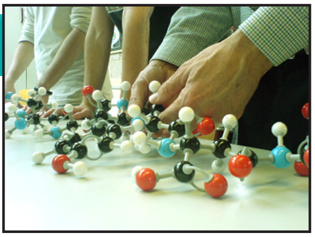
5

Chemical Bonding

CHAPTER



KEY CONCEPTS AND EQUATIONS

CHEMICAL BOND AND VALENCE

The force which results from the interaction between various atoms that form a stable molecule is referred to as a chemical bond. It is defined as a force that holds two or more atoms together as a stable molecule.

The valence is the number of bonds formed by an atom in a molecule.

OCTET RULE

Atoms interact by electron transfer or sharing so as to have the stable outer shell of eight electrons. This tendency for atoms to have eight electrons in the outer shell is known as **Octet rule.**

IONIC BOND

The electrostatic attraction between the cations and anions produced by electron transfer constitutes an **Ionic** or **Electrostatic bond.** Following factors favour the formation of Ionic bond.

(i) The ionisation energy of the metal atom which loses electrons should be low. That is why alkali metals and alkaline earth metals form Ionic bonds. The tendency to form ionic bond increases as we go down a group as there is a decrease in Ionisation energy.

(ii) The electron affinity of the electron accepting atom should be high. The elements of group VI A and VII B have high electron affinity. That is why they form ionic bonds with the metals. In moving down a group the electron affinity decreases and, therefore, the tendency to form ionic bond decrease.

(iii) The Lattice Energy is the amount of energy released when one mole of an ionic compound is formed from its cations and anions. Greater the lattice energy, greater the strength of the ionic bond.

COVALENT BOND

The covalent bond is attractive force between atom created by sharing of an electron pair. It is indicated by a dash (–) between the two bonded atoms. After sharing both atoms have eight electrons in their outer most shell.

CONDITIONS FOR THE FORMATION OF COVALENT BOND

(i) Each of the atoms should have 5, 6 or 7 valence electrons so as to have eight electrons by sharing 3, 2 or 1 electron pair. The non-metals of group VA, VIA and VIIA satisfy this condition and form covalent bonds.

(ii) Both the atom should have same for similar electronegativity.

(iii) Both the atoms should have equal or almost equal electron affinity.

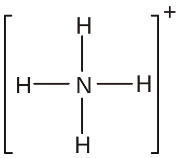
EXAMPLES OF COVALENT COMPOUNDS

H—H Cl—Cl O$=$O H—O—H N$\equiv$N O$=$C$=$O

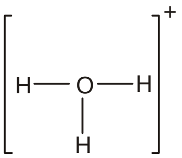
COORDINATE COVALENT BOND

In some cases a covalent bond is formed when both the electrons are supplied by one atom and sharing is done by both the atoms. Such a bond is called **Coordinate covalent bond** or **dative bond.** The atom which donates a pair of electrons is called **donor,** while the atoms which accepts the electron pair is called **acceptor.** This type of bond is represented by an arrow pointing towards the acceptor atom.

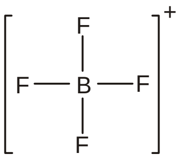
EXAMPLES OF COORDINATE COMPOUNDS OR IONS



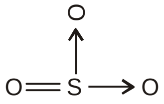
Ammonium ion



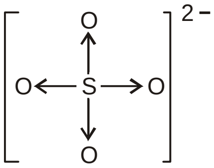
Hydronium ion



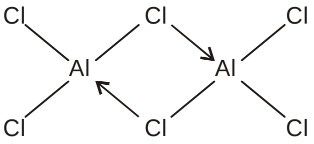
Fluoroborate ion



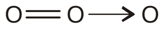
Sulphur trioxide



Sulphate ion



Aluminum chloride (Dimer)



Ozone molecule

POLAR COVALENT BOND

A covalent bond in which electrons are shared unequally and the bonded atoms acquire a partial positive and negative charge is called a polar covalent bond. The polarity of a bond is determined by the difference in electronegativity of the two bonded atoms.

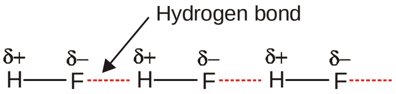
The percentage Ionic character of a bond can be calculated by using the equation

$$\%\text{age Ionic character} = 16\,[X_A - X_B] + 3.5\,[X_A + X_B]^2$$

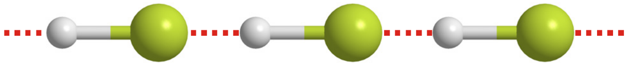
where X_A and X_B are the electronegativities of the two atoms.

HYDROGEN BONDING

The electrostatic attraction between a H atom covalently bonded to a highly electronegative atom X and lone pair of electrons on X in another molecule is called **Hydrogen bonding**. It is represented by a dotted line.



Hydrogen fluoride molecules



CONDITIONS OF HYDROGEN BONDING

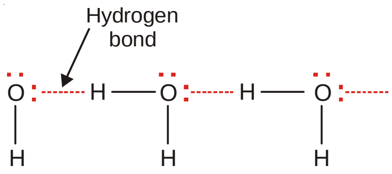
(1) The electronegativity of the atom bonded to H atom should be high. The atoms such as F,O and N form Hydrogen Bonding.

(2) The size of the atom bonded by H atom should be small. For example, N and Cl both have 3.0 electronegativity but H-bonding is effective in NH_3 due to smaller size of N atoms than Cl atom.

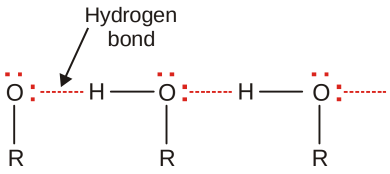
TYPES OF HYDROGEN BONDING

(1) Intermolecular H–bonding

This type of bonding occurs in two different molecules of the same or different substances. It results in the associated molecules. The substances having inter molecular H-bonding have high melting or boiling points, viscosity, surface tension etc. For example,



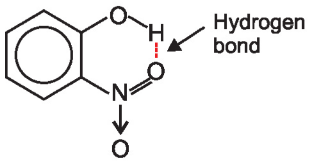
Water

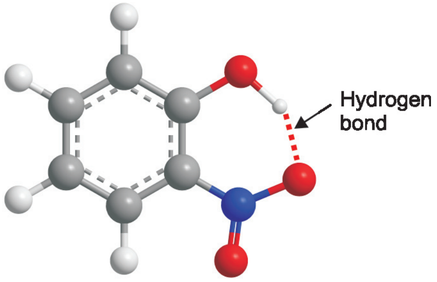


Alcohol

(2) Intramolecular H-bonding

This type of hydrogen bonding is formed between the H atoms and electronegative atom present within the same molecule. It results in cyclization of the molecule. Molecules exist as discrete unit and not in associated form. Intramolecular H-bonding has no effect of melting and boiling points, viscosity, surface tension, etc. For example,





GEOMETRY OF MOLECULES VSEPR THEORY

It states that the electron pairs both lone pairs and bond pairs surrounding the central atom will be arranged in space as far apart as possible to minimise the electrostatic repulsion between them. On the basis of VSEPR theory the shapes of some molecules with their bond angles are given in Table 5.1

TABLE 5.1 SHAPES OF MOLECULES - VSEPR THEORY

Molecule	No. of electron pairs around central atom	Shape of the molecule	Bond Angle
$BeCl_2$	2	Linear	180°
$BF_{3,}$ SO_3	3	Trigonal Planar	120°
CH_4	4	Tetrahedral	109°28'
NH_3	4	Distorted Tetrahedral	107°
H_2O	4	Distorted Tetrahedral	105°
PF_5	5	Trigonal Bipyramidal	90°, 120°
SF_6	6	Octahedral	90°

ADDITIONAL SOLVED PROBLEMS

SOLVED PROBLEM 1. Two elements X and Y occur in same period and their atoms have two and seven valence electrons respectively. Write down the most probable compound between X and Y. Will the bond between X and Y be predominantly ionic or covalent ?

SOLUTION :

Since the element X has two electrons in the valence shell, it should be electropositive and have a tendency to form X^{2+} by losing two electrons.

The element Y has seven electrons in the valence shell, it should be electronegative and have a tendency to form Y^- by gaining one electron.

X^{2+} combines with two Y^- anions to form the compound with formula $XY_{2.}$

Since the bond has been formed by the transfer of electrons the bond is purely **ionic**.

SOLVED PROBLEM 2. Calculate the percentage ionic character of C—Cl bond in CCl_4, if the electronegativities of C and Cl are 3.5 and 3.0 respectively.

SOLUTION :

Formula used

$$\%\ age\ ionic\ character = 16\,[X_A - X_B] + 3.5\,[X_A - X_B]^2$$

Quantities given

$$X_A = 3.5 \qquad X_B = 3.0$$

Substitution of values

$$\begin{aligned}\%\text{ age Ionic Character} &= 16(3.5-3.0) + 3.5\,(3.5-3.0)^2\\ &= 8.0 + 0.875\\ &= \mathbf{8.875\%}\end{aligned}$$

SOLVED PROBLEM 3. The dipole moment of KCl is 3.336×10^{-29} coulomb meter which indicates that it is highly polar molecule. The interionic distance between K^+ and Cl^- in this molecule is 2.6×10^{-10}m. Calculate the dipole moment of KCl molecule if there were opposite charges of one fundamental unit localised at each nucleus. Calculate the percentage ionic character of KCl.

SOLUTION :

Formula used :

$$\mu = e \times d$$

For complete separation of unit charge (100% ionic character)

$$\begin{aligned}\mu &= 1.602 \times 10^{-19}\text{ coulomb} \times 2.6 \times 10^{-10}\text{ m}\\ &= 4.165 \times 10^{-29}\text{ coulomb meter}\end{aligned}$$

Quantity given

$$\textit{Actual dipole moment of KCl} = 3.336 \times 10^{-29}\text{ coulomb meter.}$$

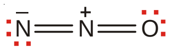
Substitution of values

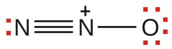
$$\begin{aligned}\%\text{ ionic character of KCl} &= 100 \times \frac{3.336 \times 10^{-29}\text{coulomb meter}}{4.165 \times 10^{-29}\text{ coulomb meter}}\\ &= \mathbf{80\%}\end{aligned}$$

SOLVED PROBLEM 4. Write the two resonance structures of N_2O that satisfy the octet rule.

SOLUTION :

The two resonating structures are

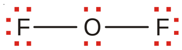




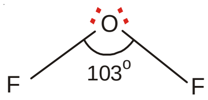
SOLVED PROBLEM 5. Using VSEPR theory, identify the type of hybridisation and draw the structure of OF_2. What are the oxidation states of O and F ?

SOLUTION :

The dot Lewis diagram of OF_2 is



There are two lone pairs and two bond pairs around central oxygen atom. Thus the hybridisation will be sp^3 and the shape will be distorted tetrahedral due to the presence of lone pairs of electrons. The angle FOF is 103° and it is V-shaped molecule.



SOLVED PROBLEM 6. Account for : The experimentally found N —— F bond length in NF_3 is greater than the sum of single covalent radii of N and F.

SOLUTION :

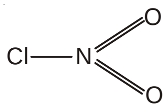
The bond length of N —— F bond in NF_3 molecule is greater than the sum of single covalent radii of N and F is due to repulsion of the bond pair by both Nitrogen and Fluorine atom. It is due to smaller size and high electron density around N atom.

ADDITIONAL PRACTICE PROBLEMS

1. Write the Lewis structure for carbon tetrachloride, CCl_4 and formaldehyde, HCHO.
2. Which of the following compounds contain bonds that are predominantly ionic in character : MgO, Ca_3P_2, $AlCl_3$, Mg_2Si and CsF.

   Answer. CsF, Mg_2Si and MgO
3. Classify the bonds in the following as ionic, polar covalent or covalent : (a) HCl (b) NaCl and (c) NCl_3.

   Answer. HCl - Polar covalent, NaCl - Ionic and NCl_3 - Covalent
4. Draw the Lewis structure for NO_3^- and PO_4^{3-} ions.
5. Complete the following structural formula by adding unshared electron pairs to the structures given.



6. The experimentally determined dipole moment, μ, of KF is 2.87 × 10^{-29} coulomb meter. The distance, *d*, separating the centers of charge in a KF dipole is 2.66 × 10^{-3} m. Calculate the percent ionic character of KF.

Answer. 67.4%

7. Write the Lewis formula for Thionyl chloride, $SOCl_2$, and Carbonyl chloride $COCl_{2.}$

8. Predict the geometry of the following molecules using VSEPR theory.

(a) CCl_4 (b) $AlCl_3$ (c) H_2Se.

Answer. (a) Tetrahedral (b) Trigonal planar (c) Bent

9. What geometry is expected for the following molecules according to the VSEPR theory ?

(a) PF_5 (b) SCl_4 (c) BrF_3

Answer. (a) Trigonal bipyramidal (b) See-saw (c) T-Shaped

10. Predict the geometry of the following ions having VSEPR model.

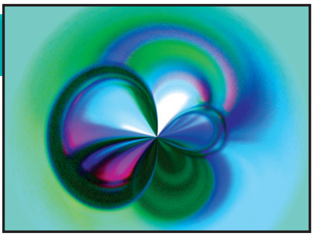
(a) H_3O^+ (b) NO_2^- (c) ClO_2^-

Answer. (a) Pyramidal (b) Bent (c) Bent

6

Chemical Bonding – Orbital Concept

CHAPTER



KEY CONCEPTS AND EQUATIONS

CHEMICAL BONDING – ENERGY CONCEPT

Two or more atoms unite to form a molecule because in doing so the energy of the system decreases and the molecule becomes stable as compared to isolated atoms. The amount of energy released per mole is termed as Bond energy or stabilisation energy.

ATOMIC ORBITAL THEORY

According to this theory a bond is formed when atomic orbital of one atom overlaps with the atomic orbital of the other atom. The strength of the bond depends upon the extent of overlapping. Greater the extent of overlap, greater the strength of the bond.

TYPES OF OVERLAPPING AND NATURE OF COVALENT BOND

A covalent bond is of two types depending on the type of overlapping between two atoms.

1. **Sigma (σ) bond**

This type of covalent bond results when there is end to end overlapping of atomic orbitals along the internuclear axis. It is formed when *s-s*, *s-p* or *p-p* head-on overlapping takes place.

2. **Pi (π) bond**

This type of covalent bond results when there is sidewise overlap of half filled atomic orbitals. It is formed when *p-p* sidewise overlapping takes place. This bond is weaker than sigma bond.

HYBRIDISATION AND SHAPE OF MOLECULES

It may be defined as the concept of mixing up of orbitals of nearly equal energy giving rise to new orbitals which are having equal energy and identical shapes. Depending upon the number and nature of the orbitals undergoing hybridisation we have various types of hybrid orbitals. The details are summarised in Table 6.1

TABLE 6.1. **HYBRIDISATION AND SHAPE OF MOLECULES**

Type of Hybridisation	No. and type of Orbitals mixed	No. and type of New orbitals formed	Shape	Examples
sp	s and p	sp Two	Linear	BeF_2, $BeCl_2$, C_2H_2
sp^2	s and two p	sp^2 Three	Trigonal	BF_3
sp^3	s and three p	sp^3 Four	Tetrahedral	CH_4, SO_4^{2-}, ClO_4^{2-}
sp^3d	s, three p and one d	sp^3d Five	Trigonal bipyramidal	PF_5
sp^3d^2	s, three p and two d	sp^3d^2 Six	Octahedral	SF_6

MOLECULAR ORBITAL THEORY

According to this theory all atomic orbitals of the participating atoms mix up and give rise to an equivalent number of new orbitals belonging to the molecule. These new orbitals are called molecular orbitals. These are of two types.

(i) Bonding Molecular orbital formed by the addition of wave functions of atomic orbitals. It lowers the energy and is responsible for the stability in the system.

(ii) Anti-Bonding Molecular orbital formed by the subtraction of wave function of atomic orbitals. It has net disruptive effect.

Since we are concerned with the few simple molecules, the only molecular orbitals which need to be considered are

$$\text{Bonding MOs} = \sigma(1s)\ \sigma(2s)\ \sigma(2p_z)\ \pi\, 2p_y\ \ \pi\, 2p_x$$

$$\text{Antibonding MOs} = \sigma^*(1s)\ \sigma^*(2s)\ \sigma^*(2p_z)\ \pi^*2p_{\mathrm{y}}\ \pi^*2p_x$$

These are arranged in their increasing order of energy as determined by spectroscopic measurements.

$$\sigma(1s)\ \sigma^*(1s)\ \sigma(2s)\ \sigma^*(2s)\ \sigma(2p_x)\ \pi(2p_y) = \pi(2p_x)\ \pi^*(2p_y) = \pi^*(2p_x)\ \sigma^*(2p_z)$$

BOND ORDER

The term bond order refers to the number of bonds that exist between two atoms. In molecular orbital theory the bond order is one half of the difference of the number of electrons in the bonding molecular orbitals and the number of electrons in the antibonding molecular orbitals. Mathematically,

$$\text{Bond Order} = \frac{N_b - N_a}{2}$$

where N_b is the number of electrons in bonding MOs
and N_a is the number of electrons in antibonding MOs.

The electronic configuration and bond order of various molecules have been summarized in Table 6.2

TABLE 6.2. ELECTRONIC CONFIGURATION AND BOND ORDERS

Molecule / Ion	Electronic Configuration	Bond Order
H_2	$\sigma(1s^2)\,\sigma^*(1s^0)$	$\frac{2-0}{2} = 1$
He_2	$\sigma(1s^2)\,\sigma^*(1s^2)$	$\frac{2-2}{2} = 0$
Li^2	$KK\sigma(2s^2)\,\sigma^*(2s^0)$	$\frac{2-0}{2} = 1$
Be_2	$KK\sigma(2s^2)\,\sigma^*\,(2s^2)$	$\frac{2-2}{2} = 0$
N_2	$KK\sigma(2s^2)\,\sigma^*(2s^2)\,\sigma 2p^2{}_z\,\pi(2p^2{}_y)\,\pi(2p^2{}_x)$	$\frac{8-2}{2} = 3$
O_2	$KK\sigma(2s^2)\,\sigma^*(2s^2)\,\sigma(2p^2{}_z)\,\pi(2p^2{}_y)\,\pi(2p^2{}_x)\,\pi^*(2p^1{}_y)\,\pi^*(2p^1{}_x)$	$\frac{8-4}{2} = 2$
$O_2{}^+$	$KK\sigma(2s^2)\,\sigma^*(2s^2)\,\sigma(2p^2{}_z)\,\pi(2p^2{}_y)\,\pi(2p^2{}_x)\,\pi^*(2p^1{}_y)$	$\frac{8-3}{2} = 2.5$
$O_2{}^-$	$KK\sigma(2s^2)\,\sigma^*(2s^2)\,\sigma(2p^2{}_z)\,\pi(2p^2{}_y)\,\pi(2p^2{}_x)\,\pi^*(2p^2{}_y)\,\pi^*(2p^1{}_x)$	$\frac{8-5}{2} = 1.5$
$O_2{}^{2-}$	$KK\sigma(2s^2)\,\sigma^*(2s^2)\,\sigma(2p^2{}_z)\,\pi(2p^2{}_y)\,\pi(2p^2{}_x)\,\pi^*(2p^2{}_y)\,\pi^*(2p^2{}_x)$	$\frac{8-6}{2} = 1$
F_2	$KK\sigma(2s^2)\,\sigma^*(2s^2)\,\sigma(2p^2{}_z)\,\pi(2p^2{}_y)\,\pi(2p^2{}_x)\,\pi^*(2p^2{}_y)\,\pi^*(2p^2{}_x)$	$\frac{8-6}{2} = 1$
Ne_2	$KK\sigma(2s^2)\,\sigma^*(2s^2)\,\sigma(2p^2{}_z)\,\pi(2p^2{}_y)\,\pi(2p^2{}_x)\,\pi^*(2p^2{}_y)\,\pi^*(2p^2{}_x)\,\pi^*(2p^2{}_Z)$	$\frac{8-8}{2} = 0$
NO	$KK\sigma(2s^2)\,\sigma^*(2s^2)\,\sigma(2p^2{}_z)\,\pi(2p^2{}_y)\,\pi(2p^2{}_x)\,\pi^*2p^1{}_y$	$\frac{8-3}{2} = 2.5$
CO	$KK\sigma(2s^2)\,\sigma^*(2s^2)\,\sigma(2p^2{}_z)\,\pi(2p^2{}_y)\,\pi(2p^2{}_x)$	$\frac{8-2}{2} = 3$

ADDITIONAL SOLVED PROBLEMS

SOLVED PROBLEM 1. Write the electronic configuration of $O_2{}^{2-}$ molecule on the basis of M.O. Theory and calculate its bond order.

SOLUTION : (i) Electronic Configuration

$$KK\sigma(2s^2)\,\sigma^*(2s^2)\,\sigma(2p^2{}_z)\,\pi(2p^2{}_y)\,\pi(2p^2{}_x)\,\pi^*(2p^2{}_y)\,\pi^*(2p^2{}_x)$$

(ii) To calculate bond order

Formula used

$$\text{Bond order} = \frac{N_b - N_a}{2}$$

$N_b = 8$ $\qquad$ $N_a = 6$

Substitution of values

$$\text{Bond order} = \frac{8-6}{2} = \mathbf{1}$$

SOLVED PROBLEM 2. Why does the molecule Ne_2 not exist ?

SOLUTION : Two electronic configuration of Ne_2 molecule is

$$\text{KK}\ \sigma(2s^2)\ \sigma^*(2s^2)\ \sigma(2p^2_z)\ \pi(2p^2_y)\ \pi(2p^2_x)\ \pi^*(2p^2_y)\ \pi^*(2p^2_x)\ \sigma^*(2p^2_z)$$

$$\begin{aligned}\text{Bond order} &= \frac{N_b - N_a}{2}\\ &= \frac{8-8}{2}\\ &= \mathbf{0}\end{aligned}$$

Since the bond order is Ne_2 is zero, it does not exist.

SOLVED PROBLEM 3. Calculate the bond order in He^+ on the basis of M.O. theory.

SOLUTION : The electronic configuration of He^+ is

$$\text{KK}\ \sigma(2s^2)\ \sigma(2s^1)$$

$$\text{Bond order} = \frac{N_b - N_a}{2} = \frac{2-1}{2} = \mathbf{0.5}$$

ADDITIONAL PRACTICE PROBLEMS

1. The O–O bond length in O_2^+ is 1.12Å and in O_2 is 1.21Å. Explain why the bond length in O_2^+ is shorter than O_2.

2. Write the molecular orbital configuration of C_2^{2-} and calculate the bond order of the acetylide in C_2^{2-}.

Answer. Three

3. Write the molecular orbital configuration of O_2^- ion.

Answer. $\text{KK}\ \sigma(2s^2)\ \sigma^*(2s^2)\ \sigma(2p^2_z)\ \pi(2p^2_y)\ \pi(2p^2_x)\ \pi^*(2p^2_y)\ \pi^*(2p^1_x)$

4. Write MO configuration for O_2 and O_2^{2-} and which of them is paramagnetic ?

Answer. O_2 is paramagnetic

5. On the basis of bond order, predict which of the following species is the most stable?

O_2^- O_2 and Ne_2^+

Answer. O_2 is most stable

6. Write the ground state electronic configuration of O_2^+ on the basis of MO theory.

Answer. $\text{KK}\ \sigma(2s^2)\ \sigma^*(2s^2)\ \sigma(2p^2_z)\ \pi(2p^2_y)\ \pi(2p^2_x)\ \pi^*(2p^1_x)$

7. Which has greater bond dissociation energy N_2 or N_2^+?

Answer. N_2, as it has bond order of three.

8. Write the electronic configuration of Be_2 molecule and calculate its bond order.

Answer. $\text{KK}\ \sigma(2s^2)\ \sigma^*(2s^2)$; zero

9. Write the ground state electronic configuration of N_2^- on the basis of MO theory and calculate its bond order.

Answer. $\text{KK}\ \sigma(2s^2)\ \sigma^*(2s^2)\ \sigma(2p^2_z)\ \pi(2p^2_y)\ \pi(2p^2_x)\ \pi^*(2p^1_y)$; 2.5

10. Calculate the number of antibonding electrons in O_2^{2-} molecule on the basis of M.O. theory.

Answer. Four

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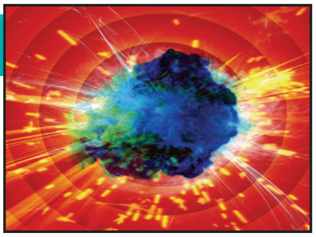
First Law of Thermodynamics

CHAPTER



KEY CONCEPTS AND EQUATIONS

THERMODYNAMICS

The study of the flow of heat or any other form of energy into or out of a system as it undergoes a physical or chemical transformation, is called Thermodynamics.

FIRST LAW OF THERMODYNAMICS

The total energy of an isolated system remains constant though it may change from one form to another, or,

Energy can neither be created nor, destroyed, it can only be converted from one form to other.

MATHEMATICAL STATEMENT OF THE FIRST LAW

$$\Delta E = q - w$$

where ΔE is the change in internal energy, q is the amount of heat supplied to the system and w is the work done by the system.

WORK DONE IN AN ISOTHERMAL REVERSIBLE EXPANSION

The work done in reversible expansion from value V_1 to V_2 at a constant temperature is given by

$$w = -2.303 \times n\,R\,T \ \log \frac{P_1}{P_2}$$

or

$$w = 2.303 \times n\,R\,T \ \log \frac{P_2}{P_1}$$

or

$$= 2.303 \times n\,R\,T \ \log \frac{V_1}{V_2}$$

where P_1 is the initial pressure, P_2 is the final pressure, n the number of moles of the gas, R the gas constant and T the absolute temperature.

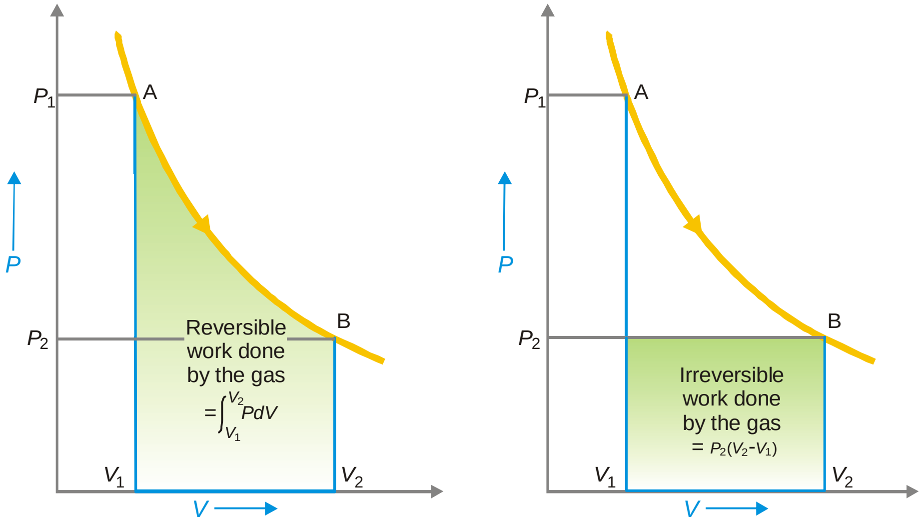
WORK DONE IN AN IRREVERSIBLE EXPANSION

The work done in an irreversible expansion of a gas from volume V_1 to V_2 is given by

$$w = P_2 (V_2 - V_1)$$

where P_2 is the final pressure ; V_1 the initial volume and V_2 the final volume.

It may be noted that work is not a state function as it depends on the path by which the process is performed rather than the initial and final states. Thus, it is path function.



(a) (b)

Figure 7.1

(*a*) The reversible work of expansion; (*b*) The irreversible work done by the gas when the external pressure is at once dropped to the final value P_2.

INTERNAL ENERGY AND ENTHALPY

The total of all possible kinds of energy of a system is called its Internal Energy. It is a state function and is an extensive property. It is denoted by *E*.

The total heat content of a system at constant pressure is equivalent to the internal energy *E* plus the *PV* energy. This is called the Enthalpy and is defined by the equation.

$$H = E + PV$$

It is state function and is independent of the path. The change in internal energy and enthalpy is denoted by

$$\Delta E = E_2 - E_1$$

and

$$\Delta E = H_2 - H_1$$

where E_1 and H_1 are internal energy and enthalpy in the initial state and E_2 and H_2 are internal energy and the enthalpy in the final state.

RELATION BETWEEN ΔH AND ΔE

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

or

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

where ΔV is the change in volume $(V_2 - V_1)$.

Δn is the change in number of moles of gaseous products and gaseous reactants and is given by $\Delta n = n_2 - n_1$ where n_2 is the no. of moles of gaseous products and n_1 is the no. of moles of gaseous reactants.

MOLAR HEAT CAPACITIES

The molar heat capacity of a system is defined as the amount of heat required to raise the temperature of one mole of the susbstance (system) by 1 K. It varies with temperature and is given by

$$C = \frac{dq}{dt}$$

where *dq* is the small quantity of heat absorbed by the system producing a small rise *dt*. It is also defined as the ratio of the amount of heat absorbed to rise in temperature. It is not a state function.

MOLAR HEAT CAPACITY AT CONSTANT VOLUME

$$C_v = \frac{\Delta E}{T_2 - T_1}$$

where ΔE is the amount of heat absorbed at constant volume. Thus the heat capacity at constant volume is defined as the rate of change of internal energy with temperature at constant volume.

MOLAR HEAT CAPACITY AT CONSTANT PRESSURE

$$C_p = \frac{\Delta H}{T_2 - T_1}$$

where ΔH is the amount of heat absorbed at constant volume. Thus heat capacity at constant pressure is defined as the rate of change of enthalpy with temperature at constant pressure.

RELATION BETWEEN C_P AND C_V

C_p is greater than C_v. These two are related to each other by the relation

$$C_p - C_v = R$$

CALCULATION OF ΔE AND ΔH

$$\Delta E = n \times C_v\ (T_2 - T_1)$$

and $$\Delta H = n \times C_p\ (T_2 - T_1)$$

ADIABATIC EXPANSION OF AN IDEAL GAS

In an adiabatic process there is no heat exchange between a system and surroundings *i.e.* $q = 0$

also $$\frac{T_2}{T_1} = \left(\frac{V_1}{V_2}\right)^{\gamma - 1} \quad \text{or} \quad TV^{\gamma-1} = \text{a constant}$$

and $$\frac{P_2}{P_1} = \left(\frac{V_1}{V_2}\right)^{\gamma - 1} \quad \text{or} \quad PV^{\gamma}$$

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

In an isothermal process, temperature of system remains constant while in an adiabatic process temperature must change. These two processes are shown in Fig 7.2.

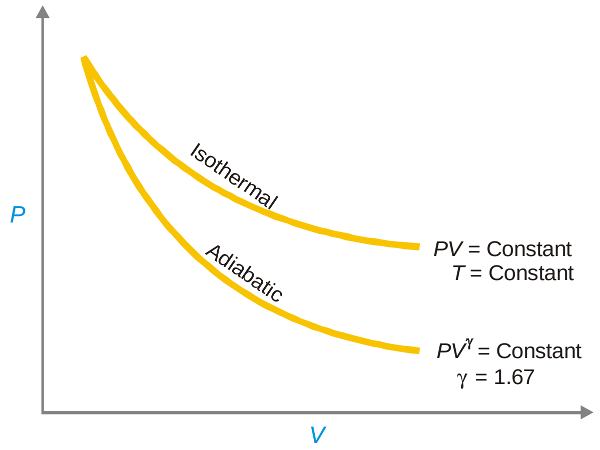


Figure 7.2
Curves for isothermal and adiabatic expansions for a monoatomic ideal gas.

ADDITIONAL SOLVED PROBLEMS

SOLVED PROBLEM 1. A dry gas at NTP is expanded adiabatically from 1 litre to 5 litre. Calculate the final temperature and pressure assuming ideal behaviour ($C_p / C_v = 1.4$)

SOLUTION : (a) To calculate the temperature

Formula used

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

Quantities given

$T_1 = 273$ K $\qquad V_1 = 1$ litre $\qquad V_2 = 5$ litres $\qquad \gamma = 1.4$

Substitution of values

$$T_2 = 273 \text{ K} \times \left(\frac{1 \text{ litre}}{5 \text{ litre}}\right)^{1.40 - 1}$$

Taking logarithms

$$\log T_2 = \log 273 + 0.40 \log \frac{1}{5}$$

or $$= 2.4361 + 0.40\,(-0.6990)$$

or $$\log T_2 = 2.4361 - 0.2796$$
$$= 2.1565$$

Taking Antilogarithms

$$T_2 = \text{Antilog } 2.1565$$
$$= 143.4 \text{ K}$$

(ii) To calculate the pressure

Formula used

$$\frac{P_1}{P_2} = \left(\frac{V_2}{V_1}\right)^{\gamma}$$

Quantities given

$P_1 = 1$ atm $\qquad V_1 = 1$ litre $\qquad V_2 = 5$ litres $\qquad \gamma = 1.4$

Substitution of values

$$\frac{1 \text{ atm}}{P_2} = \left(\frac{1 \text{ litre}}{5 \text{ litre}}\right)^{1.40}$$

or $$P_2 = \left(\frac{1}{5}\right)^{1.40} \text{ atm}$$

Taking logarithms

$$\log P_2 = 1.40 \log (0.2)$$
$$= 1.40\,(-0.6990)$$
$$= -0.9786$$

or $$P_2 = \text{Antilog}\,(-0.9786)$$
$$= \mathbf{0.1050 \text{ atm}}$$

SOLVED PROBLEM 2. Calculate the maximum work done when 44 g of Neon gas expands reversibly and isothermally from 10 atm to 2 atm pressure at constant temperature 27 ºC. (Neon at. mass = 20; $R = 2$ cal deg^{-1} mol^{-1}).

SOLUTION :

Formula used

$$w = 2.303 \times n R T \log \frac{P_1}{P_2}$$

Quantities given

$n = \frac{44}{20} = 2.2$ moles

$R = 2$ cal deg^{-1} mol^{-1}

$T = 27 + 273 = 300$ K

$P_1 = 10$ atm

$P_2 = 2$ atm

Substitution of values

$$w = 2.303 \times 2.2 \text{ mol} \times 2 \text{ cal K}^{-1} \text{ mol}^{-1} \times 300 \text{ K} \times \log \frac{10 \text{ atm}}{2 \text{ atm}}$$

$$= 3039.96 \text{ cal} \times \log 5$$

$$= \mathbf{2124.84 \text{ cal}}$$

SOLVED PROBLEM 3. How many calories of heat are required to heat 1 mole of Argon from 40 ºC to 100 ºC at (i) Constant Volume and (ii) at Constant pressure ?

Molar heat capacity of Ar at constant volume = 3 cal K^{-1}

Molar heat capacity of Ar at constant pressure = 5 cal K^{-1}

Solution : **(i) At constant volume**

Formula used

$$\Delta E = n \times C_v \times (T_2 - T_1)$$

Quantities given

$n = 1$ mole

$C_v = 3$ cal K^{-1}

$T_2 = 100 + 273 = 373$ K

$T_1 = 40 + 273 = 313$ K

Substitution of values

$$\Delta E = 1 \times 3 \times (373 - 313) \text{ cal}$$

$$= \mathbf{180 \text{ cal}}$$

(ii) At constant pressure

Formula used

$$\Delta H = n \times C_p \times (T_2 - T_1)$$

Quantities given

$n = 1$ mole

$C_p = 5$ cal K^{-1}

$T_2 = 373$ K

$T_1 = 313$ K

Substitution of values

$$\Delta H = 1 \times 5 \times (373 - 313)$$

$$= \mathbf{300 \text{ cal}}$$

SOLVED PROBLEM 4. Calculate the work of expansion of one mole of an ideal gas at 25 ºC under isothermal conditions, the pressure being changed from 1 atm to 5 atm.

SOLUTION :

Formula used

$$w = 2.303 \times n R T \log \frac{P_1}{P_2}$$

Quantities given

$n = 1$ mole

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

$T = 25 + 273 = 298$ K

$P_1 = 1$ atm $\qquad\qquad$ $P_2 = 5$ atm

Substitution of values

$$\begin{aligned} w &= 2.303 \times 1 \text{ mol} \times 8.314 \text{ J K}^{-1} \text{ mol}^{-1} \times 298 \text{ K} \times \log \frac{1 \text{ atm}}{5 \text{ atm}} \\ &= 5705.848 \times \log \frac{1}{5} \\ &= 5705.848 \times (0.6990) \\ &= \mathbf{-3988.38\ J} \end{aligned}$$

SOLVED PROBLEM 5. Calculate the value of ΔE and ΔH on heating 64.0 grams of oxygen from 0 ºC to 100 ºC. C_v and C_p on an average are 5.0 and 7.0 cal mol^{-1} deg^{-1} respectively.

SOLUTION : (i) To calculate ΔE

Formula used

$$\Delta E = n \times C_v \times (T_2 - T_1)$$

Quantities given

$n = \dfrac{64 \text{ g}}{32 \text{ g mol}^{-1}} = 2$ mol $\qquad\qquad$ $C_v = 5$ cal K mol^{-1}

$T_2 = 100 + 273 = 373$ K $\qquad\qquad$ $T_1 = 273$ K

Substitution of values

$$\begin{aligned} \Delta E &= 2 \text{ mol} \times 5 \text{ cal K}^{-1} \text{ mol}^{-1} \times (373 \text{ K} - 273 \text{ K}) \\ &= 10 \times 100 \text{ cal} \\ &= \mathbf{1000\ cal} \end{aligned}$$

(i) To calculate ΔH

Formula used

$$\Delta H = n \times C_p \times (T_2 - T_1)$$

Quantities given

$n = 2$ mol $\qquad$ $C_p = 7$ cal K^{-1} mol^{-1} $\qquad$ $T_2 = 373$ K $\qquad$ $T_1 = 273$ K

Substitution of values

$$\begin{aligned} \Delta H &= 2 \text{ mol} \times 7 \text{ cal K}^{-1} \text{ mol}^{-1} \times (373 \text{ K} - 273 \text{ K}) \\ &= 14 \times 100 \text{ cal} \\ &= \mathbf{1400\ cal} \end{aligned}$$

SOLVED PROBLEM 6. One mole of an ideal gas expands isothermally and reversibly from 1 litre to 100 litres at 27 ºC. Calculate w, q, ΔE, ΔH and ΔS for the process.

SOLUTION : (i) To calculate w

Formula used

$$w = 2.303\, n R T \times \log \frac{V_2}{V_1}$$

Quantities given

$n = 1$ mol $\qquad$ $T = 300$ K $\qquad$ $V_2 = 100$ litres $\qquad$ $V_1 = 1$ litre $\qquad$ $R = 1.987$ cal K^{-1} mol^{-1}

Substitution of values

$$\begin{aligned} w &= 2.303 \times 1 \text{ mol} \times 1.987 \text{ cal K}^{-1} \text{ mol}^{-1} \times 300 \text{ K} \times \log \frac{100 \text{ litre}}{1 \text{ litre}} \\ &= 1372.818 \text{ cal} \times \log 100 \\ &= \mathbf{2745.637\ cal} \end{aligned}$$

(ii) To calculate q and ΔE

Formula used

$$\Delta E = q - w = 0$$

or $q = w$

∴ $q = \mathbf{2745.636\ cal}$ and $\Delta E = \mathbf{0}$

(iii) To calculate ΔH

Formula used

$$\Delta H = \Delta E + \Delta n\,(R\,T)$$

Quantities given

$\Delta E = 0$ $\quad \Delta n = 1$ $\quad R = 1.987 \text{ cal K}^{-1} \text{ mol}^{-1}$ $\quad T = 300 \text{ K}$

Substitution of values

$$\Delta H = 0 + 1 \text{ mol} \times 1.987 \text{ cal K}^{-1} \text{ mol}^{-1} \times 300 \text{ K}$$
$$= \mathbf{596.1} \text{ cal}$$

(iv) To calculate ΔS

Formula used

$$\Delta S = \frac{q}{T}$$

Quantities given

$q = 2745.636 \text{ cal}$ $\quad T = 300 \text{ K}$

Substitution of values

$$\Delta S = \frac{2745.636 \text{ cal}}{300 \text{ K}}$$
$$= \mathbf{9.152\ cal\ K^{-1}}$$

SOLVED PROBLEM 7. Calculate the maximum work obtained when 2 moles of nitrogen were expanded isothermally and reversibly from 10 litres to 20 litres at 25 ºC.

SOLUTION :

Formula used

$$w = 2.303\ n\ R\,T\ \log \frac{V_2}{V_1}$$

Quantities given

$n = 2 \text{ mol}$ $\quad T = 298 \text{ K}$ $\quad R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$ $\quad V_1 = 10 \text{ litres}$ $\quad V_2 = 20 \text{ litres}$

Substitution of values

$$w = 2.303 \times 2 \text{ mol} \times 8.314 \text{ J K}^{-1} \text{ mol} \times 298 \text{ K} \times \log \frac{20 \text{ litre}}{10 \text{ litre}}$$
$$= 11411.69 \text{ cal} \times \log 2$$
$$= 11411.69 \text{ cal} \times 0.3010$$
$$= \mathbf{3434.92\ J}$$

SOLVED PROBLEM 8. Calculate ΔE and ΔH when the temperature of one mole of water is increased from 10 ºC to 70 ºC. The density of water is 0.9778 g cm^{-3} and 0.9997 g cm^{-3} at 70 ºC and 10 ºC respectively.

SOLUTION : (i) To calculate ΔH

Formula used

$$\Delta H = n \times C_p \times (T_2 - T_1)$$

Quantities given

$n = 1 \text{ mole}$ $\quad C_p = 18 \text{ cal K}^{-1} \text{ mol}^{-1}$ $\quad T_2 = 70 + 273 = 343 \text{ K}$ $\quad T_1 = 10 + 273 = 283\text{K}$

Substitution of values

$\Delta H = 1 \text{ mol} \times 18 \text{ cal K}^{-1} \text{ mol}^{-1} \times (343 \text{ K} - 283 \text{ K})$ [∵ C_p = 18 cal K^{-1} as its sp heat = 1]

$$\mathbf{= 1080\ cal = 1080\ cal}$$

(ii) To calculate ΔE

Formula used

$$\Delta E = \Delta H - P(V_2 - V_1)$$

Quantities given

$$V_1 = \frac{18 \times 24.2}{0.9997 \times 1000} = \frac{18 \times 24.2}{1000}\left[\frac{1}{0.9997}\right] \qquad \left[\because \text{Molar Vol.} = \frac{\text{Mol. mass}}{\text{Density}}\right]$$

$$V_2 = \frac{18 \times 24.2}{0.9778 \times 1000} = \frac{18 \times 24.2}{1000}\left[\frac{1}{0.9778}\right]$$

$$\Delta H = \mathbf{1080\ cal}$$

Substitution of values

$$\Delta E = 1080 \text{ cal} - \frac{24.2 \times 18}{1000}\left[\frac{1}{0.9778} - \frac{1}{0.9997}\right] \text{cal}$$

$$= 1080 \text{ cal} - 0.4356 \times (0.02240) \text{ cal}$$

$$= 1080 - 0.009757 \text{ cal}$$

$$= \mathbf{1079.99\ cal}$$

SOLVED PROBLEM 9. Calculate ΔE for the following process, for which $q = -93.78$ kJ at STP

$$N_{2\,(g)} + 3\,H_{2\,(g)} \longrightarrow 2\,NH_{3\,(g)}$$

SOLUTION : (i) To calculate the work done in the process

Formula used

$$w = P\,\Delta V = \Delta n R T$$

Quantities given

$\Delta n = n_P - n_R = 2 \text{ moles} - 4 \text{ moles} = -2 \text{ moles}$ $\quad R = 8.314 \text{ JK}^{-1} \text{ mol}^{-1}$ $\quad T = 273$ K

Substitution of values

$$w = -2 \text{ moles} \times 8.314 \text{ J K}^{-1} \text{ mol}^{-1} \times 273 \text{ K}$$

$$= -4539.44 \text{ J}$$

$$= \mathbf{-4.53944\ kJ}$$

(ii) To calculate the value of ΔE

Formula given

$$\Delta E = q - w$$

Quantities given

$q = -93.78$ k J $\qquad w = -4.5394$ k J

Substitution of values

$$\Delta E = -93.78 \text{ k J} - (-4.53944 \text{ k J})$$

$$= \mathbf{-89.240\ k\ J}$$

SOLVED PROBLEM 10. Calculate the difference between heats of reaction at constant pressure and constant volume in kJ for the reaction at 25 ºC.

$$2\,C_6H_{6\,(l)} + 15O_{2\,(g)} \longrightarrow 12\,CO_{2\,(g)} + 6\,H_2O_{\,(l)}$$

SOLUTION :

Formula used

$$\Delta H = \Delta E + \Delta n R T$$

or $$\Delta H - \Delta E = \Delta n\, R\, T$$

Quantities given

$\Delta n = n_P - n_R = 12 - 15 = -3$ *moles* [$\because$ C_6H_6 and H_2O are in liquid state]

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

Substitution of values

$$\Delta H - \Delta E = -3 \text{ mole} \times 8.314\ JK^{-1} \text{ mole}^{-1} \times 298\ K$$
$$= -7432.7\ J$$
$$= \mathbf{-7.4327\ kJ}$$

SOLVED PROBLEM 11. For the reaction

$$C_{(graphite)} + \tfrac{1}{2}O_{2\ (g)} \longrightarrow CO_{\ (g)}$$

at 298 K and l atm pressure, $\Delta H = -110.60$ kJ. Calculate ΔE if the molar volume of graphite is 0.0053 litres, assuming ideal conditions.

SOLUTION :

Formula used

$$\Delta H = \Delta E + \Delta n\, R\, T$$

Quantities given

$\Delta H = -110.60$ kJ $R = 8.314\ JK^{-1} mol^{-1} = 8.314 \times 10^{-3} kJ\ K^{-1} mol^{-1}$

$T = 298$ K $\Delta n = n_p - n_R = 1 - ½ = ½$ mole (neglecting the molar volume of graphite)

Substitution of values

$$-110.60\ kJ = \Delta E + ½ \text{ mole} \times 8.314 \times 10^{-3}\ kJ\ K^{-1} mol^{-1} \times 298K$$
$$= \Delta E + 1.238\ kJ$$
$$\Delta E = -110.60\ kJ - 1.238\ kJ$$
$$= \mathbf{-111.838\ kJ}$$

SOLVED PROBLEM 12. What is the maximum work obtainable from the isothermal expansion of 3 moles of an ideal gas at 27 °C from a pressure of 4 atm to 1 atm. Also calculate the quantity of heat evolved in the process.

SOLUTION :

(i) To calculate the maximum work obtainable

Formula used

$$w_{max} = 2.303 \times n\, R\, T \log \frac{P_1}{P_2}$$

Quantities given

$n = 3$ moles $R = 8.314\ J\ K^{-1} mol^{-1}$ $T = 27 + 273 = 300$ K

$P_1 = 4$ atm $P_2 = 1$ atm

Substitution of values

$$w_{max} = 2.303 \times 3 \text{ moles} \times 8.314\ J\ K^{-1} mol^{-1} \times 300\ K$$
$$= \mathbf{17.232\ kJ}$$

(ii) To calculate the quantity of heat absorbed

Formula used

$$q = w_{max}$$

$$\therefore \quad q = 17.232\ kJ$$

SOLVED PROBLEM 13. Five moles of a perfect gas with $C_v = 5.0$ cal mole^{-1} K^{-1} are compressed adiabatically and reversibly from a volume of 50 litres at 1 atm to a pressure of 100 atm. Calculate (i) the final volume of the gas (ii) the final temperature of the gas.

SOLUTION : (i) To calculate the final volume of the gas

Formula used

$$P_1 V_1^{\gamma} = P_2 V_2^{\gamma}$$

or
$$\frac{P_1}{P_2} = \left(\frac{V_2}{V_1}\right)^{\gamma}$$

Quantities given

$P_1 = 1$ atm $\qquad P_2 = 100$ atm $\qquad V_1 = 50$ litres

$$\gamma = \frac{C_p}{C_v} = \frac{C_v + R}{C_v} = \frac{5+2}{5} = \frac{7}{5} = 1.4$$

Substitution of values

$$\frac{1\text{atm}}{100\text{ atm}} = \left(\frac{V_2}{50\text{ lit}}\right)^{1.4}$$

or
$$\frac{1}{100} = \left(\frac{V_2}{50\text{ lit}}\right)^{1.4}$$

Taking logarithms

$$\log\frac{1}{100} = 1.4\,(\log V_2 - \log 50)$$

$$-\,2 = 1.4\,(\log V_2 - 1.6990)$$

$$\frac{-2}{1.4} = \log V_2 - 1.6990$$

or
$$1.6990 - 1.4285 = \log V_2$$

or
$$V_2 = \text{Antilog } 0.2705$$

$$= \mathbf{1.86\ litre}$$

(ii) Calculate the final temperature of the gas

Formula used

$$P_2 V_2 = n R T_2$$

or
$$T_2 = \frac{P_2 V_2}{n R}$$

Quantities given

$n = 5$ moles $\qquad P_2 = 100$ atm $\qquad R = 0.082$ atm lit^{-1} K^{-1} mol^{-1} $\qquad V_2 = 1.86$ litre

Substitution of values

$$T_2 = \frac{100\text{ atm} \times 1.86\text{ lit}}{5\text{ mole} \times 0.0821\text{ atm lit K}^{-1}\text{ mol}^{-1}}$$

$$= \mathbf{453\ K}$$

SOLVED PROBLEM 14. Certain quantity of air at 27 ºC was allowed to expand adiabatically and reversibly from 100 atm. to 20 atm. Assuming the ideal behaviour, calculate the final temperature of the air ($C_v = 5.0$ cal K^{-1}mol^{-1})

SOLUTION :

Formula used

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

Quantities given

$T_1 = 27 + 273 = 300\text{ K}$ $\qquad P_1 = 100\text{ atm}$ $\qquad P_2 = 20\text{ atm}$

$$\gamma = \frac{C_p}{C_v} = \frac{C_v + R}{C_v} = \frac{5+2\text{ cal}}{5\text{ cal}} = 1.4 \quad \text{and} \qquad 1 - \gamma = 1 - 1.4 = -0.4$$

Substitution of values

$$\frac{T_2}{300\text{ K}} = \left(\frac{100\text{ atm}}{20\text{ atm}}\right)^{\frac{-0.4}{1.4}}$$

or
$$T_2 = 300\text{ K} \times (5)^{\frac{-0.4}{1.4}}$$

Taking logarithms

$$\log T_2 = \log 300 - \left(\frac{0.4}{1.4}\right)\log 5$$
$$= 2.4771 - 0.2857 \times 0.6990$$
$$= 2.4471 - 0.1997$$

or
$$T_2 = \text{Antilog } 2.247$$
$$= 189.4\text{ K} = 189.4\text{ K} - 273 = \mathbf{-83.59\ ^\circ C}$$

ADDITIONAL PRACTICE PROBLEMS

1. The internal energy of a system was increased by 400 kJ while the system performed 125 kJ of work on the surroundings. How much heat was transferred between the system and its surrounding during this process ? In what direction did the heat flow ?
Answer. + 525 kJ ; From surroundings to system

2. In a certain chemical reaction, 20.6 kcal of heat are evolved. The volume of the reactants is 36.0 litres ; the volume of products is 9.0 litres. What is ΔE for the reaction ?
Answer. – 19.94 kcal

3. When one mole of liquid Br_2 is converted to Br_2 vapour at 25 ºC and 1 atm pressure, 7.3 kcal of heat is absorbed and 0.59 kcal of expansion work is done by the system. Calculate ΔE for this process.
Answer. + 6.7 kcal

4. The volume of a certain reaction undergoes a change from 11.2 litre to 33.6 litre during a chemical change taking place at 1.0 atm pressure. If ΔE for the reaction is 12.0 kcal, calculate ΔH for the process ?
Answer. 12.50 kcal

5. What is the maximum work which can be obtained by the isothermal reversible expansion of two moles to three moles of an ideal gas at 273 K from 1.12 litre to 11.2 litres ?
Answer. 1627.35 cal

6. Calculate *w* and ΔE for the conversion of 1 mole of water into l mole of steam at a temperature of 373 K and 1 atm pressure. Latent heat of vapourisation of water 540 cal g^{-1}.
Answer. 8.979 kcal

7. Calculate the maximum work done when pressure of 12 g of hydrogen is reduced from 10 to 1 atm at a constant temperature of 273 K. Assuming that gas behaves ideally. Also calculate ‘*q*’.
Answer. 7495 cal ; 7495 cal

8. Calculate the work done when 5 moles of hydrogen gas expand isothermally and reversibly at 298 K from 10 to 50 litres.

Answer. 4.766 kcal

9. Find the work done when 2 moles of an ideal gas expand isothermally from 2 litres to 5 litres against a constant pressure of 1 atm at 298 K.

Answer. 1085 cal

10. ΔE for the process

$$2\,CO_{(g)} + O_{2\,(g)} \longrightarrow 2\,CO_{2\,(g)}$$

is – 134.8 kcal at 298 K and 1 atm pressure. What is ΔH for this reaction ?

Answer. 135.4 kcal]

11. Calculate ΔE for the combustion of one mole of Magnesium in an open container at 298 K and 1 atm pressure, if $\Delta H_{combustion}$ = – 143.9 k cal ?

Answer. – 143.6 k cal

12. 10 g of Argon is compressed isothermally and reversibly at a temperature of 27 ºC from 10 litre to 5 litre. Calculate q, w, ΔE and ΔH for this process. $R = 2.0$ cal K^{-1} mol^{-1} ; log 2 = 0.30. At wt. of Ar = 40

Answer. 0 ; 103.6 cal ; – 103.6 ; 0

8

Thermochemistry

CHAPTER

KEY CONCEPTS AND EQUATIONS

THERMOCHEMISTRY

It is that branch of Chemistry which deals with the thermal or heat changes caused by Chemical reactions.

CHANGE IN INTERNAL ENERGY, ΔE

The difference of internal energy of the products E_P and that of reactants E_R is change in internal energy denoted by ΔE *i.e.*

$$\begin{aligned}\Delta E &= E_{Products} - E_{Reactants}\\ &= E_P - E_R\end{aligned}$$

If ΔE is + ve then the reaction is Exothermic and if ΔE is – ve then the reaction is Endothermic.

ENTHALPY OF A REACTION

The sum of Internal energy and the product of pressure and volume is called Enthalpy, denoted by *H*. That is

$$H = E + PV$$

The change in enthalpy, ΔH, is given by the expression

$$\begin{aligned}\Delta H &= H_{Products} - H_{Reactants}\\ &= H_P - H_R\end{aligned}$$

For an exothermic reaction ΔH is – ve and $H_P < H_R$ and for an endothermic reaction ΔH is + ve and $H_P < H_R$. It has been illustrated in Fig. 8.1

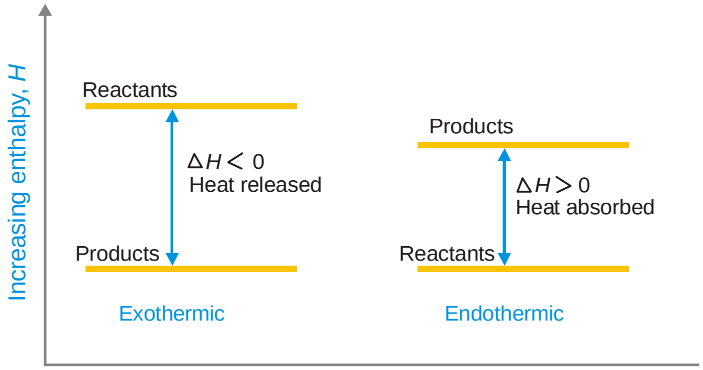


Figure 8.1
Enthalpy diagram for an exothermic and endothermic reaction.

RELATION BETWEEN ΔH AND ΔE

ΔH and ΔE are related to each other by the relation

$$\Delta H = \Delta E + \Delta n\, R\, T$$

where Δn is the difference of the number of moles of gaseous products and gaseous reactants.

THERMOCHEMICAL EQUATIONS

An equation which indicates the amount of heat change (evolved or absorbed) in the reaction or process is called a Thermochemical equation. For example,

$$H_{2\,(g)} + \tfrac{1}{2}\,O_{2\,(g)} \longrightarrow H_2O_{(l)} \qquad \Delta H = -\ 68.32 \text{ kcal}$$

$$H_{2\,(g)} + \tfrac{1}{2}\,O_{2\,(g)} \longrightarrow H_2O_{(g)} \qquad \Delta H = -\ 57.80 \text{ kcal}$$

HEAT OF REACTION AND STANDARD HEAT OF REACTION

Heat of a reaction may be defined as the amount of heat absorbed or evolved in a reaction when the number of moles of reactants as represented by the balanced chemical equation change completely into the products. It is denoted by ΔH *e.g.*

$$CO_{(g)} + \tfrac{1}{2}\,O_{2(g)} \longrightarrow CO_{2(g)} \qquad \Delta H = -\ 284.5 \text{ kJ}$$

The heat change accompanying a reaction taking place at 298 K and one atmosphere pressure is called the **standard heat change** or **standard enthalpy change.** It is denoted by ΔH^o *e.g.*

$$\tfrac{1}{2}\,H_{2\,(g)} + \tfrac{1}{2}\,Cl_{2\,(g)} \longrightarrow HCl_{(g)} \qquad \Delta H^o = -\ 92.46 \text{ kJ}$$

DIFFERENT TYPES OF HEAT (ENTHALPY) OF REACTIONS

HEAT OF FORMATION

The change in enthalpy that takes place when one mole of a compound is formed from its elements. It is denoted by ΔH_f *e.g.*

$$C_{(s)} + 2H_{2\,(g)} \longrightarrow CH_{4\,(g)} \qquad \Delta H_f = -\ 74.85 \text{ kJ}$$

By convention the standard heat of formation of all elements is assusmed to be zero.

STANDARD HEAT OF FORMATION

It is equal to the standard heat of formation of products minus the standard heat of formation of reactants *i.e.*

$$\Delta H^o = \Delta H^o_{f\,(\,Products)} - \Delta H^o_{f\,(\,Reactants)}$$

HEAT OF COMBUSTION

The change in enthalpy of a system when one mole of the substance is completely burnt in excess of air oxygen. It is denoted by ΔH_c *e.g.*

$$CH_{4\,(g)} + 2O_{2\,(g)} \longrightarrow CO_{2\,(g)} + 2H_2O_{(g)} \qquad \Delta H_c = -\ 890.3 \text{ kJ}$$

It may be noted that heat of combustion of a substance is always negative.

HEAT OF SOLUTION

The change in enthalpy when one mole of a substance is dissolved in a solvent so that further dissolution does not give any change in enthalpy. For example,

$$KCl_{(s)} + H_2O_{(l)} \longrightarrow KCl_{(aq)} \qquad \Delta H = -\ 18.40 \text{ kJ}$$

HEAT OF NEUTRALISATION

The change in enthalpy of the system when one gram equivalent of an acid is neutralised by one gram equivalent of base or vice versa in dilute solution. For example,

$$HCl_{(aq)} + NaOH_{(aq)} \longrightarrow NaCl_{(aq)} + H_2O_{(l)} \quad \Delta H = -57.3\text{ kJ}$$
$$HNO_{3\,(aq)} + KOH_{(aq)} \longrightarrow KNO_{3\,(aq)} + H_2O_{(l)} \quad \Delta H = -57.3\text{ kJ}$$

It may be noted that heat of neutralisation of a strong acid and strong base is – 57.3 kJ, no matter which acid or base is empolyed. In fact the heat of neutralisation of an acid and a base is merely the heat of formation of water from hydrogen and hydroxide ions.

$$H^+_{(aq)} + OH^-_{(aq)} \longrightarrow H_2O_{(l)} \qquad \Delta H = -57.3\text{ kJ}$$

ENERGY CHANGES DURING TRANSITION OR PHASE CHANGES, HEAT OF FUSION

The heat change when one mole of a solid substance is converted into the liquid state at its melting point is called heat of fusion. For example,

$$\underset{Ice}{H_2O_{(s)}} \longrightarrow \underset{Water}{H_2O_{(l)}} \qquad \Delta H = -5.89\text{ kJ}$$

HEAT OF VAPORISATION

It is defined as the heat change when one mole of a liquid is converted into vapour or gaseous state at its boiling point. For example,

$$\underset{Water}{H_2O_{(l)}} \longrightarrow \underset{Steam}{H_2O_{(g)}} \qquad \Delta H = 40.62\text{ kJ}$$

HEAT OF SUBLIMATION

It is defined as the heat change when one mole of an element changes from one alltropic form to another. For example,

$$\underset{Solid}{I_{2\,(s)}} \longrightarrow \underset{Vapours}{I_{2\,(g)}} \qquad \Delta H = -62.42\text{ kJ}$$

HEAT OF TRANSITION

It is defined as the heat change when one mole of an element changes from one allotropic form to another. For example,

$$C_{diamond} \longrightarrow C_{amorphous} \qquad \Delta H = +13.80\text{ kJ}$$

HESS'S LAW OF CONSTANT HEAT SUMMATION

This law states that at constant pressure the total heat change accompanying a chemical reaction is the same no matter by which method the change is brought about. For example,

For a reaction $A \longrightarrow Z \qquad \Delta H_1 = -\,Q_1$

and for a reaction $A \longrightarrow B \qquad \Delta H_2 = -\,q_1$

$B \longrightarrow C \qquad \Delta H_3 = -\,q_2$

$C \longrightarrow Z \qquad \Delta H_4 = -\,q_3$

According to Hess's Law $\Delta H_1 = \Delta H_2 + \Delta H_3 + \Delta H_4$

or $-Q_1 = -q_1 + (-q_2) + (-q_3)$

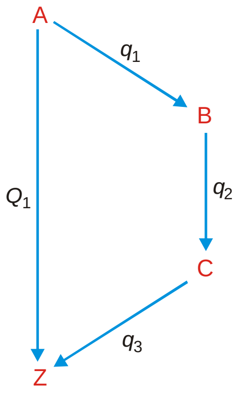
$= -\,(q_1 + q_2 + q_3)$

This is shown in the Fig. 8.2 in which the example of formation of CO_2 by two methods has been illustrated. It may be noted that thermochemical equations may be multiplied, added or subtracted like ordinary algebric equations.

BOND ENERGY

The bond energy is defined as the average of energy required to break all bonds of a particular type in one mole of the substance. It is always positive as heat is always given to the system *e.g.*

$$\underset{molecule}{H{-}H} \longrightarrow \underset{atom}{H} + \underset{atom}{H} \qquad \Delta H = 431.78\text{ kJ}$$



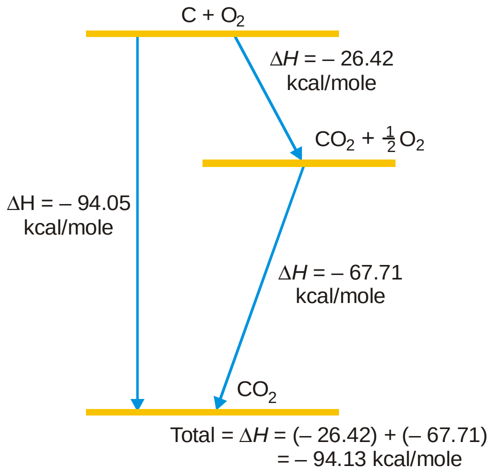


Figure 8.2
Illustration of Hess's Law.

Bond energy is a measure of strength of the bond.

Bond energy data can be used to calculate the heat of the reaction. The energy of formation of a bond is numerically equal to its bond energy with a negative sign.

ADDITIONAL SOLVED PROBLEMS

SOLVED PROBLEM 1. If the heat of formation of methane at constant pressure is – 17.9 kcal per mole at 25 °C, what is its value at constant volume ?

SOLUTION :

The equation is

$$C_{(s)} + 2\,H_{2\,(g)} \longrightarrow CH_{4\,(g)}$$

Formula used

$$\Delta H = \Delta E + \Delta n\,R\,T$$

Quantities gives

$\Delta H = -17.9\ \text{kcal mol}^{-1}$ $\quad T = 25 + 273 = 298\ \text{K}$ $\quad \Delta N = n_P - n_R = 1 - 2 = -1$

$R = 1.987\ \text{cal mol}^{-1}\text{K}^{-1} = 1.987 \times 10^{-3}\ \text{kcal mol}^{-1}\ \text{K}^{-1}$

Substitution of values

$$-17.9\ \text{kcal} = \Delta E + (-1)\ \text{mol} \times 1.987 \times 10^{-3}\ \text{kcal K}^{-1}\ \text{mol}^{-1} \times 298\ \text{K}$$

or $\quad \Delta E = -17.9\ \text{kcal} + 0.592\ \text{kcal}$

$\quad = \mathbf{-17.308\ kcal}$

SOLVED PROBLEM 2. From the following heats of formation

$$2\,C_{(s)} + 3\,H_{2\,(g)} = C_2H_{6\,(g)} + 20236\ \text{cal}$$

$$2\,C_{(s)} + 3\,H_{2\,(g)} + \tfrac{1}{2}O_{2\,(g)} = C_2H_5OH_{(l)} + 66356\ \text{cal}$$

Calculate ΔH for the reaction

$$C_2H_{6\,(g)} + \tfrac{1}{2}\,O_{2\,(g)} = C_2H_5OH_{(l)}$$

SOLUTION :

Given equation are

$$2\,C_{(s)} + 3\,H_{2\,(g)} \longrightarrow C_2H_{6\,(g)} + 20236 \text{ cal} \qquad ...(i)$$

$$2\,C_{(s)} + 3\,H_{2\,(g)} + \tfrac{1}{2}\,O_2 \longrightarrow C_2H_5\,OH_{(l)} + 66356 \text{ cal} \qquad ...(ii)$$

Subtracting (i) from (ii) we have

$$\begin{array}{lllll}
2\,C_{(s)} & + 3\,H_{2\,(g)} & + \tfrac{1}{2}\,O_{2\,(g)} & \longrightarrow & C_2H_5\,OH_{(g)} + 66356 \text{ cal} \\
2\,C_{(s)} & + 3\,H_{2\,(g)} & & \longrightarrow & C_2H_{6\,(g)} \quad + 20236 \text{ cal} \\
- & - & & & - \qquad\quad - \\
\hline
C_2H_{6\,(g)} & & + \tfrac{1}{2}\,O_{2\,(g)} & \longrightarrow & C_2H_5\,OH_{(l)} + 46120 \text{ cal} \\
\hline
\end{array}$$

$$\text{or} \quad C_2H_{6\,(g)} + \tfrac{1}{2}\,O_{2\,(g)} \longrightarrow C_2H_5\,OH_{(l)}$$

$$\mathbf{\Delta H = -46120 \text{ cal}}$$

SOLVED PROBLEM 3. Given the heat of combustion of ethylene, hydrogen and ethane are 337.2, 68.3 and 372.8 kcal respectively, calculate the heat of the reaction at 78 °C for

$$C_2\,H_{4(g)} + H_{2\,(g)} \longrightarrow C_2H_{6\,(g)}$$

SOLUTION :

From the given data we can frame the following equations

$$C_2H_{4\,(g)} + 3\,O_{2\,(g)} \longrightarrow 2\,CO_{2\,(g)} + 2\,H_2O \qquad \Delta H = -337.2 \text{ kcal} \qquad ..(i)$$

$$H_{2\,(g)} + \tfrac{1}{2}\,O_{2\,(g)} \longrightarrow H_2O_{(l)} \qquad \Delta H = -68.3 \text{ kcal} \qquad ..(ii)$$

$$C_2\,H_{6\,(g)} + \tfrac{7}{2}\,O_{2\,(g)} \longrightarrow 2\,CO_{2\,(g)} + 3\,H_2O_{(g)} \qquad \Delta H = -372.8 \text{ kcal} \qquad ..(iii)$$

Adding (i) and (ii) we get

$$C_2\,H_{4\,(g)} + \tfrac{7}{2}\,O_{2\,(g)} + H_{2\,(g)} \longrightarrow 2\,CO_{2\,(g)} + 3\,H_2O_{(g)} \qquad \Delta H = -405.5 \text{ kcal} \qquad ..(iv)$$

Subtracting (iii) from (iv) we have

$$\begin{array}{llllll}
C_2H_{4\,(g)} + \tfrac{7}{2}\,O_{2\,(g)} & + H_{2\,(g)} & \longrightarrow & 2\,CO_{2\,(g)} & + 3\,H_2O_{(g)} & \Delta H = -405.5 \text{ kcal} \\
C_2\,H_{6\,(g)} + \tfrac{7}{2}\,O_{2\,(g)} & & \longrightarrow & 2\,CO_{2\,(g)} & + 3\,H_2O_{(g)} & \Delta H = -\ 372.8 \text{ kcal} \\
- \qquad - & & & - & - & \qquad\quad + \\
\hline
C_2H_{4\,(g)} & + H_{2\,(g)} & \longrightarrow & C_2H_{6\,(g)} & & \Delta H = -\ 32.7 \text{ kcal} \\
\hline
\end{array}$$

$$\text{or} \quad \mathbf{C_2H_{4\,(g)} + H_{2\,(g)} \longrightarrow C_2H_{6\,(g)} \qquad \Delta H = -32.7 \text{ kcal}}$$

SOLVED PROBLEM 4. Heats of solution of hydrated copper sulphate and anhydrous copper sulphate are –2.80 and 15.89 kcal respectively. Calculate the heat of hydration of copper sulphate.

SOLUTION :

Heat of hydration = Heat of hydration of hydrated salt–Heat of hydration of anhydrous salt

$$\Delta H_{Hydration} = \Delta H_{Sol} \text{ of hydrated } Cu\,SO_4 5H_2O - \Delta H_{Sol} \text{ of } Cu\,SO_4$$

Quantities given

ΔH_{Sol} of $Cu\,SO_4 5H_2O = -2.80$ kcal $\qquad\qquad$ ΔH_{Sol} of $CuSO_4 = 15.89$ kcal

Substitution of values

$$\Delta H_{Hydration} = -2.80 \text{ kcal} - 15.89 \text{ kcal}$$

$$= \mathbf{-18.69 \text{ kcal}}$$

SOLVED PROBLEM 5. ΔH for the combustion of ethyl alcohol, carbon and hydrogen are –330.0, –94.3 and – 68.5 kcal respectively. Calculate the heat of formation of ethyl alcohol.

SOLUTION :

From the given data we can frame the following equations

$$C_2H_5OH_{(g)} + 3\,O_{2\,(g)} \longrightarrow 2\,CO_{2\,(g)} + 3H_{2\,(g)} \qquad \Delta H = -\ 330.0 \text{ kcal} \quad ....(i)$$

$$C_{(s)} + O_{2\,(g)} \longrightarrow CO_{2\,(g)} \qquad \Delta H = -\ 94.3 \text{ kcal} \quad ....(ii)$$

$$H_{2\,(g)} + \tfrac{1}{2}\,O_{2\,(g)} \longrightarrow H_2O_{(g)} \qquad \Delta H = -\ 68.5 \text{ kcal} \quad ....(iii)$$

Multiplying equation (ii) by 2 and (iii) by 3 and adding we have

$$2\,C_{(s)} + 2\,O_{2\,(g)} \longrightarrow 2\,CO_{2\,(g)} \qquad \Delta H = -188.6 \text{ kcal}$$

$$3\,H_{2\,(g)} + \tfrac{3}{2}\,O_{2\,(g)} \longrightarrow 3\,H_2O_{(g)} \qquad \Delta H = -195.5 \text{ kcal}$$

$$2\,C_{(s)} + 3H_{2\,(g)} + \tfrac{7}{2}\,O_{2\,(g)} \longrightarrow 2CO_{2\,(g)} + 3\,H_2O \qquad \Delta H = -394.1 \text{ kcal} \quad ....(iv)$$

Subtracting equaton (i) from (iv) we have

$$2\,C_{(s)} + 3\,H_{2\,(g)} + \tfrac{7}{2}\,O_{2\,(g)} \longrightarrow 2\,CO_{2\,(g)} + 3\,H_2O \qquad \Delta H = -394.1 \text{ kcal}$$

$$C_2H_5OH_{(g)} + 3\,O_{2\,(g)} \longrightarrow 2\,CO_{2\,(g)} + 3\,H_2O_{(g)} \qquad \Delta H = -330.0 \text{ kcal}$$

– – – – +

$$2\,C_{(s)} + 3\,H_{2\,(g)} + \tfrac{1}{2}\,O_{2\,(g)} \longrightarrow C_2H_5OH_{(l)} \qquad \Delta H = -64.1 \text{ kcal}$$

Thus the heat of combustion of ethyl alcohol = – 64.1 kcal

SOLVED PROBLEM 6. Calculate the heat of formation of benzene at 25 °C, if the heats of combustion of benzene, carbon and hydrogen are – 780.90, 94.05 and – 68.32 kcal respectively at 25 °C.

SOLUTION :

The formation of benzene is respresented by

$$6\,C_{(s)} + 3\,H_{2\,(g)} \longrightarrow C_6H_{6\,(l)} \qquad \Delta H = ?$$

From the given data we can frame the following equations

$$C_6H_{6\,(l)} + \tfrac{15}{2}O_{2(g)} \longrightarrow 6\,CO_{2\,(g)} + 3\,H_2O_{(g)} \qquad \Delta H = -780.98 \text{ kcal} \quad ...\ (i)$$

$$C_{(s)} + O_{2(g)} \longrightarrow CO_{2\,(g)} \qquad \Delta H = -\ 94.05 \text{ kcal} \quad ...(ii)$$

$$H_{2\,(g)} + \tfrac{1}{2}\,O_{2(g)} \longrightarrow H_2O_{(g)} \qquad \Delta H = -\ 68.32 \text{ kcal} \quad ...(iii)$$

Multiplying equation (ii) by 6 and (iii) by 3 and adding we get

$$6\,C_{(s)} + \tfrac{15}{2}\,O_{2\,(g)} + 3\,H_{2\,(g)} \longrightarrow 6\,CO_{2\,(g)} + 3\,H_2O_{(g)} \qquad \Delta H = -769.26 \text{ kcal} \quad ...(iv)$$

Subtracting (i) from (iv), we have

$$6\,C_{(s)} + \tfrac{15}{2}\,O_{2\,(g)} + 3\,H_{2\,(g)} \longrightarrow 6\,CO_{2\,(g)} + 3\,H_2O_{(g)} \qquad \Delta H = -769.26 \text{ kcal}$$

$$C_6H_{6\,(l)} + \tfrac{15}{2}O_{2\,(g)} \longrightarrow 6\,CO_{2\,(g)} + 3\,H_2O_{(g)} \qquad \Delta H = -780.98 \text{ kcal}$$

– – – – +

$$6\,C_{(s)} + 3\,H_{2\,(g)} \longrightarrow C_6H_{6\,(l)} \qquad \Delta H = +\ 11.72 \text{ kcal}$$

Thus the heat of formation benzene = + 11.72 kcal

SOLVED PROBLEM 7. Given following thermochemical equations :

$$C_{(graphite)} + O_{2\,(g)} \longrightarrow CO_{2\,(g)} \qquad \Delta H = -\,94.05 \text{ kcal}$$

$$C_{(graphite)} \longrightarrow C_{(diamond)} \qquad \Delta H = +\,0.5 \text{ kcal}$$

Calculate (i) Enthalpy change for burning $C_{(diamond)}$

(ii) quantity of $C_{(graphite)}$ must be burnt to evolve 100 kcal of heat.

SOLUTION : (i) To calculate the enthalpy change

Given that

$$C_{(graphite)} + O_{2\,(g)} \longrightarrow CO_{2\,(g)} \qquad \Delta H = -\,94.05 \text{ kcal} \qquad \text{...(i)}$$

$$C_{(graphite)} \longrightarrow C_{(diamond)} \qquad \Delta H = +\,0.5 \text{ kcal} \qquad \text{...(ii)}$$

Subtracting (ii) from (i) we get

$$C_{(diamond)} + O_{2\,(g)} \longrightarrow CO_{2\,(g)} \qquad \Delta H = -\,94.55 \text{ kcal}$$

Thus the enthalpy change for burning $C_{(diamond)}$ is – 94.55 kcal

(ii) To calculate the quantity of $C_{(graphite)}$ burnt to evolve 100 kcal of heat

12 *g* of $C_{(graphite)}$ burn to give heat = 94.05 kcal

∴ Amount of $C_{(graphite)}$ that burns to give 100 kcal of heat

$$= \frac{12 \text{ g} \times 100 \text{ kcal}}{94.05 \text{ kcal}}$$

$$= \mathbf{12.759 \text{ g}}$$

SOLVED PROBLEM 8. The heat of combustion of benzoic acid at constant pressure is –771400 cal at 25 °C. Calculate the heat of combustion at constant volume.

SOLUTION :

The equation representing combustion of benzoic acid is

$$C_6H_5COOH_{(g)} + {}^{15}\!/_2\, O_{2\,(g)} \longrightarrow 7\,CO_{2\,(g)} + 3\,H_2O_{(g)} \qquad \Delta H = -\,771400 \text{ cal}$$

Formula used

$$\Delta H = \Delta E + \Delta n\,R\,T \qquad \text{or} \qquad \Delta E = \Delta H - \Delta n\,R\,T$$

Quantities given

$$\Delta n = n_P - n_R = 7 - {}^{15}\!/_2 = \tfrac{1}{2} \text{ mol} \qquad T = 298 \text{ K} \qquad R = 1.987 \text{ cal}^{-1} \text{ mol}^{-1}$$

Substitution of values

$$\Delta E = -\,771400 \text{ cal} - (-\,\tfrac{1}{2} \text{ mol}) \times 298 \text{ K} \times 1.987 \text{ cal K}^{-1} \text{ mol}^{-1}$$

$$= -\,771400 \text{ cal} + 296.063 \text{ cal}$$

$$= \mathbf{-\,771103.937 \text{ cal}}$$

SOLVED PROBLEM 9. Calculate the heat of reaction, ΔH, of the following reaction

$$CH_{4\,(g)} + 4\,F_{2\,(g)} \longrightarrow CF_{4\,(g)} + 4\,HF_{(g)}$$

Bond energies of C—H, F—F, C—F and H—F bonds are 99.3, 38.0, 116.0 and 135 kcal mol^{-1} respectively.

SOLUTION :

The heat of the reaction

$$CH_{4\,(g)} + 4\,F_{2\,(g)} \longrightarrow CF_{4\,(g)} + 4\,H\text{—}F$$

is given by

$$\begin{aligned}\Delta H &= [4 \times \text{Bond energy of (C—F)} + 4 \times (\text{Bond energy of H—F})] - \\ &\quad [4 \times (\text{Bond energy of C—H}) + 4 \times (\text{Bond energy of F—F})] \\ &= [4 \times 116.0 + 4 \times 135] - [4 \times 99.3 + 4 \times 38.0] \\ &= 1004 \text{ kcal} - 549.2 \text{ kcal} \\ &= \mathbf{454.8 \ kcal}\end{aligned}$$

SOLVED PROBLEM 10. The heat of formation of methane at 27 °C is – 19.3 kcal when the measurements are made at constant pressure. What will be the heat of formation at constant volume?

SOLUTION :

Given that

$$C_{(s)} + 2H_{2\,(g)} \longrightarrow CH_{4\,(g)} \qquad \Delta H = -19.3 \text{ kcal}$$

Formula used

$$\Delta H = \Delta E + \Delta n R T \quad \text{or} \quad \Delta E = \Delta H - \Delta n R T$$

Quantities given

$$\Delta H = n_P - n_R = 1 - 2 = -1 \qquad R = 1.987 \times 10^{-3} \text{ kcal}$$

Substitution of values

$$\begin{aligned}\Delta E &= -19.3 \text{ kcal} - [(-1) \times 1.987 \times 10^{-3} \text{ kcal K}^{-1} \text{ mol}^{-1} \times 300 \text{ K}] \\ &= -19.3 \text{ kcal} - 0.5961 \text{ kcal} \\ &= \mathbf{-18.7039 \ kcal}\end{aligned}$$

SOLVED PROBLEM 11. Bond energies of F_2 and Cl_2 are 36.6 and 580 kcal mol^{-1} respectively. Heat liberated in the reaction $F_2 + Cl_2 \longrightarrow 2\,FCl$ is 26.6 kcal. Find the bond energy of F — Cl bond.

SOLUTION :

The given reaction is

$$\text{F—F} + \text{Cl—Cl} \longrightarrow 2\,\text{F—Cl} \quad \Delta H = -26.6 \text{ kcal}$$

The heat of the reaction is given by

ΔH = [2 × Bond energy of F — Cl] – [Bond energy of F — F + Bond energy of Cl — Cl]

Quantities given

$\Delta H = -26.6$ kcal *B.E.* of F — F = 36.6 kcal mol^{-1} *B.E.* of Cl — Cl = 580 kcal mol^{-1}

Substitution of values

– 26.6 kcal = [2 × Bond energy of F — Cl] – [36.6 kcal + 580 kcal]

– 26.6 kcal = 2 × Bond energy of F — Cl – 616.6 kcal

∴ 2 × Bond energy of F — Cl = 616.6 kcal – 26.6 kcal

Bond of energy of F — Cl = $^{590}/_{2}$ kcal

= 295 kcal

Thus bond energy of F — Cl bond = 295 kcal

SOLVED PROBLEM 12. Graphite and diamond are two forms of carbon. The enthalpy of combustion of graphite at 25 °C is – 393.51 kJ mol^{-1} and that of diamond is –395.41 kJ mol^{-1}. What is the enthalpy change in the process graphite ⟶ diamond at that temperature?

SOLUTION :

From the given data we can frame the following equations

$$C_{(graphite)} + O_{2\,(g)} \longrightarrow CO_{2\,(g)} \qquad \Delta H = -393.51 \text{ kJ} \qquad \text{... (i)}$$

$$C_{(diamond)} + O_{2\,(g)} \longrightarrow CO_{2\,(g)} \qquad \Delta H = -395.41 \text{ kJ} \qquad \text{... (ii)}$$

The required equation is

$$C_{(graphite)} \longrightarrow C_{(diamond)} \qquad \Delta H = ?$$

Subtracting equation (ii) from (i) we have

$$\begin{array}{llllll}
C_{(graphite)} & + O_{2\,(g)} & \longrightarrow & CO_{2\,(g)} & \Delta H & = -393.51\text{ kJ} \\
C_{(diamond)} & + O_{2\,(g)} & \longrightarrow & CO_{2\,(g)} & \Delta H & = -395.41\text{ kJ} \\
- & - & & - & & + \\
\hline
C_{(graphite)} & & \longrightarrow & C_{(diamond)} & \Delta H & = -1.90\text{ kJ} \\
\hline
\end{array}$$

Thus the enthalpy of the process $C_{(graphite)} \longrightarrow C_{(diamond)}$ is + 1.90 kJ

SOLVED PROBLEM 13. The heat of combustion of glucose at 17 °C and at constant pressure is – 651000 cal. Calculate heat of combustion at constant volume at 17 °C.

SOLUTION :

The given equation is

$$C_6H_{12}O_{6\,(s)} + O_{2\,(g)} \longrightarrow 6\,CO_{2\,(g)} + 6\,H_2O_{(l)} \qquad \Delta H = -65100\text{ cal}$$

Formula used

$$\Delta H = \Delta E + \Delta n\,R\,T \qquad \text{or} \qquad \Delta E = \Delta H - \Delta n\,R\,T$$

Quantities given

$$\Delta H = -\ 651000\text{ cal} \qquad \Delta n = n_P - n_R = 6 - 6 = 0$$

$$T = 17 + 273 = 290\text{ K} \qquad R = 1.987\text{ cal K}^{-1}\text{mol}^{-1}$$

Substitution of values

$$\Delta E = -\ 651000\text{ cal} - 0 \times 1.987\text{ cal K}^{-1}\text{ mol}^{-1} \times 290\text{ K}$$

$$= -\ \mathbf{651000\text{ cal}}$$

SOLVED PROBLEM 14. Calculate the heat of formation of acetic acid if its heat of combustion is –869.0 kJ mol^{-1}. The heat of formation of $CO_{2\,(g)}$ and $H_2O_{(l)}$ are –390.0 kJ mol^{-1} and –285.0 kJ mol^{-1} respectively.

SOLUTION :

We can frame the following equation from the given data.

$$\begin{array}{lllllll}
CH_3COOH_{(l)} & + 2\,O_{2\,(g)} & \longrightarrow & 2\,CO_{2\,(g)} & \Delta H & = -\ 869.0\text{ kJ} & ...(i) \\
C_{(s)} & + O_{2\,(g)} & \longrightarrow & CO_{2\,(g)} & \Delta H & = -390.0\text{ kJ} & ...(ii) \\
H_{2\,(g)} & + \tfrac{1}{2}\,O_{2\,(g)} & \longrightarrow & H_2O_{(g)} & \Delta H & = -285.0\text{ kJ} & ...(iii)
\end{array}$$

The required equation is

$$2\,C_{(s)} + 2\,H_{2\,(g)} + O_{2\,(g)} \longrightarrow CH_3COOH_{(l)} \qquad \Delta H = ?$$

Multiplying equations (iii) and (ii) each by 2 and adding we get

$$2\,C_{(s)} + 2\,H_{2\,(g)} + 3\,O_{2\,(g)} \longrightarrow 2\,CO_{2\,(g)} + 2\,H_2O_{(g)} \qquad \Delta H = -1350\text{ kJ} \qquad ...(iv)$$

Subtracting (i) from (iv) we have

$$\begin{array}{lllllll}
2\,C_{(s)} + 2\,H_{2\,(g)} & + 3\,O_{2\,(g)} & \longrightarrow & 2\,CO_{2\,(g)} & + 2\,H_2O_{(g)} & \Delta H & = -1350\text{ kJ} \\
CH_3COOH_{(l)} & + 2\,O_{2\,(g)} & \longrightarrow & 2\,CO_{2\,(g)} & + 2\,H_2O_{(g)} & \Delta H & = -\ 869.0\text{ kJ} \\
- & - & & - & - & & + \\
\hline
2\,C_{(s)} + 2H_{2\,(g)} & + O_{2\,(g)} & \longrightarrow & CH_3COOH_{(l)} & & \Delta H & = -\ 481.0\text{ kJ} \\
\hline
\end{array}$$

Thus the heat of formation of acetic acid is – 481.0 kJ

SOLVED PROBLEM 15. The standard heats of formation of $CO_{(g)}$ and $H_2O_{(g)}$ at 25 °C are 100.5 kJ and – 241.8 kJ per mole respectively. Calculate the heat change of following reaction at this temperature.

$$H_2O_{(g)} + C_{(s)} \longrightarrow H_2O_{(g)} + CO_{(g)}$$

SOLUTION :

We can frame the following equations from the given data

$$\begin{array}{lll} C_{(s)} + \tfrac{1}{2} O_{2\,(g)} \longrightarrow CO_{(g)} & \Delta H^o = \ 100.5\ \text{kJ} & \ldots\text{(i)} \\ H_{2\,(g)} + \tfrac{1}{2} O_{2\,(g)} \longrightarrow H_2O_{(g)} & \Delta H^o = -\ 241.8\ \text{kJ} & \ldots\text{(ii)} \end{array}$$

Subtracting equation (ii) from (i), we have

$$\begin{array}{l} C_{(s)} \quad + \tfrac{1}{2} O_{2\,(g)} \longrightarrow CO_{(g)} \qquad \Delta H^o = -100.5\ \text{kJ} \\ H_{2\,(g)} + \tfrac{1}{2} O_{2\,(g)} \longrightarrow H_2O_{(g)} \qquad \Delta H^o = -241.8\ \text{kJ} \\ - \qquad - \qquad\qquad\quad - \qquad\qquad\qquad + \\ \hline C_{(s)} + H_2O_{(g)} \longrightarrow H_{2\,(g)} + CO_{(g)} \qquad \Delta H^o = +341.8\ \text{kJ} \\ \hline \end{array}$$

Thus the heat of the reaction is + 342.3 kJ

SOLVED PROBLEM 16. On the basis of bond energies given below, calculate the heat of reaction :

$$2\,C_{(s)} + 3\,H_{2\,(g)} + \tfrac{1}{2} O_{2\,(g)} \longrightarrow CH_3 - O - CH_{3\,(g)}$$

Bond	*Bond energy (kcal mol^{-1})*
$H-H$	103
$O-O$	118
$C-H$	98
$C-O$	84
$C_{(s)} \longrightarrow C_{(g)}$	171

SOLUTION : The heat of reaction for the equation

$$2\,C_{(s)} + 3\,H_{2\,(g)} + \tfrac{1}{2} O_{2\,(g)} \longrightarrow CH_3 - O - CH_{3\,(g)}$$

is given by

$$\begin{aligned} \Delta H &= \text{Total bond energy of products} - \text{Total bond energy of reactants} \\ &= [\,6 \times \text{B.E. of } C-H + 2 \times \text{B.E. of } C-O\,] - \\ &\quad [\,2 \times \{C_{(s)} \longrightarrow C_{(g)}\} + 3 \times \text{B.E. of } H-H + \tfrac{1}{2}\,\text{B.E. of } O = O\,] \\ &= [\,6 \times 98 + 2 \times 84\,] - [\,2 \times 171 + 3 \times 103 + \tfrac{1}{2} \times 118\,] \\ &= 756 - 710\ \text{kcal} \\ &= \mathbf{46\ kcal} \end{aligned}$$

SOLVED PROBLEM 17. The heat of combustion of liquid benzene is – 326.7 kJ. The heat of formation of CO_2 and H_2O are – 393.5 kJ and – 286.2 respectively. Calculate the heat of formation of liquid benzene.

SOLUTION :

We can frame the following equation from the given data

$$\begin{array}{ll} C_{(s)} + {}^{15}\!/_{2}\, O_{2\,(g)} \longrightarrow CO_{2\,(g)} & \Delta H = -393.5\ \text{kJ} \ \ldots\text{(i)} \\ H_{2\,(g)} + \tfrac{1}{2} O_{2\,(g)} \longrightarrow H_2O_{(g)} & \Delta H = -286.2\ \text{kJ} \ \ldots\text{(ii)} \\ C_6H_{6\,(l)} + {}^{15}\!/_{2}\, O_{2\,(g)} \longrightarrow 6\,CO_{2\,(g)} + 3\,H_{2\,(l)} & \Delta H = -326.7\ \text{kJ} \ \ldots\text{(iii)} \end{array}$$

Multiplying equation (i) by 6 and equation (ii) by 3 and adding we get

$$6\,C_{(s)} + 3\,H_{2\,(g)} + O_{2\,(g)} \longrightarrow 6\,CO_{2\,(g)} + 6\,H_2O_{(l)} \qquad \Delta H = -3219.6\ \text{kJ} \ldots\text{(iv)}$$

Subtracting equation (iii) from equation (iv) we have

$$\begin{array}{llll}
6C_{(s)} + 3H_{2\,(g)} + & O_{2\,(g)} \longrightarrow 6CO_{2\,(g)} + 6H_2O_{(l)} & & \Delta H = -3219.6\text{ kJ} \\
C_6H_{6\,(l)} + & {}^{15}\!/_{2}O_{2\,(g)} \longrightarrow 6CO_{2\,(g)} + 6H_2O_{(l)} & & \Delta H = -326.7\text{ kJ} \\
\hline
6C_{(s)} + 3H_{2\,(g)} & \longrightarrow C_6H_{6\,(l)} & & \Delta H = -2826.1\text{ kJ} \\
\hline
\end{array}$$

Thus the heat of formation of liquid benzene is – 2826.1 kJ

SOLVED PROBLEM 18. The enthalpy of neutralisation of HCl with NaOH is –57.3 kJ mol^{-1} and that of CH_3COOH with NaOH is –55.2 kJ mol^{-1}. Calculate the enthalpy of ionisation of CH_3COOH.

SOLUTION :

The required equation is

$$CH_3COOH_{(aq)} \longrightarrow CH_3COO^-_{(aq)} + H^+_{(aq)} \qquad \Delta H = ?$$

Given that

$$H^+_{(aq)} + OH^-_{(aq)} \longrightarrow H_2O_{(l)} \qquad \Delta H = -57.3\text{ kJ} \quad ...(i)$$

$$CH_3COOH_{(aq)} + OH^-_{(aq)} \longrightarrow CH_3COO^-_{(aq)} + H_2O_{(l)} \qquad \Delta H = -55.2\text{ kJ} \quad ...(ii)$$

Subtracting equation (i) from (ii) we have

$$\begin{array}{lllll}
CH_3COOH_{(aq)} & + OH^-_{(aq)} & \longrightarrow CH_3COO^-_{(aq)} & + H_2O_{(l)} & \Delta H = -55.2\text{ kJ} \\
\quad H^+_{(aq)} & + OH^-_{(aq)} & \longrightarrow H_2O_{(l)} & & \Delta H = -57.3\text{ kJ} \\
\quad - & \quad - & \quad - & & \qquad + \\
\hline
CH_3COOH_{(aq)} & & \longrightarrow CH_3COO_{(aq)} & + H^+_{(aq)} & \Delta H = -\ 2.1\text{ kJ} \\
\hline
\end{array}$$

Thus the enthalpy of ionisation of CH_3COOH is + 2.1 kJ

SOLVED PROBLEM 19. Calculate the standard enthalpy of formation of napthalene ($C_{10}H_8$) when the standard enthalpy of combustion of napthalene is – 5153 kJ and standard enthalpies of formation of CO_2 and H_2O are –393.5 kJ mol^{-1} and –285.8 kJ^{-1} mol^{-1} respectively.

SOLUTION :

We can frame the following equations from the given data

$$C_{10}H_{8\,(s)} + 12O_{2\,(g)} \longrightarrow 10CO_{2\,(g)} + 4H_2O_{(g)} \qquad \Delta H^o = -5153\text{ kJ} \quad ...(i)$$

$$C_{(s)} + O_{2\,(g)} \longrightarrow CO_{2(g)} \qquad \Delta H^o = -393.5\text{ kJ} \quad ...(ii)$$

$$H_{2\,(g)} + \tfrac{1}{2}O_{2\,(g)} \longrightarrow H_2O_{(g)} \qquad \Delta H^o = -285.8\text{ kJ} \quad ...(iii)$$

The required equation is

$$10C_{(s)} + 4H_{2\,(g)} \longrightarrow C_{10}H_{8\,(s)} \qquad \Delta H^o = ?$$

Multiplying equation (ii) by 10 & (iii) by 4 and adding we get

$$10C_{(s)} + 4H_{2\,(g)} + 12O_{2\,(g)} \longrightarrow 10CO_{2\,(g)} + 4H_2O_{(l)} \qquad \Delta H^o = -5078.2\text{ kJ} \quad ..(iv)$$

Subtracting equation (i) from equation (iv) we have

$$\begin{array}{lllll}
10C_{(s)} + 4H_{2\,(g)} & + 12O_{2\,(g)} & \longrightarrow 10CO_{2\,(g)} & + 4H_2O_{(l)} & \Delta H^o = -\ 5078.2\text{ kJ} \\
C_{10}H_{8\,(s)} & + 12O_{2\,(g)} & \longrightarrow 10CO_{2\,(g)} & + 4H_2O_{(l)} & \Delta H^o = -\ 5153.0\text{ kJ} \\
- & \quad - & \quad - & \quad - & \qquad + \\
\hline
10C_{(s)} + 4H_{2\,(g)} & & \longrightarrow C_{10}H_{8\,(s)} & & \Delta H^o = +74.8\text{ kJ} \\
\hline
\end{array}$$

Thus standard enthalpy of formation of napthalene is + 74.8 kJ

SOLVED PROBLEM 20. Calculation the heat of formation of carbon disulphide. The heat of combustion of CS_2, S and C are – 26.5 kcal, – 94.3 kcal and 71.08 kcal respectively at 25 °C.

SOLUTION :

We can frame the following equations from the given data

$$C_{(s)} + O_{2\,(g)} \longrightarrow CO_{2\,(g)} \qquad \Delta H = -\ 71.08 \text{ kcal} \quad ...(i)$$

$$S_{(s)} + O_{2\,(g)} \longrightarrow SO_{2\,(g)} \qquad \Delta H = -\ 94.3 \text{ kcal} \quad ...(ii)$$

$$CS_{2\,(l)} + 3\,O_{2\,(g)} \longrightarrow CO_{2\,(g)} + 2\,SO_{2\,(g)} \qquad \Delta H = -\ 26.5 \text{ kcal} \quad ...(iii)$$

The required equation is

$$C_{(s)} + 2\,S_{(s)} \longrightarrow CS_{2\,(l)} \qquad \Delta H = \ ?$$

Multiplying equation (ii) by 2 and adding to equation (i) we get

$$C_{(s)} + 2\,S_{(s)} + 3\,O_{2\,(g)} \longrightarrow CO_{2\,(g)} + 2\,SO_{2\,(g)} \qquad \Delta H = -259.68 \text{ kcal} \ ...(iv)$$

Subtracting equation (iii) from (iv) we have

$$\begin{array}{lllllll}
C_{(s)} & +\ 2\,S_{(s)} & +\,3\,O_{2\,(g)} & \longrightarrow & CO_{2\,(g)} & +\,2\,SO_{2\,(g)} & \Delta H = -259.68 \text{ kcal} \\
CS_{2\,(l)} & & +\,3\,O_{2\,(g)} & \longrightarrow & CO_{2\,(g)} & +\,2\,SO_{2\,(g)} & \Delta H = -\ \ 26.5 \text{ kcal} \\
- & & - & & - & - & \qquad + \\
\hline
C_{(s)} & +\,2\,S_{(s)} & & \longrightarrow & C\,S_{2\,(l)} & & \Delta H = -233.18 \text{ kcal} \\
\hline
\end{array}$$

Thus the heat of formation of CS_2 is – 233.18 kcal

SOLVED PROBLEM 21. Using the data (all values are in kcal mol^{-1} at 25 °C) given below, calculate the bond energy of C — C and C — H bonds.

$\Delta H^o_{\text{combustion}}$ (*ethane*) = – 372.0 $\qquad$ $\Delta H^o_{\text{combustion}}$ (*propane*) = – 530.0

ΔH^o for C (*graphite*) $\longrightarrow$ C (*g*) = – 172.0 $\qquad$ Bond energy of H — H = 104.0

ΔH^o_f of $H_2O_{(l)}$ = – 68.0 $\qquad$ and ΔH^o_f of CO_2 = – 94.0

SOLUTION :

(i) To calculate ΔH^o_f for ethane and propane

The chemical equations representing combustion of ethane and propane are

$$C_2H_{6\,(g)} + {}^7\!/_2\,O_{2\,(g)} \longrightarrow 2\,CO_{2\,(g)} + 3\,H_2O_{(l)} \qquad \Delta H^o = -372 \text{ kcal mol}^{-1}$$

and

$$C_3H_{8\,(g)} + 5\ O_{2\,(g)} \longrightarrow 3\,CO_{2\,(g)} + 4\,H_2O_{(l)} \qquad \Delta H^o = -530 \text{ kcal mol}^{-1}$$

Formula used

$$\Delta H^o = \Delta H^o_f\ (Products) - \Delta H^o_f\ (Reactants)$$

Quantities given (i) For ethane

$\Delta H^o = -372$ kcal mol^{-1} $\qquad$ $\Delta H^o_f(CO_2) - 94$ kcal mol^{-1} $\qquad$ $\Delta H_f\,(H_2O) = -68.0$ kcal mol^{-1}

Substitution of values

$$-372 \text{ kcal mol}^{-1} = [\,2 \times -94 \text{ kcal mol}^{-1} + 3 \times -68 \text{ kcal mol}^{-1}\,] - [\,\Delta H_f\ (C_2H_6) - 0\,]$$

$$\Delta H_f\,(C_2H_6) = -392 \text{ kcal mol}^{-1} + 372 \text{ kcal mol}^{-1}$$

$$= \mathbf{20 \text{ kcal mol}^{-1}}$$

Quantities given (ii) For propane

$\Delta H^o = -530$ kcal mol^{-1} $\qquad$ $\Delta H_f\ (CO_2) = -94$ kcal mol^{-1} $\qquad$ $\Delta H_f\ (H_2O) = -68.0$ kcal mol^{-1}

Substitution of values

$$-530 \text{ kcal mol}^{-1} = [\,3 \times -94 \text{ kcal mol}^{-1} + 4 \times -68 \text{ kcal mol}^{-1}\,] - [\,\Delta H_f\,(C_3H_8) - 0\,]$$

$$\Delta H_f\,(C_3H_8) = -554 \text{ kcal mol}^{-1} + 530 \text{ kcal mol}^{-1}$$

$$= \mathbf{-\ 24 \text{ kcal mol}^{-1}}$$

(ii) To calculate the bond energy of C — C and C — H bonds.

The formation of ethane and propane are represented by

$$2\,C_{(s)} + 3\,H_{2\,(g)} \longrightarrow C_2H_{6\,(g)} \qquad \Delta H = -20 \text{ kcal mol}^{-1}$$
$$3\,C_{(s)} + 4\,H_{2\,(g)} \longrightarrow C_3H_{8\,(g)} \qquad \Delta H = -24 \text{ kcal mol}^{-1}$$

Let the bond energy of C — C be 'a' and that of C — H be 'b'

Formula used

$$\Delta H = \text{Bond energy of reactants} - \text{Bond energy of products}$$

For ethane

$$-20 \text{ kcal mol}^{-1} = [2 \times \text{B.E. of } C_{(graphite)} \longrightarrow C_{(g)} + 3 \times \text{B.E. of H — H}] - [1 \times \text{B.E. of C — C} + 6 \times \text{B.E. of C — H}]$$
$$= [2 \times 172 + 3 \times 104] - [a + 6b]$$
$$a + 6b = 676 \text{ kcal mol}^{-1}$$

and for propane

$$-24 \text{ kcal mol}^{-1} = [3 \times \text{B.E. of } C_{(graphite)} \longrightarrow C_{(g)} + 4 \times \text{B.E. of H — H}] - [2 \times \text{B.E. of C — C} + 8 \times \text{B.E. of C — H}]$$

or $\quad -24 \text{ kcal mol}^{-1} = [3 \times 172 \text{ kcal mol}^{-1} + 4 \times 104 \text{ kcal mol}^{-1}] - [2a + 8b]$

or $\quad 2a + 8b = 956 \text{ kcal mol}^{-1}$

Solving for a and b, we have

$$\mathbf{a = 99 \text{ kcal mol}^{-1} \text{ and } b = 82 \text{ kcal mol}^{-1}}$$

SOLVED PROBLEM 22. Calculate the resonance energy of N_2O from the following data : ΔH_f^o for N_2O = 82 kJ mol^{-1}. Bond energy of N≡N, N=N, O=O and N=O bond are 946, 418, 498, and 607 kJ mol^{-1} respectively.

SOLUTION :

The equation representing the formation of N_2O is

$$N \equiv N + \tfrac{1}{2}\,O = O \longrightarrow \overset{+}{N} = \overset{-}{N} = O$$

Formula used

$$\Delta H_f^o(N_2O) = \text{B.E. of Reactants} - \text{B.E. of products}$$

Quantities given

B.E. of N ≡ N = 946 kJ mol^{-1}

B.E. of O = O = 498 kJ mol^{-1}

B.E. of N ≡ N = 418 kJ mol^{-1}

B.E. of N = O = 607 kJ mol^{-1}

Substitution of values

$$\Delta H^o{}_f(N_2O) = [\text{B.E. of N} \equiv \text{N bond} + \tfrac{1}{2}\,\text{B.E. of O} = \text{O bond}] - [\text{B.E. of N} = \text{N} + \text{B.E. of N} = \text{O}]$$
$$= [946 + \tfrac{1}{2} \times 498] \text{ kJ mol}^{-1} - [418 + 607] \text{ kJ mol}^{-1}$$
$$= 170 \text{ kJ mol}^{-1}$$

But the actual value of $\Delta H_f^o(N_2O) = 82 \text{ kJ mol}^{-1}$

$\therefore$ Resonance energy of N_2O = Theoretical heat of formation – Actual heat of formation

$$= 170 \text{ kJ mol}^{-1}$$
$$= \mathbf{88 \text{ kJ mol}^{-1}}$$

SOLVED PROBLEM 23. Determine the enthalpy of the reaction

$$C_3H_{8\,(g)} + H_{2\,(g)} \longrightarrow C_2H_{6\,(g)} + CH_{4\,(g)}$$

at 25 °C, using the given heats of combustion under standard conditions.

Compound	$H_{2\,(g)}$	$CH_{4\,(g)}$	$C_2H_{6\,(g)}$	$C_{\,(graphite)}$
ΔH^o (kJ mol^{-1})	–285.8	– 890	– 1560	– 393.5

The standard heat of formation of $C_3H_{8\,(g)}$ is – 103.8 kJ mol^{-1}

SOLUTION : The given data can be used to frame the following equations

$$H_{2\,(g)} + {}^{11}\!/_{2}O_{2\,(g)} \longrightarrow H_2O_{(l)} \qquad \Delta H = -258.8 \text{ kJ mol}^{-1} \quad ...(i)$$
$$CH_{4\,(g)} + 2\ O_{2\,(g)} \longrightarrow CO_{2\,(g)} + 2\,H_2O_{(l)} \qquad \Delta H = -890.0 \text{ kJ mol}^{-1} \quad ...(ii)$$
$$C_2H_{6\,(g)} + {}^{7}\!/_{2}O_{2\,(g)} \longrightarrow CO_{2\,(g)} \qquad \Delta H = -1560.0 \text{ kJ mol}^{-1} \quad ...(iii)$$
$$C_{(s)} + O_{2\,(g)} \longrightarrow CO_{2\,(g)} \qquad \Delta H = -393.5 \text{ kJ mol}^{-1} \quad ...(iv)$$
$$3\,C_{(s)} + 4\ H_{2\,(g)} \longrightarrow C_3H_{8\,(g)} \qquad \Delta H = -103.8 \text{ kJ mol}^{-1} \quad ...(v)$$

We have to arrive at the equation

$$C_3H_{8\,(g)} + H_{2\,(g)} \longrightarrow C_2H_{6\,(g)} + CH_4 \qquad \Delta H = ?$$

Multiplying equation (i) by 5 and equation (iv) by 3 and adding

$$5\,H_{2\,(g)} + {}^{5}\!/_{2}O_{2\,(g)} \longrightarrow 5\,H_2O_{(l)} \qquad \Delta H = -1294.0 \text{ kJ mol}^{-1}$$
$$3\,C_{(s)} + 3\ O_{2\,(g)} \longrightarrow 3\,CO_{2\,(g)} \qquad \Delta H = -1180.5 \text{ kJ mol}^{-1}$$

$$3\,C_{(s)} + 5\tfrac{1}{2}\,O_{2\,(g)} + 5\ H_{2\,(g)} \longrightarrow 5\,H_2O_{(l)} + 3\,CO_{2\,(g)} \qquad \Delta H = -2474.5 \text{ kJ mol}^{-1} \quad ...(vi)$$

Adding equation (ii), (iii) and (v) we get

$$CH_{4\,(g)} + C_2H_{6\,(g)} + 3\,C_{(s)} + 4\,H_{2\,(g)} + 5\tfrac{1}{2}\,O_{2\,(g)} \longrightarrow 3\,CO_{2\,(g)} + 5\,H_2O_{(l)} + C_3H_{8\,(g)} \qquad \Delta H = -2553.8 \text{ kJ mol}^{-1}$$

...(vii)

Subtracting equation (vii) from (vi) we have

$$3\,C_{(s)} + {}^{11}\!/_{2}O_{2\,(g)} + 5\,H_2O_{(g)} \longrightarrow 5\,H_2O_{(l)} + 3\,CO_{2\,(g)} \qquad \Delta H = -2474.5 \text{ kJ mol}^{-1}$$
$$3\,C_{(s)} + {}^{11}\!/_{2}O_{2\,(g)} + 4\,H_{2(g)} + CH_{4\,(g)} + C_2H_{6\,(g)} \longrightarrow 5\,H_2O_{(l)} + 3\,CO_{2\,(g)} + C_3H_{8\,(g)} \qquad \Delta H = -5028.3 \text{ kJ mol}^{-1}$$

$$C_3H_8 + H_{2\,(g)} \longrightarrow CH_{4\,(g)} + C_2H_{6\,(g)} \qquad \boldsymbol{\Delta H = -\,5028.3\ \text{kJ mol}^{-1}}$$

SOLVED PROBLEM 24. 0.16 g of methane was subjected to combustion at 27°C in a bomb calorimeter. The temperature of calorimeter system including water was found to rise by 0.5°C. Calculate the heat of combustion of methane at (i) constant volume and (ii) at constant pressure. The thermal capacity of the calorimeter system is 17.7 kJ K^{-1}. (R = 8.314 J K^{-1} mol^{-1})

SOLUTION :

(i) To calculate the heat of combustion at constant volume

Quantity of heat liberated = Thermal capacity of calorimeter × Rise in temperature for 0.16 g of methane

$$= 17.7 \text{ kJ K}^{-1} \times 0.5 \text{ K}$$
$$= -8.85 \text{ kJ}$$
$$\Delta E = \text{Quantity of heat liberated for one mole of methane}$$
$$= \frac{8.85 \text{ kJ} \times 16 \text{ g mol}^{-1}}{0.16 \text{ g}}$$
$$= -\ 885 \text{ kJ}$$

(ii) To calculate the heat of combustion at constant pressure

The equation representing the combustion of methane is

$$CH_{4\,(g)} + 2\,O_{2\,(g)} \longrightarrow CO_{2\,(g)} + 2\,H_2O_{(l)}$$

Formula used

$$\Delta H = \Delta E + \Delta n\,R\,T$$

Quantities given

$\Delta E = -885 \text{ kJ mol}^{-1}$ $R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1} = 8.314 \times 10^{-3} \text{ kJ K}^{-1} \text{ mol}^{-1}$

$T = 27 + 273 = 300 \text{ K}$ $\Delta n = n_P - n_R = 1 - 3 = -2$

Substitution of values

$$\Delta H = -885 \text{ kJ mol}^{-1} + (-2) \times 8.314 \times 10^{-3} \text{ kJ K}^{-1} \text{ mol} \times 300 \text{ K}$$
$$= -885 - 4.9884 \text{ kJ mol}^{-1}$$
$$= \mathbf{-889.9884 \text{ kJ mol}^{-1}}$$

SOLVED PROBLEM 25. The polymerisation of ethylene to linear Polyethylene is represented by the reaction

$$n\,CH_2{=}CH_2 \longrightarrow (-CH_2-CH_2-)_n$$

where n has a large integral value. Given that the average enthalpies of bond dissociation for C$=$C and C — C at 298 K are + 590 and + 331 kJ mol^{-1} respectively, calculate the enthalpy of polymerisation per mole of ethylene at 298 K.

SOLUTION :

The polymerisation of ethylene is represented by

$$n\,CH_2{=}CH_2 \longrightarrow (-CH_2-CH_2-)_n$$

For every unit of ethylene C$=$C bond breaks and three new C — C single bonds are formed. But the net effect is the formation of two C — C single bonds per mole of ethylene *i.e.*

Total energy released = No.of bonds formed × Bond energy of C — C bond

$= 2 \times 331 \text{ kJ mol}^{-1} = 662 \text{ kJ mol}^{-1}$

Total energy absorbed = No. of bonds broken × Bond energy of C$=$C bond

$= 1 \times 590 \text{ kJ mol}^{-1} = 590 \text{ kJ mol}^{-1}$

∴ Net energy released per mole of ethylene $= 590 \text{ kJ mol}^{-1} - 662 \text{ kJ mol}^{-1}$

Thus **ΔH polymeration for ethylene** $= \mathbf{-72 \text{ kJ mol}^{-1}}$

SOLVED PROBLEM 26. At 300K, the enthalpies of formation of Benzoic acid $_{(s)}$, $CO_{2\,(g)}$ and $H_2O_{(l)}$ are – 408, – 393 and – 286 kJ mol^{-1} respectively. Calculate the heat of combustion of benzoic acid at (i) constant pressure and (ii) at constant volume. ($R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$)

SOLUTION :

(i) To calculate the heat of combustion of C_6H_5COOH at constant pressure.

The equation representing the combustion of benzoic acid is

$$C_6H_5COOH_{(s)} + O_{2\,(g)} \longrightarrow 7\,CO_{2\,(g)} + 3\,H_2O_{(l)} \qquad \Delta H = ?$$

Formula used

$$\Delta H = \Delta H_{f\,(Products)} - \Delta H_{f\,(Reactants)}$$

Quantities given

$\Delta H_f(CO_2) = -393 \text{ kJ mol}^{-1}$ $\Delta H_f(H_2O) = -286 \text{ kJ mol}^{-1}$ $\Delta H_f(C_6H_5COOH) = -408 \text{ kJ mol}^{-1}$

Substitution of values

$$\Delta H = [7 \times (-393)] + 3 \times (-286) - [-408 + {}^{15}\!/_2 \times 0] \text{ kJ mol}^{-1}$$
$$= [-2751 - 858] + [408] \text{ kJ mol}^{-1}$$
$$= -3201 \text{ kJ mol}^{-1}$$

(ii) To calculate the heat of combustion at constant volume

Formula used

$$\Delta H = \Delta E + \Delta n\, R\, T$$

Quantities given

$\Delta H = -320 \text{ kJ mol}^{-1}$ $R = 8.314 \text{ J K}^{-1}\text{mol}^{-1} = 8.314 \times 10^{-3} \text{ kJ mol}^{-1}\text{ K}^{-1}$ $T = 300 \text{ K}$

$\Delta n = n_P - n_R = 7 - {}^{15}\!/_{2} = -½$

Substitution of values

$$-320 \text{ kJ mol}^{-1} = \Delta E + (-½) \times 8.314 \times 10^{-3} \text{ kJ K}^{-1}\text{ mol}^{-1} \times 300 \text{ K}$$

or $\Delta E = -320 \text{ kJ mol}^{-1} + 1.247 \text{ kJ mol}^{-1}$

$= \mathbf{318.75 \text{ kJ mol}^{-1}}$

SOLVED PROBLEM 27. The heat liberated on complete combustion of 7.8 g benzene is 327 kJ. This heat has been measured at constant volume and at 27ºC. Calculate the heat of combustion of benzene at constant pressure. ($R = 8.314 \text{ J mol}^{-1}\text{ K}^{-1}$)

SOLUTION : (i) To calculate ΔH $_{\text{(combustion)}}$ for benzene per mole

The chemical equation representing combustion of benzene is

$$C_6H_{6\,(l)} + O_{2\,(g)} \longrightarrow 6\,CO_{2\,(g)} + 3\,H_2O_{\,(l)}$$

Quantity of heat evolved when 7.8 g of benzene is burnt $= -327$ kJ

Quantity of heat evolved when 78 g (1 mole) of benzene is burnt

$$= -\frac{327 \text{ kJ mol}^{-1} \times 78 \text{ g mol}^{-1}}{7.8 \text{ g}}$$

$$= -3270 \text{ kJ mol}^{-1}$$

(ii) To calculate ΔE

Formula used

$$\Delta H = \Delta E + \Delta n\, R\, T \quad \text{or} \quad \Delta E = \Delta H - \Delta n\, R\, T$$

Quantities given

$\Delta H = -3270 \text{ kJ mol}^{-1}$ $R = 8.314 \text{ J K}^{-1}\text{ mol}^{-1} = 8.314 \times 10^{-3} \text{ kJ K}^{-1}\text{mol}^{-1}$

$T = 27 + 273 = 300 \text{ K}$ $\Delta n = n_P - n_R = 6 - {}^{15}\!/_{2} = -{}^{3}\!/_{2}$

Substitution of values

$$\Delta H = -3270 \text{ kJ mol}^{-1} + \left(-{}^{3}\!/_{2}\right) \times 8.314 \times 10^{-3} \text{ kJ K}^{-1}\text{ mol}^{-1} \times 300 \text{ K}$$

$$= -3270 \text{ kJ mol}^{-1} - 3.741 \text{ kJ mol}^{-1}$$

$$= \mathbf{3273.741 \text{ kJ mol}^{-1}}$$

ADDTIONAL PRACTICE PROBLEMS

1. Calculate the standard internal energy change for the following reaction at 25ºC

$$C_{\,(graphite)} + H_2O_{\,(g)} \longrightarrow CO_{\,(g)} + H_{2\,(g)}$$

ΔH_f^o at 25 ºC for $H_2O_{\,(g)} = 241.8 \text{ kJ mol}^{-1}$ and for $CO_{\,(g)} = 110.5 \text{ kJ mol}^{-1}$;
Gas constant $R = 8.314 \text{ J K}^{-1}\text{ mol}^{-1}$
Answer. 128.82 kJ

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

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

ΔH_f^o at 25 °C for $H_2O_{2\,(l)}$ = – 188.0 kJ mol^{-1} and for $H_2O_{(l)}$ = – 286.0 kJ mol^{-1} ; Gas constant R = 8.314 J k^{-1} mol^{-1}

Answer. 198.477 kJ

3. The heat of combustion of methane is – 890.65 kJ mol^{-1} and heats of formation of CO_2 and H_2O are – 393.5 and –286.0 kJ mol^{-1} respectively. Calculate the heat of formation of methane.

Answer. –74.85 kJ mol^{-1}

4. Given standard enthalpy of formation of $H_2O_{(l)}$, $SO_{(g)}$, $H_2S_{(g)}$ and $O_{2(g)}$ are –286, –296.9, –20.17 and 0 kJ mol^{-1} respectively. Calculate ΔH_f^o for the reaction

$$2\,H_2S_{(g)} + 3\,O_{2\,(g)} \longrightarrow 2\,H_2O_{(l)} + 2\,SO_{2\,(g)}$$

Answer. 1125.46 kJ

5. Calculate the standard enthalpy change (ΔH^o) and standard internal energy change (ΔE^o) for the reaction

$$OF_{2\,(g)} + H_2O_{(g)} \longrightarrow O_{2\,(G)} + 2\,HF_{(G)}$$

when standard enthalpy of formation ΔH_f^o for various compounds are $OF_{2\,(g)}$ = –23.0 kJ mol^{-1},

$H_2O_{(g)}$ = –241.8 kJ mol^{-1} and $HF_{(g)}$ = – 268.6 kJ mol^{-1}.

Answer. –320.877 kJ

6. Dissociation energy of $H_{2(g)}$, $Cl_{2\,(g)}$ respectively are 435.4 and 243 kJ mol^{-1}. Enthalpy of formation of $HCl_{(g)}$ is – 92.9 kJ mol^{-1}. Calculate the dissociation energy of HCl.

Answer. – 413.4 kJ mol^{-1}

7. Calculate the enthaply change for the reaction

$$2\,S_{(s)} + 3\,O_{2\,(g)} \longrightarrow 2\,SO_{3\,(g)}$$

given the following information:

$$S_{(s)} + O_{2\,(g)} \longrightarrow SO_{2\,(g)} \qquad \Delta H = -297\ \text{kJ}$$

$$2\,SO_{3\,(g)} \longrightarrow 2\,SO_{2\,(g)} + O_{2\,(g)} \qquad \Delta H = 198\ \text{kJ}$$

Answer. – 792 kJ

8. While phosphorus, P_4, burns in an excess of oxygen to form tetraphosphorus decoxide, P_4O_{10}.

$$P_{4(s)} + 5\,O_{2\,(g)} \longrightarrow P_4O_{10\,(g)} \qquad \Delta H = -2942\ \text{kJ}$$

what is the heat evolved per gram of phosphorus burnt?

Answer. – 23.72 kJ

9. Ammonia burns in the presence of a copper catalyst to form nitrogen gas

$$4\,NH_{3\,(g)} + 3\,O_{2\,(g)} \longrightarrow 2\,N_{2\,(g)} + 6\,H_2O_{(g)} \qquad \Delta H = -1267\ \text{kJ}$$

What is the enthalpy change to burn 25.6 ammonia ?

Answer. – 476.98 kJ

10. Calculate the enthalpy change for the reaction

$$C_2H_{4\,(g)} + H_{2\,(g)} \longrightarrow C_2H_{6\,(g)}$$

using the following combustion data :

C_2H_4 = – 1401 kJ C_2H_6 = – 1550 kJ H_2 = – 286 kJ

Answer. – 137 kJ

11. Calcium carbonate on heating decomposes to calcium oxide according to equation

$$CaCO_{3\,(s)} \longrightarrow CaO_{(s)} + CO_{2\,(g)} \qquad \Delta H = -178.3 \text{ kJ}$$

How much heat is required to decompose 24.0 g of calcium carbonate ?

Answer. 42.79 kJ

12. In an experiment 5.48 g of formic acid, HCOOH, was burnt and the amount of heat evolved was 30.3 kJ. Calculate ΔH per mole of formic acid.

Answer. 42.79 kJ

13. Calculate the heat of formation of ammonia from the heats of combustion of ammonia and hydrogen which are 9.06 and 68.9 kcals respectively.

Answer. – 94.29 kcals

14. Calculate the heat of formation of anhydrous $AlCl_3$ from the following data :

$$2\,Al_{(s)} + 6\,HCl_{(aq)} \longrightarrow Al_2Cl_{6\,(aq)} + 3\,H_2O \qquad \Delta H = -244 \text{ kcal}$$

$$H_{2\,(g)} + Cl_{2\,(g)} \longrightarrow 2\,HCl_{(g)} \qquad \Delta H = -44 \text{ kcal}$$

$$HCl_{(g)} + aq. \longrightarrow HCl_{(aq.)} \qquad \Delta H = -17.5 \text{ kcal}$$

$$Al_2Cl_{6\,(s)} + aq. \longrightarrow Al_2Cl_{6\,(aq.)} \qquad \Delta H = -153.7 \text{ kcal}$$

Answer. – 327.3 kcals

15. The enthalpies for the following reaction (ΔH°) at 25 °C are given below :

$$\tfrac{1}{2}\,H_{2\,(g)} + \tfrac{1}{2}\,O_{2\,(g)} \longrightarrow OH_{(g)} \qquad \Delta H = 10.06 \text{ kcal}$$

$$H_{2\,(g)} \longrightarrow 2\,H_{(g)} \qquad \Delta H = 104.18 \text{ kcal}$$

$$O_{2\,(g)} \longrightarrow 2\,O_{(g)} \qquad \Delta H = 118.32 \text{ kcal}$$

Calculate the O — H bond energy in the hydroxyl radical.

Answer. – 101.19 kcals

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

Answer. – 22.0 kcal

17. Using the data given below, Calculate the bond of C — C and C — H bonds.

$$\Delta H^o_{\text{combustion}} \text{ (ethane)} = -372.0 \text{ kcal}$$

$$\Delta H^o_{\text{combustion}} \text{ (propane)} = -530.0 \text{ kcal}$$

$$\Delta H^o \text{ for } C_{(\text{graphite})} \longrightarrow C_{(g)} = -172.0 \text{ kcal}$$

$$\text{Bond Energy of H — H} = -104.0 \text{ kcal}$$

$$\Delta H^o_f \text{ of } H_2O_{(l)} = -\ 90.0 \text{ kcal}$$

Answer. C — C = 82 kcal ; C — H = 99 kcal

18. In order to get maximum calorific output, a burner should have an optimum fuel to oxygen ratio which corresponds to 3 times as much oxygen as required theoretically for complete combustion of the fuel. A burner which has been adjusted for methane as fuel (with x litre hr^{-1} of CH_4 and 6 x litre hr^{-1} of O_2) is to be readjusted for butane, C_4H_{10}. In order to get the same calorific output what should be the rate of supply of butane and oxygen ? Assume that losses due to incomplete combustion etc. are the same for both fuels and that the gases behave ideally. Heat of combustion : CH_4 = 809 kJ mol^{-1} ; C_4H_{10} = 2878 kJ mol^{-1}

Answer. butane = 0.2795 x litre hr^{-1} ; O_2 = 5.450 x litre hr^{-1}

19. The polymerisation of ethylene to linear polyethylene is represented by the reaction

$$n\ CH_2{=\!=}CH_2 \longrightarrow (-CH_2{-\!-}CH_2-)_n$$

where n has a large integral value. Given that the average enthalpies of bond dissociation for C $=\!=$ C and C — C at 298 K + 590 and + 331 mol^{-1} respective, calculate the enthapy of polymerisation per mole of ethylene at 298 K.

Answer. – 72 kJ mol^{-1}

20. The heat of combustion of $C_2H_{4\,(g)}$, $C_2H_{6\,(g)}$ and $H_{2\,(g)}$ are –1409 kJ, –1558.3 kJ and – 285.645 respectively. Calculate the heat of hydrogenation of ethylene.

Answer. – 136.8 kJ

21. When 2 moles of ethane are completely burnt 3129 kJ of heat is liberated. Calculate the heat of formation, ΔH_f for C_2H_6. ΔH_f for $CO_{2\,(g)}$ and $H_2O_{\,(l)}$ are – 395 and – 286 kJ respectively.

Answer. – 83.5 kJ

22. The standard heat of formation of $CH_{4\,(g)}$, $CO_{2\,(g)}$ and $H_2O_{\,(g)}$ are – 76.2, – 394.8 and –241.6 kJ mol^{-1} respectively. Calculate the amount of heat evolved by burning 1 m^3 of methane measured under normal condition.

Answer. 3.58×10^4 kJ

9

Second Law of Thermodynamics

CHAPTER

KEY CONCEPTS AND EQUATIONS

ENTROPY,S

It is a measure of the disorder or freedom or randomness of a system. The increasing order of entropy is

$$\text{Solid} < \text{Liquid} < \text{Gas}$$

It is denoted by *S*. It is a thermodynamics quantity depending upon the initial and final states of the system. It is independent of path. The change in entropy, Δ*S*, is given by

$$\Delta S = S_f - S_i$$

where S_f is the final entropy and S_i the initial entropy. The change in entropy for a reaction is given by

$$\Delta S = \Sigma S_{(Products)} - \Sigma S_{(Reactants)}$$

Δ*S* will be +ve if the system is more disorganised in the final state (products) and it will be –ve if the system is less disorganised in the final state. The units of entropy are JK^{-1} or cal K^{-1}

SECOND LAW OF THERMODYNAMICS

The total entropy of the universe is increasing *i.e.* the total entropy of a system and its surrounding is always increasing, *i.e.*

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

Thus for a spontaneous process at a given temperature the change in entropy of the system is greater than the heat divided by the absolute temperature.

EFFICIENCY OF A HEAT ENGINE, η

It is the ratio of work obtained in cyclic process (*w*) to the heat taken from the high temperature reservoir *i.e.*

$$\eta = \frac{w}{q_2} = \frac{T_2 - T_1}{T_2}$$

where T_2 and T_1 are the absolute temperatures of the reservoir and sink respectively.

THE CARNOT CYCLE

The cycle of processes which occured under reversible conditions is referred to as the Carnot cycle. It comprises of four operations :

(i) Isothermal reversible expansion (ii) Adiabatic reversible expansion
(iii) Isothermal reversible compression (iv) Adiabatic reversible compression

These four operations are shown in the Fig 9.1.

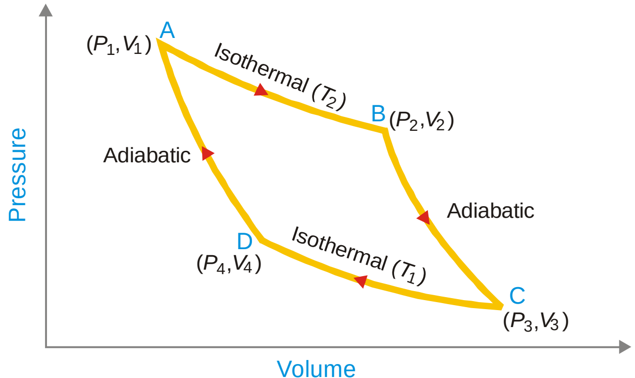


Figure 9.1
The Carnot cycle.

Work done and heat absorbed in Carnot cycle. The work done in Carnot cycle is given by

$$w = RT_2 \ln \frac{V_2}{V_1} + RT_1 \ln \frac{V_4}{V_3}$$

and the heat absorbed in Carnot cycle is given by

$$q = RT_2 \ln \frac{V_2}{V_1} - RT_1 \ln \frac{V_3}{V_4}$$

or

$$q = R(T_2 - T_1) \ln \frac{V_2}{V_1} \qquad \left[\because \frac{V_3}{V_4} = \frac{V_2}{V_1}\right]$$

More statements of Second Law of Thermodynamics

(1) It is impossible to take heat from a hotter reservoir and convert it completely into work by a cyclic process without transferring a part of heat to a cooler reservoir.

(2) It is possible for a cyclic process to transfer heat from a body at lower temperature to one at higher temperature without at the same time converting some heat to work.

THIRD LAW OF THERMODYNAMICS

All substances in their normal crystalline state at absolute zero would be the most ordered state with zero entropy. This is third law of Thermodynamics.

Entropy change for an ideal gas

It is given by

$$\Delta S = 2.303\ n\ C_v \log \frac{T_2}{T_1} + 2.303\, R \log \frac{V_2}{V_1}$$

or

$$\Delta S = 2.303\ n\ C_p \log \frac{T_2}{T_1} + 2.303\, nR \log \frac{P_1}{P_2}$$

Special Cases

Case I : At constant temperature for an isothermal process

$$\Delta S_T = 2.303\ nR \log \frac{P_1}{P_2}$$

Case II : At constant pressure (Isobaric process)

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

Case III : At constant volume (Isochoric process)

$$\Delta S_v = 2.303\ n\,C_v \log \frac{T_2}{T_1}$$

Entropy change accompanying change of phase

Certain processes occur at equilibrium, *e.g.* melting of ice at 273 K when ice is in equilibrium with liquid water. In such cases the entropy change results from the absorption of heat energy. Thus

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

For example

$$H_2O_{(s)} \rightleftharpoons H_2O_{(l)} \qquad \Delta S_{fusion} = \frac{\Delta H_{fusion}}{T_m}$$

and $$H_2O_{(l)} \rightleftharpoons H_2O_{(g)} \qquad \Delta S_{vap} = \frac{\Delta H_{vap}}{T_b}$$

where T_m and T_b are the absolute temperature at which melting and boiling of water occur.

GIBBS FREE ENERGY

The work accompanying a chemical process may be of two types - unavoidable (work of expansion) and useful work (work of non - expansion). Therefore, every system has a capacity to do useful work which is called Gibbs Free Energy, *G*, defined by the relation.

$$G = H - TS$$

and the change in free energy, ΔG, is given by

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

under standard conditions (298 K and 1 atm pressure) we have

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

when all reactants and products are in their standard states.

GIBBS HELMHOLTZ EQUATION

(i) In terms of free energy and enthalpy

$$\Delta G = \Delta H - T\,d\left(\frac{\Delta G}{dT}\right)_p$$

(ii) In terms of Internal energy and work function

$$\Delta A = \Delta E + T\,d\left(\frac{\Delta A}{dT}\right)_v$$

SPONTANEOUS REACTIONS AND CRITERION FOR SPONTANEITY

A reaction is spontaneous if the capacity of the system to do work increases during the process. In term of ΔG

the process is spontaneous if $\Delta G = -\text{ve}$

and the process is non - spontaneous if $\Delta G = +\text{ve}$

Since ΔG is the net resultant of two factors ΔH and $T\Delta S$, it becomes negative under the conditions given in Table 10.1.

TABLE 10.1. **CONDITIONS FOR SPONTANEITY OF A REACTION**

ΔH	ΔS	ΔG	Spontaneity
–ve	+ve	–ve	Spontaneous at all temperatures.
+ve	–ve	+ve	Non-spontaneous at all temperatures.
–ve	–ve	+ve or –ve	Non-spontaneous at high temperatures. Spontaneous at low temperatures.
+ve	+ve	+ve or –ve	Non-spontaneous at low temperatures. Spontaneous at high temperatures.

CLAUSIUS CLAPEYRON EQUATION

It gives us important information about a system of any two phases of a single substance in chemical equilibrium. It is given by

$$\log \frac{p_2}{p_1} = \frac{\Delta H}{2.303\,R}\left[\frac{1}{T_1} - \frac{1}{T_2}\right]$$

where p_2 is the vapour pressure at temperature T_1, P_2 the vapour pressure at temperature T_2, ΔH is the heat of reaction and R is gas constant.

VAN'T HOFF ISOTHERM AND ISOCHORE

The equilibrium constant is related to the Gibbs free energy by the relation

$$-\Delta G = RT \ln K_p$$

or

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

And the variation of equilibrium constant with temperature is given by

$$\log \frac{K_{p_2}}{K_{p_1}} = \frac{\Delta H}{2.303 \times R}\left[\frac{T_2 - T_1}{T_1\,T_2}\right]$$

ADDITIONAL SOLVED PROBLEMS

SOLVED PROBLEM 1. What is the change in entropy when 1 mole of helium gas is heated from 200K to 400K at constant pressure ? (Given: C_p for helium = 5.0 cal per degree per mole)

SOLUTION :

Formula used

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

Quantities given

n = 1 mole $\qquad$ $C_p = 5.0$ cal K^{-1} mol^{-1}

T_1 = 200K $\qquad$ T_2 = 400 K

Substitution of values

$$\Delta S = 2.303 \times 1\text{mole} \times 5\text{ cal K}^{-1}\text{ mol}^{-1} \times \log \frac{400\text{K}}{200\text{K}}$$

$$= 11.515\text{ cal K}^{-1} \times \log 2$$

$$= 11.515 \times 0.3010\text{ cal K}^{-1}$$

$$= \mathbf{3.466\ \ cal\ K^{-1}}$$

SOLVED PROBLEM 2. Calculate the total entropy change when 5 gram of ice at 0 °C is converted into steam at 100 °C. (Latent heat of evaporation = 540 cals/g ; C_p for water = 18 cals/mole ; Latent heat of fusion of water = 80 cal/mole).

SOLUTION :

(i) To calculate the entropy change for 5g of ice at 0 °C to water at 0 °C.

Formula used

$$\Delta S_1 = \frac{\Delta H_f}{T_f}$$

Quantities given

$\Delta H_f = 5 \times 80$ cal $\qquad$ $T_f = 273$ K

Substitution of values

$$\Delta S_1 = \frac{5 \times 80\text{ cal}}{273\text{ K}}$$

$$= 1.465\text{ cal K}^{-1}$$

(ii) To calculate the entropy change for 5g water at 0 °C to water at 100 °C

Formula used

$$\Delta S_2 = 2.303\ C_p \log \frac{T_2}{T_1}$$

Quantities given

$T_1 = 273\text{ K}$ $\qquad$ $T_2 = 373\text{ K}$

$C_p = 18\text{ cal mol}^{-1}$ or C_p for 5g $= 5\text{ cal}$ $\qquad$ $[\because 1\text{ mole} = 18\text{g}]$

Substitution of values

$$\Delta S = 2.303 \times 5\text{ cal} \times \log \frac{373\text{K}}{273\text{K}}$$

$$= 11.515\text{ cal} \times 0.1355$$

$$= 1.560\text{ cal K}^{-1}$$

(iii) Entropy change for 5g of water at 100 °C to steam at 100 °C.

Formula used

$$\Delta S_3 = \frac{\Delta H_v}{T_b}$$

Quantities given

$\Delta H_v = 540\text{ cal g}^{-1} \times 5\text{g} = 2700\text{ cal}$ $\qquad$ $T_b = 373\text{ K}$

Substitution of values

$$\Delta S_3 = \frac{2700\text{ cal}}{373\text{ K}}$$

$$= 7.238\text{ cal K}^{-1}$$

Total entropy change

$$\Delta S = \Delta S_1 + \Delta S_2 + \Delta S_3$$

$$= 1.465\text{ cal K}^{-1} + 1.560\text{ cal K}^{-1} + 7.238\text{ cal K}^{-1}$$

$$= \mathbf{10.263\text{ cal K}^{-1}}$$

SOLVED PROBLEM 3. Calculate the work performed when two grams of hydrogen gas is expanded isothermally and reversibly at 27 °C from ten to one hundred litres. What is the amount of heat absorbed ? What is the change in internal energy ?

SOLUTION :

(i) To calculate the work done in an isothermal reversible expansion

Formula used

$$w = n R T \times 2.303 \log \frac{V_2}{V_1}$$

Quantities given

$n = \dfrac{2\text{ g}}{2\text{ g mol}^{-1}} = 1\text{ mole}$ $\qquad$ $V_1 = 10\text{ litres}$ $\qquad$ $V_2 = 100\text{ litres}$

$T = 300\text{ K}$ $\qquad$ $R = 1.987\text{ cal K}^{-1}\text{ mol}^{-1}$

Substitution of values

$$w = 2.303 \times 1\text{ mole} \times 1.987\text{ cal K}^{-1}\text{mol}^{-1} \times 300\text{ K} \times \log \frac{100\text{ lit}}{10\text{ lit}}$$

$$= \mathbf{1372.82\text{ cal}}$$

(ii) To calculate the heat absorbed in the process

For this process $\qquad q = w =$ **1372.82 cal**

and $\qquad \Delta E = q - w$

$$= 1372.82\text{ cal} - 1372.82\text{ cal}$$
$$= \mathbf{0}$$

SOLVED PROBLEM 4. For a heat engine the source is at 500 K and the sink at 300 K. What is the efficiency of this engine ?

SOLUTION :

Formula used

$$\eta = \frac{T_2 - T_1}{T_2}$$

Quantities given

$T_2 = 500$ K $\qquad$ $T_1 = 300$ K

Substitution of values

$$\text{Efficiency, } \eta = \frac{500\text{ K} - 300\text{ K}}{500\text{ K}}$$
$$= \frac{200}{500}$$
$$= \mathbf{0.4 \text{ or } 40\%}$$

SOLVED PROBLEM 5. Calculate the work done in the expansion of 3 moles of hydrogen reversibly and isothermally at 27 °C from 21.0 litres to 70.3 litres.

SOLUTION :

Formula used

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

Quantities given

$n = 3$ moles $\qquad$ $R = 8.314 \times 10^7$ ergs

$T = 300$ K $\qquad$ $V_1 = 21$ litres $\qquad$ $V_2 = 70.3$ litres

Substitution of values

$$w = 2.303 \times 3\text{ moles} \times 8.314 \times 10^7\text{ ergs} \times 300\text{ K} \times \log \frac{70.3\text{ lit}}{21\text{ lit}}$$
$$= 17232.43 \times 10^7\text{ erg} \times \log \frac{70.3}{21}$$
$$= 17232.43 \times 10^7\text{ erg} \times \log 3.3490$$
$$= 17232.43 \times 10^7\text{ erg} \times 0.5249$$
$$= \mathbf{9045.30 \times 10^7\ ergs}$$

SOLVED PROBLEM 6. Heat supplied to a Carnot engine is 1897.86 kJ. How much useful work can be done by the engine which works between 0 °C and 100 °C ?

SOLUTION :

Formula used

$$\frac{w}{q_2} = \frac{T_2 - T_1}{T_2}$$

or

$$w = q_2 \times \frac{T_2 - T_1}{T_2}$$

Quantities given

$q_2 = 1897.86$ kJ $\qquad$ $T_2 = 100 + 273 = 373$ K $\qquad$ $T_1 = 0 + 273 = 273$ K

Substitution of values

$$w = 1897.86\text{ kJ} \times \frac{373\text{ K} - 273\text{ K}}{373\text{ K}}$$

$$= 1897.86 \text{ kJ} \times \frac{100}{373}$$

$$= \mathbf{508.81 \text{ kJ}}$$

SOLVED PROBLEM 7. A Carnot's engine works between the temperatures 27°C and 127°C. Calculate the efficiency of the engine.

SOLUTION :

Formula used :

$$\textit{Efficiency}, \eta = \frac{T_2 - T_1}{T_2}$$

Quantities given

$T_1 = 27 + 273 = 300 \text{ K}$ $\qquad$ $T_2 = 127 + 273 = 400 \text{ K}$

Substitution of values

$$\text{Efficiency}, \eta = \frac{400 \text{ K} - 300 \text{ K}}{400 \text{ K}}$$

$$= \frac{100}{400}$$

$$= \mathbf{0.25 \ \text{or} \ 25\%}$$

SOLVED PROBLEM 8. Calculate the work done on the system if one mole of an ideal gas at 300 K is compressed isothermally and reversibly to one-fifth of its original volume.

SOLUTION :

Formula used

$$w = 2.303 \times n R T \ \log \frac{V_2}{V_1}$$

Quantities given

$n = 1 \text{ mole}$ $\qquad$ $R = 8.314 \times 10^7 \text{ ergs}$ $\qquad$ $T = 300 \text{ K}$

$V_1 = \text{V litres}$ $\qquad$ $V_2 = \frac{\text{V}}{5} \text{ litres}$

Substitution of values

$$w = 2.303 \times 1 \text{ mole} \times 8.314 \times 10^7 \text{ ergs} \times 300 \text{ K} \times \log \frac{\text{V}}{5 \times \text{V}}$$

$$= 5744.14 \times 10^7 \text{ ergs} \times \log \frac{1}{5}$$

$$= 5744.14 \times 10^7 \text{ ergs} \times (-0.6990)$$

$$= \mathbf{-4015.15 \times 10^7 \text{ ergs}}$$

SOLVED PROBLEM 10. Two moles of an ideal gas undergo isothermal reversible expansion from 15 litres to 30 litres at 300 K. Calculate the work done and change in entropy.

SOLUTION :

(i) To calculate the work done

Formula used

$$w = 2.303 \times n R T \ \log \frac{V_2}{V_1}$$

Quantities given

$n_2 = 2 \text{ moles}$ $\qquad$ $R = 1.987 \text{ cal K}^{-1} \text{ mol}^{-1}$ $\qquad$ $T = 300 \text{ K}$

$V_1 = 15 \text{ litres}$ $\qquad$ $V_2 = 30 \text{ litres}$

Substitution of values

$$w = 2.303 \times 2 \text{ mole} \times 1.987 \text{ cal K}^{-1} \text{ mol}^{-1} \times 300 \times \log \frac{30 \text{ lit}}{15 \text{ lit}}$$

$$= 2745.637 \text{ cal} \times \log 2$$
$$= 2745.637 \text{ cal} \times 0.3010$$
$$= \mathbf{826.4 \text{ cal}}$$

(ii) To calculate the change in entropy

Formula used

$$\Delta S = \frac{q}{T}$$

Quantities given

q = 826.4 cal

T = 300 K

Substitution of values

$$\Delta S = \frac{826.4 \text{ cal}}{300 \text{ K}}$$
$$= \mathbf{2.755 \text{ cal K}^{-1}}$$

SOLVED PROBLEM 11. Water boils at 373 K at one atm pressure. At what temperature will it boil at a hill station where the atmospheric pressure in 500 mm. Hg. (Latent heat of vaporisation of water is 2.3 kJg^{-1} and R = 8.314 J K^{-1} mol^{-1}).

SOLUTION :

Formula used

$$\log \frac{p_2}{p_1} = \frac{\Delta H}{2.303 R} \left[\frac{1}{T_1} - \frac{1}{T_2}\right]$$

Quantities given

p_2 = 500 mm

p_1 = 760 mm

R = 8.314 JK^{-1} mol^{-1}

Latent heat of vaporisation of water = 2.3 kJg^{-1} = 2300 J g^{-1}

T_1 = 373 K

Substitution of values

$$\log \frac{500 \text{mm}}{760 \text{mm}} = \frac{2300 \text{ Jg}^{-1} \times 18 \text{ g mol}^{-1}}{2.303 \times 8.314 \text{ JK}^{-1} \text{ mol}^{-1}} \left[\frac{1}{373} - \frac{1}{T_2}\right]$$

$$-0.1818 = 2162.2025 \left[\frac{1}{373} - \frac{1}{T_2}\right]$$

$$-0.1818 = \frac{2162.2025}{373} - \frac{2162.2025}{T_2} \text{ K}$$

or
$$\frac{2162.2025}{T_2} = 5.796 + 0.1818$$
$$= 5.9785 \text{ K}$$

or
$$T_2 = \frac{2162.2025}{5.97858} \text{ K}$$
$$= \mathbf{361.65 \text{ K}}$$

SOLVED PROBLEM 12. Calculate the work performed when 4 moles of an ideal gas expand isothermally and reversibly at 25 °C from 15 to 20 dm^3. (R = 8.314 JK^{-1} mol^{-1}).

SOLUTION :

Formula used

$$w = 2.303 \times n R T \log \frac{V_2}{V_1}$$

Quantities given

$n = 4$ moles $\qquad R = 8.314\ \text{JK}^{-1}\ \text{mol}^{-1} \qquad T = 25 + 273 = 298\ \text{K}$

$V_1 = 15\ \text{dm}^3 \qquad V_2 = 20\ \text{dm}^3$

Substitution of values

$$\begin{aligned} w &= 2.303 \times 4\ \text{mole} \times 8.314\ \text{JK}^{-1}\ \text{mol}^{-1} \times 298\ \text{K} \times \log \frac{20\ \text{dm}^3}{15\ \text{dm}^3} \\ &= 22823.39\ \text{J} \times \log \frac{4}{3} \\ &= 22823.39\ \text{J} \times 0.1250 \\ &= 2852.92\ \text{J} \\ &= \mathbf{2.85292\ kJ} \end{aligned}$$

SOLVED PROBLEM 13. An engine operates between 100 °C and 0 °C and another engine operates between 100 °C and 0 K (absolute zero). Find the efficiency in two cases.

SOLUTION :

(i) For engine A operating between 100 °C and 0 °C

Formula used

$$\eta = \frac{T_2 - T_1}{T_2}$$

Quantities given

$T_2 = 100 + 273 = 373\ \text{K} \qquad T_1 = 0 + 273 = 273\ \text{K}$

Substitutions of values

$$\begin{aligned} \eta &= \frac{373\ \text{K} - 273\text{K}}{373\ \text{K}} \\ &= \frac{100}{373} \\ &= 0.268 \quad \text{or} \quad 26.8\% \end{aligned}$$

(ii) For engine B operating between 100 °C and 0 K

Formula used

$$\eta = \frac{T_2 - T_1}{T_1}$$

Quantities given

$T_2 = 100 + 273 = 373\ \text{K} \qquad T_1 = 0\ \text{K}$

Substitution of values

$$\begin{aligned} \eta &= \frac{373\ \text{K} - 0\ \text{K}}{373\ \text{K}} \\ &= \frac{373}{373} \\ &= 1 \quad \text{or} \quad 100\% \end{aligned}$$

SOLVED PROBLEM 14. Two moles of hydrogen are compressed adiabatically from NTP conditions to occupy a volume of 4.48 litre. Calculate the final pressure and temperature. (γ_1 = 1.41)

SOLUTION :

(i) To calculate the final pressure

Formula used

$$P_1 V_1^{\gamma} = P_2 V_2^{\gamma} \quad \text{or} \quad \frac{P_1}{P_2} = \left(\frac{V_2}{V_1}\right)^{\gamma}$$

Quantities given

P_1 = 1 atm T_1 = 273 K γ = 1.41

V_1 = 44.8 litre V_2 = 4.48 litre

Substitution of values

$$\frac{1 \text{ atm}}{P_2} = \left(\frac{4.48 \text{ litre}}{44.8 \text{ litre}}\right)^{1.41 \text{ atm}}$$

$$\frac{1}{P_2} = \left(\frac{1}{10}\right)^{1.41 \text{ atm}}$$

or $$P_2 = 10^{1.41}$$

Taking logarithms

$$\log P_2 = 1.41 \times \log 10$$

$$\log P_2 = 1.41 \text{ atm} \qquad [\because \log 10 = 1]$$

or $$P_2 = \text{Antilog } 1.41 \text{ atm}$$

$$= \mathbf{25.7\ atm}$$

(ii) To calculate the final temperature

Formula used

$$P_2 V_2 = n R T_2 \quad \text{or} \quad T_2 = \frac{P_2 V_2}{nR}$$

Quantities given

n = 2 moles R = 0.0820 atm lit K^{-1} mol^{-1}

P_2 = 25.7 atm V_2 = 4.48 litre

Substitution of values

$$T_2 = \frac{25.7 \text{ atm} \times 4.48 \text{ lit}}{0.0820 \text{ atm lit K}^{-1} \text{ mol}^{-1} \times 2 \text{ mol}}$$

$$= 702.1 \text{ K}$$

$$= 702.1 - 273$$

$$= \mathbf{429.1\ °C}$$

SOLVED PROBLEM 15. Calculate the change in free energy for the expansion of one mole of an ideal gas from 2.0 atm to 0.2 atm at 25 °C ($R = 8.314\ \text{JK}^{-1}\ \text{mol}^{-1}$).

SOLUTION :

Formula used

$$\Delta G = 2.303 \times n\,R\,T \log \frac{P_2}{P_1}$$

Quantities given

$n = 1$ mole $\quad T = 298$ K $\quad R = 8.314\ \text{J K}^{-1}\ \text{mol}^{-1}$

$P_1 = 2$ atm $\quad P_2 = 0.2$ atm

Substitution of values

$$\Delta G = 2.303 \times 1\ \text{mole} \times 8.314\ \text{JK}^{-1}\ \text{mol}^{-1} \times 298\ \text{K} \times \log \frac{0.2\ \text{atm}}{2.0\ \text{atm}}$$

$$\Delta G = 5705.848\ \text{J} \times \log \frac{1}{10}$$

$$= 5705.8483\ \text{J} \times (-1.0)$$

$$= \mathbf{-5705.8483\ J}$$

SOLVED PROBLEM 16. For the reaction $H_{2(g)} + \frac{1}{2}\, O_{2\,(g)} \longrightarrow H_2O_{(l)}$ the values of enthalpy change and free energy change are – 68.32 and – 56.69 kcal respectively at 25 °C. Calculate the value of free energy change at 30 °C.

SOLUTION :

(i) To calculate $\left[\dfrac{\delta\,(\Delta G)}{\delta\,T}\right]_P$

Formula used

$$\Delta G = \Delta H + T\left[\frac{\delta\,(\Delta G)}{\delta T}\right]_P$$

Quantities given

$\Delta G = -56.69$ kcal $\quad \Delta H = -68.32$ kcal $\quad T = 25 + 273 = 298$ K

Substitution of values

$$-56.69\ \text{kcal} = -68.32\ \text{kcal} + 298\ \text{K}\left[\frac{\delta\,(\Delta G)}{\delta T}\right]_P$$

or

$$\left[\frac{\delta\,(\Delta G)}{\delta T}\right]_P = \frac{-56.69\ \text{kcal} + 68.32\ \text{kcal}}{298\ \text{K}}$$

$$= \frac{11.630\ \text{kcal}}{298\ \text{K}}$$

$$= 0.0390\ \text{kcal K}^{-1}$$

(ii) To calculate ΔG at 30 °C

Assuming that $\left[\dfrac{\delta\,(\Delta G)}{\delta T}\right]_P$ remains constant over this temperature range.

Formula used

$$\Delta G = \Delta H + T\left[\frac{\delta\,(\Delta G)}{\delta T}\right]_P$$

Quantities given

$\Delta H = -68.32$ kcal $\quad T = 30 + 273 = 303$ K $\quad \left[\dfrac{\delta\,(\Delta G)}{\delta T}\right]_P = 0.0390\ \text{kcal K}^{-1}$

Substitution of values

$$\Delta G = -68.32\ \text{kcal} + 303\ \text{K} \times 0.0390\ \text{kcal K}^{-1}$$

$$= -68.32 \text{ kcal} + 11.817 \text{ kcal}$$

$$= \mathbf{-57.15\ kcal.}$$

SOLVED PROBLEM 17. 1.0 mole of steam is condensed at 100°C and water is cooled to 0 °C and frozen to ice. Calculate the entropy change for the process. Latent heat of fusion and evaporation of ice and water are 80 and 540 cal/g respectively.

SOLUTION :

(i) To calculate the entropy change for 1 mole of steam of 100 °C to water at 100 °C

Formula used

$$\Delta S_1 = \frac{\Delta H_v}{T_b}$$

Quantities given

$\Delta H_v = 540 \text{ cal g}^{-1} \times 18 \text{ g}$ $\qquad T_b = 373 \text{ K}$

Substitution of values

$$\Delta S_1 = \frac{540 \text{ cal g}^{-1} \times 18 \text{ g mol}^{-1}}{373 \text{ K}} = 26.06 \text{ cal K}^{-1} \text{mol}^{-1}$$

(ii) To calculate entropy change for 1 mole of water at 100 ºC to water at 0 ºC

Formula used

$$\Delta S_2 = C_p \times 2.303 \times \log \frac{T_2}{T_1}$$

Quantities given

$T_1 = 373 \text{ K}$ $\qquad T_2 = 273 \text{ K}$ $\qquad C_p = 18 \text{ cal K}^{-1} \text{ mol}^{-1}$

Substitution of values

$$\Delta S_2 = 18 \text{ cal K}^{-1} \text{ mol}^{-1} \times 2.303 \times \log \frac{273 \text{ K}}{373 \text{ K}}$$

$$= 41.45 \text{ cal K}^{-1} \text{mol}^{-1} \times (-0.1355)$$

$$= -5.617 \text{ cal K}^{-1} \text{ mol}^{-1}$$

(iii) To calculate entropy change for 1 mole of water at 0 ºC to ice at 0 ºC

Formula used

$$\Delta S_3 = \frac{\Delta H_f}{T_f}$$

Quantities given

$\Delta H_f = 80 \text{ cal g}^{-1} \times 18 \text{ g mol}^{-1}$ $\qquad T_f = 273 \text{ K}$

Substitution of values

$$\Delta S_3 = \frac{80 \text{ cal g}^{-1} \times 18 \text{ g mol}^{-1}}{273 \text{ K}}$$

$$= \mathbf{5.275\ cal\ K^{-1}\ mol^{-1}}$$

Total entropy change

$$\Delta S = \Delta S_1 + \Delta S_2 + \Delta S_3$$

$$\Delta S = 26.06 \text{ cal K}^{-1} \text{ mol}^{-1} + (-5.618 \text{ cal K}^{-1} \text{ mol}^{-1}) + 5.274 \text{ cal K}^{-1} \text{ mol}^{-1}$$

$$= \mathbf{25.717\ cal\ K^{-1}\ mol^{-1}}$$

SOLVED PROBLEM 18. 5.0 moles of an ideal gas ($C_v = 5/2\ R$) are allowed to expand adiabatically and reversibly at 300 K from a pressure of 10 atm to 1 atm. Calculate the final temperature and work done by the gas.

SOLUTION :

(i) To calculate the final temperature

Formula used

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

Quantities given

$T_1 = 300\text{ K}$ $P_1 = 10\text{ atm}$ $P_2 = 1\text{ atm}$ $\gamma = 1.4$

Substitution of values

$$\frac{T_2}{300\text{ K}} = \left(\frac{10}{1}\right)^{\frac{1-1.4}{1.4}}$$

or

$$T_2 = 300\text{ K} \times 10^{-\frac{0.4}{1.4}}$$

Taking logarithms

$$\log T_2 = \log 300 + \left(\frac{-0.4}{1.4}\right) \log 10$$

$$= 2.4771 - 0.2857$$

$$= 2.1914$$

Taking antilogarithms

$$T_2 = \text{Antilog } 2.1914$$

$$= \mathbf{155.38\ K}$$

(ii) To calculate the work done in an adiabatic process

Formula used

$$w = C_v\,(T_2 - T_1)$$

$$= \frac{5}{2} R \times (T_2 - T_1)$$

Quantities given

$R = 8.314\text{ JK}^{-1}\text{ mol}^{-1}$ $T_2 = 155.38\text{ K}$ $T_1 = 300\text{ K}$

Substitution of values

$$w = \frac{5}{2} \times 8.314\text{ JK}^{-1}\text{ mol}^{-1} \times (155.38 - 300)\text{ K}$$

$$= \mathbf{-3005.93\ J}$$

SOLVED PROBLEM 19. Calculate the entropy increase in the evaporation of a mole of water at 100 °C. (Heat of vaporisation = 540 cal g^{-1})

SOLUTION :

Formula used

$$\Delta S_v = \frac{\Delta H_v}{T_b}$$

Quantities given

$\Delta H_v = 540\text{ cal g}^{-1} = 540\text{ cal g}^{-1} \times 18\text{ g mol}^{-1}$ $T_b = 100 + 273 = 373\text{ K}$

Substitution of values

$$\Delta H_v = \frac{540 \times 18\text{ cal mol}^{-1}}{373\text{ K}}$$

$$= \mathbf{26.06\ cal\ K^{-1}\ mol^{-1}}$$

SOLVED PROBLEM 20. Calculate ΔS when 28 gm of N_2 gas expand reversibly from 2 litres to 20 litres at 27 °C.

SOLUTION :

Formula used

$$\Delta S = 2.303 \times nR \log \frac{V_2}{V_1}$$

Quantities given

$n = \dfrac{28 \text{ g}}{14 \text{ g mol}^{-1}} = 2$ moles $R = 8.314 \text{ JK}^{-1}\text{mol}^{-1}$

$V_1 = 2$ litres $V_2 = 20$ litre

Substitution of values

$$\Delta S = 2.303 \times 2 \text{ mole} \times 8.314 \text{ J K}^{-1} \text{ mol}^{-1} \log \frac{20 \text{ lit}}{2 \text{ lit}}$$

$$= 38.294 \text{ J K}^{-1} \times \log 10$$

$$= \mathbf{38.294 \text{ J K}^{-1}} \qquad [\because \log 10 = 1]$$

SOLVED PROBLEM 21. Calculate the entropy change in transforming 24 g of Ice into water at 0 °C. Molar heat of fusion = 6009 J mol^{-1}.

SOLUTION :

Formula used

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

Quantities given

$\Delta H_f = 6009 \text{ J mol}^{-1}$ $T_f = 273$ K

ΔH_f for 24 g of water $= \dfrac{24}{18} \times 6009 \text{ J} = 8012$ J

Substitution of values

$$\Delta S_f = \frac{8012 \text{ J}}{273 \text{ K}} = \mathbf{29.3480 \text{ JK}^{-1}}$$

SOLVED PROBLEM 22. The enthalpy change for the transition of liquid water to steam is 40.8 KJmol^{-1} at 373 K. Calculate ΔG for the process.

SOLUTION :

Formula used

$$\Delta S_v = \frac{\Delta H_v}{T_b}$$

Quantities given

$\Delta H_v = 40.8 \text{ kJ mol}^{-1} = 40800 \text{ J mol}^{-1}$ $T_b = 373$ K

Substitution of values

$$\Delta S_v = \frac{40800 \text{ J mol}^{-1}}{373 \text{ K}}$$

$$= \mathbf{109.38 \text{ JK}^{-1} \text{ mol}^{-1}}$$

SOLVED PROBLEM 23. For the reaction

$$Ag_2O_{(s)} \longrightarrow 2\,Ag_{(s)} + \tfrac{1}{2}O_{2\,(g)}$$

calculate the temperature at which free energy change is equal to zero. ΔH for the reaction is + 30.50 kJ mol^{-1} and ΔS is 0.066 kJ K^{-1} mol^{-1} at 1 atm pressure. Predict the nature of the reaction (i) below this temperature and (ii) above this temperature.

SOLUTION :

Formula used

$$\Delta G = \Delta H - T\Delta S \qquad [\because \Delta G = 0]$$

or

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

Quantities given

$\Delta H = 30.50$ kJ K^{-1} mol^{-1} $\qquad$ $\Delta S = 0.066$ kJ K^{-1} mol^{-1}

Substitution of values

$$T = \frac{30.50 \text{ kJ mol}^{-1}}{0.066 \text{ kJ mol}^{-1}\text{ K}^{-1}}$$

$$= \mathbf{462\ K}$$

(i) At temperature below 463 K $\Delta H > T\Delta S$ and

$\therefore$ ΔG = + ve. The reaction is **non - spontaneous**

(ii) At temperature above 463 K $\Delta H < T\Delta S$ and

$\therefore$ ΔG = – ve. The reaction is **spontaneous.**

SOLVED PROBLEM 24. Calculate the entropy change for the following reversible processes :

(i) 1 mole of liquid water at 1 atm and at 100 °C evaporates to 1 mole water vapour at 1 atm at 100 °C (ΔH_{Vap} for H_2O = 2257 J g^{-1})

(ii) 1 mole of *a*-tin at 1 atm pressure and 13 °C changes to 1 mole of *b*-tin at 1 atm and 13 °C. $\Delta H_{transition}$ (Sn) = 2090 J mol^{-1})

SOLUTION :

(i)

$$H_2O_{(l)} \longrightarrow H_2O_{(g)}$$

Formula used

$$\Delta S_{Vap} = \frac{\Delta H_{Vap}}{T_b}$$

Quantities given

ΔH_v = 40.626 kJ mol^{-1} $\qquad$ T_b = 373 K

Substitution of values

$$\Delta S_{Vap} = \frac{40.626 \text{ kJ mol}^{-1}}{373 \text{ K}}$$

$$= \mathbf{108.916\ JK^{-1}\,mol^{-1}}$$

(ii)

$$a\text{ - tin} \longrightarrow b\text{ - tin}$$

Formula used

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

Quantities given

$\Delta H_{transition}$ = 2090 J mol^{-1} $\qquad$ $T_{transition}$ = 13 + 273 = 286 K

Substitution of values

$$\Delta S_{transition} = \frac{2090\ \text{J mol}^{-1}}{286\ \text{K}}$$

$$= \mathbf{7.30\ J\ K^{-1}\ mol^{-1}}$$

SOLVED PROBLEM 25. For the reaction

$$M_2O_{(s)} \longrightarrow 2\,M_{(s)} + ½\,O_{2\,(g)}$$

$\Delta H = 30$ kJ mol^{-1} and $\Delta S = 0.07$ kJ K^{-1} mol^{-1} at 1 atm pressure. Calculate upto which temperature the reaction would not be spontaneous.

SOLUTION :

Formula used

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

or $$T = \frac{\Delta H}{\Delta S} \qquad \left[\because \Delta G = 0 \text{ at Equilibrium}\right]$$

Quantities given

$\Delta H = 30$ kJ mol^{-1} $\qquad \Delta S = 0.07$ kJ JK^{-1} mol^{-1}

Substitution of values

$$T = \frac{30\ \text{kJ mol}^{-1}}{0.07\ \text{kJ K}^{-1}\text{mol}^{-1}}$$

$$= \mathbf{428.57\ K}$$

Thus the reaction would not be spontaneous up to 428.57 K

SOLVED PROBLEM 26. Predict whether at 27 ºC, the following reaction is spontaneous or not :

$$4\,NH_{3\,(g)} + 5\,O_{2\,(g)} \longrightarrow 4\,NO_{(g)} + 6\,H_2O_{(l)}$$

Given $\Delta H = +9080$ J mol^{-1} and $\Delta S = +35.7$ JK^{-1} mol^{-1}.

SOLUTION :

Formula used

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

Quantities given

$\Delta H = 9080$ J mol^{-1} $\qquad T = 27 + 273 = 300$ K $\qquad \Delta S = 35.7$ J mol^{-1} K^{-1}

Substitution of values

$$\Delta G = 9080\ \text{J mol}^{-1} - 300\ \text{K} \times 35.7\ \text{J mol}^{-1}\ \text{K}^{-1}$$

$$= 9080\ \text{J mol}^{-1} - 10710\ \text{J mol}^{-1}$$

$$= \mathbf{-1630\ J\ mol^{-1}}$$

Since ΔG = – ve, the reaction is spontaneous.

SOLVED PROBLEM 27. What is the equilibrium constant K for the reaction

$$2\,NOCl \longrightarrow 2\,NO + Cl_2$$

at 27 °C if at this temperature ΔH and ΔS are 10 kJ mol^{-1} and 122 JK^{-1} mol^{-1} respectively ?

($R = 8.314$ JK^{-1} mol^{-1})

SOLUTION :

(i) To calculate the value of ΔG

Formula used

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

Quantities given

$\Delta H = 70 \text{ kJ mol}^{-1} = 70000 \text{ J mol}^{-1}$ $\qquad T = 27 + 273 \text{ K} = 300 \text{ K}$

$\Delta S = 122 \text{ JK}^{-1} \text{mol}^{-1}$

Substitution of values

$$\begin{aligned} \Delta G &= 70000 \text{ J mol}^{-1} - 300 \text{ K} \times 122 \text{ J mol}^{-1} \\ &= 70000 \text{ J mol}^{-1} - 36600 \text{ J mol}^{-1} \\ &= 33400 \text{ J mol}^{-1} \end{aligned}$$

(ii) To calculate the equilibrium constant K

Formula used

$$\Delta G = -2.303\, R\, T \log K$$

Quantities given

$\Delta G = 33400 \text{ J mol}^{-1}$ $\qquad R = 8.314 \text{ JK}^{-1} \text{mol}^{-1}$ $\qquad T = 27 + 273 = 300 \text{ K}$

Substitution of values

$$\begin{aligned} 33400 \text{ J mol}^{-1} &= -2.303 \times 8.314 \text{ JK}^{-1} \text{ mol}^{-1} \times 300 \text{ K} \times \log K \\ 33400 \text{ J mol}^{-1} &= -5744.14 \text{ J mol}^{-1} \times \log K \end{aligned}$$

or
$$\begin{aligned} \log K &= -\frac{33400 \text{ J mol}^{-1}}{5744.14 \text{ J mol}^{-1}} \\ &= -5.8146 \end{aligned}$$

or
$$K = \text{Antilog}\,(-5.8146)$$

or
$$= \mathbf{1.532 \times 10^{-6}}$$

SOLVED PROBLEM 28. Calculate the equilibrium constant at 25 ºC for the reaction

$$H_2 + I_2 \longrightarrow 2\,HI$$

if standard free energy of formation of HI is 1.30 kJ mol^{-1} mol^{-1} ($R = 8.314 \text{ JK}^{-1} \text{ mol}^{-1}$)

SOLUTION :

(i) To calculate ΔG for the reaction

$$H_2 + I_2 \longrightarrow 2\,HI$$

$$\begin{aligned} \Delta G^o &= \Delta G^o_{f\ (products)} - \Delta G^o_{f\ (Reactants)} \\ &= [2 \times \Delta G^o_{f(HI)}] - [\Delta G^o_{f(H_2)} + \Delta G^o_{f\ (I_2)}] \\ &= 2 \times 1.30 \text{ kJ mol}^{-1} - [0 + 0] \\ &= 2.60 \text{ kJ mol}^{-1} \\ &= 2.60 \times 128 \text{ kJ} \qquad [\because 1 \text{ mol}^{-1} = 128 \text{ g of HI}] \\ &= 332.8 \text{ kJ} \end{aligned}$$

(ii) To calculate the equilibrium constant K

Formula used

$$\Delta G = -2.303\, R\, T \log K$$

Quantities given

$\Delta G = 332.8 \text{ kJ}$ $\qquad R = 8.314 \text{ JK}^{-1} \text{ mol}^{-1} = 8.314 \times 10^{-3} \text{ kJ K}^{-1} \text{mol}^{-1}$

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

Substitution of values

$$332.8 \text{ kJ} = -2.303 \times 8.314 \times 10^{-3} \text{ kJK}^{-1} \text{ mol}^{-1} \times 298 \text{ K} \times \log K$$

or $$\log K = \frac{-332.8}{2.303 \times 8.314 \times 10^{-3} \times 298}$$

$$= -5.833 \times 10^{-2+3}$$

$$= -58.33$$

or $$K = \text{Antilog} - 58.33$$

$$= \mathbf{4.677 \times 10^{-59}}$$

SOLVED PROBLEM 29. For the reaction at 298 K

$$A_{(g)} + B_{(g)} \longrightarrow C_{(g)}$$

given that $\Delta E = -5$ kcal and $\Delta S = -10$ cal K^{-1}. Calculate ΔG for the reaction and predict whether the reaction may occur spontaneously.

SOLUTION :

Formula used

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

or $$\Delta G = \Delta E + \Delta n R T - T\Delta S \qquad [\because \Delta H = \Delta E + \Delta nR T]$$

Quantities given

$\Delta G = n_P - n_R = 1 - 2 = -1$ mol $\qquad \Delta E = -5$ k cal $= -5000$ cal

$R = 1.987$ cal K^{-1} mol^{-1} $\qquad T = 25 + 273 = 298$ K

Substitution of values

$$\Delta G = -5000 \text{ cal} + (-1 \text{ mol}) \times 1.987 \text{ cal K}^{-1} \text{ mol}^{-1} \times 298 \text{ K} - 298 \text{ K} (-10) \text{ cal}$$

$$= -5000 \text{ cal} - 592.13 \text{ cal} + 2980 \text{ cal}$$

$$= \mathbf{-2612.13 \text{ cal}}$$

Since ΔG is – ve, the reaction is spontaneous.

ADDITIONAL PRACTICE PROBLEMS

1. Calculate the efficiency of steam engine operating between 100 ºC and 25 ºC. What would be the efficiency of the engine if the boiler temperature is raised to 150 ºC, the temperature of the sink remaining same ?

   Answer. 22.1% ; 29.55%

2. Calculate the amount of the heat supplied to Carnot cycle working between 105 ºC and 20 ºC if the maximum work obtained is 200 cal ?

   Answer. 889.4 cal

3. Predict whether at 27 ºC the following reaction is spontaneous or not :

   $$4 \text{ NH}_{3\ (g)} + 5 \text{ O}_{2\ (g)} \longrightarrow 4 \text{ NO}_{(g)} + 6 \text{ H}_2\text{O}_{(l)}$$

   Given $\Delta H = +9080$ J mol^{-1} and $\Delta S = +35.7$ J K^{-1} mol^{-1}.

   Answer. Spontaneous

4. Calculate entropy change for the reaction

   $$A_{(s)} \longrightarrow B_{(s)} + C_{(s)}$$

   if absolute entropies (JK^{-1} mol^{-1}) are A = 130, B = 203 and C = 152

   Answer. 225 J K^{-1} mol^{-1}

5. Calculate the free energy change for the dissociation of KNO_3 in water at 298 K

   $$\text{KNO}_{3\ (s)} + \text{water} \longrightarrow \text{K}^+_{(aq)} + \text{NO}^-_{3\ (aq)}$$

   $\Delta H^o = 34$ kJ mol^{-1} $\qquad \Delta S^o = 0.116$ kJ K^{-1} mol^{-1}

   Answer. 568 J mol^{-1}

6. For the reaction $M_2O_{(s)} \longrightarrow 2M_{(s)} + ½\,O_{2\,(g)}$ $\Delta H = 30$ kJ mol^{-1} and $\Delta S = 0.07$ kJ K^{-1} mol^{-1} (at 1 atm). Calculate up to which temperature reaction would not be spontaneous.

   Answer. 428.57K

7. Ethanol boils at 78.4 ºC and standard enthalpy of vaporisation of ethanol is 42. kJ mol^{-1}. Calculate the entropy of vaporisation of ethanol.

   Answer. 120.66 JK^{-1} mol^{-1}

8. At 0 ºC, ice and water are in equilibrium and $\Delta H = 6.0$ kJ mol^{-1} for the process $H_2O_{(s)} \longrightarrow H_2O_{(g)}$, calculate ΔS for the conversion of ice to fluid water.

   Answer. 201.978 J mol^{-1}

9. What is the entropy change for conversion of one mole of ice to water at 273 K and 1 atm pressure (Given ΔH of ice = 6.025 kJ mol^{-1}).

   Answer. 22.069 J mol^{-1}

10. For the reaction $2\,NO_{(g)} + O_{2\,(g)} \longrightarrow 2\,NO_{(g)}$ calculate ΔG at 700 K when enthalpy and entropy change ΔH and ΔS are – 113.0 kJ mol^{-1} and – 145 JK^{-1} mol^{-1} respectively.

    Answer. – 11.5 kJ mol^{-1}]

11. For the reaction $Ag_2O_{(s)} \longrightarrow 2\,Ag_{(s)} + ½\,O_{2\,(g)}$ calculate the temperature at which free energy change is equal to zero. [$\Delta H = 30.56$ kJ mol^{-1} ; $\Delta S = 0.066$ kJ K^{-1} mol^{-1} at 1 atm pressure]

    Answer. 462 K

12. At 373 K the entropy change for the transition of liquid water to steam is 109 JK^{-1} mol^{-1}. Calculate the enthalpy change ΔH_{vap} for the process.

    Answer. 40.657 kJ mol^{-1}

13. Calculate the entropy change ΔS^o for the following reaction at 298K and 1 atm pressure.

$$2\,CO_{(g)} + O_{2\,(g)} \longrightarrow 2\,CO_{2\,(g)}$$

The absolute entropies (S^o) at 298 K and 1 atm pressure are as follows :

$CO_{2\,(g)} = 213.6$ J K^{-1} mol^{-1} $\quad O_{2\,(g)} = 205.03$ JK^{-1} mol^{-1} $\quad CO_{(g)} = 197.6$ JK^{-1} mol^{-1}

Answer. – 173.030 JK^{-1} mol^{-1}

14. The enthalpy change for the transition of liquid water to steam (ΔH_{vap}) is 40.8 kJ mol^{-1} at 373 K. Calculate the entropy change ΔS_{vap} for this process.

    Answer. 109.38 JK^{-1} mol^{-1}

15. The heat of vaporisation, ΔH_{vap} of carbon tetrachloride, CCl_4, at 25 ºC is 43 kJ mol^{-1}.
    If 1 mole of liquid carbon tetrachloride at 25 ºC has an entropy of 214 JK^{-1}, what is the entropy of 1 mole of the vapour in equilibrium with the liquid at this temperature ?

    Answer. 358 JK^{-1} mol^{-1}

16. If $\Delta G^o_{f\,(MgO)}$ is – 1361 kcal mol^{-1} and $\Delta G^o_{f\,(H_2O)}$ is – 56.7 kcal mol^{-1}, calculate ΔG^o of the reaction $MgO_{(s)} + H_{2\,(g)} \longrightarrow Mg_{(s)} + H_2O_{(l)}$ and predict whether the reaction is spontaneous or not.

    Answer. 79.4 kcal ; No

17. The process $NH_{3\,(g)} + HCl_{(g)} \longrightarrow NH_4Cl_{(s)}$ is exothermic by – 42.1 kcal at 1 atm and 25 ºC. Find ΔG^o for the reaction, given that $S^o_{NH_3} = +46$ cal mol^{-1} K^{-1} ; $S^o_{HCl} = +44.6$ cal K^{-1} mol^{-1} and $S^o_{NH_4Cl} = +22$ cal K^{-1} mol^{-1}. Would the reaction be spontaneous ?

    Answer. – 21.8 kcal ; Yes

18. The enthalpy change involved in oxidation of glucose is – 2880 kJ mol^{-1}. Twenty five percent of this energy is available for muscular work. If 100 kJ of muscular work is needed to walk one kilometer, what is the maximum distance a person will be able to walk after eating 120 g of glucose ?

    Answer. 4.8 km

CHAPTER

10

The Gaseous State and the Kinetic Molecular Theory

KEY CONCEPTS AND EQUATIONS

THE GASEOUS STATE

All matter exist in three states gas, liquid and solid. The behaviour of gases is very important to a chemist. On account of their compressibility and thermal expansion, gases are affected by changes in pressure and temperature. The quantitative effect of change of pressure and temperature is described by Gas Laws.

PRESSURE

It is the force exerted by the impacts of the molecules of a gas per unit surface area. It is measured in **torr** or **mm** Hg or **atmosphere.** The SI unit of pressure is **Pascal (Pa).**

$$1\text{atm} = 760\text{ mm Hg} = 760\text{ torr} = 1.013 \times 10^5\text{ Pa}$$

TEMPERATURE

It is the degree of hotness or coldness of a gas. It determines the average kinetic energy of the gas molecules and is measured in **degrees Celsius.** The absolute temperature is measured in **degrees Kelvin.**

$$K = °C + 273$$

These two scales are represented in Fig 10.1.

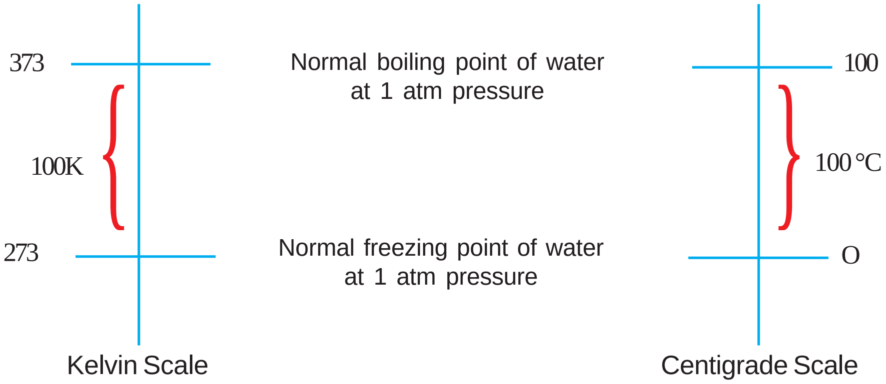


Figure 10.1
Comparison of Celsius and Kelvin Scales.

BOYLE'S LAW

The volume of a given sample of a gas varies **inversely** as its pressure at constant temperature. Mathematically, we can write

$$V \propto \frac{1}{P} \quad \text{or} \quad V = \frac{k}{P} \quad \text{or} \quad PV = k \quad (\text{At constant Temperature})$$

Graphically Boyle's law can be expressed in the following ways :

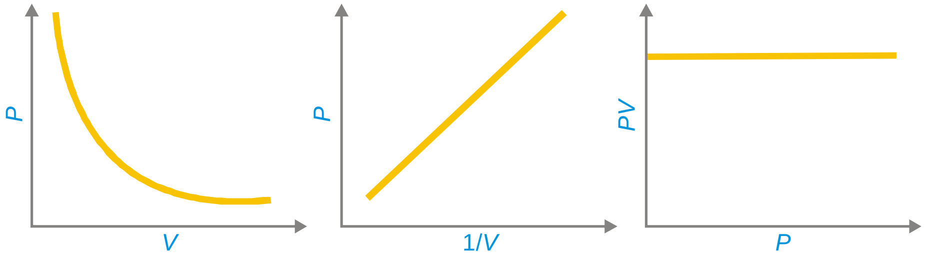


Figure 10.2
Graphical representation of Boyle's law.

CHARLE'S LAW

The volume of a given sample of a gas is **directly** proportional to its Kelvin or absolute temperature at constant pressure. Mathematically, we can write

$$V \propto T \quad \text{or} \quad V = kT \quad \text{or} \quad \frac{V}{T} = k \quad (\text{At constant pressure})$$

Graphically, Charle's law can be represented as

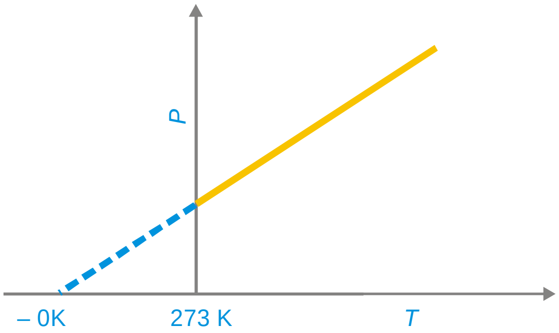


Figure 10.3
Graphical representation of Charle's law.

ABSOLUTE ZERO

The volume of the gas theoratically becomes zero at –273°C or 0 K and this *imaginary* temperature is called **absolute zero** of temperature. In actual practice, the gas changes to liquid or solid before this temperature is attained.

STANDARD CONDITIONS OF TEMPERATURE AND PRESSURE (STP)

The volume of gases present in two different samples can be compared only if these are at same temperature and pressure. For this purpose it is useful to adopt a set of standard conditions of temperature and pressure. By universal agreement, the standard temperature is chosen as 273K (0°C) and the standard pressure as exactly as one atm (760 torr). These conditions of temperature and pressure are referred to as **Standard conditions** or **Standard temperature and pressure (STP).**

AVOGADRO'S LAW

Equal volumes of all gases at same temperature and pressure contain equal number of molecules or moles. Mathematically,

$$V \propto n \quad \text{or} \quad V = A \times n \qquad (T \text{ and } P \text{ constant})$$

where A is a constant of proportionality.

For two gases we have

$$n_1 = n_2 \quad \text{if} \quad V_1 = V_2 \qquad (T \text{ and } P \text{ constant})$$

COMBINED GAS LAWS OR IDEAL GAS EQUATION

The simultaneous effect of change of pressure and temperature of a gas can be studied by combining Boyle's law and Charles' law. The derived new equation is called combined gas law or ideal gas equation.

Boyle's law $$V \propto \frac{1}{P} \qquad (T \text{ constant})$$

Charles' law $$V \propto T \qquad (P \text{ constant})$$

$$\therefore \quad V \propto \frac{T}{P}$$

or $$V = \frac{kT}{P} \quad \text{or} \quad \frac{PV}{T} = k$$

or $$\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}$$

This expression is a mathematical statement of combined gas law. If $T_1 = T_2$, the equation reduces to $P_1V_1 = P_2V_2$ (Boyle's law). Alternatively, if $P_1 = P_2$ the expression becomes $V_1/T_1 = V_2/T_2$ (Charles' law)

THE GAS CONSTANT, R

Besides temperature and pressure, the volume of a gas depends upon the number of moles of the gas. Therefore, the constant k in the combined gas law can be regarded as a product of two factors, one of which is the number of moles of the gas. Therefore, we can write

$$\frac{PV}{T} = k \quad \text{or} \quad \frac{PV}{T} = nR$$

where n is the number of moles of gas and R is a new constant called gas constant. Its value depends upon the units in which P, V and T are expressed.

$$R = 8.314 \text{ JK}^{-1}\text{mol}^{-1} = 8.314 \times 10^7 \text{ ergs K}^{-1}\text{ mol}^{-1}$$
$$= 0.0821 \text{ atm lit k}^{-1}\text{ mol}^{-1} = 1.987 \text{ cal K}^{-1}\text{ mol}^{-1}$$

SOLVING NUMERICAL PROBLEMS ON IDEAL GAS EQUATION

In numerical problems related to ideal gas equation, there are four variables (P, V, T and n). Out of these four, three are generally given and the value of fourth is to be calculated. The temperature must be expressed in absolute temperature scale (in Kelvins). The units of P and V are generally in atmosphere and litre (dm^3). If other units are given for pressure and volume, convert them to atmosphere and litre (dm^3) respectively and use $R = 0.0821$ atm lit K^{-1} mol^{-1}.

DALTON'S LAW OF PARTIAL PRESSURES

The total pressure of a mixture of non-reacting gases is equal to the sum of their partial pressures. Mathematically,

$$P_{Total} = p_A + p_B + p_C + \text{...........} \qquad (V \text{ and } T \text{ are constant})$$

where p_A, p_B, p_C .... etc. are the partial pressures of gases A, B, C .... respectively. The ideal gas equation $P\,V = n\,R\,T$ can be applied to each gas separately and we can write.

$$p_A = n_A \frac{RT}{V} \qquad p_B = n_B \frac{RT}{V} \qquad p_C = n_C \frac{RT}{V}$$

where n_A, n_B and n_C are number of moles of gases A, B and C respectively. The total pressure of gaseous mixture is

$$\begin{aligned} P_{Total} &= n_A \frac{RT}{V} + n_B \frac{RT}{V} + n_C \frac{RT}{V} + \text{...........} \\ &= (n_A + n_B + n_C + \text{...........}) \frac{RT}{V} \\ &= n_{Total} \frac{RT}{V} \end{aligned}$$

GRAHAM'S LAW OF DIFFUSION

The rate of diffusion of a gas is inversely proportional to the square root of its density. Mathematically,

$$r \propto \sqrt{\frac{1}{d}}$$

For two gases A and B, under identical conditions

$$\frac{r_A}{r_B} = \sqrt{\frac{d_B}{d_A}}$$

or in terms of molecular masses

$$\frac{r_A}{r_B} = \sqrt{\frac{\textit{molecular mass of gas B}}{\textit{molecular mass of gas A}}} \qquad [\because \; VD = 2 \times \textit{Mol. mass}]$$

THE MOLAR GAS VOLUME

The volume occupied by one mole of a gas at standard temperature and pressure is its molar volume. At STP one mole of a gas occupies volume equal to 22.4 lit (or dm^3) *i.e.*

Volume of one mole of a gas at STP = 22.4 litre.

RELATIONSHIPS DERIVED FROM KINETIC MOLECULAR THEORY OF GASES

If N molecules of a gas, each of mass m are enclosed in a container of volume V, the pressure exerted by the gas molecules derived from kinetic molecular theory is related by the equation

$$PV = \frac{1}{3}\, m\, N\, \mu^2$$

where μ is the **root mean square velocity**. It is defined as the imaginary velocity when all the gas molecules would possess if the total kinetic energy is equally divided among them. For n molecules having velocities v_1, v_2, v_3 ...., the root mean square velocity is given by

$$\mu = \sqrt{\frac{v_1^2 + v_2^2 + v_3^2 + \text{.....}}{N}}$$

$$= \sqrt{\frac{3RT}{M}} = \sqrt{\frac{3PV}{M}} = \sqrt{\frac{3P}{D}} \qquad \left[\because \; RT = PV \text{ and } M/V = D\right]$$

The **average velocity** is given by

$$\overline{v} = \frac{v_1 + v_2 + v_3 + \ldots\ldots\ldots\ldots\ldots}{N}$$

$$= \sqrt{\frac{8RT}{\pi M}} = \sqrt{\frac{8PV}{\pi M}} = \sqrt{\frac{8P}{D}}$$

The **most probable velocity** is the velocity possessed by maximum number of molecules of a gas. It is given by

$$\mu_{mp} = \sqrt{\frac{2RT}{M}} = \sqrt{\frac{2PV}{M}} = \sqrt{\frac{2P}{D}}$$

RELATION BETWEEN AVERAGE VELOCITY, ROOT MEAN SQUARE VELOCITY AND MOST PROBABLE VELOCITY

$$\overline{v} : \mu : \mu_{mp} = \sqrt{\frac{8RT}{\pi M}} : \sqrt{\frac{3RT}{M}} : \sqrt{\frac{2RT}{M}}$$

$$= 1.128 : 1.224 : 1$$

AVERAGE KINETIC ENERGY OF A GAS

The kinetic molecular gas equation is

$$PV = {}^{1}\!/_{3}\, m N \mu^2 = {}^{2}\!/_{3}\, N \times {}^{1}\!/_{2}\, m \mu^2 = {}^{2}\!/_{3}\, N \times e$$

where e is the average kinetic energy of a single molecule

or $PV = {}^{2}\!/_{3}\, E$ or $nRT = {}^{2}\!/_{3}\text{E}$ or $E = {}^{3}\!/_{2}\, nRT$

where E is the total kinetic energy of N molecules.

COLLISION PROPERTIES

Mean Free Path

The mean distance travelled by a molecule between two successive collisions is the mean free path. It is related to the coefficient of viscosity of the gas by the relation

$$\lambda = \eta \sqrt{\frac{3}{PD}}$$

where P is the pressure of the gas, D the density and η the coefficient of viscosity of the gas.

Collision Frequency

The number of molecular collisions taking place per second per unit volume of the gas is called collision frequency. It is denoted by Z and is given by the relation.

$$Z = \frac{\pi \; \overline{v} \; \sigma^2 \; \overline{N}^2}{\sqrt{2}}$$

where $\overline{v}$ is the average velocity, σ the molecular diameter and $\overline{N}$ the number of molecules of the gas per cm^3.

MOLAR HEAT CAPACITIES OF IDEAL GASES

Specific Heat

It is the amount of heat required to raise the temperature of one gram of a substance through 1°C.

Molar Heat Capacity

It is the amount of heat required to raise the temperature of one mole of a gas through 1°C. Thus

$$\text{Molar Heat Capacity} = \text{Specific heat} \times \text{molecular mass of the gas}$$

Molar Heat Capacity at constant volume (C_v)

It is the amount of heat required to raise the temperature of one mole of a gas at constant volume.

Molar Heat Capacity at constant pressure (C_p)

It is the amount of heat required to raise the temperature of one mole of a gas at constant pressure. It has been found that $C_p > C_v$ and the difference between the two is equal to the gas constant *i.e.*

$$C_p - C_v = R = 1.987 \text{ cal}$$

Specific Heat Ratio

The ratio C_p/C_v, denoted by the symbol γ, which varies with the atomicity of the gas.

For a monoatomic gas $C_p = \frac{5}{2} R$; $C_v = \frac{3}{2} R$

and $\gamma = \dfrac{C_p}{C_v} = \dfrac{\frac{5}{2}R}{\frac{3}{2}R} = 1.667$

For a diatomic gas $C_p = \frac{7}{2} R$; $C_v = \frac{5}{2} R$

and $\gamma = \dfrac{C_p}{C_v} = \dfrac{\frac{7}{2}R}{\frac{5}{2}R} = 1.40$

For polyatomic gas $C_p = \frac{8}{2} R$; $C_v = \frac{6}{2} R$

and $\gamma = \dfrac{C_p}{C_v} = \dfrac{\frac{8}{2}R}{\frac{6}{2}R} = 1.33$

REAL GASES : VANDER WAALS EQUATION

An ideal gas is one which obeys the gas laws and the gas equation ($PV = nRT$) at all pressures and temperatures. However, no gas is ideal. Almost all gases show deviations from the ideal behaviour and are called real gases. The extent to which is real gas departs from ideal behaviour is given by a factor called compressibility factor Z, given by

$$Z = \frac{PV}{RT}$$

For ideal gases $Z = 1$ and for real gas $Z < 1$ or $Z > 1$. The gases under high pressures and low temperatures deviate from the ideal behaviour. The deviations from ideality is due to faulty assumptions of the kinetic molecular theory. These are

(i) the molecules in a gas possess no volume

(ii) there are no intermolecular forces among the molecules of a gas.

vander Waals modified the gas equation and the new equation is vander Waals equation

$$\left(P + \frac{n^2 a}{V^2}\right)(V - nb) = nRT$$

where the factors $\frac{n^2 a}{V^2}$ and nb are the pressure and volume correction factors respectively. These factors account for the inter molecular attractive forces and the actual volume occupied by the gas molecules. 'a' and 'b' are constants called vander Waals constants.

Units of 'a' and 'b'

The units of vander Waals constants are

a = atm lit^2 mol^{-2} or kPa dm^3 mol^{-1}

and b = lit mol^{-1} or dm^3 mol^{-1}

The vander Waals constant '*b*' is four times the actual volume of the gas molecule *i.e.*

$$b = 4 \times \text{Avogadro's number} \times \frac{4}{3}\pi r^3$$

where *r* is the radius of the gas molecule.

CRITICAL PHENOMENON

Critical Temperature (T_c) of a gas is that temperature above which it cannot be liquified no matter how great the pressure applied.

Critical Pressure (P_c) of a gas is the minimum pressure required to liquify a gas at its critical temperature.

Critical Volume (V_c) of a gas is the volume occupied by one mole of it at its critical temperature and critical pressure.

Relations between Critical Constants and vander Waals constants

$$V_c = 3b \qquad P_c = \frac{a}{27\,b^2} \qquad T_c = \frac{8a}{27\,R\,b}$$

ADDITIONAL SOLVED PROBLEMS

SOLVED PROBLEM 1. At what temperature would ethane molecules have the same root mean square velocity as methane molecules at 27 °C.

SOLUTION :

Formula used

$$\mu = \sqrt{\frac{3RT}{M}}$$

Quantities given

$T = 27 + 273 = 300$ K

mol. mass of CH_4 = 16

mol mass of C_2H_6 = 30

Substitution of values

$$\mu_{CH_4} = \sqrt{\frac{3R \times 300}{16}} = \sqrt{\frac{900R}{16}}$$

and
$$\mu_{C_2H_6} = \sqrt{\frac{3R \times 300}{30}} = \sqrt{\frac{3RT}{30}}$$

Since two velocities are equal, we have

$$\sqrt{\frac{900R}{16}} = \sqrt{\frac{3RT}{30}}$$

Squaring both sides

$$\frac{900R}{16} = \frac{3RT}{30}$$

or
$$T = \frac{900 \times 30}{16 \times 3}\text{ K}$$
$$= 562.5\text{ K}$$
$$= 562.5 - 273\ ^\circ\text{C}$$
$$= \mathbf{289.5\ ^\circ C}$$

SOLVED PROBLEM 2. Calculate the root mean square velocity of oxygen molecules at 27 °C.

SOLUTION :

Formula used

$$\mu = \sqrt{\frac{3\,RT}{M}}$$

Quantities given

$T = 27 + 273 = 300$ K $\qquad R = 8.314 \times 10^{7}$ erg K^{-1} mol^{-1} $\qquad M = 32$ g mol^{-1}

Substitution of values

$$\mu_{o_2} = \sqrt{\frac{3 \times 8.314 \times 10^{7}\ \text{erg K}^{-1}\ \text{mol}^{-1} \times 300\ \text{K}}{32\ \text{g mol}^{-1}}}$$

$$= \sqrt{23.383 \times 10^{8}\ \text{cm sec}^{-1}}$$

$$= \mathbf{4.8356 \times 10^{4}\ \text{cm sec}^{-1}}$$

SOLVED PROBLEM 3. Calculate the critical constants V_c, P_c and T_c for C_2H_2 using vander Waals constants $a = 4.390$ atm lit mol^{-2} ; $b = 0.05316$ lit mol^{-1} ($R = 0.082$ atm lit K^{-1} mol^{-1})

SOLUTION :

(i) To calculate V_c

Formula used

$$V_c = 3\,b$$

Quantity given

$$b = 0.05136\ \text{lit mol}^{-1}$$

Substitution of values

$$V_c = 3 \times 0.05136\ \text{lit mol}^{-1} = \mathbf{0.15408\ lit}$$

(ii) To calculate P_c

Formula used

$$P_c = \frac{a}{27\,b^{2}}$$

Quantities given

$a = 4.390$ atm lit^{2} mol^{-2} $\qquad b = 0.05136$ lit mol^{-1}

Substitution of values

$$P_c = \frac{4.390\ \text{atm lit}^{2}\ \text{mol}^{-2}}{27 \times (\,0.05136\ \text{lit mol}^{-1}\,)\,2}$$

$$= \frac{4.390}{27 \times 0.002638}$$

$$= \mathbf{61.64\ atm}$$

(iii) To calculate T_c

Formula used

$$T_c = \frac{8a}{27\,R}$$

Quantities given

$a = 4.390$ atm lit^{2} mol^{-2} $\qquad R = 0.082$ atm lit K^{-1} mol^{-1}

Substitution of values

$$T_c = \frac{8 \times 4.390\ \text{atm lit}^{2}\text{mol}^{-2}}{27 \times 0.082\ \text{atm lit K}^{-1}\ \text{mol}^{-1}}$$

$$= \mathbf{15.86\ K}$$

SOLVED PROBLEM 4. Calculate the root mean square velocity of oxygen molecules at 25 °C.

SOLUTION :

Formula used

$$\mu = \sqrt{\frac{3RT}{M}}$$

Quantities given

$R = 8.314 \times 10^7 \text{ erg K}^{-1}\text{mol}^{-1}$ $\qquad$ $T = 25 + 273 = 298 \text{ K}$

$M = 32 \text{ g mol}^{-1}$

Substitution of values

$$\mu_{O_2} = \sqrt{\frac{3 \times 8.314 \times 10^7 \text{ erg K}^{-1}\text{mol}^{-1} \times 298 \text{ K}}{32 \text{ g mol}^{-1}}}$$

$$= \sqrt{23.227 \times 10^8 \text{ cm sec}^{-1}}$$

$$= \mathbf{4.819 \times 10^4 \text{ cm sec}^{-1}}$$

SOLVED PROBLEM 5. Calculate the root mean square velocity of CO_2 at 27 °C.

SOLUTION :

Formula used

$$\mu = \sqrt{\frac{3RT}{M}}$$

Quantities given

$R = 8.314 \times 10^7 \text{ erg K}^{-1}\text{ mol}^{-1}$ $\qquad$ $T = 27 + 273 = 300 \text{ K}$

$M = 44 \text{ g mol}^{-1}$

Substitution of values

$$\mu_{CO_2} = \sqrt{\frac{3 \times 8.314 \times 10^7 \text{ erg K}^{-1} \times 300 \text{ K}}{44 \text{ g mol}^{-1}}}$$

$$= \sqrt{17.059 \times 10^8 \text{ cm sec}^{-1}}$$

$$= \mathbf{4.130 \text{ cm sec}^{-1}}$$

SOLVED PROBLEM 6. One mole of diethyl ether occupies 15 litres at 227 °C. Calculate the pressure if vander Waals constants for diethyl ether are $a = 17.38 \text{ atm lit}^2 \text{ mol}^{-2}$ and $b = 0.134 \text{ lit mol}^{-1}$.

SOLUTION :

Formula used

$$\left(P + \frac{n^2 a}{V^2}\right)(V - nb) = nRT$$

or

$$P = \frac{nRT}{V - nb} - \frac{n^2 a}{V^2}$$

Quantities given

$n = 1 \text{ mol}$ $\qquad$ $V = 15 \text{ lit}$ $\qquad$ $R = 0.0821 \text{ atm lit K}^{-1}\text{mol}^{-1}$

$a = 17.38 \text{ atm lit}^2 \text{ mol}^{-2}$ $\qquad$ $T = 500 \text{ K}$ $\qquad$ $b = 0.134 \text{ lit mol}^{-1}$

Substitution of values

$$P = \frac{1 \text{ mol} \times 0.0821 \text{ atm lit K}^{-1} \text{ mol}^{-1} \times 500 \text{ K}}{15 \text{ lit} - 0.314 \text{ lit}} - \frac{(1 \text{ mol})^2 \times 17.38 \text{ atm lit}^2 \text{ mol}^{-2}}{(15 \text{ lit})^2}$$

$$= 2.795 \text{ atm} - 0.07724 \text{ atm}$$

$$= \mathbf{2.723 \text{ atm.}}$$

SOLVED PROBLEM 7. Calculate the root mean square velocity for oxygen molecules at 26.85 ºC, given that the gas constant is 8.314 × 10^7 erg mol^{-1} deg^{-1}.

SOLUTION :

Formula used

$$\mu = \sqrt{\frac{3RT}{M}}$$

Quantities given

$R = 8.314 \times 10^7 \text{ erg K}^{-1} \text{ mol}^{-1}$ $\qquad T = 273.15 + 26.85 = 300\text{K}$ $\qquad M = 32 \text{ g mol}^{-1}$

Substitution of values

$$\mu_{O_2} = \sqrt{\frac{3 \times 8.314 \times 10^7 \text{ erg K}^{-1} \text{mol}^{-1} \times 300\text{K}}{32 \text{ g mol}^{-1}}}$$

$$= \sqrt{23.383 \times 10^8} \text{ cm sec}^{-1}$$

$$= \mathbf{4.8356 \times 10^{-4} \text{ cm sec}^{-1}}$$

SOLVED PROBLEM 8. A vessel of volume 1.0 litre contains 10^{25} gas molecules of mass 10^{-24} g each. If r. m. s. velocity is 10^5 cm sec^{-1}, calculate the total kinetic energy and temperature.

SOLUTION : (i) To calculate the total Kinetic energy

Formula used

$$K.E. = ½ m v^2$$

Quantities given

Mass of the gas = no. of molecules × mass of each molecule $\qquad v = 10^5 \text{ cm sec}^{-1}$

$= 10^{25} \times 10^{-24}$ g

= 10 g

Substitution of values

$$\text{K.E. of the gas} = ½ \times 10 \text{ g} \times (10^5 \text{ cm sec}^{-1})^2$$

$$= \mathbf{5 \times 10^{10} \text{ ergs}}$$

(ii) To calculate the Temperature

Formula used

$$K.E. = \frac{3}{2} RT \text{ or } T = \frac{2\,K.E.}{3R}$$

Quantities given

$K.E. = 5 \times 10^{10}$ ergs $\qquad R = 8.314 \times 10^7 \text{ ergs K}^{-1} \text{ mol}^{-1}$

Substitution of values

$$T = \frac{2 \times 5 \times 10^{10} \text{ erg}}{3 \times 8.314 \times 10^7 \text{ ergs K}^{-1} \text{ mol}^{-1}}$$

$$= 400.93 \text{ K}$$

$$= 400.93 - 273 \text{ ºC}$$

$$= \mathbf{127.93 \text{ ºC}}$$

SOLVED PROBLEM 9. Critical density of a substance having molecular weight 111 is 0.555 g cm^{-3} and P_c = 48 atm. Calculate the vander Waals constant ‘*a*’ and ‘*b*’.

SOLUTION :

(i) To calcualte ‘b’

Formula used

$$V_c = 3b \text{ or } b = \frac{V_c}{3}$$

Quantities given

$$\text{Critical volume} = \frac{\text{Molecular mass}}{\text{Critical density}} = \frac{111 \text{ g mol}^{-1}}{0.555 \text{ g ml}^{-1}} = 200 \text{ ml mol}^{-1} = 0.2 \text{ lit mol}^{-1}$$

Substitution of values

$$b = \frac{0.2 \text{ lit mol}^{-1}}{3} = \mathbf{0.066 \text{ lit mol}^{-1}}$$

(ii) To calculate 'a'

Formula used

$$P_c = \frac{a}{27\ b^2} \quad \text{or} \quad a = 27\, b^2\, P_c$$

Quantities given

$b = 0.066 \text{ lit mol}^{-1}$

$P_c = 48 \text{ atm}$

Substitution of values

$$\begin{aligned} a &= 27 \times (0.066 \text{ lit mol}^{-1})^2 \times 48 \text{ atm} \\ &= \mathbf{5.645 \text{ atm lit}^2 \text{ mol}^{-2}} \end{aligned}$$

SOLVED PROBLEM 10. For ammonia gas vander Waals constants a and b are 4.0 litre^2 atm and 0.036 litre mol^{-1} respectively. Calculate the critical volume ($R = 0.082$ lit atm K^{-1})

SOLUTION :

Formula used

$$V_c = 3\,b$$

Quantity given

$$b = 0.036 \text{ lit mol}^{-1}$$

Substitution of values

$$\begin{aligned} V_c &= 3 \times 0.036 \times \text{lit mol}^{-1} \\ &= \mathbf{0.108 \text{ lit}} \end{aligned}$$

SOLVED PROBLEM 11. Calculate the pressure developed in a 5 litre vessel containing 88 g of CO_2 at 27 °C. Assume CO_2 as van der Waals gas (C = 12, O = 6) ; $a = 3.59$ atm lit^2 mol^{-2} ; $b = 0.043$ lit mol^{-1}.

SOLUTION :

Formula used

$$\left(P + \frac{n^2 a}{V^2}\right)(V - n\,b) = n\,R\,T$$

or

$$P = \frac{n\,R\,T}{V - n\,b} - \frac{n^2\,a}{V^2}$$

Quantities given

$n = \dfrac{88 \text{ g}}{44 \text{ g mol}^{-1}} = 2 \text{ mole}$

$R = 0.0821 \text{ atm lit K}^{-1} \text{ mol}^{-1}$

$V = 5 \text{ lit}$

$T = 27 + 273 = 300 \text{ K}$

$a = 3.59 \text{ atm lit}^2 \text{ mol}^{-2}$

$b = 0.043 \text{ lit mol}^{-1}$

Substitution of values

$$\begin{aligned} P &= \frac{2 \text{ mol} \times 0.0821 \text{ atm lit K}^{-1} \text{ mol}^{-1} \times 300 \text{ K}}{5 \text{ lit} - 2 \times 0.043 \text{ lit}} - \frac{(2 \text{ mol})^2 \times 3.59 \text{ atm lit}^2 \text{mol}^{-1}}{(5 \text{ lit})^2} \\ &= \frac{49.26}{4.914} \text{ atm} - 0.574 \text{ atm} \\ &= \mathbf{9.450 \text{ atm}} \end{aligned}$$

SOLVED PROBLEM 12. If for a gas $T_c = 31$ °C, $P_c = 72.8$ atm and $R = 0.082$ then calculate the vander Waals constant a and b.

SOLUTION :

(i) To calculate 'b'

Formula used

$$P_c = \frac{a}{27\,b_2} \quad \text{and} \quad T_c = \frac{8\,a}{27\,R\,b}$$

or $$\frac{P_c}{T_c} = \frac{a}{27\,b^2} \times \frac{27\,R\,b}{8\,a} = \frac{R}{8\,b}$$

or $$b = \frac{R\,T_c}{8\,P_c}$$

Quantities given

$T_c = 31 + 273 = 304\text{ K}$ $\qquad$ $P_c = 72.8\text{ atm}$ $\qquad$ $R = 0.0821\text{ atm lit K}^{-1}\text{ mol}^{-1}$

Substitution of values

$$b = \frac{0.0821\text{ atm lit K}^{-1}\text{ mol}^{-1} \times 304\text{ K}}{8 \times 72.8\text{ atm}}$$

$$= \mathbf{0.04285\text{ lit mol}^{-1}}$$

(ii) To calculate 'a'

Formula used

$$P_c = \frac{a}{27\,b^2} \quad \text{or} \quad a = 27\,P_c\,b^2$$

Quantities given

$P_c = 72.8\text{ atm}$ $\qquad$ $b = 0.04285\text{ lit mol}^{-1}$

Substitution of values

$$a = 27 \times 72.8\text{ atm} \times (0.04285\text{ lit mol}^{-1})^2$$

$$= \mathbf{3.6091\text{ atm lit}^2\text{ mol}^{-1}}$$

SOLVED PROBLEM 13. Calculate the root mean square, velocity, average velocity and the most probable velocity of a gas at 27 ºC, where the mass of gas molecule is 4.4688×10^{-26} kg.

SOLUTION :

(i) To calculate the molecular mass of the gas

Mass of a molecule of the gas $= 4.4688 \times 10^{-26}$ kg

$= 4{,}4688 \times 10^{-23}$ g

Molecular mass = Avogadro's number × Mass of one molecule

$= 6.023 \times 10^{23}\text{ mol}^{-1} \times 4.4688 \times 10^{-23}\text{ g}$

$= 26.90\text{ g mol}^{-1}$

(ii) To calculate the root mean square velocity

Formula used

$$\mu = \sqrt{\frac{3\,R\,T}{M}}$$

Quantities given

$R = 8.314 \times 10^7\text{ erg K}^{-1}\text{ mol}^{-1}$ $\qquad$ $T = 27 + 273 = 300\text{ K}$ $\qquad$ $M = 26.90\text{ g mol}^{-1}$

Subsitution of values

$$\mu = \sqrt{\frac{3 \times 8.314 \times 10^7\text{ erg K}^{-1}\text{mol}^{-1} \times 300\text{ K}}{26.90\text{ g mol}^{-1}}}$$

$$= \sqrt{27.816 \times 10^8}$$

$$= \mathbf{5.274 \times 10^4\ cm\ sec^{-1}}$$

(ii) To calculate the average velocity

$$v = 0.9213 \times \mu$$

$$= 0.9213 \times 5.274 \times 10^4 \text{ cm sec}^{-1}$$

$$= \mathbf{4.859 \times 10^4\ cm\ sec^{-1}}$$

(iii) To calculate the most probable velocity

$$\mu_{mp} = \sqrt{\frac{2}{3}} \times \mu$$

$$= \sqrt{\frac{2}{3}} \times 5.274 \times 10^4 \text{ cm sec}^{-1}$$

$$= \mathbf{4.306 \times 10^4\ cm\ sec^{-1}}$$

SOLVED PROBLEM 14. vander Walls constants for CO_2 are $a = 3.65 \times 10^{-1}$ Nm^4 mol^{-2}, $b = 4.28 \times 10^{-5}$ m^3 mol^{-1}. Calculate T_c and V_c of the gas.

SOLUTION :

(i) To calculae 'b'

Formula used

$$V_c = 3\,b$$

Quantity given

$$b = 4.28 \times 10^{-5} \text{ m}^3 \text{ mol}^{-3}$$

Substitution of values

$$V_c = 3 \times 4.28 \times 10^{-5} \text{ m}^3 \text{ mol}^{-1}$$

$$= \mathbf{1.284 \times 10^{-4}\ m^3}$$

(ii) To calculate 'a'

Formula used

$$T_c = \frac{8\,a}{27\,R\,b}$$

Quantities given

$a = 3.65 \times 10^{-1}$ Nm^4 mol^{-2} $R = 8.314$ Nm K^{-1} mol^{-1} $b = 4.28 \times 10^{-5}$ m^3 mol^{-1}

Subsitution of values

$$T_c = \frac{8 \times 3.65 \times 10^{-1} \text{ Nm}^4 \text{ mol}^{-2}}{27 \times 8.314 \text{ Nm K}^{-1} \text{ mol}^{-1} \times 4.28 \times 10^{-5} \text{ m}^3 \text{ mol}^{-1}}$$

$$= \mathbf{303.92\ K}$$

SOLVED PROBLEM 15. Calculate the root mean square velocity of nitrogen at 27 ºC and 700 mm pressure.

SOLUTION :

(i) To convert Gram molar volume to given conditions

At NTP	P_1 = 760 mm	V_2 = 22400 ml	T_1 = 273 K
At given conditions	P_2 = 700 mm		T_2 = 300 K

Formula used

$$\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2} \qquad \text{or} \qquad V_2 = \frac{P_1 V_1 T_2}{T_1 P_2}$$

Substitution of values

$$V_2 = \frac{760\,\text{mm} \times 22400\,\text{ml} \times 300\,\text{K}}{273\,\text{K} \times 700\,\text{mm}}$$

$$= \mathbf{26725\ ml}$$

(ii) To calculate root mean square velocity, μ

Formula used

$$\mu = \sqrt{\frac{3\,P\,V}{M}}$$

Quantities given

$V = 26725\,\text{ml}$ $P = 700\,\text{mm Hg} = 70\,\text{cm of Hg} = 70 \times 13.6 \times 981$ $M = 28\,\text{g mol}^{-1}$

Substitution of values

$$\mu = \sqrt{\frac{3 \times 70 \times 13.6 \times 981 \times 26725}{28}}$$

$$= 51712\,\text{cm sec}^{-1}$$

$$= \mathbf{5.1712 \times 10^4\ cm\ sec^{-1}}$$

SOLVED PROBLEM 16. Calculate the root mean square speed of CO_2 Molecules at 27 ºC.

SOLUTION :

Formula used

$$\mu = \sqrt{\frac{3\,R\,T}{M}}$$

Quantities given

$R = 8.314 \times 10^7\,\text{erg K}^{-1}\,\text{mol}^{-1}$ $T = 27 + 273 = 300$ $M = 44\,\text{g mol}^{-1}$

Subsitution of values

$$\mu = \sqrt{\frac{3 \times 8.314 \times 10^7\,\text{erg K}^{-1}\,\text{mol}^{-1} \times 300\,\text{K}}{44\,\text{g mol}^{-1}}}$$

$$= \sqrt{17.0059 \times 10^8}$$

$$= \mathbf{4.1238\ cm\ sec^{-1}}$$

SOLVED PROBLEM 17. What would be the pressure exerted by 0.8 mole of NO_2 in a vessel of Volume 20 dm^3 at 300 K from vander Waals equation. ($R = 8.314\,\text{J K}^{-1}\,\text{mol}^{-1}$, $a = 0.535\,\text{Nm}^{-4}\,\text{mol}^{-2}$, $b = 4.42 \times 10^{-5}\,\text{m}^3\,\text{mol}^{-1}$).

SOLUTION :

Formula used

$$\left(P + \frac{a\,n^2}{V^2}\right)(V - n\,b) = n\,R\,T$$

or

$$P = \frac{n\,R\,T}{V - n\,b} - \frac{a\,n^2}{V^2}$$

Quantities given

$n = 0.8\,\text{mole}$ $R = 8.314\,\text{JK}^{-1}\,\text{mol}^{-1}$ $V = 20\,\text{dm}^3 = 0.02\,\text{m}^3$

$T = 300\,\text{K}$ $a = 0.535\,\text{Nm}^{-4}\,\text{mol}^{-2}$ $b = 4.42 \times 10^{-5}\,\text{m}^3\,\text{mol}^{-1}$

Substitution of values

$$P = \frac{0.8\ \text{mol} \times 8.314\ \text{JK}^{-1}\ \text{mol}^{-1} \times 300\ \text{K}}{0.02\ \text{m}^3 - 0.8\ \text{mol} \times 4.42 \times 10^{-5}\ \text{m}^3\ \text{mol}^{-1}} - \frac{0.535\ \text{Nm}^4\ \text{mol}^{-2} \times (0.8\ \text{mol})^2}{(0.02\ \text{m}^3)^2}$$

$$= \frac{1995.36}{0.01996}\ \text{Nm}^{-2} - 858.6\ \text{Nm}^{-2}$$

$$= 99088\ \text{Nm}^{-2}$$

$$= \frac{99088}{1.01325 \times 10^5}\ \text{atm} \qquad [\because 1\ \text{atm} = 1.01325 \times 10^5\ \text{Nm}^{-2}]$$

$$= \mathbf{0.9779\ atm}$$

SOLVED PROBLEM 18. Calculate the mean free path for oxygen molecule at 300 K and pressure 101.325 k Pa. The collision diameter of oxygen molecule is 0.362 nm. (Avogadro's number $N_A = 6.022 \times 10^{23}$ mol^{-1}).

SOLUTION :

(i) To calculate the number of molecules of oxygen per unit volume

Formula used

$$\bar{n} = \frac{P}{RT} \times N$$

Quantities given

$P = 101.325\ \text{k Pa} = 101325\ \text{Pa}$ $\qquad T = 300\ \text{K}$

$R = 8.314\ \text{JK}^{-1}\ \text{mol}^{-1}$ $\qquad N = 6.023 \times 10^{23}\ \text{mol}^{-1}$

Substitution of values

$$\bar{n} = \frac{101325\ \text{Pa} \times 6.023 \times 10^{23}\ \text{mol}^{-1}}{8.314\ \text{JK}^{-1}\ \text{mol}^{-1} \times 300\ \text{K}}$$

$$= 2.44679 \times 10^{25}\ \text{m}^{-3}$$

(ii) To calculate the mean free path

Formula used

$$L = \frac{1}{\sqrt{2} \times \pi \sigma^2 n}$$

Quantities given

$\sigma = 0.362\ \text{nm} = 0.362 \times 10^{-9}\ \text{m}$ $\qquad \bar{n} = 2.44679 \times 10^{25}\ \text{m}^{-3}$

Substitution of values

$$L = \frac{1}{\sqrt{2} \times 3.14 \times (0.362 \times 10^{-9}\ \text{m})^2 \times (2.44679 \times 10^{25}\ \text{m}^{-3})}$$

$$= \mathbf{7.0472 \times 10^{-8}\ m}$$

SOLVED PROBLEM 19. Calculate the critical temperature of a vander Waals gas for which P_c is 100 atm and b is 50 cm^3 mol^{-1}.

SOLUTION :

(i) To calculate V_C

Formula used

$$V_c = 3b$$

Quantities given

$$b = 0.050\ \text{cm}^3\ \text{mol}^{-1} = 0.050\ \text{lit mol}^{-1}$$

Substitution of values

$$V_c = 3 \times 0.050 \text{ lit mol}^{-1}$$
$$= \mathbf{0.150 \text{ lit mol}^{-1}}$$

(ii) To calculate T_c

Formula used

$$T_c = \frac{8\,P_c\,V_c}{3\,R}$$

Quantities given

$P_c = 100$ atm

$V_c = 0.150$ lit mol^{-1}

$R = 0.0821$ atm lit K^{-1} mol^{-1}

Substitution of values

$$T_c = \frac{8 \times 100 \text{ atm} \times 0.150 \text{ lit mol}^{-1}}{3 \times 0.0821 \text{ atm lit K}^{-1} \text{ mol}^{-1}}$$
$$= 487.2 \text{ K}$$
$$= 487.2 - 273\ ^\circ\text{C}$$
$$= \mathbf{214.2\ ^\circ C}$$

SOLVED PROBLEM 20. Calculate molar volume of an ideal gas at 127 ºC and 1 atm pressure.

SOLUTION :

Formula used

$$P\,V = n\,R\,T \qquad \text{or} \qquad V = \frac{n\,R\,T}{P}$$

Quantities given

$n = 1$ mole

$R = 0.0821$ atm lit K^{-1} mol^{-1}

$T = 127 + 273 = 400$ K

Substitution of values

$$V = \frac{1 \text{ mole} \times 0.0821 \text{ atm lit K}^{-1} \text{ mol}^{-1} \times 400 \text{ K}}{1 \text{ atm}}$$
$$= \mathbf{32.84 \text{ lit}}$$

SOLVED PROBLEM 21. The average velocity at T_1 K and most probable velocity of CO_2 at T_2 K is 9×10^4 cm sec^{-1}. Calculate the value of T_1 and T_2.

SOLUTION :

(i) To calculate the value of T_1

Formula used

$$v = \sqrt{\frac{8\,R\,T_1}{\pi M}} \qquad \text{or} \qquad T_1 = \frac{v^2 \times \pi \times M}{8\,R}$$

Quantities given

$v = 9 \times 10^4$ cm sec^{-1}

$R = 8.314 \times 10^7$ erg K^{-1} mol^{-1}

$M = 44$ g mol^{-1}

Substitution of values

$$T_1 = \frac{(9 \times 10^4 \text{ cm sec}^{-1})^2 \times 3.14 \times 44 \text{ g mol}^{-1}}{8 \times 8.314 \times 10^7 \text{ erg K}^{-1} \text{mol}^{-1}}$$
$$= \frac{81 \times 10^8 \times 3.14 \times 44}{8 \times 8.314 \times 10^7} \text{ K} = \mathbf{1682.5 \text{ K}}$$

(ii) To calculate the value of T_2

Formula used

$$\mu_{mp} = \sqrt{\frac{2RT_2}{M}} \qquad \text{or} \qquad T_2 = \frac{(\mu_{mp})^2 \times M}{2R}$$

Quantities given

$\mu_{mp} = 9 \times 10^4 \text{ cm sec}^{-1}$ $\qquad R = 8.314 \times 10^7 \text{ erg K}^{-1} \text{ mol}^{-1}$ $\qquad M = 44 \text{ g mol}^{-1}$

Substitution of values

$$T_2 = \frac{(9 \times 10^4 \text{ cm sec}^{-1})^2 \times 44 \text{ g mol}^{-1}}{2 \times 8.314 \times 10^7 \text{ erg K}^{-1} \text{ mol}^{-1}}$$

$$= \frac{81 \times 10^8 \times 44}{2 \times 8.314 \times 10^7} \text{ K}$$

$$= \mathbf{2143 \text{ K}}$$

SOLVED PROBLEM 22. Calculate the volume occupied by 5 g of acetylene gas at 50 ºC and 740 mm pressure.

SOLUTION :

Formula used

$$PV = nRT \qquad \text{or} \qquad V = \frac{nRT}{P}$$

Quantities given

$n = \dfrac{5 \text{ g}}{26 \text{ g mol}^{-1}} = 0.1923 \text{ mol}^{-1}$ $\qquad R = 0.0821 \text{ atm lit K}^{-1} \text{ mol}^{-1}$

$T = 50 + 273 = 323 \text{ K}$ $\qquad P = 740 \text{ mm} = \dfrac{740 \text{ mm}}{760 \text{ mm}} \times 1 \text{ atm} = 0.9737 \text{ atm}$

Substitution of values

$$V = \frac{0.1923 \text{ mol}^{-1} \times 0.0821 \text{ atm lit K}^{-1} \text{mol}^{-1} \times 323 \text{ K}}{0.9737 \text{ atm}}$$

$$= \mathbf{5.2377 \text{ lit}}$$

SOLVED PROBLEM 23. At 27 ºC hydrogen is leaked through a tiny hole into a vessel for 20 minutes. Another unknown gas at the same temperature and pressure, as that of H_2, is leaked through the same hole for 20 minutes. After the effusion of gases the mixture exerts a pressure of 6 atm. The hydrogen content of the the mixture is 0.7 mole. If the volume of the container is 3 litres, what is the molecular mass of the unknown gas.

SOLUTION :

(i) To calculate to the total number of moles in the mixture

Formula used

$$PV = nRT \qquad \text{or} \qquad n = \frac{PV}{RT}$$

Quantities given

$P = 6 \text{ atm}$ $\qquad V = 3 \text{ lit}$ $\qquad T = 27 + 273 = 300 \text{ K}$

$R = 0.0821 \text{ atm lit K}^{-1} \text{ mol}^{-1}$

Substitution of values

$$n = \frac{6 \text{ atm} \times 3 \text{ lit}}{0.0821 \text{ atm lit K}^{-1} \text{ mol}^{-1} \times 300 \text{ K}}$$

$$= 0.7308 \text{ mol}$$

$$\begin{aligned}\text{Number of moles of unknown gas} &= \text{Total number of moles} - \text{moles of hydrogen}\\ &= 0.7308 - 0.7 \text{ mol}\\ &= 0.0308 \text{ mol}\end{aligned}$$

(ii) To calculate the molecular mass of the unknown gas

Formula used

$$\frac{r_{H_2}}{r_{gas}} = \sqrt{\frac{M_{gas}}{M_{H_2}}}$$

Quantities given

$$\frac{r_{H_2}}{r_{gas}} = \frac{\text{amt of H}_2}{\text{amt of gas}} = \frac{0.7 \text{ mol}}{0.0308 \text{ mol}}$$

$$\text{M}_{\text{H}_2} = 2 \text{ g mol}^{-1}$$

Substitution of values

$$\frac{0.7}{0.0308} = \sqrt{\frac{M_{gas}}{2}}$$

Squaring both sides

$$\frac{0.7 \times 0.7}{0.0308 \times 0.0308} = \frac{M_{gas}}{2 \text{ g mol}^{-1}}$$

or $M_{gas} = \mathbf{1033 \text{ g mol}^{-1}}$

SOLVED PROBLEM 24. A gas bulb of 1 litre capacity contains 2.0×10^{21} molecules of nitrogen exerting a pressure of 7.57×10^3 Nm^2. Calculate the RMS velocity and the temperature of the gas molecules. If the ratio of most probable velocity to RMS velocity is 0.82, calculate the most probable velocity for these molecules at this temperature.

SOLUTION :

(i) To calculate the RMS velocity of N_2 molecules

Formula used

$$\mu = \sqrt{\frac{3P}{D}}$$

Quantities given

$P = 7.57 \times 10^3 \text{ Nm}^{-2}$

$$\begin{aligned}D = \frac{\text{Mass}}{\text{Volume}} &= \frac{28 \text{ g} \times 2 \times 10^{21} \text{ molecules}}{1 \text{ lit} \times 6.023 \times 10^{23} \text{ mol}^{-1}}\\ &= 0.0929 \text{ g lit}^{-1}\\ &= \frac{0.0929 \times 10^{-3}}{10^{-3}} \text{ kg m}^{-3}\\ &= 0.0929 \text{ kg m}^{-3}\end{aligned}$$

Substitution of values

$$\begin{aligned}\mu &= \sqrt{\frac{3 \times 7.57 \times 10^3 \text{ Nm}^{-2}}{0.0929 \text{ kg m}^{-3}}}\\ &= \sqrt{244456.40}\\ &= \mathbf{494.425 \text{ m sec}^{-1}}\end{aligned}$$

(ii) To calculate the temperature of the gas

Formula used

$$\mu = \sqrt{\frac{3RT}{M}} \quad \text{or} \quad T = \frac{M\mu^2}{3R}$$

Quantities given

$M = 28 \times 10^{-3}\ \text{kg mol}^{-1}$ $\mu = 494.425\ \text{m sec}^{-1}$ $R = 8.314\ \text{J K}^{-1}\text{mol}^{-1}$

Substitution of values

$$T = \frac{(28 \times 10^{-3}\ \text{kg mol}^{-1}) \times (494.425\ \text{m sec}^{-1})^2}{3 \times (8.314\ \text{J K}^{-1}\ \text{mol}^{-1})}$$

$$= \mathbf{274.43\ K}$$

(ii) To calculate most probable velocity

$$\frac{\text{Most probable velocity, } \mu_{mp}}{\text{Root Mean Square Velocity, } \mu} = 0.82 \text{ (given)}$$

$\therefore$ Most probable velocity, μ_{mp} = RMS velocity $\times$ 0.82

$= 494.425\ \text{m sec}^{-1} \times 0.82$

$= \mathbf{405.43\ m\ sec^{-1}}$

SOLVED PROBLEM 25. A balloon of diameter 20 m. weighs 100 kg. Calculate its pay-load if it is filled with Helium at 1 atm and 27 ºC. Density of air 1.2 kg m^{-3} ($R = 0.082$ atm dm^3 K^{-1})

SOLUTION :

(i) To calculate the mass of Helium gas present in the balloon

Formula used

$$PV = nRT \quad \text{or} \quad n = \frac{PV}{RT}$$

Quantities given

$P = 1$ atm $V = \frac{4}{3}\pi r^3 = \frac{4}{3} \times 3.14 \times (10\text{m})^3 = 4186.66\ \text{m}^3 = 4186.66 \times 10^3\ \text{dm}^3$

$R = 0.082$ atm K^{-1} mol^{-1} dm^3 $T = 27 + 273 = 300$ K

Substitution of values

$$n = \frac{1\ \text{atm} \times 4186.66 \times 10^3\ \text{dm}^3}{0.082\ \text{atm dm}^3\ \text{K}^{-1}\ \text{mol}^{-1} \times 300\ \text{K}}$$

$= 170.189 \times 10^3$ mol

Mass of Helium present $= 4\text{g mol}^{-1} \times 170.189 \times 10^3$ mol

$= 680.76 \times 10^3$ g

$= 680.76$ kg

$\therefore$ Mass of the filled balloon = Mass of the balloon + Mass of Helium present

$= 100\ \text{kg} + 680.76\ \text{kg}$

$= 780.76$ kg

(ii) To calculate the pay load

Mass of the displaced air = Volume $\times$ density

$= 4186.66\ \text{m}^3 \times 1.2\ \text{kg m}^{-3}$

$= 5023.99$ kg

$\therefore$ Pay load = Mass of displaced air – Total mass of balloon

$= 5023.99\ \text{kg} - 780.76\ \text{kg}$

$= \mathbf{4243.23\ kg}$

SOLVED PROBLEM 26. An LPG (liquified petroleum gas) cylinder weighs 14.8 kg when empty. When full it weighs 29.0 kg and shows a pressure of 2.5 atm. In the course of use at 27 ºC the weight of the full cylinder reduces to 23.2 kg. Find out the volume of the gas in cubic meters used up at the normal usage conditions and the final pressure inside the gas. Assume LPG to be *n*-butane with normal boiling of 0 ºC.

SOLUTION :

(i) To calculate the volume of the gas initially present

Mol mass of LPG (n-C_4H_{10}) $= 12 \times 4 + 10 \times 1 = 58.0\ \text{g mol}^{-1} = 58 \times 10^{-3}\ \text{kg mol}^{-1}$

Weight of the full cylinder $= 29.0\ \text{kg}$

Weight of the empty cylinder $= 14.8\ \text{kg}$

Weight of gas initially present $= 29.0\ \text{kg} - 14.8\ \text{kg} = 14.2\ \text{kg}$

No. of moles of *n*-butane initially present $= \dfrac{14.2\ \text{kg}}{58 \times 10^{-3}\ \text{kg mol}^{-1}}$

$= 244.827\ \text{mol}$

Pressure of the gas before use $= 2.5\ \text{atm}$

Initial volume of the gas, $V = \dfrac{nRT}{P} = \dfrac{224.827\ \text{mol} \times 0.0821\ \text{atm lit}^{-1}\ \text{K}^{-1}\ \text{mol}^{-1} \times 300\ \text{K}}{2.5\ \text{atm}}$

$= \mathbf{2214.97\ lit}$

(ii) To calculate the pressure of the gas after use

Weight of cylinder after $= 23.2\ \text{kg}$

Weight of empty cylinder $= 14.8\ \text{kg}$

$\therefore$ Weight of the gas unused gas $= 23.2\ \text{kg} - 14.8\ \text{kg}$

$= 8.4\ \text{kg}$

Pressure of gas after use $P = \dfrac{nRT}{V}$

$$= \frac{8.4\ \text{kg}}{50 \times 10^{-3}\ \text{kg mol}} \times \frac{0.0821\ \text{atm lit K}^{-1}\ \text{mol}^{-1} \times 300\ \text{K}}{2214.97\ \text{lit}}$$

$= \mathbf{1.4788\ atm}$

(iii) To calculate the volume of the gas after used

Weight of the gas initially present $= 14.2\ \text{kg}$

Weight of gas after use $= 8.4\ \text{kg}$

Weight of the gas used up $= 14.2\ \text{kg} - 8.4\ \text{kg}$

$= 5.8\ \text{kg}$

Pressure under normal conditions of usage $= 1\ \text{atm}$

$\therefore$ Volume of the gas used up, $V = \dfrac{nRT}{P}$

$$= \frac{5.8\ \text{kg} \times 0.0821\ \text{atm lit K}^{-1}\ \text{mol}^{-1} \times 300\ \text{K}}{58 \times 10^{-3}\ \text{kg mol}^{-1} \times 1\ \text{atm}}$$

$= 2463\ \text{lit}$

$= \mathbf{2.463\ m^3}$

SOLVED PROBLEM 27. A 4 : 1 mixture of Helium and methane is contained in vessel at 20 bar pressure. Due to a hole in the vessel, the gas mixture leaks out. What is the composition of the mixture effusing out initially.

SOLUTION :

(i) To calculate the partial pressure of He and CH_4

Ratio of moles He and CH_4 = 4 : 1 (given)

Total no. of moles = 5

Pressure ∝ no. of moles of the gas at constant V and T

$$\therefore \quad \text{Partial pressure of He, } P_{He} = \frac{\text{No. of moles of He}}{\text{Total no. of moles}} \times \text{Total pressure}$$

$$= \frac{4}{5} \times (20\text{ bar})$$

$$= 16\text{ bar}$$

$$\text{and} \quad \text{Partial pressure of CH}_4,\ P_{CH_4} = \frac{\text{No. of moles of CH}_4}{\text{Total no. of moles}} \times \text{Total pressure}$$

$$= \frac{1}{5} \times (20\text{ bar})$$

$$= 4\text{ bar}$$

(ii) To calculate the rates of effusion of He and CH_4

$$\text{Rate of effusion of Helium, } r_{He} = \frac{k \times P_{He}}{\sqrt{M_{He}}}$$

$$\text{Mol. mass of He, } M_{He} = 4$$

$$\therefore \quad r_{H_e} = \frac{k \times 16\text{ bar}}{\sqrt{4}}$$

$$= 8\,k$$

$$\text{and} \quad \text{Rate of effusion of CH}_4,\ r_{CH_4} = \frac{k \times P_{CH_4}}{\sqrt{M_{CH_4}}}$$

$$\text{Mol. mass of CH}_4,\ M_{CH_4} = 16$$

$$\therefore \quad r_{CH_4} = \frac{k \times (4\text{ bar})}{\sqrt{M_{CH_4}}}$$

$$= k$$

Hence the rate of gases effusing out initially is 8 *k* : *k* or 8 : 1

SOLVED PROBLEM 28. An iron cylinder contains helium at a pressure of 250 k Pa at 300K. The cylinder can withstand a pressure of 1×10^6 Pa. The room in which cylinder is placed catches fire. Predict whether the cylinder will blow up before it melts or not. (melting point of cylinder = 1800 K)

SOLUTION :

To calculate the final pressure

Formula used

$$\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2} \quad \text{or} \quad P_2 = \frac{P_1 V_1 T_2}{T_1 V_2}$$

Quantities given

Initial conditions : $P_1 = 250\text{ k Pa} = 250 \times 10^3\text{ Pa}$ $T_1 = 300\text{K}$ $V_1 = \text{V lit}$

Final conditions : $V_2 = \text{V lit}$ $T_2 = 1800\text{ K}$ [∵ volume remains the same]

Substitution of values

$$P_2 = \frac{250 \times 10^3 \text{ Pa} \times 1800 \text{ K} \times \text{V lit}}{300 \text{ K} \times \text{V lit}}$$

$$= 1500 \times 10^3 \text{ Pa}$$

$$= \mathbf{1.5 \times 10^6 \text{ Pa}}$$

Since the cylinder can withstand a pressure of 1×10^6 Pa, it will definitely blow up at the melting point of cylinder as the pressure becomes 1.5×10^6 Pa when the cylinder melts.

SOLVED PROBLEM 29. 20 dm^3 of SO_2 diffuse through a porous partition in 60 sec. What volume of O_2 will diffuse under similar conditions in 30 sec ?

SOLUTION :

Formula used

$$\frac{r_{SO_2}}{r_{O_2}} = \sqrt{\frac{M_{O_2}}{M_{SO_2}}}$$

Quantities given

$$r_{SO_2} = \frac{\text{Vol. of } SO_2}{\text{Time taken}} = \frac{20 \text{ dm}^3}{60 \text{ sec}} \qquad M_{SO_2} = 64 \text{ g mol}^{-1}$$

$$r_{O_2} = \frac{\text{Vol. of } O_2}{\text{Time taken}} = \frac{V_{O_2} \text{ dm}^3}{30 \text{ sec}} \qquad M_{O_2} = 32 \text{ g mol}^{-1}$$

Substitution of values

$$\frac{\frac{20 \text{ dm}^3}{60 \text{ sec}}}{\frac{V_{O_2} \text{ dm}^3}{30 \text{ sec}}} = \sqrt{\frac{32 \text{ g mol}^{-1}}{64 \text{ g mol}^{-1}}}$$

$$\frac{10}{V_{O_2}} = \sqrt{\frac{1}{2}}$$

or

$$V_{O_2} = 10 \times \sqrt{2} \text{ dm}^3$$

$$= 10 \times 1.414 \text{ dm}^3$$

$$= \mathbf{14.14 \text{ dm}^3}$$

SOLVED PROBLEM 30. The molar volume of liquid benzene (density = 0.877 g ml^{-1}) increases by a factor of 2750 as it vapourises at 20ºC and that of liquid toluene (density = 0.867 g ml^{-1}) increases by a factor of 7720 at 20ºC. A solution of benzene and toluene at 20 ºC has vapour of 46.0 torr. Find the mole fraction of benzene in the vapour above the solution.

SOLUTION :

Formula used

$$p^o = \frac{n R T}{V}$$

Quantities given for benzene

$n = 1$ mole $\qquad R = 0.0821$ atm lit K^{-1} mol^{-1} $\qquad T = 20 + 273 = 293$ K

Volume of 1 mole of liquid benzene $= \frac{M}{D} = \frac{78\text{ g}}{0.877\text{ g ml}^{-1}}$

$= 88.939\text{ ml}$

and Volume of 1 mole of benzene vapours $= 2750 \times 88.939\text{ ml}$

$= 244582\text{ ml}$

$= 244.582\text{ lit}$

Substitution of values

$$p^o_{benzene} = \frac{1\text{ mole} \times 0.0821\text{ atm lit K}^{-1}\text{ mol}^{-1} \times 293\text{ K}}{244.582\text{ lit}}$$

$$= 0.098\text{ atm}$$

Quantities given for toluene

$n = 1$ mole $R = 0.0821\text{ atm lit K}^{-1}\text{ mol}^{-1}$ $T = 293\text{ K}$

Volume of 1 mole of liquid toluene $= \frac{M}{D} = \frac{92\text{ g}}{0.867\text{ g ml}^{-1}}$

$= 106.11\text{ ml}$

and Volume of 1 mole toluene vapours $= 7720 \times 106.11\text{ ml}$

$= 819169\text{ ml}$

$= 819.169\text{ lit}$

Substitution of values

$$p^o_{toluene} = \frac{1\text{ mole} \times 0.0821\text{ atm lit K}^{-1}\text{ mol}^{-1} \times 293\text{ K}}{819.169\text{ lit}}$$

$$= 0.029\text{ atm}$$

(ii) To calculate the mole fraction of benzene

Formula used

$$x_{benzene} \times p^o_{benzene} + x_{toluene} \times p^o_{toluene} = \textit{Total pressure}$$

Quantities given

$\textit{Total pressure} = 46\text{ torr} = \frac{46\text{ torr}}{760\text{ torr}} = 0.06\text{ atm}$

$p^o_{benzene} = 0.98$ $p^o_{toluene} = 0.029\text{ atm}$ $x_{toluene} = 1 - x_{benzene}$

Substitution of values

$$x_{benzene} \times 0.098\text{ atm} + (1 - x_{benzene})\, 0.029\text{ atm} = 0.06\text{ atm}$$

or $$x_{benzene} = \frac{0.06 - 0.029}{(0.098 - 0.029)}$$

$$= \mathbf{0.449}$$

ADDITIONAL PRACTICE PROBLEMS

1. A 5.0 litre sample of gas has its pressure doubled while its absolute temperature is increased by 25%. What is its new volume ?

Answer. 3.125 lit

2. The total pressure of a mixture of gases is 1.50 atm. The mixture contains 0.1 mole of N_2 and 0.2 mole of O_2. What is the partial pressure of O_2 ?

Answer. 1.0 atm

3. Calculate the RMS, average and most probable velocity of a gas at 25 ºC, when the mass of a gas molecule is 4.468×10^{26}g.

Answer. 5.274×10^4 cm sec^{-1} ; 4.859×10^4 cm sec^{-1} ; 4.306×10^4 cm sec^{-1}

4. Calculate the RMS velocity of CO_2 at 27 ºC.

Answer. 4.1328×10^4 cm sec^{-1}

5. Calculate the mean free path for O_2 molecule at 300 K and pressure 101.325 kPa. The collision diameter of oxygen molecule is 0.326 nm.

Answer. 7.0169×10^{-8} m

6. Calculate the pressure developed in 95 litre vessel containing 88 g of CO_2 at 27ºC. Assume CO_2 is vander Waals gas (C = 12 ; O = 16 $a = 3.59$ atm lit^2 mol^{-2} ; $b = 0.043$ lit mol^{-1})

Answer. 9.450 atm

7. Calculate the critical temperature of a vander Waals gas for which P_c is 100 atm and b is 50 cm^3 mol^{-1}.

Answer. 214.2 ºC

8. The pressure in a bulb dropped from 2000 to 150 mm of Hg in 47 minutes when the contained oxygen leaked through a small hole. The bulb was then evacuated. A mixture of oxygen and another gas with molar ratio1:1 at a pressure of 4000 mm Hg was introduced. Find the molar ratio of two gas remaining in the bulb after 74 minutes.

Answer. 4 : 5

9. Calculate the average kinetic energy in Joules of the molecules in 8.0 g of methane at 27 ºC.

Answer. 1870.65 J

10. At room temperature ammonia gas at 1 atm pressure and hydrogen chloride at P atm pressure are allowed to effuse through indentical pin holes from opposite ends of a glass tube of one meter length and of uniform cross-section. Ammonium Chloride is first formed at 60 cm from the end through which hydrogen chloride is sent in. What is the value of P?

Answer. 2.197 atm

11. When 2 g of a gas is introduced into an evacuated flask kept at 25 ºC, the pressure is found to be 1 atm. If 3 g of another gas B is then added to same flask the total pressure becomes 1.5 atm. Assuming ideal behaviour, calculate the ratio of their molecular mass $M_A : M_B$.

Answer. 1.3

12. Oxygen is present in 1 litre flask at a pressure of 7.6×10^{-10} mm of Hg. Calculate the number of oxygen molecules in the flask at 0 ºC.

Answer. 3.224×10^{11} molecules

13. Calculate the root mean square velocity of Ozone kept in a closed vessel at 20 ºC and 82 cm mercury pressure.

Answer. 3.9032×10^4 cm sec^{-1}

14. A spherical balloon of 21 cm diameter is to be filled up with hydrogen at NTP from a cylinder containing the gas at 27 ºC and 27 atm pressure. If the cylinder can hold 2.82 litre of water, calculate the number of balloons that can be filled up.

Answer. 10

15. At 27 ºC, hydrogen is leaked through a tiny hole into a vessel for 22 minutes. Another unknown gas at the same temperature and pressure as that of H_2 is leaked through the same hole for 20 minutes. After the effusion of the gases, the mixture exerts a pressure of one atmosphere. The hydrogen content of the mixture is 0.7 mole. If the volume of container is 3.0 litre, what is the molecular mass of the unknown gas.

Answer. 1020 g mol^{-1}

16. The composition of the equilibrium mixture (Cl_2 = 2 Cl), which is attained at 1200 ºC, is determined by measuring the rate of effusion through a pin-hole. It is observed that at 1.80 mm Hg pressure, the mixture effuses 1.16 times as fast as Krypton effuses under the same conditions. Calculate the fraction of chlorine molecules dissociated into atoms (Atomic weight of Kr = 84).

Answer. 0.137

17. What weight of AgCl would be precipitated if 10 ml of HCl gas, measured at 12 ºC and 750 mm pressure were passed into excess of a solution of silver nitrate?

Answer. 0.606 g

18. Calculate the total pressure in a mixture of 4 g of oxygen and 3 g of hydrogen confined in a total volume of one litre at 0 ºC.

Answer. 25.18 atm

19. Calculate the volume occupied by 7 g of nitrogen gas at 27 ºC and 750 mm pressure.

Answer. 6.23 litre

20. Two gases P and Q having molecular masses 44 and 64 respectively are enclosed in a vessel. Their masses are 0.5 g and 0.3 g respectively and the total pressure of the mixture is 740 mm. Calculate the partial pressures of the two gases.

Answer. 524 mm ; 216 mm

21. Calculate the total pressure in a 10 Litre cylinder which contains 0.4 g of helium, 1.6 g of oxygen and 1.4 of nitrogen at 27 ºC. Also calculate the partial pressure of helium gas in the cylinder. Assume ideal behaviour for gases.

Answer. 0.492 atm ; 0.246 atm