation of a compound is equal to its standard enthalpy

$$\Delta_f H^0 \text{ (Compound)} = H^0 \text{ (Compound)}$$

Consider the reaction

aA + bB → cC + dD

Standard enthalpy of the reaction is given by

$$\Delta_f H^0 = (cH^0{}_c + dH^0{}_D) - (aH^0{}_A + bH^0{}_B)$$

$$= [c\ \Delta_f H^0 (C) + d\ \Delta_f H^0 (D)] - [a\ \Delta_f H^0 (A) + b\ \Delta_f H^0 (\text{reactants})]$$

$$= \sum \Delta_f H^0 (\text{Products}) - \sum \Delta_f H^0 (\text{reactants})$$

Q68. What is standard enthalpy of combustion? Give an example ?

Ans:

i. The standard enthalpy of combustion of a substance is the standard enthalpy change accompanying a reaction in which one mole of the substance state is completely oxidised

ii. Consider the reaction

$$C_2H_{2(g)} + \frac{5}{2}O_{2(g)} \rightarrow 2CO_{2(g)} + H_2O_{(l)},$$

$$\Delta_r H^0 = -1300\,kJ$$

iii. In the above reaction, the standard enthalpy change of the oxidation reaction , –1300 kJ is the standard enthalpy of combustion of $C_2H_{2(g).}$

+ Q.69 Try this

Write thermochemical equation for complete oxidation of one mole of $H_{2(g)}$. Standard enthalpy change of the reaction is –286 kJ. Is the value –286 kJ, enthalpy of formation or enthalpy of combustion or both? Explain

Ans:

i. The Thermochemical equation is

$$H_{2(g)} + \frac{1}{2}O_{2(g)} \rightarrow H_2O_{(l)} \Delta rH^0 = -286\,kJ$$

ii. The Valur –286 kJ represents both enthalpy of formation and enthalpy of combustion

(a) The Value –286 kJ represents enthalpy of combustion because one mole of H_2 is completely oxidised in its standard state

(b) The value –286 kJ represents enthalpy of formation because 1 mole of H_2O is formed in its standard states.

Q70. Define bond enthalpy and give examples

Ans:

i. The enthalpy change required to break particular covalent bond in one mole of gaseous molecule to produce gaseous atoms and / or radicals, is called bond enthalpy.

ii. Consider the reaction

$$H_{2(g)} \longrightarrow H_{(g)} + H_{(g)} + H_{(g)}, \Delta_r H^0 = 436.4\,kJ$$

It shows that H–H bond in one mole of $H_{2(g)}$ is decomposed producing gaseous H atoms. The enthalpy change of the reaction 436.4 kJ is bond enthalpy of the H–H bond

iii. HCl molecule dissociates as

$$HCl_{(g)} \longrightarrow H_{(g)} + Cl_{(g)}, \Delta_r H^0 = 431.9\,kJ$$

$$\Delta H^0(\mathrm{H-Cl\,bond}) = 431.9\ \mathrm{kJ\ mol^{-1}}$$

+Q71. Try this
Write equation for bond enthalpy of Cl – Cl bond in Cl_2 molecule $\Delta_r H^0$ for dissociation of Cl_2 molecule is 242.7 kJ

Ans: The equation is

$$Cl_{2(g)} \rightarrow 2Cl_{(g)}, \qquad \Delta_r H^0 = 242.7\,\mathrm{kJ}$$

Note : Remember

For diatomic molecules the bond enthalpy is the same as enthalpy of atomization

Q.72 Explain average bond enthalpy in polyatomic molecules using an example

Ans:

i. Each covalent bond in polyatomic molecules is associated with its own specific bond enthalpy

ii. The thermochemical equation for dissociation of H_2O molecules is

$$H_2O_{(g)} \longrightarrow 2H_{(g)} + O_{(g)}, \Delta_r H^0 = 927\,\mathrm{kJ}$$

iii. The above equation implies that the enthalpy change for breaking of two O–H bonds in one mole of gaseous H_2O are identical the energies needed to break individual O–H bonds are different.

iv. The bonds in H_2O are broken in successsive steps as shown

a. $H_2O_{(g)} \longrightarrow OH_{(g)} + H_{(g)}\ \Delta_r H^0 = 499\ \mathrm{kJ}$

b. $OH_{(g)} \longrightarrow O_{(g)} + H_{(g)}\ \ \Delta_r H^0 = 428\ \mathrm{kJ}$

$$H_2O_{(g)} \longrightarrow 2H_{(g)} + O_{(g)}\ \Delta_r H^0 = 927\ \mathrm{kJ}$$

v. The total enthalpy change, 927 kJ, not twice as large of the O–H bond enthalpy

vi. For polyatomic molecules the average bond enthalpy of a particular bond would be considered . Thus, the average bond enthalpy of the O–H = 927 2 = 463.5 kJ or ΔH^0 (O–H) = 463.5 kJ $\mathrm{mol^{-1}}$

⋆Q.73 What is the enthalpy of O–H bond in H_2O molecule?

Ans:

The average bond enthalpy of the O–H bond enthalpy of the O–H bond = 927/2 = 463.5 kJ or ΔH^0 (O–H) = 463.5 kJ $\mathrm{mol^{-1}}$

⋆Q.74 How will you calculate reaction enthalpy from data on bond enthalpies?

Ans:

i. Reaction and bond enthalpies

ii. In a chemical reaction bonds are broken and formed

iii. The enthalpies of reaction involving substances having covalent bonds are calculated by knowing the bond enthalpies of reactants and those in products

iv. The calculations assume all the bonds of a given type are identical

v. Enthalpy change of a reaction

$$\Delta_r H^0 = \sum \Delta H^0(\text{reactant}) - \sum \Delta H^0(\text{product}) \qquad \text{..... (i)}$$

Consider the reaction

$$H_{2(g)} + I_{2(g)} \longrightarrow 2\,HI_{(g)}$$

The enthalpy is given by

$$\Delta_r H^0 = \left[\Delta H^0(\mathrm{H-H}) + \Delta H^0(\mathrm{I-I})\right] - \left[2\Delta H^0(\mathrm{H-I})\right]$$

Note:

If reactants and products are diatomic molecules the Eq. (i) gives accurate results. The bond enthalpies are known accurately. For reactions involving polyatomic molecules the reaction enthalpies calculated via. Eq. (i) would be approximate and refer to average bond enthalpies

Q75. State Hess's law of constant heat summation Illustrate with an example state its example

Ans:

i. The law states that, "Overall the enthalpy change for a reaction is equal to sum of enthalpy changes of individual steps in the reaction".

ii. The enthalpy change for a chemical reaction is the same regardless of the path by which the reaction occurs

iii. Hess's law is a direct consequence of the fact that enthalpy is state function

iv. The enthalpy change of a reaction depends only on the initial and final states and not on the path by which the reaction occcurs

v. To determine the overall equation of reaction, reactants and products in the individual steps are added or subtracted like algebraic entities

Consider the synthesis of NH_3

$$2H_{2(g)} + N_{2(g)} \longrightarrow N_2H_{2(g)}, \Delta_f H_l^0 = +95.4\,kJ \text{......}[1]$$

$$N_2H_{4(g)} + H_{2(g)} \longrightarrow 2NH_{3(g)}, \quad \text{.........}[1]$$

$$\Delta_r H_2^0 = -187.6\,kJ$$

$$3H_{2(g)} + N_{2(g)} \longrightarrow 2NH_{3(g)}, \Delta_r H^0 = -92.2\,kJ$$

The sum of the enthalpy changes for step (i) and (ii) is equal to enthalpy change for the overall reaction

Q.76 State application of Hess's law?

Ans : The Hess's law has been useful to calculate the enthalpy changes for the reaction with their enthalpies being not known experimentally

Types – 4

Numericals based on standard enthalpyies of a reaction, formations, combustion and enthalpy change of reaction

+Q.1 Calculate standard enthalpy of reaction,

$$\mathbf{2C_2H_{6(g)} + 7O_{2(g)} \rightarrow 4CO_{2(g)} + 6H_2O_{(l)}}$$

Given that

$\Delta_f H^0 (CO_2) = -393.5\ kJ\ mol^{-1}$

$\Delta_f H^0 (H_2O) = -285.8\ kJ\ mol^{-1}$ **and**

$\Delta_f H^0 (C_2H_6) = -84.9\ kJ\ mol^{-1}$

Solution:

$$\Delta_f H^0 = \sum \Delta_f H^0 (\text{products}) - \sum \Delta_f H^0 (\text{reactants})$$

$= [4\Delta_f H^0 (CO_2) + 6\ \Delta_f H^0\ (H_2O)]$

$\quad - [2\Delta_f H^0 (C_2H_6) + 7\ \Delta_f H^0 (O_2)]$

$= [4mol \times (-393.5\ kJ\ mol^{-1}) + 6\ mol \times (-285.8\ kJ\ mol^{-1})]$

$\quad - [2\ mol \times (-84.9\ kJ\ mol^{-1}) + 0]$

$= -1574\ kJ - 1714.8\ kJ + 169.8\ kJ$

$= -3119 kJ$

★ Q2. Calculate standard enthalpy of reaction , $\mathbf{Fe_2O_{3(s)} + 3CO_{(g)} \rightarrow 2Fe_{(s)} + 3CO_{2\,(g)}}$**, from the following data.**

$\mathbf{\Delta_f H^o (Fe_2O_3) = -824\ kJ/\ mol}$ **,**

$\mathbf{\Delta_f H^o (CO) = -110\ kJ/mol}$

$\mathbf{\Delta_f H^o (CO_2) = -393\ kJ/\ mol}$

Solution :

Given : $\Delta_f H^o (Fe_2O_3) = -824\ kJ/\ mol$,

$\Delta_f H^o (CO) = -110\ kJ/mol$

$\Delta_f H^o (CO_2) = -393\ kJ/\ mol$

To find : Standard enthalpy of the given reaction $(\Delta_r H^o)$

Formula :

$$\Delta H^o = \sum \Delta_f H^o (\text{products}) - \sum \Delta_f H^o (\text{reac tan ts})$$

Calculation : The reaction is

$$Fe_2O_{3\,(s)} + 3CO_{(g)} \rightarrow 2Fe_{(s)} + 3CO_{2\,(g)}$$

$$\Delta_r H^o = \sum \Delta_f H^o\ (\text{products}) - \sum \Delta_f H^o\ (\text{reactants})$$

$$= \left[2\Delta_f H^o (Fe) + 3\Delta_f H^o\ (CO_2)\right]$$
$$- \left[\Delta_f H^o\ (Fe_2O_3) + 3\Delta_f H^o\ (CO)\right]$$

$$= \left[0 + 3\,mol \times \left(-393\,kJ\,mol^{-1}\right)\right]$$

$$- \left[1\,mol \times \left(-824\,kJ\,mol^{-1}\right) + 3\ mol \times (-110\,kJ\,mol^{-1})\right]$$

$= -1179 + 824 + 330$

$= -25\,kJ$

Ans : The standard enthalpy of the given reaction is - 25 kJ.

★ Q3. When 6.0 g of O_2 reacts with CIF as per

$$\mathbf{2CIF_{(g)} + O_{2(g)} \rightarrow Cl_2O_{(g)} + OF_{2(g)}}$$

The enthalpy change is 38.55 kJ. What is standard enthalpy of the reaction ?

solution :

Given : Enthalpy change for a given mass = 38.55 kJ

Mass of O_2 = 6.0 g

To find : Standard enthalpy of the given reaction.

Calculation :

Number of moles of O_2 =

$$\frac{\text{Mass of } O_2}{\text{Molar mass of } O_2} = \frac{6\text{ g}}{32\text{ g mol}^{-1}} = 0.1875\text{ mol}$$

The enthalpy change when 0.1875 mol of O_2 react with CIF is 38.55 kJ.

∴ Enthalpy change for 1 mole of $O_2 = \frac{38.55}{0.1875}$

$= \text{Antilog}[\log 38.55 - \log 0.1875]$
$= \text{Antilog}[1.5860 - (-0.7269)]$
$= \text{Antilog}[1.5860 + 0.7269]$
$= \text{Antilog}(2.3129]$
$= 205.5$ KJ
From the reaction, 2 moles of CIF react with 1 mole of O_2.
So, standard enthalpy of reaction is
+ 205.6 kJ.

Ans : Standard enthalpy of the given reaction is
+ 205.6 kJ .

★ Q4. How much heat is evolved when 12 g of CO reacts with NO_2? The reaction is

$$\mathbf{4CO_{(g)} + 2NO_{2(g)} \longrightarrow 4CO_{2(g)} + N_{2(g)},\ \Delta_r H^0 = -1200\text{ kJ}}$$

Ans:
Given:

★ Q6. Calculate $\Delta_r H^o$ for the following reaction at 298 K :

i. $\mathbf{2H_3BO_{3(aq)} \rightarrow B_2O_{3(s)} + 3H_2O_{(l)},\ \Delta_r H^o = +14.4\text{kJ}}$

ii. $\mathbf{H_3BO_{3(aq)} \rightarrow HBO_{2(aq)} + H_2O_{(l)},\ \Delta_r H^o = -0.02\text{kJ}}$

iii. $\mathbf{H_2B_4O_{7(s)} \rightarrow 2B_2O_{3\,(s)} + H_2O_{(l)},\ \Delta_r H^o = +17.3\text{kJ}}$

solution :

Given : Given equations are,

$2H_3BO_{3(aq)} \rightarrow B_2O_{3(s)} + 3H_2O_{(l)},\quad \Delta_r H^o = +14.4\text{kJ}$ ...(i)

$H_3BO_{3(aq)} \rightarrow HBO_{2(aq)} + H_2O_{(l)},\quad \Delta_r H^o = -0.02\text{kJ}$ ...(ii)

$H_2B_4O_{7(s)} \rightarrow 2B_2O_{3\,(s)} + H_2O_{(l)},\quad \Delta_r H^o = +17.3\text{kJ}$ ..(iii)

To find : The standard enthalpy of the given reaction ($\Delta_r H^o$)

Calculation : Reverse equation (i) and multiply by 2,

$2B_2O_{3(s)} + 6H_2O_{(l)} \rightarrow 4H_3BO_{3\,(aq)},\ \Delta_r H^o = -28.8\text{ kJ}$ ..(iv)

Multiply equation (ii) by 4,

$4H_3BO_{3(aq)} \rightarrow 4HBO_{2(aq)} + 4H_2O_{(l)},\ \Delta_r H^o = -0.08\text{ kJ}$ ..(v)

Add equation (iv), (v) and (iii),

$$2B_2O_{3(s)} + 6H_2O_{(l)} \rightarrow 4H_3BO_{3\,(aq)} \qquad \Delta_r H^o = -28.8 \text{ kJ}$$

$$4H_3BO_{3(aq)} \rightarrow 4HBO_{2(aq)} + 4H_2O_{(l)}, \qquad \Delta_r H^o = -0.08 \text{ kJ}$$

$$H_2B_4O_{7(s)} \rightarrow 2B_2O_{3\,(s)} + H_2O_{(l)}, \qquad \Delta_r H^o = +17.3 \text{kJ}$$

$$H_2B_4O_{7(s)} + H_2O_{(l)} \rightarrow 4HBO_{2(aq)} \qquad \Delta_r H^o = -28.8 + (-0.08) + 17.3 = -11.58 \text{kJ}$$

Ans : The standard enthalpy ($\Delta_r H^o$) of the given reaction is –11.58 kJ.

4.11 Spontaneous (irreversible) process

Q76. What is spontaneous process? Give examples?

Ans: Spontaneous Processes have a natural tendency to occur and do not require any external influence for their occurrence

Examples:

i. The aqueous NaOH and HCl solutions mixed together NaOH immediately combines with HCl to form NaCl and water

$$NaOH_{(aq)} + HCl_{(aq)} \longrightarrow NaCl_{(aq)} + H_2O_{(l)},$$
$$\Delta_f H^0 = -57 \text{kJ}$$

No external force or energy is required for the reaction to occur .This process stops when HCl or NaOH is consumed.

NaCl is dissolved in water, it does not react with water to produce NaOH and HCl.

ii. Water flows from higher level to lower level. It is not necessary to apply external force. It is a spontaneous process .The flow ceases when two levels become equal or when the equilibrium is reached

iii. Ice melts spontaneously above 0 °C.

iv. Hot coffee in a cup placed in a room cools down releasing heat to the surroundings .This is spantaneous

Q.77 Enlist the key points of spontaneous process.

Ans:

i. It occurs of its own and does not require any external agency to occur

ii. It proceeds in one direction and cannot take place in the opposite direction unless the external stimulant is present

iii. The spontaneous processes can be rapid or slow or spontaneity is not concerned with the rate of the reaction

iv. The processes continues till equilibrium is reached . The spontaneous (natural) processes tend to occur in a direction that leads to equilibrium.

Q.78 Explain why exothermicity is not the sufficient criterion for deciding of spontaneity

Ans:

The spontaneous reaction takes place in a direction in which energy of the system is lowered

It is accompanied by release of energy .The reaction between NaOH and HCl is exothermic $\left(\Delta_r H^0 = -57 \text{ kJ}\right)$ and is spontaneous.

On the other hand :

i. Ice melts spontanoeusly above 0 ºC by absorbing heat from the surroundings. It is endothermic.

ii. Likewise, NaCl dissolves spontaneously in water with the absorbtion of heat from the surroundings.

$$NaCl_{(s)} + aq \longrightarrow Na^{-}_{(aq)} + Cl^{-}_{(aq)}$$
$$\Delta H^0 = +3.9 \text{ kJ mol}^{-1}$$

These are endothermic and spontaneous. It is therefore, clear that the exothermicity is not the sufficient criterion for deciding of spontaneity.

Q.79 Entropy of water increases as the phase transform from ice to water to vapour explain.

Ans:

i. Consider the phase transformation in water from ice to liquid to vapour as shown in the diagram below

ii. In solid state water molecules in ice are arranged in a definite order.

iii. When ice melts, this highly crystalline arrangements of water molecules collapse. The molecules become free in liquid state. An ordered state thus tends to become more disordered.

iv. When liquid water vaporises, gaseous water molecules move freely and randomly in the available space. A less disordered state becomes highly disordered as shown in the figure.

v. During melting of ice or the vaporisation of liquid water the disorder or randomness increases. The disorder or randomness is measured by entropy, denoted by S.
Greater the disorder of a system larger is its entropy.
The melting of ice and vaporisation of liquid water show that disorder and hence, entropy of substance increases as it passes from solid to liquid to gas.
In both processes entropy change $\Delta S > 0$.

Q.80 Explain the entropy change in the following processes.

i. Dissolution of solid I_2 in water

ii. Dissolution of H_2 molecule into atoms

Ans:

i. Dissolution of solid I_2 in water :

$I_{2(s)} + aq. \longrightarrow I_{2(aq)}$ (ΔS is positive)

ordered state disordered state

When solid iodine dissolves in water I_2 molecules move randomly. Thus disorder and hence, entropy of the system increases or ΔS is positive for the dissolution process.

ii. Dissociation of H_2 molecule into atoms

$H_{2(g)} \longrightarrow 2H_{(g)}$ (ΔS is positive)

One mole of H_2 gas is converted into two H atoms. Larger disorder is associated with separated H atoms than with H_2 molecule.
Thus, disorder and hence entropy ncreases or sS is positive.

Q.81 State whether ΔS is positive or negative or zero for the reaction.

$2H_{(g)} \longrightarrow H_{2(g)}$ Explain.

Ans:

In this process two gaseous hydrogen atom associate into one molecule of hudrogen gas i.e. the number of particles decreases leading to a less disordered state. Therefore ΔS is negative.

+Q.82 Try this

State whether ΔS is positive, negative or zero for the following reactions.

i. $2H_{2(g)} + O_{(g)} \longrightarrow 2H_2O_{(l)}$

ii. $CaCO_{3(s)} \xrightarrow{\Delta} CaO_{(s)} + CO_{2(g)}$

Ans:

i. 3 moles of gaseous reactants are convertd into liquid product. from liquid to gas. entropy increases therefore entropy of the decreases or ΔS is negative.

ii. Caco3 dissociates into one solid product and one gaseous product. Gases have greater disorder than liquids, therefore the entropy of the system increases and ΔS is positive **.**

Q.83 What is entropy? Give its units.

Ans:

Entropy is a measure of molecular disorder or randomness.
An entropy change of a system is equal to the amount of heat transferred (Q_{rev}) to it in a reversible manner divided by the temperature in kelvin T at which the transfer takes place. Thus

$$\Delta S = \frac{Q_{rew}}{T}$$

the ΔS is thus expressed in J K^{-1}.
Entropy or its change ΔS is a state function and depends on the initial and final states of the system and not on the path connecting two states.

Q.84 Explain : Entropy change (ΔS) relates reciprocally to temperature at which of the heat is added.

Ans:

i. When heat is added to a system the molecular motions increase owing to increase of their kinetic energies. This results in increased molecular disorder and thus entropy of the system. ΔS is proportional to Q_{rev}.

ii. The effectiveness of the addition of heat to increase randomness depends on temperature.

If a certain amount of heat is added to system at the higher temperature then the disorder caused is lesser than that caused by adding the same amount of heat is added to system at the lower temperature.

Thus, ΔS relates reciprocally to temperature at which the of heat is added.

Q.85 Explain : The increase in entropy of a system alone does not guarantce the spontaneity of a process.

Ans:

i. The entropy increases when ice melts above 0 ºC and water vaporizes at 100 ºC. Both are spontaneous.

ii. Consider the spontaneous reaction at room temperature

$$2H_2O_{2(l)} \longrightarrow 2H_2O_{(l)} + O_{2(g)}, \quad \Delta S = +126 \text{ J K}^{-1}$$

iii. Entropy increases due to the formation of O_2 gas.

iv. From above examples, it is clear that the entropy of the system increases in the spontaneous processes.

Consider the reaction.

v. $2H_{2(g)} + O_{2(g)} \longrightarrow 2H_2O_{(l)}$,

$$\Delta S = -27 \text{ J K}^{-1}.$$

The entropy of the system decreases.

⋆Q.86 State second law of thermodynamics in terms of entropy

Ans:

i. The second law of thermodynamics states that total entropy of a system and its surroundings increases in a spontaneous process. For the process to be spontaneous $\Delta S_{total} = \Delta S_{sys} + \Delta S_{surr} > 0$

⋆Q.87 Although for the formation of two moles of water form H_2 and O_2 is -327 J K^{-1}, it is spontaneous Explain (Given ΔH For the reaction is –572 kJ)

Ans: For the process to be spontaneous

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

Consider

$$2H_{2(g)} + O_{2(g)} \longrightarrow 2H_2O_{(l)}$$

$\Delta S = -327 \text{ JK}^{-1}$, and $\Delta H = -572$ kJ (both at 298 K)

When 2 moles of H_2 and 1 mole of O_2 gas combine to form 2 moles of liquid water, 527 kJ of heat is released which is received by surroundings at constant pressure (and 298 K).

The entropy change of surroundings is

$$\Delta S_{surr} = \frac{Q_{rew}}{T} = \frac{572 \times 10^3 \text{ J}}{298\text{K}} = 1919 \text{ JK}^{-1}$$

$$\Delta S_{total} = \Delta S_{sys} + \Delta S_{sur}$$

$$= -327 \text{ JK}^{-1} + 1919 \text{ J K}^{-1}$$

$$= +1592 \text{ JK}^{-1}$$

$$\Delta S_{total} > 0$$

Since Total , the reaction is spontaneous at 298 k.

Therefore to decide spontanceity of reaction we need to consider the entropy of system and its surrounding.

Q.88 Consider the entropy of the system and surrounding and state whether the process is spontaneous, non spontaneous or at equilibrium.

Ans:

i. The total entropy increases during as pontaneous process that finally reaches equilibrium.

ii. The equilibrium corresponds to maximum total entropy.

iii. The total entropy change, ΔS_{total} must be zero for a process at equilibrium.

from above.

iv. $\Delta_{total} > 0$, the process is spontaneous

v. $\Delta S_{total} < 0$, the process is nonspontaneous

vi. $\Delta S_{total} = 0$, the process is at equilibrium

Q.89 Write a short note on : Gibbs energy.

Ans:

i. As pointed out in the preceding section, it is necessary to determine, ΔS_{sys} and ΔS_{surr}, for predicting the spontaneity of a reaction.

ii. We are more interested in the system (reaction mixture) .

iii. It. is, convenient to consider the criterion of spontaneity in terms of the thermodynamic properties of a system.

iv. This problem was solved by American theoretician J. W. Gibbs. He introduced a new thermodynamic property called Gibbs energy usually denoted by G.

v. The Gibbs energy is defined as
$G = H - TS$

vi. where H is enthalpy and S entropy of the system.

vii. Since H, T and S are state functions, G is state function.

viii. A change in Gibbs energy depends on initial and final states of the system and not on a path connecting the two states.

ix. The change in Gibbs energy at constant temperature and constant pressure is given by
$\Delta G = \Delta H - T\Delta S$

Q.90 Obtain the relation between ΔG and $\Delta S_{total.}$ Comment on spontaneity of the reaction

Ans:

i. The total entropy change that accompanies a process is given by
$\Delta S_{total} = \Delta S_{sys} + \Delta S_{surr}$
$= \Delta S + \Delta S_{surrr}$ .... (i)
The subscript sys that refers to the system is dropped hereafter.

ii. Relation between ΔG and ΔS total
According to second law of thermodynamics for a process to be spontaneous, $\Delta S_{total} > 0$.

iii. If ΔH is the enthalpy change accompanying a reaction (system) the enthalpy change of the surroundings is $-\Delta H$. With

$$\Delta S_{surr} = -\frac{\Delta H}{T} \text{ .... (ii)}$$

iv. Substituting above into Eq.

$$\Delta S_{total} = \Delta S - \frac{\Delta H}{T} \text{ ....(iii)}$$

v. Thus ΔS_{total} is expressed in terms of the properties of the system only. Rearranging
$T\Delta S_{total} = \Delta H - T\Delta S$ .... (iv)

vi. Substituting in Eq.
$\Delta G = -T\Delta S$ .... (v)

vii. For a spontaneous reaction $S_{total} > 0$ and hence, $\Delta G < 0$. At constant temperature and pressure Gibbs energy of the system decreases in a spontaneous process.

viii. The second law leads to the conditions of spontaneity which are summarised here.
  a. $\Delta S_{total} > 0$ and $\Delta G < 0$, the process is spontaneous.
  b. $\Delta S_{total} < 0$ and $\Delta G > 0$, the process is nonspontaneous.
  c. $\Delta S_{total} = 0$ and $\Delta G = 0$, the process is at equilibrium.

Q.91 If the enthalpy change of a reaction is ΔH how will you calculate entropy change of surrounding?

Ans: If ΔH is the enthalpy change of a reaction (system) then the enthalpy change of the surrounding in $-\Delta H$. The entropy change of the surrounding can be calculated using the expression.

$$\Delta S_{surr} = -\frac{\Delta H}{T}$$

Q.92 Comment on the spontaneity of reactions when
i. ΔH and ΔS are both negative?
ii. ΔH and ΔS are both positive?
iii. ΔH is negative and ΔS is positive?

Ans:

The temperature term determines relative contributions of ΔH and ΔS to ΔG.

i. ΔH and ΔS are both negative then ΔG will be negative only when ΔH is more negative than $T\Delta S$. This is possible at low temperatures only.

ii. ΔH amd ΔS both positive ΔG will be negative only if $T\Delta S > \Delta H$. This is possible only at high temperatures.

iii. For ΔH negative and ΔS is positive it follows that ΔG is negative regardless of temperature.

iv. For ΔH positive and ΔS is negative then ΔG is positive regardless of temperature. Such reactions are nonspontaneous at all temperatures.

Q.93 Comment on spontaneity of ractions for which ΔH is positive and ΔS is negative.

Ans: When ΔH positive and ΔS is negative, then

ΔH is positive regardless of temperature. Such reacions are non spontaneous at all temperatures.

★ Q.94 For a certain reaction ΔH^o = 219 kJ and ΔS^o = –21 J/K. Determine whether the reaction is spontaneous at all temperatures.

Ans: When ΔH positive and ΔS is negative, then ΔG is positive regardless of temperature. Hence, the reaction is nonspontaneous at all temperatures.

★ Q.95 Determine whether the following reaction is spontaneous nuder standard state conditions.

$$2H_2O_{(l)} + O_{2(g)} \rightarrow 2H_2O_{2(l)}$$

If ΔH^o = 196 kJ, ΔS^o = – 126 J/K, does it have a cross-over temerature?

Ans: When ΔH is positive and ΔS is negative then ΔG is positive regardless of temperature. Therefore the reaction is non spontaneous at all temperatures. Hence, it does not have a cross-over temperature.

Q.96 How equilibrium temperature can be calculated using ΔH and ΔS.

Ans:

i. For equilibrium

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

$$\therefore\ T = \frac{\Delta H}{\Delta S}$$

ii. T is the temperature at which the change over from spontaneous to non spontaneous behavior occurs.

★ Q.97 Obtain the relationship between ΔG^o of a reaction and the equilibrium constant.

Ans:

i. Gibbs energy change for a chemical reaction is given by

$\Delta G = \Delta G^o + RT \ln Q$

ii. where ΔG^o is standard Gibbs energy change that is, the Gibbs energy change when the reactants and products in a reaction are in their standard states.

iii. Q is called reaction quotient Q is analogus to that of the equilibrium constant. and involves nonequilibrium concentrations or partial pressures in case of gaseous reaction.

iv. Consider

$$aA + bB \rightarrow cC + dD$$

$$G = G^o + RT \text{ In } Q_c$$

$$= \Delta G^o + RT \text{ In } \frac{[C]^c [D]^d}{[A]^a [B]^b}$$

v. or $\Delta G = \Delta G^o + RT \text{ In } Q_p$

$$= \Delta G^o + RT \text{ In } \frac{P_C^c \times P_D^d}{P_A^a \times P_B^b}$$

vi. When the reaction reaches equilibrium, $\Delta G^o = 0$ and Q_c and Q_p become K_c and K_p, respectively. Thus,

$0 = \Delta G^o + RT \ln K_c$ and $0 = \Delta G^o + RT \ln K_p$

or

$\Delta G^o = -RT \ln K_c$ and $\Delta G^o = -RT \ln K_p$

or $\Delta G^o = -2.303\ RT \log_{10} K_c$

and

$\Delta G^o = -2.303\ RT \log_{10} K_p$.

Type-5

Numericals based on spontaneous and non spontaneous reactions and Gibbs energy.

+1. State whether following reactions are spontaneious or not. Furthere state whether they are exothermic or endothermic.

a. $\boldsymbol{\Delta H = -110\,kJ \text{ and } \Delta S = +40\,Jk^{-1} \text{ at } 400K}$

b. $\boldsymbol{\Delta H = +50kJ \text{ and } \Delta S = -130\,JK^{-1} \text{ at } 250\,K}$

Solution:

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

$\Delta H = 110kJ, \Delta S = +40\,J\,K^{-1}$

$= +40 \times 10^{-3} kJ\,K^{-1}$, T = 400 K

Therefore, $\Delta G = -110\,kJ - 400\,K \times 40 \times 10^{-3}\ kJ\ K^{-1}$

$= -110\ kJ - 16\ kJ = -126\ kJ$

Since ΔG is negative, the reaction is spontaneous. It is exothermic since ΔH is negative

b. $\Delta H = +50kJ, \Delta S = -130 \times JK^{-1}$

$= -130 \times 10^{-3}\ \text{kJ}^{-1}\ T = 250\ \text{K}$

$\Delta G = +50\ \text{kJ} - 250\ \text{K} \times (-130 \times 10^{-3}\text{kJ K}^{-1})$

$= 50\ \text{kJ} + 32.5\ \text{kJ} = +82.5\ \text{kJ}$

As ΔG is positive, the reaction is nonspontaneous. It is endothermic since ΔH is positive.

+2. For a certain reaction ΔH^0 is –224 kJ and ΔS^0 is –153 J K^{-1}. At what temperature the change over from spontaneous to nonspontaneous will occur?

Solution :

$$T = \frac{\Delta H^0}{\Delta S^0}$$

$$\Delta H^0 = -224\text{kJ}, \Delta S^0 = -153\text{JK}^{-1} = -0.153\text{kJK}^{-1}$$

Therefore, $T = \dfrac{\text{-224 kJ}}{\text{-0.153 J K}^{-1}} = +1464\text{K}$

Since ΔH^0 and ΔS^0 are both negative, the reaction is spontaneous at low temperatures. A change over will occur at 1464 K. The reaction is spontaneous below 1464 K .

+3. For the reaction,

$$\mathbf{CH_{4(g)} + H_{2(g)} \rightarrow C_2H_{6(g)},}$$

$$\mathbf{K_p = 3.356 \times 10^{17}}$$

Calculate ΔG^0 for the reaction at 25⁰C.

Solution:

$$\Delta G^0 = -2.303RT \log 10 K_p$$

$R = 8.314\ \text{JK}^{-1}\ \text{mol}^{-1}$, $T = 298$ K,

$K_p = 3.356 \times 10^{17}$

$$\Delta G^0 = -2.303 \times 8.314 \times 298 \times \log_{10}(3.356 \times 10^{17})$$

$= -2.303 \times 8.314\ \text{J mol}^{-1} \times 298 \times 17.526$

$= -100{,}000\ \text{J mol}^{-1}$

$= -100\ \text{kJ mol}^{-1}$

+4. Calculate ΔS_{total} and state whether the reaction is spontaneous or nonspontaneous at 25⁰C.

$$\mathbf{HgS_{(s)} + O_2 \rightarrow Hg(\mathit{l}) + SO_{2(g)},}$$

$$\mathbf{\Delta H^0 = -238.6\,kJ, \Delta S^0 = +36.7\,J\,K^{-1}}$$

Solution:

$$\Delta S_{surr} = -\frac{\Delta H^0}{T}$$

$$= \frac{(-238.6\,\text{kJ})}{298\,\text{K}}$$

$= +0.8007\ \text{kJ K}^{-1} = +800.7\ \text{J K}^{-1}$

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

$= +36.7\ \text{JK}^{-1} + 800.7\ \text{JK}^{-1}$

$= +837.4\ \text{J K}^{-1}$

$\Delta S_{total} > 0$, the reaction is spontaneous at 25⁰C.

+5. Calculate ΔG for the reaction at 25⁰C $CO_{(g)} + 2H_{2(g)}$ ® $CH_3OH_{(g)}$, $\Delta G^0 = -24.8\,\text{kJ mol}^{-1}$ .The partial pressures of gases are P_{CO} = 4 bar, P_{H_2} = 2 bar and $P_{CH_3OH} = 2\text{bar}$

Solution:

$$\Delta G = \Delta G^0 + RT\,\text{In}\,Q_p$$

$$= \Delta G^0 + 2.303RT \log 10 \frac{P_{CH_3OH}}{P_{CO} \times P^2_{H_2}}$$

$\Delta G^0 = -24.8\text{kJmol}^{-1}$, $R = 8.314 \times 10^{-3}$ kJ $\text{K}^{-1}\text{mol}^{-1}$, $T = 298$ K

Calculate Q_p,

$$Q_p = \frac{P_{CH_3CH}}{P_{CO} \times P^2_{H_2}} = \frac{2}{4 \times 4} = \frac{1}{8} = 0.125$$

$\Delta G = -248\ \text{kJ mol}^{-1} + 2.303 \times 8.314 \times 10^{-3}$ kJ $\text{K}^{-1}\ \text{mol}^{-1} \times 298\ \text{K} \times \log_{10} 0.125$

$= -248\ \text{kJ mol}^{-1} + 5.706 \times (-0.903)\ \text{kJ mol}^{-1}$

$= -24.8\ \text{kJ mol}^{-1} - 5.153\ \text{kJ mol}^{-1}$

$= -29.953\ \text{kJ mol}^{-1}$.

❍❍❍

MCQ. from Textbook

1. The correct thermodynamic conditions for the spontaneous reaction at all temperatures are
   a. $\Delta H < 0$ and $\Delta S > 0$
   b. $\Delta H > 0$ and $\Delta S < 0$
   c. $\Delta H < 0$ and $\Delta S < 0$
   d. $\Delta H < 0$ and $\Delta S = 0$
2. A gas is allowed to expand in a well insulated container against a constant external pressure of 2.5 bar from an initial volume of 2.5 L to a final volume of 4.5 L. The change in internal energy, ΔU of the gas will be
   a. – 500 J
   b. + 500 J
   c. – 1013 J
   d. + 1013 J
3. In which of the following, entropy of the system decreases?
   a. Crystallization of liquid into solid
   b. Temperature of crystalline solid is increased from 0 K to 115 K
   c. $H_{2(g)} \rightarrow 2H_{(g)}$
   d. $2NaHCO_{3(s)} \rightarrow Na_2CO_{3(s)} + CO_{2(g)} + H_2O_{(g)}$
4. The enthalpy of formation for all elements in their standard states is
   a. unity
   b. zero
   c. less than zero
   d. different elements
5. Which of the following reactions is exothermic?
   a. $H_{2(g)} \rightarrow 2H_{(g)}$
   b. $C_{(s)} \rightarrow C_{(g)}$
   c. $2Cl_{(g)} \rightarrow Cl_{2(g)}$
   d. $H_2O_{(s)} \rightarrow H_2O(l)$
6. 6.24 g of ethanol are vaporized by supplying 5.89 kJ of heat. Enthalpy of vaporization of ethanol will be
   a. 43.4 kJ mol^{-1}
   b. 60.2 kJ mol^{-1}
   c. 38.9 kJ mol^{-1}
   d. 20.4 kJ mol^{-1}
7. If the standard enthalpy of formation of methanol is – 238.9 kJ mol^{-1} then entropy change of the surroundings will be
   a. – 801.7 J K^{-1}
   b. 801.7 J K^{-1}
   c. 0.8017 J K^{-1}
   d. –0.8017 J K^{-1}
8. Which of the following are not state functions?
   i. $Q + W$
   ii. Q
   iii. W
   iv. $H–TS$
   a. i, ii and iii
   b. ii and iii
   c. i and iv
   d. ii, iii and iv
9. For vaporization of water at 1 bar, $\Delta H = 40.63$ kJ mol^{-1} and $\Delta S = 108.8$ J K^{-1} mol^{-1}. At what temperature, $\Delta G = 0$?
   a. 273.4 K
   b. 393.4 K
   c. 373.4 K
   d. 293.4 K
10. Bond enthalpies of H-H, Cl-Cl and H-Cl bonds are 434 kJ mol-1, 242 kJ mol-1 and 431 kJ mol-1, respectively. Enthalpy of formation of HCl is
    a. 245 kJ mol^{-1}
    b. –93 kJmol^{-1}
    c. –245 kJ mol^{-1}
    d. 93 kJ mol^{-1}

Answer Key

1. a 2. a 3. a 4. b 5. c 6. a
7. b 8. c 9. c 10. b