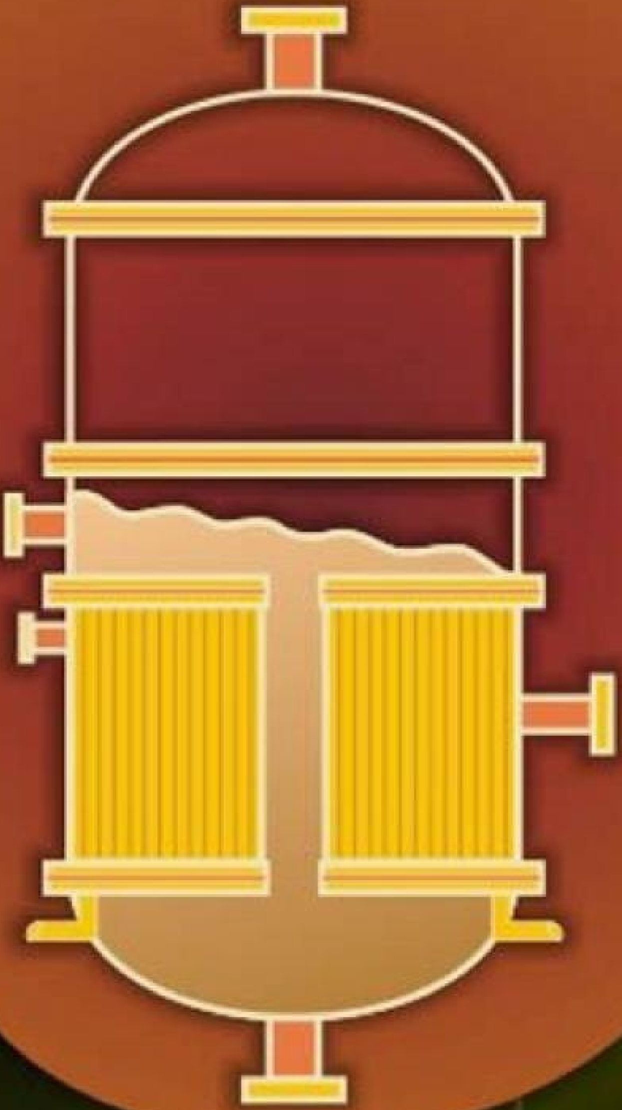

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Chemical Process Calculations

D.C. Sikdar

PHI

Chemical Process Calculations

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CHEMICAL PROCESS CALCULATIONS
D.C. Sikdar

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To
My wife BULU, son ATANU
and Parents
for their Love, Understanding and Support

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Foreword

Chemical Process Calculations is one of the core courses at the undergraduate level of Chemical Engineering curriculum. In this course, more emphasis is given on the units and conversions, basic concept of calculations, material balance with or without chemical reactions, combustion of fuels and energy balances.

Professor D.C. Sikdar has written this book on Chemical Process Calculations with his vast experience in teaching and research. He has received awards from the Government of Karnataka for guiding M.Tech. thesis in the field of Bio-fuel. Professor Sikdar is well known for his teaching skills. He has taken a keen interest in writing this book.

This book is meant to provide the fundamental concepts and practical tools needed by all Chemical Engineers, regardless of the particular area they eventually enter. The chapters and topics are organized in a systematic way in order that the students get a thorough knowledge and understanding of the subject.

I strongly recommend the student to make use of this book and learn Chemical Process Calculations in a very easy way.

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Preface

The importance of Chemical Process Calculations and applications is well-known in the various fields of Engineering and Technology. For example, the knowledge of material and energy balance with or without chemical reaction is very essential for process design. Thus, we can say that material balance and energy balance are the basic tools of Process Calculations. The design of equipment starts only after completion of material and energy balance calculation of the process. Based on these calculations the feasibility of the process or performance of the equipment can be judged. A mistake in the calculations can be easily corrected at the initial stage of the process; whereas a mistake carried forward to the execution stage can result in considerable loss in investment and time. Therefore, a strong foundation in Chemical Process Calculations is must for the success of chemical engineers in their professional life.

Chemical Process Calculations is one of the core courses at the undergraduate level of chemical engineering course curriculum. In this course, more emphasis is given to the units and conversions, basic concept of calculations, material balance without chemical reactions, material balance with chemical reactions, combustion of fuels and energy balances, all coming under the realm of Chemical Process Calculations. The chapters and topics are organized in a systematic way in order that the students get a thorough knowledge and understanding of the subject. The usefulness of the book has been further enhanced by the inclusion of a large number of illustrative figures, solved examples and exercises at the end of the chapters for bridging the gap between theoretical learning and practical implementation.

During the two and half decades of my experience in teaching chemical process calculations to the undergraduate students, I have come across the students who have feeling of liking and disliking towards this subject. Unfortunately, the disliking outnumbers the liking. The difficulty in process calculations of industrial based chemical reaction is to be partly blamed for this scenario. The major reason is the scarcity of students friendly textbooks that help the students in providing a sound knowledge and act as catalyst for going deeper into the subject. This kind of feeling of students is kept in mind while preparing the context of the book. An attempt is also made to eliminate avoidable rigor and intricacy that usually make the subject dry.

This book is intended to serve as a simple textbook for the undergraduate students in Chemical Engineering and other related branches of engineering, such as Polymer Science and Engineering, Petroleum Engineering, Biotechnology and Diploma in Chemical Engineering. A large number of examples are given under each chapter which would help the students gain a better insight into the theory. In this book, only SI unit is used. The exercise questions at the end of the chapters would help the student to check his or her understanding of the topics discussed in each chapter before going to the next.

This book is an outgrowth of the several lectures I have delivered to chemical engineering students in Dayananda Sagar College of Engineering, Bangalore. The continuous demand for detailed information about the Process Calculations during the teaching–learning process made me to write this textbook for the benefit of all aspiring chemical engineering students.

Valuable help and suggestions at various stages in its evolution have been contributed towards bringing it out in the present form.

D.C. SIKDAR

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I recall with gratitude the stimulating experiences, I spent at NITK Surathkal during my undergraduate and postgraduate study and interaction with Prof. M.G. Subba Rao, which contributed much in sustaining my interest in the subject of chemical process calculations.

I express my deep sense of gratitude to Dr. D. Hemachandra Sagar, Chairman and Dr. D. Premachandra Sagar, Vice-Chairman and CEO, Dayananda Sagar Institutions, who has enthused me with the spirit of writing the book that would be useful to the student community.

I am thankful to Sri Galiswamy, Secretary, Dayananda Sagar Institutions, Dr. A.N.N. Murthy, Principal, DSCE and Dr. R. Ravishankar, Head of the Department of Chemical Engineering, DSCE, Bangalore, for their sustained support rendered during the writing of this book.

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I thank my family and relatives for their direct and indirect support. My wife Bulu, son Atanu, need a special mention for their patience and graceful support during the writing of this book.

Finally, last but not least, I express my thanks to the Management, and Editorial and Production Departments of PHI Learning for their careful evaluation and constructive suggestions. It is my duty to thank Mr. Asoke Ghosh, Managing Director of PHI learning for publishing my book. My thanks are also due to Mr. Chandira Devadiga for his constant support and encouragement in shaping this text as a publishable material. My thanks are also due to Ms. Shivani Garg and her team of editors for providing necessary guidelines for the preparation of the text.

I hope that this book will be very useful to the readers in all aspects.

I welcome helpful comments and suggestions from the readers for its further improvement.

D.C. SIKDAR

List of Symbols

A Area
A Empirical constant
a Vander Waals constant
a Constant
B Virial co-efficient
b Vander Waals constant
b Constant
C Heat capacity
C Empirical constant
c Constant
C_P Specific heat at constant pressure
$C_{pm}{}^{o}$ Mean molal heat capacity at standard condition
C_v Specific at constant volume
C_A Specific heat of Air
C_W Specific heat of water
D Diameter
D Distillate
d Constant
E Energy
E_K Kinetic energy
E_p Potential energy
f_i Fugacity
F Feed
G Mass velocity
g Acceleration due to gravity
g Gram
H Enthalpy
H Humidity
H Molal humidity
H Henry’s law constant
h Heat transfer coefficient
H_H Humid heat
H_p Percentage humidity
H_R Relative humidity
H_S Saturated humidity

ΔH	Change in enthalpy
ΔH_c^o	Standard heat of combustion
ΔH_{con}	Heat of condensation
ΔH_R^o	Standard heat of reaction
ΔH_f^o	Standard heat of formation
ΔH_s	Heat of solution
ΔH_m	Heat of mixing
ΔH_{cr}	Heat of crystallization
ΔH_v	Heat of vaporization
k	Relative vapour pressure
k	Thermal conductivity
k	Dimensional constant
K	Degree kelvin
l	Dimension of length
L	Thick liquor
l	Length of a body
M	Molality
M	Molarity
M	Molecular weight
M	Dimension of mass
m	Mass
M_A	Molecular weight of component A
M_B	Molecular weight of component B
M_i	Moles of component i
M_{Avg}	Average molecular weight
N	Normality
n_a	Number of moles of component a
n_b	Number of moles of component b
n_c	Number of moles of component c
Δn	Change in mole
N_{pr}	Prandtl number
P	Product
P	Final pressure
P_A	Saturated vapour pressure of component A
P_A^o	Vapour pressure of pure liquid
P_B	Saturated vapour pressure of component B
P_C	Saturated vapour pressure of component C

P_c Critical pressure
P_0 Initial pressure
p_a Partial pressure of component a
p_b Partial pressure of component b
p_c Partial pressure of component c
P_s Vapor pressure of pure solvent
p_t Total pressure
p_T Partial pressure of Toluene
p_B Partial pressure of Benzene
p_X Partial pressure of Xylene
Q Heat transferred
r Regression
R Universal gas constant
R Product
R Resistance force
R Reflux ratio
T Absolute temperature
T Dimensionless time
T_C Critical temperature
T_o Standard temperature
T_B Boiling temperature
U Internal energy
ΔU Change in internal energy
V Vapour
V Volume
V Specific volume
V Velocity
V_A Pure component volume of A
V_B Pure component volume of B
V_C Pure component volume of C
V_a Pure component volume of a
V_b Pure component volume of b
V_c Pure component volume of c
ΔV_i^I Residual volume
W Bottom product
W_A Weight of component A
W_B Weight of component B

x Independent variable
x_i Mole fraction of component i
x_F Mole fraction of feed
x_D Mole fraction of distillate
x_W Mole fraction of bottom product
x_A Mole fraction of component A in the liquid phase
y Dependent variable
y_A Mole fraction of component A in the Gas phase
r Density
r_{mix} Density of mixture
μ Viscosity
π Buckingham terms
a Constant
s Standard deviation
l Latent heat of vaporization

1

Units and Dimensions

1.1

Introduction

Physical theory does not have definite boundary. Hence, to give definite boundary to physical theory, it is generally expressed in mathematical form in terms of model equation. In order to reproduce the physical theory uniformly, the numbering and measuring is very much essential for model equations.

Without units and dimensions much of our work is meaningless. For example, consider a box containing ripe mangoes. The number of mangoes contained in the box can be counted, the same mangoes can be weighed also. Now, suppose if we did not have any units and dimension, both the quantities would have represented by a number that would lead to throw into disorder for the others. Hence, for logical understanding of the subjects, a complete knowledge of various system of units and dimensions is essential.

Units and dimensions are the powerful tools for systematic study of Science and Technology. They are useful in solving material balance and energy balance problems in a chemical industry.

1.2

Fundamental and Derived Units

The study of chemical process calculations is no way different than that of other science and one must start with the understanding of fundamental quantities, namely dimensions. This will facilitate the use of appropriate and consistent units in solving process calculation problems. Physical quantities can be classified into two groups namely:

1. Fundamental quantities
2. Derived quantities.

1.2.1 Fundamental Quantities

It consists of four quantities, length, mass, time and temperature. These are called dimensions or base units and are represented by the symbols L, M, q and T respectively. The fundamental quantities are represented by a system of units according to the system of measurement. Basically, the physical system representing the base unit differs in different systems of units.

1.2.2 Derived Quantities

It consists of quantities which derived from the fundamental quantities, such as area, force, pressure, energy etc. It follows, therefore, that derived quantities are represented algebraically in terms of base units by means of the mathematical symbols of multiplication and division.

1.3

System of Units

System of units is initially developed by England in 18th century. They considered foot, pound and second as standard measurements for length, mass and time respectively. They faced little difficulties in the measurement of small length in terms of feet and very small weight in terms of pounds. To overcome these difficulties, in 1860, British association developed CGS system in which base units are chosen as centimetre, gram and second. Again, some difficulties arises with the measurement of CGS system. For example, the large length need to express in terms of multiple of centimetres and large weight in terms of multiple of grams. Hence, this system of units was not accepted internationally.

To overcome these difficulties, in 1971, France association developed MKS system in which base units are chosen as metre, kilogram and second. This system of measurement is also known as Metric system. It is needless to say that this MKS system is derived from the CGS system eventhough the base standard of the MKS system is similar to those of the CGS system. In practice, it is difficult to work with either CGS system or MKS system alone. Therefore, this two systems are used side by side depending on the convenience. For example, it is common to express the density in g/cm^3 rather than in kg/m^3.

Later, it was felt by international society that there is a need for an international system for better understanding of system of units. To meet this, in 1954, a general conference on weight and measurement was held at Paris. In this general conference, they decided to have an international practical system of units in which base units are chosen as metre, kilogram, second, Ampere, Kelvin and Candela. Later, in 1960, again a general conference on weight and measurement was held in Paris and gave the name to this system as system international units. It is also known as International system of units and abbreviated as SI units in all language.

The various systems of units and the fundamental quantities associated with them are given in Table 1.1.

TABLE 1.1 System of Units

Fundamental quantity	System of units				Dimension
	SI	MKS	CGS	FPS	
Length	metre (m)	metre (m)	centimetre (cm)	foot (ft)	L
Mass	kilogram (kg)	kilogram (kg)	gram (g)	pound (lb)	M
Time	second (s)	second (s)	second (s)	second (s)	q
Temperature	kelvin (K)	celsius (°C)	celsius (°C)	fahrenheit (°F)	T

The official international system of units is SI units. The International system of units covers the entire field of science and technology. SI units are probably the most important for engineering calculations.

Basic SI Units:

Mass : kilogram (kg)
Length : metre (m)
Time : second (s)
Temperature : kelvin (K)
Mole : kilogram mole (kgmol)
Force : newton (N)
Pressure : newton/metre^2 (N/m^2 = Pa)

Energy : newton . metre (N . m = J)
Power : newton . metre/second (N . m/s = J/s = W)

1.4

Conversion of Units

The conversion of units of a particular quantity from one system of units to another system of units is done with the help of conversion factors when quantity is expressed in terms of fundamental units of mass, length, time and temperature. Some conversion factors are given in Table 1.2.

TABLE 1.2 Conversion Factors

Length	1 in = 2.54 cm
	1 ft = 30.48 cm
	1 mile = 1.6093 km
	1 yd = 0.9144 m
Area	1 in^2 = 6.452 cm^2
	1 ft^2 = 0.0929 m^2
	1 Acre = 4046.9 m^2
Volume	1 in^3 = 16.386 cm^3
	1 ft^3 = 0.0283 m^3
	1 barrel = 0.1589 m^3
Capacity	1 UK gal = 4.546 l
	1 US gal = 3.7854 l
	1 ft^3 = 28.3168 l
Mass	1 lb = 0.4535 kg
	1 grain = 0.0647 g
Density	1 lb/ft^3 = 0.016 g/cm^3
Specific volume	1 ft^3/lb = 0.0624 m^3/kg
Force	1 lbf = 0.4535 kgf
	1 N = 0.1019 kgf
	1 N = 1 × 10^5 dyn
Pressure	1 lbf/in^2 = 0.0689 bar
	1 kPa = 0.0101 kgf/cm^2
	1 lbf/in^2 = 0.068 atmosphere
	1 in Hg = 25.3999 torr (1 mmHg)
	760 mmHg = 101.325 kPa
Energy	1 Btu = 1055 J
	1 lbf ┘ ft = 1.3558 J
	1 Btu = 2.9307 × 10^{-4} kWh
	1 Btu = 0.2519 kcal
Power	1 hp = 746 W
	1 hp = 1.0138 metric hp
	1 kW = 1.3596 metric hp
Heat capacity	1 Btu/(lb ┘ °F) = 4186.7 J/(kg ┘ °C)

	1 Btu/(lb°F) = 1 kcal/(kg°C)
Temperature	(5/9) (°F – 32) = 1 °C (9/5) °C + 32 = 1 °F
Temperature interval difference	1 °C = 1.8 °F = 1 K

EXAMPLE 1.1 Convert 150 lb/ft^3 into g/cm^3.

Solution: We know that

1 lb = 0.4535 kg

1 ft = 30.48 cm

Therefore,

$$\begin{aligned} 150\ \text{lb/ft}^3 &= 150 \times \frac{0.4535 \times 1000}{(30.48)^3} \\ &= 2.4022\ \text{g/cm}^3 \end{aligned}$$

EXAMPLE 1.2 Convert 50 Btu to kWh.

Solution: We know that

$$\begin{aligned} 1\ \text{Btu} &= 1055\ \text{J} \\ &= 1055\ \frac{\text{J}}{\text{h}} \cdot \text{h} \\ &= \frac{1055}{3600}\left(\frac{\text{J}}{\text{s}}\right) \cdot \text{h} \\ &= \frac{1055}{3600}\ \text{Wh} \\ &= \frac{1055}{3600 \times 1000}\ \text{kWh} \\ 1\ \text{Btu} &= 2.9305 \times 10^{-4}\ \text{kWh} \end{aligned}$$

Therefore,

$$\begin{aligned} 50\ \text{Btu} &= 50 \times 2.9305 \times 10^{-4}\ \text{kWh} \\ &= 0.0146\ \text{kWh} \end{aligned}$$

EXAMPLE 1.3 Convert 2 kWh to Btu.

Solution: We know that

$$\begin{aligned} 1\ \text{kWh} &= 1 \times 1000\ \text{W} \cdot \text{h} \\ &= 1 \times 1000 \times 3600\ \text{W} \cdot \text{s} \\ &= 1 \times 1000 \times 3600\ \frac{\text{J}}{\text{s}} \cdot \text{s} \\ &= 3600 \times 1000\ \text{J} \\ &= \frac{3600 \times 1000}{1055}\ \text{Btu} \\ &= 3412\ \text{Btu} \end{aligned}$$

Therefore, 2 kWh = 6824.64 Btu

EXAMPLE 1.4 Convert 1200 mmHg into atm.

Solution:

Since 760 mmHg = 1 atm

1200 mmHg = $1 \times \frac{1200}{760}$

Therefore, = 1.5789 atm

EXAMPLE 1.5 Convert 1000 W in hp and kgf ⊣ m/s

Solution:

Since 746 W = 1 hp

Therefore, 1000 W = $1 \times \frac{1000}{746}$

= 1.34 hp

Also, 1 hp = 746 W

= 746 N ⊣ m/s

= 746 × 0.019 kgf ⊣ m/s

1 hp = 76.01 kgf ⊣ m/s

⌃ 1.34 hp = 76.01 × 1.34

⌃ = 101.86 kgf ⊣ m/s

EXAMPLE 1.6 Convert volumetric flow rate of 5 m^3/s to l/s.

Solution:

5 m^3/s = $5 \times \frac{1000}{1}$ l/s

= 5000 l/s

EXAMPLE 1.7 In a double effect evaporator plant, the second effect is maintained under vacuum of 455 torr (mmHg). Find the absolute pressure in kPa.

Solution: Absolute pressure = Atmospheric pressure – Vacuum

= 760 – 455

= 305 torr (mmHg)

Absolute pressure = $305 \times \frac{101.325}{760}$

= 40.66 kPa

EXAMPLE 1.8 A force equal to 25 kgf is applied on the piston with a diameter of 2 cm. Find the pressure exerted on a piston in kPa.

Solution: We know that $P = \frac{F}{A}$

and $A = \pi\left(\frac{d^2}{4}\right) = \frac{\pi}{4}(2)^2$

$= 3.1415\ \text{cm}^2$

Also, $F = 25$ kgf (given)

Therefore, $P = \frac{25}{3.1415} = 7.958\ \text{kgf/cm}^2$

$= 7.958 \times \frac{1}{0.0101} = 787.9$ kPa

EXAMPLE 1.9 Convert 40 l/(m^2)(h) to m^3/(cm)^2 (s).

Solution:

$$40\,\frac{1}{(\text{m}^2)(\text{h})} = 40 \times \frac{1 \times 10^{-3}\ \text{m}^3}{1 \times 10^{4}\ (\text{cm}^2)} \times \frac{1}{3600\ \text{s}}$$

$$= 40 \times \frac{1 \times 10^{-3}}{(1 \times 10^{4})\ 3600\ \text{s}}\,\frac{\text{m}^3}{(\text{cm}^2)(\text{s})}$$

$$= 1.11 \times 10^{-9}\ \text{m}^3/(\text{cm}^2)(\text{s})$$

EXAMPLE 1.10 The thermal conductivity of steel is 16.5 Btu/(h)(ft)(°F). What is the value of the thermal conductivity in W/(m)(°C)?

Solution:

$$16.5\,\frac{\text{Btu}}{(\text{h})(\text{ft})(°\text{F})} = 16.5 \times \frac{1055 \times (1.8)}{(3600) \times 0.3048 \times 1}$$

$$= 2.6529\ \text{W/m °C}$$

EXAMPLE 1.11 Convert – 40 °C to °F.

Solution: We know that

$°\text{F} = \frac{9}{5}(°\text{C}) + 32$

$= \frac{9}{5}(-40) + 32$

$°\text{F} = -40$

Therefore, – 40 °F = – 40 °C

EXAMPLE 1.12 Prove that kcal/h = 1.163 (N ⏌ m)/s.

Solution:

$$\frac{\text{kcal}}{\text{h}} = \frac{1000 \times 4.187}{3600}\ \text{J/s}$$
$$= 1.163\ \text{J/s}$$
$$= 1.163\ (\text{N}\cdot\text{m})/\text{s}$$

EXAMPLE 1.13 Verify that 1 lbf/ft^2 = 47.88 N/m^2.

Solution:

$$1\ \text{lbf/ft}^2 = \frac{1 \times 0.4535}{0.1019} \times \frac{1}{(0.3048)^2}\ \text{N/m}^2$$
$$= 47.88\ \text{N/m}^2$$

EXAMPLE 1.14 Prove that Btu/(ft^2)(h) = 3.155 W/m^2.

Solution:

$$1\frac{\text{Btu}}{(\text{ft}^2)(\text{h})} = 1 \times \frac{1055}{(0.3048)^2\,(3600)}\ \frac{\text{J}}{(\text{s})(\text{m}^2)}$$
$$= 3.155\ \text{W/m}^2$$

EXAMPLE 1.15 Show that Btu/(lb)(°F) = 4187 J/(kg) (K)

Solution:

$$1\frac{\text{Btu}}{(\text{lb})(°\text{F})} = 1 \times \frac{(1055)(1.8)}{(0.4535)}\ \frac{\text{J}}{(\text{kg})(\text{K})}$$
$$= 4187\ \text{J/(kg)(K)}$$

1.5

Dimensional Consistency of Equations

The Vander Waals equation

$$\left(P + \frac{a}{V^2}\right)(V - b) = RT \qquad (1.1)$$

where

P = Absolute pressure (N/m^2)

a = Vander Waals constant (N ⊣ m^4/kgmol^2)

V = Specific volume (m^3/kgmol)

b = Vander Waals constant (m^2/kgmol)

R = Universal gas constant (J/kgmol ⊣ K)

T = Absolute temperature (K)

In Eq. (1.1), each term has a specific unit as shown. Therefore, Vander Waals equation exhibits dimensional consistency.

EXAMPLE 1.16 An empirical equation for calculating the inside heat transfer coefficient h_i for the turbulent flow of liquids in a pipe is given by

$$h_i = \frac{0.023\, G^{0.8}\, k^{0.67}\, C_p^{\;0.33}}{D^{0.2}\, \mu^{0.47}} \qquad \text{(i)}$$

where

h_i = Heat transfer co-efficient (W/m^2 °C)

G = Mass velocity of the liquid (kg/m^2 · s)
k = Thermal conductivity of the liquid (W/m · °C)
C_p = Heat capacity of the liquid (J/kg °C)
m = Viscosity of the liquid (kg/m · s)
D = Inside diameter of the pipe (m)

Verify, if the equation is dimensionally consistent.

Solution: We have from Eq. (i).

$$h_i = \frac{0.023\, G^{0.8}\, k^{0.67}\, C_p^{\;0.33}}{D^{0.2}\, \mu^{0.47}}$$

$$h_i = \frac{(0.023)\ (\text{lb/h} \cdot \text{ft}^2)^{0.8}\ [\text{Btu/(h)(ft)(°F)}]^{0.67}\ [\text{Btu/lb (°F)}]^{0.33}}{(\text{ft})^{0.2}\ [\text{lb/(ft)(h)}]^{0.47}}$$

$$h_i = \frac{(0.023)\,(\text{Btu})^{0.67}\,(\text{Btu})^{0.33}\,(\text{lb})^{0.8}\,(\text{ft})^{0.47}\,(\text{h})^{0.47}}{(\text{h})^{0.8}(\text{ft})^{1.6}(\text{h})^{0.67}(\text{ft})^{0.67}(°\text{F})^{0.67}(\text{lb})^{0.33}(°\text{F})^{0.33}(\text{ft})^{0.2}(\text{lb})^{0.47}}$$

$$h_i = \frac{(0.023)\,(\text{Btu})^{0.67}(\text{Btu})^{0.33}\,(\text{lbm})^{0.8}}{(\text{lb})^{0.33}\,(\text{lb})^{0.47}} \times \frac{(\text{h})^{0.47}}{(\text{h})^{0.8}\,(\text{h})^{0.67}} \times \frac{(\text{ft})^{0.47}}{(\text{ft})^{1.6}(\text{ft})^{0.67}(\text{ft})^{0.2}} \times \frac{1}{(°\text{F})^{0.67}(°\text{F})^{0.33}}$$

$$h_i = 0.023 \frac{\text{Btu}}{(\text{h})(\text{ft}^2)(°\text{F})} \qquad \text{(ii)}$$

Hence, the equation is dimensionally consistent.

1.6

Dimensional Equations

A dimensional equation is one in which physical quantities are expressed in terms of power of fundamental quantities, such as length, mass, time and temperature. It is a useful tool for dimensional analysis. It establishes the relationship between two or more physical quantities in an equation.

For example, consider the enthalpy relation

$$H = U + PV \qquad (1.2)$$

where

H = Enthalpy (J/kg)
U = Internal energy (J/kg)
P = Absolute pressure (N/m^2)
V = Specific volume (m^3/kg)

The dimensional equation of enthalpy relation may be expressed as

$$(MLT^{-2})\,(LM^{-1}) = (MLT^{-2})\,(LM^{-1}) + (MLT^{-2})\,(L^{-2})(L^3M^{-1}) \qquad (1.3)$$

where

M = Dimension of mass
L = Dimension of length
T = Dimension of time.

1.7

Dimensionless Group and Constant

A dimensionless group is one in which two or more physical quantities, such as velocity, density and viscosity are expressed in terms of single group to give rise to zero overall dimension. A typical example of dimensionless group is the Prandtl number

$$N_{\mathrm{pr}} = \frac{C_p\mu}{k} \qquad (1.4)$$

where

N_{pr} = Prandtl number
C_p = Specific heat (J/kg °C)
m = Viscosity (kg/m ⊣ s)
k = Thermal conductivity (W/m °C)

The dimensions of the physical quantities involved are

$$C_p = \frac{(L^2)}{(T^2)(\theta)} \qquad (1.5)$$

$$\mu = \frac{(M)}{(L)(T)} \qquad (1.6)$$

$$k = \frac{(M)(L)}{(T^3)(\theta)} \qquad (1.7)$$

The fundamental units of length, mass, time and temperature, L, M, T and q reduces the Prandtl number to a dimensionless group. Substituting Eqs. (1.5), (1.6) and (1.7) in Eq. (1.4), we get

$$N_{\mathrm{pr}} = \frac{[(L^2)/(T^2)(\theta)] \times [(M)/(L)(T)]}{(M)(L)/(T^3)(\theta)} \qquad (1.8)$$

$$N_{\mathrm{pr}} = 1 \qquad (1.9)$$

Thus, we can observe that by substituting the dimension of physical quantities in dimensionless group

N_{pr}, the group reduces to a pure number 1. Hence, it is also called dimensionless number.

The significance of the dimensionless group is that each dimensionless group containing several physical quantities acts as a single compound variable. Hence, it reduces the number of experiment needed to correlate and interpret the experimental data.

1.8

Dimensionless Equation

A dimensionless equation is one in which physical quantities are expressed in terms of two or more groups in such a way that the dimension of each term cancel. For example, consider the other form of Virial equation of state.

$$PV = RT + PB \qquad (1.10)$$

where

P = Absolute pressure (N/m^2)
V = Specific volume (m^3/kg)
R = Universal gas constant (J/kg ⊣ K)
T = Absolute temperature (K)
B = Virial co-efficient (m^3/kg)

Dividing Eq. (1.10) by RT, we get

$$\frac{PV}{RT} = 1 + \frac{PB}{RT} \qquad (1.11)$$

The dimensions of the physical quantities involved are:

$$P = \frac{(M)}{(T^2)(L)} \qquad (1.12)$$

$$V = \frac{(L^3)}{(M)} \qquad (1.13)$$

$$R = \frac{(L^2)}{(T^2)(\theta)} \qquad (1.14)$$

$$T = q \qquad (1.15)$$

$$B = \frac{(L^3)}{(M)} \qquad (1.16)$$

Substituting Eqs. (1.12), (1.13), (1.14), (1.15) and (1.16) in Eq. (1.11), we get

$$\frac{[(M)/(T^2)(L)] \times [(L^3)/(M)]}{(L^2)/(T^2)(\theta) \times \theta} = 1 + \frac{[(M)/(T^2)(L)] \times [(L^3)/(M)]}{(L^2)/(T^2)(\theta) \times \theta} \qquad (1.17)$$

From Eq. (1.17), it is observed that the dimension of each term is cancelled and each term is dimensionless.

The significance of dimensionless equation is that it reduces the group containing physical variable, Hence, it reduces the time required to conduct the experiment as well as interpret the experimental data.

1.9

Dimensional Analysis

Dimensional analysis is a method to determine relationships among the physical quantities, such as velocity, density and viscosity by using their fundamental properties length L, mass M, time T and temperature q. It is a simple mathematical technique to determine the expression for dependent variable. It is used in research work for conducting model tests. Dimensional analysis can be carried out by the following methods:

1. Rayleigh’s method
2. Buckingham’s *p*-method.

1.9.1 Rayleigh’s Method

Rayleigh’s method of dimensional analysis is generally used when the expression contains maximum of three independent variables. If the number of independent variables is three or less, then it is very easy to determine the expression for the dependent variable. If the number of independent variable is four or more, then it is very difficult to determine the expression for the dependent variable.

In this method, the expression can be written as

$$x = k(x_1^a \cdot x_2^b \cdot x_3^c) \qquad (1.18)$$

where

x = Dependent variable

x_1 = Independent variable

x_2 = Independent variable

x_3 = Independent variable

k = Dimensional constant

a = Arbitrary power of independent variable x_1

b = Arbitrary power of independent variable x_2

c = Arbitrary power of independent variable x_3.

1.9.2 Buckingham’s *p*-method

This method of dimensional analysis is generally used when the Rayleigh’s method becomes difficult. This difficulty is overcome by using Buckingham’s *p*-method of dimensional analysis while determining the expression for dependent variable.

In this method, there are ‘n’ number of independent and dependent variables and ‘m’ number of fundamental variables. The difference of these variables $(n - m)$ will give rise to number of dimensionless terms. Each of this term is called Buckingham’s *p*-term.

In Buckingham’s *p*-method of dimensional analysis, the expression can be written as

$$x_1 = f(x_2, x_3, \ldots, x_n) \qquad (1.19)$$

where

x_1 = Dependent variable

x_2 = Independent variable

x_3 = Independent variable

x_n = Independent variable

According to *p*-theorem, Eq. (1.19) can be written as

$$f(p_1, p_2, \ldots, p_{n-m}) = 0 \qquad (1.20)$$

where

p_1 = Dimensionless term 1

p_2 = Dimensionless term 2

p_{n-m} = Dimensionless term $n - m$

EXAMPLE 1.17 Using Rayleigh’s method, show that the resistance force *R* of a partially submerged body in water can be expressed in the form

$$R = \rho l^2 V^2 \phi\left[\frac{\mu}{lV\rho}, \frac{lg}{V^2}\right]$$

where

R = Resistance force (kg · m/s^2)

l = Length of the body (m)

V = Velocity of the partially submerged body (m/s)

r = Density of water (kg/m^3)

m = Viscosity of water (kg/m · s)

g = Acceleration due to gravity (m/s^2)

Solution: *R* is a function of *l*, *V*, *r*, *m*, *g*

$$R = f(l, V, r, m, g) \qquad \text{(i)}$$

The dimensions of the physical quantities involved are

Resistance force (R) = MLT^{-2}

Length of the body (l) = L

Velocity of the body (V) = LT^{-1}

Density of water (r) = ML^{-3}

Viscosity of water (m) = $ML^{-1}T^{-1}$

Acceleration due to gravity (g) = LT^{-2}

$$R = [l^a \cdot V^b \cdot r^c \cdot m^d \cdot g^e] \qquad \text{(ii)}$$

Substituting the dimensions on both sides of Eq. (ii), we get

$$MLT^{-2} = (L)^a \cdot (LT^{-1})^b \cdot (ML^{-3})^c \cdot (ML^{-1}T^{-1})^d \cdot (LT^{-2})^e \qquad \text{(iii)}$$

Comparing the power of *MLT* on both side of Eq. (iii), we get

$$M: 1 = c + d \quad \Rightarrow \quad c = 1 - d \qquad \text{(iv)}$$

$$L: 1 = a + b - 3c - d + e \quad \Rightarrow \quad a = 2 - d + e \qquad \text{(v)}$$

$$T: -2 = -b - d - 2e \quad \Rightarrow \quad b = 2 - d - 2e \qquad \text{(vi)}$$

Substituting Eqs. (iv), (v) and (vi) in Eq. (ii), we get

$$R = (l)^{2-d+e} \cdot (V)^{2-d-2e} \cdot (r)^{1-d} \cdot (m)^{d} \cdot (g)^{e}$$

$$\therefore \quad R = \left(\frac{l^2 \cdot l^e}{l^d}\right) \cdot \left(\frac{V^2}{V^d \cdot V^{2e}}\right) \cdot \left(\frac{\rho^1}{\rho^d}\right) \cdot (\mu)^d \cdot (g)^e \qquad \text{(vii)}$$

Combining the like term of Eq. (vii), we get

$$R = (\rho l^2 V^2) \cdot \left(\frac{\mu}{\rho V l}\right)^d \cdot \left(\frac{lg}{V^2}\right)^e$$

$$R = \rho l^2 V^2 \phi \left[\left(\frac{\mu}{\rho V l}\right), \left(\frac{lg}{V^2}\right)\right] \qquad \text{(viii)}$$

EXAMPLE 1.18 Using Buckingham’s *p*-theorem show that the resistance force *R* of a partially submerged body in water can be expressed in the form

$$R = \rho l^2 V^2 \phi \left[\left(\frac{\mu}{\rho V l}\right), \left(\frac{lg}{V^2}\right)\right]$$

where

R = Resistance force (kg $\cdot$ m/s^2)
l = Length of the body (m)
V = Velocity of the partially submerged body (m/s)
r = Density of water (kg/m^3)
m = Viscosity of water (kg/m $\cdot$ s)
g = Acceleration due to gravity (m/s^2)

Solution: R is a function of l, V, r, m, g.

Therefore, $R = f(l, V, r, m, g)$

$\therefore \; f(R, l, V, r, m, g) = 0 \qquad$ (i)

Number of independent and dependent variables (n) = 6
Number of fundamental variables (m) = 3
Number of p-terms ($n - m$) = 3

Therefore, $f(p_1, p_2, p_3) = 0 \qquad$ (ii)

Choosing l, V, r, as repeating variables, we have

$$p_1 = l^{a1} \cdot V^{b1} \cdot r^{c1} \cdot R \qquad \text{(iii)}$$

$$p_2 = l^{a2} \cdot V^{b2} \cdot r^{c2} \cdot m \qquad \text{(iv)}$$

$$p_3 = l^{a3} \cdot V^{b3} \cdot r^{c3} \cdot g \qquad \text{(v)}$$

The dimensions of the physical quantities involved are:

Resistance force (R) = MLT^{-2}

Length of the body (l) = L

Velocity of the body (V) = LT^{-1}

Density of water (r) = ML^{-3}

Viscosity of water (m) = $ML^{-1}T^{-1}$

Acceleration due to gravity (g) = LT^{-2}

First p-term:

$$p_1 = l^{a_1} \times V^{b_1} \times r^{c_1} \times R \qquad \text{(iii)}$$

Substituting the dimension of physical quantities in Eq. (iii), we get

$$M^0L^0T^0 = (L)^{a_1} \times (LT^{-1})^{b_1} \times (ML^{-3})^{c_1} \times MLT^{-2} \qquad \text{(vi)}$$

Comparing the power of M, L, T on both sides of Eq. (vi), we get

$$M: 0 = c_1 + 1 \quad \Rightarrow \quad c_1 = -1 \qquad \text{(vii)}$$

$$L: 0 = a_1 + b_1 - 3c_1 + 1 \quad \Rightarrow \quad a_1 = -2 \qquad \text{(viii)}$$

$$T: 0 = -b_1 - 2 \quad \Rightarrow \quad b_1 = -2 \qquad \text{(ix)}$$

Substituting Eqs. (vii), (viii) and (ix) in Eq. (iii), we get

$$p_1 = l^{-2} \times V^{-2} \times r^{-1} \times R$$

$$\pi_1 = \left(\frac{R}{\rho l^2 V^2}\right) \qquad \text{(x)}$$

Second p-term:

$$p_2 = l^{a_2} \times V^{b_2} \times r^{c_2} \times m \qquad \text{(iv)}$$

Substituting the dimensions of physical quatities in Eq. (iv), we get

$$M^0L^0T^0 = (L)^{a_2} \times (LT^{-1})^{b_2} \times (ML^{-3})^{c_2} \times ML^{-1}T^{-1} \qquad \text{(xi)}$$

Comparing the power of M, L, T on both sides of Eq. (xi), we get

$$M: 0 = c_2 + 1 \quad \Rightarrow \quad c_2 = -1 \qquad \text{(xii)}$$

$$L: 0 = a_2 + b_2 - 3c_2 - 1 \quad \Rightarrow \quad a_2 = -1 \qquad \text{(xiii)}$$

$$T: 0 = -b_2 - 1 \quad \Rightarrow \quad b_2 = -1 \qquad \text{(xiv)}$$

Substituting Eqs. (xii), (xiii) and (xiv) in Eq. (iv), we get

$$p_2 = l^{-1} \times V^{-1} \times r^{-1} \times m$$

$$\pi_2 = \left(\frac{\mu}{lV\rho}\right) \qquad \text{(xv)}$$

Third p-term:

$$p_3 = l^{a_3} \times V^{b_3} \times r^{c_3} \times g \qquad \text{(v)}$$

Substituting the dimensions of physical quantities in Eq. (v), we get

$$M^0L^0T^0 = (L)^{a3} \cdot (LT^{-1})^{b3} \cdot (ML^{-3})^{c3} \cdot LT^{-2} \qquad \text{(xvi)}$$

Comparing the power of M, L, T on both sides of Eq. (vi), we get

$$M\text{: } 0 = c_3 \qquad \Rightarrow \quad c_3 = 0 \qquad \text{(xvii)}$$

$$L\text{: } 0 = a_3 + b_3 - 3c_3 + 1 \qquad \Rightarrow \quad a_3 = 1 \qquad \text{(xviii)}$$

$$T\text{: } 0 = -b_3 - 2 \qquad \Rightarrow \quad b_3 = -2 \qquad \text{(xix)}$$

Substituting Eqs. (xvii), (xviii) and (xix) in Eq. (v), we get

$$p_3 = l^1 \cdot V^{-2} \cdot r^0 \cdot g$$

$$\pi_3 = \frac{lg}{V^2} \qquad \text{(xx)}$$

Substituting Eqs. (x), (xv) and (xx) in Eq. (ii), we get

$$f\left(\frac{R}{\rho l^2 V^2}, \frac{\mu}{lV\rho}, \frac{lg}{V^2}\right) = 0 \qquad \text{(xxi)}$$

$$\therefore \qquad \frac{R}{\rho l^2 V^2} = \phi\left(\frac{\mu}{lV\rho}, \frac{lg}{V^2}\right) \qquad \text{(xxii)}$$

$$\therefore \qquad R = \rho l^2 V^2 \phi\left(\frac{\mu}{lV\rho}, \frac{lg}{V^2}\right) \qquad \text{(xxiii)}$$

1.10

Conversion of Equation

The conversion of equation from one particular unit system to another system of units is done with the help of conversion factors when quantity is expressed in terms of fundamental units of mass, length, time and temperature.

EXAMPLE 1.19 In the case of liquid, the total heat transfer coefficient for a long tube is expressed by the empirical equation

$$h = 0.023 \frac{G^{0.8} k^{0.67} C_p^{\ 0.33}}{D^{0.2} \mu^{0.47}}$$

where

h = Heat transfer coefficient (W/m^2 °C)
G = Mass velocity (kg/m^{2}s)
k = Thermal conductivity (W/m°C)
C_p = Heat capacity (J/kg°C)
D = Diameter of the tube (m)
m = Viscosity of the liquid (kg/m $\cdot$ s)

Convert the empirical equation to suit FPS system of units.

Solution:

$$h = 0.023\frac{G^{0.8}K^{0.67}C_p{}^{0.33}}{D^{0.2}\mu^{0.47}}$$

$$= 0.023\frac{(\text{lb/h}\cdot\text{ft}^2)^{0.8}\ [\text{Btu/(h)(ft)°F}]^{0.67}[\text{Btu/lb(°F)}]^{0.33}}{(\text{ft})^{0.2}[\text{lb/(ft)(h)}]^{0.47}}$$

$$h_i = 0.023\frac{(\text{Btu})^{0.67}(\text{Btu})^{0.33}(\text{lb})^{0.8}}{(\text{lb})^{0.33}(\text{lb})^{0.47}}\times\frac{(\text{h})^{0.47}}{(\text{h})^{0.8}(\text{h})^{0.67}}\times\frac{(\text{ft})^{0.47}}{(\text{ft})^{1.6}(\text{ft})^{0.67}(\text{ft})^{0.2}}\times\frac{1}{(\text{°F})^{0.47}(\text{°F})^{0.33}}$$

$$h_i = 0.023\frac{\text{Btu}}{(\text{h})(\text{ft})^2(\text{°F})}$$

EXAMPLE 1.20 The equation for the heat transfer to or from a stream of gas flowing in turbulent motion is as follows:

$$h = \frac{\alpha C_p G^{0.8}}{D^{0.2}} = \frac{16.6 C_p G^{0.8}}{D^{0.2}}$$

where

h = Heat transfer coefficient (kcal/(h)(m^2)(°C))
C_p = Heat capacity (kcal/(kg) (°C))
D = Internal diameter of pipe (m)
G = Mass velocity (kg/(m^2)(s))
a = Constant

It is desired to transform the equation into a new form

$$h' = \frac{\alpha' C_p'(G')^{0.8}}{(D')^{0.2}}$$

where

h' = Btu/(h)(ft^2)(°F)
C_p' = Btu/(lb)(°F)
D' = ft
G' = (lb)/(ft^2)(s)

Solution: Let us consider

$$h\frac{\text{kcal}}{(\text{h})(\text{m}^2)(\text{°C})} = h'\frac{\text{Btu}}{(\text{h})(\text{ft})^2(\text{°F})}$$

$$h\frac{\text{kcal}}{(\text{h})(\text{m}^2)(\text{°C})} = h'\times\frac{1055\times 1.8}{1000\times 4.187\times(0.3048)^2}\frac{\text{kcal}}{(\text{h})(\text{m}^2)(\text{°C})}$$

$$h = 4.882\,h' \qquad \text{(i)}$$

$$C_p \frac{\text{kcal}}{(\text{kg})(^\circ\text{C})} = C'_p \frac{\text{Btu}}{(\text{lb})(^\circ\text{F})}$$

∴

$$C_p \frac{\text{kcal}}{(\text{kg})(^\circ\text{C})} = C'_p \times \frac{1055}{1000 \times 4.187} \times \frac{1}{0.453} \times \frac{1.8}{1} \frac{\text{kcal}}{(\text{kg})(^\circ\text{C})}$$

$C_p = C_p'$ (ii)

∴ D (m) = D'(ft)

∴ D (m) = D' × 0.3048 m

∴ $D = 0.3048D'$ (iii)

$$G \frac{\text{kg}}{(\text{m}^2)(\text{s})} = G' \frac{\text{lb}}{(\text{ft})^2(\text{s})}$$

∴

$$G \frac{\text{kg}}{(\text{m}^2)(\text{s})} = G' \times \frac{0.453}{(0.3048)^2} \frac{\text{kg}}{(\text{m}^2)(\text{s})}$$

∴ $G = 4.876G'$ (iv)

Substituting Eqs. (i), (ii), (iii) and (iv) in original equation, we get

$$4.882h' = \frac{\alpha'(C'_p)(4.876G')^{0.8}}{(0.3048D')^{0.2}}$$

$$4.882h' = \frac{1 \times (4.876)^{0.8}}{(0.3048)^{0.2}} \frac{C'_p(G')^{0.8}}{(D')^{0.2}}$$

Therefore,

$$h' = \frac{1 \times (4.876)^{0.8}}{4.882 \times (0.3048)^{0.2}} \frac{C'_p(G')^{0.8}}{(D')^{0.2}} \qquad \text{(v)}$$

$$h' = 0.9226 \frac{C'_p(G')^{0.8}}{(D')^{0.2}}$$

This is the converted equation from given unit to FPS unit.

EXAMPLE 1.21 The value of heat transfer coefficient in a particular heat exchange operation is found to be 200 Btu/h · ft^2 · °F. Convert its value in W/m^2 °C.

Solution:

$$200 \frac{\text{Btu}}{\text{h} \cdot \text{ft}^2 \cdot {^\circ\text{F}}} = 200 \times \frac{1055}{1} \times \frac{1}{3600} \times \frac{1}{(0.3048)^2} \times \frac{1.8}{1}$$

$$= 1136 \text{ W/m}^2\ {^\circ\text{C}}$$

EXAMPLE 1.22 The value of heat transfer coefficient in a particular heat exchange operation is found to be

300 Btu/h · ft^2 · °F.

Convert its value in kcal/(s)(m^2)(°C).

Solution: We know that

1 Btu = 1055 J
1 cal = 4.187 J
1 h = 3600 s
1 ft = 0.3048 m
1°C = 1.8°F

$$300\ \text{Btu/h} \cdot \text{ft}^2 \cdot {}^\circ\text{F} = 300 \times 0.252 \times \frac{1}{3600} \times \frac{1}{(0.3048)^2} \times \frac{1.8}{1}$$
$$= 0.4068\ \text{kcal/(s)(m}^2\text{)(}^\circ\text{C)}$$

EXAMPLE 1.23 Convert 125 lb/ft^3 into g/cm^3.

Solution: We know that

l lb = 0.453 × 1000 g
1 ft = 30.48 cm

$$125\ \text{lb/ft}^3 = 125 \times 0.453 \times 10^3 \times \frac{1}{(30.48)^3}$$
$$= 1.99\ \text{g/cm}^3$$

1.11

Graphical Method of Integration

It is a useful tool for the calculation of area under the curve. In this method, a curve is obtained by plotting the function *f* (*x*) against *x*. Then, vertical lines are drawn through the value of *x* corresponding to the given two limits. Then, area enclosed between the curve, the given limits and *x*-axis is measured.

For example, consider the method of calculation of fugacity using the equation

$$\ln \frac{f_i}{P} = \frac{-1}{RT} \int_0^P (\Delta V_i') \, dp$$
$$\ln \frac{f_i}{P} = -\frac{1}{RT} \times A$$

where

f_i = Fugacity of component *i* (N/m^2)
P = Absolute pressure (N/m^2)
R = Universal gas constant (J/kgmol ⌋ K)
T = Absolute temperature (K)
A = Area under the curve

In this case, definite integral $\int_0^P (\Delta V_i')\,dp$ may be calculated by graphical method. By plotting ㅅ V ㄴㅎ i against P, we get a curve ABCDE as shown in Figure 1.1. Let, BF and DG are the vertical lines drawn corresponds to the value of $x = x_1$ and $x = x_2$ respectively. The entire area bounded by the points BDGF is the desired integral. The calculations of area under the curve follows. Count the number of 1 cm × 1 cm square units under the enclosed area. Then, multiply the number of units by the scale of x-axis and y-axis. Thus, area may be calculated as

$$A = \int_0^P (\Delta V_i')\,dp$$

$$= (\text{Number of square units}) \times (\text{Scale of } x\text{-axis}) \times (\text{Scale of } y\text{-axis})$$

$$= 128 \times (1 \times 10^5) \times (0.001)$$

$$= 12{,}800$$

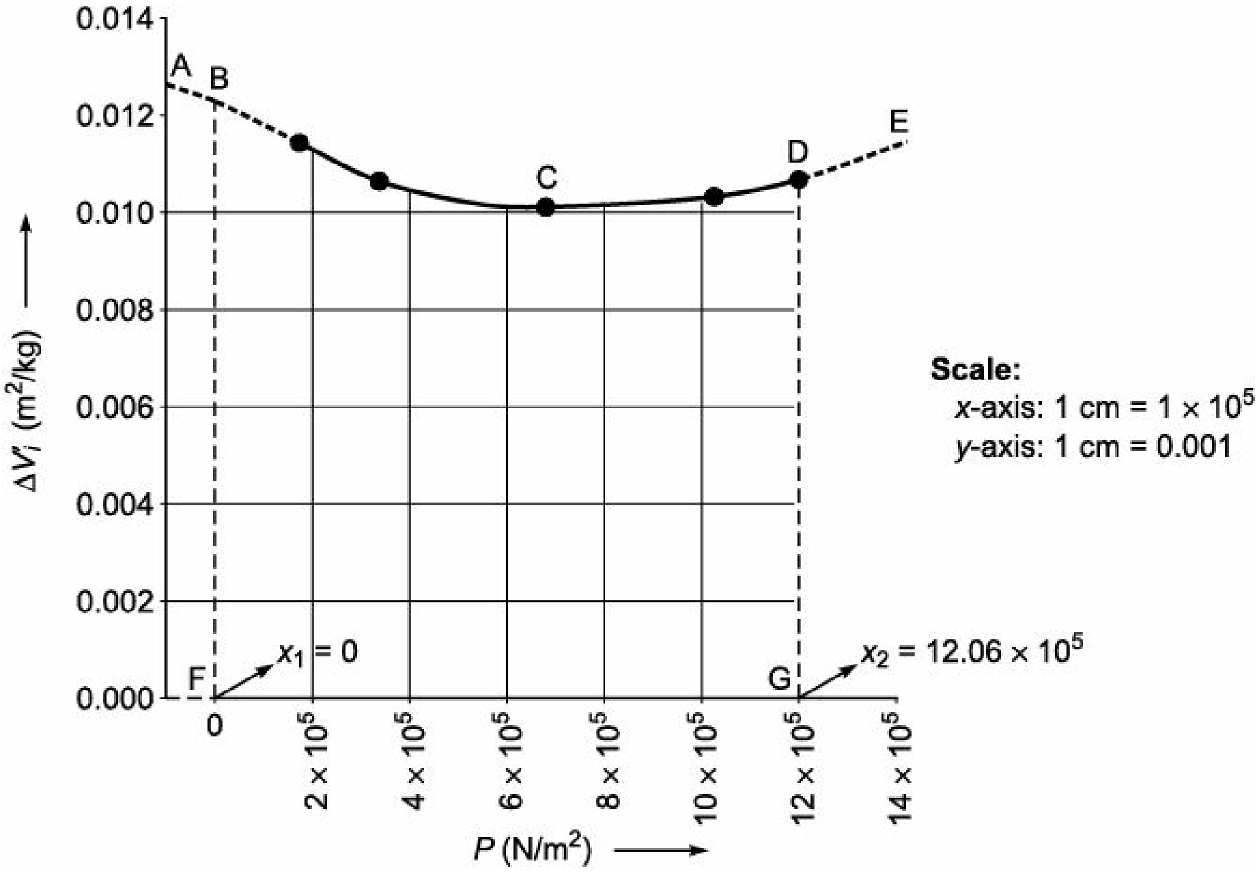


FIGURE 1.1 Determination of area under the curve.

1.12

Least Square Method

It is a popular technique in which the overall solution of a system minimizes the sum of the square of the mistake made in the results of every single equation. Approximately, it gives the solution of a set of equations which consists of more equations than unknowns. This technique is available with two different version. Version one is called Ordinary Least Square (OLS) and the other version is called Weighted Least Square (WLS). Weighted least square is a most sophisticated technique which can regulate the importance of any observation in the final solution. Hence, its performance is better than

OLS. The best fit, in the sense of least square minimizes the difference between an observed values and the fitted values provided by the model equation. For example, consider the best fit of a set of data points with a straight line function. A typical result of best fit of a set of data for a straight line function by least square method is shown in Figure 1.2.

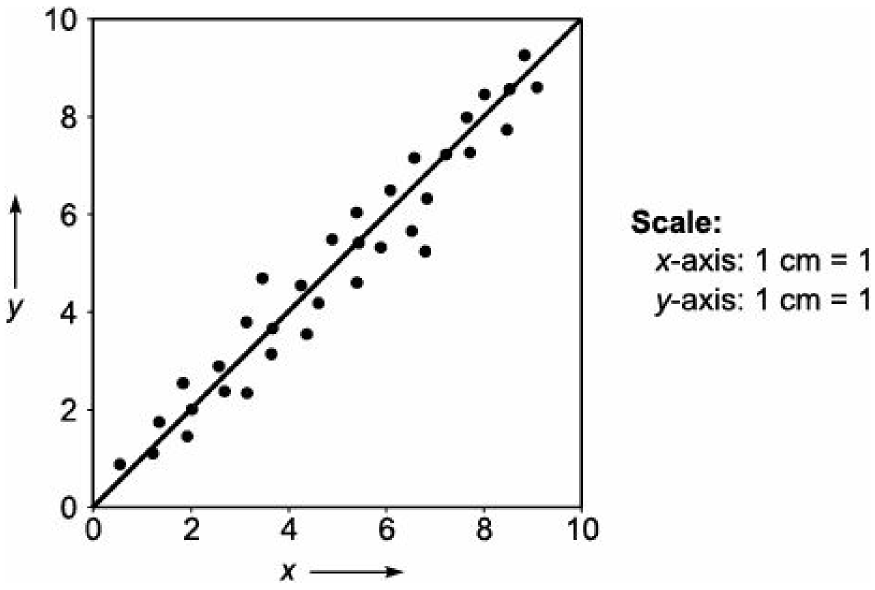


FIGURE 1.2 Results of best fit of a set of data for a straight line function by least square.

1.13

Curve Fitting

Let us consider that we have experimental data comprising the values of two variables x and y. We need to find a possible relationship between these two variables. The method of obtaining the specific relation in the form

$$y = f(x)$$

for the given set of experimental data to satisfy as accurately as possible is called curve fitting. This technique is generally used for the verification of experimental results.

EXAMPLE 1.24 Fit a straight line

$$y = ax + b$$

in the least square sense for the data

x	1	2	3	6	4	5
y	1	3	5	7	9	11

Solution: The normal equations for curve fitting

$$y = ax + b \qquad \text{(i)}$$

are given by

$$\sum y = a\sum x + nb \qquad \text{(ii)}$$

$$\sum xy = a\sum x^2 + b\sum x \qquad \text{(iii)}$$

We construct the table based on the requirement.

x	y	xy	x^2	
1	1	1	1	
2	3	6	4	
3	5	15	9	
6	7	42	36	
4	9	36	16	
5	11	55	25	
S $x = 21$	S $y = 36$	S $xy = 155$	S $x^2 = 91$	$n = 6$

$$21a + 6b = 36 \qquad \text{(iv)}$$

$$91a + 21b = 155 \qquad \text{(v)}$$

Multiplying Eq. (iv) by 21 and Eq. (v) by 6, we get

$$\begin{array}{rcrl}
441a + 126b & = & 756 & \qquad \text{(vi)} \\
\underset{-}{} 546a \underset{-}{+} 126b & = & \underset{-}{} 930 & \qquad \text{(vii)} \\
\hline
-\,105a & = & -\,174 & \\
a & = & 1.6571 & \qquad \text{(viii)} \\
b & = & 0.2 & \qquad \text{(ix)}
\end{array}$$

Substituting Eqs. (viii) and (ix) in Eq. (i), we get

$$y = 1.6571x + 0.2$$

This is the best fit of a straight line.

1.14

Regression

Let us consider that we have experimental data comprising the values of two variables x and y. We need to find the possible relationship for y in terms of x or x in terms of y. The method of obtaining the specific relation of one independent variable in terms of the other in the form

$$y - \bar{y} = r \frac{\sigma_y}{\sigma_x} (x - \bar{x})$$

is called Regression

where

y = Dependent variable

$$\bar{y} = \frac{\sum y}{n}$$

x = Independent variable

r = Regression

s = Standard deviation

$$\bar{x} = \frac{\sum x}{n}$$

n = Number of set of data.

Now,

$$\sigma_x^2 = \frac{\sum x^2}{n} - (\bar{x})^2$$

$$\sigma_y^2 = \frac{\sum y^2}{n} - (\bar{y})^2$$

$$r = \frac{\sigma_x^2 + \sigma_y^2 - \sigma_{x-y}^2}{2\sigma_x \sigma_y}$$

Exercises

1.1 Discuss the fundamental and derived units with suitable examples.

1.2 What is dimensional consistency?

1.3 What is dimensional consistency equation? Explain with suitable example.

1.4 What is dimensionless group? Explain with suitable example.

1.5 One hundred pounds of water is flowing through a pipe at the rate of 10 ft/s. What is the kinetic energy of this water in joules?

1.6 The volumetric flow rate of kerosene in 80 mm nominal diameter pipe is 75 Imperial gallons per minute. Density of kerosene is 0.8 g/cm^3. Find the mass flow rate in kg/h.

1.7 Iron metal weighing 500 lb occupies a volume of 29.25 l. Calculate the density of Fe in kg/m^3.

1.8 The diameter and height of a vertical cylindrical tank are 5 ft and 6.5 ft respectively. It is full up to 75% height with carbon tetrachloride (CCl_4), the density of which is 1.6 kg/l. Find the mass in kilogram.

1.9 Show that Reynolds number defined as

$$N_{\text{Re}} = \frac{DV\rho}{\mu}$$

is dimensionless

where

D = Diameter of the pipe (m)

V = Average velocity of fluid (m/s)

r = Density of the fluid (kg/m^3)

m = Viscosity of the fluid (kg/m ⊣ s)

1.10 Find the mass flow rate of the liquid in lb/min flowing through a pipe of 5 cm diameter which has density of 960 kg/m^3 and viscosity 0.9 centipose. The Reynolds number is reported to be 3200 for the flow. **[VTU Exam, Dec 2009]**

1.11 Steam is flowing at the rate of 2000 kg/h in a 3° NB, 40 schedule pipe at 440 kPa absolute and 453 K. Calculate the velocity of the steam in the pipeline.

Data: Internal diameter of 3° NB, 40 schedule pipe = 3.068° . Specific volume of steam at 440 kPa and 453 K = 0.461 m^3/kg.

1.12 The conductance of a fluid flow system is defined as the volumetric flow rate referred to a pressure of one torr. For an orifice, the conductance C can be computed from

$$C = 89.2A\sqrt{\frac{T}{M}},\ \text{ft}^3/\text{s}$$

where

A = Area of opening (ft^2)
T = Temperature (°F)
M = Molecular weight.

Convert the empirical equation into SI units.

1.13 A handbook shows that microchip etching roughly follows the relation

$$d = 16.2 - 16.2\ e^{-0.021t} \text{ for } t > 200$$

where

d = Depth of etch (μm)
t = Time of etch (second)

What are the units associated with the number 16.2 and 0.021?

Convert the relation so that d can be expressed in inches and 't' can be used in minutes.

1.14 The conductance of a fluid flow system is defined as the volumetric flow rate referred to a pressure of one torr. For an orifice, the conductance C can be computed from

$$C = 89.2A\sqrt{\frac{T}{M}},\ \text{ft}^3/\text{s}$$

where

A = Area of opening (ft^2)
T = Temperature (°F)
M = Molecular weight

Convert the empirical equation into metric units.

1.15 What are the advantages of SI system of units?

1.16 Convert 23.16 lb · ft/min^2 to kg · cm/s^2.

1.17 Covnert 120 hp to kJ/min.

1.18 Convert $\dfrac{\text{Btu}}{(\text{h})(\text{ft}^2)\,°\text{F}}$ to $\dfrac{\text{kJ}}{(\text{day})\,(\text{m}^2)(\text{K})}$

1.19 A quantity k depends on temperature T in the following manner:

$$k\left(\frac{\text{mol}}{\text{cm}^3\cdot\text{s}}\right) = 1.2\times10^5\exp\left(-\frac{20{,}000}{1.987T}\right)$$

where, units of quantity 20,000 is cal/mol and temperature T in K. What are the units of the value 1.2×10^5 and 1.987?

1.20 Is the following equation dimensionally homogeneous?

$$\Delta P = \frac{14L\bar{V}\mu}{D^2}$$

where

DP = Pressure drop (lb/ft^2)
L = Pipe length (ft)
$\bar{V}$ = Fluid velocity (ft/s)
m = Fluid viscosity (lb/ft ⊣ s)
D = Pipe diameter (ft)

If so, are the units consistent? If not, what factor must be added to the right hand side of the equation to provide consistency.

1.21 Convert 40 l/(m^2)(h) to m^3/(cm^2)(s).

1.22 The thermal conductivity of steel is

16 Btu/(h)(ft)(°F)

What is the value of the thermal conductivity in W/m °C?

1.23 The heat transfer coefficient for the gas flowing over a solid surface is calculated by the empirical equation

$$h = 0.01G^{0.8}$$

where

h = Heat transfer coefficient (Btu/(h)(ft^2)(°F))
G = Mass velocity (lb/(hr)(ft^2))

Convert this equation to suit SI units.

1.24 Convert 1 kWh to Btu.

1.25 Convert – 40 °C to °F.

1.26 The equation for the heat transfer from a stream of gas flowing in turbulent motion is as follows

$$h = \frac{16.6C_pG^{0.8}}{D^{0.2}}$$

where

C_p = Heat capacity (Btu/(lb)(°F))
G = Mass velocity (lb/(ft^2) ⊣ (s))
D = Internal diameter of pipe (m)

Convert this equation into SI units and find out the new constant.

1.27 In case of liquids, the local heat transfer coefficient for long tube is expressed by the empirical equation.

$$h = \frac{0.023G^{0.8}k^{0.67}C_p^{\ 0.33}}{D^{0.2}\mu^{0.47}}$$

where

h = Heat transfer coefficient (Btu/(h)(ft^2)°F)

G = Mass velocity (lb/(ft^2)(s))

C_p = Heat capacity (Btu/(lb)(°F))

k = Thermal conductivity (Btu/(h)(ft)(°F))

D = Diameter of the tube (ft).

m = Viscosity of the liquid (lb/(ft) ⊣ (s))

Convert the empirical equation to suit SI system of units.

1.28 Convert a volumetric flow rate of 2m^3/s to l/s.

1.29 In double effect evaporator plant, the second effect is maintained under vacuum of 475 torr (mmHg). Find the absolute pressure in kPa.

1.30 A force equal to 19.635 kgf is applied on the piston with a diameter of 5 cm. Find pressure exerted on a piston in kPa.

1.31 Convert the pressure of 2 atm into mmHg.

1.32 Convert 2000 W in hp and (kgf ⊣ m)/s.

1.33 Convert 1000 dyne into Newton.

1.34 Convert 1500 mmHg into atm.

1.35 Convert 130 lb/ft^3 into g/cm^3.

1.36 Make the following conversions:

(i) 350 l per minute to m^3/s

(ii) 475 mmHg to kN/m^2.

1.37 The equation for the heat transfer to or from a stream of gas flowing in turbulent motion is as follows:

$$h = \frac{\alpha C_p G^{0.8}}{D^{0.2}} = \frac{16.6 C_p G^{0.8}}{D^{0.2}}$$

where

C_p = Heat capacity as (Btu/lbm°F)

D = Internal diameter of pipe (in)

G = Mass velocity (lb/ft^2 ⊣ s)

h = Heat transfer co-efficient (Btu/(h)(ft^2) ⊣ (°F))

It is desired to transform the equation into a new form

$$h' = \frac{\alpha' C_p' (G')^{0.8}}{(D')^{0.2}}$$

where

C ㄴㅎ p = Heat capacity (kcal/(kg)(°C))

D ㄴㅎ = Internal diameter of pipe (cm)

G ㄴㅎ = Mass velocity (kg/(m^2)(s)) h ㄴㅎ = Heat transfer co-efficient (kcal/(h)(m^2)(°C))

1.38 Prove the following:

(i) 1 g/cm^3 = 62.42 lb/ft^3

(ii) 1 Btu/(lb)(°F) = 1 kcal/(kg)(°C)

1.39 Prove the following:

(i) 1 Bar = 750 mmHg

(ii) – 40 °C = – 40 °F

1.40 An empirical equation for calculating the inside heat transfer coefficient h_i for the turbulent flow of liquids in a pipe is given by

$$h_i = \frac{0.023\, G^{0.8}\, k^{0.67}\, C_p{}^{0.33}}{D^{0.2}\, \mu^{0.47}}$$

where

h_i = Heat transfer coefficient (Btu/(h)(ft^2)(°F))

G = Mass velocity of the liquid (lbm/(ft^2)(h))

k = Thermal conductivity of the liquid (Btu/(h)(ft)(°F))

C_p = Heat capacity of the liquid (Btu/(lbm)(°F))

m = Viscosity of the liquid (lbm/(ft)(h))

D = Inside diameter of the pipe (ft)

(i) Verify whether the equation is dimensionally consistent or not.

(ii) What will be the value of the constant given as 0.023, if all the variables in the equation are inserted in SI units and h_i is in SI units.

1.41 Iron metal weighing 500 lb occupies a volume of 29.25 ft^3. Calculate the density of Fe in g/cm^3.

1.42 The diameter and height of a vertical cylindrical tank are 5 ft and 6.5 ft respectively. It is full up to 75% height with carbon tetrachloride, the density of which is 1.6 g/cm^3. Find the mass in tonnes. **[Ans.** 4.34*t***]**

1.43 Corrosion rate are normally reported in miles per year (mpy) in the chemical process industry. For the measurement of the rate, a corrosion test coupon is inserted in the process stream for a definite period. The loss of weight is measured during the period of insertion.

In a particular test, a coupon of carbon steel was kept in a cooling water circuit. The dimensions of the coupon were measured to be 7.5 cm × 1.3 cm × 0.15 cm. Weight of the coupon before insertion in the circuit and after exposure for 50 days were measured to be 15 g and 14.6 g respectively. Calculate the rate of corrosion. Take the density of the carbon steel = 7.754 g/cm^3.

Note: 1 mpy = 0.001 in per year. **[Ans.** 5.3 mpy**]**

1.44 Show that Prandtl number defined as

$$N_{\mathrm{Pr}} = \frac{C_p \mu}{k}$$

is dimensionless

where

N_{Pr} = Prandtl number

C_p = Specific heat (J/kg °C)

m = Viscosity of the fluid (kg/m ⊣ s)

k = Thermal conductivity of fluid (W/m °C)

1.45 Show that Dittus number defined as

$$N_{\mathrm{Di}} = \frac{hd}{k}$$

is dimensionless

where

N_{Di} = Dittus number

h = Heat transfer coefficient

d = Diameter of the pipe

k = Thermal conductivity of the fluid.

1.46 What are the different system of units in common use? With a suitable example, explain how a quantity of one system be converted into other system.

1.47 Make the following conversions

(i) 325 l/min to m^3/s

(ii) 450 mmHg to kN/m^2

1.48 When a gas is flowing in a tube and the tube is heated from outside. The heat transfer coefficient is found to be related by the following equation:

$$h = 120\,(1 + 2V^{1/2})$$

where

h = Heat transfer coefficient (Btu/h ⊣ ft^2 ⊣ °F)

V = Velocity (ft/s)

If so convert the relation for other units.

1.49 What are the limitations of FPS system? Explain with example.

1.50 Define the following terms and mention their dimensions in all the four unit system.

(i) Acceleration due to gravity

(ii) Heat

(iii) Pressure

(iv) Velocity

1.51 Prove the following:

(i) 1 g/cm^3 = 62.42 lb/ft^3

(ii) 1 Btu/lb °F = 1 kcal/kg °C

1.52 What are the fundamental quantities in FPS, CGS, MKS and SI units?

1.53 What is a derived quantity? Establish relation between Dyne and Newton.

1.54 The variation of heat capacity for carbon dioxide with temperature is given by the equation

$$C_p = 6.34 + 10.15 \times 10^{-3}\,\mathrm{T} - 3.41 \times 10^{-6}\,\mathrm{T}^2$$

where, C_p is in cal/gmol °C and T is in K.

Transform the above equation in FPS unit on mass basis.

1.55 The value of heat transfer coefficient in a particular heat exchange operation is found to be

$$0.125\ \mathrm{kcal/(s)(m^2)(°C)}$$

Convert its value in Btu/h ⊣ ft^2 ⊣ °C

1.56 Convert 2 g/cm^3 into lb/ft^3.

1.57 The value of heat transfer coefficient in a particular heat exchange operation is given by 350 W/m^2 °C. Convert its value in Btu/h ⊣ ft^2 ⊣ °C.

1.58 The superficial mass velocity of air through a dehumidifier is found to be 250 lb/(h)(ft^2).Calculate its equivalent value in kg/(h)(m^2).

1.59 The superficial mass velocity of air through a dehumidifier is found to be 2000 kg/(h)(m^2).Convert its value in lb/(h)(ft^2).

1.60 The variation of heat capacity data for gaseous SO_2 is given by the following equation:

$$C_p = 43.46 + 10.64 \times 10^{-3}\, T - \frac{5.95 \times 10^5}{T^2}$$

where C_p = cal/(gmol)(°C) and T is in K.

Transform the above equation in FPS units on mole basis.

1.61 The variation of heat capacity data for gaseous N_2 is given by the following equation:

$$C_p = 29.49 - 5.14 \times 10^{-3}\, T + 13.18 \times 10^{-6}\, T^2 - 4.95 \times 10^{-9}\, T^3$$

where C_p is in kJ/kmol ⊣ K and T is in K. Transform the above equation in FPS units on mole basis.

1.62 At 350 °C the heat transfer by conduction and convection of a spherical mild steel ball to air is reported to be 16 W/m^2 °C. Convert this result into FPS unit.

1.63 The variation of heat capacity data for toluene is given by the equation

$$C_p = 1.8 + 812.21 \times 10^{-3}\, T - 1512.67 \times 10^{-6}\, T^2$$

where C_p is in kJ/kmol ⊣ K and T is in K. Transform the equation in FPS unit on mole basis.

1.64 Convert 390 Btu/(ft^2)(h) °F to kcal/(m^2)(h) °C.

1.65 Prove that

$$1\,\frac{\text{cal}}{(\text{g})(°\text{C})} = 1\,\frac{\text{Btu}}{(\text{lb})(°\text{F})}$$

1.66 The variation of heat capacity data for O_2 is given by the equation

$$C_p = 26.0 + 11.76 \times 10^{-3}\, T - 2.34 \times 10^{-6}\, T^2$$

where C_p is in kJ/kmol ⊣ K and T is in K.

Transform the equation in FPS unit on mole basis.

1.67 A flow system has been found to obey

$$f\,(Q, H, g, V_0, f) = 0$$

where

Q = Volumetric flow rate

H = Liquid level

g = Acceleration due to gravity
V_0 = Velocity of approach
f = Angle of the flow meter

Derive an equation for *Q* using dimensional analysis.

1.68 Explain Rayleigh's method of dimensional analysis.

1.69 Using Buckingham's *p*-theorem show that the velocity through a circular orifice is given by

$$V = \sqrt{2gH}\ \phi\left(\frac{D}{H}, \frac{\mu}{HV\rho}\right)$$

where

V = Velocity of fluid flowing
H = Head causing flow
D = Diameter of orifice
m = Viscosity of fluid flowing
r = Density of fluid flowing
g = Acceleration due to gravity

1.70 State the Buckingham's *p*-theorem and explain the procedure to solve the problem for resistance for *R* of a supersonic plane during flight which can be considered as dependent upon the length of the aircraft *l*, velocity *V*, air viscosity *m*, air density *r* and bulk modulus of air *k*. Express the functional relationship between these variables and the resistance force.

1.71 The pressure drop D*P* in a pipe of diameter *D* and length *l* due to turbulent flow depends on the velocity *V*, viscosity *m*, density *r* and roughness *k*. Using Buckingham's *p*-theorem, obtain an expression for D*P*.

1.72 Show by Rayleigh's method of dimensional analysis that the resistance *R* to the motion of sphere of diameter *D* moving with a uniform velocity *V* through a real fluid having density *r* and viscosity *m* is given by

$$R = \rho D^2 V^2\ \phi\left(\frac{\mu}{DV\rho}\right)$$

2

Basic Chemical Calculations

2.1

Introduction

A basic chemical process ascribes to any operation or a number of operations in series which causes a chemical or physical changes in a substance or group of substances. The substance or group of substances under consideration is called system. In this context, before dealing with chemical process calculations, we need to be familiar with basic chemical principles underlying the subject of discussion of the following terms.

(i) Atomic weight
(ii) Molecular weight
(iii) Basis of calculation.

Atomic weight

It may be defined as the mass of an atom that assigns carbon a mass of twelve exactly.

Molecular weight

It may be defined as the sum of the atomic weights of the atoms using which a molecule of a compound is formed.

Basis of calculation

Basis of calculations is very important in solving the problems on material and energy balances of a given process. Hence, before we start solving the problems on material and energy balances of a given process, we must assume a suitable basis on which further calculations are based.

The calculations must be presented by assuming some suitable basis of calculation. The assumption of basis of calculation must be some specific quantity or composition or flow rate of stream entering or leaving the process. If the flow rate is specified as a basis in the problem, assume it as a basis of calculation. If the basis is not specified in the problem, assume a suitable basis which will simplify the given problem. While assuming a new basis of calculation, we have to see that it must contain the maximum amount of information of the process. For example, if the stream amounts and flow rate are not specified, assume some amount of stream for which composition is known. Assumption of the basis of calculation of some amount or quantity of stream of which composition is known makes the calculation simplified.

If the given problem is specified in weight units, assume a quantity of either entering stream or leaving stream in weight units, for example, 500 g, 500 kg etc. If the given problem is specified in molar units, assume a quantity of either entering stream or leaving stream in molar units, such as 50 moles, 50 kgmol.

In problems involving chemical reaction or gases, it is better to specify the basis of calculation in molar units. Whenever a composition is specified the assumption of basis of calculations, a quantity, such as 100 in weight or 100 in molar units make the calculation simple.

2.2

Concept of Atom

An atom is the smallest particle of chemical element that can take part in a chemical reaction. It consists of negatively charged electrons, no charged neutrons and positively charged protons.

An atom has a nucleus at the centre. Nucleus contains mixed of protons and neutrons and it is surrounded by electrons. These electrons are bounded to the nucleus by the electromagnetic force within the atom.

If the number of electrons present in the atom is equal to the number of protons, then the atom is said to be electrically neutral.

If the number of electrons present in the atom is few, then the atom is said to be positively charged. For example, consider the Na atom. Its atomic number is 11. The electronic configuration of Na is

$$1s^2, 2s^2, 2p^6, 3s^1$$

It is observed from the electronic configuration of Na that the number of electron present in the outer shell of the orbit is 1. This number is small. Hence, the Na atom is positively charged. It is represented by the symbol Na^+. Its valency is 1.

On the other hand, if the number of electrons present in the atom is more, then the atom is said to be negatively charged. For example, consider the Cl atom. Its atomic number is 17. The electronics configuration of Cl is

$$1s^2, 2s^2, 2p^6, 3s^2, 3p^5$$

It is observed from the electronics configuration of Cl that the number of electron present in the outer shell of the orbit is 5. This number is large. Hence, the Cl atom is negatively charged. It is represented by the symbol Cl^-. Its valency is 1. One atom of Na react with one atom of Cl to give rise to one molecule of NaCl.

In general, gram atom is used to specify the amounts of chemical elements. It is defined as a mass in gram of an element which is numerically equal to its atomic weight. It can be represented as

$$\text{Gram atom of element} = \frac{\text{Weight in grams}}{\text{Atomic weight}} \qquad (2.1)$$

The concept of atom is required to study the formation of molecule and chemical compound. It also helps in basic chemical calculations.

2.3

Moles and Mole Fraction

When a group of atom of elements joined together to give rise to a specific structure is called a molecule.

These molecules may be formed using either atoms of the same element or the atoms of the different element. For example, consider the molecule of chlorine. Its molecular formula is Cl_2. Here, two atoms of the same element joined together to form a chlorine molecule. Consider an another example of molecule as a table salt. It is a crystalline solids in which constituents are present in a definite geometric pattern. Its molecular formula is NaCl. Here, one atom of sodium of one element joined with one atom of chlorine of another element to form one molecule of sodium chloride. The bonding between sodium (a metal) and chlorine (a non-metal) give rise to a specific structure. This type of bonding between the atoms of metal and non-metal is called ionic bond.

When a substance is formed by the combination of two or more different elements is called a compound. In the case of sodium chloride, sodium and chlorine are of two different elements combine together. Hence, we can say that NaCl is a compound.

For example, consider the chemical reaction

$$2Fe + 3H_2O \rightleftharpoons Fe_2O_3 + 3H_2$$

Here, iron reacts with water to give rise to iron oxide and hydrogen. In this chemical reaction, iron and water are the reactants and iron oxide and hydrogen are the products. The molecular formula of the compound and element present in this reaction can help us to calculate the amount of iron and water necessary to produce any desired amount of hydrogen.

In general gmol or kgmol is used to specify the amounts of chemical compounds. It is defined as the mass in grams of substance that is numerically equal to its molecular weight. It can be represented as

$$\text{gram mole of compound} = \frac{\text{Weight in grams}}{\text{Molecular weight}} \qquad (2.2)$$

or

$$\text{kg mole of compound} = \frac{\text{Weight in kg}}{\text{Molecular weight}} \qquad (2.3)$$

Molecular weight of the compound is found from the atomic weights of elements involved in the formation of compound.

Mole fraction is the ratio of moles of individual components to the total moles of the system. For binary system of A and B, the mole fraction may be represented as

$$\text{Mole fraction of } A = \frac{\text{Moles of } A}{\text{Total moles of the system}} \qquad (2.4)$$

It may also be represented by the equation

$$X_A = \frac{W_A/M_A}{(W_A/M_A) + (W_B/M_B)} \qquad (2.5)$$

where

X_A = Mole fraction of component A

W_A = Weight of component A

M_A = Molecular weight of component A

W_B = Weight of component B

M_B = Molecular weight of component B.

For determining moles and mole fraction, we need to use molecular weight of the element. Hence, to make the task easy, molecular weight of various elements are given in Table 2.1.

TABLE 2.1 Molecular weight of some elements

Element	Molecular weight	Element	Molecular weight	Element	Molecular weight
H	1	Mg	24.3	Th	232.04
C	12	Ba	137.36	U	238.03
K	39	As	74.9	Li	6.94
O	16	Br	80	Be	9.01

S	32	Zn	65.38	V	51.0
N	14	Ti	47.90	Cr	52.0
P	31	Pb	207.20	Ni	58.70
Na	23	Hg	200.59	Ga	69.72
Mn	55	Pt	195.09	Ge	72.59
Cu	63.5	Au	196.97	Se	78.96
Cl	35.5	Ra	226.02	Kr	83.80
Ca	40	Co	58.93	Bi	208.98
Al	27	Si	28.09	Cd	112.40
Fe	56	Ar	39.95		

2.4

Method of Expressing the Composition of Mixtures

Various methods are used to express the composition of mixtures of solids, liquids and gases.

The methods given here are explained by considering a system composed of two components, namely *A* and *B*. Same methods are used for system containing more than two components. The compositions can be expressed in weight per cent, volume per cent and mole per cent.

The composition of solid systems and also of liquid system is expressed in terms of weight per cent and also in terms of mole per cent. The composition of gases is expressed in terms of volume per cent.

The method of expressing the composition in ppm (i.e. one part in 10^6 part) is used specifying the contents of trace impurities in solids or liquids.

Considering a binary system composed of components *A* and *B*.

Mass Per cent: It is the mass of any component expressed as the percentage of total mass of the system. It can be expressed as

$$\text{Mass\% of } A = \frac{\text{Mass of } A}{\text{Total mass of the system}} \times 100 \qquad (2.6)$$

or

$$\text{Mass\% of } A = \frac{W_A}{W_A + W_B} \times 100 \qquad (2.7)$$

where

W_A = Weight of component *A*

W_B = Weight of component *B*

$W_A + W_B$ = Total weight of the system

Volume Per cent: It is the pure component volume of any component expressed as a percentage of the total volume of the system. It can be expressed as

$$\text{Volume\% of } A = \frac{\text{Pure component volume of } A}{\text{Total volume of the system}} \times 100 \qquad (2.8)$$

$$\text{Volume\% of } A = \frac{V_A}{V_A + V_B} \times 100 \qquad (2.9)$$

where

V_A = Volume of the pure component A

V_B = Volume of pure component B

$V_A + V_B$ = Total volume of the system

Mole Per cent: It is the moles of any component expressed as the percentage of the total moles of the system. It can be expressed as

$$\text{Moles\% of } A = \frac{\text{Moles of A}}{\text{Total moles of the system}} \times 100 \qquad (2.10)$$

$$\text{Moles\% of } A = \frac{W_A/M_B}{W_A/M_A + W_B/M_B} \times 100 \qquad (2.11)$$

where

W_A = Weight of component A

M_A = Molecular weight of component A

W_B = Weight of component B

M_B = Molecular weight of component B

W_A/M_A = Moles of component A

$W_A/M_A + W_B/M_B$ = Total moles of the system.

EXAMPLE 2.1 Calculate the kg atoms of carbon which weigh 48 kg.

Solution: Basis: 48 kg of carbon

Atomic weight of carbon = 12

$$\text{kg atom of carbon} = \frac{\text{Weight of carbon in kg}}{\text{Atomic weight of carbon}} = \frac{48}{12} = 4$$

EXAMPLE 2.2 Determine the molecular weight of the following compounds.

(i) Na_2CO_3

(ii) HNO_3

(iii) $MgSO_4$

(iv) H_2SO_4

(v) HCl

Solution:

(i) Na_2CO_3

Atomic weights: Na = 23, C = 12 and O = 16

Molecular weight of $Na_2CO_3 = 2 \times 23 + 1 \times 12 + 3 \times 16$

$= 46 + 12 + 48 = 106$

(ii) HNO_3

Atomic weights: H = 1, N = 14 and O = 16

Molecular weight of HNO_3 = 1 × 1 + 1 × 14 + 3 × 16

= 1 + 14 + 48 = 63

(iii) $MgSO_4$

Atomic weights: Mg = 24, S = 32 and O = 16

Molecular weight of $MgSO_4$ = 1 × 24 + 1 × 32 + 4 × 16

= 24 + 32 + 64 = 120

(iv) H_2SO_4

Atomic weights: H = 1, S = 32 and O = 16

Molecular weight of H_2SO_4 = 2 × 1 + 1 × 32 + 4 × 16

= 2 + 32 + 64 = 98

(v) HCl

Atomic weights: H = 1, and Cl = 35.5

Molecular weight of HCl = 1 × 1 + 1 × 35.5

= 1 + 35.5 = 36.5

EXAMPLE 2.3 Calculate the kg of Na of which amount is specified as 4 kgatom.

Solution: Basis: 4 kgatom of Na

Atomic weight of Na = 23

$$\text{kgatom of Na} = \frac{\text{kg of Na}}{\text{Atomic weight of Na}}$$

$$4 = \frac{\text{kg of Na}}{23}$$

$$4 \times 23 = \text{kg of Na}$$

$$\text{kg of Na} = 92$$

EXAMPLE 2.4 How many kilograms of ethane are there in 220 kgmol?

Solution: Basis: 220 kgmol of ethane

Chemical formula of ethane = C_2H_6

Atomic weights: C = 12 and H = 1

Molecular weight of ethane = 2 × 12 + 6 × 1

= 24 + 6 = 30

$$\text{kgmol of ethane} = \frac{\text{Weight of ethane in kg}}{\text{Molecular weight of ethane}}$$

kg of ethane = kgmol of ethane × Molecular weight of ethane

= 220 × 30 = 6600

EXAMPLE 2.5 Calculate the moles of oxygen present in 640 grams.

Solution: Basis: 640 g of oxygen

Molecular weight of oxygen = 32

$$\text{Moles of oxygen} = \frac{\text{Weight of oxygen in g}}{\text{Molecular weight of oxygen}}$$
$$= \frac{640}{32}$$
$$= 20$$

EXAMPLE 2.6 Convert 998 g of $CuSO_4$ ⊣ $5H_2O$ into moles.

Solution: Basis: 998 g of $CuSO_4$ ⊣ $5H_2O$

Atomic weights: Cu = 63.5, S = 32, O = 16 and H = 1

Molecular weight = 1 × 63.5 + 1 × 32 + 4 × 16 + 5(2 × 1 + 1 × 16)

= 63.5 + 32 + 64 + 5(18) = 249.5

$$\text{Moles of } CuSO_4 \cdot 5H_2O = \frac{\text{Weight of } CuSO_4 \cdot 5H_2O}{\text{Molecular weight of } CuSO_4 \cdot 5H_2O}$$
$$= \frac{998}{249.5}$$
$$= 4$$

EXAMPLE 2.7 How many moles of H_2SO_4 will contain 64 kg of S?

Solution: Basis: 64 kg of S

Atomic weight of S = 32 kg

Molecular weight of H_2SO_4 = 98 kg

Each mole of H_2SO_4 contains one atom of S

32 kg of S ⊣ 98 kg of H_2SO_4

64 kg of S ⊣ ?

Amount of H_2SO_4 = $\frac{98}{32} \times 64$

= 196 kg

Therefore, moles of H_2SO_4 = $\frac{\text{Weight of } H_2SO_4 \text{ in kg}}{\text{Molecular weight of } H_2SO_4}$

= $\frac{196}{98}$

Hence, moles of H_2SO_4 = 2

EXAMPLE 2.8 How many moles of K_2CO_3 will contain 78 kg of K?

Solution: Basis: 78 kg of K

Atomic weight of K = 39 kg

Molecular weight of K_2CO_3 = 138 kg

Each mole of K_2CO_3 contains 2 atoms of K.

Now, 78 kg of K → 138 kg of K_2CO_3

Amount of K_2CO_3 = 138 kg

$$\text{Moles of } K_2CO_3 = \frac{\text{Weight of } K_2CO_3 \text{ in kg}}{\text{Molecular weight of } K_2CO_3}$$
$$= \frac{138}{138}$$
$$= 1$$

EXAMPLE 2.9 How many moles of HNO_3 will contain 56 kg of N?

Solution: Basis: 56 kg of N
Atomic weight of N = 14

$$\text{Atoms of N} = \frac{\text{kg of N}}{\text{Atomic weight of N}}$$
$$= \frac{56}{14}$$
$$= 4$$

Each mole of HNO_3 contains one atom of N.

1 kg atom of N = 1 kgmol of HNO_3

4 kg atom of N = 1 × 4 = 4

That is, moles of HNO_3 = 4 kgmol

EXAMPLE 2.10 How many kg of carbon are present in 80 kg of methane?
Solution: Basis: 80 kg of methane (CH_4)
Atomic weights: C = 12 and H = 1

Molecular weight of CH_4 = 1 × 12 + 4 × 1

= 16

Now, 1 kg atom of C = 1 kgmol of CH_4

Also, 12 kg of C = 16 kg of CH_4

∴ 16 kg of CH_4 = 12 kg of C

80 kg of CH_4 = $\frac{12}{16} \times 80$

That is, amount of carbon = 60 kg

EXAMPLE 2.11 Calculate the N content of 100 kg urea sample containing 96.43% of urea.
Solution: Basis: 100 kg urea sample
Amount of urea present = 96.43 kg
Molecular weight of urea (NH_2CONH_2) = 60

Now, 1 kgmol of NH_2CONH_2 → 2 kgatom of N

Also, 60 kg of NH_2CONH_2 ⏌ 28 kg of N

96.43 kg of NH_2COHN_2 ⏌ ?

Nitrogen content of the sample = $\frac{28}{60} \times 96.43$

= 45 kg

EXAMPLE 2.12 Calculate the equivalent moles of Na_2SO_4 in 1288 g of Na_2SO_4⏌$10H_2O$ crystals.

Solution: Basis: 1288 g of Na_2SO_4⏌$10H_2O$ crystals

$$\begin{aligned}\text{Molecular weight of } Na_2SO_4 &= 2 \times 23 + 1 \times 32 + 4 \times 16\\ &= 142\end{aligned}$$

$$\begin{aligned}\text{Molecular weight of } Na_2SO_4 \cdot 10H_2O &= 142 + 10\,(2 \times 1 + 1 \times 16)\\ &= 142 + 180\\ &= 322\end{aligned}$$

$$\begin{aligned}\text{Moles of } Na_2SO_4 \cdot 10H_2O &= \frac{\text{Weight of } Na_2SO_4 \cdot 10H_2O \text{ in g}}{\text{Molecular weight of } Na_2SO_4 \cdot 10H_2O}\\ &= \frac{1288}{322}\\ &= 4 \text{ mole}\end{aligned}$$

$$1 \text{ mole of } Na_2SO_4 \cdot 10H_2O \equiv 1 \text{ mole of } Na_2SO_4$$

$$4 \text{ mole of } Na_2SO_4 \cdot 10H_2O \equiv ?$$

$$\begin{aligned}\text{Amount of } Na_2SO_4 &= \frac{1 \times 4}{1}\\ &= 4 \text{ moles}\end{aligned}$$

The equivalent moles of Na_2SO_4 in crystals are 4 moles.

2.5

Equivalent Weight

It is defined as the ratio of the atomic weight or molecular weight to its valency.

The valency of an element or a compound does depend on the number of hydrogen ions H^+ accepted or the hydroxyl ion OH^- donated for each atomic weight or molecular weight. It can be expressed as

$$\text{Equivalent weight} = \frac{\text{Molecular weight}}{\text{Valency}} \qquad (2.12)$$

EXAMPLE 2.13 Calculate the equivalent weight of the following:

(i) NaOH

(ii) H_2SO_4

(iii) HCl

(iv) Na_2CO_3

Solution:

(i) NaOH

Molecular weight of NaOH = 1 × 23 + 1 × 16 + 1 × 1

= 23 + 16 + 1 = 40

Valency of NaOH = 1

$$\begin{aligned}\text{Equivalent weight of NaOH} &= \frac{\text{Molecular weight of NaOH}}{\text{Valency of NaOH}}\\ &= \frac{40}{1}\\ &= 40\end{aligned}$$

(ii) H_2SO_4

Molecular weight of H_2SO_4 = 2 × 1 + 1 × 32 + 4 × 16

= 2 + 32 + 64 = 98

Valency of H_2SO_4 = 2

$$\begin{aligned}\text{Equivalent weight of } H_2SO_4 &= \frac{\text{Molecular weight of } H_2SO_4}{\text{Valency of } H_2SO_4}\\ &= \frac{98}{2}\\ &= 49\end{aligned}$$

(iii) HCl

Molecular weight of HCl = 1 × 1 + 1 × 35.5

= 1 + 35.5 = 36.5

Valency of HCl = 1.

$$\begin{aligned}\text{Equivalent weight of HCl} &= \frac{\text{Molecular weight of HCl}}{\text{Valency of HCl}}\\ &= \frac{36.5}{1}\\ &= 36.5\end{aligned}$$

(iv) Na_2CO_3

Molecular weight of Na_2CO_3 = 2 × 23 + 1 × 12 + 3 × 16

= 46 + 12 + 48 = 106

Valency of Na_2CO_3 = 2

$$\text{Therefore, equivalent weight of } Na_2CO_3 = \frac{\text{Molecular weight of } Na_2CO_3}{\text{Valency of } Na_2CO_3} = \frac{106}{2} = 53$$

EXAMPLE 2.14 Determine the equivalent weight of the following:

(i) NH_4NO_3

(ii) $(NH_4)_2SO_4$

Solution:

(i) NH_4NO_3

Molecular weight of $NH_4NO_3 = 1 \times 14 + 4 \times 1 + 1 \times 14 + 3 \times 16$

$= 14 + 4 + 4 + 48 = 70$

Valency of $NH_4NO_3 = 1$

Hence, equivalent weight of $NH_4NO_3 = \frac{70}{1} = 70$

(ii) $(NH_4)_2SO_4$

Molecular weight of $(NH_4)_2SO_4 = (1 \times 14 + 4 \times 1)\ 2 + 1 \times 32 + 4 \times 16$

$= (14 + 4)\ 2 + 32 + 64$

$= 132$

Valency of $(NH_4)_2SO_4 = 2$

$$\text{Therefore, equivalent weight of } (NH_4)_2SO_4 = \frac{\text{Molecular weight of } (NH_4)_2SO_4}{\text{Valency of } (NH_4)_2SO_4} = \frac{132}{2} = 66$$

2.6

Concept of Normality, Molarity and Molality

There are three ways of expressing the concentration of solution containing either solid or liquid solute, namely

1. Normality
2. Molarity
3. Molality

2.6.1 Normality

It is defined as the number of gram equivalents of solute dissolved in one litre of solution. It is designated by the symbol *N*. It can be expressed as

$$\text{Normality } (N) = \frac{\text{Gram equivalent of solute}}{\text{Volume of solution in litre}} \qquad (2.13)$$

2.6.2 Molarity

It is defined as the number of gram moles of the solute dissolved in one litre of solution. It is designated by the symbol *M*. It can be expressed as

$$\text{Molarity } (M) = \frac{\text{Gram moles of solute}}{\text{Volume of solution in litre}} \qquad (2.14)$$

2.6.3 Molality

It is defined as the gram moles of the solute dissolved in one kilogram of the solvent. It can be expressed as

$$\text{Molality } (M) = \frac{\text{Gram mole of solute}}{\text{Mass of solvent in kg}} \qquad (2.15)$$

EXAMPLE 2.15 196 grams of sulphuric acid (H_2SO_4) are dissolved in water to prepare one litre of solution. Determine the normality.

Solution: Basis: One litre of solution.

Amount of H_2SO_4 dissolved = 196 g

$$\begin{aligned}
\text{Molecular weight of } H_2SO_4 &= 2 \times 1 + 1 \times 32 + 4 \times 16 \\
&= 2 + 32 + 64 \\
&= 98 \\
\text{Equivalent weight of } H_2SO_4 &= \frac{\text{Molecular weight of } H_2SO_4}{\text{Valency of } H_2SO_4} \\
&= \frac{98}{2} \\
&= 49
\end{aligned}$$

$$\begin{aligned}
\text{Gram-equivalent of } H_2SO_4 &= \frac{\text{Weight of } H_2SO_4 \text{ in g}}{\text{Equivalent weight of } H_2SO_4} \\
&= \frac{196}{49} \\
&= 4 \text{ moles} \\
\text{Therefore,} \qquad \text{Normality } (N) &= \frac{\text{Gram equivalent of } H_2SO_4}{\text{Volume of solution in litre}} \\
&= \frac{4}{1} \\
&= 4
\end{aligned}$$

EXAMPLE 2.16 196 grams of sulphuric acid (H_2SO_4) are dissolved in water to prepare one litre of solution. Calculate the molarity.

Solution: Weight of sulphuric acid (H_2SO_4) = 196 g

Molecular weight of H_2SO_4 = 98

$$\begin{aligned}\text{Moles of } H_2SO_4 &= \frac{\text{Weight of } H_2SO_4 \text{ in g}}{\text{Molecular weight of } H_2SO_4}\\ &= \frac{196}{98}\\ &= 2 \text{ moles}\\ \text{Molarity } (M) &= \frac{\text{Gram moles of solute } (H_2SO_4)}{\text{Volume of solution in litre}}\\ &= \frac{2}{1}\\ &= 2\end{aligned}$$

EXAMPLE 2.17 196 grams of sulphuric acid (H_2SO_4) are dissolved in water to prepare one litre of solution. Calculate the molality.

Solution:

Amount of solvent = 1 litre

$$\rho = \frac{M}{V}$$

Therefore, $$M = \rho \cdot \mathrm{V}$$

$$\begin{aligned}\text{Amount of solvent in kg} &= 1000\,\frac{\text{kg}}{\text{m}^3} \times 1000 \text{ cm}^3\\ &= \frac{10^6 \text{ kg}}{10^6 \text{ cm}^3} \cdot \text{cm}^3\\ &= 1 \text{ kg}\end{aligned}$$

$$\begin{aligned}\text{Molality } (M) &= \frac{\text{Gram moles of solute}}{\text{Mass of solvent in kg}}\\ &= \frac{2}{1}\\ &= 2\end{aligned}$$

EXAMPLE 2.18 10 g of caustic soda are dissolved in water to prepare 500 ml of solution. Calculate the normality.

Solution: Basis: 500 ml of solution

Molecular weight of NaOH = 40

Valency of NaOH = 1

$$\text{Equivalent weight of NaOH} = \frac{\text{Molecular weight of NaOH}}{\text{Valency of NaOH}}$$

$$= \frac{40}{1}$$

$$= 40$$

$$\text{Volume of solution} = 500 \text{ ml}$$

$$= 0.5 \text{ l}$$

$$\text{Gram equivalent of NaOH} = \frac{\text{Weight of NaOH in g}}{\text{Equivalent weight of NaOH}}$$

$$= \frac{10}{40}$$

$$= 0.25$$

$$\text{Normality of NaOH} = \frac{\text{Gram equivalent of NaOH}}{\text{Volume of solution in litre}}$$

$$= \frac{0.25}{0.5}$$

$$= 0.5$$

EXAMPLE 2.19 Find out g of HCl needed to prepare 1 litre of 2N HCl solution.

Solution: Basis: 1 litre 2N HCl solution.

$$\text{Normality} = \frac{\text{Gram equivalent of HCl}}{\text{Volume of solution in litre}}$$

$$\therefore\ 2 = \frac{\text{Gram equivalent of HCl}}{1}$$

∴ Gram equivalent of HCl = 2 × 1 = 2

Molecular weight of HCl = 1 × 1 + 1 × 35.5

= 1 + 35.5 = 36.5

$$\text{Equivalent weight of HCl} = \frac{\text{Molecular weight of HCl}}{\text{Valency of HCl}}$$

$$= \frac{36.5}{1} = 36.5$$

$$\text{Gram equivalent weight of HCl} = \frac{\text{Weight of HCl in g}}{\text{Equivalent weight of HCl}}$$

Weight of HCl in g = Gram equivalent weight of HCl × Equivalent weight of HCl

= 2 × 36.5 = 73

EXAMPLE 2.20 Convert 588 g/l H_2SO_4 to normality.

Solution: Basis: 1 litre of solution

H_2SO_4 in solution = 588 g

Molecular weight of H_2SO_4 = 2 × 1 + 1 × 32 + 4 × 16

= 2 + 32 + 64

= 98

Valency of H_2SO_4 = 2

$$\text{Equivalent weight of } H_2SO_4 = \frac{\text{Molecular weight of } H_2SO_4}{\text{Valency of } H_2SO_4}$$

$$= \frac{98}{2}$$

$$= 49$$

$$\text{Gram equivalent weight of } H_2SO_4 = \frac{\text{Weight of } H_2SO_4 \text{ in g}}{\text{Equivalent weight of } H_2SO_4}$$

$$= \frac{588}{49}$$

$$= 12 \text{ N}$$

EXAMPLE 2.21 Convert 5N H_3PO_4 to g/l.

Solution: Basis = 1 litre of solution

Molecular weight of H_3PO_4 = 3 × 1 + 1 × 31 + 4 × 16

= 3 + 31 + 64 = 98

Valency of H_3PO_4 = 3

$$\text{Equivalent weight of } H_3PO_4 = \frac{\text{Molecular weight of } H_3PO_4}{\text{Valency of } H_3PO_4}$$

$$= \frac{98}{3}$$

$$= 32.67$$

$$\text{Gram equivalent weight of } H_3PO_4 = \frac{\text{Weight of } H_3PO_4 \text{ in g}}{\text{Equivalent weight of } H_3PO_4}$$

$$\text{Weight of } H_3PO_4 \text{ in } g = \text{Gram equivalent weight of } H_3PO_4 \times \text{Equivalent weight of } H_3PO_4$$

$$\text{Normality} = \frac{\text{Gram equivalent of } H_3PO_4}{\text{Volume of solution in litre}}$$

$$\text{Gram equivalent of } H_3PO_4 = \text{Normality} \times \text{Volume of solution in litre}$$

$$\text{Weight of } H_3PO_4 \text{ in g} = \text{Normality} \times \text{Volume of solution in litre} \times \text{Equivalent weight of } H_3PO_4$$

$$= 5 \times 1 \times 32.67$$

$$= 163.35 \text{ g}$$

$$\text{Concentration (g/l)} = \frac{\text{Mass of } H_3PO_4 \text{ in g}}{\text{Volume of solution in litre}}$$

$$= \frac{163.35}{1}$$

$$= 163.35$$

EXAMPLE 2.22 An aqueous solution of sodium chloride is prepared by dissolving 20 kg of NaCl in 100 kg of water. Calculate weight% composition of solution.

Solution: Basis: 20 kg of NaCl in 100 kg of water

$$\begin{aligned}
\text{Amount of solution} &= 20 + 100 \\
&= 120 \text{ kg} \\
\text{Weight\% of NaCl} &= \frac{\text{kg of NaCl}}{\text{kg of solution}} \times 100 \\
&= \frac{20}{120} \times 100 \\
&= 16.66\% \\
\text{Weight\% of } H_2O &= \frac{\text{kg of } H_2O}{\text{kg of solution}} \times 100 \\
&= \frac{100}{120} \times 100 \\
&= 83.34\%
\end{aligned}$$

EXAMPLE 2.23 An aqueous solution of sodium chloride is prepared by dissolving 20 kg of NaCl in 80 kg of water. Calculate mole% composition of solution.

Solution: Basis: 20 kg of NaCl and 80 kg of water

Molecular weight of NaCl = 1 × 23 + 1 × 35.5 = 23 + 35.5 = 58.5

Molecular weight of H_2O = 2 × 1 + 1 × 16 = 2 + 16 = 18

Now, $$\text{moles of NaCl} = \frac{\text{Mass of NaCl in kg}}{\text{Molecular weight of NaCl}} = \frac{20}{58.5} = 0.3418$$

Also, $$\text{moles of water } (H_2O) = \frac{\text{Mass of water in kg}}{\text{Molecular weight of } H_2O} = \frac{80}{18} = 4.444$$

$$\text{Total moles of solution} = \text{Moles of NaCl} + \text{Moles of } H_2O = 0.3418 + 4.444 = 4.7858$$

Therefore, $$\text{mole\% of NaCl} = \frac{\text{Moles of NaCl}}{\text{Total moles of solution}} \times 100 = \frac{0.3418}{4.7858} \times 100 = 7.14\%$$

and $$\text{mole\% of water} = \frac{\text{Moles of water}}{\text{Total moles of solution}} \times 100 = \frac{4.444}{4.7858} \times 100 = 92.86\%$$

EXAMPLE 2.24 The strength of aqueous solution of soda ash is specified as 15% Na_2O by weight. Express the composition in terms of weight per cent soda ash.

Solution: Basis: 100 kg of aqueous solution.

The aqueous solution contains 15 kg of Na_2O.

$Na_2CO_3 = Na_2O + CO_2$

Molecular weight of $Na_2CO_3 = 2 \times 23 + 1 \times 12 + 3 \times 16 = 46 + 12 + 48 = 106$

Molecular weight of $Na_2O = 2 \times 23 + 1 \times 16 = 46 + 16 = 62$

1 kgmol of Na_2CO_3 → 1 kgmol of Na_2O

106 kg of Na_2CO_3 → 62 kg of Na_2O

or, 62 kg of Na_2O → 106 kg of Na_2CO_3

Therefore, 15 kg of Na_2O → $\frac{106}{62} \times 15$ kg of Na_2CO_3

= 25.65 kg of Na_2CO_3

Therefore, weight% of Na_2CO_3 in solution = $\dfrac{\text{Weight of soda ash}}{\text{Total weight of aqueous solution}}$

$= \dfrac{25.65}{100} \times 100$

$= 25.65$

EXAMPLE 2.25 The strength of a phosphoric acid sample is found to be 40% P_2O_5 by weight. Find out the actual concentration of H_3PO_4 (weight%) in the acid.

Solution: Basis: 100 kg of phosphoric acid sample.
It contains 40 kg of P_2O_5.

Now, $2H_3PO_4 = P_2O_5 + 3H_2O$

Molecular weight of $H_3PO_4 = 3 \times 1 + 1 \times 31 + 4 \times 16 = 3 + 31 + 64 = 98$

Molecular weight of $P_2O_5 = 2 \times 31 + 5 \times 16 = 62 + 80 = 142$

2 kgmol of H_3PO_4 ≡ 1 kgmol of P_2O_5

196 kg of H_3PO_4 ≡ 142 kg of P_2O_5

142 kg of P_2O_5 ≡ 196 kg of H_3PO_4

Hence, 40 kg of P_2O_5 ≡ $\dfrac{196}{142} \times 40$ kg of H_3PO_4

$= 55.21$ kg

Weight% of H_3PO_4 in phosphoric acid sample = $\dfrac{\text{Weight of phosphoric acid in kg}}{\text{Total weight of phosphoric acid sample}} \times 100$

$= \dfrac{55.21}{100} \times 100$

$= 55.21$

EXAMPLE 2.26 Nitric acid and water form maximum boiling azeotrope containing 65 mole% water. Find the composition of azeotrope by weight per cent.

Solution: Basis: 100 kgmol of HNO_3 + water azeotrope sample. It contains 65 kgmol of water and 35 kgmol of HNO_3.

Molecular weight of $H_2O = 2 \times 1 + 1 \times 16 = 2 + 16 = 18$

Molecular weight of $HNO_3 = 1 \times 1 + 1 \times 14 + 3 \times 16 = 1 + 14 + 48 = 63$

Amount of H_2O in azeotrope = $65 \times 18 = 1170$ kg

Amount of HNO_3 in azeotrope = $35 \times 63 = 2205$ kg

Therefore, total amount of ($HNO_3 + H_2O$) azeotrope = $2205 + 1170 = 3375$ kg

Hence, weight% of HNO_3 in azeotrope = $\dfrac{\text{Weight of } HNO_3 \text{ in kg}}{\text{Total weight of azeotrope sample}} \times 100$

$= \dfrac{2205}{3375} \times 100 = 65.33$

EXAMPLE 2.27 Spent acid from a fertilizer plant has the following composition by weight.

H_2SO_4 = 20%

NH_4HSO_4 = 45%

H_2O = 30%

Organic compound = 05%

Calculate the total acid content of the spent acid in terms of H_2SO_4 after adding the acid content chemically bound in ammonium hydrogen sulphate.

Solution: Basis: 100 kg of spent acid.
It contains 20 kg of H_2SO_4 and 45 kg of NH_4HSO_4.

1 kgmol NH_4HSO_4 → 1 kgmol H_2SO_4

115 kg NH_4HSO_4 → 98 kg H_2SO_4

H_2SO_4 chemically bound in 45 kg NH_4HSO_4 = $\frac{98}{115} \times 45$ = 38.35 kg

H_2SO_4 from spent acid = Free H_2SO_4 + H_2SO_4 chemically bound in NH_4HSO_4.

= 20 + 38.35 = 58.35 kg

Total acid content of spent acid = $\frac{H_2SO_4 \text{ from spent acid}}{\text{Total acid content of spent acid}} \times 100$

$= \frac{58.35}{100} \times 100$

= 58.35%

2.7

Concept of PPM (Parts Per Million)

It is the short form of parts per million, i.e. parts of one substance present in million parts of another substance, specially solvent. It is commonly used as a unit of concentration.

Concentration may be defined as the amount of solute present in known amount of solvent. It has the unit g/l or g/cc. For example, consider the concentration of NaOH in water. When 5 g of Sodium hydroxide is dissolved in 1 litre of water, it gives the concentration of Sodium Hydroxide in water as 5 g/l.

When a large amount of solute substance is present in a solvent, it can be comfortably represented by the unit g/l. But, when the solute substance present in solvent is very very small, the uncomfortness arises to represent the unit as g/l. To overcome this difficulties, ppm unit is used.

The unit as ppm is commonly used to measure the small level of pollutants present in air. For example, Permissible Exposure Limit (PEL) of CO in air is 50 ppm.

It is also used as a measure of small level of pollutant present in drinking water. For example, permissible exposure limit of Arsenic in drinking water is 1 ppm.

EXAMPLE 2.28 A sample of water contains 2000 ppm solids. Find the concentration of solids by weight percentage.

Solution: Basis: 10^6 kg of water sample

Solids in water = 2000 ppm.

Now, 1 ppm = $\frac{1}{1000000} \frac{\text{mg}}{\text{mg}}$

2000 ppm = $\frac{2000 \times 1}{1000000} \frac{\text{mg}}{\text{mg}}$

1000000 mg → 2000 mg

Amounts of solids in 10^6 kg water = $\frac{2000}{10^6} \times 10^6 \frac{(\text{mg})(\text{kg})}{\text{mg}}$

= 2000 kg

Weight% of solids = $\frac{\text{Weight of solids in kg}}{\text{Total water sample in kg}} \times 100$

= $\frac{2000}{10^6} \times 100$

= 0.20

2.8

Application of Different Types of Graph

In science and technology, the different types of graph generally used are:

1. Ordinary graph
2. Semi-log graph
3. Log-log graph
4. Triangular graph.

2.8.1 Ordinary Graph

In ordinary graph, data are plotted between *X*-axis and *Y*-axis to obtain a straight line or curve. This is generally used when both the variables have the restricted range of values. The data can be plotted on first, second, third and fourth quadrant of the graph. It is the simplest among all kinds of graph. A typical ordinary graph is shown in Figure 2.1.

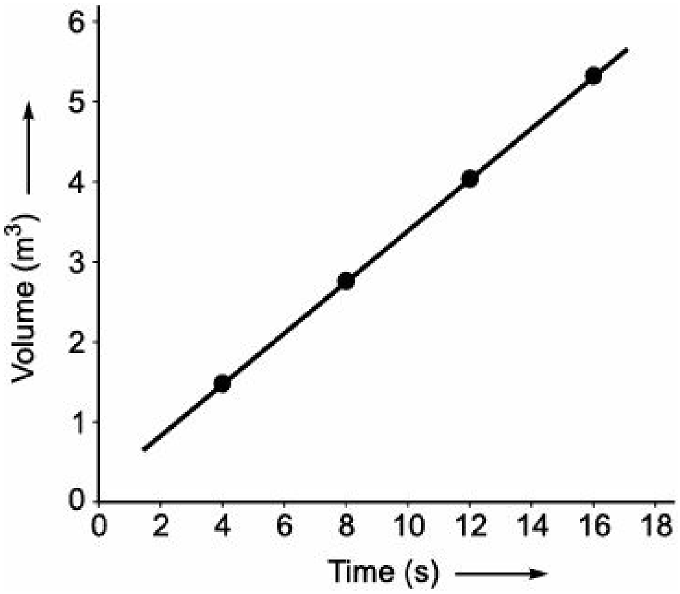


FIGURE 2.1 Ordinary graph.

2.8.2 Semi-log Graph

Semi-log graph consists of one axis ordinary (generally *Y*-axis) and other axis logarithmic (generally *X*-axis). Semi-log paper (3 cycles) is written at the top of the graph. While plotting the data, it is to be remember to hold the graph in such a way that semi-log paper (3 cycles) should represent the top right hand side corner of the graph.

The number of cycles in semi-log graph is not fixed. It varies depending on the requirement of plotting the data. It is generally available in 1 to 2 cycles, 1 to 3 cycles and 1 to 4 cycles. A typical semi-log graph of 1 to 3 cycles is shown in Figure 2.2. It is observed from the graph that the horizontal axis is very peculiar as the number moves horizontally from 1 to 9 for a cycle and again it start with 1 for next cycle and so on. This is because of the fact that it represents the logarithmic distance and there is no log of zero.

It is also observed that in horizontal axis, first cycle vertical line started with 0.1, second cycle started with 1.0 and third cycle started with 10 and end with 100. But, the line of basic numerical values does not change. The placement of decimal point is allowed to change and they always differ by one decimal point per cycle.

Semi-log graph is useful when one of the variable being plotted to cover a large range of values and the other has only a restricted range. For example, in control engineering, it is useful in plotting phase margin diagram where *wt* has large range of values and *f* has restricted range of values.

2.8.3 Log-Log Graph

In log-log graph both *x*-axis and *y*-axis consist of logarithmic scale. Log-log paper (3 cycles × 4 cycles) is written at the top of the graph. While plotting the data, it is to be remembered to hold the graph in such a way that log-log paper (3 cycles × 4 cycles) should represent the top right hand side corner of the graph.

The number of cycles in log-log graph is not fixed in either *x*-axis or *y*-axis. It varies depending on the size of the data. It is generally available in 2 cycles × 3 cycles and 3 cycles × 4 cycles. A typical log-log graph of 3 cycles × 4 cycles is shown in Figure 2.3. It is observed from the graph that in the vertical axis as well as horizontal axis, the number moves from 1 to 9 for a cycle and again it starts with 1 for next cycle and so on. This is because of the fact that both *x*-axis and *y*-axis represent the logarithmic distance and there in no log of zero.

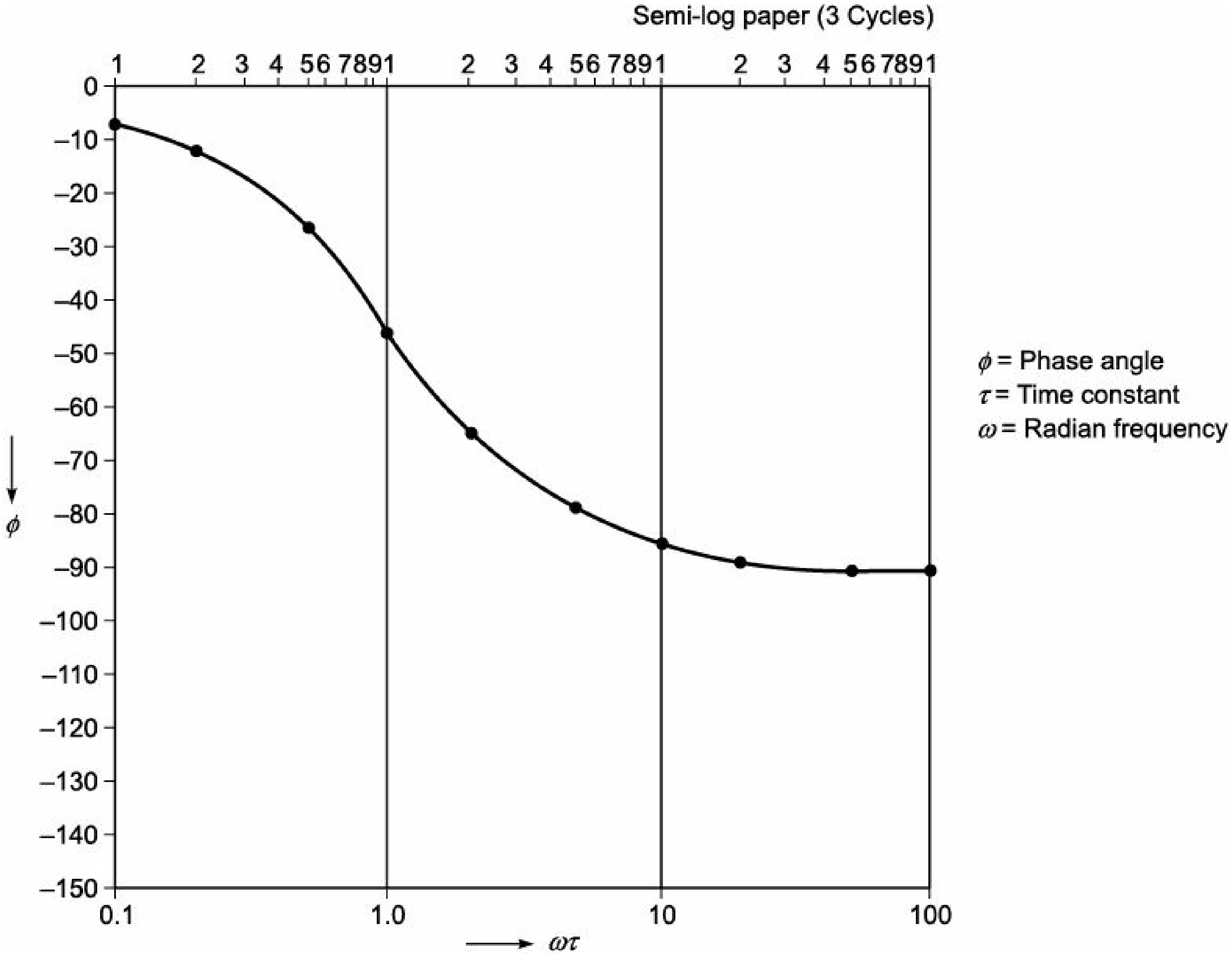


FIGURE 2.2 Semi-log graph.

It is also observed that in horizontal axis, first cycle vertical line is started with 0.1, second cycle is started with 1.0, third with 10 and fourth with 100, and end with 1000. Whereas, in vertical axis, the first cycle horizontal line is started with 0.01, second with 0.1, third with 1.0 and end with 10. But the line of basic numerical values in case of vertical axis as well as horizontal axis does not change. The placement of decimal point is allowed to change and they always differ by one decimal point per cycle.

Log-log graph is useful when both of the variables being plotted to cover a large range of values. For example, in control engineering, it is useful in plotting phase margin diagram for the determination of stability of the system.

2.8.4 Triangular Graph

A triangular graph is of the form of equilateral triangle. It has three sides AB, BC and CA of equal length, and all of its angles A, B and C are of same measure of 60°.

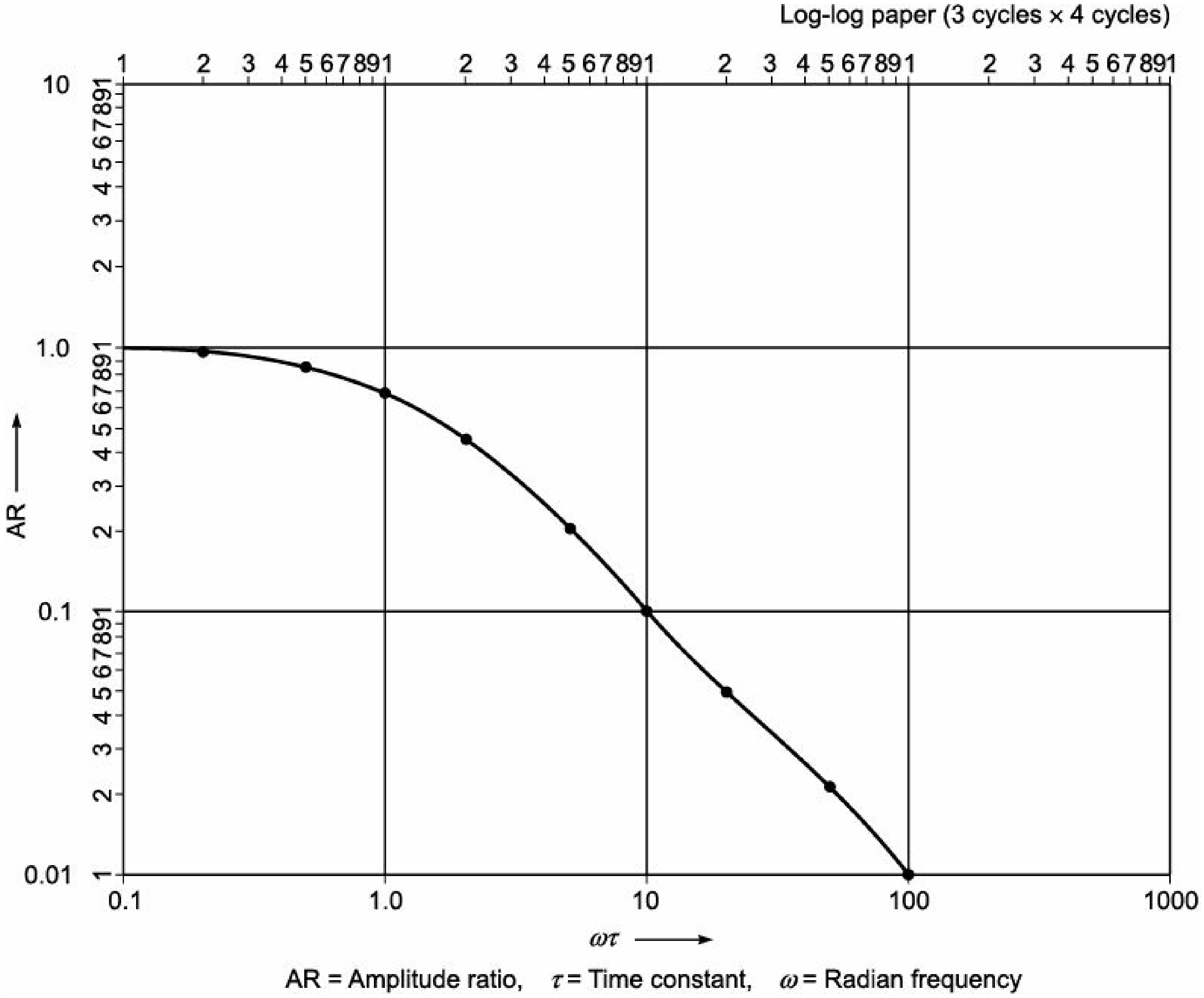


FIGURE 2.3 Log-log graph.

It has three axes, A, B and C. These axes move in either clockwise or anticlockwise directions. A typical graph is shown in Figure 2.4. It is observed from the graph that the number moves from 0 to 100 for a axis and again it starts from '0' and so on. The data represents the axis in the form of percentage. A triangular graph is generally used for plotting the data of liquid-liquid extraction system. For example, consider the liquid-liquid extraction system of benzene, acetic acid and water. If A = 30, B = 10 and C = 60, a graph can be plotted on the triangular graph.

It is a useful method for examining the varying proportion of three related set of data. Also, it is the only graph which enables three variables to be plotted. It has one disadvantage that it cannot be used to represent the absolute values.

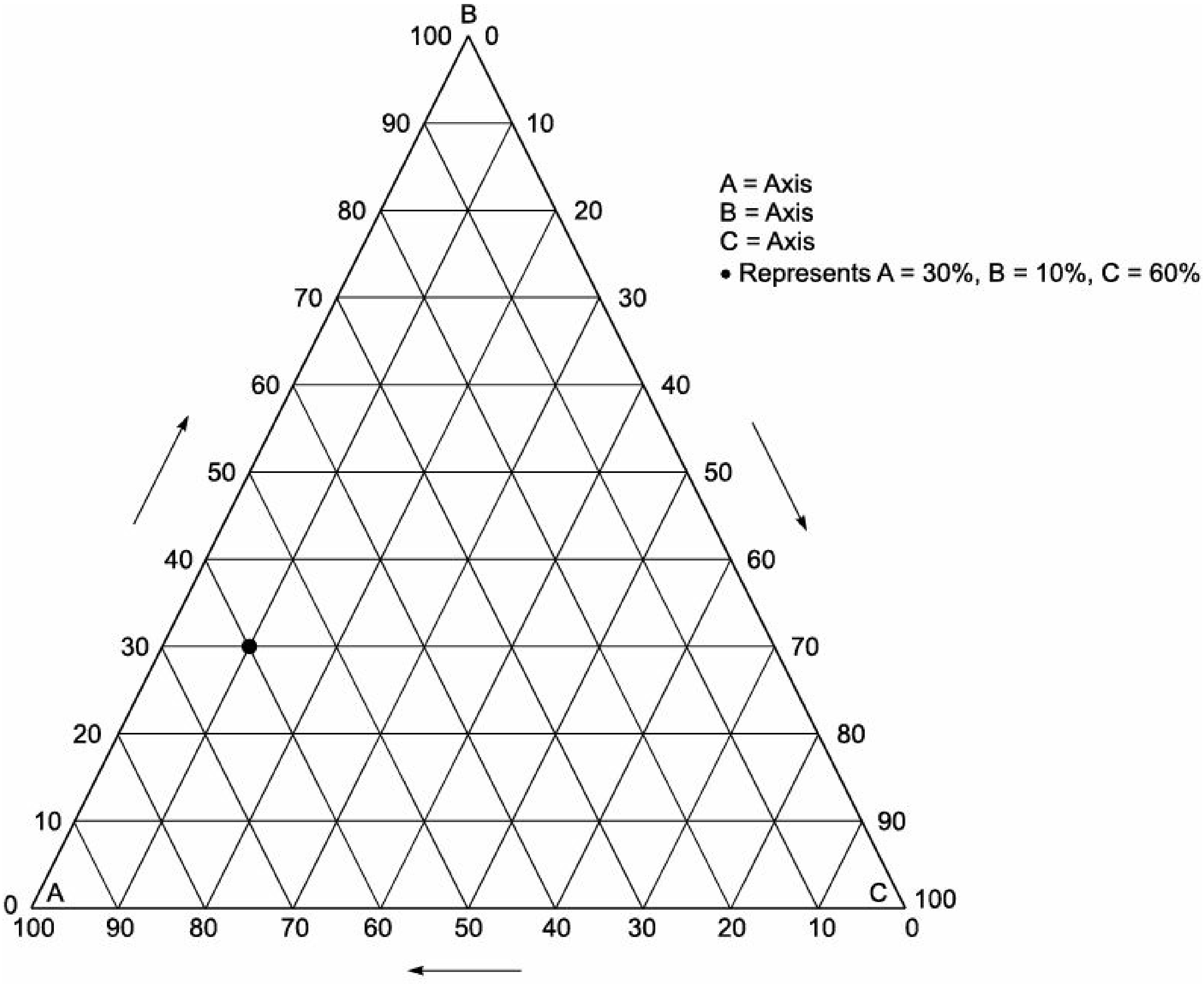


FIGURE 2.4 Triangular group.

2.9

Gases

The volume of gases can be measured easily. Hence, the composition of gases can be expressed in terms of volume per cent. If parameters, such as temperature and pressure of the gas are known, then the density of the gas can be calculated. This, in turn, gives the mass of the gas. While dealing with substances existing in the gaseous state, the relationship among the temperature, pressure, mass and volume must be known.

2.9.1 Ideal Gas Law

According to Boyle's law, for a given mass of an ideal gas, the product of the pressure and volume is constant at a constant temperature, i.e.

$$P \times V = \text{Constant} \qquad (2.16)$$

where

P = Absolute pressure (N/m^2)

V = Volume occupied by the gas (m^3)

According to Charle’s law, for a given mass of an ideal gas, the ratio of the volume to temperature is constant at a given pressure, i.e.

$$\frac{V}{T} = \text{Constant} \qquad (2.17)$$

where

V = Volume occupied by the gas (m^3)
T = Absolute temperature (K)

Combining Eqs. (2.16) and (2.17), we get

$$\frac{PV}{T} = \text{Constant} \qquad (2.18)$$

The constant is designated by the symbol R, known as universal gas constant.

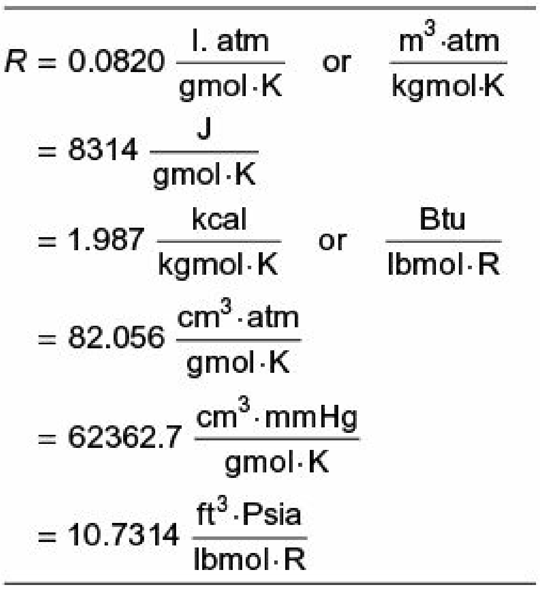
Therefore, $PV = RT$ (2.19)

This is called ideal gas law. Here, P, V and T are expressed in atmosphere (absolute), litre per gmol and kelvin respectively. When V is the volume of a gas in litre of n moles, Eq. (2.19) get modified as

$$PV = nRT \qquad (2.20)$$

The value of R changes with different units and it is given in Table 2.2.

TABLE 2.2 Numerical Value of Universal Gas Constant



$$R = 0.0820 \frac{\text{l. atm}}{\text{gmol}\cdot\text{K}} \quad \text{or} \quad \frac{\text{m}^3\cdot\text{atm}}{\text{kgmol}\cdot\text{K}}$$

$$= 8314 \frac{\text{J}}{\text{gmol}\cdot\text{K}}$$

$$= 1.987 \frac{\text{kcal}}{\text{kgmol}\cdot\text{K}} \quad \text{or} \quad \frac{\text{Btu}}{\text{lbmol}\cdot\text{R}}$$

$$= 82.056 \frac{\text{cm}^3\cdot\text{atm}}{\text{gmol}\cdot\text{K}}$$

$$= 62362.7 \frac{\text{cm}^3\cdot\text{mmHg}}{\text{gmol}\cdot\text{K}}$$

$$= 10.7314 \frac{\text{ft}^3\cdot\text{Psia}}{\text{lbmol}\cdot\text{R}}$$

In Eq. (2.20) V is called molal volume. At 0°C (32 °F) and 1 atm (14.696 Psia), V = 22.4136 l/gmol or m^3/kgmol. These conditions are said to be normal temperature and pressure (NTP). In the FPS system, the molal volume at NTP equals 359.03 ft^3/lbmol.

Local conditions vary from place to place and, therefore, if standard temperature and pressure (STP) are considered, the molal volume will differ at different places. In India, 1 atm and 25 °C are considered to be STP. Knowing the values of P and T, it is easy to calculate the molal volume using the equation

$$\frac{PV}{T} = R \qquad (2.21)$$

If P_1, V_1 and T_1 are the conditions of an ideal gas under one situation, and if P_2, V_2 and T_2 are the conditions of the gas under another situation. It follows that

$$\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2} \qquad (2.22)$$

At one situation may be taken as NTP, i.e.

P_1 = 1 atm

V_1 = 22.4136 l/gmol

T_1 = 273 K

2.10

Dalton's Law

It states that the total pressure exerted by a gaseous mixture is equal to the sum of the partial pressures of component gases. Thus, it expresses the additive nature of partial pressures. Mathematically, it can be expressed as

$$P = p_A + p_B + p_C + \ldots \qquad (2.23)$$

where

P = Total pressure

p_A = Partial pressure of component A

p_B = Partial pressure of component B

p_C = Partial pressure of component C.

2.10.1 Partial Pressure

It is the pressure in the mixture of gases that would be exerted by that component gases if they were present in the same volume and temperature.

2.11

Amagat's Law

It states that the total volume occupied by gaseous mixture is equal to the sum of the pure component volumes. Thus, it expresses the additive nature of pure component volumes of component gases. Mathematically, it can be expressed as:

$$V = V_A + V_B + V_C + \ldots \qquad (2.24)$$

where

V = Total volume

V_A = Pure component volume of A

V_B = Pure component volume of B

V_C = Pure component volume of C

2.11.1 Pure Component Volume

It is the volume that would be occupied by that component gases if they were present at the same pressure and temperature as the mixture.

2.12

Gaseous Mixtures

The composition of component gases present in gas mixture is generally expressed in terms of volume per cent. In case of gas mixture containing in closed vessel, the molecules of each component gases are distributed throughout the entire volume of the container. The total pressure exerted by the entire mixture is equal to the sum of pressure exerted by each component gas.

2.13

Relationship between Partial Pressure, Mole Fraction of Component Gas to Total Pressure

Consider a gas mixture consisting of components *a*, *b*, *c*.
Let V be the total volume of gas mixture.
P be the total pressure exerted by the mixture, and
V_a, V_b and V_c are the pure component volumes of *a*, *b*, and *c* respectively.
p_a, p_b and p_c are the partial pressures of components *a*, *b*, *c* respectively.
From the ideal gas law, we know that

$$PV = nRT$$

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

$$\text{or } p_a = \frac{n_a RT}{V} \qquad (2.25)$$

$$p_b = \frac{n_b RT}{V} \qquad (2.26)$$

$$p_c = \frac{n_c RT}{V} \qquad (2.27)$$

Adding Eqs. (2.25), (2.26) and (2.27), we get

$$P = p_a + p_b + p_c = \frac{(n_a + n_b + n_c)\,RT}{V} \qquad (2.28)$$

Dividing Eq. (2.25) by Eq. (2.28), we get

$$\frac{p_a}{p_a + p_b + p_c} = \frac{n_a RT/V}{(n_a + n_b + n_c)\,RT/V}$$

$$\text{or } \frac{p_a}{p_a + p_b + p_c} = \frac{n_a}{n_a + n_b + n_c} \qquad (2.29)$$

or $\dfrac{p_a}{p_a + p_b + p_c} \times 100 = \dfrac{n_a}{n_a + n_b + n_c} \times 100$

That is, Pressure% = Mole% (2.30)

From Eq. (2.29), we get

$$\frac{p_a}{P} = x_a$$

or $p_a = x_a P$ (2.31)

When ideal gas law is applicable, it can be written for gas components, *a*, *b* and *c* as

$pV_a = n_a RT$ (2.32)

$pV_b = n_b RT$ (2.33)

$pV_c = n_c RT$ (2.34)

Adding Eqs. (2.32), (2.33) and (2.34), we get

$P(V_a + V_b + V_c) = (n_a + n_b + n_c)\, RT$ (2.35)

Dividing Eq. (2.32) by Eq. (2.35), we get

$$\frac{PV_a}{P(V_a + V_b + V_c)} = \frac{n_a RT}{(n_a + n_b + n_c)\, RT}$$

or $\dfrac{V_a}{(V_a + V_b + V_c)} = \dfrac{n_a}{(n_a + n_b + n_c)}$ (2.36)

or $\dfrac{V_a}{(V_a + V_b + V_c)} \times 100 = \dfrac{n_a}{(n_a + n_b + n_c)} \times 100$

That is, Volume% = Mole% (2.37)

Combining Eqs. (2.30) and (2.37), we get

Pressure% = Mole% = Volume% (2.38)

2.14

Average Molecular Weight of Gas Mixture

Generally, it is required for calculating the weight of a gas mixture. It is assumed that the quantity of gas mixture has one mole as the weight of one mole of gas mixture represents its average molecular weight. If the composition of gas mixture is specified in terms of volume%, assuming ideal gas applicability, we have to treat the same as mole%. Then mole fraction to be calculated, which is needed for calculating average molecular weight of gas mixture.

Let us consider a gas mixture consisting of components *a*, *b*, and *c*.

Let M_a, M_b and M_c are the molecular weight of the components *a*, *b*, *c* and x_a, x_b and x_c are the mole fractions of component gases.

Then,

$$M_{\text{avg}} = M_a \dashv x_a + M_b \dashv x_b + M_c \dashv x_c \qquad (2.39)$$

where

M_{avg} = Average molecular weight of gas mixture.

Average molecular weight of gas mixture is the sum of the products of molecular weight and mole fraction of component gases. It can be expressed as

$$M_{\text{avg}} = \sum_{i=1}^{n} M_i \cdot x_i \qquad (2.40)$$

2.15

Density of Gas Mixture

The density of a gas mixture can be easily calculated by the use of ideal gas law at a given temperature and pressure of the gas mixture.

For calculating the density, one must know the average molecular weight of the gas mixture. From the ideal gas law, we know that

$$PV = nRT \qquad (2.41)$$

$$\wedge \quad \frac{P}{RT} = \frac{n}{V}$$

$$\wedge \quad \frac{P}{RT} = n \times \frac{1}{V}$$

$$\wedge \quad \frac{P}{RT} = \frac{\text{Weight of gas mixture in kg}}{\text{Average molecular weight}} \times \frac{1}{V}$$

$$\wedge \quad \frac{P}{RT} = \frac{\text{Weight of gas mixture in kg}}{M_{\text{Avg}}} \times \frac{1}{V}$$

$$\wedge \quad \frac{PM_{\text{avg}}}{RT} = \frac{\text{Weight of gas mixture in kg}}{V}$$

$$\frac{PM_{\text{avg}}}{RT} = \rho_{\text{mix}}$$

Therefore, Density (r_{mix}) = $\dfrac{PM_{\text{Avg}}}{RT}$ (2.42)

where

r_{mix} = Density of the gas mixture (kg/m^3)

P = Pressure (atm)

M_{avg} = Average molecular weight

R = Universal gas constant $\left(\dfrac{\text{m}^3.\text{atm}}{\text{kgmol}\cdot\text{K}}\right)$

T = Absolute temperature (K)

2.16

Non-ideal Behaviour of Gases

According to Boyles law, the volume occupied by a gas is inversely proportional to its pressure. However, real gases exhibit considerable deviation from ideal behaviour. For every gas, the ratio

$$\frac{PV}{RT} = \text{Constant} \qquad (2.43)$$

covers only a definite range of pressure. Within this range, Boyle's law is obeyed.

In general, the extent of the deviation from Boyle's law is small at low pressure, especially when the temperature is relatively high. The lower the pressure, the better is the ideal behaviour of the gas.

In order to account for non-ideal behaviour of gases, Vander Waals proposed an equation of state as

$$\left(P + \frac{a}{V^2}\right)(V - b) = RT \qquad (2.44)$$

where

P = Pressure

a = Constant

b = Constant

V = Volume

R = Universal gas constant and

T = Absolute temperature.

The values of constants a and b depend on the gas. The values of a and b can be evaluated using the following equations.

$$a = \frac{27R^2T_c^2}{64P_c}\left(\frac{\text{l-atm}}{(\text{gmol})^2}\right) \qquad (2.45)$$

$$b = \frac{RT_c}{8P_c}\left(\frac{1}{\text{gmol}}\right) \qquad (2.46)$$

where

P_C = Critical pressure

T_C = Critical temperature.

The critical temperature is the maximum temperature at which a gas can be liquefied. The critical pressure is the saturation pressure corresponding to the critical temperature. Above the critical temperature, a gas cannot be liquefied regardless of the pressure. The volume occupied by a gas under critical condition is called the critical volume V_C.

EXAMPLE 2.29 A compound whose molecular weight is 103, analyses C = 81.5%, H = 4.9% and N = 13.6%. What is its molecular formula?

Solution: Basis: 103 kg of compound.

$$\text{Weight of C} = \frac{81.5}{100} \times 103$$

$$= 83.95 \text{ kg}$$

$$\text{kg atom of C} = \frac{\text{Weight in kg}}{\text{Atomic weight}}$$

$= \frac{83.95}{12}$

= 6.995

= 7

Weight of H = $\frac{4.9}{100} \times 103$

= 5.05 kg

kg atom of H = $\frac{\text{Weight in kg}}{\text{Atomic weight}}$

$= \frac{5.05}{1}$

= 5.05

= 5

Weight of N = $\frac{13.6}{100} \times 103$

= 14.01

kg atom of N = $\frac{\text{Weight in kg}}{\text{Atomic weight}}$

$= \frac{14.01}{14}$

= 1

Therefore, molecular formula = C_7H_5N.

EXAMPLE 2.30 Calculate the volume occupied by 1 gmol of water vapour at 900 °C and 100 atm.

(i) By perfect gas law

(ii) By using Vander Waals equations.

The Vander Waals constant for water are

$$a = 5.404 \frac{(\text{l})^2 \cdot \text{atm}}{(\text{gmol})^2}$$

$$b = 0.3049 \frac{1}{\text{gmol}}$$

Solution:

(i) By perfect gas law

$PV = nRT$

ˆ $V = \frac{nRT}{P}$

where

n = 1 gmol

$R = 0.082 \frac{(\text{l})(\text{atm})}{(\text{gmol})(\text{K})}$

$T = 1173$ K
$P = 100$ atm

Therefore,
$$V = \frac{(1) \times (0.082) \times (1173)}{100}$$
$$V = 0.962\ \text{l}$$

(ii) By Vander Waals equation

$$\left(P + \frac{a}{V^2}\right)(V - b) = RT$$

where

$P = 100$ atm

$$a = 5.404\ \frac{(\text{l})^2 \cdot \text{atm}}{(\text{gmol})^2}$$

$$b = 0.3049\ \frac{\text{l}}{\text{gmol}}$$

$$R = 0.082\ \frac{\text{l} \cdot \text{atm}}{\text{gmol K}}$$

$T = 1173$ K

Now,
$$\left(100 + \frac{5.404}{V^2}\right)(V - 0.3049) = (0.082) \times 1173$$
$$\left(100 + \frac{5.404}{V^2}\right)(V - 0.3049) = 96.2$$

By using trial and error method,
Trial and error method is as follows:

Assumed values of V (l)	LHS	RHS
1.0	73.26	96.2
1.2	92.87	96.2
1.24	96.79	96.2
$V = 1.24$ l/gmol		

2.17

Gas–Liquid System

The approximate relationship that governs the distribution of a substance between a gas and a liquid phase are Raoult’s and Henry’s laws which assume reasonably accurate results in many cases.

2.17.1 Raoult’s Law

It states that the equilibrium partial pressure of component ‘*A*’ is equal to the product of vapour pressure and mole fraction of component ‘*A*’ in the liquid phase. It can be expressed as

$$p_A = P°_A \times x_A = P \times y_A \qquad (2.47)$$

where,

p_A = Partial pressure of component 'A' in liquid phase
$P°_A$ = Vapour pressure of pure liquid 'A'
x_A = Mole fraction of 'A' in the liquid phase
P = Total pressure of the system
y_A = Mole fraction of 'A' in the vapour phase.

Raoult's law is generally valid when x_A is close to 1, i.e. when the liquid phase is almost pure. It is also valid over entire range of compositions for mixture of similar substances, such as straight chain hydrocarbons of similar molecular weights.

2.17.2 Henry's Law

It states that the partial pressure of solute gas is proportional to mole fraction of that component in liquid phase. It can be expressed as

$$p_A = H \times x_A = P \times y_A \qquad (2.48)$$

where

p_A = Partial pressure of component 'A'
x_A = Mole fraction of A in the liquid phase
H = Henry's law constant
y_A = Mole fraction of 'A' in the vapour phase
P = Total pressure of the system.

Henry's law is valid when x_A is close to zero, i.e. for dilute solution of component 'A'.

2.18

Vapour Pressure

It may be defined as the absolute pressure at which the liquid and its vapour are in equilibrium at a given temperature. When the liquid is heated, evaporation takes place. During the evaporation, two opposing process occurs.

1. The process of vaporisation
2. The process of condensation.

As the vaporisation proceeds, the pressure of vaporisation increases and the rate of condensation also increases. The moment at which the rate of vaporisation is equal to the rate of condensation, a sort of dynamic equilibrium exists and the vapour remains unchanged. The pressure exerted by the vapour at this condition is termed vapour pressure of the liquid. All liquids and solids exhibit a definite vapour pressure at a given temperature.

2.18.1 Saturated Vapour Pressure

When the vapour of a liquid exists under conditions so that its partial pressure is equal to the equilibrium vapour pressure, then it is called saturated vapour pressure. That means, at this condition the vapour is ready to condense.

2.18.2 Unsaturated Vapour Pressure

When the vapour of a liquid exists under conditions, such that its partial pressure is less than the equilibrium vapour pressure, then it is called unsaturated vapour pressure. That means, at this condition the vapour is not ready to condense. It is also called superheated vapour.

2.18.3 Boiling Point

The temperature of the liquid at which the equilibrium vapour pressure is equal to the total pressure surrounding the liquid surface is called boiling point. It is dependent on the total pressure surrounding the liquid surface. It increases with increase in total pressure and decreases with decrease in total pressure. Therefore, liquid can be made to boil at any desired temperature by sufficiently altering the total pressure surrounding its surface. The boiling point of a liquid may be determined by using the equation

$$T_B = \left(\frac{R \ln P_V}{\Delta H_V} + \frac{1}{T} \right)^{-1} \qquad (2.49)$$

where,

T_B = Temperature at which the liquid boil

P_V = Vapour pressure of the liquid at given temperatures (atm)

ㅅ H_V = Heat of vaporization of the liquid (J/mol)

2.18.4 Normal Boiling Point

The temperature of the liquid at which the equilibrium vapour pressure is equal to the atmospheric pressure at sea level is called normal boiling point. It is also known as atmospheric pressure boiling point. When the boiling of a liquid takes place under a pressure of 760 mmHg, then it is called standard boiling.

2.18.5 Effect of Temperature on Vapour Pressure

The effect of temperature on vapour pressure of a liquid is given by Clausius Clapeyron equation. It can be expressed as

$$\frac{dP}{P} = \frac{\lambda \, dT}{RT^2} \qquad (2.50)$$

where

P = Vapour pressure (atm)

l = Latent heat of vaporization (J/mol)

R = Universal gas constant (J/mol ㅓ K)

T = Absolute temperature (K)

If the vapour of the liquid obey’s the ideal gas law, then the Clausius Clapeyron equation is more accurate at low temperature and low pressure.

Assuming the molal heat of vaporization is constant. When the temperature does not vary over a wide range of limit, Eq. (2.50) may be integrated between the limit P_0, T_0 and P, T, we get

$$\ln \frac{P}{P_0} = \frac{\lambda}{R}\left(\frac{1}{T_0} - \frac{1}{T}\right) \qquad (2.51)$$

where

P_0 = Initial pressure (atm)

P = Final pressure (atm)

l = Latent heat of vaporization (J/mol)

T_0 = Initial temperature

T = Final temperature

This equation can be used for the calculation of vapour pressure of a liquid at a given temperature if the initial pressure P_0, initial temperature T_0 and the latent heat of vaporization are known.

The limitation of Clausius Clapeyron equation is that the latent heat of vaporization (l) is constant. It obeys ideal gas law.

EXAMPLE 2.31 Find the volume of CO_2 at 25 °C and 750 mmHg if the volume of CO_2 is 15 m^3 at 760 mmHg and 20 °C.

Solution: We know from the ideal gas equation

$$\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}$$

$$V_2 = V_1 \times \frac{P_1}{P_2} \times \frac{T_2}{T_1}$$

$$= 15 \times \frac{760}{750} \times \frac{298}{293}$$

$$= 15.459 \text{ m}^3$$

EXAMPLE 2.32 Calculate the volume occupied by 20 kg of Cl_2 gas at a pressure of 100 kPaand 25 °C.

Solution: Basis: 20 kg chlorine gas

$$\text{kg moles of chlorine gas} = \frac{\text{Mass of chlorine gas in kg}}{\text{Molecular weight of chlorine gas}}$$

$$= \frac{20}{71}$$

$$= 0.2816$$

From the ideal gas law, we know that

$$PV = nRT$$

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

where

n = 0.2816 kmol

$$R = 0.082 \frac{\text{m}^3 \cdot \text{atm}}{\text{kmol} \cdot \text{K}}$$

$T = 298$ K

$P = 100$ kPa or 0.9869 atm

Therefore, $V = \dfrac{0.2816 \times 0.082 \times 298}{0.9869}$ m^3

or, $V = 6.972$ m^3

EXAMPLE 2.33 10 kg of O_2 contained in a closed container of volume 2 m^3 is heated without exceeding a pressure of 709.28 kPa. Calculate the maximum temperature of gas attained.

Solution: Basis: 10 kg of oxygen

Molecular weight of $O_2 = 2 \times 16$

= 32

$$\text{Moles of oxygen} = \frac{\text{Weight of oxygen in kg}}{\text{Molecular weight}}$$

$$= \frac{10}{32}$$

$$= 0.3125$$

From ideal gas law, we know that

$$PV = nRT$$

$$T = \frac{PV}{nR}$$

where

$P = 709.28$ kPa = 7 atm

$V = 2$ m^3

$n = 0.3125$

$R = 0.082 \dfrac{\text{m}^3 \cdot \text{atm}}{\text{kgmol} \cdot \text{K}}$

Therefore, $T = \dfrac{7 \times 2}{0.3125 \times 0.082}$ K

$= 546.34$ K

EXAMPLE 2.34 Calculate the weight of SO_2 in a vessel having 5 m^3 volume, pressure 96 kPa and temperature 392 K.

Solution: Basis: 5 m^3 of SO_2 gas

$$PV = nRT$$

$$n = \frac{PV}{RT}$$

where

$P = 96$ kPa = 0.947 atm

$V = 5$ m^3

$R = 0.082 \dfrac{\text{m}^3 \cdot \text{atm}}{\text{kgmol} \cdot \text{K}}$

$T = 392$ K

Now, $n = \dfrac{0.947 \times 5}{0.082 \times 392}$ kgmol

$n = 0.1473$ kgmol

$\text{kgmol} = \dfrac{\text{Weight of SO}_2 \text{ in kg}}{\text{Molecular weight of SO}_2}$

Weight of SO_2 in kg = kgmol of SO_2 × Molecular weight of SO_2

= 0.1473 × 64

= 9.42 kg

EXAMPLE 2.35 A gas contained in a closed vessel at a pressure of 1.2 atm and 299 K is heated to a temperature of 1250 K. Calculate the pressure to which a closed vessel should be designed.

Solution: Basis: A gas at 299 K in closed vessel

From ideal gas law, we know that

$$\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2}$$

As vessel being closed, $V_1 = V_2$

Therefore,
$$\frac{P_1}{T_1} = \frac{P_2}{T_2}$$
$$P_2 = P_1 \times \frac{T_2}{T_1}$$

where

$P_1 = 1.2$ atm

$T_2 = 1250$ K

$T_1 = 299$ K

$$P_2 = 1.2 \times \frac{1250}{299}$$

= 5.01 atm

Pressure to which vessel should be designed is 5.01 atm.

EXAMPLE 2.36 A cylinder contains 14.2 kg of liquid propane. What volume in m^3 will propane occupy if it is released and brought to NTP condition?

Solution: Basis: 14.2 kg of liquid propane

Molecular weight of propane (C_3H_8) = 3 × 12 + 8 × 1

= 36 + 8 = 44

$\text{Moles of propane} = \dfrac{\text{Weight of propane in kg}}{\text{Molecular weight of propane}}$

$= \frac{14.2}{44} = 0.3227$

From ideal gas law, we know that

$PV = nRT$

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

where

$n = 0.3227$ kgmol

$R = 0.082\ \frac{\text{m}^3 \cdot \text{atm}}{\text{kgmol} \cdot \text{K}}$

$T = 273$ K

$P = 1$ atm

Therefore, $V = \frac{0.3227 \times 0.082 \times 273}{1}$

$V = 7.223\ \text{m}^3$

EXAMPLE 2.37 A gas mixture contains 0.28 kgmol of HCl, 0.34 kmol of N_2 and 0.09 kgmol of O_2. Calculate:

(i) Average molecular weight of gas

(ii) Volume occupied by this mixture at 4 atm and 303 K.

Solution: Basis: A gas mixture containing 0.28 kgmol HCl, 0.34 kgmol N_2 and 0.09 kgmol O_2.

Total moles of gas mixture = 0.28 + 0.34 + 0.09 kgmol

= 0.71 kgmol

Mole fraction of HCl (x_{HCl}) = $\frac{0.28}{0.71} = 0.394$

Mole fraction of N_2 (x_{N2}) = $\frac{0.34}{0.71} = 0.478$

Mole fraction of O_2 (x_{O2}) = $\frac{0.09}{0.71} = 0.126$

Molecular weight of HCl (M_{HCl}) = 36.5

Molecular weight of N_2 (M_{N2}) = 28

Molecular weight of O_2 (M_{O2}) = 32

(i) Average molecular weight (M_{avg}) = $\sum_{i=1}^{n} M_i \cdot x_i$

$= M_{HCl} \dashv x_{HCl} + M_{N2} \dashv x_{N2} + M_{O2} \dashv x_{O2}$

$= (36.5 \times 0.394) + (28 \times 0.478) + (32 \times 0.126)$

$= 14.381 + 13.384 + 4.032$

$= 31.797$

(ii) From ideal gas law, we know that

$PV = nRT$

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

where

n = 0.71 kgmol

$R = 0.082\ \frac{\text{m}^3 \cdot \text{atm}}{\text{kgmol} \cdot \text{K}}$

T = 303 K

P = 4 atm

Hence, $V = \frac{0.71 \times 0.082 \times 303}{4}$

or $V = 4.41\ \text{m}^3$

EXAMPLE 2.38 The analysis of the gas sample is given below (volume basis):

CH_4 = 66%, CO_2 = 30%, NH_3 = 4%.

Calculate:

(i) The average molecular weight of the gas

(ii) The density of the gas at 2 atm and 303 K.

Solution: Basis: 100 m^3 of gas sample.

Component	*Molecular weight*	*Volume* (m^3)	*Volume%*	*Mole%*	*Mole fraction*
CH_4	16	66	66	66	0.66
CO_2	44	30	30	30	0.30
NH_3	17	4	4	4	0.04
Total volumes = 100 m^3					

(i) Average molecular weight (M_{avg}) = $\sum_{i=1}^{n} M_i \cdot x_i$

$= \text{M}_{CH_4} \dashv x_{CH_4} + M_{CO_2} \dashv x_{CO_2} + M_{NH_3} \dashv x_{NH_3}$

$= 16 \times 0.66 + 44 \times 0.30 + 17 \times 0.04$

$= 24.44$

(ii) Density of the gas mixture (r_{mix}) = $\frac{PM_{avg}}{RT}$

$$= \frac{2 \times 24.44}{0.082 \times 303}$$

$= 1.967$ kg/m^3

EXAMPLE 2.39 By electrolysing a mixed brine, a gaseous mixture is obtained at the cathode having the following composition by weight:

$Cl_2 = 67\%$, $Br_2 = 28\%$, $O_2 = 5\%$

Calculate:

(i) Composition of the gas by volume

(ii) Average molecular weight

(iii) Density of gas mixture at 298 K and 1 atm.

Solution: Basis: 100 kg of gas mixture

(i) Composition of the gas by volume:

Component	*Weight in* kg	*Molecular weight*	kgmol	*Mole%*	*Volume%*
Cl_2	67	71	0.9437	74.02	74.02
Br_2	28	160	0.1750	13.72	13.72
O_2	5	32	0.1563	12.26	12.26
		Total moles = 1.2750			

(ii) Average molecular weight:

Component	*Molecular weight*	*Mole fraction*
Cl_2	71	0.7402
Br_2	160	0.1372
O_2	32	0.1226

Average molecular weight (M_{avg}) = $\sum_{i=1}^{n} M_i \cdot x_i$

$= M_{Cl2} \dashv x_{Cl2} + M_{Br2} \dashv x_{Br2} + M_{O2} \dashv x_{O2}$

$= 71 \times 0.7402 + 160 \times 0.1372 + 32 \times 0.1226$

$= 78.43$

(iii) Density of gas mixture (r_{mix}) = $\frac{PM_{avg}}{RT} = \frac{1 \times 78.43}{0.082 \times 298}$

$= 3.20$ kg/m^3

EXAMPLE 2.40 A mixture of CH_4 and C_2H_6 has the average molecular weight 22.4. Find mole% of CH_4 and C_2H_6 in the mixture.

Solution: Basis: Average molecular weight of gas mixture 22.4.

$$M_{avg} = \sum_{i=1}^{n} M_i \cdot x_i$$

$$M_{avg} = M_{CH_4} \cdot x_{CH_4} + M_{C_2H_6} \cdot x_{C_2H_6}$$

$$22.4 = 16 \times x_{CH_4} + 30 \times x_{C_2H_6}$$

We know that

$$x_{CH_4} + x_{C_2H_6} = 1$$

$$\Rightarrow \; x_{C_2H_6} = (1 - x_{CH_4})$$

$$\Rightarrow \; 22.4 = 16x_{CH_4} + 30(1 - x_{CH_4})$$

$$\Rightarrow \; 22.4 = 16x_{CH_4} + 30 - 30x_{CH_4}$$

$$\Rightarrow \; 30x_{CH_4} - 16x_{CH_4} = 30 - 22.4$$

$$\Rightarrow \; 14x_{CH_4} = 7.6$$

$$\Rightarrow \; x_{CH_4} = 7.6/14$$

$$\Rightarrow \; x_{CH_4} = 0.543$$

$$\Rightarrow \; x_{C_2H_6} = 1 - 0.543$$

$$\Rightarrow \; x_{C_2H_6} = 0.457$$

Mole% of CH_4 = 54.30

Therefore, Mole% of C_2H_6 = 45.70

EXAMPLE 2.41 In a vessel, 26.6 litres of NO_2 at 0.789 atm and 298 K is allowed to stand until the equilibrium is reached. At equilibrium, the pressure is found to be 0.657 atm. Calculate the partial pressure of N_2O_4 in the final mixture.

Solution: Basis: 26.6 litres of NO_2 at 0.789 atm and 298 K. From the ideal gas law, we know that

$$P_1V_1 = n_1RT_1$$

Initial mole, $n_1 = \frac{P_1V_1}{RT_1}$

where

$P_1 = 0.789$ atm

$V_1 = 26.6$ l or $V_1 = 0.0266$ m^3

$R = 0.082 \; \frac{\text{m}^3 \cdot \text{atm}}{\text{kgmol} \cdot \text{K}}$

$T_1 = 298$ K

$$n_1 = \frac{0.789 \times 0.0266}{0.082 \times 298}$$

Now,

$$n_1 = 8.58 \times 10^{-4} \text{ kgmol}$$

$$n_1 = 0.858 \text{ mole}$$

Chemical reaction:

$$2NO_2 = N_2O_4$$

Let x be the mole of N_2O_4 in final gas mixture.

NO_2 reacted = $2x$ mole

NO_2 unreacted = $(0.858 - 2x)$ mole

Final moles, $n_2 = (x + 0.858 - 2x)$ mole

$$n_2 = (0.858 - x) \text{ moles}$$

For final condition, $P_2V_2 = n_2RT_2$

$$\frac{P_1V_1}{P_2V_2} = \frac{n_1RT_1}{n_2RT_2}$$

But, $V_1 = V_2$

and $T_1 = T_2$

Now,
$$\frac{P_1}{P_2} = \frac{n_1}{n_2}$$
$$\frac{0.789}{0.657} = \frac{0.858}{0.858 - x}$$

Solving, we get $x = 0.1435$

Final mole $(n_2) = 0.858 - x$

$= 0.858 - 0.1435$

$= 0.7145$

Mole fraction of $N_2O_4 = \frac{x_1}{n_2}$

$$= \frac{0.1435}{0.7145}$$

$= 0.20$

From Raoult’s law, we know that

$$P_{N_2O_4} = x_{N_2O_4} \times P$$

$= 0.20 \times 0.657$

$= 0.1314$ atm

The partial pressure of N_2O_4 in the final mixture is 0.1314 atm.

EXAMPLE 2.42 A solution containing 55% benzene, 28% toluene and 17% xylene by weight is in contact with its vapour at 373 K. Calculate the total pressure and molar composition of the liquid and vapour.

Solution: Basis: 100 kg of solution

Component	*Molecular weight*	*Amount in* kg	*Amount in* kgmol	*Mole*%

C_6H_6	78	55	0.7051	60.28
$C_6H_5CH_3$	92	28	0.3043	26.01
$C_6H_5(CH_3)_2$	106	17	0.1604	13.71
		Total moles = 1.1698		

According to Raoult's law

$$p_i = P_i \dashv x_i$$

where

p_i = Partial pressure of component '*i*' over a solution

P_i = Vapour pressure of pure '*i*'

x_i = Mole fraction of '*i*' in solution.

Vapour pressure of C_6H_6 ($P°_B$) at 373 K = 1.762 atm

Vapour pressure of $C_6H_5CH_3$ ($P°_T$) at 373 K = 0.737 atm

Vapour pressure of $C_6H_4(CH_3)_2$ ($P°_X$) at 373 K = 0.276 atm

Partial pressure, $p_B = 0.6028 \times 1.762$

$= 1.062$ atm

$p_T = 0.2601 \times 0.737$

$= 0.192$ atm

and $p_X = 0.1371 \times 0.276$

$= 0.038$ atm

Total pressure, $P = p_B + p_T + p_X$

$= 1.062 + 0.192 + 0.038$

$= 1.292$ atm

Composition of vapours:

$$\text{Pressure\% of benzene} = \frac{\text{Partial pressure of benzene}}{\text{Total pressure}} \times 100$$

$$\text{Pressure\% of } C_6H_6 = \frac{1.062}{1.292} \times 100 = 82.19$$

$$\text{Pressure\% of } C_6H_5CH_3 = \frac{0.192}{1.292} \times 100 = 14.86$$

$$\text{Pressure\% of } C_6H_4(CH_3)_2 = \frac{0.038}{1.292} \times 100 = 2.95$$

We know that pressure% = Mole%.

The composition of the vapours in mole% are:

Mole% of benzene = 82.19

Mole% of toluene = 14.86

Mole% of xylene = 2.95

EXAMPLE 2.43 Calculate the total pressure and composition of vapour in contact with the solution at 100 °C containing 35% benzene, 40% toluene and 25% o-xylene by weight.

Data:

Component	*Vapour pressure at* 100°C (mmHg)	*Molecular weight*
Benzene	1340	78
Toluene	560	92
O-xylene	210	106

Solution: Basis: 100 kg of solution

Component	*Weight in* kg	*Molecular weight*	*Moles*	*Mole% (vapour%)*
Benzene	35	78	0.449	40.08
Toluene	40	92	0.435	38.84
O-xylene	25	106	0.236	21.08
		Total moles = 1.120		

We know that

$$p_i = P_i^\circ \dashv x_i$$

where

p_i = Partial pressure

P°_i = Vapour pressure of pure component

x_i = Mole fraction of ‘*i*’ in solution.

Component	*Vapour pressure* (mmHg)	*Mole fraction*	*Partial pressure*
Benzene	1340	0.4008	537
Toluene	560	0.3884	217
O-xylene	210	0.2108	44

Total pressure

$$P = p_B + p_T + p_X$$

$$= 537 + 217 + 44$$

$$= 798 \text{ mmHg}$$

2.19

Vapour Pressure of Immiscible Liquid Mixture

The vapour pressure of immiscible liquid mixture is the sum of vapour pressure exerted by the individual components of the system with no change in temperature. Depending on the temperature, each component of the mixture will add its own vapour pressure. This mixture will boil, when the sum of the individual components pressure equals the existing total pressure above its surface.

The boiling point of immiscible liquid mixture is always less than the boiling point of its any of the individual component present in the system. This logic is generally used in steam distillation. For example, in separation of petroleum fraction.

2.19.1 Hansbrand Chart

The Hansbrand chart is a plot of two graphs.

1. $(p_t - p_B)$ vs T
2. p_A vs T

This chart is generally used in steam distillation process to determine the distillation temperature. After plotting the graphs, we can see that the two curves intersect at a particular point. We draw a vertical line from the point of intersection towards the *x*-axis which meets at a particular point on temperature axis. This temperature is the boiling point of the substance under distillation. A Hansbrand chart is shown in Figure 2.5.

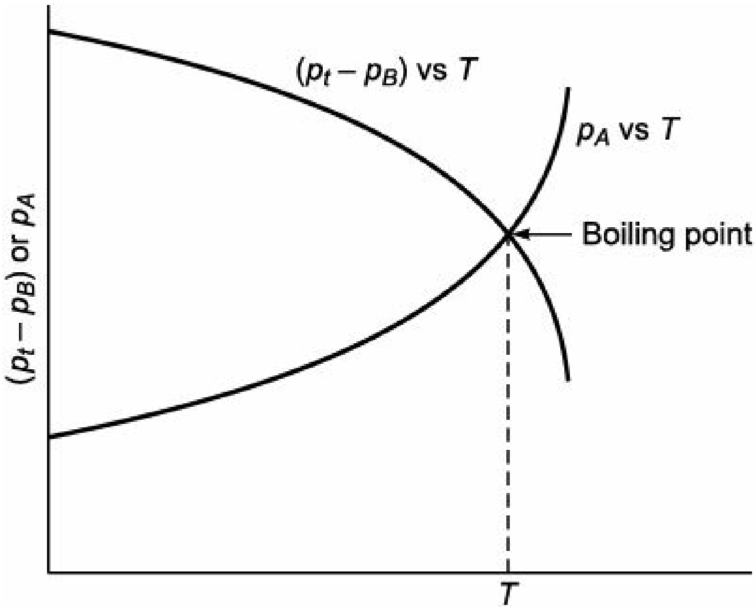


Figure 2.5 Hansbrand chart.

2.20

Cox Chart

It is a plot of logarithmic vapour pressure of a substance vs logarithmic vapour pressure of a reference substance both at the same temperature. A typical cox chart is shown in Figure 2.6. It is observed from the chart that the plot is almost a straight line and available for wide variety of substances. Calingert and Davis found the method of cox in which reference substance is water. In this method, the equivalent vapour pressure of the substance is calculated using the following equation.

$$\ln P = A - \frac{B}{(T - 43)} \qquad (2.52)$$

where

P = Vapour pressure (mmHg)
T = Temperature (K)
A = Empirical constant
B = Empirical constant

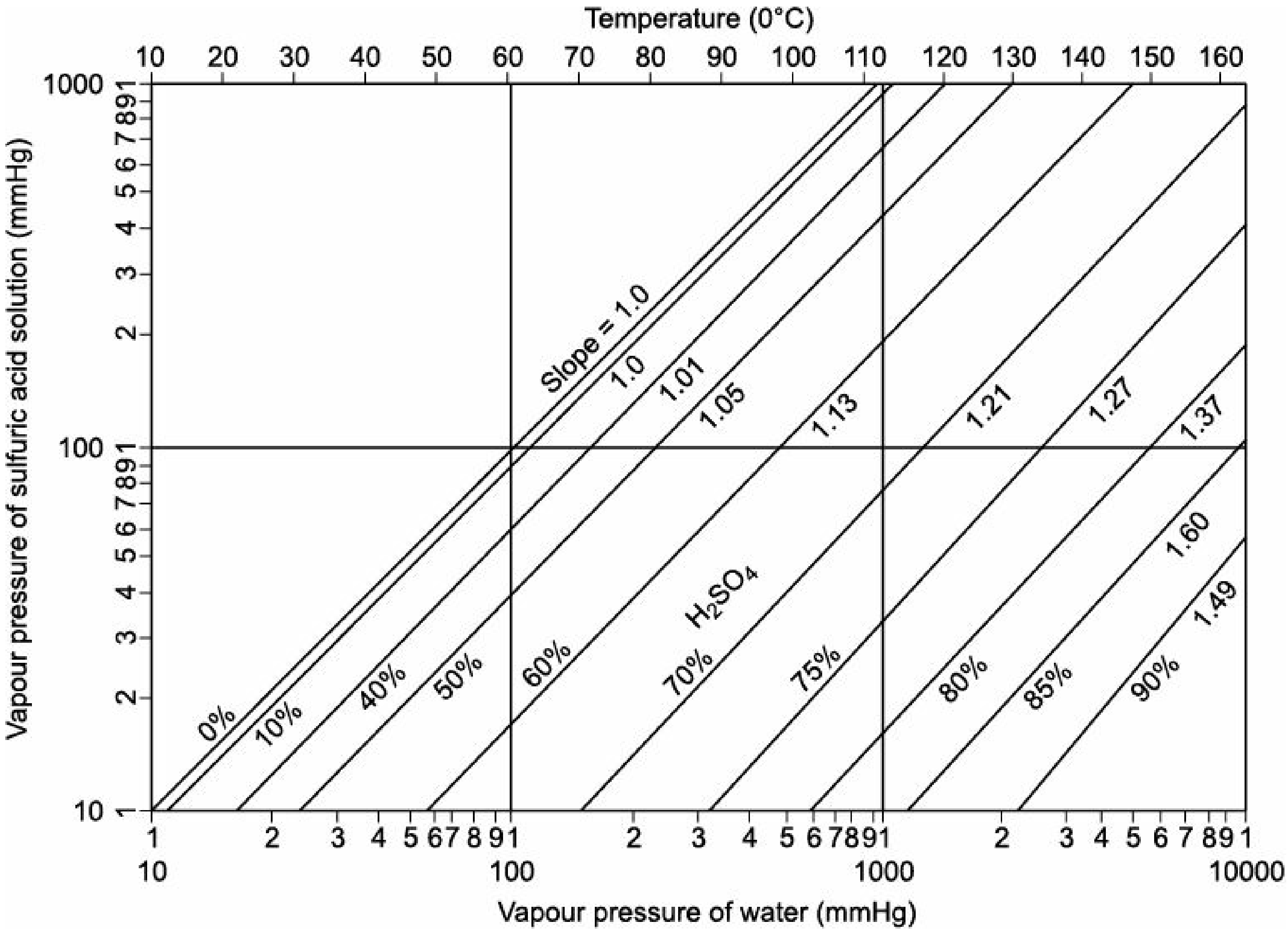


FIGURE 2.6 Cox chart.

In this method, when ln P is plotted against $1/(T - 43)$, we get a straight line.
Later, Antonie proposed an equation to calculate the vapour pressure of the substance by the following equation

$$\log P = A - \frac{B}{T + C} \qquad (2.53)$$

where

P = Vapour pressure (mmHg)
A = Empirical constant
B = Empirical constant
T = Temperature (K)
C = Empirical constant

A graph relating to Antonies equation is called cox chart.

2.21

Non-volatile Solution

Consider a binary solution in which two components are present. If one of the components has negligible vapour pressure, then its presence will not have any effect on the composition of the vapour in equilibrium with the solution. The vapour of this solution will have more volatile component, but its equilibrium vapour pressure is always less than that of the pure liquid at no change in temperature.

Therefore, we can say that a non-volatile solute produces a vapour pressure which lower the boiling point of the solvent. The difference found between the boiling point of the solution and that of the pure solvent is called boiling point elevation of the solution.

2.22

Relative Vapour Pressure

Consider a binary solution in which two components are present. Both the components present in the solution exert an individual vapour pressure. The vapour pressure of pure solvent related to the vapour pressure of the solution is called Relative vapour pressure. The relative vapour pressure of the solution can be calculated using the following equation

$$p = kP_S \qquad (2.54)$$

where

p = Vapour pressure of the solution
k = Relative vapour pressure
P_S = Vapour pressure of pure solvent

The value of k for a solution may be obtained by the method of determination of boiling point.

EXAMPLE 2.44 The vapour pressure of ether is 0.58 atm at 298 K. If 3 g of a compound A are introduced and dissolved in 50 g of ether at this temperature, the vapour pressure falls to 0.56 atm.Calculate the molecular weight of A. Assume that the solution of A in ether is very dilute.

Solution: Basis: 3 g of a compound A in 50 g of ether at 298 K. We know from the relative vapour pressure

Vapour pressure of ether in solution = Vapour pressure of ether × Mole fraction of ether

$$0.56 = 0.58 \times x_E$$

$$\hat{} \; x_E = 0.9655$$

$$\hat{} \; x_A + x_E = 1$$

$$\hat{} \; x_A = 1 - x_E$$

$$\hat{} \; x_A = 1 - 0.9655$$

$$\hat{} \; x_A = 0.0344$$

Mole fraction of A in solution = 0.0345
Mole fraction of ether in solution = 0.9655

Now, moles of ether in solution = $\dfrac{\text{Weight of ether in g}}{\text{Molecular weight of ether}}$

$$= \frac{50}{74}$$

$$= 0.6756$$

Therefore, mole fraction of ether = $\dfrac{\text{Moles of ether}}{\text{Moles of ether + Moles of } A}$

$$0.9655 = \frac{0.6756}{(0.6756) + \text{Moles of } A}$$

Moles of $A = 0.0241$

$$\text{Moles of } A = \frac{\text{Weight of } A \text{ in g}}{\text{Molecular weight of } A}$$

$$\text{Hence, Molecular weight of } A = \frac{\text{Weight of } A \text{ in g}}{\text{Moles of } A}$$

$$= \frac{3}{0.0241}$$

$= 124.5$

2.23

Humidity

Humidity is the term which gives the information of amount of water vapour present in the air. It is not constant. It differs from place to place. For example, humidity in Kerala and Kolkata is very high, whereas in Rajasthan, it is low. It has a lot of effects on human kind.

Humidity may be defined as the ratio of mass of water vapour present in the air in kg to mass of dry air in kg. Mathematically, humidity can be expressed under any given set of condition as

$$\text{Humidity } (H) = \frac{\text{Mass of water vapour present in the air in kg}}{\text{Mass of dry air in kg}} \qquad (2.55)$$

Normally, the amount of water present in the air is measured in terms of partial pressure, but not in terms of weight. Let the partial pressure of water vapour present in the air sample is p_A. Then, the humidity may be expressed as

$$\text{Humidity } (H) = \frac{\text{Partial pressure of water vapour in air}}{\text{Partial pressure of dry air}}$$

$$\text{Humidity } (H) = \frac{p_A}{P_t - p_A} \qquad (2.56)$$

Since, the molecular weight of water vapour and air is 18 and 29 respectively. Therefore, the humidity at a given temperature and pressure may be expressed as

$$\text{Humidity } (H) = \frac{M_W(p_A)}{M_A(P_t - p_A)} \qquad (2.57)$$

$$\text{or Humidity } (H) = \frac{18p_A}{29(P_t - p_A)} \qquad (2.58)$$

where

H = Humidity

M_W = Molecular weight of water vapour

M_A = Molecular weight of air

p_A = Partial pressure of water vapour in air

P_t = Total pressure of the system.

2.23.1 Saturated Humidity

If the vapour pressure of water in air is in equilibrium with the liquid vapour, then the air is said to be saturated at a given temperature and pressure. Mathematically, saturated humidity can be expressed as

$$\text{Humidity } (H_S) = \frac{M_W(p_A)}{M_A(P_t - p_A)} \qquad (2.59)$$

where

H_S = Saturated humidity

M_W = Molecular weight of water

M_A = Molecular weight of air

P_A = Saturated vapour pressure

P_t = Total pressure

2.23.2 Percentage of Humidity

The percentage of humidity at a given temperature and pressure may be expressed as

$$\text{Percentage humidity } (H_P) = \frac{\text{Actual humidity } (H)}{\text{Saturated humidity } (H_s)} \times 100 \qquad (2.60)$$

Humidity, other than zero and hundred per cent, is less than relative humidity in percentage.

2.23.3 Relative Humidity

The relative humidity at a given temperature and pressure may be expressed as

$$\text{Relative humidity } (H_R) = \frac{\text{Actual partial pressure of water in air } (P)}{\text{Partial pressure of water at saturation } (P_s)} \times 100 \qquad (2.61)$$

2.23.4 Humid Volume

The volume occupied by a unit mass of dry gas and its associated vapour is called Humid volume. It is denoted by V_H.

2.23.5 Humid Heat

The amount of heat required to rise the temperature of unit mass of dry air and its associated vapour by 1°C at no change in pressure is called Humid heat. Mathematically, it can be expressed as

$$H_H = C_A + HC_W \qquad (2.62)$$

where

H_H = Humid heat

C_A = Heat capacity of air (kJ/kgmol K)

H = Humidity

C_W = Heat capacity of water vapour (kJ/kgmol K)

For air water system, Eq. (2.62) may be simplified and expressed as

$$H_H = 1.0 + 1.9H \qquad (2.63)$$

2.23.6 Dew Point (D.P.)

It is the temperature at which the dry air associated with water vapour must be cooled to become saturated with respect to a plane water surface. It is denoted by D.P.

2.23.7 Dry Bulb Temperature

It is the temperature of the moist air measured by ordinary thermometer. It is commonly referred as DBT.

2.23.8 Wet Bulb Temperature

It is the temperature of the moist air measured by ordinary thermometer when the bulb of the thermometer is covered by wet cloth or wick. It is commonly referred as WBT.

When the bulb of the thermometer is surrounded by wet cloth, it absorbs some amount of moisture from the air and gives up some amount of heat. Due to this fact, temperature of the surrounding air decreases. Hence, wet bulb temperature (WBT) is always less than dry bulb temperature (DBT).

2.24

Humidity Chart

Humidity chart gives the information of amount of moisture present in unit mass of dry air at any given temperature. This properties of mixture of air water vapour is necessary in designing the humidifier. It is also known as psychrometry chart. This chart mainly consists the plots of four curves.

1. Humidity vs Temperature curve
2. Humidity vs Humid heat line
3. Specific volume vs Temperature curve
4. Adiabatic cooling lines.

2.24.1 Humidity vs Temperature Curve

In this plot, humidity is plotted on *y*-axis and temperature is plotted on *x*-axis at atmospheric pressure. The humidity is expressed in kg of water per kg of dry air. There are many curves in this plot and each curve represents a definite relative humidity value. The following information may be obtained from this plot.

1. Any point on the curved line represents the temperature and humidity of the sample of air.
2. The curved line marked 100% gives the relative humidity of saturated air at various temperature.
3. There is no air and water vapour mixture to the left of the 100% relative humidity curve.
4. There are many curves representing between 90% to 10% to the right of 100% relative humidity curved line.

A typical humidity chart is shown in Figure 2.7.

2.24.2 Humidity vs Humid Heat Line

In this plot, humid heat is plotted against the humidity. It is observed from the chart that it is a straight line which started from the bottom of the chart and reached the top with an angle of 60°. This plot is useful in designing the air conditioner. A typical humid heat line is shown in Figure 2.7.

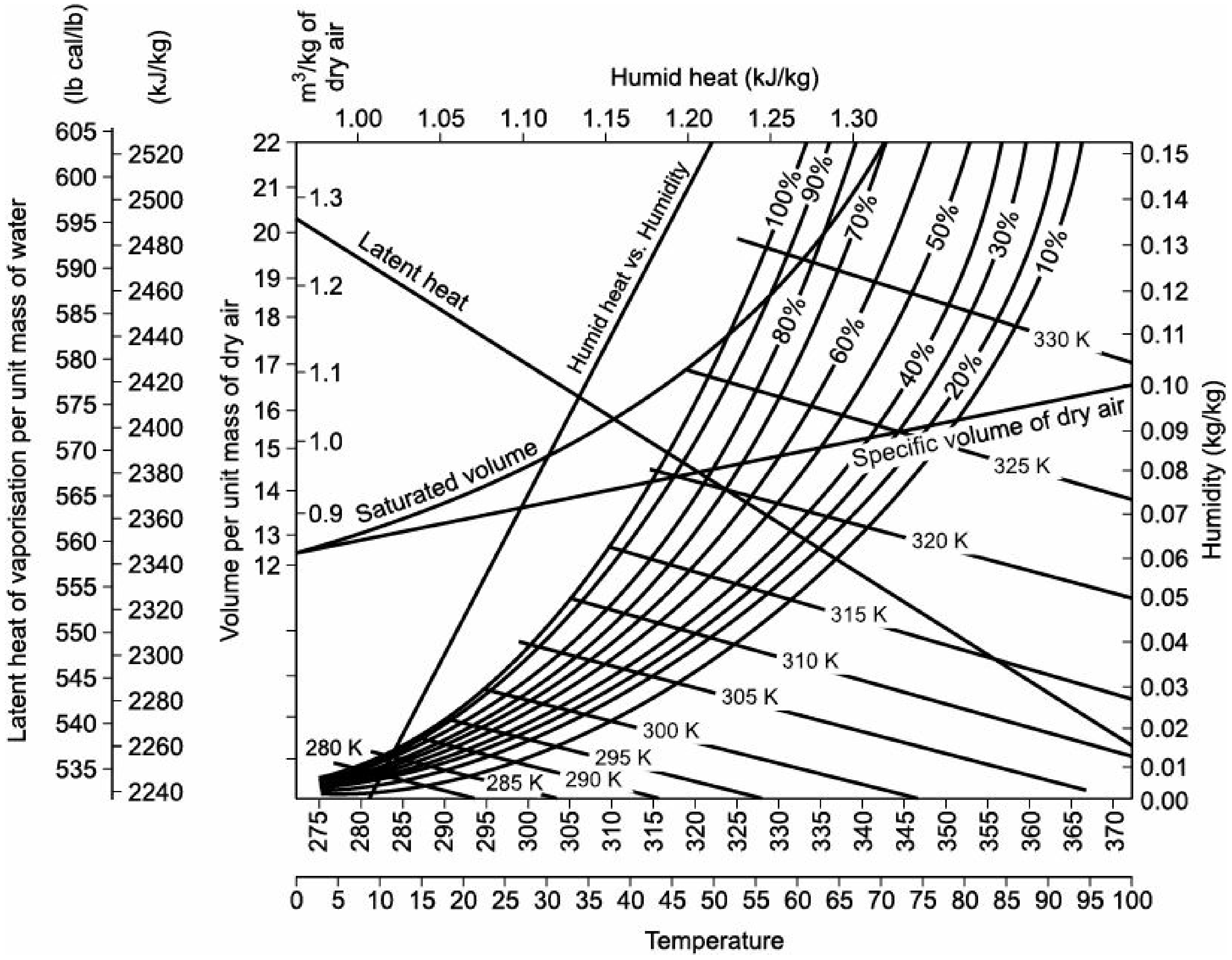


FIGURE 2.7 Humidity chart.

2.24.3 Specific Volume vs Temperature Line

In this plot specific volume of dry air is plotted against the temperature. It is observed from the chart that it is a straight line which started from the one end of *y*-axis and reached the other end of the *y*-axis with an angle of 30°. The humid volume of a sample of air may be determined at a given temperature and humidity by linear interpolation of the humidity temperature line. This plot is useful in engineering calculation. A typical specific volume line is shown in Figure 2.7.

2.24.4 Adiabatic Cooling Lines

In this plot, a group of lines are plotted with a negative slope from the 100% relative humidity curve. These lines are also called Adiabatic cooling lines. This plot is useful for two purposes. Firstly, they can be used to determine the humidity from the knowledge of dry bulb temperature and wet bulb temperature. Secondly, these lines show the changes in humidity during drying under adiabatic condition. A typical adiabatic lines are shown in Figure 2.7.

2.24.5 Application of Humidity Chart

Humidity chart represents the source data of a definite air-water mixture. A simplified portion of humidity chart is shown in Figure 2.8.

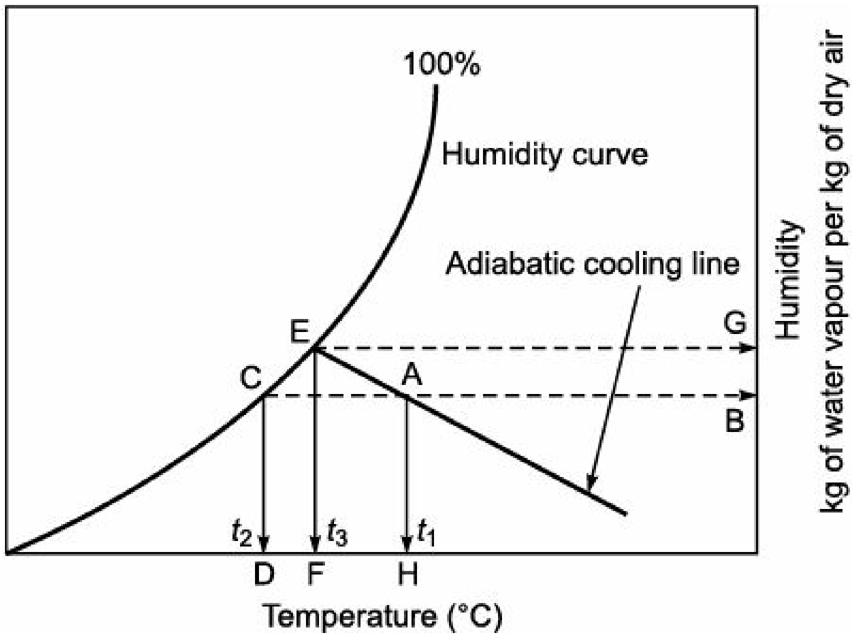


FIGURE 2.8 Application of humidity chart.

Assume a stream of unsaturated air water mixture at a point A on humidity chart shown in Figure 2.8. By moving vertically downwards from this point, we get temperature t_1, which is the dry bulb temperature. The application of humidity chart is explained by using point A. The following data can be obtained from the humidity chart:

1. *Humidity:* From point A moving horizontally towards the *y*-axis, gives an intercept point B, which is the humidity of the sample air.
2. *Dew point:* From point A moving horizontally towards the left to the 100% relative humidity line, gives an intersection point C. Moving vertically downwards from this point, we get point D. This is the dew point, which represents temperature t_2.
3. *Adiabatic saturation temperature:* From point A moving along the adiabatic cooling line towards the 100% relative humidity curve, gives an intersection point E. Moving vertically downwards from this point, we get point F. The line drawn from E to F is called Adiabatic cooling line. It represents the adiabatic saturation temperature t_3.
4. *Humidity at adiabatic saturation:* From point E moving horizontally right towards the *y*-axis gives an intersection point G. The point G represents the humidity at adiabatic saturation line.

In similar way, humid volume, humid heat can be determined using humidity chart.

EXAMPLE 2.45 A sample of air at 40°C, has a wet bulb temperature of 25°C. Calculate the humidity, % humidity and molal humidity of this air sample.

Solution:

1. *Humidity:* Draw a vertical line upward at 40°C on humidity chart, which will meet the 100% relative humidity curve at a particular point. From this point, draw a horizontal line which will meet the *y*-axis at a particular point. This point is read as saturated humidity. The value from the chart is 0.051 kg of water/kg of dry air. Draw another vertical line upwards at 25°C on humidity chart, which will meet 100% relative humidity curve at a particular point. From this point, draw a horizontal line which will meet the *y*-axis at a particular point. This point is read as actual humidity. The corresponding value from the chart is 0.018 kg of water/kg of dry air.

2. Percentage humidity = $\dfrac{\text{Actual humidity}}{\text{Saturated humidity}} \times 100$

$$= \frac{0.018}{0.051} \times 100$$

$$= 35.29$$

3. Molal humidity = $\text{Humidity} \times \dfrac{\text{Molecular weight of air}}{\text{Molecular weight of water}}$

$$= 0.018 \times \frac{29}{18}$$

= 0.029 kg of water/kg of dry air

EXAMPLE 2.46 30,000 m^3 of coal gas measured at 289 K and 1 atm is saturated with water vapour. This is compressed to 340 kN/m^2 pressure and cooled to 289 K and the condensed water is drained off. Subsequently, the pressure is reduced to 170 kN/m^2 and gas is distributed at this pressure and 289 K. What is the % humidity after treatment? The vapour pressure of water at 289 K is 1.8 kN/m^2.

Solution: From the definition of humidity, we know that

$$H_1 = \frac{M_A}{M_B} \cdot \frac{P_A}{(P_t - P_A)}$$

where

H_1 = Humidity at initial condition

M_A = 18

P_A = 1.8 kN/m^2

P_t = 340 kN/m^2

$$H_1 = \frac{18}{M_B} \cdot \frac{1.8}{(340 - 1.8)}$$

$$H_1 = \frac{0.0958}{M_B} \frac{\text{kg of water vapour}}{\text{kg of dry air}}$$

Humidity for reduced pressure

$$H_2 = \frac{M_A}{M_B} \cdot \frac{P_A}{P_t - P_A}$$

where

P_t = 170 kN/m^2

M_A = 18 (Molecular weight of water)

$$H_2 = \frac{18}{M_B} \cdot \frac{P_A}{170 - P_A}$$

It should be noted that humidity remains same even on compression or expansion of gas keeping temperature constant. Therefore,

$$H_1 = H_2$$

$$\frac{0.0958}{M_B} = \frac{18}{M_B} \cdot \frac{P_A}{170 - P_A}$$

∴ $P_W = P_A = 0.899 \text{ kN/m}^2$

$$\text{Relative humidity} = \frac{\text{Actual partial pressure of water in the air-water mixture}}{\text{Partial pressure of water at saturation}} \times 100$$

$$= \frac{0.899}{1.8} \times 100$$

$$= 49.94\%$$

2.25
Humidification

It may be defined as the process of increasing the moisture content in the air.

Many chemical and biochemical processes are required to maintain the temperature from 25°C to 28°C and the corresponding relative humidity of 20% to 30%. Therefore, in dry weather, humidification is necessary. Humidification may be achieved to the desired condition by spraying water into the circulation of air path, at a temperature lower than the dry bulb temperature and higher than the wet bulb temperature. To meet this purpose, absorption refrigeration system is employed. The mechanism of a simple adiabatic humidification process is shown in Figure 2.9.

In this plot, *x*-axis indicates the perpendicular distance to the interface and *y*-axis represents the humidity and temperature. Broken arrows represent the diffusion of vapour into the gas phase and the continuous arrows represent the flow of heat through the gas and liquid phase.

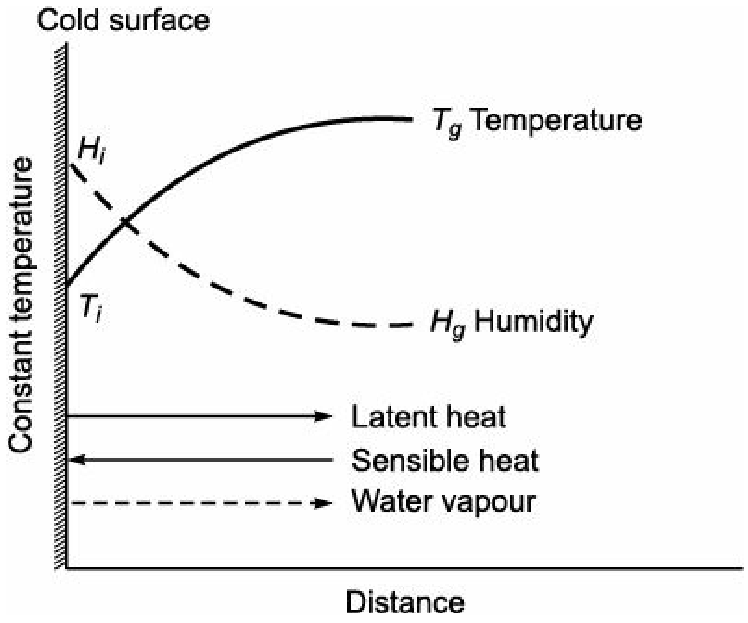


FIGURE 2.9 Adiabatic humidification process.

In adiabatic humidification process, water sprayed in the path of circulated air at constant temperature. The air to get humidified, it is necessary that the humidity at the interface is higher than the humidity of the circulated air. Since the water is vaporised, the latent heat is transferred from water to air. In order to flow of sensible heat to the interface, the air temperature must be higher than the interface temperature. The latent heat flows from the water to air and the sensible heat flows from the air to water. Thus, the flow of heat get balanced and there is no temperature gradient in the liquid.

2.26

Dehumidification

It is the process of removal of moisture from the air. The process of dehumidification accomplished when the moist air bring into contact with either liquid or solid surface. For example, large air conditioner incorporate automatic control of temperature and humidity. The temperature is controlled with the aid of thermocouple and the humidity is controlled by using the recorded data of difference between the wet bulb temperature and dry bulb temperature.

Generally, the dehumidifiers are used in special heat transfer devices. In this process, the removal of moisture is accomplished by removing the latent heat. The air is very humid in West Bengal, Kerala, Tamil Nadu and some other parts of India. It is very difficult to carry out the desired operations in such places with hygroscopic substances even in air conditioned room. Hence, dehumidifiers are essential to use under this circumstances.

2.26.1 Mechanism of Dehumidification

When the temperature of the surface is less than the dew point of the air, condensation of moisture takes place at this circumstances. Hence, the temperature of the air falls. This is the mechanism of dehumidification. A simple mechanism of dehumidification process is shown in Figure 2.10.

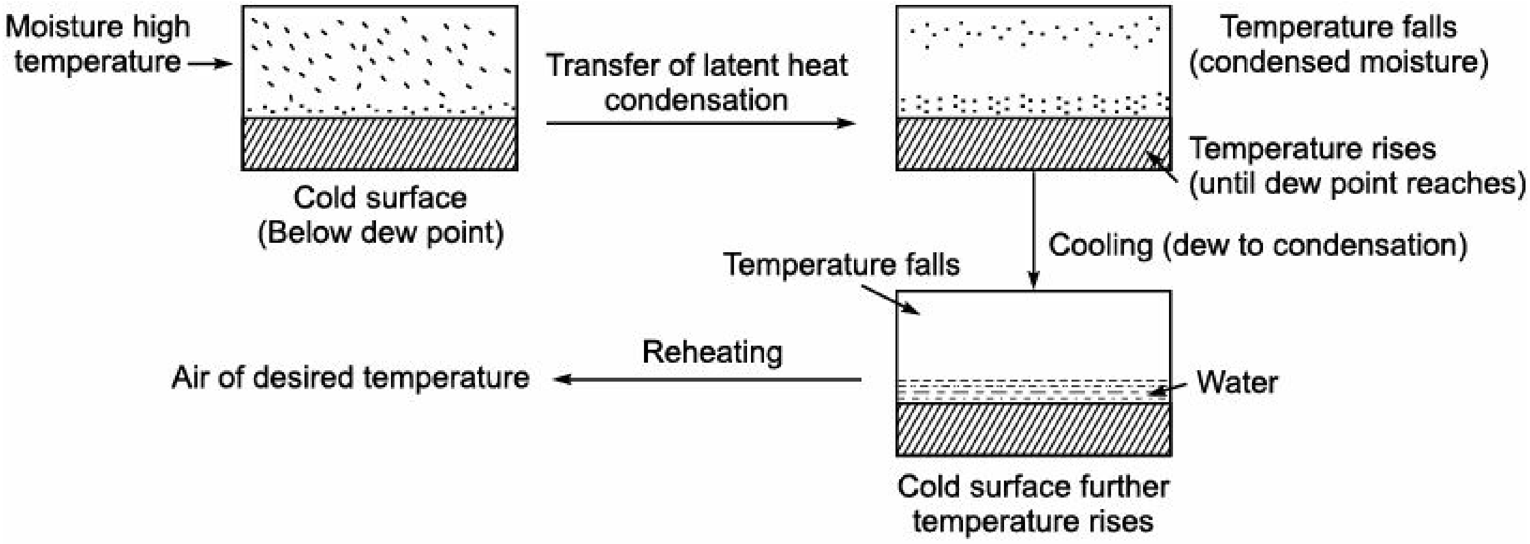


FIGURE 2.10 Principle of dehumidification.

The condition at a particular point of a dehumidifier is shown in Figure 2.11.

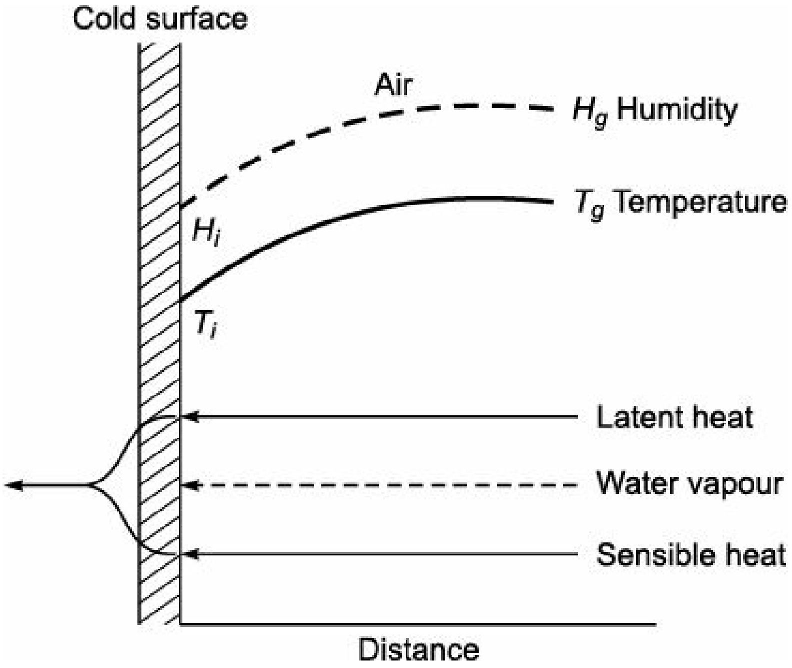


FIGURE 2.11 Condition of dehumidifier.

In this plot, the *x*-axis indicates the perpendicular distance to the interface and *y*-axis represents the humidity and temperature. The broken arrows represent the diffusion of vapour into the gas phase and the continuous arrows represent the flow of heat through the gas and liquid phase. In this case, the humidity at interface is lesser than the humidity of air. Hence, the water vapour diffuses into the interface. Because of this reason, temperature of the surface tends to rise and the temperature of the air decreases. Therefore, it is expected that the air would cool at constant humidity until the dew point is reached. In the case of saturated air, temperature at interface must be less than the temperature of the air. Hence, the bulk of the air would be saturated with the water vapour at that temperature. This is the way in which sensible heat is transferred into the water. The air in contact with the surface get cooled below its dew point and the air from a distant place get condensed, which requires more time to cool. Therefore, the dehumidification get enhanced by effective mixing. Normally, the temperature as well as humidity reduced simultaneously throughout the process. After dehumidification process, the gas can be reheated to its original dry bulb temperature.

2.26.2 Approaches to Dehumidification

The approaches to dehumidification are as follows:

1. The temperature of the moist air is in contact with the spray of cold water is less than the dew point of the entering air.
2. Humidity of the air can be reduced by compressing it. During the compression, partial pressure of the water vapour increases. As soon as the water vapour reaches the saturation, condensation takes place. Due to the condensation, water vapour gets liquefied and drained off.
3. When moist air is passed over a solid adsorbent surface or it is passed through a liquid adsorbent spray, dehumidification bounds to take place. In this case, the dehumidification takes place because of lowering the water vapour pressure. The solid adsorbents used here are silica gel or activated alumina. The liquid adsorbents are the solution of inorganic salt, such as brine, lithium chloride and the organic compound, such as ethylene glycol. A typical approaches to dehumidification process is shown in Figures 2.12 and 2.13. The adsorbents are reactivated time to time and reused.

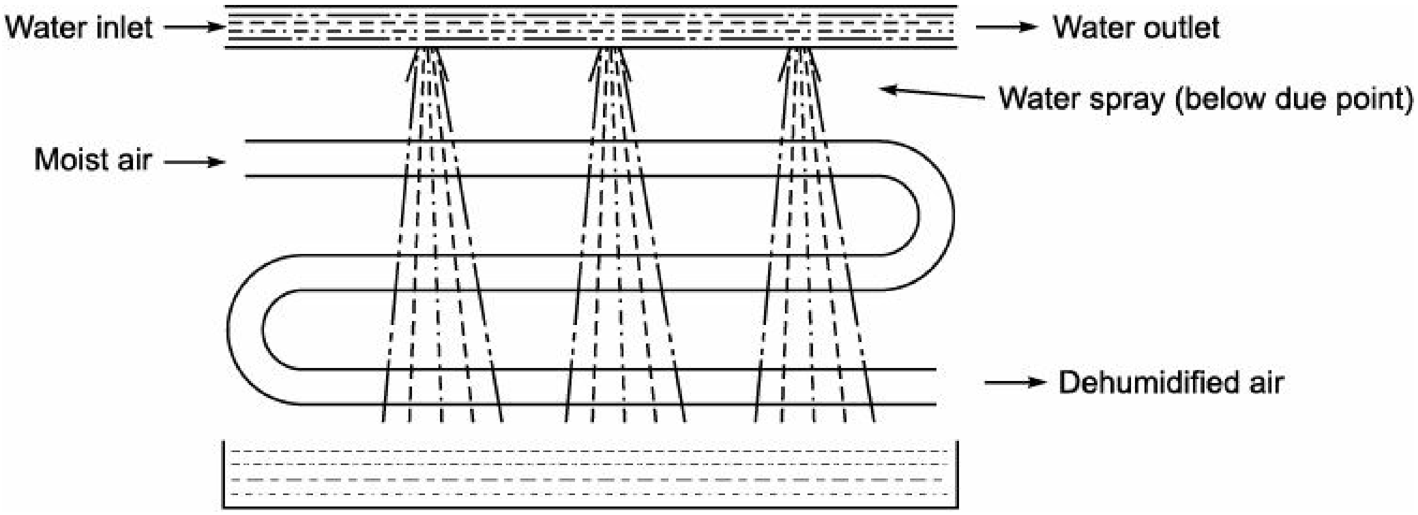


FIGURE 2.12 Spraying of water on moist air.

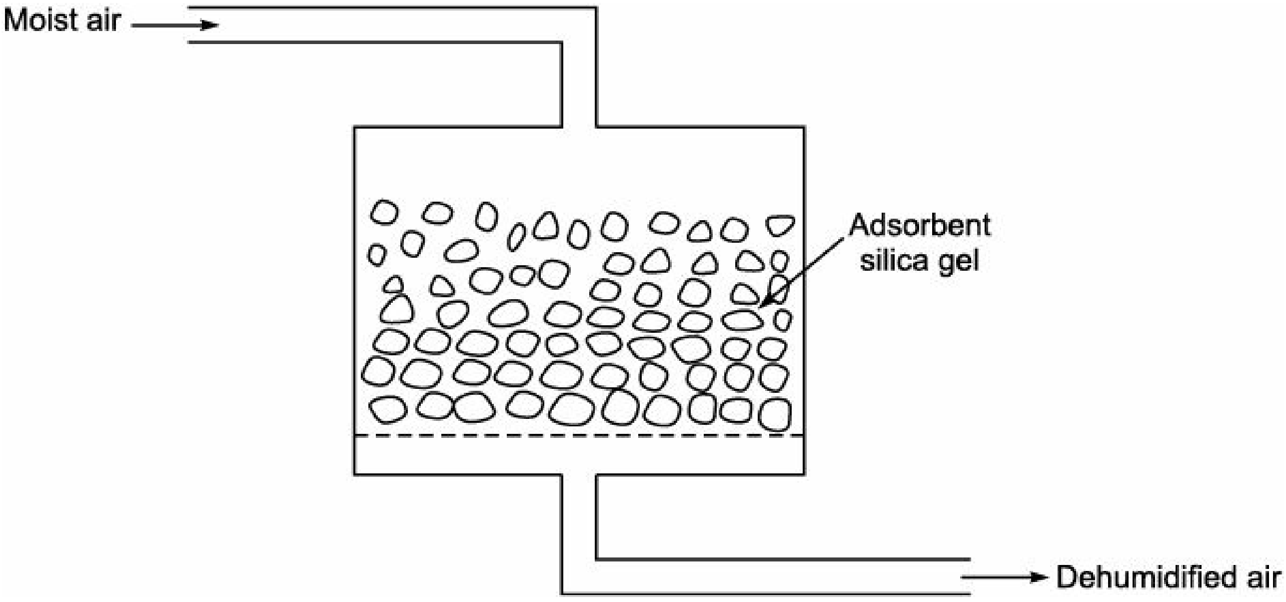


FIGURE 2.13 Adsorption of moist air.

EXAMPLE 2.47 An air (B)–water (A) sample has a dry bulb temperature 55°C and an absolute humidity 0.030 kg water/kg dry air at 1 std. atm pressure.

Calculate:

(i) The percentage humidity

(ii) The molal absolute humidity

(iii) The partial pressure of water vapour in the sample

(iv) The relative humidity

(v) Dew point

(vi) Humid volume

(vii) Humid heat

(viii) Enthalpy.

Solution:

(i) *The percentage humidity:* Draw a vertical line at 55°C on humidity chart and extend the same till it meet the 100% saturation humidity curve. From the meet point draw a horizontal line towards the absolute humidity axis, which gives the saturation humidity. Then, percentage humidity can be calculated as

$$\text{Percentage humidity } (H_P) = \frac{\text{Actual humidity}}{\text{Saturated humidity}} \times 100$$

where

Actual humidity = 0.030

Saturated humidity (Fig. 2.7) = 0.115

$$H_P = \frac{0.030}{0.115} \times 100$$
$$= 26.08\%$$

(ii) *Molal absolute humidity:*

$$\text{Molal absolute humidity} = \text{Humidity} \times \frac{\text{Molecular weight of air}}{\text{Molecular weight of water}}$$

$$= H_a \times \frac{M_B}{M_A}$$

$$= 0.030 \times \frac{29}{18}$$

$$= 0.0483\ \frac{\text{kg of water}}{\text{kg of dry air}}$$

(iii) *Partial pressure of water vapour in the sample:* The partial pressure of water vapour in the sample may be calculated using the equation

$$p_A = \frac{HP_t}{(1+H)}$$

where

p_A = Partial pressure of water vapour

H = Molal absolute humidity

P_t = Total pressure

$$\text{Now, } p_A = \frac{0.0483 \times 1.013 \times 10^5}{(1 + 0.0483)}\ \text{N/m}^2$$
$$= 4667.35\ \text{N/m}^2$$

(iv) *Relative humidity:* The relative humidity (RH) may be calculated as

$$\text{RH} = \frac{\text{Actual partial pressure of water vapour } (p_A)}{\text{Partial pressure of water at saturation } (p_S)} \times 100$$

where

p_A = 4667.35 N/m^2

P_S = 15,730 N/m^2 (from data book)

Therefore, $$\text{RH} = \frac{4667.35}{15{,}730} \times 100$$
$$= 29.67\,\%$$

(v) *Dew point:* Draw a vertical line upward at 55 °C on humidity chart (Fig. 2.7). Also draw a horizontal line from the point of absolute humidity 0.030. This will meet the vertical line at a particular point. Extend the horizontal line through the meet point towards the 100% saturation humidity curve. It will meet the curve at a particular point. From this point, draw a line vertically downwards till it meet *x*-axis. Thus, we will get a temperature 31.5°C. This temperature is called dew point.

(vi) *Humid volume:* Draw a vertical line upward at 55°C on humidity chart Fig. 2.7. Extend the line upward till it meet the line of specific volume of dry air. From this meet point draw a horizontal line towards the y-axis which represents the specific volume of dry air. From the humidity chart, at 55°C, the specific volume of dry air is 0.93 m^3/kg. The humid volume of saturated air is 1.10 m^3/kg. Interpolating for 26.08 % humidity.

$$V_H = 0.93 + (1.10 - 0.93)\,(0.2608)$$

$$= 0.974\ m^3/kg$$

(vii) *Humid heat:* Humid heat (H_H) may be calculated using the equation

$$H_H = C_g + H -\!\rceil\ C_V$$

where

C_g = 1005 kJ/kg °C (From the data book)

H = 0.03 kg of water/kg of dry air

C_V = 1884 kJ/kg °C (From the data book)

Note: Data is from Chemical Engineer’s Perry Handbook.

Therefore, H_H = 1005 + (0.03)(1884)

= 1061.52 J (for wet air)/kg of dry air . K

(viii) *Enthalpy:* The enthalpy may be calculated using the equation

Enthalpy = Enthalpy of dry air + (Enthalpy of saturated air – Enthalpy of dry air)
× humidity

where

Enthalpy of dry air = 56,000 J/kg (From data book)

Enthalpy of saturated air = 3,52,000 J/kg (From data book)

Humidity = 0.2608

Therefore, Enthalpy = 56,000 + (352000 – 56000) × 0.2608

= 133.197 kJ/kg of dry air.

Note: Data is from Chemical Engineer’s Perry Handbook.

EXAMPLE 2.48 Air at a temperature of 25°C and pressure 750 mmHg has a relative humidity of 75%.

Calculate:

(i) Humidity of air

(ii) Molal humidity of air

(iii) Weight of water condensed from 100 m^3 of original wet air, if the temperature of the air is reduced to 15°C and the pressure is increased to 2 bar. At 25°C the vapour pressure of the water is 2.5 kN/m^2.

Solution: (i) Humidity of air:

$$\text{RH} = \frac{\text{Actual partial pressure of water vapour } (p_w)}{\text{Partial pressure of water at saturation } (p_s)} \times 100$$

$$\text{RH} = \frac{p_w}{p_s} \times 100$$

Therefore,
$$75 = \frac{p_w}{p_s} \times 100$$

$$75 = \frac{p_w}{2.5} \times 100$$

$$p_w = 1.875 \text{ kN/m}^2$$

Now, total pressure (P_t) = 750 mmHg

$$= \frac{750}{760} \times 1.013 \times 10^5 \text{ N/m}^2$$

= 99.967 kN/m^2

Humidity (H) = $$\frac{M_w p_w}{M_A (P_t - p_w)}$$

$$= \frac{18 \times 1.875}{29 \times (99.967 - 1.875)}$$

$$= 0.01186 \frac{\text{kg of water vapour}}{\text{kg of dry air}}$$

(ii) Molal humidity:

$$H_m = H \times \frac{M_A}{M_w}$$

$$= 0.01186 \times \frac{29}{18}$$

$$= 0.0191 \frac{\text{kgmol of water vapour}}{\text{kgmol of dry air}}$$

(iii) Weight of water condensed:

$$H = \frac{M_w}{M_A} \frac{p_A}{p_t - p_A}$$

where

H = Humidity at given temperature

$M_W = 18$

$M_A = 29$

$p_A = 2.5$ kN/m^2 from steam table at 15°C

$P_t = 197.43$ kN/m^2 (2 bar)

Therefore,

$$H = \frac{18}{29} \times \frac{2.5}{(197.43 - 2.5)}$$

$$H = 0.00796 \, \frac{\text{kg of water vapour}}{\text{kg of dry air}}$$

Water condensed = Initial humidity – Final humidity

= 0.01186 – 0.00796

$$= 0.0039 \, \frac{\text{kg of water vapour}}{\text{kg of dry air}}$$

$$H = \frac{0.00796}{(1 + 0.00796)} \, \frac{\text{kg of water vapour}}{\text{kg of wet air}}$$

$$H = 0.00789 \, \frac{\text{kg of water vapour}}{\text{kg of wet air}}$$

$$\text{Humid volume} = 22.414\left(\frac{H}{M_A} + \frac{1}{M_B}\right)\left(\frac{T}{273}\right)\left(\frac{1}{P}\right)$$

$$= 22.414\left(\frac{0.00789}{29} + \frac{1}{18}\right)\left(\frac{288}{273}\right)\left(\frac{1}{2}\right)$$

= 0.66 m^3 of wet air/kg of dry air

0.66 m^3 of wet air = 1 kg of dry air

100 m^3 of wet air = $\frac{1 \times 100}{0.66}$ kg of dry air

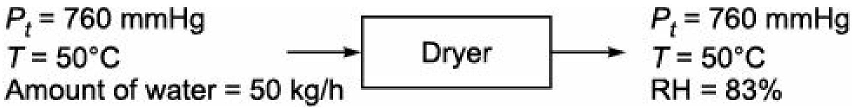
Amount of dry air = 151.52 kg

Water condensed from 100 m^3 of air = 151.52 × 0.0039

= 0.591 kg of water.

EXAMPLE 2.49 Conditioned air at 760 mmHg total pressure, 50°C and at a humidity of 0.01 kg water per kg of bone dry air enters the drier. It leaves the drier at 760 mmHg total pressure and 50°C, with RH 83%. Vapour pressure of water at 50°C is 92.5 mmHg. If 50 kg of water enters into the air stream per hour, calculate the rate of bone dry air flowing through the dryer.

Solution: Here,



$$H = 0.01\ \frac{\text{kg of water}}{\text{kg of dry air}}$$

$$\text{RH} = \frac{\text{Actual partial pressure of water vapour}}{\text{Partial pressure of water vapour at saturation}} \times 100$$

where

RH = 83%

p_W = ?

p_S = 92.5 mmHg

Therefore, $83 = \frac{p_w}{92.5} \times 100$

^ p_W = 76.775 mmHg

Now, $H = \frac{M_A}{M_B} \times \left(\frac{p_A}{P_t - p_A}\right)$

where

M_A = 18

M_B = 29

p_A = 76.775 mmHg

P_t = 760 mmHg

Therefore, $H = \frac{18}{29} \times \left(\frac{76.775}{760 - 76.775}\right)$

^ $H = 0.0697\ \frac{\text{kg of water}}{\text{kg of dry air}}$

Water removed = Humidity at removal – Humidity at entry level

= 0.0697 – 0.01

$= 0.0597\ \frac{\text{kg of water}}{\text{kg of dry air}}$

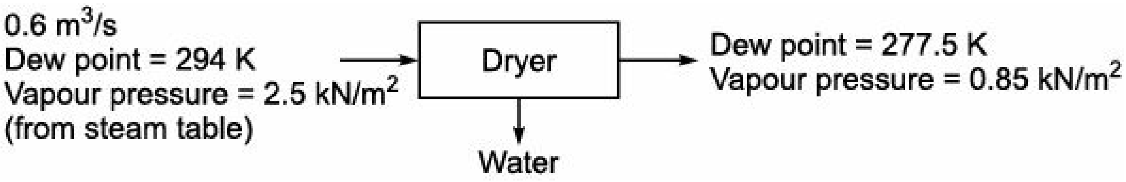
0.0597 kg of water = 1 kg of dry air

50 kg of water = $\frac{1 \times 50}{0.0597}$ kg of dry air

= 837.52 kg

EXAMPLE 2.50 0.6 m^3/s of gas is to be dried from a dew point of 294 K to a dew point 277.5 K.How much water must be removed and what will be the volume of the gas after drying? The vapour pressure of the gas at 294 K is 0.85 kN/m^2.

Solution:



Mole fraction of water in the inlet = $\frac{2.5}{101.3}$

= 0.0246

Mole fraction of water in the outlet = $\frac{0.85}{101.3}$

= 0.00839

Mole fraction of air in the inlet = 0.975

Mole fraction of air in the outlet = 0.9916

22.414 m^3 ≅ 1 kgmol

Amount of moist air = $\frac{1 \times 0.6}{22.414} \times \frac{273}{294}$

= 0.0248 kgmol/s

Dry air balance over the dryer:

$0.0248 \times 0.975 = G \times 0.9916$

^ $G = 0.0243$ kgmol/s

Now, 1 kgmol contain 22.414 m^3

Therefore, in 0.0243 kgmol the amount of dry air leaving = $\frac{22.414 \times 0.0243}{1} \times \frac{277.5}{273}$

= 0.554 m^3

Amount of water removed = (0.0246)(0.0248) – (0.00839)(0.0243)

= 0.000406 kgmol/s

= 0.00731 kg/s

Also, kgmol = $\frac{\text{Mass of vapour (in kg)}}{\text{Molecular weight}}$

^ Mass of vapour = Molecular weight × kgmol

Now, 22.414 m^3 contains 1 kgmol

Therefore, 1 m^3 will contain $\frac{1 \times 1}{22.414} \times \left(\frac{2.5}{101.3}\right) \times \left(\frac{273}{294}\right)$ kgmol

Amount of vapour (in kg) per m^3 of vapour at the inlet = $18 \times \frac{1}{22.414} \times \left(\frac{2.5}{101.3}\right) \times \left(\frac{273}{294}\right)$

$= 0.0184 \ \frac{\text{kg of vapour}}{\text{m}^3 \text{ of gas}}$

kg of vapour per m^3 of gas at the outlet = $18 \times \frac{1}{22.414} \times \left(\frac{0.85}{101.3}\right) \times \left(\frac{273}{277.5}\right)$

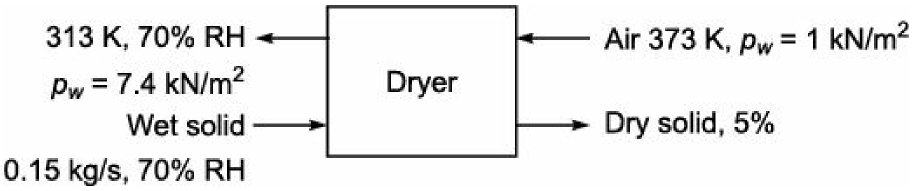
$$= 0.0066 \ \frac{\text{kg of vapour}}{\text{m}^3 \text{ of gas}}$$

Water removed/s = (0.0184 – 0.0066) × 0.6

$$= 0.00708 \ \frac{\text{kg of vapour}}{\text{m}^3 \text{ of gas}}$$

EXAMPLE 2.51 Brick material containing 70% moisture is to be dried at the rate of 0.15 kg/s in a counter current drier to give a product containing 5% moisture (wet basis). The drying medium consists of air heated to 373 K and containing water vapour equivalent to a partial pressure of 1 kN/m^2. The air leaves the drier at 313 K and 70% RH. Calculate how much air is required to remove the moisture. The vapour pressure of water at 313 K is 7.4 kN/m^2.

Solution:



Feed water (in Brick) = 0.15 × 0.7 = 0.105 kg/s

Weight of dry solids = 0.15 × 0.3 = 0.045 kg/s

Weight of water in the product = 0.05 kg/s (wet basis)

Weight fraction of water present in the product stream of bricks

$$\frac{M_w}{M_w + M_s} = 0.05$$

where

M_W = Mass of water in kg

M_S = Mass of solids in kg (0.045 kg/s)

Therefore, $\frac{M_w}{M_w + 0.045} = 0.05$

$$\therefore \ M_W = 0.00237 \text{ kg/s}$$

Water to be removed from the brick = 0.105 – 0.00237 = 0.10263 kg/s

Humidity of entering air = $\frac{M_w}{M_A} \times \left(\frac{p_w}{P_t - p_w}\right)$

$$= \frac{18}{29} \times \left(\frac{1}{101.3 - 1}\right)$$

$$= 0.006 \frac{\text{kg of water}}{\text{kg of dry air}}$$

For exit air,

$$\text{RH} = \frac{\text{Actual partial pressure of water}}{\text{Partial pressure of water vapour at saturation}} \times 100$$

$$\hat{} \; 70 = \frac{p_w}{7.4} \times 100$$

$$\hat{} \; p_w = \frac{70 \times 7.4}{100}$$

$$p_w = 5.18 \text{ kN/m}^2$$

$$\text{Humidity at exit air} = \frac{M_w}{M_A} \times \left(\frac{p_w}{P_t - p_w}\right)$$

$$= \frac{18}{29} \times \left(\frac{5.18}{101.3 - 5.18}\right)$$

$$= 0.0335 \frac{\text{kg of vapour}}{\text{kg of dry air}}$$

Increase in humidity = 0.0335 – 0.006

$$= 0.0275 \frac{\text{kg of water vapour}}{\text{kg of dry air}}$$

Let '*m*' be the mass flow rate of dry air in kg/s then,

$m \times 0.0275 = 0.10263$

$\hat{}\; m = 3.732$ kg of dry air/s

Weight of (wet) moist air entering = 3.732 + 0.02345

= 3.7554 kg/s

Exercises

2.1 Calculate the kilogram atoms of carbon which weigh 36 kg.

2.2 Calculate the kg of Na of which amount is specified as 5 kgatom.

2.3 Determine the molecular weight of the following compounds.

(i) K_2CO_3

(ii) NH_2CONH_2 (urea)

(iii) $Al_2(SO_4)_3$

(iv) $FeCl_3$

(v) NaOH

2.4 Determine the molecular weight of the following compounds.

(i) H_3PO_4

(ii) K_2SO_4

(iii) $CaCl_2$

(iv) NaCl

(v) NH_4NO_3

2.5 Determine the molecular weight of the following compounds.

(i) NH_4HSO_4

(ii) P_2O_5

(iii) Na_2O

(iv) KCl

(v) CO_2

(vi) $KMnO_4$

2.6 Calculate the kg of K of which amount is specified as 3 kgatom.

2.7 How many kilogram of ethane are there in 110 kgmol?

2.8 Calculate the moles of oxygen present in 650 g.

2.9 Convert 748.5 g of $CuSO_4 \cdot 5H_2O$ into moles.

2.10 How many moles of H_2SO_4 will contain 128 kg of S?

2.11 How many moles of K_2CO_3 will contain 234 kg of K?

2.12 How many kilograms of C_2H_6 will contain 8 kgatom of carbon?

2.13 How many grams of carbon are present in 528 g CO_2?

2.14 Calculate the equivalent moles of Na_2SO_4 in 966 g of $Na_2SO_4 \cdot 10H_2O$ crystals.

2.15 Find the equivalent weight of the following compounds.

(i) $CaCl_2$

(ii) $FeCl_3$

(iii) $Al_2(SO_4)_3$

(iv) H_3PO_4

2.16 Determine the equivalent weight of the following compounds.

(i) $KMnO_4$

(ii) $NaHCO_3$

(iii) HNO_3

(iv) $MgCO_3$

2.17 25 g of caustic soda is dissolved in water to prepare 1500 ml of solution. Calculate the normality of the solution.

2.18 20 g of caustic soda is dissolved in water to prepare 750 ml of solution. Calculate the molarity of the solution.

2.19 A H_2SO_4 solution has a molarity of 12 and molality of 96. Calculate the density of solution.

2.20 5 litres of NH_3 at 303 K and 21 kPa is neutralised by 140 ml of solution of H_2SO_4. Determine the normality of the acid.

2.21 A sample of $Na_2CO_3 \dashv H_2O$ weighing 0.65 g is added to 100 ml of 0.1 N H_2SO_4 solution. Will the resulting solution acidic, basic or neutral?

2.22 Make the following conversions:

(i) 294 g/l H_2SO_4 to normality

(ii) 54.75 g/l HCl to molarity.

2.23 Make the following conversions:

(i) 5N H_3PO_4 to g/l

(ii) 4.8 mg/ml $CaCl_2$ to normality

(iii) 4 M K_2SO_4 to g/l.

2.24 Sodium chloride weighing 200 kg is mixed with 500 kg of potassium chloride. Find the composition of the mixture in weight%.

2.25 Sodium chloride weighing 100 kg is mixed with 400 kg of potassium chloride. Find the composition of the mixture in mole%.

2.26 The strength of aqueous solution of soda ash is specified as 14% Na_2O by weight. Express the composition in terms of weight per cent soda ash.

2.27 The strength of phosphoric acid sample is found to be 25% P_2O_5 by weight. Calculate the actual concentration of H_3PO_4 (weight%) in the acid.

2.28 A sample of caustic soda flakes contains 70% Na_2O by weight. Find the purity of the flakes. ***Hint:*** $2NaOH = Na_2O + H_2O$.

2.29 Calculate the percentage of Na_2O content of lye containing 75% caustic soda (NaOH).

Hint: $2NaOH = Na_2O + H_2O$.

2.30 A solution of methanol in water contains 30 mole% of methanol. Express the composition as weight% methanol.

2.31 Nitric acid and water forms maximum boiling azeotrope containing 60 mole% water. Find the composition of the azeotrope by weight.

2.32 Ethanol and water form an azeotrope containing 96.5% by weight of ethanol. Find the composition of azeotrope by mole%.

2.33 The solubility of methyl bromide in methanol at 298 K is 44 kg per 100 kg. Find the weight fraction of methanol in saturated solution.

2.34 The solubility of methyl bromide in methanol at 298 K is 42 kg per 100 kg. Find the mole fraction of methanol in saturated solution.

2.35 A saturated solution of salicylic acid (HOC_6H_4COOH) in methanol contains 62 kg of salicyclic acid per 100 kg of methanol at 298 K. Calculate the composition of the solution in weight per cent.

2.36 A saturated solution of salicylic acid in methanol contains 60 kg of salicyclic acid per 100 kg of methanol at 298 K. Calculate the composition of the solution in mole per cent.

2.37 Caustic soda flakes obtained from a manufacturer are found to contain 50 ppm silica (SiO_2). Convert this impurity into weight%.

2.38 20 kg of CO_2 is compressed at a temperature of 303 K to a volume of 1.5 m^3. Calculate the pressure required for given duty. Assume ideal gas law is applicable.

2.39 A sample of a gas having volume of 0.5 m^3 is compressed in such a manner so that pressure is increased by 75 %. The operation is done for a fixed mass of a gas at constant temperature. Calculate the final volume of the gas.

2.40 A sample of gas having volume of 2 m^3 is compressed in such a manner so that its pressure is increased by 75 %. The operation is done for a fixed mass of gas at constant temperature. Calculate the final volume of gas.

2.41 A certain sample of gas at a pressure of 2 atm pressure is expanded so that its volume is increased by 60 %. The operation is done for a fixed mass of gas at constant temperature. Calculate the final pressure of gas.

2.42 A gas mixture has the following composition by volume:

Ethylene = 30.6%
Benzene = 24.5%
Oxygen = 1.3%
Methane = 15.5%
Ethane = 25.0%
Nitrogen = 3.1%

Calculate:

(i) Average molecular weight of the gas mixture.
(ii) The composition by weight.
(iii) The density of the gas mixture in kg/m^3 at NTP.

2.43 The analysis of a sewage gas sample from a municipal sewage plant is given below (volume basis):

Methane = 68%
Carbon dioxide = 30%
Ammonia = 2%
H_2S, SO_2 etc. = Traces

Calculate:

(i) The average molecular weight of the gas.
(ii) The density of the gas at NTP.

2.44 In the manufacture of nitric acid, initially ammonia and air are mixed at 7 atm and 650 °C. The composition of the mixture (volume basis) is as follows:

Nitrogen = 70.5%
Oxygen = 18.8%
Water = 1.2%
Ammonia = 9.5%

Calculate the density of the gas mixture using ideal gas law.

2.45 A natural gas has the following composition by volume.

Methane (CH_4) = 80%
Ethane (C_2H_6) = 12%
n-Butane (C_4H_{10}) = 3%

and the rest nitrogen (N_2).

Calculate:

(i) Composition of the gas by weight.

(ii) Average molecular weight.

(iii) Density of the gas at 30 °C and 200 kN/m^2.

2.46 A natural gas has the following composition by volume

CH_4 = 94.1%

C_2H_6 = 3.0%

and rest is N_2. This gas is piped from the well at a temperature of 27°C and an absolute pressure of 1300 mmHg. Using ideal gas law calculate:

(i) Partial pressure of N_2.

(ii) Pure component volume of N_2 per 100 m^3 of gas.

(iii) Density of the natural gas in kg/m^3 at the existing conditions. **[B.U. M/A 1998]**

2.47 A mixture of gas has the following composition by volume:

Methane = 80%

Ethane = 12%

and Nitrogen = 8%.

Calculate:

(i) The composition of gas by weight%.

(ii) Average molecular weight.

(iii) Density of the gas mixture at 30°C and 750 mmHg.

(iv) Specific gravity.

2.48 A by-product of coke oven produces 30,000 m^3 of gas per hour having the following analysis:

C_6H_6 = 5%

C_7H_8 = 5%

CH_4 = 40%

CO = 7%

H_2 = 35%

CO_2 = 5%

N_2 = 3%

The gas leaves the oven at 1.4 atm and 390 °C. After cooling to 40°C, the benzene and toluene are completely removed by absorption. Calculate:

(i) Average molecular weight of the gas entering the absorber.

(ii) Weight of gas leaving the oven per hour.

(iii) Volumetric composition of the gas leaving the absorber.

(iv) Weight of benzene and toluene absorbed.

2.49 A gas mixture is found to contain the following composition by volume:

Ethylene = 30.6%

Benzene = 24.5%

Oxygen = 1.3%

Methane = 15.5%
Ethane = 25.0 %
Nitrogen = 3.1%.

Find the composition in mole%, average molecular weight of the gas sample, density and specific gravity of the gas mixture at 20°C and 765 mmHg.

2.50 Calculate the total pressure and the composition of the vapours in contact with a solution at 100°C containing 35% benzene (C_6H_6), 40% toluene ($C_6H_5CH_3$) and 25% orthoxylene [$C_6H_4(CH_3)_2$] by weight.

Vapour pressure at 100°C:
Benzene = 1340 mmHg
Toluene = 560 mmHg
O-xylene = 210 mmHg.

2.51 A producer gas has the following composition by volume:
CO = 25.3%
CO_2 = 5.4%
H_2 = 13.2%
O_2 = 0.5%
CH_4 = 0.4%
and N_2 = 55.2%

Calculate:
(i) The average molecular weight of the gas.
(ii) The composition in weight per cent.
(iii) The density at standard conditions.

2.52 State Dalton's and Amagat's law.

2.53 Cracked gas from a petroleum refinery has the following composition by weight.
Methane = 27.13%
Ethane = 11.30%
Ethylene = 26.37%
Propane = 11.61%
Propylene = 12.66%
n-Butane = 10.93%.

Find the average molecular weight of the gas mixture.

2.54 A limestone analyses
$CaCO_3$ = 92.89%
$MgCO_3$ = 5.41%
Insoluble = 1.7%.
(i) How many kilograms of calcium oxide can be made from 5 tonnes of this limestone?
(ii) How many kilograms of CO_2 can be recovered per kg of limestone?
(iii) How many kilograms of limestone are needed to make 1 tonne of lime?

2.55 The analysis of a gas sample has the following volume per cent:

Methane = 68%

CO_2 = 30%

Ammonia = 2%.

Find

(i) The average molecular weight of the gas.

(ii) The density of the gas at NTP.

2.56 A mixture of nitrogen and carbon dioxide at 298 K and 1 atm has an average molecular weight of 31. What is the partial pressure of nitrogen?

2.57 Assuming air to contain 79% N_2 and 21% O_2 by volume. Calculate the density of air at NTP.

2.58 A natural gas has the following composition by volume:

CH_4 = 82%

C_2H_6 = 12%

and N_2 = 6%.

Calculate the density of gas at 288 K and 1 atm and composition in weight per cent.

2.59 Calculate the density of air containing 21% O_2, 79% N_2 by volume at 503 K and15 atm.

2.60 A gas mixture has the following composition by volume:

SO_2 = 8.5%

O_2 = 10%

and N_2 = 81.5%.

Calculate:

(i) The density of gas mixture at a temperature of 473 K and 2 atm.

(ii) The composition by weight.

2.61 A gaseous mixture has the following composition by volume:

CO_2 = 8%

CO = 14%

O_2 = 6%

H_2O = 5%

CH_4 = 1%

and N_2 = 66%

Calculate:

(i) Average molecular weight of gas mixture.

(ii) Density of gas mixture at 303 K and 1 atm.

2.62 Calculate the total pressure and the composition of vapour in contact with a solution at 100 °C, containing 35% Benzene, 40% Toluene and 25% Orthoxylene by weight.

Data: Vapour pressure at 100°C

Benzene = 1340 mmHg

Toluene = 560 mmHg

O-Xylene = 210 mmHg

2.63 Derive the empirical formula of the following:

Ag = 9.09%
N = 20.77%
O = 70.14%.

2.64 A solid compound is found to contain
C = 42.11%
O = 51.46%
H = 6.43%

Its molecular weight is about 341. What is the formula of the compound?

2.65 How many ppb are there in 1 ppm?

2.66 A gas mixture consists of 3 components A, B and C. The following is the analysis of this mixture.
A 40 mole% ... Molecular weight = 40
B ... 18.75 weight% Molecular weight = ?
C 20 mole% ... Molecular weight = 50

Calculate:
(i) Molecular weight of B.
(ii) Average molecular weight of the mixture. **[Ans. 42]**

2.67 A mixture of CH_4 and C_2H_6 has average molecular weight 22.4. Find the mole% of CH_4 and C_2H_6 in the mixture.

2.68 Two different engineers calculate the average molecular weight of a flue gas sample. One engineer uses correct mass of 28 for Nitrogen and determines average molecular to be 30.08. The other using an incorrect value of 14, calculates the average molecular weight to be 18.74.
(i) Calculate the volume% of Nitrogen in the flue gas sample.
(ii) If the remaining component of the flue gases are CO_2 and O_2, calculate the volume per cent of each of them.

2.69 Two engineers are calculating the average molecular weight of gaseous mixture containing oxygen and other gases. One of them using the correct molecular weight 32 for oxygen determines molecular weight correctly as 39.8. The other using an incorrect value of 16 determines molecular weight as 32.8. This is only an error in his calculations. What is the mole% of oxygen in the mixture?

2.70 Two thermometers are to be checked against standard thermometer, which are calibrated in °C and K. The standard reads – 22°F. What should be the other two thermometers read?

2.71 A mixture of CH_4 and C_2H_6 has density 1.0 kg/m^3 at 273 K and 1 atm. Calculate the mole% and weight% of CH_4 and C_2H_6 in the mixture.

2.72 A mixture of gases is analyzed and found to have the following composition:
CO_2 = 12.0%
CH_4 = 27.3%
H_2 = 9.9%
N_2 = 44.8%
CO = 6.0%

How much will the weight of 3 lb moles of this gas mixtures?

2.73 A gas mixture from a reaction has the following composition by weight.

Cl_2 = 67%

Br_2 = 28%

O_2 = 5%

Using the ideal gas law, calculate:

(i) The composition of gas by volume
(ii) The density of the gas mixture in g/l at 25°C
(iii) Specific gravity of the mixture
(iv) Average molecular weight of the mixture.

2.74 A gas mixture is found to contain the following composition by volume.

Ethylene = 30.6%
Benzene = 24.5%
Oxygen = 1.3%
Ethane = 25.0%
Nitrogen = 3.1%.

Calculate:

(i) Composition in mole%
(ii) Weight%
(iii) Average molecular weight of gas sample
(iv) Density of gas at NTP.

2.75 A compound having molecular weight 60 has the following percentages of the elements:

C = 20%

O_2 = 26.66%

N_2 = 46.66%

and rest hydrogen.

Find out the empirical formula of the compound and the probable name of the compound.

2.76 A producer gas has the following composition by volume:

CO = 22%

CO_2 = 5%

O_2 = 3%

and N_2 = 70%.

Calculate the volume of the gas in cubic meters at 308 K and 1 atm pressure per 10 kgof carbon present.

2.77 A gas mixture has the following composition by volume:

O_2 = 15.1%

CO_2 = 3.7%

N_2 = 75%

H_2O = 6.2%.

Find (i) Composition by weight and (ii) Density of gas mixture at 0.9934 atm and 303 K.

2.78 In a vessel at 1 bar and 300 K, the % RH of water vapour in the air is 25. If partial pressure of water vapour when air is saturated with vapour at 300 K is 3.6 kN/m^2. Calculate

(i) Partial pressure of water

(ii) The humidity of air

(iii) The percentage humidity

(iv) The humid volume.

2.79 It is proposed to construct a drier for removing 50 kg water/h. Air is supplied to the drying chamber at a temperature of 65°C and pressure of 760 mmHg and a dew point of 4.5°C. If the air leaves the dryer at a temperature of 35°C and a pressure of 755 mmHgand a dew point of 24°C, calculate the volume of air at initial conditions that must be supplied per hour.

Data: Vapour pressure of water at 4.5°C = 6.5 mmHg

Vapour pressure of water at 24°C = 22.5 mmHg.

2.80 Air at a temperature of 20°C and a pressure of 750 mmHg has a relative humidity of 80%.

(i) Calculate the molal humidity of the air.

(ii) Calculate the molal humidity of the air if its temperature is reduced to 10 °C and its pressure increased to 2.5 atm, condensing out some of water.

(iii) Calculate the weight of water condensed from 100 m^3 of original wet air in cooling and compressing to the condition of part '*b*'.

(iv) Calculate the final volume of wet air of part '*c*'.

2.81 Air at a temperature of 40°C and atmospheric pressure has wet bulb temperature of 30 °C.

(i) Estimate the molal humidity, the percentage saturation and dew point of this air.

(ii) The air of part (i) is passed into a humidifier from which it emerges having a dry bulb temperature of 50°C and wet bulb temperature of 45°C. Estimate the percentage saturation of the air leaving the humidifier and calculate the weight of water gained per 1000 m^3 of entering air.

2.82 The gas acetylene is produced as per the reaction

$$CaC_2 + 2H_2O \rightleftarrows C_2H_2 + Ca(OH)_2$$

Calculate the number of hours of service that can be obtained from 1.0 kg of carbide in an acetylene lamp burning 2 m^3 of gas per hour at a temperature of 24°C and a pressure of 743 mmHg.

2.83 A wet solid containing 60% water by weight is to be dried to a water content of 9%. For each kg of dry solid 53.2 kg of dry air is passed. The air leaving the drier has humidity of 0.05. Fresh air is supplied at a humidity of 0.015. Determine the fraction of air recirculated.

2.84 Liquid water and air are flowing into a humidification chamber in which water evaporates completely. The entering air contains one mole% of water vapour and 20.8% of O_2 and the rest N_2. The humidified air should contain 10 mole% of H_2O. Calculate the flow rate of liquid to humidity 200 kgmol/min of entering air.

2.85 The percentage humidity of air at 30 °C and a total pressure of 750 mmHg is 20%. Calculate the RH and the partial pressure of water vapour in the air. What is the dew point of the air?

2.86 Acetone which is being used as a solvent in an extraction process, is being recovered by evaporation into a stream of Nitrogen. The nitrogen enters the evaporator at a temperature of 30°C containing acetone such that its dew point is 10°C. It leaves at a temperature of 25°C with a dew point of 20°C. The barometric pressure is constant at 760 mmHg.

Calculate:

(i) The weight of acetone evaporated per 1000 litres of gases entering the evaporator.
(ii) The volume of the gases leaving the evaporator per 1000 litres of gases entering.

The vapour pressure of acetone is 116 mmHg at 10°C and 185 mmHg at 20°C.

2.87 A volume of moist air of 100 m^3 at 740 mmHg and 30°C contains water vapour in such proportion that its pressure is 22 mmHg. Without changing the total pressure temperature is reduced to 15°C and some of the water vapour is removed by condensation. After cooling, it is found that the partial pressure of water vapour is 12.7 mmHg.

Calculate:

(i) Volume of air after cooling
(ii) Weight of water vapour condensed.

2.88 1000 m^3 of moist air at 740 mmHg and 30°C contains water vapour in such proportions that its partial pressure is 22 mmHg. The air is cooled at constant total pressure to 15°C and partial pressure dropped to 12.7 mmHg. Compute the mass of water removed and volume of gas after cooling.

2.89 At 297 K and 1 bar, the mixture of N_2 and C_6H_6 has the RH 60%. It is required to recover 80% of C_6H_6 present by cooling to 283 K and compressing to a suitable pressure. What is that pressure?

Vapour pressure of C_6H_6 at 297 K = 12.2 kN/m^2

Vapour pressure of C_6H_6 at 283 K = 6 kN/m^2.

2.90 Humid air at 75°C, 1.1 bar and 30% RH is fed to a process unit at a rate of 1000 m^3/h.Determine the molar flow rates of water, dry air and oxygen entering the process, the molal humidity, absolute humidity, the percentage humidity of air and the dew point.

2.91 30,000 m^3 of coal gas measured at 289 K and 1 atmosphere saturated with water vapour. This is compressed to 340 kN/m^2 pressure and cooled to 289 K and the condensed water is drained off. Subsequently, the pressure is reduced to 170 kN/m^2 and the gas is distributed at this pressure and 289 K. What is the % humidity after treatment? The vapour pressure of water at 289 K is 1.8 kN/m^2.

2.92 In a vessel at 1 bar and 300 K, the RH of water vapour in the air is 25%, if the partial pressure of water vapour when air is saturated with vapour at 300 K is 3.6 kN/m^2.

Calculate:

(i) Partial pressure of water
(ii) The humidity of air
(iii) Percentage humidity
(iv) Humid volume.

2.93 A humidifier is conditioning air to 45°C DBT and 30 °C WBT by heating outside air passing it through an adiabatic spray chamber in which it reaches 85% humidity and then reheated to the desired temperature. The outside air is at 5°C and foggy carrying 0.006 kg liquid per m^3 air. To what temperature of the air it leaves from the spray chamber, before the final heating operation?

2.94 Wet air with DP 35°C is compressed from 1 atm to 10 atm in a compressor. After compression only 25% of the original water remains in the air. Compute:

(i) The final temperature of wet air after compression

(ii) How much original in volume is required to make 10 m^3 of compressed air?

(iii) Relative humidity of compressed air.

(iv) The pressure to which air must be compressed if only 10% of the original water were to remain after compression, the temperature remaining as before. Humidity chart may be used for getting data.

2.95 We have sample of air at 1.013 bar (std atm pressure), 35°C and with a percentage saturation of 60. It is required to alter the condition to

(i) Temperature 25°C and humidity 70%

(ii) Temperature 50°C and humidity 30%.

What operations do you recommend to achieve the above conditions?

2.96 Liquid water and air are flowing into a humidification chamber in which water evaporates completely. The entering air contains one mole% of water vapour and 21% of O_2 and the rest is N_2. The humidified air should contain 10 mole% of H_2O. Calculate the flow rate of liquid to humidify 200 kgmol/min of entering air.

2.97 A wet solid containing 60% water by weight is to be dried to a water content of 9 %. For each kg of dry solid 53.2 kg of dry air is passed. The air leaving the drier has a humidity of 0.05. Fresh air is supplied at a humidity of 0.015. Determine the fraction of air recirculated.

2.98 The vapour pressure of benzene is measured at two temperatures with the following results

T_1 = 7.6°C, p_1 = 40 mmHg

T_2 = 15.4°C, p_2 = 60 mmHg

Calculate the parameters of the Clausius Clapeyron equation and then estimate the vapour pressure at 42.2°C.

2.99 The percentage humidity of air at 30°C and a total pressure of 750 mmHg is 20%. Calculate RH and the partial pressure of water vapour in the air. What is the dew point of the air?

2.100 Acetone which is being used as a solvent in an extraction process, is being recovered by evaporation into a stream of Nitrogen. The Nitrogen enters the evaporator at a temperature of 30°C containing acetone, such that its dew point is 10°C. It leaves at a temperature of 25°C with a dew point of 20°C. The barometric pressure is constant at 760 mmHg. Calculate:

(i) The weight of acetone evaporated per 1000 litres of gases entering the evaporator.

(ii) The volume of the gases leaving the evaporator per 1000 litres entering. The vapour pressure of acetone is 116 mmHg at 10°C and 185 mmHg at 20°C.

2.101 A mixture of Benzene and dry air at a temperature of 30°C and a pressure of 760 mmHgis found to have a dew point of 15°C. Calculate:

(i) Percentage by volume of Benzene

(ii) Moles of Benzene per mole of air

(iii) Weight of Benzene per unit weight of air.

Data: Vapour pressure of Benzene at 15°C is 60 mmHg.

2.102 A mixture of dry flue gases and acetone at pressure of 750 mmHg and a temperature of 30°C has a dew point 25°C. It is proposed to condense 90% of the acetone in this mixture by cooling to 5°C and compressing. Calculate the necessary pressure in mmHg.

Data:

At 25°C, vapour pressure of acetone = 229.2 mmHg

At 5°C, vapour pressure of acetone = 89.1 mmHg.

3

Material Balance without Chemical Reactions

3.1

Introduction

The knowledge of material balance with or without chemical reaction is very essential for process design. In similar way, energy balance with or without chemical reaction is also essential for process design related to heat transfer unit operations. Thus, we can say that material and energy balances are the basic tools of process calculations. The design of equipment starts only after the completion of material and energy balance of the process. The material balance calculations give the information regarding the amount of material coming in, material going out, material accumulated or depleted during the unit operations. Based on these calculations, the feasibility of the process or performance of the equipment can be judged.

The law of conservation of mass is the basis for material balance calculations. It states that the total mass of various components involved in a unit process remains constant. Thus, for any unit process

$$\text{Input} - \text{Output} = \text{Accumulation} \qquad (3.1)$$

For steady state unit process where accumulation is constant, we have

$$\text{Input} - \text{Output} = 0 \qquad (3.2)$$

3.2

Classification of Material Balance without Chemical Reaction

The material balance problems without chemical reaction can be classified as follows:

1. Material balance at steady state operation.
2. Material balance at unsteady state operation.

3.3

Guidelines for Material Balance without Chemical Reactions

The general guidelines for solving material balance problems for system involving without chemical reactions are as follows:

1. If the basis of calculations is given in the problem, then the same basis may be selected for the calculations. If the basis of calculations is not given in the problem, then a suitable basis of calculations should be selected. The basis of calculations should be specified in weight units. For example, g or kg.
2. If the system involves a type of material which does not change during the unit operation is called tie material. For simplification, make the material balance of such tie material. For example, consider 200 g of solids NaOH is dissolved in 1 litre of water and is subjected to evaporation. The quantity of dissolved solids NaOH is remain same both in weak liquor before evaporation and in thick liquor after evaporation. It is the quantity of water which changes during the operation. Hence, in this case of evaporation, dissolved solid NaOH is the tie

material.

3. If the system involves with an inert material which does not take part in unit operation, then for simplification of calculations, we make the material balance of such inert material. For example, consider the burning of coal. The amount of ash present in the coal does not take part in combustion process. Therefore, ash present in coal is an inert material.
4. If the system involves two or more components which undergoes chemical changes in a unit operation, then for simplification of calculations, we make the material balance of such compositions of the system. Depending on the number of components present in the system, we generate the independent material balance equations and then solve the equations simultaneously. For example, consider the preparation of desired mixed acids from weak acids by blending it with concentrated acids. In this process, the mixed acid composition simultaneously get affected.
5. The process of operations for material balance should be represented by a suitable block diagram. A simple block diagram of a unit operation is shown in Figure 3.1.

FIGURE 3.1 General block diagram of material balance.

3.4

Various Important Operations Carried Out in Industry

The various important operations carried out in industry are as follows:

1. Distillation
2. Absorption
3. Extraction
4. Crystallization
5. Drying
6. Mixing
7. Evaporation.

3.4.1 Distillation

It is a method of separation of mixture based on differences in volatilities of components in a boiling liquid mixture. It is a unit operation or physical separation process. Fractional distillation can give almost pure product. The product obtained from the top is called distillate or overhead product. The product removed from the bottom is called residue or bottom product.

A typical distillation column is shown in Figure 3.2. The number of tray in distillation column is required to separate the components from the feed. The material balance for distillation column can be represented by the simple block diagram as shown in Figure 3.3.

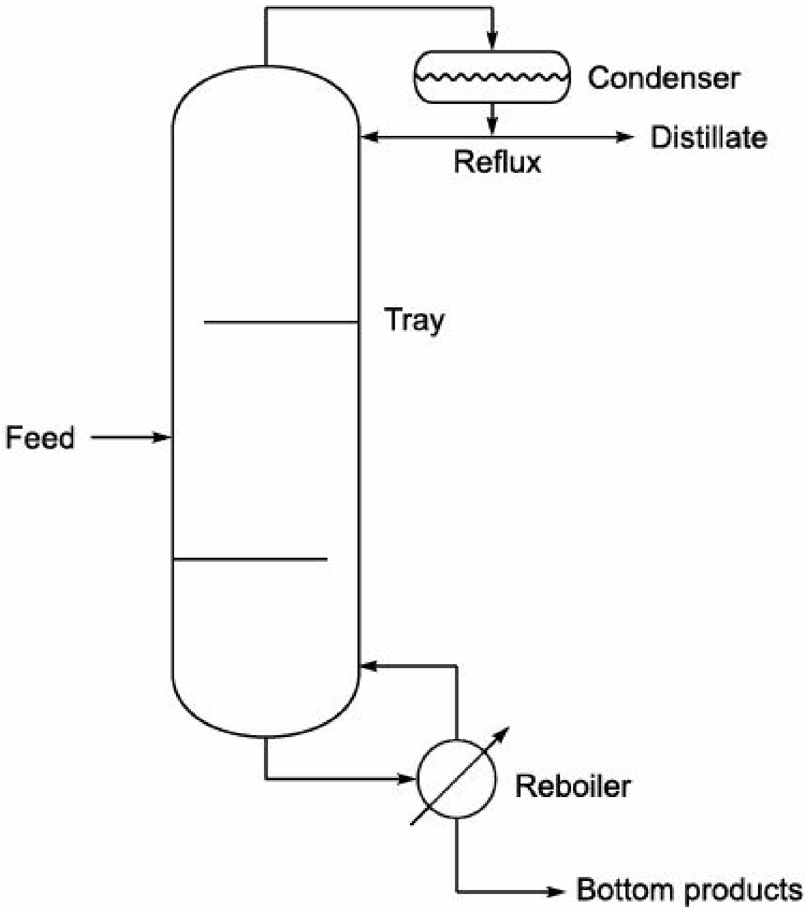


FIGURE 3.2 Distillation column.

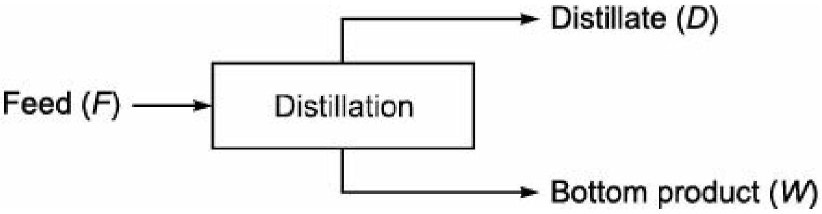


FIGURE 3.3 Block diagram of distillation column.

The overall material balance of distillation column can be written as

$$F = D + W \qquad (3.3)$$

where

F = Feed (kg)
D = Distillate (kg)
W = Bottoms (kg)

Material balance of component '*A*' in distillation column can be written as

A in feed = *A* in distillate + *A* in bottoms

$$\text{or } F \times x_F = D \times x_D + W \times x_W \qquad (3.4)$$

where

x_F = Mole fraction of *A* in feed
x_D = Mole fraction of *A* in distillate
x_W = Mole fraction of *A* in bottoms.

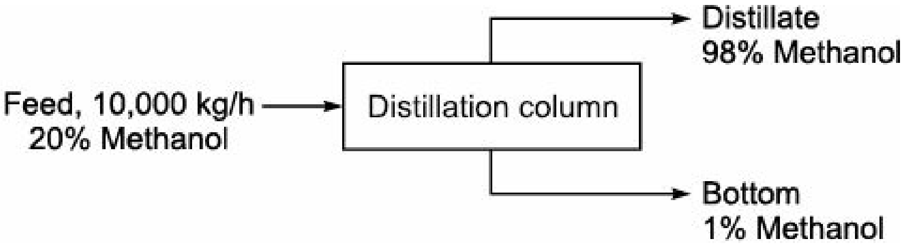
EXAMPLE 3.1 10,000 kg/h of solution containing 20% methanol is continuously fed to a distillation column. Distillate is found to contain 98% methanol and waste solution from the column carries 1%

methanol. All percentage are by weight. Calculate:

(i) The mass flow rates of distillate and bottom product

(ii) The percentage loss of methyl alcohol.

Solution: Basis: 10,000 kg/h of 20% methanol feed solution



Let x = Mass flow rates of distillate and
y = Mass flow rates of (bottom) waste solution.

Overall material balance:

$$10{,}000 = x + y \qquad \text{(i)}$$

Material balance of methanol:

$$10{,}000 \times 0.2 = x \times 0.98 + y \times 0.01$$

$$\therefore\ 2000 = 0.98x + 0.01y \qquad \text{(ii)}$$

Now $x + y = 10{,}000$ (i)

Also, $0.98x + 0.01y = 2000$ (ii)

Multiplying Eq. (i) by 0.98, we get

$$0.98x + 0.98y = 9800 \qquad \text{(iii)}$$

Subtracting Eq. (ii) from Eq. (iii), we get

$$\begin{array}{rcrcll} 0.98x & + & 0.98y & = & 9800 & \qquad \text{(iii)} \\ 0.98x & + & 0.01y & = & 2000 & \qquad \text{(ii)} \\ - & & - & & - & \\ \hline & & 0.97y & = & 7800 & \end{array}$$

Therefore,

y = 8041.2 kg/h and

x = 1958.8 kg/h

Mass flow rate of distillate = 1958.8 kg/h

Mass flow rate of bottoms = 8041.2 kg/h

Methanol in waste solution = 8041.2 × 0.01 = 80.412 kg/h

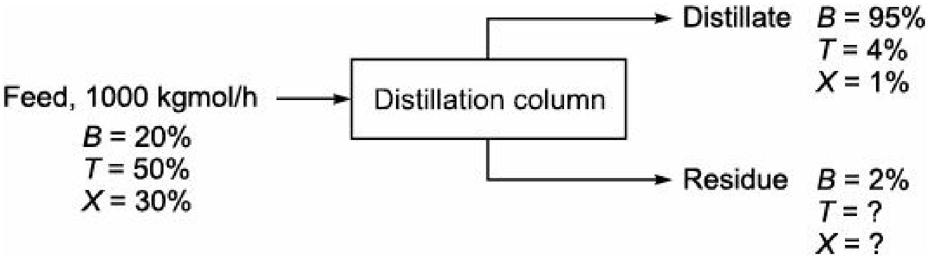
Methanol in feed solution = 10,000 × 0.2 = 2000 kg/h

Therefore, percentage loss of methanol = $\dfrac{\text{Methanol in waste solution}}{\text{Methanol in feed solution}} \times 100$

$$= \frac{80.412}{2000} \times 100 = 4.02$$

EXAMPLE 3.2 A distillation column separates 20% C_6H_6, 50 % Toluene, 30 % Xylene into 95 % C_6H_6, 4% Toluene and 1% Xylene and waste product containing 2 % C_6H_6. Calculate the quantities of distillate and residue if 1000 kgmol/h of feed is fed.

Solution: Basis: 1000 kgmol/h



Material balance:

$F = D + W$

$1000 = D + W$ (i)

Material balance of Benzene:

$1000 \times 0.2 = D \times 0.95 + W \times 0.02$

∴ $200 = 0.95D + 0.02W$ (ii)

Now, $D + W = 1000$ (i)

Also, $0.95D + 0.02W = 200$ (ii)

Multiplying Eq. (i) by 0.02, we get

$0.02D + 0.02W = 20$ (iii)

Subtracting Eq. (iii) from Eq. (ii), we get

$$\begin{array}{rcrcl} 0.95D & + & 0.02W & = & 200 \\ 0.02D & + & 0.02W & = & 20 \\ - & & - & & - \\ \hline 0.93D & & & = & 180 \end{array}$$

Therefore,

$D = 193.55$ kgmol/h

$W = 806.45$ kgmol/h

Mass flow rate of distillate = 193.55 kgmol/h

Mass flow rate of residue = 806.45 kgmol/h

Material balance for Toluene:

$1000 \times 0.5 = 193.55 \times 0.04 + 806.45 \times T_R$

∴ $T_R = 61\%$

Material balance for Xylene:

$1000 \times 0.3 = 193.55 \times 0.01 + 806.45 \times X_R$

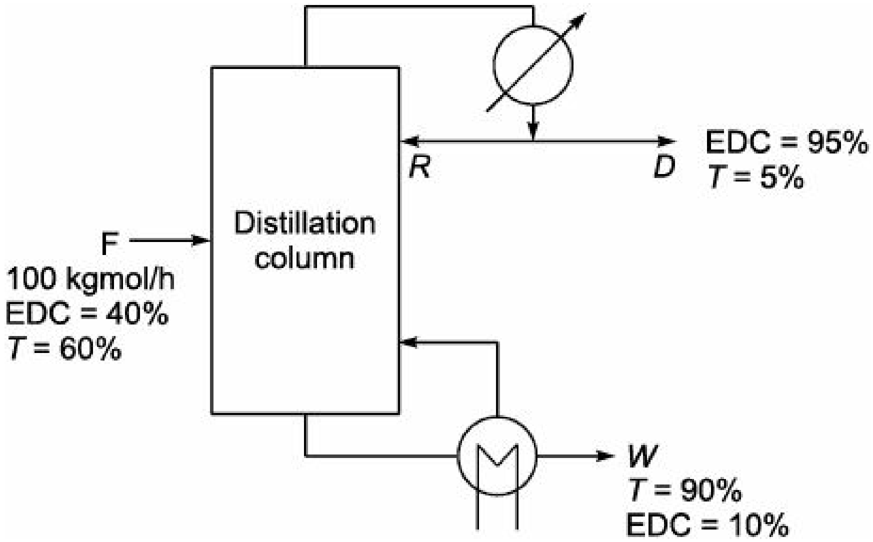
∴ $X_R = 37\%$

Quantities in distillate = 193.55 × (78 × 0.95 + 92 × 0.04 + 106 × 0.01) = 15259.48 kg

Quantities in residue = 806.45 (78 × 0.02 + 92 × 0.61 + 106 × 0.37) = 78145 kg

EXAMPLE 3.3 100 kg mol/h of 40 mole% of solution of Ethylene dichloride in Toluene is fed to middle of the distillation column. The distillate contains 95 mole% Ethylene dichloride and the bottoms consists of 90 mole% Toluene. What is the rate of flow of each stream?

Solution: Basis: 100 kgmol/h



Overall material balance:

$$F = D + W$$

$$100 = D + W \qquad \text{(i)}$$

Material balance for EDC:

$$100 \times 0.4 = D \times 0.95 + W \times 0.1$$

$$40 = 0.95D + 0.1W \qquad \text{(ii)}$$

Rearranging Eqs. (i) and (ii), we get

$$0.95D + 0.1W = 40 \qquad \text{(ii)}$$

$$D + W = 100 \qquad \text{(i)}$$

Multiplying Eq. (i) by 0.1, we get

$$\begin{array}{rcrcl} 0.95D & + & 0.1W & = & 40 \qquad \text{(ii)} \\ 0.1D & + & 0.1W & = & 10 \qquad \text{(iii)} \\ - & & - & & - \\ \hline 0.94D & & & = & 30 \end{array}$$

Therefore,

$D = 31.92$ kgmol/h and

$W = 68.08$ kgmol/h.

3.4.2 Absorption

It is a method of separation of solute gas component from its mixture using another component gas with the help of suitable liquid solvent in which solute gas is absorbed. The component gases help to remove solute gases is termed an inert gas with respect to absorption. Packed column is commonly used for absorption. A typical absorption column is shown in Figure 3.4. The material balance for absorption column can be represented by the simple block diagram as shown in Figure 3.5.

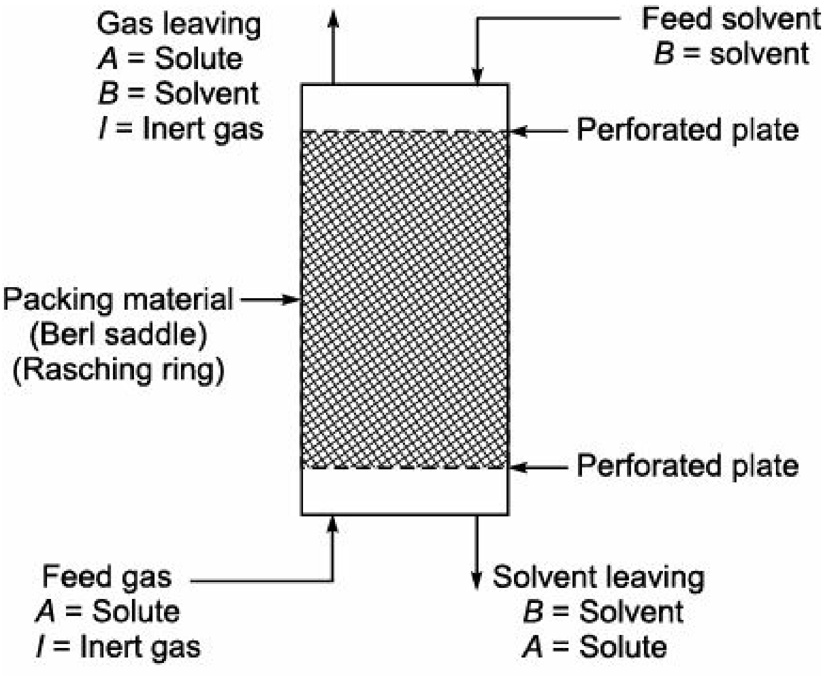


FIGURE 3.4 Absorption column.

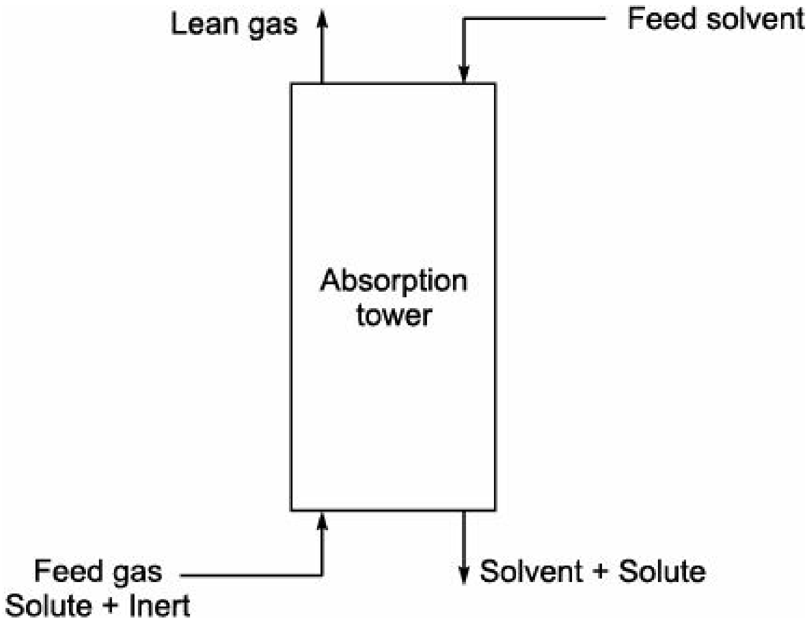


FIGURE 3.5 Block diagram of absorption column.

Material balance of Inert gas:

Inert gas in inlet = Inert gas in lean gas (3.5)

Material balance of Solute:

Solute in inlet gas = Solute in outlet gas + Solute absorbed in solvent (3.6)

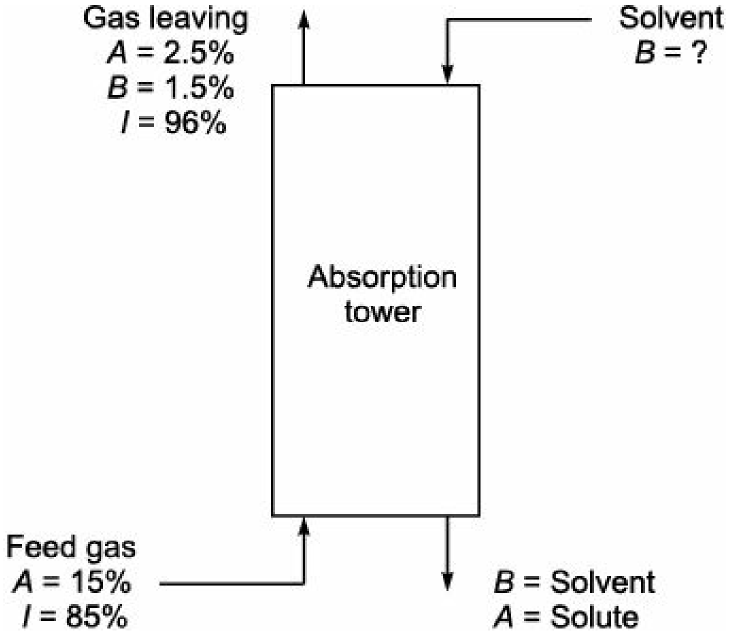
EXAMPLE 3.4 A gas mixture containing 15 mole% *A* and 85 mole% inerts is fed to an absorption tower where it is contacted with liquid solvent *B* which absorbs *A*. The mole ratio of solvent to gas entering tower is 2 : 1. The gas leaving the absorber contains 2.5% *A*, 1.5% *B*and rest inerts on mole basis. Calculate:

(i) The percentage recovery of solute ‘*A*’ and

(ii) The fraction of solvent ‘*B*’ fed to column lost in gas leaving the tower.

During the process, some solvent evaporates and gets added in gas leaving the tower.

Solution: Basis: 100 kgmol of gas entering the Absorption tower.



Mole ratio of solvent to gas entering is 2 : 1

Solvent fed to tower per unit time = $\frac{2}{1} \times 100$

= 200 kgmol

Material balance for Inert gas:

Now, Inerts in inlet gas = Inerts in lean gas (outlet gas)

Therefore, Inerts in inlet gas = 100 × 0.85 = 85 kgmol/time

Mole% of inerts in gas leaving = 100 – (2.5 + 1.5) = 96

Let x be the kgmol of gas leaving the tower per unit time.

Mole% of inerts in inlet gas = $\frac{85}{x} \times 100$ = 96

∴ x = 88.54 kgmol/time

Material balance for solute ‘*A*’:

‘*A*’ in inlet gas = ‘*A*’ in outlet gas + ‘*A*’ absorbed in solvent

∴ 100 × 0.15 = 88.54 × 0.025 + ‘*A*’ absorbed in solvent

‘*A*’ absorbed in solvent = 15 – 2.2135

= 12.7865 kgmol/time

Percentage recovery of ‘*A*’ = $\frac{\text{‘}A\text{’ absorbed}}{\text{‘}A\text{’ in inlet gas}} \times 100$

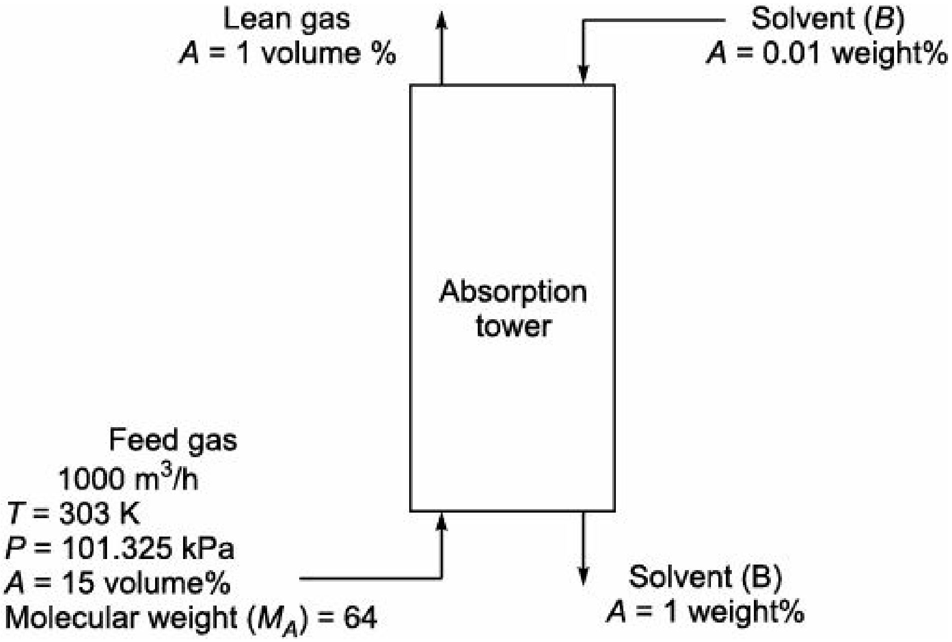
= $\frac{12.7865}{15} \times 100$ = 85.24%

Solvent ‘*B*’ in gas leaving = 88.54 × 0.015 = 1.3281 kgmol/time

The fraction of solvent ‘*B*’ fed to column lost in gas leaving = $\frac{\text{‘}B\text{’ in gas leaving}}{\text{‘}B\text{’ entering the tower}}$

= $\frac{1.3281}{200}$ = 0.0066

EXAMPLE 3.5 Absorption system utilized for absorption of solute gas '*A*' is shown schematically as follows:



Calculate the mass flow rate of solvent to the absorption tower.

Solution: Basis: 1000 m^3/h of gas entering the tower.

Molal flow rate of gas entering the tower, $n = \frac{PV}{RT}$

where,

n = Number of kgmol

P = 1 atm

V = 1000 m^3

$R = 0.082 \ \frac{m^3 \cdot atm}{kgmol \cdot K}$

T = 303 K

Therefore, $n = \frac{1 \times 1000}{0.082 \times 303}$

∴ n = 40.24 kgmol

Solute gas '*A*' in inlet gas = 40.24 × 0.15 = 6.037 kgmol/h

Inert gas *I* in inlet gas = 40.24 – 6.037 = 34.203 kgmol/h

Inert gas in lean gas = 34.203 kgmol/h

Let *y* be the kgmol/h of solute gas *A* in lean gas.

Therefore, lean gas = (34.203 + *y*) kgmol/h

Now, mole% of $A = \frac{\text{Moles of } A}{\text{Moles of lean gas}} \times 100$

∴ $1 = \frac{y}{(34.203 + y)} \times 100$

⌃ y = 0.3455 kgmol/h

Solute *A* removed from gas = Solute in inlet gas – Solute in lean gas

= 6.037 – 0.3455

= 5.6915 kgmol/h

= 5.6915 × 64

= 364.256 kg/h

Let x be the mass flow rate of solvent to the tower.

Solute balance over the Tower:

Solute ‘*A*’ in solvent at outlet – Solute ‘*A*’ in solvent at inlet = Soute ‘*A*’ removed from the gas

⌃ $0.01x - 0.0001x = 364.256$

⌃ $0.0099x = 364.256$

⌃ $x = 36{,}767.67$ kg/h

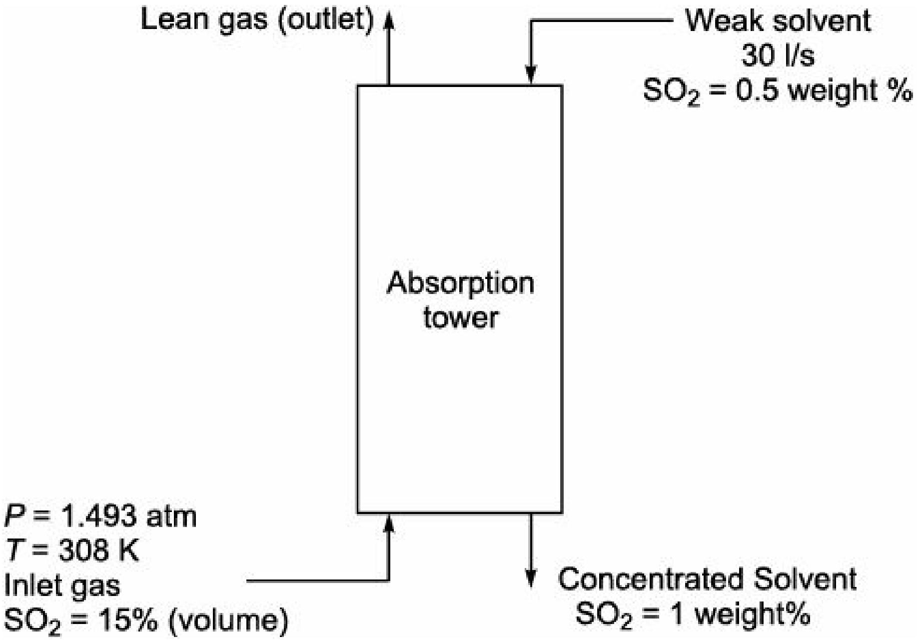
Therefore, mass flow rate of solvent to absorption tower is 36,767.67 kg/h.

EXAMPLE 3.6 In the preparation of cooking liquor for a sulphite pulp mill, an absorption tower is used for absorbing SO_2 in a weak liquor. The weak liquor enters the tower at a rate of 30 l/s from top with SO_2 concentration of 0.5% by weight and leaves from bottom with SO_2 concentration of 1% by weight. The gas stream entering the bottom of the tower contains 15% by volume of SO_2. When the gas leaves the tower from top, 70% of SO_2 get absorbed. The pressure in the tower becomes 50 kPa and operates isothermally at 308 K. Assuming that the liquor has a specific gravity of 1.0, calculate:

(i) Molal flow rate of entering gas

(ii) Volumetric flow rate of entering gas.

Solution: Basis: 30 l/s of weak liquor flowing to absorption tower.



$$\text{Mass flow rate of weak liquor} = \left(30 \times \frac{1}{1000}\right) \times 1000 = 30 \text{ kg/s}$$

SO_2 entering the tower with weak liquor = (30) × (0.005) = 0.15 kg/s

SO_2 leaving the tower with concentrated liquor = 1% by weight

Liquor free of SO_2 = 30 – 0.15 = 29.85 kg/s

Let 'x' be the kg/s of SO_2 in concentrated liquor leaving the tower, then

$$\left(\frac{x}{29.85 + x}\right) \times 100 = 1$$

$$x = 0.302 \text{ kg/s}$$

SO_2 absorbed in liquor = 0.302 – 0.15

= 0.152 kg/s

$$= \frac{0.152}{64}$$

= 0.0024 kgmol/s

Material balance for SO_2:

SO_2 removed from gas stream = SO_2 added in liquor

= 0.0024 kgmol/s

Let 'y' be the kgmol/s of SO_2 in gas entering the tower, then

$0.7y = 0.0024$

$y = 0.0034$ kgmol/s

SO_2 content of entering gas = 15% (by volume)

= 15% (by mole)

Molal flow rate of gas entering the tower = $\dfrac{0.0034}{0.15}$

= 0.023 kgmol/s

Volumetric flow rate of gas entering the tower, $V = \dfrac{nRT}{P}$

where

$n = 0.023$ kgmol/s

$R = 0.082 \dfrac{\text{m}^3 \cdot \text{atm}}{\text{kgmol} \cdot \text{K}}$

$T = 308$ K

$$V = \frac{(0.023) \times (0.082) \times 308}{1.493}$$

$$= 0.389 \text{ m}^3\text{/s}$$

Volumetric flow rate of gas entering the tower is 0.389 m^3/s.

3.4.3 Extraction

It is a method of separation of solute constituent present in solid or liquid by using a solvent. It is used in industry for separation of components of liquid mixture with the help of suitable liquid solvent.

Here, the solute from the feed solution is transferred in feed solvent heavy liquid yielding raffinate phase and extract phase. The raffinate phase rich in feed solvent is heavy liquid and the extract phase rich in feed solvent is light liquid. It does not give pure product. Hence, further processing is required. For example, consider the liquid-liquid packed column extractor. A typical packed column extractor is shown in Figure 3.6.

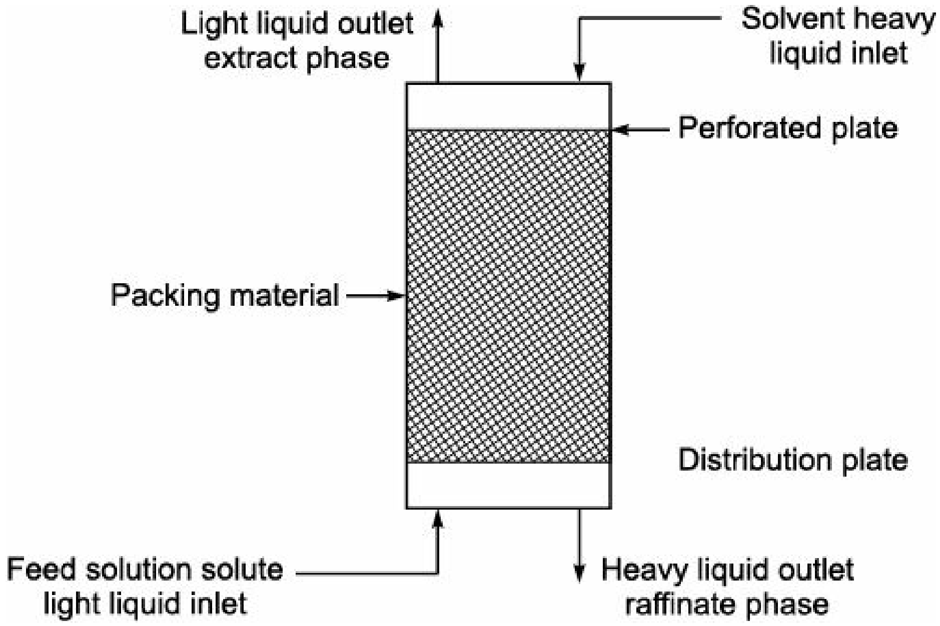


FIGURE 3.6 Packed column extraction unit.

Soluble constituents present in solids can be separated with the help of a suitable solvent by extraction process. For example, consider the oil seed extraction and leaching of valuable mineral from the ores. A typical block diagram of extraction unit is shown in Figure 3.7.

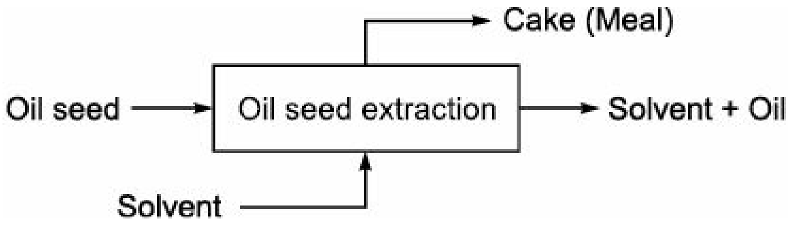


FIGURE 3.7 Block diagram of extraction unit.

Overall material balance:

Feed solution + Solvent = Extract phase + Raffinate phase (3.7)

If '*A*' is the solute to be extracted, then material balance of *A* for fresh solvent:

A in feed solution = *A* in extract phase + *A* in Raffinate phase (3.8)

Material balance for Solids:

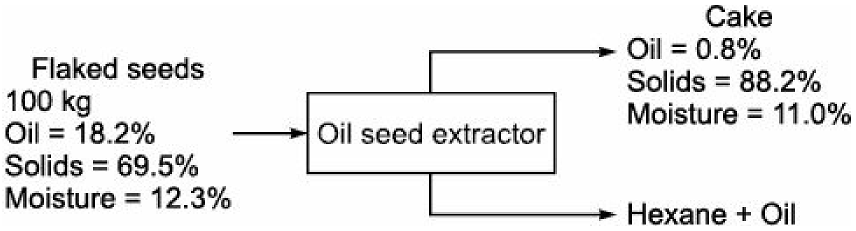
Solids in seeds = Solids in meal (if no solids in solvent) (3.9)

Material balance for Oil:

Oil in seeds = Oil in meal + Oil in solvent (3.10)

EXAMPLE 3.7 Soyabean seeds oil is extracted with hexane in a batch extractors. The flaked seeds contain 18.2% oil, 69.5% solid and 12.3% moisture. At the end of the process, cake is separated from hexane oil mixture. The cake analysis yields 0.8% oil, 88.2% solids and 11.0% moisture. Find the percentage recovery of oil. All percentage are by weight.

Solution: Basis: 100 kg of flaked seeds



Let x be the quantity of cake (meal) obtained.

Material balance for Solids:

Solids in seeds = Solids in cake

$100 \times 0.695 = x \times 0.882$

$x = 78.79$ kg

Also, Oil in the cake = 78.79×0.008

= 0.63 kg

Material balance for Oil:

Oil in seeds = Oil recovered + Oil in cake

⌃ 100×0.182 = Oil recovered + 0.63

⌃ 18.2 = Oil recovered + 0.63

Also, Oil recovered = 18.2 – 0.63

= 17.57 kg

Therefore, Percentage recovery of oil = $\dfrac{\text{Oil recovered}}{\text{Oil in seeds}} \times 100$

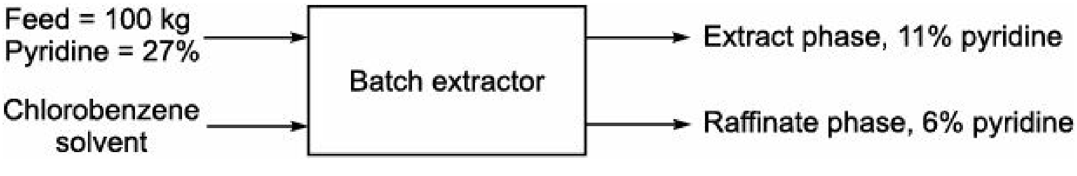
$$= \frac{17.57}{18.2} \times 100 = 96.54\%$$

EXAMPLE 3.8 An aqueous solution of pyridine containing 27% (by weight) pyridine and 73% (by weight) water is to be extracted with chlorobenzene. The feed and solvent are mixed well in batch extractor and the mixture is then allowed to stand for phase separation. The extract phase contains 11% pyridine, 88% chlorobenzene and 1% water by weight. The raffinate phase contains 6% pyridine and 94% water by weight. Calculate:

(i) The quantities of two phases (layers)

(ii) The weight ratio of solvent to feed based on 100 kg of feed.

Solution: Basis: 100 kg of feed



Let x be the quantity of extract phase, y be the quantity of raffinate phase, and z be the quantity of solvent required.

Overall material balance:

Feed + Solvent = Raffinate phase + Extract phase

⌃ $100 + z = x + y$ (i)

Material balance for Pyridine:

$100 \times 0.27 + 0 = x \times 0.11 + y \times 0.06$

⌃ $27 = 0.11x + 0.06y$

⌃ $0.11x + 0.06y = 27$ (ii)

Material balance for Water:

$100 \times 0.73 + 0 = x \times 0.01 + y \times 0.94$

⌃ $73 = 0.01x + 0.94y$

⌃ $0.01x + 0.94y = 73$ (iii)

Solving Eqs. (ii) and (iii), we get

$y = 75.48$ kg

and $x = 204.28$ kg.

The quantity of extract phase = 204.28 kg

The quantity of raffinate phase = 75.48 kg

Substituting the value of x and y in Eq. (i), we get

$100 + z = 204.28 + 75.48$

⌃ $z = 204.28 + 75.48 - 100$

$= 179.76$ kg.

The quantity of solvent required is 179.76 kg

The weight ratio of solvent to feed = $\frac{179.76}{100}$

$= 1.7976$

3.4.4 Crystallization

It is a process for the formation of solid crystals from a homogeneous solution.

In solids, particles are present randomly due to thermal agitation. In liquids it is moderate and in gases the disorderlines is highest. The liquids can transform into crystalline form whenever attraction forces between particles are strong enough to overcome the disorderlines. Crystals are commonly obtained from liquid state. For example, the formation of salt from brine. Crystallization can also proceed directly from vapour of a substance. For example, the formation of solid camphor from camphor vapour and formation of solid iodine from iodine vapour. These processes are known as sublimation.

Crystallization is used as a purification process. It is used to remove impurities from chemical products.

When a solution is heated, it loses the water vapour to the atmosphere and slowly it becomes saturated. When the solubility of a compound in a solvent exceeds the saturation solubility, the solution becomes supersaturated and the compound crystallize. Supersaturation can also be achieved by cooling the solution and by addition of a substance, which is more soluble in solvent than the solid to be crystallize.

In the absence of seed crystals, supersaturation is necessary to initiate the crystallization through the formation of nuclei. The rate of formation of crystals, particle size, its uniformity and distribution depends on the following two largely independent processes:

1. Nucleation
2. Growth of nuclei.

Solubility curves are useful tools in predicting the experimental conditions desired for crystallizing a substance from the solution. The influence of temperature on the solubility of a substance is very important, since supersaturation is achieved by reducing the temperature. If the solution is not saturated, a substance is dissolved and goes into the solution. This process continues till the solution becomes supersaturated and crystallization takes place.

There are different types of crystallizers in commerical practice:

1. Agitated batch crystallizer
2. Swenson walker crystallizer
3. Krystal crystallizer
4. Vacuum crystallizer.

A typical Agitated Batch Crystallizer is shown in Figure 3.8.

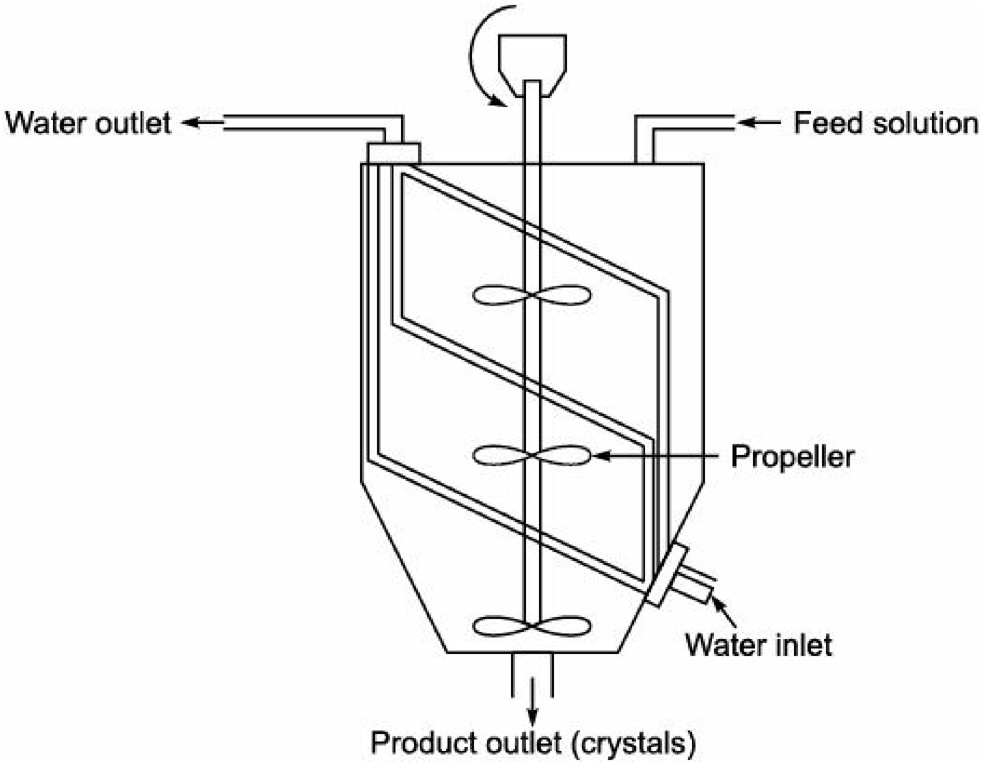


FIGURE 3.8 Agitated batch crystallizer.

The solution to be subjected for crystallization is placed in the crystallizer from the top. Cold water is passed continuously from the bottom through the pipes. In this process, temperature of the solution reduced and the solution becomes supersaturated. As the solution becomes supersaturated, formation of the crystals begins. The propeller is allowed to rotate, which serves two purposes. Firstly, it increases the rate of heat transfer thereby helps in cooling and maintains the temperature of the solution almost uniform. Secondly, it keeps fine crystal in suspension which facilitates the crystal to grow uniformly. This prevents to form large crystals or aggregates. The crystals and mother liquors are collected from the bottom of the crystallizer. Crystals are separated from mother liquor by filtration. After separation of crystals mother liquor is sent for reuse.

A simple block diagram of a crystallization unit is shown in Figure 3.9.

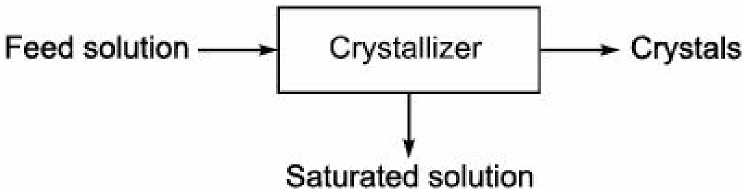


Figure 3.9 Block diagram of crystallizer.

Overall material balance:

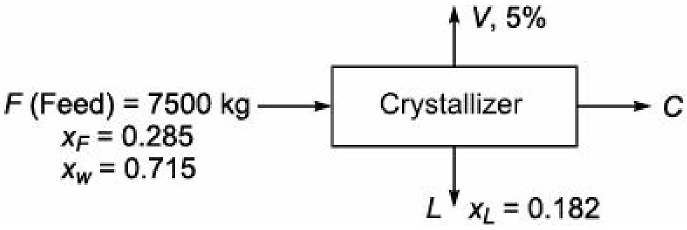
$$\text{Feed solution} = \text{Saturated solution} + \text{Crystals} \qquad (3.11)$$

Material balance for crystals (Solute):

$$\text{Crystals in feed solution} = \text{Crystals obtained} + \text{Crystals in saturated solution} \qquad (3.12)$$

EXAMPLE 3.9 A crystallizer is charged with 7500 kg of an aqueous solution at 104°C, 28.5% by weight which is anhydrous sodium sulphate. The solution is cooled. During cooling operation 5% of water originally present was lost. As a result, the crystals of $Na_2SO_4 \cdot 10H_2O$ crystallize out. The mother liquor is found to contain 18.2% by weight of anhydrous salt. Calculate the yield of crystals and quantity of mother liquor.

Solution: Basis: 7500 kg of feed.



Water present in the feed solution = 7500 × 0.715 = 5362.5 kg

Amount of water lost during cooling (V) = 5362.5 × 0.05 = 268.13 kg

Overall material balance:

$$F = V + L + C$$

$$7500 = 268.13 + L + C$$

$$L + C = 7500 - 268.13$$

$$L + C = 7231.87 \qquad \text{(i)}$$

Balance for Na_2SO_4:

$$F \cdot x_F = V \cdot x_V + L \cdot x_L + C \cdot x_C$$

$$7500 \times 0.285 = 0 + L \times 0.182 + C \times 0.441$$

$$2137.5 = 0.182L + 0.441C$$

$$0.182L + 0.441C = 2137.5 \qquad \text{(ii)}$$

Solving Eqs. (i) and (ii), we get

$$C = 3171.43 \text{ kg}$$

$$L = 4059.70 \text{ kg}$$

The yield of crystals (C) = 3171.43 kg

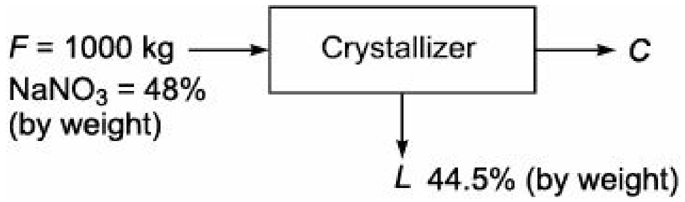
The quantity of mother liquor (L) = 4059.70 kg

EXAMPLE 3.10 A solution of $NaNO_3$ in water at 40°C contains 48% $NaNO_3$ by weight. Calculate the percentage saturation of this solution. Calculate the weight of $NaNO_3$ that may be crystallized from 1000 kg of this solution by reducing the temperature to 10°C. Calculate the percentage yield.

Solubility of $NaNO_3$ at 40°C is 51.4% by weight

Solubility of $NaNO_3$ at 10°C is 44.5% by weight.

Solution: Basis: 1000 kg of feed



Percentage saturation of $NaNO_3$ solution = $\frac{48}{51.4} \times 100$ = 93.38

Overall material balance:

$F = L + C$

$1000 = L + C$

$L + C = 1000$ (i)

Material balance for $NaNO_3$:

$1000 \times 0.48 = L \times 0.445 + C$

$480 = 0.445L + C$ (ii)

Solving Eqs. (i) and (ii), we get

$C = 63.06$ kg

$L = 936.94$ kg

Therefore, percentage yield of $NaNO_3$ = $\frac{63.06}{480} \times 100$ = 13.14

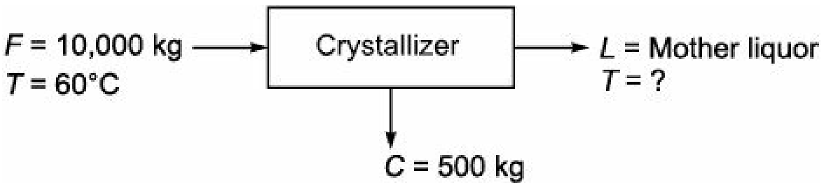
The percentage yield of $NaNO_3$ crystals is 13.14.

EXAMPLE 3.11 A tank holds 10,000 kg saturated solution of $NaHCO_3$ at 60°C. It is required to crystallize 500 kg $NaHCO_3$ from this solution. To what temperature the solution must be cooled?

Data:

Temperature (°C)	:	60	50	40	30	20	10
Solubility $\left(\frac{\text{g } NaHCO_3}{\text{100 g of water}}\right)$	:	16.4	14.45	12.70	11.11	9.6	8.15

Solution: Basis: 10,000 kg of saturated solution.



At 60 °C, the solubility of $NaHCO_3$ = $\frac{16.4}{100} \frac{\text{g } NaHCO_3}{\text{g of water}}$

$$x_F = \frac{16.4}{(16.4 + 100)}$$
$$= 0.1409$$

Overall material balance:

$F = L + C$

$10{,}000 = L + 500$

$L = 9500$ kg

Material balance for $NaHCO_3$:

$$F \dashv x_F = L \dashv x_L + C \dashv x_C$$

$$10{,}000 \times 0.1409 = 9500 \times x_L + 500 \times 1$$

$$x_L = 0.0956$$

Temperature (°C)	*Solubility* $\left(\frac{\text{g NaHCO}_3}{\text{100 g of water}}\right)$	*Weight fraction* (*x*)
60	16.40	0.1409
50	14.45	0.1263
40	12.70	0.1127
30	11.11	0.0999
20	9.60	0.0876
10	8.15	0.0754

We plot the graph temperature vs weight fraction of $NaHCO_3$. From the graph, we calculate the temperature corresponding to the value of $x_L = 0.0956$. The temperature is 27°C. The solubility of $NaHCO_3$ with respect to temperature is shown in Figure 3.10.

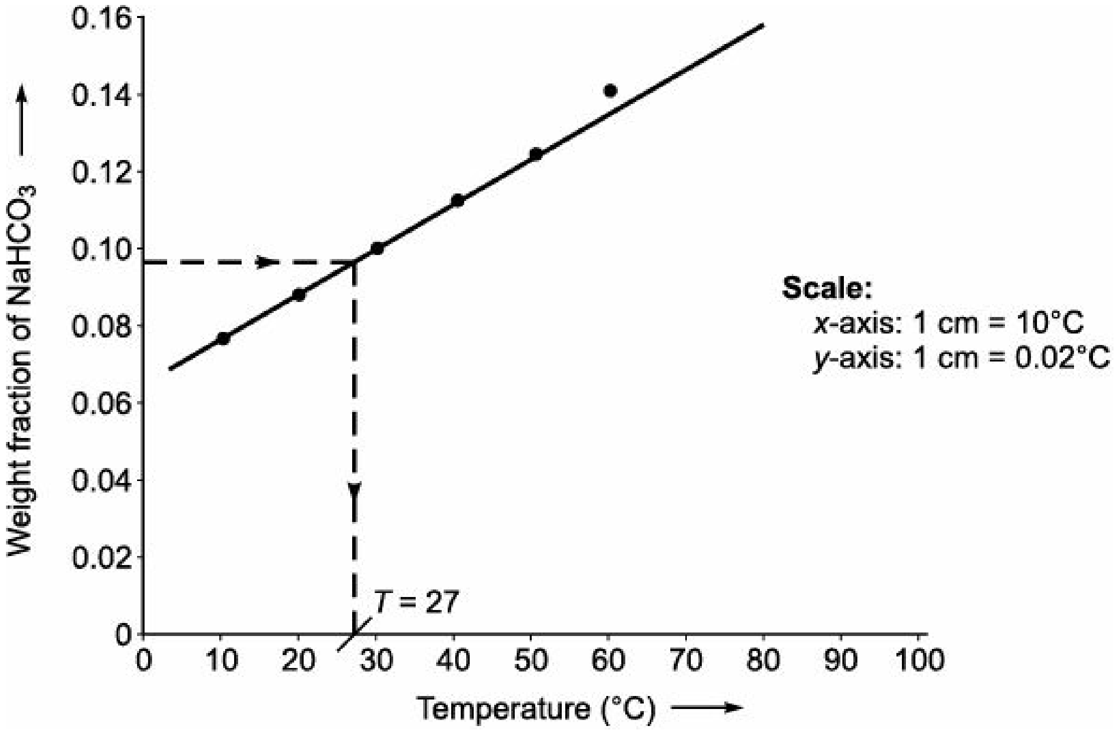


FIGURE 3.10 Solubility curve of $NaHCO_3$.

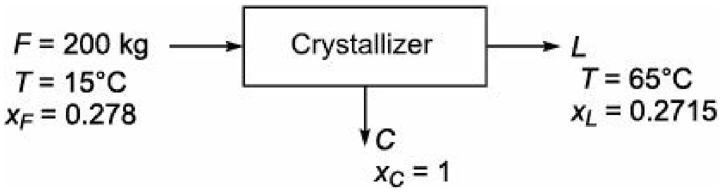
EXAMPLE 3.12 A solution of NaCl in water is saturated at 15°C. Calculate the amount of NaCl that can be dissolved by 200 kg of this solution if heated to a temperature of 65°C.

Data:

$$\text{Solubility of NaCl at 15°C} = \frac{385}{1000}\ \frac{\text{kg NaCl}}{\text{kg of water}}$$

$$\text{Solubility of NaCl at 65°C} = \frac{372.65}{1000}\ \frac{\text{kg NaCl}}{\text{kg of water}}$$

Solution: Basis: 200 kg of solution



Overall material balance:

$F = L + C$

Material balance for NaCl:

$F \dashv x_F = L \dashv x_L + \mathrm{C} \dashv x_C$

⌃ $200 \times 0.278 = (F - C) \times 0.2715 + C \times 1$

⌃ $55.6 = (200 - C) \times 0.2715 + C$

⌃ $55.6 = 54.3 - 0.2715C + C$

⌃ $55.6 = 54.3 + 0.7285C$

⌃ $0.7285C = 55.6 - 54.3$

⌃ $0.7285C = 1.3$

Therefore, $C = 1.784$ kg.

The amount of NaCl that can be dissolved if the solution is heated to a temperature of 65 °C is 1.784 kg.

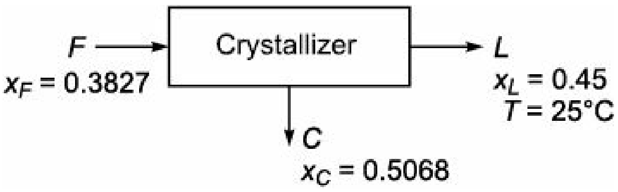
EXAMPLE 3.13 A solution of $CaCl_2$ in water contains 62 kg of $CaCl_2$ per 100 kg of water. Calculate the weight of this solution necessary to dissolve 300 kg of $CaCl_2 \dashv 6H_2O$ at 25°C.

Solubility of $CaCl_2$ at 25°C = $\frac{7.38}{1000} \frac{\text{kgmol } CaCl_2}{\text{kg of } H_2O}$

Molecular weight of $CaCl_2$ = 111

Molecular weight of $CaCl_2 \dashv 6H_2O$ = 219

Solution: Basis: 300 kg



Overall material balance:

$F = L + C$

Material balance for $CaCl_2$:

$F \dashv x_F = L \dashv x_L + C \dashv x_C$

$300 \times 0.3827 = L \times 0.45 + (F - L) \times 0.5068$

$114.81 = 0.45L + (300 - L) \times 0.5068$

$114.81 = 0.45L + 152.04 - 0.5068L$

$114.81 = 152.04 - 0.0568L$

$0.0568L = 152.04 - 114.81$

$0.0568L = 37.23$

$L = 655.46$ kg.

Solubility curves

When a particular substance (solute) dissolved in a particular solvent which yield a saturated solution is called solubility.

The solubility of a compound ranges from infinitely soluble to very poorly soluble. For example, ethanol in water is infinitely soluble or we can say fully soluble. Silver chloride in water is the example of very poorly soluble. Sometimes, very poorly soluble compound is called insoluble compound.

Solubility of a compound increases with increase of temperature. Solubility data of various compounds are necessary for basic chemical calculations involved in crystallization process. Generally, solubility data are presented through solubility curves of different compounds. Solubility curves is the plot of temperature on *x*-axis and solubility (g of solute/100 g of solvent) on *y*-axis. A typical solubility curves of a few compounds is shown in Figure 3.11.

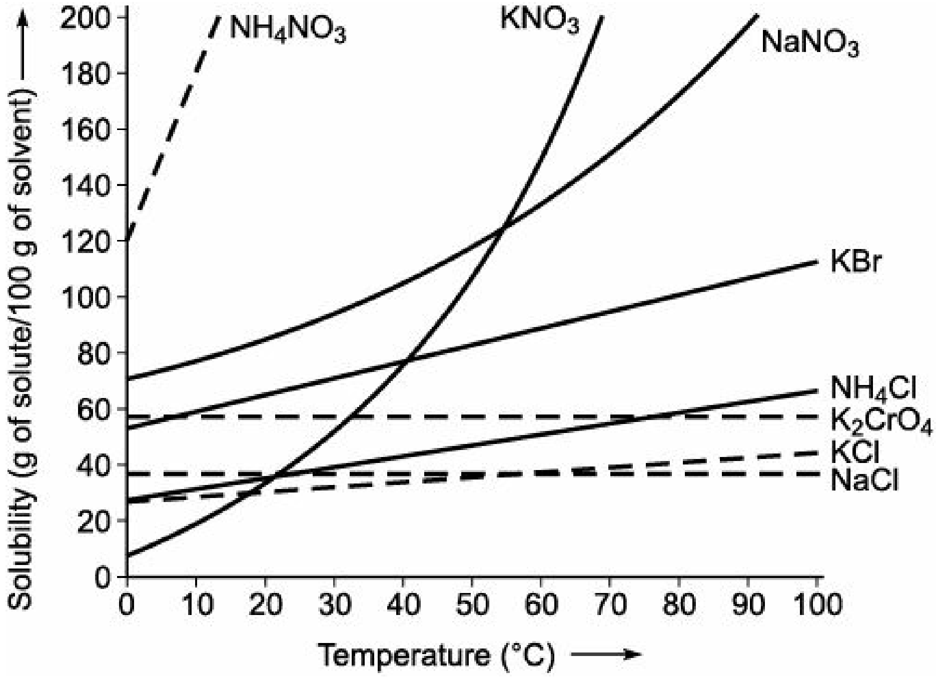


FIGURE 3.11 Solubility curves.

3.4.5 Drying

Drying is the process of removal of small amount of moisture or other liquid from a solid substance by the application of heat. The water or other liquid may be removed from the solid substances either mechanically by filtration or by thermal vaporization. The process of removal of water from the solid surface is cheaper by mechanical process rather than thermal process. Therefore, it is advisable to reduce the water present in the solid as much as it is possible before subjecting to the drying process.

In drying process, dry solid is the product. Drying of wet solid substances is possible when the surrounding environment is unsaturated with the water vapour. Hence, the humidity present in the environment is an important factor for drying solids. The various drying equipments industrially used are:

1. Tray dryer
2. Drum dryer
3. Spray dryer

4. Fluidised bed dryer
5. Vacuum dryer
6. Freeze dryer.

In tray dryer, solid materials are dried by hot air which is forced to pass over the solid substances. A typical tray dryer is shown in Figure 3.12.

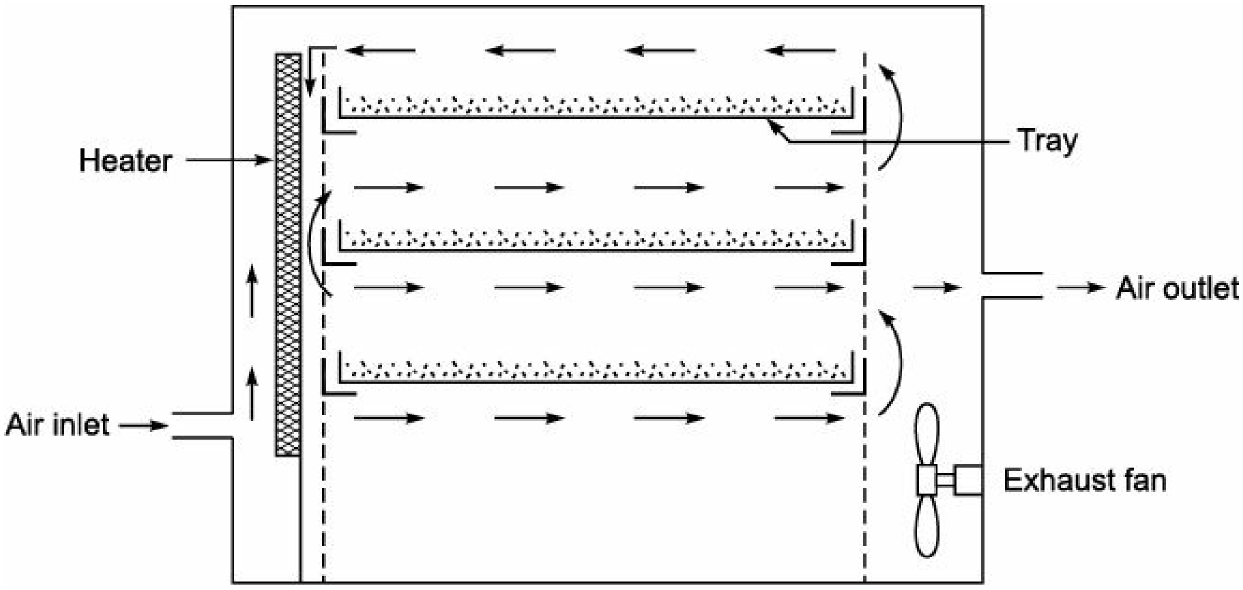


FIGURE 3.12 Tray dryer.

In tray dryer, trays are placed in the drying chamber and wet solids are loaded into it. Fresh air is introduced through the inlet, which passes over the heater. It heats the air introduced at a required temperature. The hot air is circulated surrounding the wet substances by means of a fan. The water molecules present in the solid substances move towards the upper surface of the solids and is picked up by the circulated air. This event occurs in a single pass of air and latter it moves out from the air outlet. The time of contact between wet surface of the solid and hot circulated air is short. Hence, the amount of water picked up from the wet solid surface in a single pass is very small. Therefore, 80% of the discharged air which is having some amount of heat, circulated back through the fan and 20% fresh air after heating introduced to it. In this way, uniform air flow is maintained over the material and constant temperature is achieved for drying. The process is continued until the desired moisture content is achieved. At the end of the drying period, the trays are pulled out from the drying chamber and materials are sent for packing. Sticky materials and granules are easily dried using tray dryer.

Material balance for moisture:

Moisture removed from solids = Moisture added in air

Moisture in wet solid – Moisture in dry solids = Moisture in outlet air – Moisture in inlet air (3.13)

Material balance for Solids:

Solids in wet solids (Feed) = Solids in dried product (3.14)

A simple block diagram of a dryer is shown in Figure 3.13.

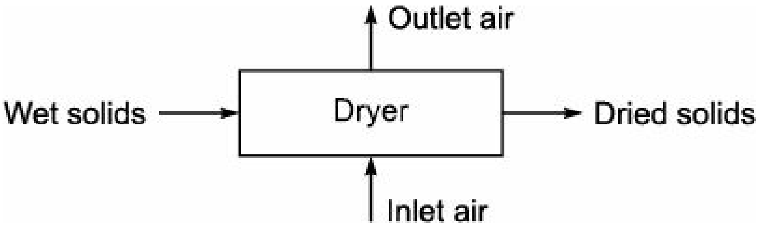


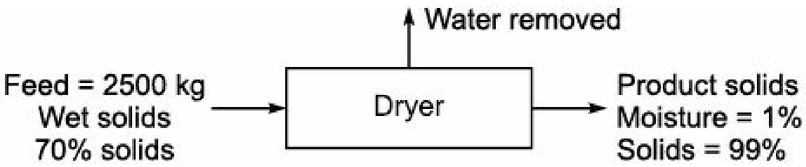
FIGURE 3.13 Block diagram of dryer.

EXAMPLE 3.14 2500 kg of wet solids containing 70% solids by weight are fed to tray dryer where it is dried by hot air. The product finally obtained is found to contain 1% moisture by weight. Calculate:

(i) Amount (in kg) of water removed from wet solids

(ii) Amount (in kg) of product obtained.

Solution: Basis: 2500 kg of wet solids



Let x be the amount of product obtained, and
y be the amount of water removed.

Material balance for Solids:

Solids in wet solids = Solids in product

$\therefore\ 2500 \times 0.70 = x \times 0.99$

$\therefore\ 1750 = 0.99x$

$\therefore\ x = 1767.68$ kg

Overall material balance:

$F = x + y$

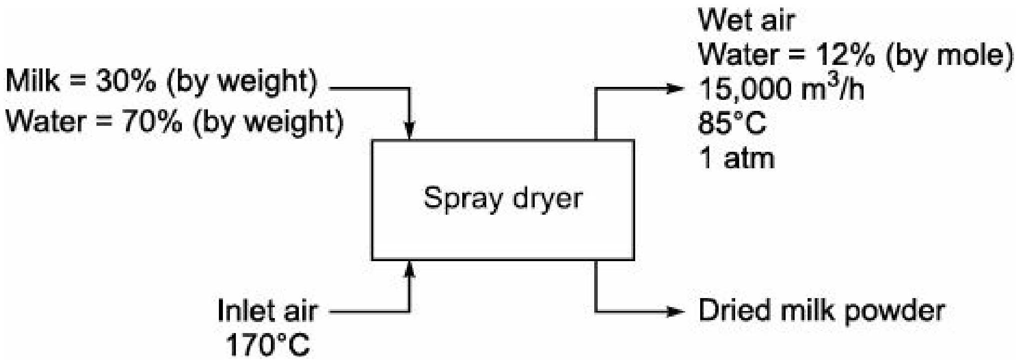
$2500 = 1767.68 + y$

$y = 732.32$ kg

Therefore, amount of water removed = 732.32 kg

Amount of product obtained = 1767.68 kg.

EXAMPLE 3.15 Milk powder is produced in a spray dryer which evaporates all of liquid (H_2O). The operation is shown in figure below.

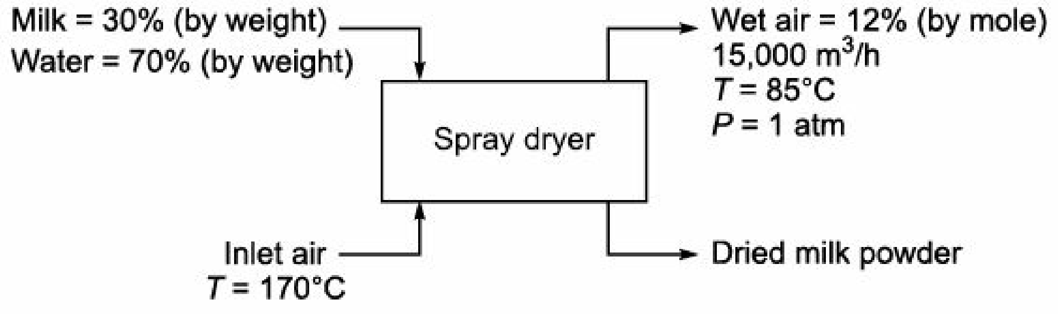


Assuming inlet air contains no water. Calculate:

(i) Production rate of powdered milk

(ii) Molal flow rate of the inlet air.

Solution: Basis: 15,000 m^3/h of wet air leaving the dryer.



Molal flow rate of air leaving the dryer,

$$n = \frac{PV}{RT}$$

where

$P = 1$ atm

$V = 15{,}000\ \text{m}^3/\text{h}$

$R = 0.082\ \dfrac{\text{m}^3\cdot\text{atm}}{\text{kgmol}\cdot\text{K}}$

$T = 358$ K

Therefore, $n = \dfrac{1 \times 15{,}000}{(0.082)(358)}$

∴ $= 510.97$ kgmol/h

Water in wet air $= 510.97 \times 0.12 = 61.32$ kgmol/h

Dry air in air leaving the dryer $= 510.97 - 61.32 = 449.65$ kgmol/h

If air entering dryer contains no water, therefore,

Air entering dryer = Dry air in air leaving the dryer

$= 449.65$ kgmol/h

Water in wet air leaving the dryer $= 61.32 \times 18 = 1103.76$ kg/h

Let x be the flow rate of milk in kg/h and y be the flow rate of powder milk in kg/h.

Material balance for water:

Water in wet air leaving the dryer = Water removed from milk

∴ $1103.76 = x \times 0.70$

∴ $x = 1576.8$ kg/h

Overall material balance for milk:

$x = y$ + water in wet air leaving

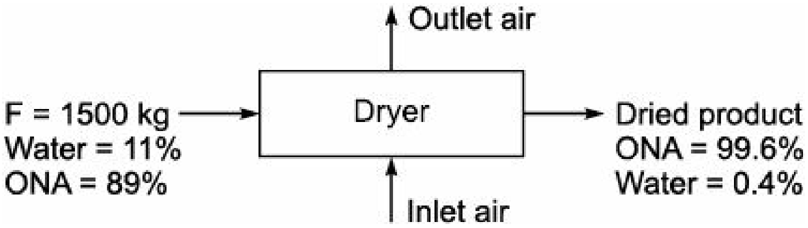
∴ $1576.8 = y + 1103.76$

∴ $y = 473.04$ kg/h

The production rate of powdered milk is 473.04 kg/h.

EXAMPLE 3.16 A tray dryer is fed with 1500 kg of wet orthonitroaniline containing 11% water. The dried product contains 99.6% orthonitroaniline and the rest is water. Find the percentage of original water that is removed in the dryer.

Solution: Basis: 1500 kg of wet orthonitroaniline



Amount of water present in the feed = 1500 × 0.11 = 165 kg

Let x be the amount of product obtained.

Material balance for Solids:

$$1500 \times 0.89 = x \times 0.966$$

$$\therefore\ 1335 = 0.996x$$

$$\therefore\ x = 1340.36 \text{ kg}$$

Amount of water present with the product = 1340.36 × 0.004 = 5.36 kg

Amount of water removed = 165 – 5.36 = 159.64 kg

$$\text{Percentage of water removed} = \frac{\text{Water removed}}{\text{Water in feed}} \times 100 = \frac{159.64}{165.00} \times 100 = 96.75$$

3.4.6 Mixing

It is a process of putting together of two or more dissimilar particles within a system. Mixing may be of the following different types:

1. Solid-solid
2. Liquid-liquid
3. Gas-gas
4. Solid-liquid.

Liquid-liquid mixing is a simple operation. It involves the formation of homogeneous system. Gas-gas mixing is seldom difficult, whereas solid-solid and solid-liquid mixing is quite difficult, because it involves the application of shear force.

Mixing device consists of a container and an impeller. These devices can be arranged to make a batch process or continuous process. A typical mixing tank is shown in Figure 3.14.

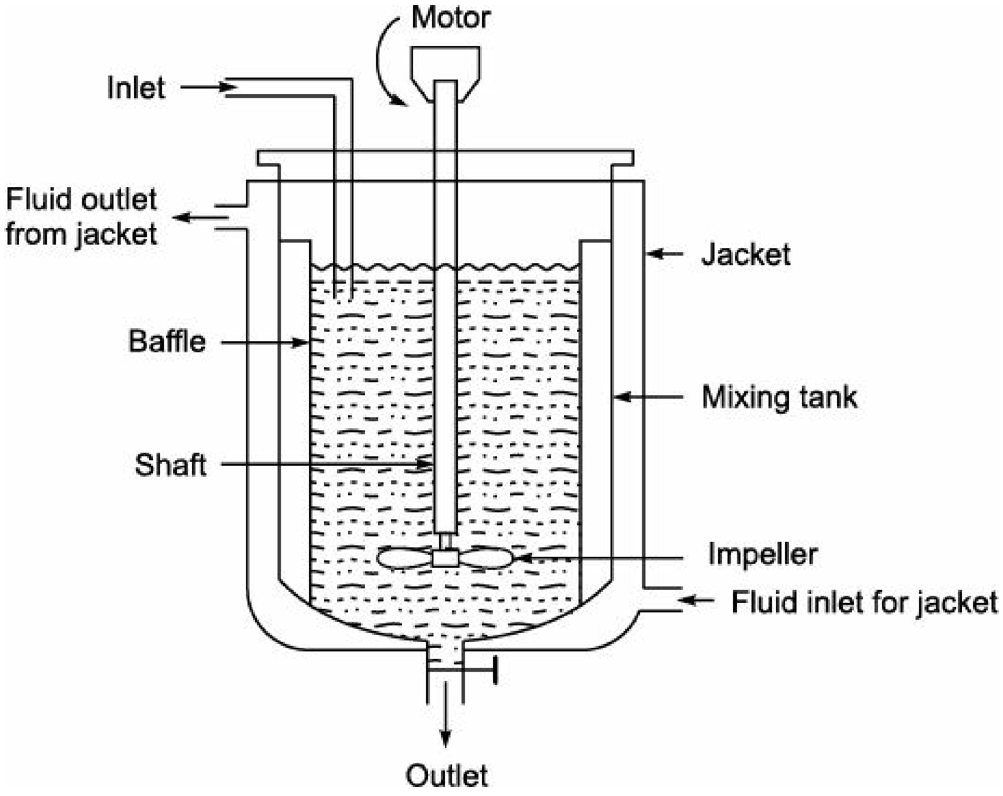


FIGURE 3.14 Mixing tank.

The mixing of fluid is done by impeller, which is mounted with the help of a shaft. The shaft is driven by a motor.

The mixing tank is a cylindrical stainless steel vessel. It is constructed with tank diameter to height ratio of 2 : 3. The top of the tank is closed with a flat plate, whereas the bottom is of round shaped to eliminate the sharp corners. The capacity of the tank depends on the nature of agitation involved with mixing. It also has inlet, outlet, jackets, baffles and temperature measuring devices. Mixing is also known by another name blending. In process industries, this operation is carried out to mix weak streams with concentrated streams. For example, the desired strength of mixed acid is prepared by blending acids of higher strength. A simple block diagram of mixing is shown in Figure 3.15.

FIGURE 3.15 Block diagram of mixing.

Overall material balance:

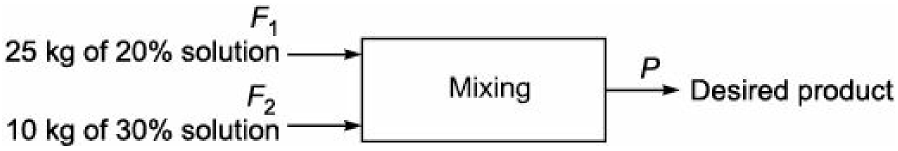
Feed stream 1 + Feed stream 2 + Feed stream 3 = Desired product (3.15)

EXAMPLE 3.17 In a mixing process, two salt solutions having the following compositions are mixed:

1. 25 kg of 20% solution
2. 10 kg of 30% solution.

Calculate the amount and the concentration of the final salt solution.

Solution: Basis: 25 kg of 20% solution and 10 kg of 30% solution.



Overall material balance:

$$F_1 + F_2 = P$$

$$\Rightarrow\ 25 + 10 = P$$

$$\Rightarrow\ P = 35 \text{ kg}$$

The amount of final salt solution = 35 kg

Material balance for salt:

$$F_1 \times x_{F1} + F_2 \times x_{F2} = P \times x_P$$

$$\Rightarrow\ 25 \times 0.20 + 10 \times 0.30 = 35 \times x_p$$

$$\Rightarrow\ 5 + 3 = 35 \times x_p$$

$$\Rightarrow\ 8 = 35 \times x_p$$

$$\Rightarrow\ x_p = 0.2286$$

Therefore, the concentration of final salt solution is 0.2286.

EXAMPLE 3.18 It is required to make 100 kg of 30% NaOH solution by mixing the following liquids; 20% NaOH solution and 36% NaOH solution. Calculate the quantities of the two solutions to be mixed.

Solution: Basis: 100 kg of 30% NaOH solution.

Overall material balance:

$$x + y = 100 \qquad \text{(i)}$$

Material balance for NaOH:

$$x \times 0.20 + y \times 0.36 = 100 \times 0.30$$

$$0.20x + 0.36y = 30 \qquad \text{(ii)}$$

Solving Eqs. (i) and (ii), we get

$$x = 37.5 \text{ kg}$$

$$y = 62.5 \text{ kg}$$

Hence, the amount of 20% NaOH solution = 37.5 kg and the amount of 36% NaOH solution = 62.5 kg.

EXAMPLE 3.19 It is required to make 1000 kg of mixed acid containing 60% H_2SO_4, 32% HNO_3 and 8% water by blending

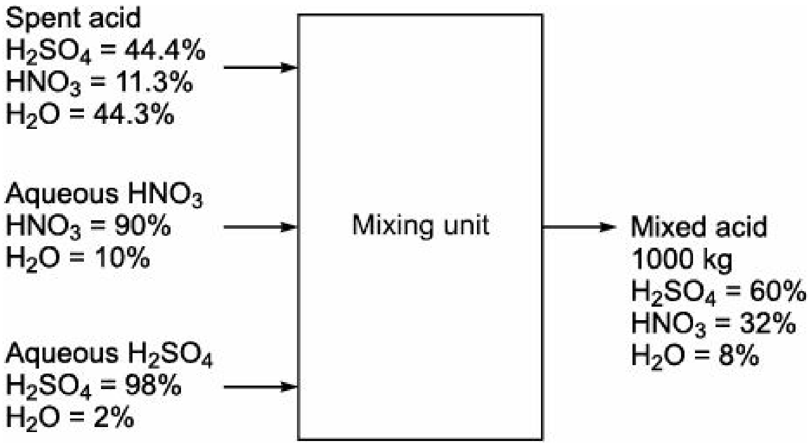
(i) The spent acid containing 11.3% HNO_3, 44.4% H_2SO_4 and 44.3% H_2O.

(ii) Aqueous 90% HNO_3 and

(iii) Aqueous H_2SO_4 98%.

All percentage are by weight. Calculate the quantities of each of the three acids required for blending.

Solution: Basis: 1000 kg of mixed acid



Let x be the amount of spent acid (in kg)

y be the amount of aqueous HNO_3 (in kg)

z be the amount of aqueous H_2SO_4 (in kg)

Overall material balance:

$$x + y + z = 1000 \qquad \text{(i)}$$

Material balance for H_2SO_4:

$$x \times 0.444 + y \times 0 + z \times 0.98 = 1000 \times 0.60$$

$$\therefore\ 0.444x + 0.98z = 600 \qquad \text{(ii)}$$

Material balance for HNO_3:

$$x \times 0.113 + y \times 0.90 + z \times 0 = 1000 \times 0.32$$

$$\therefore\ 0.113x + 0.90y = 320 \qquad \text{(iii)}$$

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

$$(x + y + z = 1000) \times 0.98$$

$$0.444x + 0.98z = 600$$

$$\begin{array}{rcrcrcl} 0.98x & + & 0.98y & + & 0.98z & = & 980 \\ 0.444x & & & + & 0.98z & = & 600 \\ - & & & & - & & - \\ \hline 0.536x & + & 0.98y & & & = & 380 \end{array} \qquad \text{(iv)}$$

From Eqs. (iii) and (iv), we get

$$(0.113x + 0.90y = 320) \times 0.536$$

$$(0.536x + 0.98y = 380) \times 0.113$$

Subtracting, we get

$$\begin{array}{rcrcl} 0.061x & + & 0.482y & = & 171.52 \\ 0.061x & + & 0.111y & = & 42.94 \\ - & & - & & - \\ \hline & & 0.371y & = & 128.58 \end{array}$$

Therefore, $y = 346.58$

$x = 71.49$

$z = 581.93$

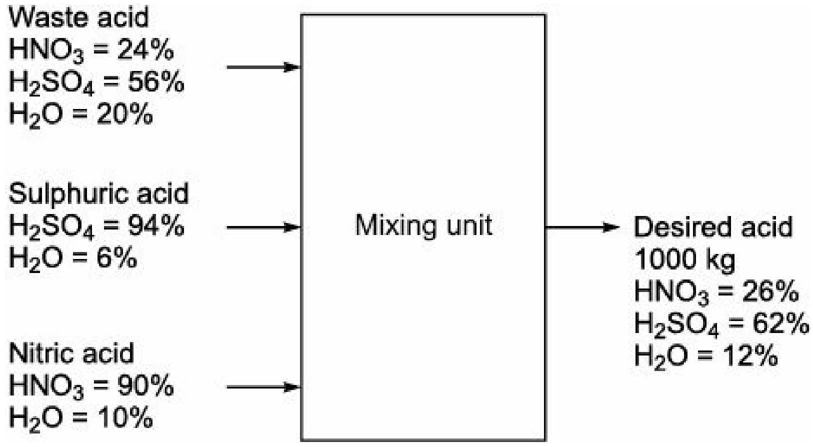
Hence, the amount of spent acid = 71.49 kg

The amount of aqueous HNO_3 = 346.58 kg

The amount of aqueous H_2SO_4 = 581.93 kg.

EXAMPLE 3.20 The waste acid from a nitrating process containing HNO_3 24%, H_2SO_4 56% and H_2O 20% by weight. This acid is to be concentrated to contain 26% HNO_3, 62% H_2SO_4 by the addition of 94% H_2SO_4 and 90% HNO_3. Calculate the weight of waste acid and concentrated acids that must be combined to obtain 1000 kg of desired mixture.

Solution: Basis: 1000 kg of desired mixed acid:



Let x be the amount of waste acid (in kg), y be the amount of sulphuric acid (in kg), z be the amount of nitric acid (in kg).

Overall material balance:

$$x + y + z = 1000 \qquad \text{(i)}$$

Material balance for H_2SO_4:

$$x \times 0.56 + y \times 0.94 + z \times 0 = 1000 \times 0.62$$

$$\hat{} \quad 0.56x + 0.94y = 620 \qquad \text{(ii)}$$

Material balance for HNO_3:

$$x \times 0.24 + y \times 0 + z \times 0.90 = 1000 \times 0.26$$

$$\hat{} \quad 0.24x + 0.9z = 260 \qquad \text{(iii)}$$

Solving Eqs. (i), (ii) and (iii), we get

x = 372.11 kg

y = 438.23 kg

and z = 189.66 kg

Therefore, the amount of waste acid = 372.11 kg.

The amount of concentrated H_2SO_4 = 438.23 kg.

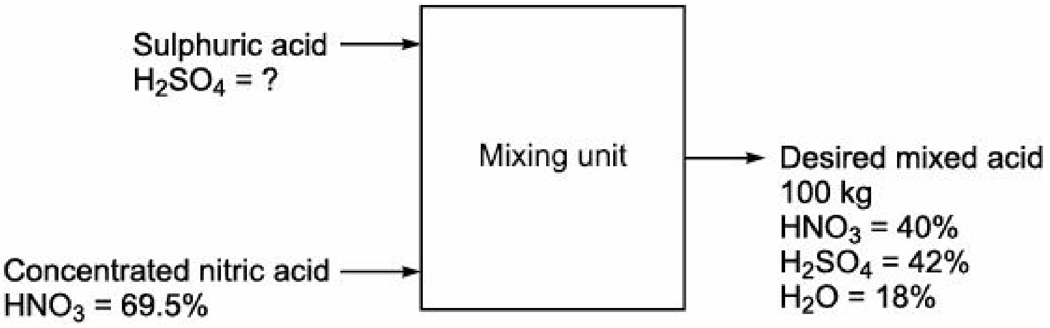
and the amount of concentrated HNO_3 = 189.66 kg.

EXAMPLE 3.21 For carrying out nitration reaction, it is desired to have mixed acid containing 40% HNO_3, 42% H_2SO_4 and 18% H_2O by weight. Nitric acid of 69.5% by weight is readily available. Calculate:

(i) Required strength of sulfuric acid to obtain the above mixed acid.

(ii) The weight ratio of nitric acid to sulfuric acid to be mixed.

Solution: Basis: 100 kg of desired mixed acid.



Let x be the amount of sulphuric acid (in kg) and y be the amount of nitric acid (in kg).

Overall material balance:

$$x + y = 100 \qquad \text{(i)}$$

Material balance for HNO_3:

$$x \times 0 + y \times 0.695 = 100 \times 0.40$$

$$\therefore \; y = 57.55 \text{ kg}$$

Material balance for H_2SO_4:

H_2SO_4 in sulphuric acid = H_2SO_4 in desired mixed acid

= 42 kg

We have,

$$x + y = 100$$

$$\therefore \; x + 57.55 = 100$$

$$\therefore \; x = 42.45 \text{ kg}$$

$$\text{Strength of } H_2SO_4 \text{ (by weight\%)} = \frac{\text{kg of } H_2SO_4 \text{ in desired acid}}{\text{kg of } H_2SO_4 \text{ in feed}} \times 100 = \frac{42}{42.45} \times 100 = 98.94$$

$$\text{Weight ratio of nitric acid to sulphuric acid} = \frac{\text{kg of nitric acid}}{\text{kg of sulphuric acid}} = \frac{57.55}{42.45} = 1.356$$

3.4.7 Evaporation

It is the process of removal of relatively large amounts of water from solution under boiling condition. The process may be of single effect or multiple effect. It is the unit operation used in process industry for concentrating weak liquor to produce thick liquor by evaporating a portion of the solvent. Some industrially used evaporators are:

1. Vertical tube evaporator
2. Horizontal tube evaporator
3. Steam jacketted kettle.

We discuss the vertical tube evaporator here.

Vertical tube evaporator

The vertical tube evaporator is made up of stainless steel in the form of vertical cylinder. It is the liquor compartment of the evaporator. The top and bottom of the evaporator is closed with a semispherical dish head. The bottom of the evaporator also may be conical. There are two tube sheet, one attached at the top and the other at the bottom of the liquor compartment. A number of vertical tubes are fastened between these tube sheets. Steam is introduced into the steam chest outside the tube. As the steam flows in, it washes the non-condensed gases and withdrawn from the vent attached at the top of the steam chest. It also washes the condensate ahead of it and withdrawn from the drips attached at the bottom of the steam chest. The feed inlet may be attached to the body of the evaporator above the tube sheets at any convenient point. The outlet for the product is made usually at the centre of the bottom dish. To view the operation of the process, most of the evaporators are provided with sight glasses. As the steam supply heat, the liquor boils, it loses density, becomes lighter and moves up through the tube. On the other hand, as the liquor comes at the upper surface of the tube, it contacts with vapours, loses temperature, becomes denser and returns through the central downtakes. The vapour is withdrawn from the top of the evaporator. This process is continued till the desired product is obtained. The vertical tube evaporator is used for both viscous and non-viscous solutions. A typical vertical tube evaporator is shown in Figure 3.16.

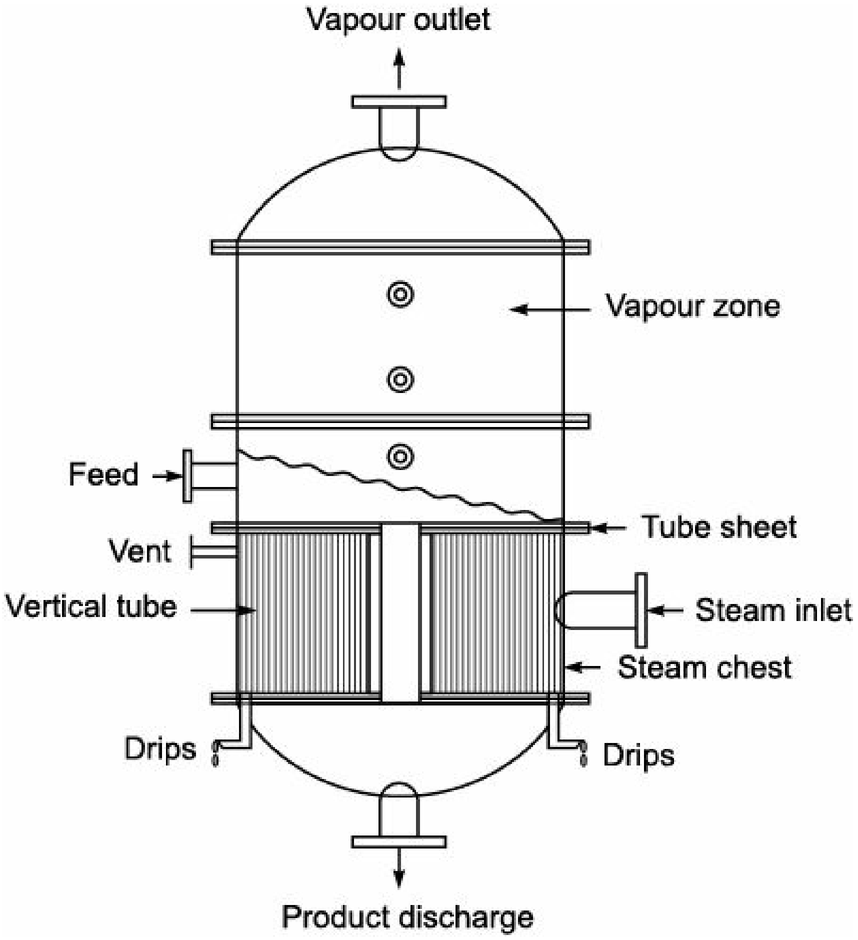


FIGURE 3.16 Vertical tube evaporator.

The block diagram of evaporator system is shown in Figure 3.17.

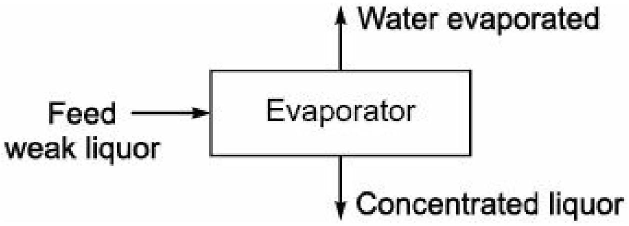


FIGURE 3.17 Block diagram of evaporator.

Overall material balance:

$$F = V + L \qquad (3.16)$$

Material balance for solids:

$$F \dashv x_F = V \dashv x_V + L \dashv x_L \qquad (3.17)$$

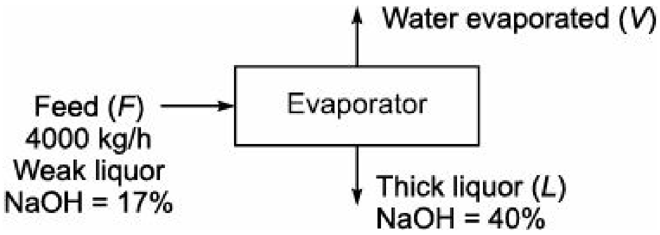
Above material balance equations may be written in terms of quantity in kg or flow rate in kg/h.

EXAMPLE 3.22 A single effect evaporator is fed with 4000 kg/h of weak liquor containing 17% caustic by weight and is concentrated to get thick liquor containing 40% by weight caustic (NaOH). Calculate:

(i) Amount (in kg) of water evaporated and

(ii) Amount (in kg) of thick liquor obtained

Solution: Basis: 4000 kg/h of weak liquor



Let x be the amount of water evaporated in kg/h and y be the amount of thick liquor in kg/h.

Overall material balance:

$$F = V + L$$

$$\wedge \quad 4000 = x + y$$

$$\wedge \quad x + y = 4000 \qquad \text{(i)}$$

Material balance for NaOH:

$$4000 \times 0.17 = x \times 0 + y \times 0.40$$

$$\wedge \quad y = 1700 \text{ kg/h}$$

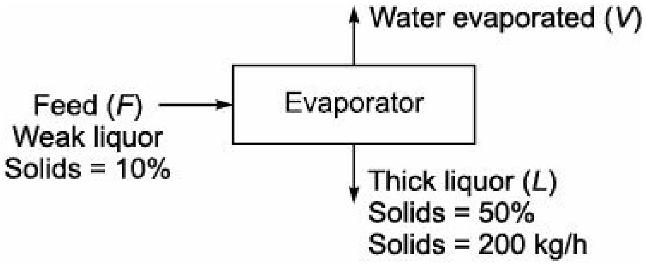
$$\wedge \quad x = 2300 \text{ kg/h}$$

Therefore, the amount of water evaporated = 2300 kg/h and the amount of thick liquor obtained = 1700 kg/h.

EXAMPLE 3.23 An evaporator system concentrating a weak liquor from 10% to 50% solids, handles 200 kg of solids per hour. If the same system is to concentrate a weak liquor from 5% to 40%, find the capacity of the system in terms of solids that can be handled per hour assuming water evaporating capacity to be same in both the cases.

Solution:

Case I Basis: 200 kg/h of solids handling capacity of evaporator.



Let x be the amount of weak liquor in kg/h and y be the amount of thick liquor in kg/h.

Overall material balance:

$F = V + L$

Material balance for Solids:

$x \times 0.10 = V \times 0 + 200$

$\therefore\ x = 2000$ kg/h

Material balance for solids in thick liquor:

$y \times 0.50 = 200$

$y = 400$ kg/h

$2000 = V + 400$

$V = 1600$ kg/h

Amount of water evaporated = 1600 kg/h

Water handling capacity in Case I and Case II is same.

Case II Basis: 1600 kg/h of water evaporated.

Let x_1 be the amount of weak liquor entering in kg/h and y_1 be the amount of thick liquor leaving in kg/h.

Overall material balance:

$F = V + L$

$\therefore\ x_1 = 1600 + y_1 \qquad \text{(i)}$

Material balance for Solids:

$x_1 \times 0.05 = 1600 \times 0 + y_1 \times 0.40$

$\therefore\ 0.05x_1 = 0.40y_1$

$\therefore\ x_1 = 8y_1 \qquad \text{(ii)}$

Substituting Eq. (ii) in Eq. (i), we get

$8y_1 = 1600 + y_1$

$7y_1 = 1600$

$\therefore\ y_1 = 228.57$ kg/h

$\therefore\ x_1 = 1828.57$ kg/h

Hence, Amount of solids in weak liquor = 1828.57 × 0.05 = 91.43 kg/h

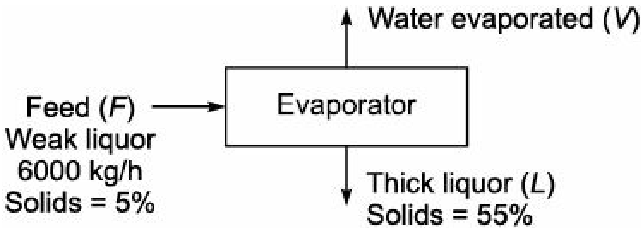
The solids handling capacity in Case II is 91.43 kg/h.

EXAMPLE 3.24 A single effect evaporator concentrating a weak liquor containing 5% solids to 55% solids (by weight) is fed with 6000 kg/h of weak liquor. Calculate:

(i) Amount (in kg) of water evaporated per hour and

(ii) Flow rate of thick liquor.

Solution: Basis: 6000 kg/h of weak liquor.



Let x be the amount of thick liquor in kg/h.

Overall material balance:

$$F = V + L$$

Material balance for Solids:

$$6000 \times 0.05 = V \times 0 + x \times 0.55$$

$$\therefore\ 300 = 0.55x$$

$$\therefore\ x = 545.45 \text{ kg/h}$$

$$\text{Also, } 6000 = V + 545.45$$

$$\therefore\ V = 5454.55 \text{ kg/h}$$

The amount of water evaporated per hour = 5454.55 kg/h

The flow rate of thick liquor = 545.45 kg/h.

3.5

Bypass Operation

The operation in which the fraction of the feed stream is diverted without chemical reaction to combined with output stream is called bypass. It is practiced in chemical industry to maintain the composition and properties of the products. For example, consider the process of concentrating the fruit juice. In this process, if the concentration of the product is higher, then the feed stream is bypassed to combine with product stream to get the desired concentration. A typical block diagram for bypass operation is shown in Figure 3.18.

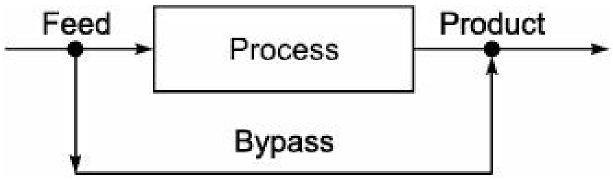


FIGURE 3.18 Bypass operation.

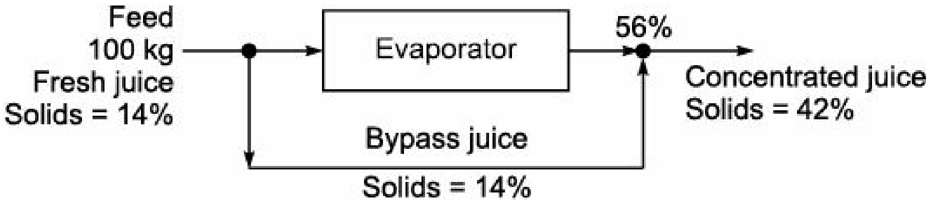
EXAMPLE 3.25 Fresh juice contains 14% solids and 86% water by weight and is to be concentrated to contain 42% solids by weight.

In a single evaporator system, it is found that the volatile constituents of juice escape with water leaving the concentrated juice 56%, with a flat taste. To overcome this problem part of the fresh juice bypass the evaporator. Calculate:

(i) The fraction of juice that bypass the evaporator

(ii) The concentrated juice produced containing 42% solids by weight.

Solution: Basis: 100 kg of fresh juice fed to process.



Let x be the amount of juice fed to the evaporator in kg; y be the amount of juice bypasses the evaporator in kg; z be the amount of juice leaving the evaporator in kg; and P be the amount of concentrated juice obtained in kg.

Overall material balance before entering the evaporator:

$x + y = 100$ (i)

Material balance for solids over evaporator:

$x \times 0.14 = z \times 0.56$

⌃ $0.14x = 0.56z$ (ii)

Overall material balance after leaving the evaporator:

$z + y = P$ (iii)

Material balance for solids after leaving the evaporator:

$z \times 0.56 + y \times 0.14 = P \times 0.42$

⌃ $0.56z + 0.14y = 0.42P$ (iv)

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

$x + y = 100$

and $0.14x = 0.56z$

⌃ $0.14(100 – y) = 0.56z$

⌃ $14 – 0.14y = 0.56z$

⌃ $0.14y + 0.56z = 14$ (v)

From Eqs. (iii) and (iv), we get

$z + y = P$

⌃ $0.56z + 0.14y = 0.42P$

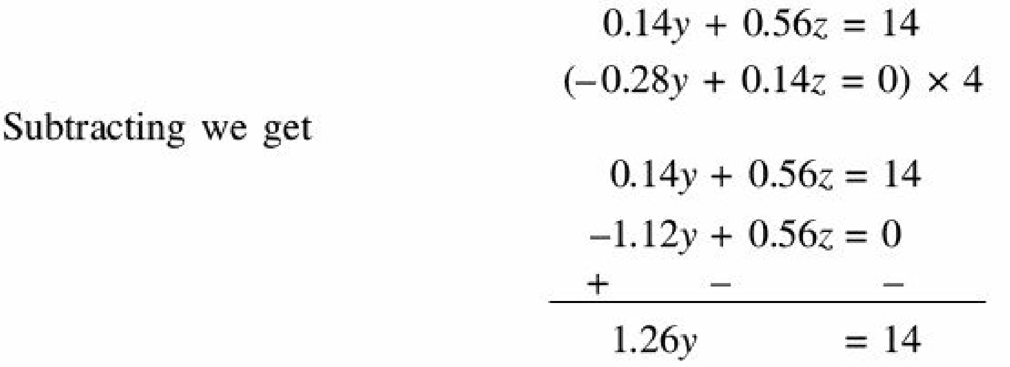
⌃ $0.56z + 0.14y = 0.42(z + y)$

⌃ $0.56z + 0.14y = 0.42z + 0.42y$

⌃ $0.14z – 0.28y = 0$

⌃ $– 0.28y + 0.14z = 0$ (vi)

From Eqs. (v) and (vi), we get



$$\begin{array}{r}0.14y + 0.56z = 14\\ (-0.28y + 0.14z = 0) \times 4\end{array}$$

Subtracting we get

$$\begin{array}{rcrcl} 0.14y & + & 0.56z & = & 14\\ -1.12y & + & 0.56z & = & 0\\ + & & - & & -\\ \hline 1.26y & & & = & 14\end{array}$$

Therefore, $y = 11.11$ kg

$z = 22.22$ kg

$x = 88.89$ kg

and $P = 33.33$ kg.

The amount of juice fed to the evaporator = 88.89 kg

The amount of juice bypasses the evaporator = 11.11 kg

The amount of juice leaving the evaporator = 22.22 kg

The amount of concentrated juice obtained = 33.33 kg.

Fraction of juice that bypasses the evaporator in percentage = $\frac{11.11}{100} \times 100$ = 11.11%

Therefore, the quantities of concentrated juice obtained = 33.33 kg.

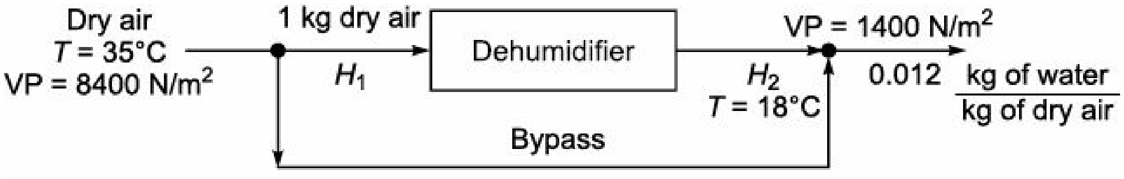
EXAMPLE 3.26 Air at 35°C saturated with water vapour is to be dehumidified. Part of the air is sent through a unit where it is cooled and some water is condensed. This air leaves the unit saturated. At 18°C, it is then mixed with air, which is bypassed the unit. The final air contains 0.012 kg water vapour per kg of dry air. The vapour pressure of water at 35°C is 8400 N/m^{2}and at 18°C is 1400 N/m^2.

Calculate:

(i) The ratio of amount of dry air bypassed to the amount of dry air sent through the dehumidifer.

(ii) The volume of final air on the basis of 20,000 m^3 of original wet air/h.

Solution: Basis: 1 kg of dry air



$$H_1 = \frac{p_w}{p_T - p_w} \times \frac{M_w}{M_A}$$

$$= \frac{8400}{(1.013 \times 10^5 - 8400)} \times \frac{18}{29}$$

$$= 0.056 \frac{\text{kg of water}}{\text{kg of dry air}}$$

$$= 0.09 \frac{\text{kgmol of water}}{\text{kgmol of dry air}}$$

$$H_2 = \frac{p_w}{p_T - p_w} \times \frac{M_w}{M_A}$$

$$= \frac{1400}{(1.013 \times 10^5 - 1400)} \times \frac{18}{29}$$

$$= 0.0087 \frac{\text{kg of water}}{\text{kg of dry air}}$$

$$= 0.014 \frac{\text{kgmol of water}}{\text{kgmol of dry air}}$$

Let x be the amount of dry air bypasses in kg.

Material balance for water after air leaving the dehumidifier:

$$1 \times 0.0087 + x \times 0.056 = (1 + x) \times 0.012 \qquad \text{(i)}$$

Solving Eq. (i), we get

$x = 0.075$ kg of dry air

Volume of wet air entering = $(1 + 0.09)(22.414) \times \left(\frac{308}{273}\right)$ = 27.546 m^3

Volume of wet air leaving = $(1 + 0.014)(22.414) \times \left(\frac{291}{273}\right)$ = 24.23 m^3

Volume of final air for 20,000 m^3 of feed, wet air/h = $20{,}000 \times \frac{24.23}{27.546}$ = 17,592.4 m^3

Therefore, the ratio of amount of dry air bypassed to the amount of dry air sent through the dehumidifier

$$= \frac{0.075}{1} = 0.075$$

3.6

Recycle Operation

We feed reactants into the reactor. But all reactants do not take part in the reaction. Some of them remains unreacted in the reactor. We take out the products and adopt a suitable method to separate the unreacted reactant from it. The unit operation in which the unreacted reactant sent back to combined with fresh feed is called Recycle Operation. The recycling is a common practice in chemical industry. This method is adopted in unit operation to maximize the utilization of raw material and to reduce the wastage.

A typical block diagram for recycle operation is shown in Figure 3.19.

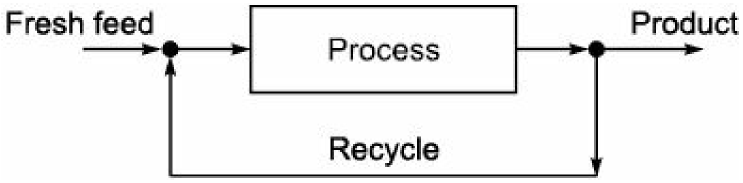
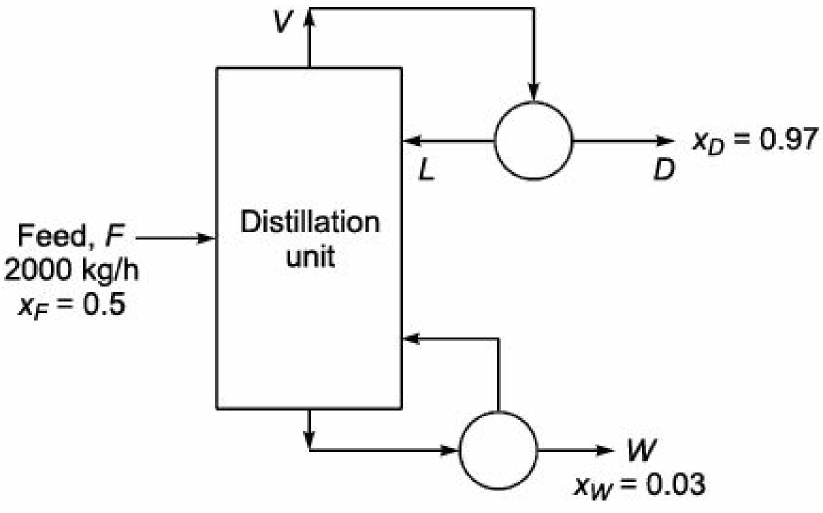


FIGURE 3.19 Recycle operation.

EXAMPLE 3.27 A continuous fractionating column separates 2000 kg/h of a solution of benzene and toluene containing 0.5 mass fraction benzene into an overhead product containing 0.97 mass fraction benzene and bottom product containing 0.03 mass fraction of benzene. A reflux ratio of 2.5 kg of reflux per kg of product is to be used. Calculate the quantity of top and bottom product in kg/h.

Solution: Basis: 2000 kg/h of a solution of benzene and toluene.



Now, $F = D + W$

Also, $F \times x_F = D \times x_D + W \times x_W$

$2000 \times 0.5 = D \times 0.97 + (2000 - D) \times 0.03$

$\therefore\ 1000 = 0.97D + 60 - 0.03D$

$\therefore\ 0.94D = 1000 - 60$

$\therefore\ D = 1000$ kg/h

$\therefore\ W = 1000$ kg/h

Reflux ratio, $R = \dfrac{L}{D}$

$\therefore\ L = 2.5 \times 1000$

or $L = 2500$ kg/h

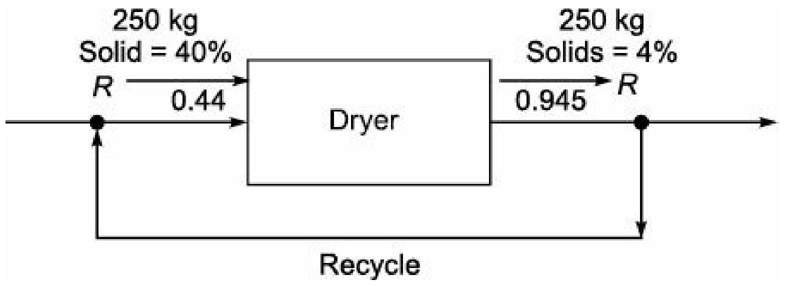
Therefore, $V = L + D$

$= 2500 + 1000$

$= 3500$ kg/h.

EXAMPLE 3.28 A wet organic pigment containing 40% by weight CCl_4 is to be dried to 4% by weight. The dryer is to operate adiabatically with fresh and recycled air entering the dryer with 0.44 kg. CCl_4 per kg of dry air. This air leaves the dryer at 0.945 kg CCl_4 per kg of dry air. The capacity of the dryer is 250 kg bone dry solid per hour. Calculate the ratio of recycle to fresh air.

Solution: Basis: 250 kg of bone dry solid



Let R be the quantity of fresh air.

Material balance for CCl_4:

$$[CCl_4 \text{ in solid} + CCl_4 \text{ in air}]_{\text{inlet}} = [CCl_4 \text{ in solid} + CCl_4 \text{ in air}]_{\text{outlet}}$$

$$250 \times \left(\frac{40}{60}\right) + R \times (0) = 250 \times \left(\frac{4}{96}\right) + R(0.945)$$

R = 165.34 kg of fresh air.

Material balance for CC1$_4$ around the drier:

Let x be the quantity of dry air.

$$250 \times \left(\frac{40}{60}\right) + (R + x) \times 0.44 = 250 \times \left(\frac{4}{96}\right) + (R + x) \times 0.945$$

Therefore,

$$166.67 + 72.75 + 0.44x = 10.42 + 156.25 + 0.945x$$

$$166.67 + 72.75 + 0.44x = 166.67 + 0.945x$$

$$x = 144.06 \text{ kg of dry air}$$

CCl_4 in recycle = 144.06 × 0.945 = 136.14 kg

Total recycle with CCl_4 = 144.06 + 136.14 = 280.2 kg

Recycle ratio, $\frac{x}{R} = \frac{280.2}{165.34} = 1.69$

EXAMPLE 3.29 In a contact process for H_2SO_4, a gas mixture of 8% (by volume) SO_3 and rest inert is sent to a absorption tower at the rate of 28 kgmol/h where it is contacted with 97.3% H_2SO_4 counter currently fed from top of the tower. 98.5% SO_3 is absorbed to produce 98% (by weight) H_2SO_4. Part of this solution is withdrawn as final product and the rest is mixed with 95.6% H_2SO_4 coming from a air drying tower to produce 97.3% H_2SO_4, which is fed from top. Calculate:

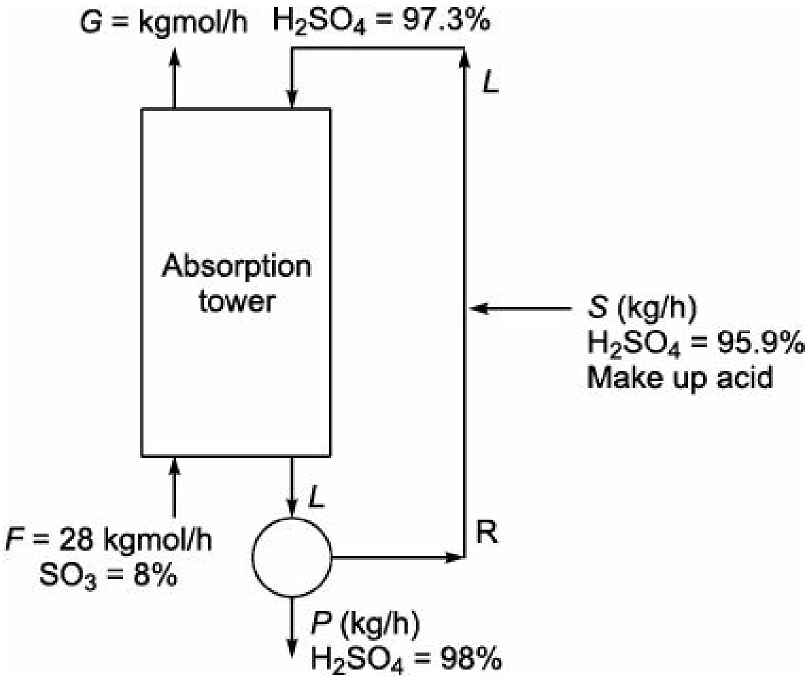
(i) Mass of 95.9% H_2SO_4 make up acid required per hour.

(ii) Mass of 97.3% H_2SO_4 fed from top of tower per hour.

(iii) Mass of 98% H_2SO_4 solution produced per hour.

(iv) Recycle ratio. Assume physical absorption.

Solution: Basis: 28 kmol/h.



Amount of inert in feed = 28 × (1 – 0.08) = 25.76 kgmol/h

Amount of SO_3 unabsorbed = 28(0.08)(1 – 0.985) = 0.0336 kgmol/h

Gas leaving the tower = 25.76 + 0.0336 = 25.7936 kgmol/h

Material balance for SO_3 over the absorption tower:

$$(28)(0.08)(80) + S(0.959)\left(\frac{80}{98}\right) = (0.0336)(80) + P(0.98)\left(\frac{80}{98}\right)$$

^ $179.2 + 0.783S = 2.688 + 0.8P$

^ $0.8P - 0.783S = 176.51$ (i)

Material balance for H_2O:

$S(1 - 0.959) = P(1 - 0.98)$

^ $0.041S = 0.02P$ (ii)

Solving Eqs. (i) and (ii), we get

$P = 422.23$ kg/h and

^ $S = 205.96$ kg/h

Overall material balance at the point of make-up acid:

$S + R = L$

^ $205.96 + R = L$ (iii)

Material balance for H_2SO_4 at the point of make-up acid:

$(205.96)(0.959) + R(0.98) = L(0.973)$

^ $197.52 + 0.98R = 0.973L$ (iv)

Solving Eqs. (iii) and (iv), we get

$L = 617.14$ kg/h

and $R = 411.18$ kg/h.

Therefore, the amount of product withdrawn, $P = 422.23$ kg/h.

The amount of make-up acid, $S = 205.96$ kg/h

The amount of feed from the top, $L = 617.14$ kg/h

The recycle ratio, $R = 0.974$.

3.7

Purging Operation

Consider, two or more reactants are continuously fed into a reactor to produce the products. Also, consider one of the reactants is impure. It contains some unwanted material. At the completion of the reaction, this unwanted material remains in a recycle stream rather than being carried out as a products. This unwanted material goes on increasing, as the substance would continuously enter the process along with fresh feed.

In this situation, if nothing were done about the unwanted material, then the attainment of steady state condition for the process is highly impossible. At this stage, a portion of the recycle stream is withdrawn and steady state condition is maintained. The withdrawal of recycle stream under this situation is called purging operation. A block diagram for purging operation is shown in Figure 3.20.

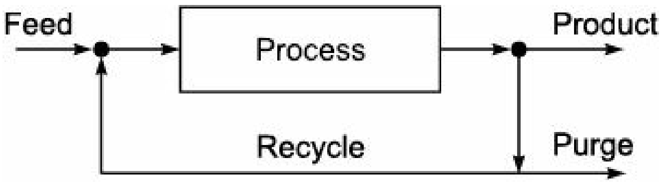


FIGURE 3.20 Purging operation.

Exercises

3.1 A distillation column separates 10,000 kg/h of a 50% Benzene and 50% Toluene mixture. The product removed from the top of the column contains 95% Benzene and the bottom of the column contains 96% Toluene. The vapour entering the condenser from the top of the column is 8000 kg/h. A portion of the product is returned to the column as reflux and the rest is withdrawn for use elsewhere. Find the ratio of the amount reflux to the product withdrawn. [**Ans.** $D = 5055$ kg/h, $W = 4945$ kg/h, $R = 0.5825$]

3.2 The feed containing 50% Benzene and 50% Toluene is fed to a distillation column at a rate of 4000 kg/h. The top product contains 95% Benzene and bottom product contains 92% Toluene. All percentage are by weight. Calculate:

(i) The mass flow rate of top and bottom products

(ii) The percentage recovery of benzene.

3.3 A continuous still is to be used separate acetic acid, water and benzene. The data are given with Figure E3.1. The data recording the Benzene composition of the feed were not taken because of instrument defect. Calculate the benzene flow in feed per hour.

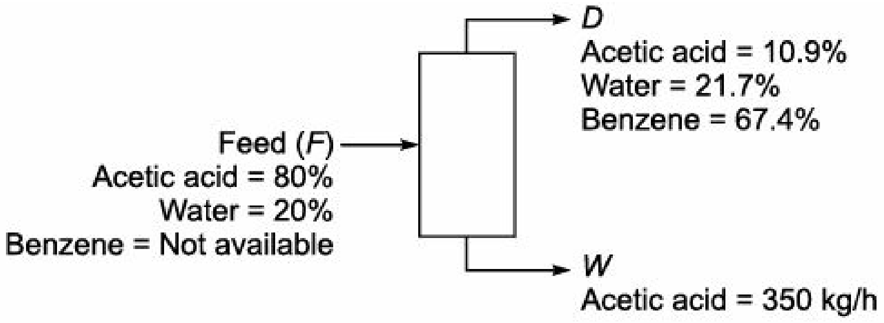


FIGURE E3.1 Continuous still.

3.4 The feed to a continuous fractionating column analyses by weight 28% Benzene and 72% Toluene. The analysis of the distillate shows 56 weight% Benzene and 4 weight% Benzene was found in the bottom product. Calculate the amount of distillate and bottom product per 1000 kg of feed per hour. Also, calculate the percentage recovery of Benzene.

3.5 A continuous fractionating column separates 1000 kg/h of a solution of Benzene and Toluene containing 0.4 mass fraction benzene into an overhead product containing 0.94 mass fraction of Benzene and bottom product containing 0.03 mass fraction of Benzene. A reflux ratio of 3.5 kg of reflux per kg of product is to be used. Calculate the quantity of top and bottom product in kg/h.

3.6 In contact process for H_2SO_4, a gas mixture of 8 volume% of SO_3 is sent to a absorption tower at the rate of 28 kgmol/h, where it is contacted with 96% H_2SO_4 counter currently fed from the top of the tower. 98.5% SO_3 is absorbed to produce 98% by weight H_2SO_4. Part of this solution is withdrawn as final product and rest of the solution is mixed with 95.9% H_2SO_4 (coming from a air drying tower) to produce 97.3% H_2SO_4 which is fed from top. Calculate:

(i) Mass of 95.9% H_2SO_4 make-up acid required per hour.

(ii) Mass of 97.3% H_2SO_4 fed from top of the tower per hour.

(iii) Mass of 98% H_2SO_4 solution, produced per hour.

Assume physical absorption

3.7 Wet air containing 4.0 mole% of water vapour is passed through a column of $CaCl_2$ pellets. The pellets absorb 97% of water and none other components of air. The column packing was initially dry and had a mass of 3.5 kg. Following 5 hours operation, the pellets are reweighed and found to have a mass of 3.6 kg. Calculate the molal flow rate of the feed gas (mol/h) and the mole fraction of water vapour in the product gas.

3.8 A mixture of Ammonia and air at a pressure of 730 mmHg and a temperature of 30°C contains 5.1% NH_3 by volume. The gas is passed at a rate of 100 m^3 per min through an absorption tower in which only NH_3 is absorbed. The gases leaves the tower at a pressure of 725 mmHg and at a temperature of 20°C and contain 0.05% NH_3 by volume. Using ideal gas law, calculate:

(i) Rate of flow of gases leaving the tower in m^3 per minutes and
(ii) Weight of NH_3 absorbed in the tower.

3.9 NH_3 and Nitrogen gas mixture contains 10% NH_3 by volume at 20°C and 760 mmHg pressure. This gas is sent into an absorption tower where 90% of the NH_3 brought originally is removed by solvent. Find out the volume of the gases after absorption if 100 m^3 of original gas mixture is sent to the tower and the outlet temperature is 15°C and pressure is 740 mmHg. Also, find average molecular weight, density and mole% of the exit gas mixtures.

3.10 In the manufacture of hydrochloric acid, a gas is obtained that contains 25% HCl and 75% air by volume. This gas is passed through an absorption system in which 98% of HCl is removed. The gas enters the system at a temperature of 50°C and pressure of 743 mmHg and leaves at 27°C and 738 mmHg. Calculate:

(i) The volume of gas leaving per 100 m^3 entering the absorption apparatus.
(ii) The percentage composition by volume of the gases leaving the absorption apparatus.

(iii) The weight of HCl removed per 100 m^3 of gas entering the apparatus.

3.11 The NH_3-air mixture containing 0.3 kg NH_3 per kg air enters into absorption system where ammonia is absorbed in water. The gas leaving the system is found to contain 0.006 kg NH_3 per kg of air. Find the percentage recovery of ammonia.

3.12 Oil is extracted from levers in a multiple counter current extractor using ethyl ether as a solvent. The fresh levers are charged into the extractor at the rate of 1000 kg/h and contains 25.6% oil. Pure ether enters from the bottom of the extractor and overflows from the extractor contains 70% oil. The underflow contains 0.23 kg solution per kg oil free solid and is known to contain 12.8% oil. Find the flow rate of ether and % recovery of oil.

3.13 Ethylene tetrachloride (C_2Cl_4), water and isopropyl alcohol separate into two phases in certain composition. The equilibrium data are given below.

Phases	C_2Cl_4	C_3H_7OH	H_2O
Water rich layer	0.9%	28%	71.1%
C_2Cl_4 rich layer	94%	5.0%	1%

To this a 100 kg mixture containing 30% C_3H_7OH and 70% water, 50 kg of C_2Cl_4 is added thoroughly, mixed and allowed to settle. Calculate the amount of the phases formed.

3.14 Phenol and water when mixed form two separate liquid phases, one rich in phenol and the other rich in water. At a temperature of 30°C, the composition of upper and lower layers are 70% and 8% by weight of phenol. If 40 kg phenol and 60 kg water are mixed and layers are allowed to separate at 30°C. What will be the weight of two layers.

3.15 In the manufacture of soda ash by the Le Blank process sodium sulphate is heated with charcoal and calcium carbonate. The resulting black ash has the following composition.

Sodium carbonate (Na_2CO_3) = 42%
Other water soluble material = 4%
Insoluble material (charcoal) = 54%.

The black ash is treated with water to extract the sodium carbonate. The solid residue from this treatment has the following composition.

Sodium carbonate (Na_2CO_3) = 5%
Other water soluble material = 85%
Water = 10%

Find the percentage of original Na_2CO_3 extracted.

3.16 2000 kg of salt solution containing 30% salt are heated to evaporate a part of H_2O and then cooled to 20°C to crystallize the salt. If 50% of dissolved salt in the original solution is to be crystallized out, calculate:

(i) The weight of water to be evaporated and

(ii) The weight of mother liquor left after crystallization.

Data:

$$\text{Solubility of salt at 20°C} = \frac{36}{100}\,\frac{\text{g salt}}{\text{g of water}}.$$

3.17 The solubility of $Ba(NO_3)_2$ at 100 °C is 34 g/100 g water and at 0°C is 5 g/100 g water. You start with 200 kg of Barium nitrate and make a saturated solution in water at 100°C. How much of water is required? If solution is cooled to 0°C, how much Barium nitrate is precipitated out of the solution?

3.18 1500 kg of 25% by weight solution of $NaNO_3$ is concentrated to saturation by evaporation. The solution is then cooled to 20°C. The crystals of $NaNO_3$ are removed by filtration. The wet crystals carry 10% by weight of mother liquor. This is dried. The solubility of $NaNO_3$ is 1.76 kg/kg of water at 100°C and 0.88 kg/kg of water at 20°C.

Calculate:

(i) The amount of water evaporated to achieve saturation at 100°C.

(ii) The weight of $NaNO_3$ obtained.

3.19 250 kg of saturated solution of $AgNO_3$ at 100°C is cooled to 20°C. The crystals are filtered out. The wet filter cake contains 80% solid crystals and 20% saturated by mass, is sent to the dryer. Calculate the amount of water that must be removed to get moisture free product. Also, calculate the weight of dry $AgNO_3$ obtained.

Solubility of $AgNO_3$ at 100°C = $\frac{952}{100}\ \frac{\text{g } AgNO_3}{\text{g of water}}$

Solubility of $AgNO_3$ at 20°C = $\frac{222}{100}\ \frac{\text{g } AgNO_3}{\text{g of water}}$.

3.20 A solution of potassium dichromate in water contains 15% $K_2Cr_2O_7$ by weight. From 500 kg of this solution, 320 kg of water is evaporated and the solution is cooled to 20°C. Calculate the amount and percentage yield of potassium dichromate crystals.

Solubility of $K_2Cr_2O_7$ at 20°C = $\frac{114.66}{1000}\ \frac{\text{kg } K_2Cr_2O_7}{\text{kg of water}}$.

3.21 A solution of $FeCl_3$ in water contains 65% by weight. Calculate the yield of $FeCl_3 \cdot 6H_2O$ crystals obtained from 800 kg solution, if cooled to 27°C. Solubility of $FeCl_3$ at 27°C is 68.3% by weight.

3.22 A solution of $NaNO_3$ in water contains 150 kg of $NaNO_3$ per 1000 kg of water. Calculate the amount of ice formed in cooling 1000 kg of this solution to a temperature of 15°C.Concentration of saturated water in $NaNO_3$ solution at

15°C = $\frac{6.2}{1000}\ \frac{\text{kgmol of } NaNO_3}{\text{kg of water}}$.

3.23 After a crystallization operation, the solution of calcium chloride in water contains 60 g of $CaCl_2$ per 100 g of water. Calculate the amount of this solution necessary to dissolve 300 kg of $CaCl_2 \cdot 6H_2O$ crystals at a temperature of 298 K.

The solubility of $CaCl_2$ at 298 K = $\frac{819.2}{1000}\ \frac{\text{g of } CaCl_2}{\text{g of water}}$.

3.24 How many kg of potassium nitrate will crystallize from 250 kg of a solution saturated at 60°C, if it is cooled to 0°C. The solubility of potassium nitrate at 60°C is 110 kg per 100 kg of water and at 0°C is 13 kg per 100 kg of water. Assume no evaporation takes place during crystallization process.

3.25 In a solution of naphthalene in benzene, the mole fraction of naphthalene is 0.15. Calculate the weight of the solution necessary to dissolve 150 kg of naphthalene at a temperature of 40°C.

Naphthalene solubility at 40°C is 56% by weight.

3.26 An aqueous solution of Na_2SO_4 is saturated at 35°C. Calculate the percentage of solute crystallized as Na_2SO_4⊣$10H_2O$ if it is cooled to 27°C. The solubility of Na_2SO_4 at 27°C is 23.5% by weight and at 35°C is 32% by weight.

3.27 What will be the yield of Glauber's salt Na_2SO_4⊣$10H_2O$ if pure 32% by weight of solution in water is cooled to 20°C without any loss due to evaporation. The solubility of Na_2SO_4 in water at 20°C is 19.2 g per 100 g of water.

3.28 1000 kg of a solution containing 50% by weight of a certain salt is cooled to 20°C in a crystallizer and the crystals formed are separated. The solubility of the salt at the crystallization temperature is 20 kg per 100 kg of water. Calculate the theoretical amount of crystals that can be produced from the solution.

3.29 A spent lye sample obtained from a soap making unit contains 9.5% glycerol and 10.2% salt. It is concentrated at a rate of 5000 kg/h in an evaporator until the solution contains 80% glycerol and 6% salt. Calculate the amount of salt crystallized in the salt box of the evaporator. What is the quantity of water evaporated? What is the quantity of salt crystallized in the evaporator?

3.30 2000 kg of a 5% slurry of calcium hydroxide in water is to be prepared by diluting a 20% slurry. Calculate the quantities required. The percentage are by weight.

3.31 A solution of sodium sulfate in water is saturated at a temperature of 40°C. Calculate the weight of Na_2SO_4⊣$10H_2O$ crystals and the percentage yield obtained by cooling 150 kgof this solution to a temperature of 5°C.

Solubility of Na_2SO_4 at 40°C = 32.6% by weight

Solubility of Na_2SO_4 at 5°C = 5.75% by weight.

3.32 A crystallizer is charged with 7500 kg of an aqueous solution at 104°C containing 29.6% by weight Na_2SO_4. The solution is cooled. During cooling, 5% of initial water is lost by evaporation. As a result, the crystals of Na_2SO_4⊣$10H_2O$ crystallize out. If the mother liquor is found to contain 18.1% Na_2SO_4 by weight, calculate the yield of crystals and the amount of mother liquor.

3.33 Calculate the amount of ice formed in cooling 1000 kg of sodium nitrate solution containing 10 parts of $NaNO_3$ per 100 parts of water by weight at –15°C. The concentration of saturated $NaNO_3$ in water solution at –15°C = $\frac{6.0}{1}\,\frac{\text{g mole}}{\text{kg of water}}$.

3.34 An aqueous solution of Na_2SO_4 is saturated at 35°C. Calculate the percentage of solute crystallized as Na_2SO_4⊣$10H_2O$ if it were cooled to 27°C.

Solubility of Na_2SO_4 at 35°C = 32.5% by weight

Solubility of Na_2SO_4 at 27°C = 23.3% by weight.

3.35 250 kg saturated solution of silver nitrate at 100°C is cooled to 20°C. The crystals are filtered out. The wet filter cake contains 80% solid crystals and 20% saturated solution by mass and is sent to a drier. Calculate the amount of water that must be removed to get a moisture free product. Also, calculate the weight of dry silver nitrate obtained.

Solubility of silver nitrate:

At 100°C: 952 g per 100 g of water

At 20°C: 222 g per 100 g of water.

3.36 Wet air containing 5.0 mole% of water vapour is passed through a column of $CaCl_2$ pellets. The pellets absorb 96% of water and none other components of air. The column packing was initially dry and had a mass of 3.5 kg. Following 5 hours operation, the pellets are reweighed and found to have a mass of 3.64 kg. Calculate the molar flow rate of the feed gas (mole/h) and the mole fraction of water vapour in the product gas.

3.37 A mixture of $CuSO_4 \cdot 5H_2O$ and $FeSO_4 \cdot 7H_2O$ weighs 200 g. It is heated in an oven at 100°C for the removal of water by hydration. The weight of the mixture after drying is found to be 120 g. Calculate the weight ratio of $CuSO_4 \cdot 5H_2O$ to $FeSO_4 \cdot 7H_2O$ in the original mixture.

3.38 A solution containing 53.6 g $MgSO_4$ per 100 g water is cooled from 80°C to 50°C. During the process 5% of the water evaporates. How many kg of $MgSO_4 \cdot 7H_2O$ crystals obtained per 100 kg of the original solution? At 50°C the solution contains only 0.4 massfraction of $MgSO_4$.

3.39 A wet solid contains 20% moisture and is to dried to a water content of 1.5% by circulating hot air over them. Fresh air contains 0.018 kg water vapour per kg dry air and exhaust air contains 0.092 kg water vapour per kg dry air. Calculate the volumetric flow rate of fresh air required per 2000 kg/h of wet solids. The fresh air is available at 27°C and 1 atm pressure.

3.40 Calcium hypochloride is produced by absorbing chlorine in milk lime. A gas produced by the Deacon Chlorine process enters the absorption apparatus at a pressure of 750 mmHgand a temperature of 24°C. The partial pressure of the chlorine is 59.5 mmHg. The remainder being inert gases. The gas leaves the absorption apparatus at a temperature of 27°C and a pressure of 742 mmHg with a partial pressure of chlorine of 1.0 mmHg. Calculate:

(i) Volume of gas leaving the apparatus per 100 ft^3 entering.

(ii) Weight of chlorine absorbed per 100 ft^3 of gas entering.

3.41 It is required to prepare 100 kg of 25%, salt solution from a two streams of solution containing 20% and 30% salt. What are the quantities of two solutions that should be mixed?

3.42 The waste acid from a nitration operation contains 23% HNO_3, 58% H_2SO_4 and 19% H_2O by weight. It is specified that the concentrated acid product should contain 26% HNO_3, 60% H_2SO_4 and 14% H_2O. If the sulphuric acid available contains 7% H_2O and HNO_3 contains 10% H_2O, then how many kg of each stream must be added to produce 1000 kgof product? **[B.U. Exam Oct. 1983]**

3.43 A sample of mixed acid contains 53% HNO_3 and 48% H_2SO_4 with 3% negative water by weight. Find the actual constituents present in it.

The above mixed acid is prepared by mixing 100% HNO_3 and Oleum. Find the required strength of Oleum and the proportion of the two acids in which they should be mixed. [**Ans.** Strength of Oleum = 22.85%]

3.44 1450 kg of a solution of methanol in water is to be prepared. The required composition being

15% by weight. One storage tank contains a methanol solution having 8% methanol and the other tank contains 30% methanol in water. All percentage are by weight. What is the percentage of the solution to be mixed from the two tanks to get the required solution?

3.45 The waste acid from a nitrating process contains 20% HNO_3, 60% H_2SO_4 and 20% H_2O by weight. The acid is to be concentrated to contain 25% HNO_3 and 60% H_2SO_4 by the addition of concentrated 95% H_2SO_4 and concentrated 90% HNO_3. Calculate the weight of waste acid and concentrated acids, which must be mixed to obtain 5000 kg of desired composition.

3.46 Waste acid from a nitrating process contains 21% HNO_3, 55% H_2SO_4 and 24% H_2O by weight. This acid is to be concentrated to contain 28% HNO_3 and 62% H_2SO_4 by the addition of concentrated H_2SO_4 containing 93% H_2SO_4 and concentrated nitric acid containing 90% HNO_3. Calculate the weight of the waste acid and concentrated acid that must be combined to obtain 500 kg of the desired mixture.

3.47 A feed stream to a process is to consist of 1000 kg/h of gas containing 30 mole% N_2 and 70 mole% H_2. The stream is obtained by blending gases from two tanks. Both tanks contains H_2–N_2 mixture. Tank 1 contains 10% N_2 and Tank 2 contains 50 mole% N_2. Calculate the required flow rates of gas mixture from tank 1 and tank 2.

3.48 The spent acid from a nitrating process contains 33% H_2SO_4, 37% HNO_3 and 30% H_2O by weight. This acid is to be strengthened by the addition of concentrated sulphuric acid containing 96% H_2SO_4 and concentrated nitric acid containing 77% HNO_3. The strengthened mixed acid is to contain 40% H_2SO_4 and 45% HNO_3. Calculate the quantities of spent acid and concentrated acids that should be mixed to yield 2500 kg of desired mixture.

3.49 A wet solid contains 25% moisture and is to be dried to a water content of 2% by circulating hot air over them. Fresh air contains 0.017 kg water vapour per kg dry air and exhaust air contains 0.11 kg water vapour per kg dry air. Calculate the volumetric flow rate of fresh air for drying 1500 kg/h of wet solids if it is available at 300 K and 1 atm pressure.

3.50 It is desired to make 200 kg of solution containing 45% salt by weight. Two solutions are available. One contains 15% salt and the other contains 65% salt. Calculate:

(i) The kg of each solution to be mixed for preparing above solution.

(ii) If 100 kg of each of the above solution is mixed, then what will be the concentration of resulting solution?

3.51 A tray dryer is fed with 2000 kg of wet orthonitroaniline containing 15% water. The dried product contains 98.5% orthonitroaniline and rest water. Find the percentage of original water that is removed in dryer.

3.52 A spent solution of chloroacetic acid in ether contains 25 mole% chloroacetic acid. It is desired to prepare 700 kg of saturated solution at 298 K. Calculate the quantities of spent solution and chloroacetic acid required to make the above solution. The solubility of chloroacetic acid in ether is 190 g per 100 g at 298 K.

3.53 Soyabean seeds are extracted with hexane in a batch extractor. The flaked seeds contain 19% oil, 70% solids and 11% moisture. At the end of the extraction process, cake is separated from the hexane oil mixture. The cake analysis yields 0.7% oil, 89.3% solids and 10% moisture. Find the percentage recovery of oil. All percentage are by weight.

3.54 The waste acid from a nitrating process contains:

HNO_3 = 21%

H_2SO_4 = 55%

H_2O = 24%

The acid is to be concentrated to contain:

HNO_3 = 28%

H_2SO_4 = 62%

H_2O = 10%

by using the addition of 90% HNO_3 and 93% H_2SO_4. All percentage are by weight. Calculate the weight of waste acid and concentrated acids to be mixed to produce 2000 kgof concentrated acid.

3.55 A stream containing 25% (by weight) methanol in water is to be diluted with a second stream containing 15% (by weight) of methanol to form a product containing 17% (by weight) CH_3OH. If the final product required is 10,000 kg. Calculate the other flow rates.

If the above compositions are taken in mole%, what will be the flow rate?

3.56 One thousand kg of a solution containing 50% by weight of a carbon salt is cooled to 20°C in a crystallizer and the crystals formed are separated. The solubility of the salt at the crystallization temperature is 20 kg/100 kg of water. Calculate the theoretical amount of crystals that can be produced from the solution.

3.57 It is required to make 2000 kg mixed acid containing 60% H_2SO_4, 32% HNO_3 and 8% H_2O by mixing (i) spent acid containing 11.4% HNO_3, 44.3% H_2SO_4 and 44.3% H_2O. (ii) aqueous 90% HNO_3 and (iii) aqueous 98% H_2SO_4 all are in weight%. Calculate the weight of these acids to be blended to set the required mixed acid.

3.58 A spent lye sample obtained from a soap making unit contains 9.6% glycerol and 10.3% salt. It is concentrated at the rate of 5000 kg/h in an evaporator until the solution contains 80% glycerol and 6% salt. Calculate the amount of salt crystallized in the salt box of the evaporator. What is the quantity of water evaporated? What is the quantity of the salt crystallized in the evaporator?

3.59 In a wood dryer, the hot air must contain at least 2% (by weight) water to prevent the wood from drying too rapidly and splitting or wraping. The original fresh air fed contains 1% (by weight) water. Wood is dried from 20% (by weight) to 5% (by weight) water. The wet air leaving the dryer contains 4% water. Calculate the amount of wet air that must be returned to the dryer if 1000 kg per hour of wet wood is dried.

3.60 Write the material balance equation for a crystallizer explaining the terms.

3.61 1000 kg of a 5% slurry of $Ca(OH)_2$ in water is to be prepared by diluting a 20% slurry. Calculate the quantities required. The percentage are by weight.

3.62 What do you understand by supersaturation? Briefly explain.

3.63 A solution of sodium sulphate in water is saturated at a temperature of 40°C. Calculate the weight of Na_2SO_4–┘$10H_2O$ crystals and the percentage yield obtained by cooling 200 kgof this solution to a temperature of 5°C.

Solubility data of sodium sulphate:

At 40°C, 32.6% Na_2SO_4

At 5°C, 5.75% Na_2SO_4.

3.64 The waste acid from a nitrating process contains 21% HNO_3, 56% H_2SO_4 and 23% H_2O by weight. This acid is to be concentrated to contain 28% HNO_3 and 62% H_2SO_4 by the addition of concentrated sulphuric acid containing 93% H_2SO_4 and concentrated nitric acid containing 90% HNO_3. Calculate the weight of waste acid and concentrated acids that must be combined to obtain 2000 kg of the desired mixture.

3.65 Write the material balance equation for a dryer explaining the terms.

3.66 If a crystallizer is charged with 7000 kg of an aqueous solution at 104°C containing 29.6% by weight Na_2SO_4. This solution is cooled. During cooling 5% of initial water is lost by evaporation. As a result, the crystals of Na_2SO_4⏌$10H_2O$ crystallize out. If the mother liquor is found to contain 18.1% by weight Na_2SO_4, calculate the yield of crystals and amount of mother liquor.

3.67 Vapour is passing continuously through a tunnel drier. The entering vapour contains 12% (by weight) water. The leaving vapour contains 3% (by weight) water. How many kilogram of water has evaporated per hour if 2000 kg/h of vapour enters the dryer. If the moisture content is made on wet basis and dry basis.

3.68 250 kg/h of 40% NH_3 liquor is flash vaporised to produce vapours containing 85% NH_3 and liquid containing 16% NH_3. All percentage are by weight. Calculate the flow rates of vapour and liquid stream leaving the flash vaporiser.

3.69 A spent lye sample obtained from a soap making unit contains 9.6% glycerol and 10.3% salt. It is concentrated at a rate of 5000 kg/h in an evaporator until the solution contains 80% glycerol and 6% salt. Calculate the amount of salt crystallized in the salt box of the evaporator. What is the quantity of water evaporated? What is the quantity of salt crystallized in the evaporator?

3.70 Write the material balance equation for an evaporator explaining the terms.

3.71 3000 kg of a 6% slurry of calcium hydroxide in water is to be prepared by diluting a 20% slurry. Calculate the quantities required. The percentage are by weight.

3.72 350 kg of saturated solution of silver nitrate at 100°C is cooled to 20°C. The crystals are filtered out. The wet filter cake contains 80% solids crystals and 20% saturated solution by mass and is sent to a dryer. Calculate the amount of water that must be removed to get a moisture free product. Also, calculate the weight of dry silver nitrate obtained.

Solubility of silver nitrate:
At 100°C: 952 g per 100 g of water
At 20°C: 222 g per 100 g of water.

3.73 A multiple effect evaporator system has a capacity of processing 2000 kg/d of solid caustic soda when it concentrate weak liquor from 5 to 30% (by on weight basis). When the same plant is fed with 8% weak liquor and if it is concentrated to 50% (both on weight basis), find the capacity of the plant in terms of solid caustic soda assuming that the water evaporating capacity to be same in both the cases.

3.74 In a textile industry, it is desired to make 25% caustic soda solution by weight for a mercerisation process. Due to very high heat of dissolution of caustic soda in water, the above solution is prepared by two step process. First, in a dissolution tank, caustic soda is dissolved in the correct quantity of water to prepare 48% (by weight) solution. After complete dissolution and cooling, this solution is taken to a dilution tank where some more water is added to produce 25% caustic soda solution. Assume no loss of water by evaporation. Calculate the weight ratio of water fed to dissolution tank to bypass water to dilution tank.

3.75 Stock containing 2.5 kg water per kg of dry material is to be dried to 0.1 kg water per kgof dry material. For each kg of dry material 60 kg of dry air passes through the drier. The air leaves at 0.05 humidity. The fresh air is supplied at 0.015 humidity. Calculate the fraction of air recirculated.

3.76 Fresh orange juice contains 13% solids and rest water. It is concentrated to contain 45% solids. In the present process, the evaporator is bypassed with a fraction of fresh juice. Juice that enters the evaporator is concentrated to 60% solids and is mixed with bypass juice to achieve the desired final concentration. Calculate the amount of final juice per kg of fresh juice fed to the process and the fraction of the feed in percentage that bypasses the evaporator.

3.77 Air at 35°C saturated with water vapour is to be dehumidified. Part of the air is sent through a unit where it is cooled and some water vapour is condensed. This air leaves the unit saturated at 15°C. It is then remixed with the air which bypassed the unit. The final air should have a humidity of 0.01. The vapour pressure of water at 35°C is 5.622 kN/m^2 and 15°C is 1.704 kN/m^2. The entire operation is performed at standard atmospheric pressure. Calculate:

(i) The ratio of kg of dry air bypassed to the kg of dry air passed through the unit.

(ii) The volume of final air on the basis of 10,000 m^3 per hour of original air.

(iii) The rate of condensation of water vapour on the same basis as above.

3.78 A mixture of $CuSO_4 \cdot 5H_2O$ and $FeSO_4 \cdot 7H_2O$ weighs 100 g. It is heated in an oven at 110°C to evaporate the water of hydration. The weight of the mixture after the removal of water is 59.78 g. Calculate the weight per cent of each compound in the original mixture.

3.79 Sea water containing 3.5% by weight salts passes through series of 10 evaporators. Roughly, equal quantities of water is evaporated in each evaporator which are condensed to get fresh water. The brine which is coming out at the last evaporator contains 5% salt. If the sea water fed into system is 50,000 kg/h. Calculate the fractional yield of fresh water and weight per cent of salt in solution leaving the 4th and 8th evaporator.

3.80 Fresh orange juice containing 12% by weight solids and rest is water. This juice is to be concentrated to 48% of solids. It was found that it was better to concentrate to 58% and mix with fresh juice to get the required 48% solids product. If so, calculate the amount of concentrated juice produced per 1000 kg of fresh juice fed to the processor and fraction of feed that by passes. Instead of 58% concentration, if concentrated to 68% and then mixed with the fresh juice, find out the required quantity of bypass.

3.81 Write the material balance equation for a distillation column explaining the terms.

3.82 A solid material with 15% of H_2O is dried to 7% H_2O under the following condition. Fresh air is mixed with recycled air and is blown over the solids. The fresh air contains 0.01 kg of H_2O per kg of dry air and the recycled air which is a part of the air leaving the dryer contains 0.1 kg of H_2O per kg of dry air. The proportions of fresh and recycled air are adjusted so that the mixture entering the dryer contains 0.03 kg of H_2O per kg of dry air. On the basis of 100 kg of wet solid material, calculate:

(i) Weight of water removed from wet solid

(ii) Weight of dry air in the fresh air
(iii) Weight of dry air in the recycled air
(iv) Draw a diagram of the process indicating the amounts of material in each stream.

3.83 Acetone which is being used as a solvent in an extraction process, is being recovered by evaporation into a stream of nitrogen. The nitrogen enters the evaporator at a temperature of 30°C containing acetone such that its dew point is 10°C. It leaves at a temperature of 25°C with a dew point of 20°C. The barometric pressure is constant at 760 mmHg. Calculate:
(i) The weight of acetone evaporated per 1000 litres of gases entering the evaporator.
(ii) The volume of the gases leaving the evaporator per 1000 litres entering. The vapour pressure of acetone is 116 mmHg at 10°C and 185 mmHg at 20°C.

3.84 Stock containing 1.5 kg water per kg of dry material is to be dried to 0.1 kg of water per kg of dry material. For each kg of dry material, 60 kg of dry air passes through the dryer. The air leaves at a humidity of 0.05. The fresh air is supplied at a humidity of 0.015. Calculate the fraction of air recirculated.

3.85 A crystallizer is charged with 8000 kg of an aqueous solution at 104°C containing 29.6% Na_2SO_4 by weight. The solution is cooled. During the cooling, 8% of initial water is lost by evaporation. As a result, the crystals of $Na_2SO_4 \cdot 10H_2O$ crystallize out. If the mother liquor is found to contain 18.2% Na_2SO_4 by weight. Calculate:
(i) The yield of crystals
(ii) The amount of mother liquor.

3.86 The spent acid from a nitrating process contains 33% H_2SO_4, 36% HNO_3 and 31% H_2O. This is to be strengthened by the addition of concentrated H_2SO_4 containing 95% H_2SO_4 and nitric acid containing 78% HNO_3. The final strengths of mixed acid should contain 40% H_2SO_4, 43% HNO_3 and rest water. Calculate:
(i) The amount of spent acid
(ii) The amount of concentrate H_2SO_4 and
(iii) The amount of concentrated HNO_3 to be mixed to produce 1500 kg of the desired acid.

3.87 The solubility of Barium nitrate at 100 °C is 34 g/100 g of H_2O and at 0°C 5 g/100 gof H_2O. If you start with 100 g of Barium nitrate and make a saturated solution in water at 100°C, how much of water is required? If this solution is cooled to 0°C, how much barium nitrate is precipitated out of solution?

3.88 The slabs of building boards contain 17% moisture by weight. They are dried to a water content of 1% by weight by circulating hot air over them. The fresh air contains 0.17 kgof moisture per kg. The exhaust air contains 0.075 kg of moisture per kg. How many cubic metres of fresh air at standard conditions must be used per 2000 kg of the wet building boards?

3.89 What will be the yield of Hypo ($Na_2S_2O_3 \cdot 5H_2O$) if 100 kg of a 42% solution is cooled to 25°C?

Data: The solubility of $Na_2S_2O_3$ at 25°C is 70 parts per 100 parts of water.

3.90 A distillation column separates a feed mixture containing 30% benzene, 50% toluene and rest is xylene on mole basis into a overhead fraction containing 95% benzene, 4% toluene and rest xylene and a bottom product of 2% benzene. The reflux ratio is 2.5 on the basis of 1000 kgmoles of feed per hour. Calculate:

(i) Mass top and bottom products
(ii) Recovery of benzene in top product and xylene in bottom product
(iii) Recycle ratio.

3.91 Define and explain the following terms.

(i) Recycle ratio
(ii) Bypass
(iii) Purge ratio

3.92 In the operation of a synthetic ammonia plant, a 1 : 3 mixture of nitrogen and hydrogen is fed to the converter resulting in a 25% conversion to ammonia. The ammonia formed is separated by condensation and the unconverted gases are recycled to the reactor. The initial nitrogen and hydrogen mixture contains 0.2 parts of argon per 100 parts of nitrogen and hydrogen mixture. The toleration limit of argon entering the reactor is assumed to be 5 parts per 100 parts of nitrogen and hydrogen by volume. Estimate the fraction of the recycle that must be continuously purged. Find also the recycle ratio and purge ratio.

3.93 A stock containing 1.4 kg of water per kg of dry material is to be dried to 0.08 kg of water per kg of dry material. For each kg of dry material, 60 kg of dry air passes through the dryer. The air leaves at a humidity of 0.055. The fresh air is supplied at a humidity of 0.014. Calculate the fraction of air recirculated.

4

Material Balance with Chemical Reactions

4.1

Introduction

A series of steps are involved in the process of manufacturing, a desired products from a given raw material. During this process chemical and physical changes take place. The step at which chemical and physical changes take place, the raw material undergoes a series of chemical reactions. This reaction may proceed with or without catalyst. The catalyst may help to increase the rate of reaction. The desired product and by-product are the heart of the process which decide the economy as a whole. In design point of view, the material balance of the chemical reactor where chemical reaction takes place is very important. The presence of single or multiple chemical reaction makes the material balance calculations complicated. Because, in this calculations, in addition to input and output term formation or disappearances term is also involved. In such processes, the total mass of various components entering the reactor is equal to the total mass of the components leaving the reactor. While doing the material balance with chemical reaction, it is very convenient to use molar unit as a basis of calculations. In general, material balance calculations should be based on limiting reactant. The chemical reactions and limiting reactants help in calculations of quantity of new products formed.

4.2

Principle of Stoichiometry

Stoichiometry is the basic tools for chemical process calculation. In chemical reactions, the mass and volumetric relationships are generally presented together with the basic units for expressing the changes in mass and compositions. This relationship is designated as the principle of stoichiometry. It is the branch of science that deals with the relative quantities of reactants and products in chemical reactions. While applying the stoichiometry, a balanced chemical reaction is used for calculations. In balanced chemical reaction, the relations among the reactants and products forms a ratio of whole numbers. For example, consider the chemical reaction

$$N_2 + 3H_2 = 2NH_3 \qquad (4.1)$$

In this reaction, 1 molecule of Nitrogen reacts with 3 molecules of Hydrogen to produce 2 molecules of Ammonia. The nitrogen, hydrogen and ammonia are in the stoichiometric proportion of 1 : 3 : 2. The stoichiometry of a chemical reaction can be used to calculate the amount of products that can be produced with the given quantity of reactants. For example, if 100 kgmol of nitrogen and 300 kgmol of hydrogen is given as reactants, we can produce 200 kgmol of ammonia. The stoichiometry can help in calculations of theoretical percentage yield of the products. It can also help in predicting the component diluted in a standard solution. It works on the basis of the law of conservation of mass.

4.2.1 Stoichiometric Coefficient

The number that proceeds with the molecular formula of each component involved in a chemical reaction is called stoichiometric coefficient. It is also called stoichiometric number. For example, consider the chemical reaction

$$N_2 + 3H_2 = 2NH_3$$

In this chemical reaction, the stoichiometric coefficient of N_2 is one, stoichiometric coefficient of H_2 is three and that of NH_3 is two.

4.2.2 Stoichiometric Ratio

The ratio of stoichiometric number of two components or molecular species that are involved in a balanced chemical reaction is called stoichiometric ratio. For example, consider the chemical reaction

$$N_2 + 3H_2 = 2NH_3$$

In this reaction, the stoichiometric ratio of H_2 to N_2 is 3 : 1.

4.2.3 Stoichiometric Proportion

Consider a general chemical reaction

$$B + C \rightleftharpoons P \qquad (4.2)$$

Here, B and C are the reactants and P is the product. When the ratio of moles of component B to the moles of component C is equal to the stoichiometric ratio obtained from the balanced chemical reaction, then the chemical reaction is said to be in stoichiometric proportion. For example, consider the chemical reaction

$$N_2 + 3H_2 = 2NH_3$$

In this chemical reaction, N_2 and H_2 are the reactants and NH_3 is the product.

If 100 kgmol of N_2 and 300 kgmol of H_2 are fed to the reactor to produce 200 kgmol of NH_3, then the reaction is said to be in stoichiometric proportion. If the reactants fed to the reactor in stoichiometric proportion, there is a possibility of reaction goes to completion. On the other hand, if 100 kgmol of N_2 and 200 kgmol of H_2 are fed to the reactor to produce 200 kgmol of NH_3, then the reaction is said to be not in stoichiometric proportion and the reaction will not proceed towards the completion.

4.3

Limiting Reactants

If two or more reactants are fed to a chemical reactor according to the stoichiometric proportion to produce the products, then the reactant that would disappear first at completion of reaction is called limiting reactant. The limiting reactant is always present in lesser quantity than the other reactants. It is the decision making component at which the reaction can proceed. For example, consider the chemical reaction

$$N_2 + 3H_2 = 2NH_3$$

In this reaction, 1 kgmol of N_2 and 3 kgmol of H_2 are reacted to produce 2 kgmol of NH_3. Here, N_2 and H_2 are the reactants. The quantity of N_2 added is less than the quantity of H_2. Hence, N_2 is the limiting reactant.

4.4

Excess Reactant

If two or more reactants are fed to a chemical reactor according to the stoichiometric proportion to produce the products, then the reactant that would still remain at the completion of reaction is called excess reactant. The excess reactant is always present in larger quantity than the other reactants. The excess reactant remains because there is nothing left with which it can react. For example, consider the chemical reaction

$$C_3H_8 + 5O_2 = 3CO_2 + 4H_2O \qquad (4.3)$$

In this chemical reaction, C_3H_8 and O_2 are reactants. O_2 is supplied from the air which is always in excess of theoretical requirement. Hence, C_3H_8 is a limiting reactant and O_2 is an excess reactant.

4.4.1 Percentage of Excess Reactants

If two or more reactants are fed to a chemical reactor according to the stoichiometric proportion to produce the product, then the reactant that would still remain in excess that of theoretically required is expressed in terms of per cent of excess. For example, consider the chemical reaction

$$C_3H_8 + 5O_2 = 3CO_2 + 4H_2O$$

In this chemical reaction C_3H_8 is the limiting reactant and O_2 is the excess reactant.

Let us assume,

$A = C_3H_8$ (reactant)

$B = O_2$ (reactant)

$C = CO_2$ (product)

$D = H_2O$ (product)

Then, the percentage of excess reactant may be expressed as

$$\text{Percentage of excess } B = \frac{\text{Moles of } B \text{ supplied} - \text{Moles of } B \text{ theoretically required}}{\text{Moles of } B \text{ theoretically required}} \times 100$$

(4.4)

The moles of excess reactant theoretically required are the moles of B that would corresponds to stoichiometric proportion. The quantity of excess reactant actually supplied may be calculated as

$$\text{Moles of } B \text{ actually supplied} = \text{Moles of } B \text{ theoretically required} \times \left(1 + \frac{\%\text{ excess of } B}{100}\right)$$

(4.5)

The quantity of excess reactant for a specific balanced chemical reaction can be calculated based on the quantity of limiting reactant fed to the reactor. For example, consider 100 kgmol/h of C_3H_8 and 600 kgmol/h of O_2 are fed to a chemical reactor. As per the stoichiometric proportion, the excess reactant O_2 would have to be 500 kgmol/h. Hence, O_2 is supplied in excess. The percentage of excess O_2 can be calculated as

$$\text{Percentage of excess } O_2 = \frac{\text{Moles of } O_2 \text{ supplied} - \text{Moles of } O_2 \text{ theoretically required}}{\text{Moles of } O_2 \text{ theoretically required}} \times 100$$

(4.6)

$$= \frac{600 - 500}{500} \times 100 = 20\%$$

4.5

Inerts

A substance that does not react with other elements or compounds is called an inert material. For example, Helium. It does not participate in the chemical reaction. Hence, helium is an inert material.
When an inert gas is added into a gas phase equilibrium reaction at constant volume, it does not help in shifting the reaction. This is because, the addition of non-reactive gas into a gas phase equilibrium reaction does not change the partial pressure of other gases in the reactor. It is true that by adding inert gas into the reactor, the total pressure of the system increases, but this total pressure does not have any effect on the equilibrium constant. However, if the volume of the system is allowed to increase, the partial pressure of all gaseous component decreases resulting in a shift towards the greater number of molecules of gas.
For example, consider the chemical reaction

$$N_2 + 3H_2 = 2NH_3$$

Here, in this chemical reaction, more number of molecules are present in the left hand side of the reaction. Hence, at higher pressure, the reaction is favourable for forward direction and vice versa. Neon and Argon are the other inert gases which are commonly used in chemical process industries.

4.6

Percentage Conversion

If two or more reactants are fed to a chemical reactor according to the stoichiometric proportion to produce the products, then one of the reactant would disappear at the completion of reaction is called limiting reactant. This limiting reactant is the key component for the calculation of percentage conversion. For example, consider the general chemical reaction

$$A + B \rightleftharpoons P \qquad (4.7)$$

where

A = Limiting reactant

B = Excess reactant

The ratio of amount of A reacted to the amount of A fed to the reactor is called conversion. The amount of A may be in moles or weight. The percentage conversion may by mathematically expressed as

$$\text{Percentage conversion of } A = \frac{\text{Moles of `}A\text{' reacted}}{\text{Moles of `}A\text{' in feed}} \times 100 \qquad (4.8)$$

For example, consider 100 kgmol of N_2 reacts with 250 kgmol of H_2 to produce 200 kgmolof NH_3. Assume, 85 kgmol of N_2 is consumed during the reaction. Then, the percentage conversion of N_2 can be calculated as

$$\text{Percentage conversion} = \frac{85}{100} \times 100 \qquad (4.9)$$

= 85

The fraction unreacted is 0.15.

4.7

Percentage Yield

The total amount of limiting reactant reacts to produce the amount of desired product is called yield. It is generally expressed in percentage. For example, consider the general chemical reactions

$$A \rightleftarrows P \qquad (4.10)$$

$$A \rightleftarrows R \qquad (4.11)$$

where

P = Desired product
R = Undesired product
A = Limiting reactant

The percentage yield can be expressed as

$$\%\ \text{yield} = \frac{\text{Moles of } A \text{ reacted to produce `}P\text{'}}{\text{Moles of } A \text{ totally reacted}} \times 100 \qquad (4.12)$$

4.8

Selectivity

When two or more reactants are fed to a chemical reactor to produce the products, then products may formed through multiple reactions.

Among these multiple reactions, the desired reaction predominate over the side reaction resulting wanted and unwanted products. The information regarding the amount of wanted product formed by desired reaction relative to amount of unwanted product formed by side reaction is called selectivity. For example, consider the general multiple reactions

$$A \rightleftarrows P \qquad (4.10)$$

$$A \rightleftarrows R \qquad (4.11)$$

where

A = Reactant
P = Wanted product
R = Unwanted product

In this multiple chemical reactions, the selectivity of P relative to R may be expressed as

$$\text{Selectivity of } P \text{ relative to } R = \frac{\text{kgmol of } P \text{ formed}}{\text{kgmol of } R \text{ formed}} \qquad (4.13)$$

The unwanted product has reverse effect on the economy of the process. Hence, it is required to minimize the unwanted products by using suitable catalyst or inhibitors.

4.9

Material Balance with Single Chemical Reaction

If material balance of a system involved with a single chemical reaction which is responsible to produce the product is called material balance with single chemical reaction.

For example, consider the process of manufacturing of sulfur trioxide by reacting sulfur dioxide with oxygen. The equation of chemical reaction may be expressed as

$$SO_2 + \frac{1}{2}O_2 = SO_3 \qquad (4.14)$$

where

SO_2 = Sulfur dioxide

O_2 = Oxygen

SO_3 = Sulfur trioxide

In this chemical reaction 1 kgmol of SO_2 react with ½ kgmol O_2 to give rise to 1 kgmol of SO_3. Here, SO_2 is the limiting reactant, O_2 is the excess reactant and SO_3 is the product. The excess reactant O_2 is generally supplied from air.

4.10

Material Balance with Multiple Chemical Reaction

If material balance of a system involves with two or more chemical reactions which are responsible to produce the desired products is called material balance with multiple chemical reactions. For example, consider the process of manufacturing of ethylene oxide by reacting ethylene and oxygen. Here, ethylene reacts with Oxygen as per the following reactions.

Reaction 1: $C_2H_4 + ½O_2 \rightleftharpoons C_2H_4O$

Reaction 2: $C_2H_4 + 3O_2 \rightleftharpoons 2CO_2 + 2H_2O$

This is a multiple chemical reaction. To calculate the percentage conversion of ethylene in this process, we need to calculate the total amount of ethylene reacted. To calculate the total amount of ethylene reacted, we have to calculate the ethylene reacted from reaction 1 and reaction 2 independently and then to add it up. Multiple reaction either may be of series type or parallel type.

4.11

Bypass Operation

The unit operation with chemical reaction in which fraction of the feed stream is diverted to combine with product stream is called bypass operation. It is practical in industry to maintain the desired properties of the product. For example, consider the dehumidification operation. In this process, part of the dry air is passed through the dehumidifier and mixed with air which bypasses the unit to achieve the desired humidity in air. A typical block diagram of bypass operation is shown in Figure 4.1.

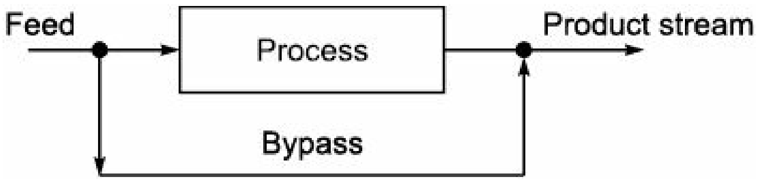


FIGURE 4.1 Bypass operation.

4.12

Recycle Operation

We feed reactants into the reactor. But all the reactants do not participate in the reactions. Some reactant remains unreacted in the reactor. We adopt a suitable method to separate the unreacted reactants from the products. The unit operation with chemical reaction in which, the unreacted reactant sent back to combined with fresh feed is called Recycle operation. This is common practice in chemical industry. The recycle operation is adopted in unit operation to maximize the utilization of raw material and to reduce the wastage. A typical block diagram of recycle operation is shown in Figure 4.2.

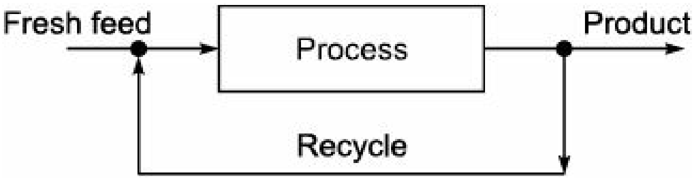


FIGURE 4.2 Recycle operation.

4.13

Purging Operation

Consider two or more reactants which are continuously fed into a chemical reactor to produce the products. Also, consider one of the reactants is impure. It contains unwanted materials. At the completion of the chemical reaction, this unwanted material remains in a recycle stream rather than being withdrawn as a product. This unwanted material goes on increasing, as the substance would continuously enter the process along with fresh feed. In this situation, if nothing were done about the unwanted material accumulated, then the attainment of steady state condition for the process is highly impossible.

At this stage, a portion of the recycle stream is withdrawn and steady state condition is maintained. The removal of impurities along with recycle stream partly under this situation is called purging operation. A typical block diagram for purging operation is shown in Figure 4.3.

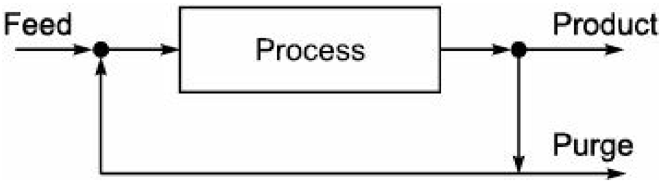


FIGURE 4.3 Purging operation.

EXAMPLE 4.1 Ammonia is produced by the following reaction.

$$N_2 + 3H_2 \rightleftharpoons 2NH_3$$

Calculate:

(i) The molal flow rate of hydrogen corresponding to nitrogen feed rate of 50 kgmol/h if they are fed in stoichiometric proportion.

(ii) The amount of ammonia produced per hour if percentage conversion is 30 and nitrogen feed rate is 50 kgmol/h.

Solution: Basis: 50 kgmol/h of nitrogen is fed to the reactor.

Reaction: $N_2 + 3H_2 \rightarrow 2NH_3$

Stoichiometric proportion of N_2 to H_2 from reaction is 1 : 3.

i.e. 1 kgmol of $N_2 \rightarrow$ 3 kgmol of H_2

Therefore, 50 kgmol of $N_2 = \frac{3}{1} \times 50$ = 150 kgmol/h

The molal flow rate of hydrogen corresponding to nitrogen feed rate is 150 kgmol/h.

Percentage conversion of $N_2 = \frac{\text{Moles of } N_2 \text{ reacted}}{\text{Moles of } N_2 \text{ feed per hour}} \times 100$ (4.8)

$30 = \frac{\text{Moles of } N_2 \text{ reacted}}{50} \times 100$

Hence, moles of N_2 reacted = 15 kgmol/h.

From the reaction, we have

1 kgmol of $N_2 \rightarrow$ 2 kgmol of NH_3

Therefore, 15 kgmol of $N_2 = \frac{2}{1} \times 15$ = 30 kgmol/h

The amount of NH_3 produced = 30 kgmol/h

= 30 × 17 = 510 kg/h

Thus, the amount of NH_3 produced per hour is 510 kg.

EXAMPLE 4.2 Write balanced reaction equation for the following reactions.

$C_9H_{18} + O_2 \rightarrow CO_2 + H_2O$

Solution: The balanced chemical reaction equation is given as follows:

$C_9H_{18} + 13.5O_2 \rightarrow 9CO_2 + 9H_2O$

EXAMPLE 4.3 Write balanced reaction equation for the following reactions.

$FeS_2 + O_2 \rightarrow Fe_2O_3 + SO_2$

Solution: The balanced chemical reaction equation is given as follows:

$2FeS_2 + 7.5O_2 = Fe_2O_3 + 4SO_2$

EXAMPLE 4.4 If 10 kg of C_6H_6 is oxidised with O_2. How much quantities of O_2 are needed to convert all the C_6H_6 to CO_2 and H_2O?

Solution:

Reaction: $C_6H_6 + O_2 \rightarrow CO_2 + H_2O$

$C_6H_6 + 7.5O_2 = 6CO_2 + 3H_2O$

From the balanced chemical reaction, we have

1 kgmol of $C_6H_6 \rightarrow$ 7.5 kgmol of O_2

78 kg of C_6H_6 → 240 kg of O_2

Therefore, 10 kg of C_6H_6 = $\frac{240}{78} \times 10$ = 30.76 kg

The amount of O_2 needed to convert all the C_6H_6 to CO_2 and H_2O is 30.76 kg.

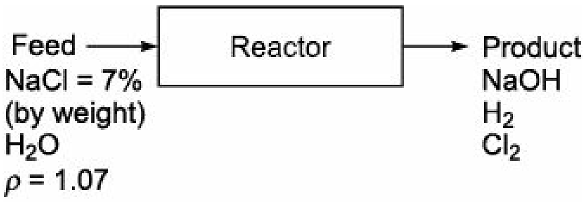
EXAMPLE 4.5 The electrolytic manufacture of Cl_2 gas from a NaCl solution is carried out by the following reaction

$2NaCl + 2H_2O \rightleftharpoons 2NaOH + H_2 + Cl_2$

How many kg of Cl_2 can be produced from 100 m^3 of a brine solution containing 7% by weight of NaCl? The specific gravity of the solution relative to water at 4 °C is 1.07.

Solution:

Reaction: $2NaCl + 2H_2O = 2NaOH + H_2 + Cl_2$



Amount of NaCl present in brine solution = 7490 kg.
From the balanced chemical reaction, we have

2 kgmol of NaCl → 1 kgmol of Cl_2

117 kg of NaCl → 71 kg of Cl_2

Therefore, 7490 kg of NaCl = $\frac{71}{117} \times 7490$

= 4545.21 kg of Cl_2

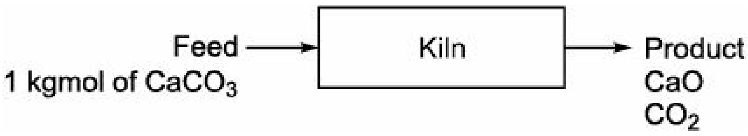
The amount of Cl_2 can be produced from 100 m^3 of a brine solution containing 7% by weight of NaCl is 4545.21 kg.

EXAMPLE 4.6 Calcium oxide is formed by decomposing limestone pure $CaCO_3$. In kiln, the reaction goes to 70% completion.

(i) What is the composition of the solid product withdrawn from the kiln?
(ii) What is the yield in kg of CO_2 produced per kg of limestone charged?

Solution: Basis: 1 kgmol of $CaCO_3$ is fed to the kiln.

Reaction: $CaCO_3 = CaO + CO_2$



The reaction goes to completion = 70%
0.70 kgmol of $CaCO_3$ takes part in the reaction.

From the balanced chemical reaction, we have

1 kgmol of $CaCO_3 \rightarrow$ 1 kgmol of CO_2

Also, 100 kg of $CaCO_3 \rightarrow$ 56 kg of CaO

Therefore, 70 kg of $CaCO_3 = \frac{56}{100} \times 70$

Hence, the amount of CaO = 39.2 kg.

Composition of the solid product:

Component	*Weight* (kg)	*Weight* %
CaO	39.2	56.65
$CaCO_3$	30.0	43.35
	Total = 69.2 kg	

From the balanced chemical reaction, we have

1 kgmol of $CaCO_3 \rightarrow$ 1 kgmol CO_2

100 kg of $CaCO_3 \rightarrow$ 44 kg of CO_2

1 kg of $CaCO_3$ = 0.44 kg of CO_2

Therefore, 0.7 kg of $CaCO_3 = \frac{0.44}{1} \times 0.7$

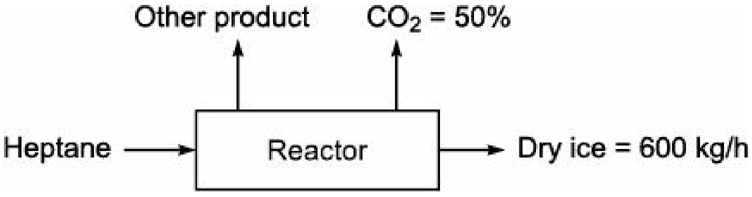
The amount of CO_2 = 0.308 kg.

The yield of CO_2 produced per kg of limestone charged is 0.308 kg.

EXAMPLE 4.7 In the combustion of Heptane, CO_2 is produced. Assume that you want to produce 600 kg of dry ice per hour and 50% of that CO_2 can be converted into dry ice. How many kg of Heptane must by burned per hour?

Solution: Basis: 600 kg of dry ice per hour.

Reaction: $C_7H_{16} + 11O_2 \rightleftharpoons 7CO_2 + 8H_2O$



From the balanced chemical reaction, we have

1 kgmol of $C_7H_{16} \rightarrow$ 7 kgmol of CO_2

100 kg of $C_7H_{16} \rightarrow$ 308 kg of CO_2

50% of the CO_2 produced get converted into dry ice.

Now, 154 kg of $CO_2 \rightarrow$ 100 kg of C_7H_{16}

Therefore, 600 kg of $CO_2 = \frac{100}{154} \times 600$

The amount of C_7H_{16} = 389.16 kg.

Therefore, the amount of C_7H_{16} must be burned per hour is 389.61 kg.

EXAMPLE 4.8 A limestone analysis is shown below.

$CaCO_3$ = 92.89%

$MgCO_3$ = 5.41%

Insoluble = 1.70% (All percentage are by weight)

(i) How many kilograms of CaO can be made from 6 tonnes of this limestone?
(ii) How many kilograms of CO_2 can be recovered per kg of limestone?
(iii) How many kilograms of limestone are needed to make 2 tonnes of lime?

Solution: Basis: 100 kg of limestone.

Reaction: $CaCO_3 \rightleftharpoons CaO + CO_2$

$MgCO_3 \rightleftharpoons MgO + CO_2$

(i) From the balanced chemical reaction, we have

1 kgmol of $CaCO_3 \rightarrow$ 1 kgmol of CaO

100 kg of $CaCO_3 \rightarrow$ 56 kg of CaO

Therefore, 92.89 kg of $CaCO_3$ = $\frac{56}{100} \times 92.89$ = 52.01 kg

Now, 100 kg of $CaCO_3 \rightarrow$ 52.01 kg of CaO

Hence, 6000 kg of $CaCO_3$ = $\frac{52.01}{100} \times 6000$ = 3120.6 kg

Therefore, the amount of calcium oxide that can be made from 6 tonnes of this limestone is 3120.6 kg.

(ii) 1 kgmol of $CaCO_3 \rightarrow$ 1 kgmol of CO_2

100 kg of $CaCO_3 \rightarrow$ 44 kg of CO_2

92.89 kg of $CaCO_3$ = $\frac{44}{100} \times 92.89$ = 40.87 kg

Now, 1 kgmol of $MgCO_3 \rightarrow$ 1 kgmol of CO_2

84 kg of $MgCO_3 \rightarrow$ 44 kg of CO_2

Hence, 5.41 kg of $MgCO_3$ = $\frac{44}{84} \times 5.41$ = 2.833 kg

Total amount of CO_2 produced per 100 kg of limestone = 40.87 + 2.833 = 43.703 kg

The amount of CO_2 produced per kg of limestone = $\frac{43.703}{100}$ = 0.437 kg

Therefore, the amount of CO_2 that can be recovered per kg of limestone is 0.437 kg.

(iii) 1 kgmol of $CaCO_3 \rightarrow$ 1 kgmol of CaO

100 kg of $CaCO_3 \rightarrow$ 56 kg of CaO

92.89 kg of $CaCO_3$ = $\frac{56}{100} \times 92.89$ = 52.01 kg

Now, 1 kgmol of $MgCO_3$ → 1 kgmol of MgO

84 kg of $MgCO_3$ → 40 kg of MgO

Hence, 5.41 kg of $MgCO_3$ = $\frac{40}{84} \times 5.41$ = 2.576 kg

Total amount of lime produced per 100 kg of limestone = 52.01 + 2.576 = 54.586 kg

Now, 54.586 kg of lime → 100 kg of limestone

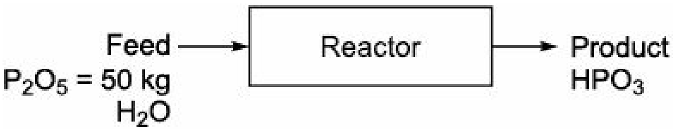
Therefore, 2000 kg of lime = $\frac{100}{54.586} \times 2000$ = 3663.9 kg

Hence, the amount of limestone that is needed to make 2 tonnes of lime is 3663.9 kg.

EXAMPLE 4.9 Metal phosphoric acid is obtained by dissolving phosphorous pentaoxide in cold water. What is the yield in kg of metal phosphoric acid produced from 50 kg of P_2O_5 charged in the reactor?

Solution: Basis: 1 kgmol of P_2O_5

Reaction: $P_2O_5 + H_2O = 2HPO_3$



From the balanced chemical reaction, we have

1 kgmol of P_2O_5 → 2 kgmol of HPO_3

142 kg of P_2O_5 → 160 kg of HPO_3

Therefore, 50 kg of P_2O_5 = $\frac{160}{142} \times 50$

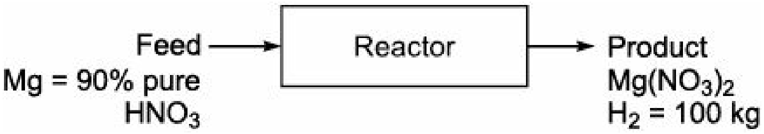
Hence, the amount of HPO_3 = 56.34 kg

The yield of metal phosphoric acid produced from 50 kg of P_2O_5 charged is 56.34 kg.

EXAMPLE 4.10 When magnesium is react with dilute HNO_3 hydrogen liberate. If the magnesium used for the reaction having 10% impurity, calculate the amount of this magnesium required to produce 100 kg of hydrogen?

Solution: Basis: 1 kgmol of magnesium

Reaction: $Mg + 2HNO_3 = Mg(NO_3)_2 + H_2$



From the balanced chemical equation, we have

1 kgmol of Mg → 1 kgmol of H_2

Also, 24.3 kg of Mg → 2 kg of H_2

Therefore, 21.87 kg of Mg = $\frac{2}{24.3} \times 21.87$

Now, 21.87 kg of Mg $\rightarrow$ 1.8 kg of H_2

1.8 kg of H_2 = 21.87 kg of Mg

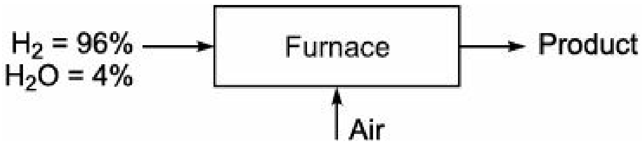
Therefore, 100 kg of H_2 = $\frac{21.87}{1.8} \times 100$

Therefore, the amount of Mg = 1215 kg.
The amount of pure Mg required is 1215 kg.
The amount of Mg with 10% impurity required to produce 100 kg of H_2 is 1350 kg.

EXAMPLE 4.11 Moist hydrogen containing 4 mole% H_2O is burnt completely in a furnace with 30% excess air. Calculate the Orsat analysis of the flue gas.

Solution: Basis: 100 kgmol of fuel.

Reaction: $H_2 + ½O_2 \rightleftharpoons H_2O$



O_2 required:

From the chemical reaction we have,

1 kgmol of H_2 $\rightarrow$ ½ kgmol O_2

96 kgmol of H_2 = $\frac{1 \times 96}{2 \times 1}$

The amount of O_2 required = 48 kgmol.

Total O_2 supplied with 30% excess air = 48(1 + 0.3) = 62.4 kgmol

N_2 along with 62.4 kgmol of O_2 = 234.74 kgmol

From the chemical reaction, we have

1 kgmol or H_2 $\rightarrow$ 1 kgmol of H_2O

Therefore, 96 kgmol of H_2 = $\frac{1 \times 96}{1}$

The amount of H_2O formed = 96 kgmol.

Total amount of H_2O in the product stream = 96 + 4 = 100 kgmol

The amount of O_2 unreacted = 62.4 – 48 = 14.4 kgmol

Product stream	kgmol	*Mole%*
H_2O	100	28.64
O_2	14.4	4.13
N_2	234.74	67.23
	Total 349.14 kgmol	

EXAMPLE 4.12 A combustion reactor is fed with 50 kgmol/h of butane and 2500 kgmol/h of air. Calculate the percentage of excess (O_2) air and composition of gases leaving the combustion reactor.

Assume complete combustion of butane.

Solution: Basis: 2500 kgmol/h of air and 50 kgmol of C_4H_{10}

Reaction: $C_4H_{10} + \left(\frac{13}{2}\right)O_2 \rightarrow 4CO_2 + 5H_2O$

O_2 in air supplied = 2500 × (0.21) = 525 kgmol

O_2 required:

From the chemical reaction, we have

1 kgmol of $C_4H_{10} \rightarrow \left(\frac{13}{2}\right)$ kgmol of O_2

Therefore, 50 kgmol of $C_4H_{10} = \frac{13 \times 50}{2 \times 1}$

The amount of O_2 required = 325 kgmol

The amount of excess air supplied = 525 – 325 = 200 kgmol

Percentage of excess of O_2 supplied = $\frac{525 - 325}{325} \times 100$ = 61.54

From the chemical reaction, we have

1 kgmol of $C_4H_{10} \rightarrow$ 4 kgmol of CO_2

Therefore, 50 kgmol of $C_4H_{10} = \frac{4 \times 50}{1}$

The amount of CO_2 formed = 200 kgmol.

From the chemical reaction, we have

1 kgmol of $C_4H_{10} \rightarrow$ 5 kgmol of H_2O

Therefore, 50 kgmol of $C_4H_{10} = \frac{5 \times 50}{1}$

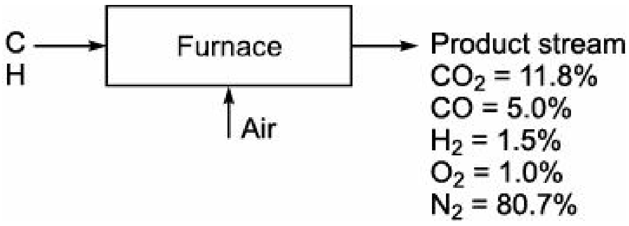
Hence, the amount of H_2O formed = 250 kgmol.

The amount of N_2 associated with supplied air = 2500 × 0.79 = 1975 kgmol

Composition	kgmol	*Mole*%
O_2	200	7.62
N_2	1975	75.24
CO_2	200	7.62
H_2O	250	9.52
	Total = 2625 kgmol	

EXAMPLE 4.13 A lab assistant reports the exit Orsat gas analysis from a furnace, CO_2 = 11.8%,CO = 5%, H_2 = 1.5%, O_2 = 1.0% and N_2 = 80.7%. The oil is being burnt with 20% excess air. Would you compliment him on his work?

Solution: Basis: 100 kgmol of flue gas.



O_2 in flue gas = $11.8 + \left(\frac{5.0}{2}\right) + 1.0 = 15.3$ kgmol

O_2 supplied from air = $(80.7) \times \left(\frac{21}{79}\right) = 21.45$ kgmol

O_2 unaccounted = 21.45 – 15.3 = 6.15 kgmol

O_2 unaccounted is not reported in the flue gas analysis. This amount of O_2 might have used in the formation of H_2O.

H_2 in fuel = 6.15 × 2 = 12.30 kgmol

O_2 required for complete combustion of fuel = 6.15 + (11.8 + 5) = 22.95 kgmol
20% excess air means 27.54 kgmol.

Now, 27.54 kgmol of $O_2 \equiv 27.54 \times \left(\frac{79}{21}\right)$ kgmol of N_2

Therefore, the amount of N_2 associated with air = 103.6 kgmol.
There is a large difference in N_2 reported in the flue gas analysis and N_2 present in the air. Hence, it is no way good to compliment him on his work.

EXAMPLE 4.14 The carbon monoxide is reacted with hydrogen to produce methanol. Calculate the stoichiometric ratio of H_2 to CO.

Solution: Basis: 1 kgmol of CO.

Reaction: $CO + 2H_2 \rightleftharpoons CH_3OH$

2 kgmol of $H_2 \equiv$ 1 kgmol of CO

Therefore, stoichiometric ratio of H_2 to CO = $\frac{2}{1} = 2$

EXAMPLE 4.15 The carbon monoxide is reacted with hydrogen to produce methanol. Calculate the kgmol of CH_3OH produced per 50 kgmol of CO reacted.

Solution: Basis: 50 kgmol of CO.

Reaction: $CO + 2H_2 \rightleftharpoons CH_3OH$

From the chemical reaction, we have

1 kgmol of CO $\equiv$ 1 kgmol of CH_3OH

Therefore, 50 kgmol of CO = $\frac{1 \times 50}{1}$

Therefore, the amount of CH_3OH produced = 50 kgmol.

EXAMPLE 4.16 The carbon monoxide is reacted with hydrogen to produce CH_3OH. Calculate the weight ratio of CO to H_2 if both are fed to the reactor in stoichiometric proportion.

Solution: Basis: 1 kgmol of CO.

Reaction: $CO + 2H_2 \rightleftharpoons CH_3OH$

From the chemical reaction, we have

1 kgmol of CO $\rightarrow$ 2 kgmol of H_2

Also, 28 kg of CO $\rightarrow$ 4 kg of H_2

Therefore, weight ratio of CO to $H_2 = \frac{28}{4} = 7$.

EXAMPLE 4.17 In production of SO_3, 50 kgmol of SO_2 and 100 kgmol of O_2 are fed to the reactor. The product stream is found to contain 40 kgmol of SO_3. Determine the percentage conversion of SO_2.

Solution: Basis: 50 kgmol of SO_2.

Reaction: $SO_2 + \frac{1}{2}O_2 = SO_3$

From the chemical reaction, we have

1 kgmol of SO_3 $\rightarrow$ 1 kgmol of SO_2

40 kgmol of $SO_3 = \frac{1 \times 40}{1}$

Therefore, the amount of SO_2 required = 40 kgmol.

$$\text{Percentage conversion of } SO_2 = \frac{\text{kgmol of } SO_2 \text{ reacted}}{\text{kgmol of } SO_2 \text{ charged}} \times 100 = \frac{40}{50} \times 100 = 80\%.$$

EXAMPLE 4.18 The gas obtained from the furnace fired with a hydrocarbon fuel analyses:

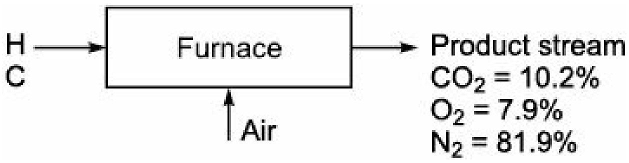
$CO_2 = 10.2\%$

$O_2 = 7.9\%$

$N_2 = 81.9\%$

by Orsat analysis. Calculate the percentage of excess air.

Solution: Basis: 100 kgmol of flue gas.



O_2 supplied = $81.9 \times \left(\frac{21}{79}\right)$ = 21.77 kgmol.

O_2 accounted = 10.2 + 7.9 = 18.1 kgmol.

O_2 unaccounted = 3.67 kgmol.

O_2 theoretically required = 10.2 + 3.67 = 21.77 – 18.1 = 3.67 kgmol.

Percentage of excess air = $\dfrac{O_2 \text{ supplied} - O_2 \text{ theoretically required}}{O_2 \text{ theoretically required}} = \dfrac{21.77 - 13.87}{13.87}$ = 56.95.

EXAMPLE 4.19 A fuel oil contains 87% C and 13% H_2. It is burnt to form flue gas of following composition:

CO_2 = 13.2%

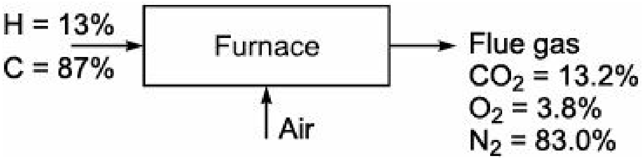
O_2 = 3.8%

and N_2 = 83.0%

Calculate the percentage of excess air used.

Solution: Basis: 100 kgmol of flue gas.

Reaction: $C + O_2 \rightleftharpoons CO_2$



O_2 supplied = 83 × $\left(\dfrac{21}{79}\right)$ = 22.063 kgmol.

O_2 accounted = 13.2 + 3.8 = 17 kgmol.

O_2 unaccounted = 22.063 – 17.0 = 5.063 kgmol.

Unaccounted O_2 might have used in the formation of H_2O.

O_2 theoretically required for complete combustion = 13.2 + 5.063 = 18.263 kgmol.

Percentage of excess air = $\dfrac{O_2 \text{ supplied} - O_2 \text{ theoretically required}}{O_2 \text{ theoretically required}} \times 100$

= $\dfrac{22.063 - 18.263}{18.263} \times 100$ = 20.81

EXAMPLE 4.20 A fuel oil contains 85% C and 15% H_2. It is burnt to form flue gas of following composition:

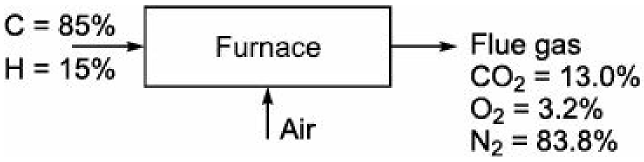
CO_2 = 13.0%

O_2 = 3.2%

and N_2 = 83.8%

How many kgmol of flue gas are produced per kg of fuel oil?

Solution: Basis: 100 kgmol of flue gas.



O_2 supplied = 83.8 × $\left(\dfrac{21}{79}\right)$ = 22.78 kgmol.

O_2 accounted = 13.0 + 3.2 = 16.2 kgmol.

O_2 unaccounted = 22.78 – 16.2 = 6.58 kgmol.

H_2 present = 6.58 × 2 = 13.16 kgmol.

C in fuel = C in flue gas = 13.0 kgmol.

Let x be the quantity of fuel supplied in kgmol.

Material balance for carbon:

$x \times 0.85 = 13.0$

$x = \frac{13.0}{0.85}$

= 15.294 kgmol

= (15.294) × 12

Therefore, fuel supplied = 183.53 kg

kgmol of flue gas produced per kg of fuel oil supplied = $\frac{100}{183.53}$ = 0.545 kgmol

EXAMPLE 4.21 A fuel gas consists of a mixture of CH_4 and N_2. This mixture is burnt with air. The flue gas analysis is:

CO_2 = 7.3%

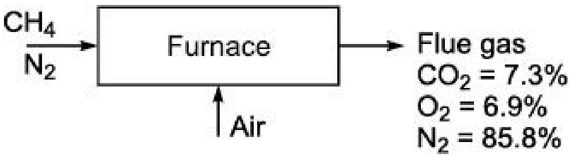
O_2 = 6.9%

and N_2 = 85.8%.

Calculate the percentage of excess air and composition of fuel gas mixture.

Solution: Basis: 100 kgmol of dry flue gas.

Reaction: $CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$



C in fuel $\rightarrow$ C in flue gas

= 7.3 kgmol

From the chemical reaction, we have

1 kgmol of CO_2 $\rightarrow$ 2 kgmol of H_2O

Therefore, 7.3 kgmol of CO_2 = $\frac{2 \times 7.3}{1}$ = 14.6 kgmol of H_2O.

The amount of H_2O formed during the reaction is 14.6 kgmol. Therefore, O_2 used for the formation of water is = $\frac{14.6}{2}$ = 7.3 kgmol.

O_2 theoretically required = 7.3 + 7.3 = 14.6 kgmol

O_2 Supplied = 14.6 + 6.9 = 21.5 kgmol

N_2 supplied from air = $21.5 \times \left(\frac{79}{21}\right)$ = 80.88 kgmol

N_2 present in the fuel = 85.8 – 80.88 = 4.92 kgmol.

From the chemical reaction, we have

1 kgmol of CH_4 → 1 kgmol of CO_2

= 7.3 kgmol

Fuel composition	kgmol	*Mole%*
CH_4	7.3	59.73
N_2	4.92	40.27
	Total = 12.22 kgmol	

Percentage of excess air = $\dfrac{O_2 \text{ supplied} - O_2 \text{ theoretically required}}{O_2 \text{ theoretically required}}$ × 100 = $\dfrac{21.5 - 14.6}{14.6}$ = 47.26%

EXAMPLE 4.22 A producer gas with composition by volume is as follows:

CO = 27.5%

CO_2 = 5.3%

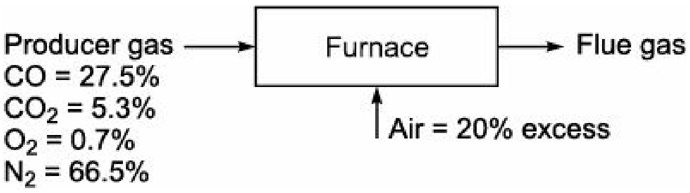
O_2 = 0.7%

and N_2 = 66.5%.

It is burnt with 20% excess air. If the combustion is 96% complete, calculate the composition by mole of the flue gas.

Solution: Basis: 100 kgmol of producer gas

Reaction: $CO + \frac{1}{2}O_2 \rightarrow CO_2$



O_2 balance:

From the chemical reaction, we have

1 kgmol of CO → $\frac{1}{2}$ kgmol of O_2

Therefore, 27.5 kgmol of CO = $\dfrac{1 \times 27.5}{2 \times 1}$ = 13.75 kgmol

O_2 required for converting CO to CO_2 = 13.75 kgmol

O_2 present in the producer gas = 0.70 kgmol.

Net O_2 required = 13.05 kgmol

Air supplied with 20% excess = (13.05) × (1.20) = 15.66 kgmol

O_2 used for 96% combustion of CO = (13.05) × 0.96 = 12.528 kgmol

Excess O_2 after combustion = 15.66 – 12.528 = 3.132 kgmol.

N_2 balance:

N_2 from air supplied = $15.66 \times \left(\frac{79}{21}\right)$ = 58.91 kgmol

N_2 present in the producer gas = 66.50 kgmol

Total amount of N_2 in the flue gas = 125.41 kgmol

CO_2 balance:

From the chemical reaction, we have

1 kgmol CO → 1 kgmol of CO_2

27.5 kgmol CO = $\frac{1 \times 27.5}{1}$

The amount of CO_2 from CO = 27.5 kgmol.

Also, the amount of CO_2 from 96% combustion of CO = 27.5 × 0.96 = 26.4 kgmol

CO_2 present in the producer gas = 5.3 kgmol.

Therefore, total amount of CO_2 present in the flue gas = 31.7 kgmol

CO balance:
CO present in the producer gas = 27.5 kgmol
CO left after 96% combustion = (27.5) × (0.04) = 1.1 kgmol.
CO present in the flue gas = 1.1 kgmol.

Composition	kgmol	*Mole%*
O_2	3.132	1.94
N_2	125.410	77.73
CO_2	31.700	19.65
CO	1.100	0.68
	Total = 161.342 kgmol	

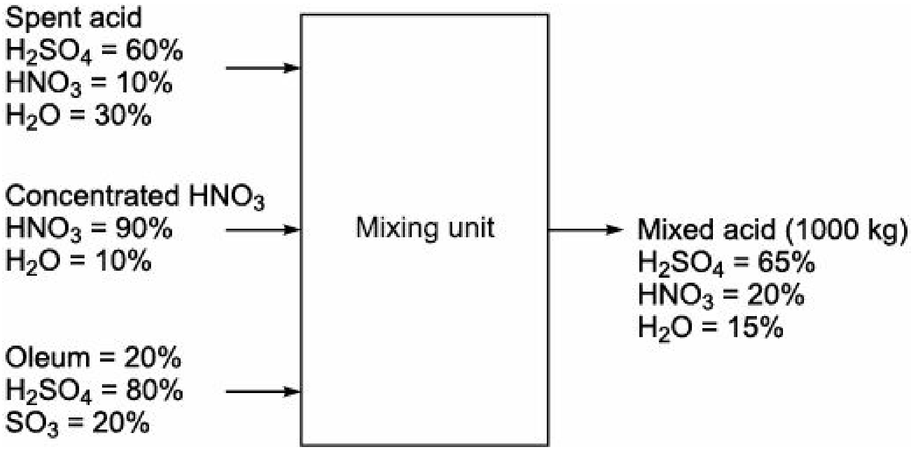
EXAMPLE 4.23 A mixed acid containing 65% H_2SO_4, 20% HNO_3 and 15% H_2O is to be made by blending the following liquids:

(i) A spend acid containing 10% HNO_3, 60% H_2SO_4 and 30% H_2O.

(ii) A concentrated HNO_3 containing 90% HNO_3 and 10% H_2O.

(iii) 20% Oleum (80% H_2SO_4 and 20% SO_3). How many kg of the acid must be used to obtain 1000 kg of the mixed acid.

Solution: Basis: 1000 kg of mixed acid.



Let x be the amount of spent acid (in kg), y be the amount of concentrated HNO_3 (in kg) and z be the amount of Oleum (in kg).

Overall material balance:

$$x + y + z = 1000 \qquad \text{(i)}$$

Material balance for H_2SO_4:

$$x \times 0.60 + y \times 0 + z \times (0.8 + 0.245) = 1000 \times 0.65$$

$$0.60x + 1.045z = 650 \qquad \text{(ii)}$$

Material balance for HNO_3:

$$x \times 0.10 + y \times 0.90 + z \times 0 = 1000 \times 0.20$$

$$0.10x + 0.90\,y = 200 \qquad \text{(iii)}$$

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

$$0.60x + 1.045z = 650$$

$$[x + y + z = 1000] \times 0.6$$

$$\begin{array}{rcrcrcl}
0.60x & + & & + & 1.045z & = & 650 \qquad \text{(iv)}\\
0.60x & + & 0.6y & + & 0.6z & = & 600 \qquad \text{(v)}\\
- & & - & & - & & - \\
\hline
 & & -0.6y & + & 0.445z & = & 50 \qquad \text{(vi)}
\end{array}$$

From Eqs. (i) and (iii), we get

$$0.10x + 0.90y = 200$$

$$[x + y + z = 1000] \times 0.1$$

or $\quad 0.1x + 0.9y = 200$

and $\quad 0.1x + 0.1y + 0.1z = 100$

$$\begin{array}{rcrcrcl}
0.1x & + & 0.9y & & & = & 200\\
0.1x & + & 0.1y & + & 0.1z & = & 100\\
- & & - & & - & & -\\
\hline
 & & 0.8y & - & 0.1z & = & 100 \qquad \text{(vii)}
\end{array}$$

From Eqs. (vi) and (vii), we get

$$-0.6y + 0.445z = 50$$

$$[0.8y - 0.1z = 100] \times 4.45$$

$$\begin{array}{rcrcl}
-0.6y & + & 0.445z & = & 50\\
3.56y & - & 0.445z & = & 445\\
\hline
2.96y & & & = & 495
\end{array}$$

$y = 167.23$

$z = 337.84$

$x = 494.93$

The amount of spent acid = 494.93 kg,

The amount of concentrated HNO_3 = 167.23 kg,

and the amount of Oleum = 337.84 kg.

EXAMPLE 4.24 In production of SO_3, 150 kgmol of SO_2 and 250 kgmol of O_2 are fed to a reactor. The product stream is found to contain 90 kgmol of SO_3. Calculate the percentage conversion of SO_2.

Solution: Basis: 150 kgmol of SO_2 fed to the reactor.

Reaction: $SO_2 + ½O_2 \rightleftharpoons SO_3$

From the chemical reaction, we have

1 kgmol of $SO_3 \equiv$ 1 kgmol of SO_2

Therefore, 90 kgmol of SO_3 = $\dfrac{1 \times 90}{1}$

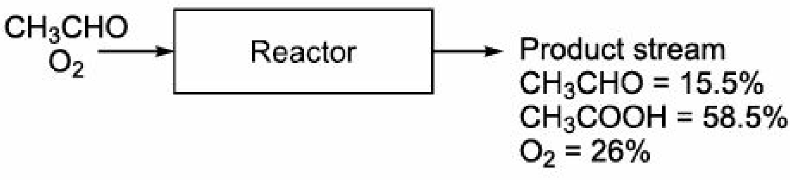
SO_2 reacted = 90 kgmol

Percentage conversion of SO_2 = $\dfrac{\text{kgmol of } SO_2 \text{ reacted}}{\text{kgmol of } SO_2 \text{ charged}} \times 100 = \dfrac{90}{150} \times 100$ = 60

EXAMPLE 4.25 Acetic acid is manufactured by the oxidation of acetaldehyde. 120 kgmol/h of acetaldehyde is fed to the reactor. The product leaving the reactor contains 15.5% acetaldehyde, 58.5% acetic acid and rest oxygen (mole basis). Calculate the percentage conversion of acetaldehyde.

Solution: Basis: 120 kgmol/h of acetaldehyde charged to the reactor.

Reaction: $CH_3CHO + ½O_2 \rightleftharpoons CH_3COOH$



Let x be the kgmol of product stream obtained per hour.

CH_3COOH formed = $0.585x$ kgmol.

From the chemical reaction, we have

1 kgmol of $CH_3CHO \rightarrow$ 1 kgmol of CH_3COOH.

CH_3CHO reacted = $0.585x$ kgmol.

CH_3CHO unreacted = $0.155x$ kgmol.

Now, material balance for CH_3CHO:

$120 = 0.585x + 0.155x$

$120 = 0.74x$

$x = 162.16$ kgmol/h

CH_3CHO reacted = 162.16×0.585

= 94.86 kgmol/h

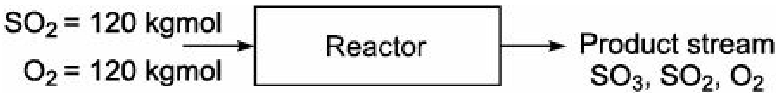
Percentage conversion of CH_3CHO = $\dfrac{CH_3CHO \text{ reacted}}{CH_3CHO \text{ in feed}} \times 100$

$= \dfrac{94.86}{120} \times 100 = 79.05\%$

EXAMPLE 4.26 Sulphur trioxide is manufactured by the reaction of SO_2 and O_2. 120 kgmol of SO_2 and 120 kgmol O_2 are fed to the reactor. If the percentage conversion of SO_2 is 60, calculate the composition of product stream on mole basis.

Solution: Basis: 120 kgmol of SO_2 and 120 kgmol of O_2 fed to the reactor.

Reaction: $SO_2 + ½O_2 \rightleftharpoons SO_3$



Percentage conversion of SO_2 = $\dfrac{\text{Moles of } SO_2 \text{ reacted}}{\text{Moles of } SO_2 \text{ in feed}} \times 100$ $60 = \dfrac{\text{Moles of } SO_2 \text{ reacted}}{\text{Moles of } SO_2 \text{ in feed}} \times 100$

Moles of SO_2 reacted = $\dfrac{60 \times 120}{100}$ = 72 kgmol

Material balance for SO_2:

SO_2 charged = SO_2 reacted + SO_2 unreacted

∴ 120 = 72 + SO_2 unreacted

∴ SO_2 unreacted = 120 – 72

= 48 kgmol

From the chemical reaction, we have

1 kgmol of SO_3 → 1 kgmol of SO_3

Therefore, 72 kgmol of SO_2 = $\frac{1 \times 72}{1}$

Therefore, the amount of SO_3 formed = 72 kgmol.

From the chemical reaction, we have

1 kgmol of SO_2 → $\frac{1}{2}$ kgmol of O_2

Therefore, 72 kgmol of SO_2 = $\frac{1 \times 72}{2 \times 1}$

Amount of O_2 reacted = 36 kgmol.

Hence, the amount of O_2 unreacted = 120 – 36 = 84 kgmol.

Composition of product stream

Component	kgmol	*Mole%*
SO_2	48	23.53
SO_3	72	35.29
O_2	84	41.18
	Total = 204 kgmol	

EXAMPLE 4.27 C_2H_4O is manufactured by the oxidation of ethylene. 120 kgmol of C_2H_4 is fed to the reactor. The product found to contain 90 kgmol of ethylene oxide and 8 kgmol of CO_2. Calculate:

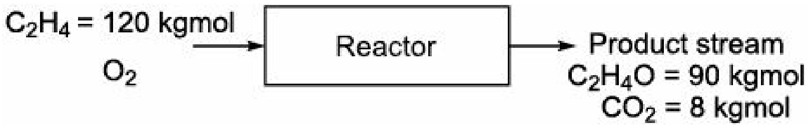
(i) Percentage conversion of ethylene

(ii) Percentage yield of C_2H_4O.

Solution: Basis: 120 kgmol of ethylene fed to the reactor.

Reaction:

1. $C_2H_4 + \frac{1}{2}O_2 \rightarrow C_2H_4O$
2. $C_2H_4 + 3O_2 \rightarrow 2CO_2 + 2H_2O$



From chemical reaction 1, we have

1 kgmol of C_2H_4O → 1 kgmol of C_2H_4

Therefore, 90 kgmol of C_2H_4O = $\frac{1 \times 90}{1}$

Thus, the amount of C_2H_4 reacted = 90 kgmol.

From chemical reaction 2, we have

$2 \text{ kgmol of } CO_2 \rightarrow 1 \text{ kgmol of } C_2H_4$

Therefore, 8 kgmol of $CO_2 = \frac{1 \times 8}{2}$

Amount of C_2H_4 reacted = 4 kgmol

Therefore, total amount of C_2H_4 reacted = 90 + 4 = 94 kgmol

Percentage conversion of $C_2H_4 = \frac{\text{Moles of } C_2H_4 \text{ reacted}}{\text{Moles of } C_2H_4 \text{ in feed}} \times 100 = \frac{94}{120} \times 100 = 78.33\%$

Percentage yield of $C_2H_4O = \frac{\text{Moles of } C_2H_4 \text{ reacted to produce } C_2H_4O}{\text{Moles of } C_2H_4 \text{ totally reacted}} \times 100 = \frac{90}{94} \times 100 =$ 95.74%

EXAMPLE 4.28 Ethylene oxide is manufactured by the oxidation of ethylene. 120 kgmol of ethylene and 120 kgmol of oxygen are fed to the reactor. The conversion of ethylene is 75% and the percentage yield of C_2H_4O is 95. Calculate the composition of product stream leaving the reactor. The reactions taking place in reactor are:

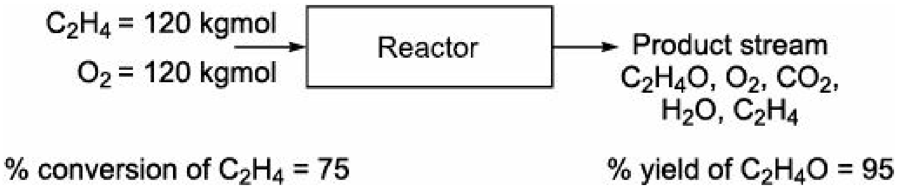
$$C_2H_4 + \frac{1}{2}O_2 \rightleftharpoons C_2H_4O$$

$$C_2H_4 + 3O_2 \rightleftharpoons 2CO_2 + 2H_2O$$

Solution: Basis: 120 kgmol of C_2H_4 and 120 kgmol O_2 fed to the reactor.

Reaction:

1. $C_2H_4 + \frac{1}{2}O_2 \rightleftharpoons C_2H_4O$
2. $C_2H_4 + 3O_2 \rightleftharpoons 2CO_2 + 2H_2O$



Moles of C_2H_4 totally reacted = 120 × 0.75 = 90 kgmol

From chemical reaction 1, we have

Moles of C_2H_4 reacted to form C_2H_4O = 0.95 × 90 = 85.5 kgmol

From chemical reaction 2, we have

Moles of C_2H_4 reacted to form CO_2, H_2O = 90 – 85.5 = 4.5 kgmol

Moles of C_2H_4 unreacted = 120 – 90 = 30 kgmol.

From chemical reaction, we have

$1 \text{ kgmol of } C_2H_4 \rightarrow 2 \text{ kgmol of } CO_2$

Therefore, 4.5 kgmol of $C_2H_4 = \frac{2 \times 4.5}{1}$

Amount of CO_2 formed = 9 kgmol.

From chemical reaction, we have

1 kgmol of $C_2H_4 \rightarrow$ 2 kgmol of H_2O

Therefore, 4.5 kgmol of $C_2H_4 = \frac{2 \times 4.5}{1}$

Amount of water formed = 9 kgmol.

From chemical reaction, we have

1 kgmol of $C_2H_4 \rightarrow \frac{1}{2}$ kgmol of O_2

Therefore, 85.5 kgmol of $C_2H_4 = \frac{1 \times 85.5}{2 \times 1}$

Amount of O_2 reacted for reaction 1 = 42.75 kgmol.

From chemical reaction, we have

1 kgmol of $C_2H_4 \rightarrow$ 3 kgmol of O_2

Therefore, 4.5 kgmol of $C_2H_4 = \frac{3 \times 4.5}{1}$

Amount of O_2 reacted for reaction 2 = 13.5 kgmol.

Total amount of O_2 reacted = 42.75 + 13.5 = 56.25 kgmol.

Amount of O_2 unreacted = 120 – 56.25 = 63.75 kgmol.

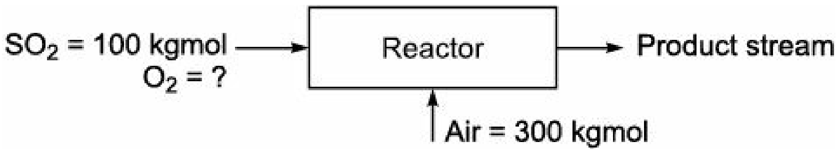
Composition of product stream

Component	kgmol	*Mole%*
C_2H_4	30.00	15.21
C_2H_4O	85.50	43.35
O_2	63.75	32.32
CO_2	9.00	4.56
H_2O	9.00	4.56
	Total = 197.25 kgmol	

EXAMPLE 4.29 In manufacture of SO_3, fed to the reactor consists of 100 kgmol of SO_2 and 300 kgmol of air. Calculate the percentage of excess air is used.

Solution: Basis: 100 kgmol of SO_2 fed to the reactor.

Reaction: $SO_2 + \frac{1}{2}O_2 \rightleftharpoons SO_3$



Air supplied = 300 kgmol

O_2 in supplied air = 300 × (0.21) = 63 kgmol

From the chemical reaction, we have

1 kgmol of SO_2 → $\frac{1}{2}$ kgmol of O_2

Therefore, 100 kgmol of SO_2 = $\frac{1 \times 100}{2 \times 1}$

O_2 required theoretically = 50 kgmol

Percentage of excess O_2 = $\frac{O_2 \text{ in supplied air} - O_2 \text{ theoretically required}}{O_2 \text{ theoretically required}} \times 100$

= $\frac{63 - 50}{50} \times 100$ = 26

Note: Percentage of excess O_2 = percentage of excess air.

Also, 21 kgmol of O_2 → 100 kgmol of air

Therefore, 50 kgmol of O_2 = $\frac{100 \times 50}{21}$

Air theoretically required = 238.09 kgmol

Air supplied = 300 kgmol

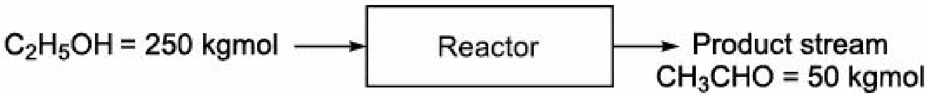
Percentage of excess air = $\frac{\text{Air supplied} - \text{Air theoretically required}}{\text{Air theoretically required}} \times 100$

= $\frac{300 - 238.09}{238.09} \times 100$ = 26

EXAMPLE 4.30 250 kgmol of ethanol are charged to a dehydrogenation reactor to produce acetaldehyde. The product stream is found to contain 50 kgmol of acetaldehyde. Calculate the % conversion of ethanol.

Solution: Basis: 250 kgmol of ethanol charged to reactor.

Reaction: $C_2H_5OH \rightleftharpoons CH_3CHO + H_2$



From the chemical reaction, we have

1 kgmol of CH_3CHO → 1 kgmol of C_2H_5OH

Therefore, 50 kgmol of CH_3CHO = $\frac{1 \times 50}{1}$

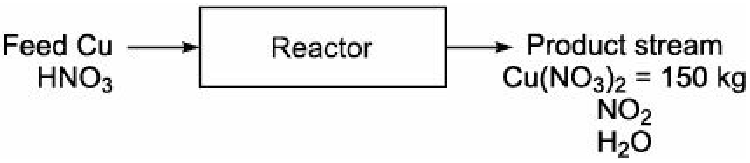
Hence, the amount of C_2H_5OH reacted = 50 kgmol.

Percentage conversion of C_2H_5OH = $\frac{\text{Moles of } C_2H_5OH \text{ reacted}}{\text{Moles of } C_2H_5OH \text{ in feed}} \times 100$ = $\frac{50}{250} \times 100$ = 20

EXAMPLE 4.31 $Cu(NO_3)_2$ is prepared by reacting copper with concentrated HNO_3. Calculate the quantity (in kg) of copper required to produce 150 kg of copper nitrate if the reaction is 96% complete.

Solution: Basis: 150 kg of $Cu(NO_3)_2$.

Reaction: $Cu + 4HNO_3 \rightarrow Cu(NO_3)_2 + 2NO_2 + 2H_2O$



From the chemical reaction, we have

187.5 kg of $Cu(NO_3)_2$ $\rightarrow$ 63.5 kg of Cu

Therefore, 150 kg of $Cu(NO_3)_2$ = $\frac{63.5 \times 150}{187.5}$

Hence, the amount of Cu required = 50.8 kg.

100% completion of reaction $\rightarrow$ Required 50.8 kg of Cu

Therefore, 96% completion of reaction = $\frac{50.8 \times 100}{96}$.

Thus, the amount of Cu required = 52.92 kg.

Therefore, to produce 150 kg of $Cu(NO_3)_2$, the amount of copper required is 52.92 kg.

EXAMPLE 4.32 Zinc nitrate is produced by reacting powdered zinc with concentrated nitric acid. Calculate the amount $Zn(NO_3)_2$ can be prepared using 120 kg of powdered zinc.

Solution: Basis: 120 kg of powdered zinc.

Reaction: $Zn + 4HNO_3 \rightarrow Zn(NO_3)_2 + 2NO_2 + 2H_2O$

From the chemical reaction, we have

65.38 kg of Zn $\rightarrow$ 189.38 kg of $Zn(NO_3)_2$

Therefore, 120 kg of Zn = $\frac{189.38 \times 120}{65.38}$

Hence, the amount of $Zn(NO_3)_2$ can be prepared = 347.59 kg.

EXAMPLE 4.33 In a reactor, 130 kg of Zn powder and 160 kg of HNO_3 are fed. The reaction is 80% complete. The products formed are $Zn(NO_3)_2$, NO_2 and H_2O. Calculate the amount of $Zn(NO_3)_2$ and NO_2 formed as a product.

Solution: Basis: 130 kg of powdered zinc.

Reaction: $Zn + 4HNO_3 \rightarrow Zn(NO_3)_2 + 2NO_2 + 2H_2O$

From the chemical reaction, we have

65.38 kg of Zn $\rightarrow$ 189.38 kg of $Zn(NO_3)_2$

Therefore, 130 kg of Zn = $\frac{189.38 \times 130}{65.38}$

Now, the amount of $Zn(NO_3)_2$ = 376.56 kg.

Amount of $Zn(NO_3)_2$ actually formed = 301.25 kg.

From the chemical reaction, we have

1 kgmol of Zn → 2 kgmol of NO_2

65.38 kg of Zn → 2 × 46 kg of NO_2

Hence, 130 kg of Zn = $\frac{2 \times 46 \times 130}{65.38}$

That is, the amount of NO_2 formed = 182.93 kg.

Now, 100% completion of reaction → 182.93 kg of NO_2

Therefore, 80% completion of reaction = $\frac{182.93 \times 80}{100}$

Thus, the amount of NO_2 actually formed = 146.34 kg.

EXAMPLE 4.34 When Mg reacts with dilute HNO_3, hydrogen liberates as per the reaction given below.

$Mg + 2HNO_3 \rightarrow Mg(NO_3)_2 + H_2$.

Calculate the amount of Mg required to produce 250 kg of hydrogen.

Solution: Basis: 250 kg of Hydrogen.

Reaction: $Mg + 2HNO_3 \rightarrow Mg(NO_3)_2 + H_2$

From the chemical reaction, we have

1 kgmol of Mg → 1 kgmol of H_2

2.0 kg of H_2 → 24.3 kg of Mg

Therefore, 250 kg of H_2 = $\frac{24.3 \times 250}{2}$

Hence, the amount of Mg required = 3,037.5 kg.

EXAMPLE 4.35 Mn and dilute HNO_3 are fed into a reactor. During the process, H_2 liberated and $Mn(NO_3)_2$ is formed as per the reaction given below.

$Mn + 2HNO_3 \rightarrow Mn(NO_3)_2 + H_2$

Consider that Mn used for reaction is 80% pure. Calculate the amount of HNO_3 required to produce 150 kg of H_2.

Solution: Basis: 150 kg of H_2.

Reaction: $Mn + 2HNO_3 \rightarrow Mn(NO_3)_2 + H_2$

From the chemical reaction, we have

1 kgmol of $H_2 \rightarrow$ 2 kgmol of HNO_3

2 kg of $H_2 \rightarrow 2 \times 63$ kg of HNO_3

150 kg of $H_2 \rightarrow$?

$$= \frac{2 \times 63 \times 150}{2}$$

Hence, the amount of HNO_3 required = 9,450 kg.

Manganese (Mn) is 80% pure. Hence, HNO_3 actually required to produce 150 kg of H_2 is 7560 kg.

EXAMPLE 4.36 Metal phosphoric acid is obtained by dissolving P_2O_5 in cold water. If 50 kgof phosphorous pentaoxide is dissolved in water, calculate the amount of metal phosphoric acid formed.

Solution: Basis: 50 kg of P_2O_5.

Reaction: $P_2O_5 + H_2O \rightleftharpoons 2HPO_3$

From the chemical reaction, we have

1 kgmol of $P_2O_5 \rightarrow$ 2 kgmol of HPO_3

Also, 142 kg of $P_2O_5 \rightarrow 2 \times 80$ kg of HPO_3

Therefore, 50 kg of $P_2O_5 = \frac{2 \times 80 \times 50}{142}$

Hence, the amount of HPO_3 formed = 56.34 kg.

EXAMPLE 4.37 A fuel oil is burnt in a furnace. The Orsat analysis of flue gas found to contain

CO_2 = 11.2%

O_2 = 5.8%

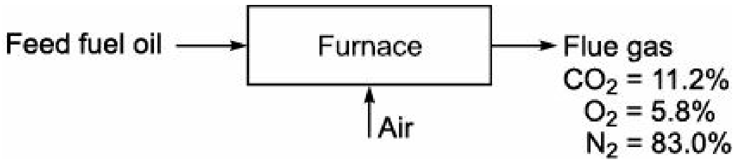
and N_2 = 83.0%.

All percentage are by mole. Calculate the C: H ratio of the fuel oil. Assume that fuel does not contain nitrogen.

Solution: Basis: 100 kgmol of flue gas.

Reaction:

1. $C + O_2 \rightleftharpoons CO_2$
2. $H_2 + \frac{1}{2}O_2 \rightleftharpoons H_2O$



From the chemical reaction 1, we have

1 kgmol of $O_2 \rightarrow$ 1 kgmol of CO_2

O_2 required for combustion of C = 11.2 kgmol

O_2 present in the flue gas = 5.8 kgmol

O_2 accounted = 11.2 + 5.8 = 17 kgmol

O_2 supplied from air = 83 × (21/79) = 22.06 kgmol

O_2 unaccounted = 22.06 – 17.00 = 5.06 kgmol.

The O_2 unaccounted is not reported in the flue gas analysis. This amount of O_2 is used for burning of Hydrogen to form water.

Form the chemical reaction 2, we have

$\frac{1}{2}$ kgmol of $O_2 \rightarrow$ 1 kgmol H_2

5.06 kgmol $O_2 = \dfrac{1 \times 5.06 \times 2}{1}$

Therefore, the amount of H_2 burnt = 10.12 kgmol

Weight of H_2 burnt = 10.12 × 2 = 20.24 kg

Weight of C burnt = 11.2 × 12 = 134.4 kg

The C:H ratio of fuel oil is = $\dfrac{134.4}{20.24}$ = 6.64.

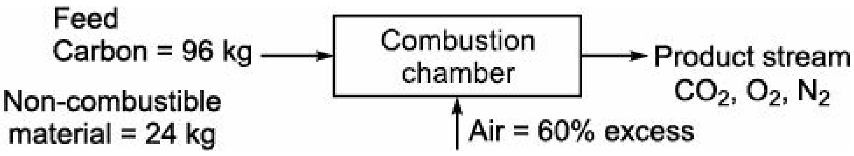
EXAMPLE 4.38 A coke contain 80% carbon and 20% non-combustible material by weight.

(i) Calculate the amount of O_2 theoretically required to burn 120 kg of coke completely.

(ii) If 60% excess air is supplied, calculate the composition of gases in the product stream.

Solution: Basis: 120 kg of coke.

Reaction: $C + O_2 \rightarrow CO_2$



From the chemical reaction, we have

1 kg atom of C = 1 kgmol of O_2

12 kg of C $\rightarrow$ 32 kg of O_2

Therefore, 96 kg of C = $\dfrac{32 \times 96}{12}$

Hence, the amount of O_2 required = 256 kg.

Amount of O_2 required = $\dfrac{256}{32}$

Amount of O_2 theoretically required = 8 kgmol

Now, 21 kgmol of $O_2 \rightarrow$ 100 kgmol of air

Therefore, 8 kgmol of $O_2 = \dfrac{100 \times 8}{21}$

Air theoretically required = 38.09 kgmol.

$$\text{Air supplied} = 38.09\left(1 + \frac{60}{100}\right) = 60.95 \text{ kgmol}$$

O_2 in supplied air = 60.95 × 0.21 = 12.8 kgmol

N_2 in supplied air = 60.95 × 0.79 = 48.15 kgmol

Unaccounted O_2 = O_2 in supplied air – O_2 theoretically required = 12.8 – 8.0 = 4.8 kgmol.

From the chemical reaction, we have

1 kg atom of C → 1 kgmol of CO_2

12 kg of C → 44 kg of CO_2

$$\text{Therefore, 96 kg of C} = \frac{44 \times 96}{12}$$

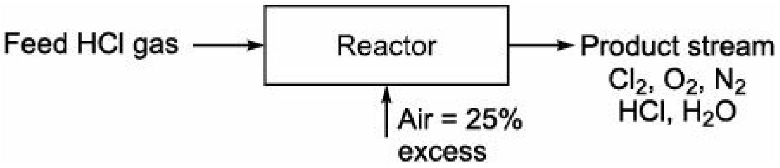
$$\text{Hence, the amount of } CO_2 \text{ formed} = 352 \text{ kg} = \frac{352}{44} = 8 \text{ kgmol.}$$

Composition of gases in product stream		
Component	*Quantity* (kgmol)	*Mole%*
CO_2	8.00	13.13
O_2	4.80	7.86
N_2	48.15	78.99
	Total = 60.95 kgmol	

EXAMPLE 4.39 Chlorine gas is manufactured by Decon process. A mixture of dry hydrochloric acid gas and air is passed over a heated catalyst which promote the oxidation of acid. Air is used in 25% excess of that theoretically required. Calculate the weight of air supplied per kilogram of acid.

Solution: Basis: 1 kg of HCl acid gas charged

Reaction: $4HCl + O_2 \rightleftharpoons 2Cl_2 + 2H_2O$



$$\text{HCl acid gas charged} = 1 \text{ kg} = \frac{1}{36.5} = 0.0274 \text{ kgmol}$$

From the chemical reaction, we have

4 kgmol of HCl → 1 kgmol of O_2

$$\text{Therefore, 0.0274 kgmol of HCl} = \frac{1 \times 0.0274}{4}$$

Amount of O_2 theoretically required = 0.00685 kgmol

$$\text{Percentage excess air} = \frac{O_2 \text{ in supplied air} - O_2 \text{ theoretically required}}{O_2 \text{ theoretically required}} \times 100$$

O_2 in supplied air = O_2 theoretically required × $\left(1 + \frac{\%\text{ excess air}}{100}\right) = 0.00685 \times \left(1 + \frac{25}{100}\right)$

Amount of O_2 supplied = 0.00856 kgmol

21 kgmol of O_2 = 100 kgmol of air

0.00856 kgmol of O_2 = $\frac{100 \times 0.00856}{21}$

Amount of air supplied = 0.0408 kgmol

= 0.0408 × 29 = 1.182 kg

Therefore, the weight of air supplied per kg of acid = 1.182.

EXAMPLE 4.40 Soda ash is manufactured as per the reaction

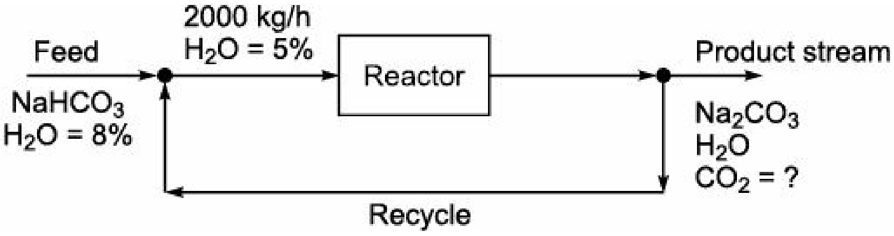
$$2NaHCO_3 \rightarrow Na_2CO_3 + CO_2 + H_2O$$

In an experimental investigation, wet $NaHCO_3$ containing 8% water is pre-mixed with recycled dry soda ash so as to reduce the water content to 5% before introducing into the calciner. The calciner is being fed with 2000 kg of wet bicarbonate per hour. Calculate:

(i) Quantity of soda ash produced per hour as the final product.
(ii) Quantity of off gases produced per hour.
(iii) Mole ratio of CO_2 to H_2O in the off gases.
(iv) Quantity of soda ash recycled per hour. **[B.U. August, 1997]**

Solution: Basis: 2000 kg of wet $NaHCO_3$ fed to the reactor.

Reaction: $2NaHCO_3 \rightarrow Na_2CO_3 + CO_2 + H_2O$



Amount of $NaHCO_3$ enter the calciner = 2000 × (1 – 0.05) = 1900 kg

From the chemical reaction, we have

168 kg of $NaHCO_3$ $\rightarrow$ 106 kg of Na_2CO_3

1900 kg of $NaHCO_3$ = $\frac{106 \times 1900}{168}$ = 1198.81 kg

Amount of soda ash produced per hour = 1198.81 kg.

From the chemical reaction, we have

168 kg of $NaHCO_3$ $\rightarrow$ 44 kg of CO_2

Therefore, 1900 kg of $NaHCO_3$ = $\frac{44 \times 1900}{168}$ = 497.62 kg

Amount of CO_2 produced per hour = 497.62 kg

Moles of CO_2 produced per hour = 11.31

From the chemical reaction, we have

168 kg of $NaHCO_3 \equiv 18$ kg of H_2O

$$1900 \text{ kg of } NaHCO_3 = \frac{18 \times 1900}{168}$$

Amount of H_2O produced per hour = 203.57 kg

Moles of H_2O produced per hour = 11.31

Quantity of off gases produced per hour

$CO_2 = 497.62$ kg

$H_2O = 203.57$ kg

Mole ratio of CO_2 to H_2O in the off gases $= \dfrac{11.31}{11.31} = 1.0$

Let 'x' be the amount of wet $NaHCO_3$ entering the junction point in kg/h and 'y' be the amount of dry Na_2CO_3 entering the junction point in kg/h.

Overall material balance around the junction point:

$$x + y = 2000$$

Material balance for water:

$$x \times 0.08 + y \times 0 = 2000 \times 0.05$$

$$0.08x + 0 = 100$$

$$x = \frac{100}{0.08}$$

Therefore, $x = 1250$ kg and $y = 750$ kg.

Thus, the amount of dry Na_2CO_3 recycled per hour = 750 kg.

EXAMPLE 4.41 A furnace uses producer gas. The analysis of the gas is as given below.

$CO_2 = 6.2\%$

$CO = 21.4\%$

$H_2 = 13.6\%$

$CH_4 = 1.1\%$

and $N_2 = 57.7\%$.

The flue gas contains

$CO_2 = 13.1\%$

$O_2 = 2.3\%$

and $N_2 = 84.6\%$.

Both analysis were conducted using Orsat apparatus. Calculate the percentage of excess air used in the furnace.

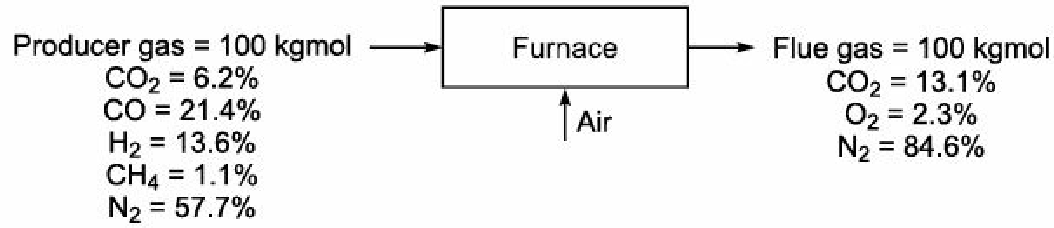
Solution: Basis: 100 kgmol of producer gas entering the furnace.

Reaction: $CO + \frac{1}{2}O_2 \rightarrow CO_2$

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

$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$

$C + O_2 \rightarrow CO_2$



The amount of C atm in producer gas = 28.7
The amount of C atm in flue gas = 13.1.
Let us assume that
'*x*' kgmol of producer gas entering the furnace and '*y*' kgmol of air is introduced into the furnace.
Overall material balance for carbon:

$$x \times \left(\frac{28.7}{100}\right) + y(0) = 13.1$$

$$\Rightarrow\ 0.287x = 13.1$$

$$\Rightarrow\ x = 45.64 \text{ kgmol.}$$

Overall material balance for nitrogen:

$$x \times \left(\frac{57.7}{100}\right) + y\left(\frac{79}{100}\right) = 84.6$$

$$\Rightarrow\ 0.577x + 0.79y = 84.6$$

$$\Rightarrow\ 0.577 \times (45.64) + 0.79y = 84.6$$

$$\Rightarrow\ y = 73.75 \text{ kgmol.}$$

Amount of O_2 supplied with N_2 = 15.49 kgmol.

From the chemical reaction, we have

Amount of O_2 theoretically required = $21.4\left(\frac{1}{2}\right) + 13.6\left(\frac{1}{2}\right) + 1.1(2)$

$$= \frac{19.7 \text{ kgmol}}{100 \text{ kgmol}} \text{ of producer gas}$$

Now, 100 kgmol of produer gas → 19.7 kgmol of O_2

Therefore, 45.64 kgmol of producer gas = $\dfrac{19.7 \times 45.64}{100}$

Amount of O_2 required theoretically = 8.99 kgmol

Percentage of excess air = $\dfrac{O_2 \text{ supplied} - O_2 \text{ theoretically required}}{O_2 \text{ theoretically required}} \times 100$

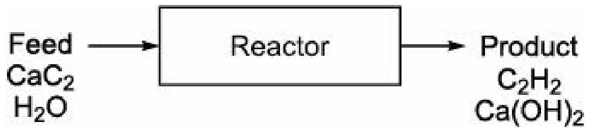
$$= \frac{15.49 - 8.99}{8.99} \times 100 = 72.30\%$$

EXAMPLE 4.42 Calcium carbide is reacted with water to produce acetylene and calcium hydroxide as per the reaction

$$CaC_2 + 2H_2O \rightleftharpoons C_2H_2 + Ca(OH)_2.$$

If 200 l of gas is burnt per hour at 298 K and 0.98 atm pressure, calculate the amount of CaC_2 in kg which must be used in the acetylene lamp at the above temperature and pressure to get 24 hours service of the lamp. The CaC_2 reacts to give acetylene to burn in the lamp.

Solution: Basis: 24 hours of operation of the lamp.



In 1 hour = amount of C_2H_2 burnt 200 l

In 24 hour = 200 × 24.

Hence, the amount of C_2H_2 burnt = 4800 l.

Amount of C_2H_2 burnt is the amount of C_2H_2 generated.

From ideal gas law, we know that

$$PV = nRT$$

$$\therefore \; n = \frac{PV}{RT}$$

where

n = Moles

P = Pressure (atm)

V = Volume (l)

$R = 0.082 \dfrac{(\text{l})\,(\text{atm})}{(\text{gmol})(\text{K})}$

T = 298 K

$$\text{Now, } n = \frac{0.98 \times 4800}{0.082 \times 298}$$

Therefore, the amount of C_2H_2 generated = 192.5 gmol.

From the chemical reaction, we have

1 mole of $C_2H_2 \rightarrow$ 1 mole of CaC_2

Hence, 192.5 mole of $C_2H_2 = \dfrac{1 \times 192.5}{1}$

Thus, amount of CaC_2 required = 192.5 mole

= 192.5 × 64 = 12,320 g

Amount of CaC_2 required = 12.32 kg.

EXAMPLE 4.43 A pure hydrocarbon 220 kg/h is fired in a furnace of the boiler at atmospheric pressure and 25°C. The flue gas analysis on dry basis at atmospheric pressure and 30°C is as given below:

CO_2 = 13%

O_2 = 3.5%

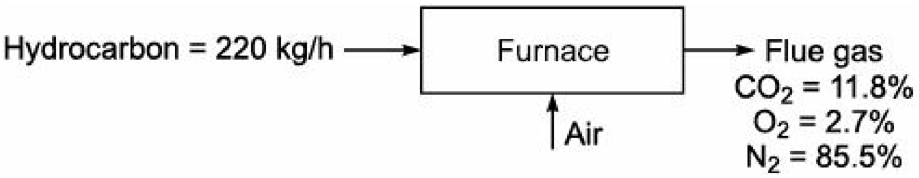
and N_2 = 83.5%.

Estimate the formula of the fuel and volumetric flow rate of the gas.

Solution: Basis: 100 kgmol of flue gas (dry basis).

Reaction: $C + O_2 \rightleftharpoons CO_2$

$H_2 + \frac{1}{2}O_2 \rightleftharpoons H_2O$



N_2 supplied from air = 85.5 kgmol.

O_2 supplied = $85.5 \times \left(\frac{21}{79}\right)$

= 22.73 kgmol

O_2 accounted = 11.8 + 2.7

= 14.5 kgmol

O_2 unaccounted = 22.73 – 14.5

= 8.23 kgmol

From the chemical reaction, we have

$\frac{1}{2}$ kgmol of $O_2 \rightarrow$ 1 kgmol of H_2

Therefore, 8.23 kgmol of O_2 = $\frac{1 \times 8.23 \times 2}{1}$

Hence, the amount of H_2 reacted = 16.46 kgmol.

Atoms of H_2 reacted = 32.92 kg atom

Amount of C in fuel = Amount of C in flue gas

= 11.8 kgmol

= 11.8 kg atom

Now, $\frac{\text{Atom of H}}{\text{Atom of C}} = \frac{32.92}{11.8}$ = 2.78

The H/C ratio in fuel is greater than 2. Hence, the fuel is paraffin base. Its formula is C_nH_{2n+2}.

Now, $\frac{n}{2n+2} = \frac{1}{2.78}$

$n = 2.56$

$C_nH_{2n+2} = C_3H_8$

Therefore, molecular weight of fuel = 44.

Fuel supplied = 220 kg/h

$$= \frac{220}{44} \text{ kgmol/h} = 5 \text{ kgmol/h}$$

Now, 1 kgmol of gas occupies = 22.414 m^3

Therefore, 5 kgmol of gas = $\frac{22.414 \times 5}{1}$ = 112.07 m^3/h

$$= \frac{112.07 \times 298}{273} = 122.33 \text{ m}^3\text{/h.}$$

EXAMPLE 4.44 A certain fuel is burnt in a furnace and its flue gas sample is carefully analyzed in a mercury filled Orsat apparatus. The flue gas was found to contain

CO_2 = 13.3%

CO = 2.1%

O_2 = 6.5%

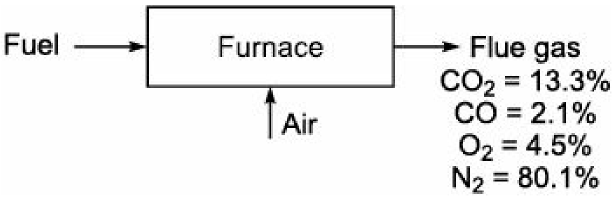
and N_2 = 78.1%.

Calculate the percentage of excess air used.

Solution: Basis: 100 kgmol of flue gas.

Reaction: $C + \frac{1}{2}O_2 \rightleftharpoons CO$

$H_2 + \frac{1}{2}O_2 \rightleftharpoons H_2O$



N_2 supplied from air = 80.1 kgmol

O_2 supplied = $80.1 \times \left(\frac{21}{79}\right)$ = 21.29 kgmol

O_2 accounted in flue gas = $13.3 + \left(\frac{2.1}{2}\right) + 4.5$ = 18.85 kgmol

O_2 unaccounted = 21.29 – 18.85 = 2.44 kgmol

O_2 unaccounted is not reported in the flue gas analysis. This amount of O_2 is used in the formation of H_2O.

O_2 theoretically required = $13.3 + \left(\frac{2.1}{2}\right) + 2.44$ = 16.79 kgmol

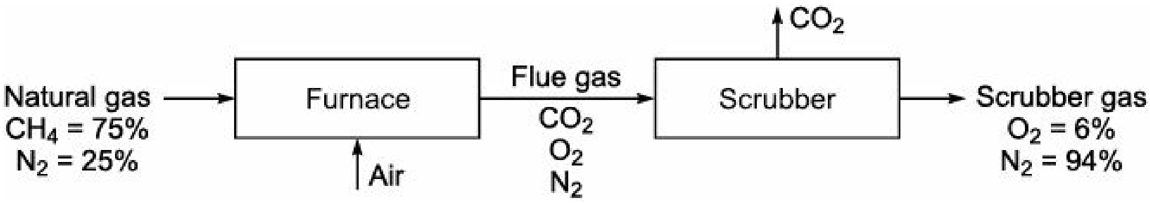
Percentage of excess air = $\frac{O_2 \text{ supplied} - O_2 \text{ theoretically required}}{O_2 \text{ theoretically required}} \times 100 = \frac{21.29 - 16.79}{16.79} \times 100$

= 26.80.

EXAMPLE 4.45 A natural gas consists of 75% CH_4 and 25% N_2 is burnt in a furnace. The CO_2 is scrubbed out of the resulting products for use in else where. The exit gases from the scrubber analyze 6% O_2 and 94% N_2. Calculate the percentage of excess air used.

Solution: Basis: 100 moles of exit gas.

Reaction: $CH_4 + 2O_2 \rightarrow CO_2 + H_2O$



Let us assume that *x* moles of natural gas and *y* moles of air enters the furnace.

Overall material balance for nitrogen:

$$0.25x + 0.79y = 94 \qquad \text{(i)}$$

From the chemical reaction, we have

1 mole of $CH_4 \rightarrow$ 2 moles of O_2

Therefore, $0.75x$ moles of $CH_4 = \dfrac{2 \times 0.75x}{1}$

Therefore, the amounts of O_2 required = $1.5x$.

Overall material balance for oxygen:

$$0.21y - 1.5x = 6 \qquad \text{(ii)}$$

$$-1.5x + 0.21y = 6 \qquad \text{(iii)}$$

Solving Eqs. (i) and (iii), we get

$$(0.25x + 0.79y = 94) \times 1.5$$

$$(-1.5x + 0.21y = 6) \times 0.25$$

Adding Eqs. (iv) and (v) we get

$$\begin{array}{rrcll} 0.375x & +\ 1.185y & = & 141 & \text{(iv)} \\ -0.375x & +\ 0.0525y & = & 1.5 & \text{(v)} \\ \hline & 1.2375y & = & 142.5 & \end{array}$$

$$y = \frac{142.5}{1.2375}$$

y = 115.15 moles and

x = 12.126 moles.

Moles of O_2 theoretically required = 18.19 moles

Moles of O_2 supplied from air = 115.15 × 0.21 = 24.18 moles

$$\text{Percentage of excess air} = \frac{O_2 \text{ supplied} - O_2 \text{ theoretically required}}{O_2 \text{ theoretically required}} \times 100$$

$$= \frac{24.18 - 18.19}{18.19} \times 100 = 33$$

EXAMPLE 4.46 A fuel oil has the following composition:

C = 83%
H = 13%
S = 2.5%

and impurities = 1.5%.

It is burnt in a furnace and dry flue gas is analyzed using a Orsat analyzer. The flue gas found to contain

CO_2 = 11.3%
O_2 = 5.9%
N_2 = 82.8%.

Calculate:

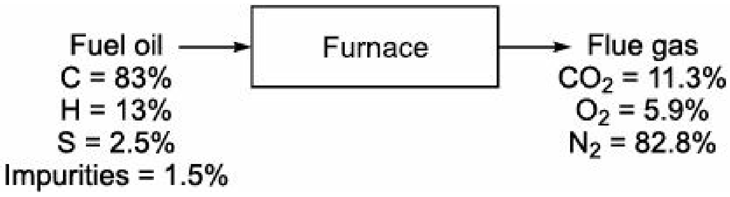
(i) The percentage of excess air
(ii) The weight of air per kg of oil fired.

Solution: Basis: 100 kg of oil.

Reaction: $C + O_2 \rightarrow CO_2$

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

$S + O_2 \rightarrow SO_2$



O_2 required:

From the chemical reaction, we have

1 kgmol of C $\equiv$ 1 kgmol of O_2

12 kg of C $\equiv$ 32 kg of O_2

83 kg of C = $\dfrac{32 \times 83}{12}$

O_2 required for C = 221.33 kg

= 6.92 kgmol

From the chemical reaction, we have

1 kgmol of H_2 $\equiv$ $\frac{1}{2}$ kgmol of O_2

2 kg of H_2 $\equiv$ $\frac{1}{2} \times 32$ kg of O_2

Therefore, 13 kg of H_2 = $\dfrac{1 \times 32 \times 13}{2 \times 2}$

Hence, O_2 required for H_2 = 104 kg

= 3.25 kgmol.

From the chemical reaction, we have

1 kgmol of S → 1 kgmol of O_2

32 kg of S → 32 kg of O_2

2.5 kg of S = $\frac{32 \times 2.5}{32}$

O_2 required for S = 2.5 kg

= 0.078 kgmol.

Total amount of O_2 required = 6.92 + 3.25 + 0.078 = 10.248 kgmol

Let us assume that '*x*' kgmol of flue gas coming out from the furnace.

Overall material balance for carbon:

$x \times \left(\frac{11.3}{100}\right) = 6.92$

$x = 61.24$ kgmol.

N_2 present in flue gas = 61.24 × $\left(\frac{82.8}{100}\right)$ = 50.71 kgmol

O_2 supplied = 50.71 × $\left(\frac{21}{79}\right)$ = 13.48 kgmol

Percentage of excess air = $\frac{O_2 \text{ supplied} - O_2 \text{ theoretically required}}{O_2 \text{ theoretically required}} \times 100 = \frac{13.48 - 10.248}{10.248} \times 100$

= 31.54%

79 kgmol of N_2 → 100 kgmol of air

50.71 kgmol of N_2 = $\frac{100 \times 50.71}{79}$ = 64.189 kgmol

Amount of air used = 1861.48 kg.

Weight of air per kg of oil fired = $\frac{1861.48}{100}$ = 18.61.

EXAMPLE 4.47 A coal containing

C = 69.7%

H_2 = 3.5%

S = 1.3%

N_2 = 1.7%

O_2 = 7.7%

Ash = 4.3%

H_2O = 11.8%

is burnt in a furnace. The combustion of dry gas has the following composition:

CO_2 = 13.9%

O_2 = 4.5%

and N_2 = 81.6%

Calculate:

(i) The percentage of excess air

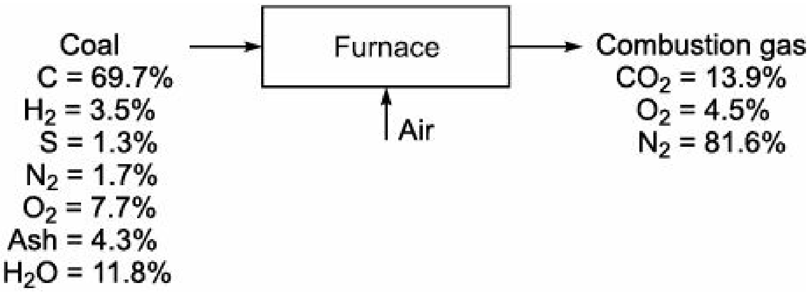
(ii) Theoretical volume of air per 100 kg of coal.

Solution: Basis: 100 kg of coal

Reaction: $C + O_2 = CO_2$

$H_2 + \frac{1}{2}O_2 = H_2O$

$S + O_2 = SO_2$



Let us assume that '*x*' kg of coal is burnt in a furnace.

Overall material balance for carbon:

$$x \times \left(\frac{69.7}{100}\right) = 13.9$$

$x = 19.94$ kg

N_2 present in combustion gas = 81.6 kg

N_2 present in coal = $19.94 \times \left(\frac{1.7}{100}\right) = 0.34$ kg

N_2 supplied from air = 81.6 – 0.34 = 81.26 kg

O_2 supplied = $81.26 \times \left(\frac{21}{79}\right) = 21.60$ kg

O_2 accounted = 13.9 + 4.5 = 18.4 kg

O_2 unaccounted = 21.60 – 18.4 = 3.2 kg

O_2 required theoretically = 13.9 + 3.2 = 17.1 kg

Percentage of excess air = $\dfrac{O_2 \text{ supplied} - O_2 \text{ theoretically required}}{O_2 \text{ theoretically required}} \times 100$

$= \dfrac{21.60 - 17.1}{17.1} \times 100 = 26.31\%$

Now, 1 kgmol of air → 22.414 m^3

Therefore, 3.546 kgmol of air = $\dfrac{22.414 \times 3.546}{1} = 79.48\ m^3$

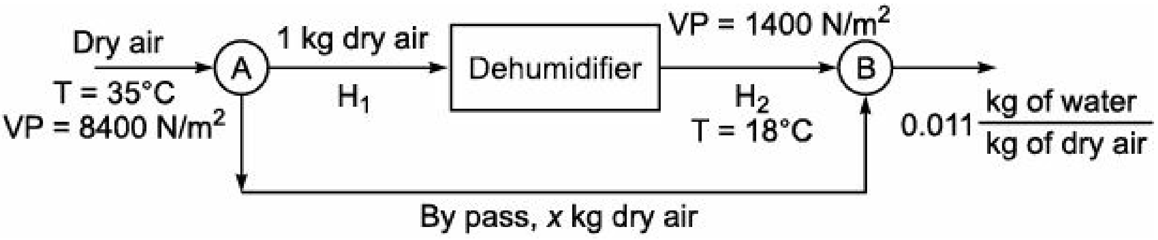
Hence, theoretical volume of air per 100 kg of coal = 79.48 m^3.

EXAMPLE 4.48 Air at 35°C saturated with water vapour is to be dehumidified. Part of the air is sent through a unit where it is cooled and some water is condensed. This air leaves the unit saturated. At 18°C, it is then mixed with air, which is bypassed the unit. The final air contains 0.011 kg water vapour per kg of dry air. The vapour pressure of water at 35°C is 8400 N/m^{2}and at 18°C is 1400 N/m^2. Calculate:

(i) The ratio of kg of dry air bypassed to the kg of dry air sent through the dehumidifier.

(ii) The volume of final air on the basis of 15,000 m^3 of original wet air/h.

Solution: Basis: 1 kg of dry air



Let *x* be the kg of dry air bypassed.

$$H_1 = \frac{p_w}{p_T - p_w} \times \frac{M_w}{M_A}$$

$$= \frac{8400}{1.013 \times 10^5 - 8400} \times \frac{18}{29}$$

$$= 0.056 \frac{\text{kg of water}}{\text{kg of dry air}}$$

= 0.09 kgmol of water/kgmol of dry air.

$$H_2 = \frac{p_w}{p_T - p_w} \times \frac{M_w}{M_A}$$

$$= \frac{1400}{1.013 \times 10^5 - 1400} \times \frac{18}{29}$$

$$= 0.0087 \frac{\text{kg of water}}{\text{kg of dry air}}$$

= 0.014 kgmol of water/kgmol of dry air.

Material balance for water at B:

$$1 \times 0.0087 + x \times 0.056 = (1 + x) \times 0.011 \qquad \text{(i)}$$

Solving Eq. (i), we get

$x = 0.0511$ kg dry air

The ratio of amount (in kg) of dry air bypassed to the amount (in kg) of dry air sent through the dehumidifier

$$= \frac{0.0511}{1} = 0.0511$$

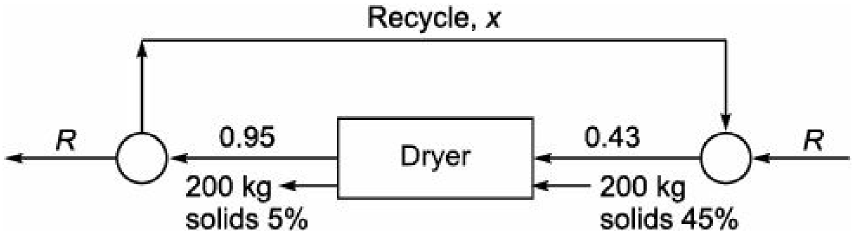
Volume of wet air entering = $(1 + 0.09)(22.414) \times \left(\frac{308}{273}\right) = 27.546$ m^3

Volume of wet air leaving = (1 + 0.014) (22.414) × $\left(\frac{291}{273}\right)$ = 24.23 m^3

Volume of final air for 15,000 m^3 of fed, wet air/h = $15,000 \times \frac{24.23}{27.546}$ = 13,194.3 m^3.

EXAMPLE 4.49 A wet organic pigment containing 45% CCl_4 by weight is to be dried to 5% by weight. The dryer is to operate adiabatically with fresh and recycle air entering the dryer with 0.43 kg of CCl_4 per kg of dry air. This air leaves the dryer at 0.95 kg of CCl_4 per kg of dry air. The capacity of the dryer is 200 kg bone dry solids per hour. Calculate the ratio of recycle to fresh air.

Solution: Basis: 200 kg of bone dry solids.



Overall material balance for CCl_4:

Let *R* be the kg of fresh air.

$$[CCl_4 \text{ in solid} + CCl_4 \text{ in air}]_{\text{inlet}} = [CCl_4 \text{ in solid} + CCl_4 \text{ in air}]_{\text{outlet}}$$

$$200 \times \left(\frac{45}{55}\right) + R(0) = 200 \times \left(\frac{5}{95}\right) + R(0.95)$$

Therefore, *R* = 161.16 kg of fresh air.

Material balance for CCl_4 around the dryer:

$$200 \times \left(\frac{45}{55}\right) + (R + x) \times 0.43 = 200 \times \left(\frac{5}{95}\right) + (R + x) \times 0.95$$

$$163.64 + 69.29 + 0.43x = 10.53 + 153.10 + 0.95x$$

$$69.3 = 0.95x - 0.43x$$

x = 133.26 kg of dry air

CCl_4 in recycle = 133.26 × (0.95) = 126.59 kg

Total recycle with CCl_4 = 133.26 + 126.59 = 259.85 kg

Hence, recycle ratio, $\frac{x}{R} = \frac{259.85}{161.16}$ = 1.61.

EXAMPLE 4.50 In a chemical process industry, methanol is synthesized as per the chemical reaction

$$CO + 2H_2 \rightleftharpoons CH_3OH$$

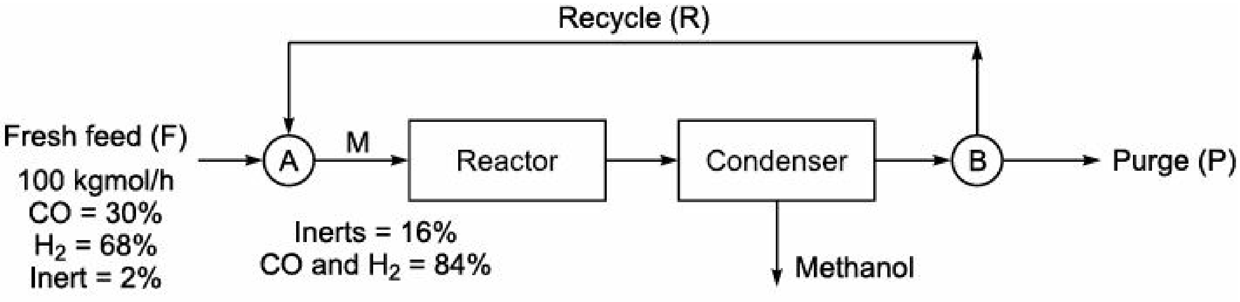
Fresh feed to the process contains 30 mole% CO, 68 mole% H_2 and 2 mole% inert, is mixed with recycle feed. The single pass conversion of CO is 25%. The product stream from the reactor is fed to the condenser where all methanol formed gets condensed and the gases from the condenser are recycled. In order to prevent the build up or inerts in recycle loop, a portion of the gases leaving the condenser is continuously purged. If mixed feed contains 16% inerts, calculate:

(i) Recycle ratio

(ii) Purge ratio

Solution: Basis: 100 kgmol/h of fresh feed.

Chemical reaction: $CO + 2H_2 \rightleftharpoons CH_3OH$



Let F be the fresh feed in kgmol/h; R be the recycle feed in kgmol/h; P be the purge in kgmol/h and M be the mixed feed in kgmol/h.

We have,

CO in fresh feed = 30 kgmol/h

H_2 in fresh feed = 68 kgmol/h

Inerts in fresh feed = 2 kgmol/h

Inerts in mixed feed = $0.16M$

CO and H_2 in mixed feed = $0.84M$

Material balance at A:

$M = F + R$ (i)

$M = 100 + R$ (ii)

$CO + H_2$ reacted = $0.25\ (0.84\ M)$ kgmol

$CO + H_2$ unreacted = $(1 - 0.25)\ (0.84\ M)$

$= 0.63\ M$ kgmol

$CO + H_2$ + Inerts, leaving the condenser per hour = $0.63\ M + 0.16M = 0.79\ M$ kgmol/h

Mole percentage of inerts in gas leaving the condenser = $\dfrac{0.16M}{0.79M} \times 100 = 20.25$

For steady state operation, we have

Inerts in fresh feed = Inerts in purge

2 kgmol = Inerts in purge

Concentration of inerts in purge = $\dfrac{2}{P} \times 100$

$20.25 = \dfrac{2}{P} \times 100$

$\therefore\ P = 9.88$ kgmol/h.

Material balance at B:

Gas leaving the condenser = Gas purged + Gas recycled

$0.79M = 9.88 + R$ (iii)

Substituting Eq. (ii) in Eq. (iii), we get

$0.79 \times (100 + R) = 9.88 + R$

$R = 329.14$ kgmol/h. (iv)

Substituting Eq. (iv) in Eq. (ii), we get

$M = 100 + 329.14$

$M = 429.14$ kgmol/h.

$$\text{Recycle ratio} = \frac{R}{F} = \frac{329.14}{100}$$

$= 3.29$

$$\text{Purge ratio} = \frac{P}{R}$$

$$= \frac{9.88}{329.14}$$

$= 0.03.$

Exercises

4.1 Write balanced reaction equation for the following reactions.

(i) $Ti + H_2SO_4 \rightleftharpoons Ti(SO_4)_2 + SO_2 + H_2O$

(ii) $Ti + HCl \rightleftharpoons TiCl_3 + H_2$.

4.2 Write balanced reaction equation for the following reactions.

(i) $TiCl_4 + Na \rightleftharpoons Ti + NaCl$

(ii) $TiO_2 + Al + BaO_2 \rightleftharpoons Al_2O_3 + Ti + BaO$.

4.3 Write balanced reaction equation for the following reactions.

(i) $TiI_4 \rightleftharpoons Ti + 2I_2$

(ii) $FeTiO_3 + K_2CO_3 + HF + [O] \rightleftharpoons K_2TiF_6 + H_2O + Fe_2O_3 + CO_2$.

4.4 Write balanced reaction equation for the following reactions.

(i) $ZrO_2 + Na_2CO_3 \rightleftharpoons Na_2ZrO_3 + CO_2$

(ii) $ZrCl_4 + NH_4OH \rightleftharpoons Zr(OH)_4 + NH_4Cl$.

4.5 Write balanced reaction equation for the following reactions.

(i) $ZrCl_4 + Al \rightleftharpoons Zr + AlCl_3$

(ii) $KHSO_4 + S \rightleftharpoons K_2S_3O_6 + K_2S_2O_3 + H_2O$.

4.6 Titanium is produced by the following reaction:

$TiCl_4 + Na \rightleftharpoons Ti + NaCl$

Calculate the kg of Titanium produced per hour if percentage conversion is 90 and $TiCl_4$ feed rate is 40 kgmol/h.

4.7 A combustion reactor is fed with 60 kgmol/h of butane and 2200 kgmol/h of air. Calculate the percentage of excess air used. Assume complete combustion of butane.

4.8 A combustion reactor is fed with 75 kgmol/h of butane and 2500 kgmol/h of air. Calculate the composition of gases leaving the combustion reactor. Assume 90% combustion of butane.

4.9 The carbon monoxide is reacted to produce methanol. Calculate the quantity of CO required to produce 500 kg of methanol.

4.10 In production of sulphur trioxide, 50 kgmol SO_2 and 100 kgmol of O_2 are fed to the reactor. The product stream is found to contain 40 kgmol of SO_3. Calculate the percentage of excess air and the composition of product stream.

4.11 The gas obtained from the furnace fired with a hydrogen fuel analysis:

CO_2 = 10.0%
O_2 = 8.1%
N_2 = 81.9%

by Orsat analysis. Calculate the carbon to hydrogen ratio.

4.12 10 kg PbS and 3 kg of O_2 react to yield 6 kg of Pb and 1 kg of PbO_2 according to the reaction

$$PbS + O_2 \rightleftharpoons Pb + SO_2$$

$$PbS + 2O_2 \rightleftharpoons PbO_2 + SO_2.$$

Calculate:

(i) The amount of PbS that does not react.
(ii) The percentage excess of O_2 based on the amount of PbS that actually reacts.
(iii) The amount of SO_2 formed.
(iv) The percentage conversion of PbS to Pb and overall % conversion of the PbS into products.

4.13 A solid fuel with a composition by weight

C = 78%
H_2 = 6%
O_2 = 9.8%
N_2 = 1.2%
and Ash = 5%

is burnt in air. The products of combustion gives on Orsat analysis by volume

CO_2 = 12.5%
CO = 0.09%
O_2 = 5.6%
and N_2 = 81.81%.

The refuse removed from ash Pit contains 30% carbon by weight. Find % of excess air used.

4.14 Analysis of flue gas is found to be

CO_2 = 4.7%
CO = 3.1%
O_2 = 8.7%
and N_2 = 83.5%.

Calculate:

(i) Moles of dry air supplied per moles of dry flue gas.
(ii) The percentage of excess air (assume complete combustion).
(iii) Amount of H_2 burnt per moles of dry flue gas.

4.15 Powdered zinc produces these product when treated with concentrated HNO_3.

$$Zn + 4HNO_3 \rightleftharpoons Zn(NO_3)_2 + 2NO_2 + 2H_2O$$

Calculate the amount of zinc powder required to produce 100 kg of $Zn(NO_3)_2$.

4.16 When Mg reacts with dilute HNO_3, hydrogen liberates. If the reaction is 80% complete, calculate the amount of Mg required to produce 100 kg of Hydrogen.

4.17 Oxidation of ethylene to produce ethylene oxide is given by the reaction

$$C_2H_4 + \frac{1}{2}O_2 \rightleftharpoons C_2H_4O$$

If air is used 30% in excess of that theoretically required, calculate the quantity of air supplied based on 150 kgmol of ethylene fed to the reactor.

4.18 Consider the chemical reaction

$$C_2H_4 + 2Cl_2 \rightleftharpoons C_2HCl_3 + H_2 + HCl$$

Calculate the following for the reaction:

(i) The stoichiometric ratio of Cl_2 to C_2H_4.

(ii) If 5 kgmol of Cl_2 are used per kgmol C_2H_4, find the percentage of excess Cl_2.

(iii) The amount of HCl produced from 65 kg of C_2H_4 assuming reaction goes to 96% completion.

4.19 Methane oxidation reactions are

$$CH_4 + O_2 \rightleftharpoons HCHO + H_2O$$

$$CH_4 + 2O_2 \rightleftharpoons CO_2 + 2H_2O.$$

150 kgmol of methane is charged to the reactor. The product stream is found to contain 20 kgmol of CO_2 and 50 kgmol of HCHO. Calculate:

(i) Percentage conversion of CH_4

(ii) Percentage yield of HCHO.

4.20 A combustion reactor is fed with 75 kgmol/h of Butane and 2500 kgmol/h of air. Calculate the percentage of excess air used. The reaction taking place in reactor is

$$C_4H_{10} + \frac{13}{2}O_2 \rightarrow 4CO_2 + 5H_2O.$$

4.21 A combustion reactor is fed with 60 kgmol/h of Butane and 2300 kgmol/h of air. Calculate the composition of the gases leaving the combustion reactor assuming 90% combustion of butane.

4.22 A combustion chamber is fed with Butane and excess air. The combustion of butane is 96% complete. The composition of combustion gases on mole basis is given below:

CO_2 = 9.5%

H_2O = 11.5%

O_2 = 4.4%

and N_2 = 74.6%.

Calculate the percentage of excess air used.

4.23 Carbon monoxide and steam are fed to a reactor for the production of H_2 and CO_2. The product gas is found to contain 36.5% H_2, 38.2% CO_2 and 25.3% H_2O. All percentage are in mole. Calculate the mole ratio of steam to carbon monoxide.

4.24 Zirconium is produced by reacting $ZrCl_4$ with Al. Calculate the amount (in kg) of Al required to produce 100 kg of Zr. Assume the reaction is 90% complete.

4.25 Assume you would like to produce 60 kg of Zirconium by reacting $ZrCl_4$ and Al. Calculate the amount of reactants required if the reaction goes to completion.

4.26 Pure CH_4 is burnt in the presence of pure O_2 using a burner to produce acetylene. The composition of the cracked gases from the burner on dry basis is as follows:

$CH_4 = 5.4\%$
$C_2H_4 = 0.5\%$
$C_2H_2 = 8.2\%$
$C_3H_6 = 0.3\%$
$CO = 26.2\%$
$CO_2 = 5.0\%$
$O_2 = 0.2\%$
and $H_2 = 55.4\%$.

All % are by volume. Calculate:

(i) Methane required
(ii) Oxygen required
(iii) Water produced

for production of 120 kgmol of cracked gas.

4.27 $Cu(NO_3)_2$ is prepared by reacting copper with concentrated HNO_3. Calculate the amount (in kg) of copper required to produce 100 kg of copper nitrate if the reaction is 90% complete.

4.28 Copper nitrate is prepared by reacting copper with concentrated HNO_3. Calculate the amount of concentrated HNO_3 required to produce 186 kg of $Cu(NO_3)_2$ if the reaction is 90% complete.

4.29 In a reactor 120 kg of zinc powder and 480 kg of concentrated HNO_3 are fed. The reaction is 85% complete. Calculate the amount of $Zn(NO_3)_2$ is formed.

4.30 125 kg of zinc powder and 500 kg of concentrated HNO_3 are fed into a reactor. Assume that the reaction goes to completion. Calculate the amount of zinc nitrate and NO_2 formed in the product stream.

4.31 When Mg reacts with dilute HNO_3, hydrogen liberates as per the reaction given below.

$$Mg + 2HNO_3 \rightleftharpoons Mg(NO_3)_2 + H_2$$

To produce 100 kg of H_2, what is the amount of Mg required?

4.32 When Mg reacts with dilute HNO_3, hydrogen liberates as per the reaction given below.

$$Mg + 2HNO_3 \rightleftharpoons Mg(NO_3)_2 + H_2$$

Consider the Mg used during the process is 80% pure. Calculate the amount of Mg required to produce 100 kg of H_2.

4.33 When Mn reacts with dilute HNO_3, hydrogen liberates as per the reaction given below.

$$Mn + 2HNO_3 \rightleftharpoons Mn(NO_3)_2 + H_2$$

To produce 150 kg of H_2, what is the amount of Mn required?

4.34 Mn reacts with dilute HNO_3 to liberate H_2 as per the reaction given below.

$$Mn + 2HNO_3 \rightleftharpoons Mn(NO_3)_2 + H_2$$

Consider the Mn used for the reaction is 90% pure. Calculate the amount of Mn required to produce 200 kg of H_2.

4.35 Phosphorous pentaoxide and cold water are fed into a reactor to produce metal phosphoric acid as per the reaction given below.

$$P_2O_5 + H_2O \rightleftharpoons 2HPO_3$$

Calculate the amount of P_2O_5 required to produce 60 kg of HPO_3. Assume reaction goes to completion.

4.36 Acetaldehyde is oxidised in the presence of air with the help of silica gel as catalyst to produce acetic acid. The reaction takes place at 390 K. The outgoing dry gases from the reactor are analysed to contain

$CH_3CHO = 8.85\%$

$CH_3COOH = 16.20\%$

$CO_2 = 5.32\%$

$O_2 = 3.12\%$

and $N_2 = 66.51\%$.

All % are by mole (dry basis). In order to carry out dry analysis, water was first removed from the mixture. Some acetic acid is also condensed at the time of removal of water. Calculate:

(i) The percentage conversion of acetaldehyde.
(ii) The percentage yield of acetic acid.
(iii) The ratio of air to acetaldehyde in the incoming feed on weight basis.
(iv) The percentage removal of acetic acid during the water removal.
(v) The actual analysis of the gases leaving the reactor.

4.37 A producer gas contains

$CO_2 = 9.6\%$

$C_2H_4 = 0.4\%$

$CO = 19.2\%$

$H_2 = 14.5\%$

$CH_4 = 2.1\%$

and $N_2 = 54.2\%$.

When it is burnt, the products of combustion are found to contain

$CO_2 = 11.0\%$

$CO = 0.6\%$

$O_2 = 9.1\%$

and rest $N_2 = 79.3\%$.

Compute:

(i) Volume of air used in the combustion of one m^3 of producer gas, both being at the same temperature and pressure.
(ii) The percentage of excess air used in the combustion.

(iii) The percentage of nitrogen in the product of combustion which came from the producer gas.

4.38 20 kg of Pb and 6 kg of O_2 react to yield 12 kg of Pb and 2 kg of PbO_2 according to the reaction

$$PbS + O_2 \rightleftharpoons Pb + SO_2$$

$$PbS + 2O_2 \rightleftharpoons PbO_2 + SO_2$$

Calculate:

(i) The amount of PbS that does not react.

(ii) The percentage of excess O_2 based on amount of PbS that actually reacts.

(iii) The amount of SO_2 formed.

(iv) The percentage conversion of PbS to Pb and overall percentage conversion of the Pbs into products.

4.39 A fuel gas contains

CO_2 = 3.5%

C_2H_4 = 0.6%

C_6H_6 = 1.4%

O_2 = 0.3%

CO = 17.5%

H_2 = 36.9%

CH_4 = 24.8%

and N_2 = 15%

All percentage are by volume. It is burnt with air in a furnace. The CO_2 analyzer indicated CO_2 = 10% (by mole) on dry basis in the flue gas. Calculate:

(i) The percentage excess air used.

(ii) The complete Orsat analysis of the flue gas.

4.40 Chlorobenzene is nitrated using a mixture of nitric acid and sulfuric acid as per the reaction

$$C_6H_5Cl + HNO_3 \rightleftharpoons ClC_6H_4NO_2 + H_2O$$

A charge consisted of 100 kg of chlorobenzene, 106.5 kg of 65.5% nitric acid and 108 kgof 93.6% sulfuric acid (by weight). After two hours of operation, the final mixture was analysed. The final product contained 2% unreacted chlorobenzene. Also, the product distribution was found to contain

P-nitrochlorobenzene = 66%

and O-nitrochlorobenzene = 34%.

Calculate:

(i) The analysis of charge.

(ii) The percentage conversion of chlorobenzene.

(iii) The composition of the product mixture.

4.41 One method for producing chlorobenzene is to react benzene, HCl and air. The following reaction takes place:

$$C_6H_6 + HCl + \tfrac{1}{2}O_2 \rightleftharpoons C_6H_5Cl + H_2O$$

After the waste gas from such a process has been scrubbed to remove any unreacted HCl and benzene and the other products, its composition is

N_2 = 88.8% (by mole)

O_2 = 11.2% (by mole).

Determine the number of moles of chlorobenzene produced per mole of air fed to the reactor.

4.42 A combustible gas with a composition by volume of

H_2 = 45%

CH_4 = 30%

C_6H_6 = 15%

N_2 = 10%

is burnt in air. The composition of the dry products of combustion is

CO_2 = 7.18%

CO = 0.16%

O_2 = 6.89%

and N_2 = 85.77%

by volume. Calculate the air-fuel ratio on the volume basis. Also, calculate the percentage of the theoretical air.

4.43 How much super phosphate fertilizer can be made from 760 kg of calcium phosphate of 94.5% pure. The reaction is

$$Ca_3(PO_4)_2 + 2H_2SO_4 \rightleftharpoons CaH_4(PO_4)_2 + 2CaSO_4$$

4.44 Hydrogen free carbon in the form of coke is burnt

(a) with complete combustion using theoretical air.

(b) with complete combustion using 50% excess air.

(c) using 50% excess air but with 10% of the carbon burning to CO only. In each case calculate the gas analysis which will be found by testing the flue gases with an Orsat apparatus.

4.45 The combustion of cracked ammonia, a mixture of $N_2 + 3H_2$ with air takes place in an annealing furnace. The flue gas analysis indicates

O_2 = 3%

N_2 = 97%.

What is the percentage of excess air used in the combustion process?

4.46 A fuel oil contains 87% carbon and 13% hydrogen. It is burnt to a flue gas of the following composition:

CO_2 = 14.1% O_2 = 3.8%

and N_2 = 82.1%.

Calculate:

(i) How many kgmol of flue gas are produced per 100 kg of fuel oil?

(ii) What is the percentage of excess air used?

4.47 A flue gas sample carefully analysed in a mercury filled Orsat apparatus gave the following composition.

CO_2 = 11.3%

CO = 1.2%
O_2 = 7.7%
and rest N_2 = 79.8%.

Calculate:

(i) The percentage of excess air used.

(ii) If all the fuel burnt, could you guess the type of fuel used?

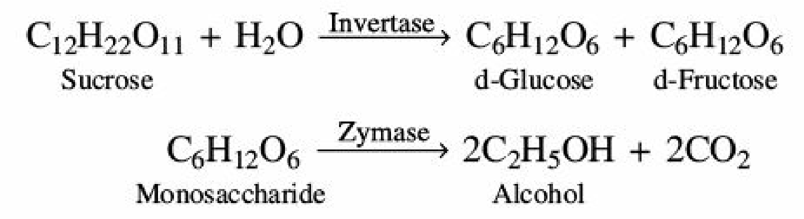
4.48 A natural gas that analyzes 80% CH_4 and 20% N_2 is burnt in a furnace. The CO_2 is scrubbed out of the resulting products for use in the manufacture of dry ice. The exit gases from the scrubber analyze 5% O_2 and 95% N_2. Calculate:

(i) Air to gas ratio and

(ii) The percentage of excess air.

4.49 A contact process sulphuric acid plant, burns essentially pure sulfur with air. The products of combustion pass to a converter where some of the SO_2 is converted to SO_3 at a high rate owing to the high temperature of the gas. The gas is then cooled and sent to a final converter where the oxidation can be carried further at the lower temperature, that is more favourable from the stand point of greater conversion of SO_2 to SO_3. The gas from the first converter was found to contain 2.4% of SO_2. The gas from the final converter contained 0.2% SO_2 and 9.4% O_2. What percentage of the total SO_2 was converted to SO_3 in the first and second converters? What was the excess of air used to burn the sulphur?

4.50 In an industry, ethyl alcohol is produced by the fermentation of molasses. The molasses sample contains 42% by weight fermentable sugar in the form of sucrose. The reactions taking place in the fermenter are:



$$\underset{\text{Sucrose}}{C_{12}H_{22}O_{11}} + H_2O \xrightarrow{\text{Invertase}} \underset{\text{d-Glucose}}{C_6H_{12}O_6} + \underset{\text{d-Fructose}}{C_6H_{12}O_6}$$

$$\underset{\text{Monosaccharide}}{C_6H_{12}O_6} \xrightarrow{\text{Zymase}} \underset{\text{Alcohol}}{2C_2H_5OH} + 2CO_2$$

Calculate the theoretical production of rectified spirit having density of 0.789 kg/l in litres per tonne of molasses.

4.51 A coke contain 85% carbon and 15% non-combustible material by weight.

(i) Calculate the amount of O_2 theoretically required to burn 150 kg of coke completely.

(ii) If 40% excess air is supplied, calculate the composition of gases in the product stream.

4.52 Chlorine gas is manufactured by Decon process. A mixture of dry hydrochloric acid gas and air is passed over a heated catalyst which promotes oxidation of acid. 40% excess air is used for the reaction.

Calculate:

(i) Weight of air supplied per kilogram of acid.

(ii) Composition of gases in the product stream.

4.53 Soda ash is manufactured as per the reaction given below:

$$2NaHCO_3 \rightleftharpoons Na_2CO_3 + CO_2 + H_2O$$

Wet $NaHCO_3$ containing 6% water is pre-mixed with recycled dry soda ash so as to reduce the water content to 2% before entering into the calciner. The calciner is being feed with 2500 kg of wet bicarbonate per hour. Calculate:

(i) Quantity of soda ash produced per hour as the final product.
(ii) Quantity of off gases produced per hour.
(iii) Mole ratio of CO_2 to H_2O in the off gases.
(iv) Recycle ratio of Na_2CO_3 per hour.

4.54 The equation for methanol synthesis is

$$CO_2 + 3H_2 \rightleftharpoons CH_3OH + H_2O.$$

The CO_2 and H_2 are reacting in stoichiometric quantities and contain 0.45% inerts by volume. All gases are ideal. The process is under steady state. The concentration of inerts going into the reactor must be below 2.4% by volume.

Calculate:

(i) Moles recycled per moles of feed.
(ii) Moles purged per moles of fresh feed.

4.55 A wet organic pigment containing 36% by weight of CCl_4 is to be dried to 6% by weight (wet basis). The drier is to operate adiabatically with fresh plus recycle air entering the dryer with 0.45 kg of CCl_4 per kg of dry air. The air leaves the dryer with 0.895 kg of CCl_4/kg of dry air. The capacity of the dryer is 250 kg of bone dry solid per hour. Calculate the ratio of the recycled air to fresh air.

4.56 Methane is burnt with oxygen to yield CO_2 and H_2O. The feed contains 19% CH_4, 61% O_2 and 20% CO_2. The percentage conversion of CH_4 is 90%. Calculate the molar composition of product stream using

(i) Balance of molecular species
(ii) Atomic balance
(iii) Excess reactant.

4.57 Propane (C_3H_8) is dehydrogenated to form propylene (C_3H_6) in a catalytic reactor. The process is to be designed for 96% overall conversion. The reaction products are separated into 2 streams one containing H_2, C_3H_6 and 0.5% of C_3H_8 that leaves the reactor which is taken as product. The other stream contains the balance of unreacted propane and 4% of propylene which is recycled into reactor. Calculate:

(i) The composition of the product.
(ii) The ratio of moles recycled to moles of fresh feed.
(iii) The single pass conversion.

4.58 A fuel gas contains

$CO_2 = 3.5\%$
$C_2H_4 = 3.8\%$
$C_6H_6 = 1.4\%$
$O_2 = 0.5\%$
$CO = 16.8\%$

H_2 = 34.6%

CH_4 = 25.2%

and N_2 = 14.2%

by volume. It is burnt with air in a furnace. The CO_2 analyzer indicates 9.8 mole% of CO_2 on dry basis in the flue gas. Calculate:

(i) The percentage excess air used.

(ii) The complete analysis of flue gas.

4.59 Chlorobenzene is nitrated using a mixture of nitric acid and sulphuric acid. The reaction is

$$C_6H_5Cl + [HNO_3 + H_2SO_4] \rightleftharpoons ClC_6H_4NO_2 + H_2O.$$

A charge consists of 102 kg of chlorobenzene, 104 kg of 64.5% HNO_3 and 108 kg of 94.6% H_2SO_4 by weight. After two hours of operation, the final mixture was analyzed. The final product contained 2.5% unreacted chlorobenzene. Also, the product distribution was found to be 64% P-nitrochlorobenzene and 36% O-nitrochlorobenzene. Calculate

(i) Analysis of charge,

(ii) The percentage conversion of chlorobenzene, and

(iii) The composition of the product stream.

Data:

Molecular weight of chlorobenzene = 112.5

Molecular weight of Nitrochlorobenze = 157.5.

4.60 A furnace uses a producer gas of the following analysis:

CO_2 = 5.2%

CO = 22.2%

H_2 = 14.4%

CH_4 = 1.1%

and N_2 = 57.1%.

The flue gas contains

CO_2 = 14.2%

O_2 = 2.2%

and N_2 = 83.6%.

Both analysis were conducted using Orsat apparatus. Calculate the percentage of excess air used in the furnace.

4.61 A quantity of Barytes containing only pure Barium sulphate and infusible matter is fused with an excess of pure anhydrous soda ash. The analysis of the fusion mass is as follows:

$BaSO_4$ = 12.1%

Na_2SO_4 = 26.9%

Na_2CO_3 = 20.4%

and remaining is barium carbonate and infusible matter. Calculate:

(i) The percentage conversion of barium sulfate to carbonate.

(ii) The percentage composition of original barytes.

(iii) Complete analysis of fusion mass.

(iv) Percentage of Na_2CO_3 used in excess.

4.62 A fuel oil contains 86% C, 14% H_2 is burnt to yield a flue gas of the following composition.

CO_2 = 12.4%

O_2 = 3.5%

and N_2 = 84.1%.

Calculate the weight of flue gas produced per 120 kg of fuel oil and percentage of excess air used.

4.63 A furnace uses coke containing 82% carbon, 0.6% hydrogen and the rest ash. The furnace operates with 50% excess air. The solid residue (ash) contains 1% unburnt carbon of the carbon burnt and 4% goes to form CO. Calculate:

(i) The composition of flue gas.

(ii) The solid residue per 120 kg of coke burnt.

(iii) The kg of carbon lost per 120 kg of coke burnt.

4.64 A contact process sulphuric acid plant burns essentially pure sulphur with air. The products of combustion pass to a converter where some of the SO_2 is converted to SO_3 at a high rate owing to the high temperature of the gas. The gas is then cooled and sent to a final converter where the oxidation can be carried further at the lower temperature, that is more favourable from the stand point of greater conversion of SO_2 of SO_3. The gas from the first converter was found to contain 2.5% of SO_2. The gas from the final converter contained 0.15% SO_2 and 9.5% O_2. Calculate:

(i) The percentage of the total SO_2 was converted to SO_3 in the first converter.

(ii) The percentage of the total SO_2 was converted to SO_3 in the second converter.

(iii) The amount of excess air used to burn the sulphur.

4.65 A producer gas made from coke has the following composition by volume.

CO = 28.0% CO_2 = 3.4% O_2 = 0.6%

and N_2 = 68.0%.

The gas is burnt with such a quantity of air that the oxygen from air is 50% in excess of the net oxygen required for complete combustion. If the combustion is 96% complete, calculate the composition of product stream by volume.

4.66 In producing activated charcoal for adsorption purposes, coconut shells are destructively distilled and treated with superheated steam. This results in the evolution of gases which leave the processing equipment mixed with steam. In a plant employing such a process, the gas yield is 1000 m^3/h at 600°C and 1.0 atmospheric pressure absolute, with the following volumetric analysis.

N_2 = 11.0%

H_2 = 19.0

NH_3 = 19.9%

CO_2 = 5.1%

CO = 24.9%

H_2O = 14.6%

C_2H_4 = 5.5%.

Before absorption of the NH_3 in H_2SO_4, the gases are cooled to 90°C in a heat exchanger. This results the removal of 95% of water by condensation. The NH_3 absorbed by the hot condensed gases are negligible. The absorption of NH_3 is accomplished by the absorption of sulphuric acid solution. Calculate:

(i) The weight of gases leaving the processing equipment in kg/h.
(ii) The weight of H_2O condensed in the heat exchanger.
(iii) The weight of $(NH_4)_2\ SO_4$ produced in kg/h.

4.67 Air at 40°C saturated with water vapour is to be dehumidified. Part of the air is sent through a unit where it is cooled and some water is condensed. This air leaves the unit saturated. At 20°C, it is then mixed with air which is bypassed the unit. The final air contains 0.013 kg of water vapour per kg of dry air. The vapour pressure of water at 40°C is 9600 N/m^2 and at 20°C is 1550 N/m^2. Calculate:

(i) The ratio of amount (in kg) of dry air bypassed to the kg of dry air sent through the dehumidifier.
(ii) The volume of final air on the basis of 25,000 m^3 of original wet air per hour.

4.68 A wet organic pigment containing 40% CCl_4 by weight is to be dried to 4% by weight. The dryer is to operate adiabatically with fresh and recycle air entering the dryer with 0.42 kg of CCl_4 per kg of dry air. This air leaves the dryer at 0.90 kg of CCl_4 per kg of dry air. The capacity of the dryer is 350 kg bone dry solids per hour. Calculate the ratio of recycle to fresh air.

4.69 The stock containing 1.6 kg of water per kg of dry material is to be dried to 0.12 kg of water per kg of dry material. For each kg of dry material, 50 kg of dry air passes through the dryer. The air leaves at 0.05 humidity. The fresh air is supplied at 0.015 humidity. Calculate the fraction of air recycled.

4.70 In a chemical process industry, methanol is synthesized as per the chemical reaction

$$CO + 2H_2 \rightleftharpoons CH_3OH$$

The fresh feed to the process contains 30 moles% CO, 66 mole% H_2 and 4 mole%inerts. It is mixed with recycle feed. The single pass conversion of CO is 24%. The product stream from the reactor is fed to the condenser where all methanol formed gets condensed and the gases from the condenser are recycled. In order to prevent the build up of inerts in recycle loop, a portion of the gases leaving the condenser is continuously purged. If mixed feed contains 14% inert, calculate:

(i) Recycle ratio
(ii) Purge ratio.

5

Combustion of Fuels

5.1

Introduction

A substance that produces light and heat energy when burnt in excess air is called a fuel. The main elements present in fuels are carbon and hydrogen. During the combustion process of fuel, carbon gets converted into carbon dioxide and hydrogen gets converted into water. The product of combustion of fuels have less heat content than the reactants. Therefore, fuels release heat energy during the combustion process. Fuels are generally used for heating and producing energy. Fuels can be classified as:

1. Solid fuels
2. Liquid fuels and
3. Gaseous fuels.

According to their physical state, they are classified.

5.1.1 Solid Fuels

Solid fuels are classified into two types; primary solid fuels and secondary solid fuels. The fuel which comes from the natural source is called primary fuel. The examples of primary fuels are coal, wood, bagasse etc. The fuels which is derived from the natural solid fuel is called secondary fuel. The examples of secondary solid fuels are charcoal, coke, etc. Generally, the solid fuels contain carbon, hydrogen, non-combustible ash, water and sulphur.

5.1.2 Liquid Fuels

The liquid fuels are also classified into two types; primary liquid fuel and secondary liquid fuel. The example of primary liquid fuel is petroleum and the examples of secondary liquid fuels are Synthetic petrol, Diesel, Kerosene, Gasoline, etc. Generally, the solid fuel contains Carbon, Hydrogen, Nitrogen, Oxygen and Sulphur.

5.1.3 Gaseous Fuels

The gaseous fuels are classified into two types; Primary gaseous fuel and secondary gaseous fuel. The example of a primary gaseous fuel is Natural gas and the examples of secondary gaseous fuels are producer gas, water gas, LPG, coal gas and biogas.

The natural gas contains 80% to 90% methane and the rest is ethane and propane. It also contains small amount of other gases like light hydrocarbon and acetylene.

In the process of combustion of fuel, carbon, hydrogen and sulphur react with oxygen to form carbon dioxide, water and sulphur dioxide respectively. A combustion process in which elements present in the fuel are completely get converted into products is called complete combustion. For example, carbon reacts with oxygen to form carbon dioxide is a complete combustion process.

$$C + O_2 \rightarrow CO_2 \qquad (5.1)$$

Other examples of complete combustion are:

$$S + O_2 \rightarrow SO_2 \qquad (5.2)$$

$$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O \qquad (5.3)$$

$$C_2H_4 + 3O_2 \rightarrow 2CO_2 + 2H_2O \qquad (5.4)$$

$$C_3H_8 + 5O_2 \rightarrow 3CO_2 + 4H_2O \qquad (5.5)$$

A combustion process in which elements present in the fuel do not get converted completely into products is called incomplete combustion. It is also known as Partial combustion. When insufficient amount of oxygen reacts with carbon to form carbon monoxide is an example of incomplete combustion.

$$C + \frac{1}{2}O_2 \rightarrow CO \qquad (5.6)$$

Other examples of incomplete combustions are:

$$C_2H_4 + 2O_2 \rightarrow 2CO + 2H_2O \qquad (5.7)$$

$$C_3H_8 + \frac{7}{2}O_2 \rightarrow 3CO + 4H_2O \qquad (5.8)$$

Always excess amount of oxygen is needed to supply for complete combustion of fuels. Generally, air is used as a source of oxygen in most of the combustion operation.

After burning of fuel, the gases CO, CO_2, H_2O, SO_2, SO_3 and N_2 leave the combustion chamber are referred to as flue gases. They are also known as stack gases. These combustion products of fuel are worthless. The flue gas analysis is very essential for many useful purpose. The flue gas analysis can be carried out by wet basis or dry basis. If the mole of water is accounted in the calculation of composition of flue gas analysis, then it is called the composition on wet basis. If the mole of water is not accounted in the calculation of composition of flue gas analysis, then it is called composition on dry basis.

5.2

Calorific Value of Fuels

It is defined as the total amount of heat released when a unit mass of fuel is completely burnt in the presence of air. The calorific value is also known as heating value or energy value. It is the characteristics of a combustible substance. The calorific value of fuel is always positive. It is measured in units of energy per unit of substance, usually in mass. The units may be expressed as kcal/kg or kJ/kg. For examples, the calorific value of Methane = 50 MJ/kg, kerosene = 43 MJ/kg and coal = 20 MJ/kg. The calorific value of fuel is commonly determined by using Bomb Calorimeter.

When a fuel is burnt, hydrogen present in the fuel reacts with oxygen supplied from the air and results in the formation of water in the process. Because of this reason, the latent heat of vaporisation is lost. Hence, this amount of heat is not available for any useful purpose. The latent heat of vaporisation of water can be made available for useful purpose if the water vapour in the flue gas are removed completely by the process of condensation.

The net calorific value (NCV) is also known as low heating value (LHV). It is the calorific value of the fuel which is determined in the presence of water. It is expressed in kJ/kg.

The gross calorific value (GCV) is also known as high heating value (HHV). It is the calorific value of the fuel which is determined in the absence of water vapour. It is expressed in unit of kJ/kg. The relation between HHV and LHV may be expressed as:

$$\text{HHV} = \text{LHV} + nH_V \qquad (5.9)$$

where

HHV = High heating value (kJ/kg)
LHV = Low heating value (kJ/kg)
n = Number of moles of water vapour
H_V = Heat of vaporisation of water (kJ/mol)

But, we know that

$$nH_V = ml \qquad (5.10)$$

where

m = Mass of water (kg)
l = Latent heat of water vapour (kJ/kg)

Substituting Eq. (5.10) in Eq. (5.9), we get

$$\text{HHV} = \text{LHV} + ml \qquad (5.11)$$

If any two properties of the fuel are known, then unknown properties may be calculated using this equation.

5.3

Analysis of Fuel

The analysis of fuel can be made by the following method:

1. Ultimate analysis
2. Proximate analysis.

5.3.1 Ultimate Analysis

When analysis of fuel involves the determination of carbon, nitrogen, hydrogen, sulphur and oxygen, it is called ultimate analysis.

5.3.2 Proximate Analysis

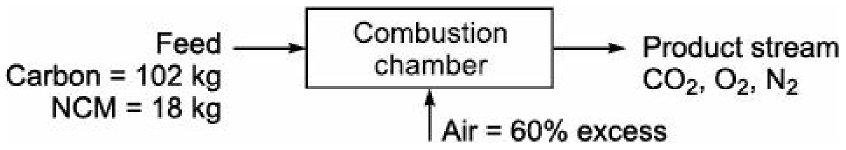
When analysis of fuel involves the determination of ash, moisture, volatile matter and fixed carbon, it is called proximate analysis.

EXAMPLE 5.1 A coke contains 85% carbon and 15% non-combustible material by weight. Calculate:

(i) The amount of oxygen theoretically required to burn 120 kg of coke completely.
(ii) The composition of gases in the product stream if 60% excess air is supplied.

Solution: Basis: 120 kg of coke.

Reaction: $C + O_2 \rightleftarrows CO_2$



(i) From the chemical reaction, we have

1 kgatom of C → 1 kgmol of O_2

12 kg of C → 32 kg of O_2

102 kg of C → $\frac{32 \times 102}{12}$

That is, the amount of O_2 required = 272 kg.

(ii) Amount of O_2 theoretically required = 8.5 kgmol

Now, 21 kgmol of O_2 → 100 kgmol of air

Therefore, 8.5 kgmol of O_2 → $\frac{100 \times 8.5}{21}$

So, air theoretically required = 40.48 kgmol.

Air supplied = $40.48\left(1 + \frac{60}{100}\right)$ = 64.77 kgmol

O_2 in supplied air = (64.77) × (0.21) = 13.60 kgmol

N_2 in supplied air = 64.77 × (0.79) = 51.17 kgmol

Unaccounted O_2 = O_2 in supplied air – O_2 theoretically required

= 13.60 – 8.5 = 5.1 kgmol

From the chemical reaction, we have

1 kg atom of C → 1 kgmol of CO_2

Also, 12 kg of C → 44 kg of CO_2

Therefore, 102 kg of C = $\frac{44 \times 102}{12}$

Amount of CO_2 formed = 474 kg

= $\frac{374}{44}$

= 8.5 kgmol

Composition of gases in product stream

Component	*Quantity* (kgmol)	*Mole*%
CO_2	8.5	13.12
O_2	5.1	7.87
N_2	51.17	79.01
	Total = 64.77 kgmol	

EXAMPLE 5.2 Coal containing

C = 68.2%

H = 4.5%

S = 0.7%

N = 1.7%

O = 7.8%
Ash = 4.4%
and water = 12.7%

is burnt in a furnace. The product of combustion dry gas, analyses CO_2 = 14.4%, O_2 = 4.6% and rest N_2. Calculate:

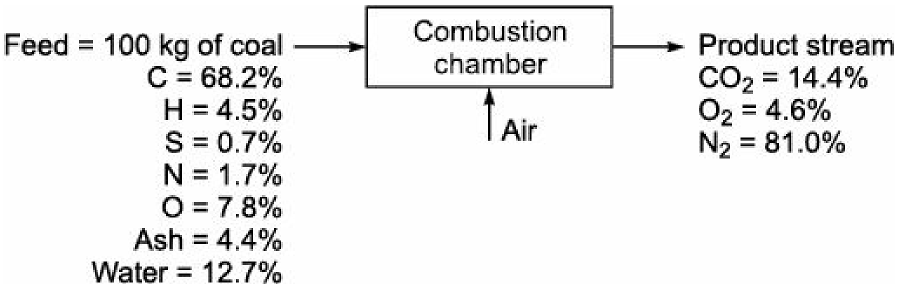
(i) The theoretical volume of air used for the complete combustion of 100 kg of coal.
(ii) The percentage of excess air used.

Solution: Basis: 100 kg of coal burnt.

Reaction: $C + O_2 = CO_2$

$H_2 + 1/2O_2 = H_2O$

$S + O_2 = SO_2$



(i) Total O_2 required = O_2 required for C + O_2 required for H + O_2 required for S

$$= \frac{68.2}{12} + \frac{4.5/2}{2} + \frac{0.7}{32}$$

= 6.83 kgmol

Now, O_2 present in coal = 7.8 kg

$$= \left(\frac{7.8}{32}\right) = 0.244 \text{ kgmol}$$

Hence, O_2 to be supplied = 6.83 – 0.244 = 6.586 kgmol

Now, 21 kgmol of O_2 → 100 kgmol of air

Therefore, 6.586 kgmol of O_2 → $\frac{100 \times 6.586}{21}$ = 31.35 kgmol

Also, 1 kgmol of air = 22.414 m^3

So, 31.35 kgmol of air = $\frac{22.414 \times 31.35}{1}$

That is the amount of air required for combustion = 702.94 m^3.

(ii) Let ‘x’ be the amount of flue gas in kgmol. Overall material balance for carbon:

$x(0.144) = 5.683$

$x = 39.465$ kgmol

Now, N_2 present in flue gas = 81%.

Therefore, the amount of N_2 in flue gas = (39.465) × (0.81)

= 31.967 kgmol

N_2 present is coal = $\frac{1.7}{28}$

= 0.061 kgmol

N_2 supplied from air = 31.967 – 0.061

= 31.906 kgmol

Air supplied = $\frac{31.906 \times 100}{79}$

Amount of air supplied = 40.39 kgmol

Amount of O_2 supplied = 40.39 × (0.21) = 8.48 kg mol

$$\text{Percentage of excess air} = \frac{O_2 \text{ supplied} - O_2 \text{ theoretically required}}{O_2 \text{ theoretically required}} \times 100 = \frac{8.48 - 6.586}{6.586} \times 100$$

= 28.76

EXAMPLE 5.3 A sample of coke having the percentage composition

C = 79.8%
H = 5.9%
O = 8.1%
N = 1.3%
S = 0.63%

and the rest is ash is gasified in a generator. The gas in the product stream has the % composition; CO_2 = 5.1%, CO = 31.9%, H_2 = 11.8% and the rest N_2. Calculate:

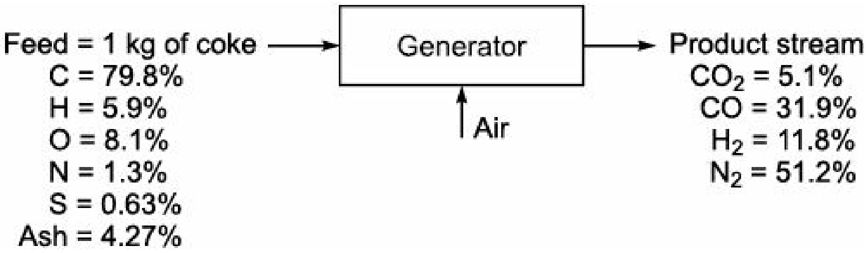
(i) m^3 of gas produced per kg of coke gasified.

(ii) The amount of air used for gasification per m^3 of gas produced.

Solution: Basis: 1 kg of coke gasified.

Reaction: $C + O_2 \rightleftharpoons CO_2$

$H + \frac{1}{2}O_2 \rightleftharpoons H_2O$



(i) Amount of C in coke = 0.798 kg

= $\frac{0.798}{12}$ = 0.0665 kg atom

Let 'x' be the amount of product stream in kgmol.

Material balance for carbon:

$x \times (0.37) = 0.0665$

$x = 0.1797$ kgmol

1 kgmol of air = 22.414 m^3

0.1797 kgmol of air = $\frac{22.414 \times 0.1797}{1}$

Gas produced per kg of coke = 4.028 m^3.

(ii) Amount of N_2 present in the product stream = $x \times (0.512)$

= 0.1797 × 0.512 = 0.092 kgmol

N_2 present in coke = $\left(\frac{1.3}{100}\right)$ kg

= $\frac{0.013}{28}$ = 0.00046 kgmol

N_2 supplied from air = 0.092 – 0.00046 = 0.0915 kgmol

Now, 79 kgmol of N_2 → 100 kgmol of air

Therefore, 0.0915 kgmol of N_2 → $\frac{100 \times 0.0915}{79}$ = 0.1158 kgmol

Therefore, the amount of air = 2.596 m^3.

$$\frac{\text{m}^3 \text{ of air}}{\text{m}^3 \text{ of gas}} = \frac{2.596}{4.028}$$

$$= 0.645$$

EXAMPLE 5.4 Wood having an analysis of

C = 45.9%

O = 23.1%

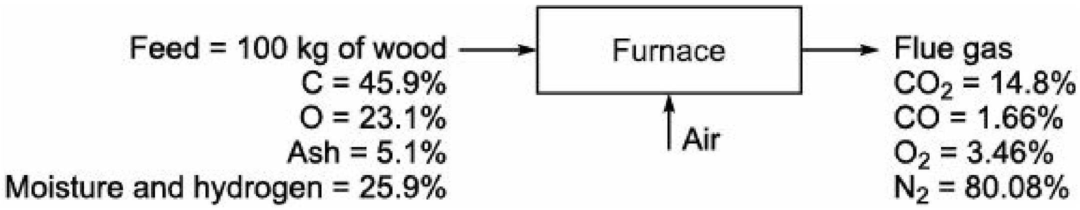
Ash = 5.1%

and rest containing moisture and hydrogen is burnt in a furnace. An Orsat analysis of the flue gas during a run shows CO_2 = 14.8%, CO = 1.66%, O_2 = 3.46% and N_2 = 80.08%. Calculate:

(i) The complete analysis of the wood used.
(ii) The fuel to air ratio by weight.
(iii) The percentage of excess air used.
(iv) The composition of the flue gas.

Solution: Basis: 100 kg of wood.

Reaction:



Now, Amount of carbon present = 45.9 kg

= $\frac{45.9}{12}$

= 3.825 kgatom

Carbon present in flue gas = (14.8 + 1.66)%

= 16.46%

Let ‘x’ be the amount of flue gas in kgmol.

Overall material balance for carbon:

$x \times (0.1646) = 3.825$

$\therefore\ x = 23.24$ kgmol

Also, N_2 present in flue gas = 80.08%

Amount of N_2 present in flue gas = 23.24 × (0.8008) = 18.61 kgmol.

Now, 79 kgmol of N_2 → 100 kgmol of air

Therefore, 18.61 kgmol of $N_2 = \frac{100 \times 18.61}{79}$

Amount of air in flue gas = 23.56 kgmol

Amount of air supplied = Amount of air in flue gas

= 23.56 kgmol

= 683.24 kg

Material balance for oxygen:

Oxygen supplied = $18.61 \times \left(\frac{21}{79}\right) = 4.946$ kgmol

Oxygen present in fuel = 23.1 kg

$= \frac{23.1}{32} = 0.722$ kgmol

O_2 accounted = 4.946 + 0.722 = 5.668 kgmol

O_2 present in flue gas = $\frac{14.8 + (1.66/2) + 3.46}{100}$

$= \left(\frac{19.09}{100}\right) \times 23.24 = 4.436$ kgmol

O_2 unaccounted = 5.668 – 4.436 = 1.232 kgmol

Unaccounted O_2 required for burning of Hydrogen.

Moles of H_2 reacted = 1.232 × 2 = 2.464 kgmol

Amount of hydrogen reacted = 4.928 kg.

Moisture and hydrogen in wood = 25.9 kg.

H_2 in wood = 4.928 kg

Moisture present in wood = 25.9 – 4.928 = 20.972 kg

$= \frac{20.972}{18} = 1.165$ kgmol

Moisture formed from H_2 = 2.464 kgmol

Moisture present in flue gas = 1.165 + 2.464

Therefore, = 3.629 kgmol

(i) Analysis of wood:

Components	*Amount* (kg)	*Weight*%
C	45.9	45.9
O	23.1	23.1
Ash	5.1	5.1
H	4.928	4.928
Moisture	20.972	20.972
	Total = 100.00 kg	

(ii) Fuel to air ratio = $\dfrac{100}{683.24}$ = 0.1464

(iii) O_2 required for complete combustion = 3.825 + 1.232 = 5.057 kgmol

O_2 present in fuel = 0.722 kgmol

O_2 theoretically required = 5.057 – 0.722 = 4.335 kgmol

Percentage of excess air = $\dfrac{O_2 \text{ supplied} - O_2 \text{ theoretically required}}{O_2 \text{ theoretically required}} \times 100$ = $\dfrac{4.946 - 4.335}{4.335} \times 100$ = 14.09

(iv) Amount of CO_2 in flue gas = 23.24 × (0.148) = 3.44 kgmol

Amount of CO in flue gas = 23.24 × (0.0166) = 0.386 kgmol

Amount of O_2 in flue gas = 23.24 × (0.0346) = 0.804 kgmol

Amount of N_2 in flue gas = 23.24 × (0.8005) = 18.60 kgmol

Amount of H_2O in flue gas = 3.629 kgmol

CO gas analysis:

Components	*Amount* (kgmol)	*Mole*%
CO_2	3.44	12.81
CO	0.386	1.44
O_2	0.804	2.99
N_2	18.60	69.25
H_2O	3.629	13.51
	Total = 26.859 kgmol	

EXAMPLE 5.5 A coal fired furnace emits 56,000 m^3/h of flue gas at 260 °C. The coal used analyses as

C = 57.4%
H = 4.3%
N = 2.3%

S = 0.3%
O = 7.6%
H_2O = 9.0%
Ash = 19.1%

If the burning rate is 4 tonnes of coal per hour. Calculate:

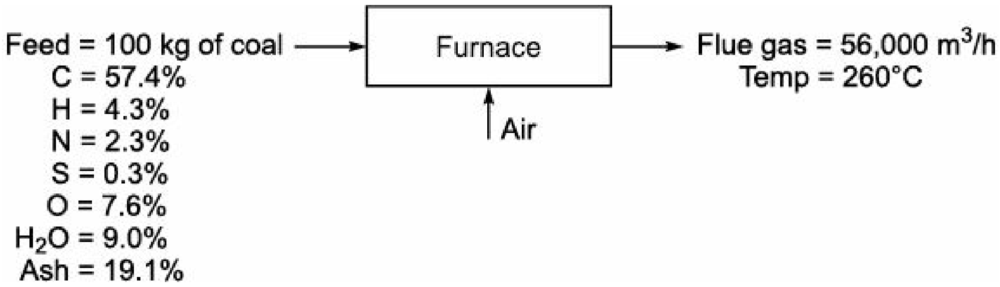
(i) Orsat analysis of flue gas
(ii) The percentage excess air used

Solution: Basis: 100 kg of coal burnt.

Reaction: $C + O_2 = CO_2$

$H_2 + \frac{1}{2}O_2 = H_2O$

$S + O_2 = SO_2$



Amount of O_2 required = 153.07 + 34.4 + 0.3 = 187.77 kg

= 5.87 kgmol

Amount of O_2 present in coal = 7.6 kg

= 0.24 kgmol

O_2 theoretically required = 5.87 – 0.24 = 5.63 kgmol

N_2 supplied from air = $5.63 \times \frac{79}{21}$ = 21.18 kgmol

Amount of flue gas from coal = 4.783 + 2.15 + 0.082 + 0.0094 + 0.5 = 7.524 kgmol

Wet flue gas obtained from 100 kg of coal = 21.18 + 7.524 = 28.704 kgmol

Actual flue gas obtained = 56,000 m^3/h = $\frac{56{,}000}{40}$

Actual flue gas obtained from 100 kg of coal = 1400 m^3

Moles of flue gas = $\frac{PV}{RT} = \frac{1 \times 1400}{0.082 \times 533}$ = 32.03 kgmol

Excess flue gas = 32.03 – 28.704 = 3.326 kgmol

Excess air used = 3.326 kgmol

Excess O_2 used = 0.698 kgmol

N_2 with excess air = 2.63 kgmol

Total amount of N_2 in flue gas = (21.18) + (2.63) + (0.082)= 23.862 kgmol

(i) Orsat analysis of flue gas:

Components	*Amount* (kgmol)	*Mole*%

CO_2	4.783	16.29
SO_2	0.0094	0.03
N_2	23.862	81.30
O_2	0.698	2.38
	Total = 29.35 kgmol	

(ii) Percentage of excess air = $\dfrac{O_2 \text{ supplied} - O_2 \text{ theoretically required}}{O_2 \text{ theoretically required}} \times 100 = \dfrac{0.698}{5.63} \times 100 =$ 12.40%

EXAMPLE 5.6 A pulverised coal is burnt in a boiler furnace having the following ultimate analysis:

C = 68.9%
H = 4.9%
O = 17.7%
N = 1.6%

and Ash = 6.9% (by weight of dry sample).

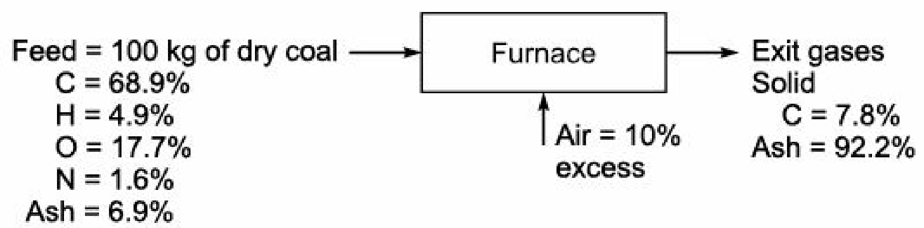
Coal contains 22.5% moisture. The exit gases carry solid which analyses; 7.8% carbon and 92.2% ash. Air used is 10% in excess and under these conditions, 0.8% of total combined carbon in the exit gases pass as CO and rest being as CO_2. Calculate:

(i) What percentage of total carbon of coal is lost in the exit material.
(ii) The exit gas analysis.
(iii) The weight of water vapour accompanies per m^3 of dry gas at 320°C and 1 atmosphere. Air may be considered as dry.

Solution: Basis: 100 kg of dry pulverised coal

Reaction: $C + O_2 = CO_2$

$H_2 + \frac{1}{2}O_2 = CO$



Amount of C lost = $6.9 \times \left(\dfrac{7.8}{92.2}\right) = 0.584$ kg

Amount of C burnt = 68.9 – 0.584 = 68.32 kg

CO in the exit gas = $68.32 \times \left(\dfrac{0.8}{100}\right) = 0.546$ kg

CO_2 in the exit gas = 68.9 – 0.584 = 68.316 kg

Oxygen balance:

O_2 required for combustion = 183.73 + 39.2 = 222.93 kg

= 6.96 kgmol

Amount of O_2 present in coal = 17.7 kg

= 0.553 kgmol

O_2 theoretically required = 6.96 – 0.553 = 6.407 kgmol

Excess air used = 10%

Therefore, O_2 supplied = $6.407 \times \left(1 + \frac{10}{100}\right)$ = 7.05 kgmol

Now, O_2 used for converting C to CO = $0.584 \times \left(\frac{16}{12}\right)$ = 0.778 kg

Also, O_2 used for converting C to CO_2 = $68.32 \times \left(\frac{32}{12}\right)$ = 182.19 kg

Therefore, the amount of O_2 used = 0.778 + 182.19 = 182.968 kg

O_2 available = 225.6 + 17.7 = 243.3 kg

O_2 excess = 243.3 – 182.968 = 60.332 kg

Nitrogen balance:

N_2 supplied from air = $225.6 \times \left(\frac{77}{23}\right)$ = 755.27 kg

N_2 from coal = 1.6 kg

Amount of N_2 in flue gas = 755.27 + 1.6 = 756.87 kg

Flue gas:

CO_2 formed = 68.316 + 182.19 = 250.51 kg

CO formed = 0.546 + 0.778 = 1.324 kg

Water formed = 4.9 + 39.2 = 44.1 kg

(i) The percentage of total carbon coal lost = $\frac{0.584}{68.9} \times 100$ = 0.85

(ii) The exit gas analysis:

Components	*Amount* (kg)	*Amount* (kgmol)	*Mole*%
CO_2	250.51	5.693	16.43
CO	1.324	0.047	0.14
O_2	60.332	1.885	5.44
N_2	756.87	27.031	77.99
		Total = 34.656 kgmol	

(iii) Coal contains 22.5% moisture:

77.5 kg dry coal = 22.5 kg water

100 kg dry coal = $\frac{22.5 \times 100}{77.5}$

Amount of water present in coal = 29.03 kg

Total water vapour in flue gas = 44.1 + 29.03 = 73.13 kg

1 kgmol of dry flue gas = 22.414 m^3

34.656 kgmol of dry flue gas = $\frac{22.414 \times 34.656}{1}$ = 776.78 m^3

= 776.78 × $\frac{320 + 273}{273}$

Total volume of dry flue gas = 1687.29 m^3

Water vapour per m^3 dry flue gas = $\frac{73.13}{1687.29}$ = 0.043.

EXAMPLE 5.7 A fuel oil contains 86.5% C and 13.5% H. It is burnt to form flue gas of following composition:

CO_2 = 12.4%

O_2 = 3.7%

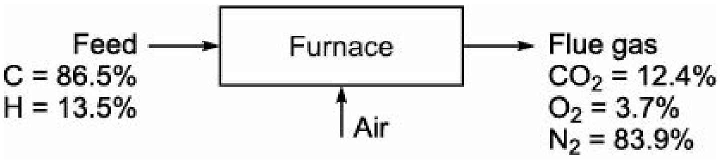
and N_2 = 83.9%

Calculate the percentage of excess air used.

Solution: Basis: 100 kgmol of flue gas.

Reaction: $C + O_2 = CO_2$

$H_2 + 1/2O_2 = H_2O$



N_2 present in flue gas = 83.9 kgmol

O_2 supplied from air = 83.9 × $\left(\frac{21}{79}\right)$ = 22.30 kgmol

O_2 accounted = 12.4 + 3.7 = 16.1 kgmol

O_2 unaccounted = 22.30 – 16.1 = 6.2 kgmol

Unaccounted O_2 used in the formation of water:

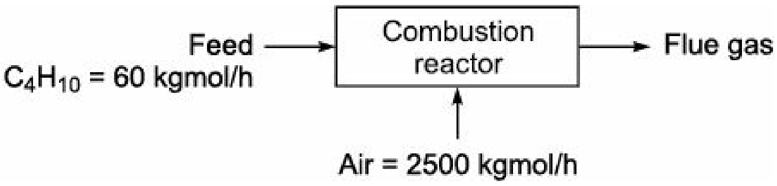
O_2 theoretically required = 12.4 + 6.2 = 18.6 kgmol

The percentage of excess air = $\frac{O_2 \text{ supplied} - O_2 \text{ theoretically required}}{O_2 \text{ theoretically required}} \times 100$ = $\frac{22.30 - 18.60}{18.60} \times 100$ = 19.89%

EXAMPLE 5.8 A combustion reactor is fed with 60 kgmol/h of butane and 2500 kgmol/h of air. Calculate the percentage of excess O_2 and composition of gases leaving the combustion reactor. Assume complete combustion of butane.

Solution: Basis: 60 kgmol/h of butane and 2500 kgmol/h of air.

Reaction: $C_4H_{10} + \left(\frac{13}{2}\right)O_2 \rightarrow 4CO_2 + 5H_2O$



O_2 in supplied air = 2500 × (0.21)

= 525 kgmol

O_2 required:

From the chemical reaction, we have

1 kgmol of $C_4H_{10} \rightarrow \left(\frac{13}{2}\right)$ kgmol of O_2

60 kgmol of $C_4H_{10} = \frac{13 \times 60}{2 \times 1}$

Amount of O_2 required = 390 kgmol

The percentage of excess O_2 $= \frac{O_2 \text{ supplied} - O_2 \text{ theoretically required}}{O_2 \text{ theoretically required}} \times 100 =$

$\frac{525 - 390}{390} \times 100 = 34.62\%$

From the chemical reaction, we have

1 kgmol of $C_4H_{10} \rightarrow$ 4 kgmol of CO_2

60 kgmol of $C_4H_{10} \rightarrow \frac{4 \times 60}{1}$

Amount of CO_2 formed = 260 kgmol

From the chemical reaction, we have

1 kgmol of $C_4H_{10} \rightarrow$ 5 kgmol of H_2O

60 kgmol of $C_4H_{10} \rightarrow \frac{5 \times 60}{1}$

Amount of H_2O formed = 300 kgmol

The amount of N_2 associated with supplied air = 2500 × 0.79 = 1975 kgmol

Composition of flue gas

Components	*Amounts* (kgmol)	*Mole*%
O_2	135	5.06
N_2	1975	73.97
CO_2	260	9.74
H_2O	300	11.23
	Total = 2670 kgmol	

EXAMPLE 5.9 A fuel oil contains 84% C and 16% H. It is burnt to form flue gas of following composition:

$CO_2 = 14.1\%$

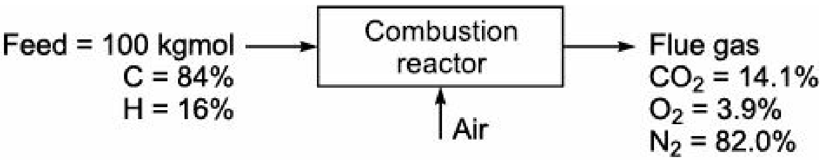
$O_2 = 3.9\%$

and $N_2 = 82.0\%$

Calculate the percentage of excess air used.

Solution: Basis: 100 kgmol of flue gas

Reaction: $C + O_2 \rightleftharpoons CO_2$



N_2 present in flue gas = 82 kgmol

O_2 supplied = $82 \times \left(\frac{21}{79}\right)$ = 21.80 kgmol

O_2 accounted = 14.1 + 3.9 = 18 kgmol

O_2 unaccounted = 21.80 – 18 = 3.8 kgmol

O_2 used for the formation of water = 3.8 kgmol

Therefore, O_2 theoretically required for complete combustion = 14.1 + 3.8 = 17.9 kgmol

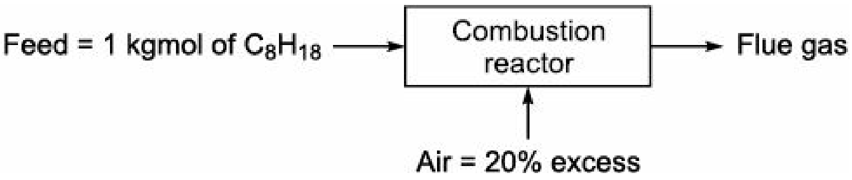
Percentage of excess air = $\frac{O_2 \text{ supplied} - O_2 \text{ theoretically required}}{O_2 \text{ theoretically required}} \times 100$ = $\frac{21.80 - 17.9}{17.9} \times 100$ = 21.78%

EXAMPLE 5.10 Octane is burnt with 20% excess air. Calculate:

(i) Air fuel ratio by weight
(ii) Air fuel ratio by volume
(iii) Weight of dry exhaust gas formed per unit of fuel
(iv) Moles of O_2 in the exhaust gas per unit weight of fuel. (Sp. gravity of Octane = 0.7).

Solution: Basis: 1 kgmol of octane burnt

Reaction: $C_8H_{18} + 12.5O_2 \rightleftharpoons 8CO_2 + 9H_2O$



From the chemical reaction, we have

O_2 theoretically required = 12.5 kgmol

Excess air used = 20%

Therefore, O_2 supplied = $12.5 \times \left(1 + \frac{20}{100}\right)$ = 15 kg mol = 480 kg

Also, N_2 supplied = $15 \times \left(\frac{79}{21}\right)$ = 56.428 kgmol = 1579.98 kg

Amount of air supplied = 71.428 kgmol = 2071.4 kg

Molecular weight of C_8H_{18} = 12 × 8 + 18 × 1 = 114

(i) Air fuel ratio (by weight) = $\frac{2071.4}{114}$ = 18.17

(ii) Density of octane = 700 kg/m^3

Volume of fuel = $\frac{\text{Mass}}{\text{Density}} = \frac{114}{700}$ = 0.163 m^3

Now, 1 kgmol of air → 22.414 m^3

Therefore, 56.428 kgmol of air → $\frac{22.414 \times 56.428}{1}$

Volume of air = 1264.78 m^3

Air fuel ratio (by volume) = $\frac{1264.78}{0.163}$ = 7759.36

(iii) Excess O_2 = O_2 supplied – O_2 theoretically required

= 15 – 12.5 = 2.5 kgmol

Dry flue gas analysis

Components	*Amount* (kgmol)	*Amount* (kg)	*Mole*%
CO_2	8.0	352	11.95
O_2	2.5	80	3.74
N_2	56.428	1580	84.31
	Total = 66.928 kgmol	Total = 2012 kg	

…

$$\frac{\text{Weight of dry exhaust gas}}{\text{Weight of fuel}} = \frac{2012}{114}$$
$$= 17.65$$

(iv) $$\frac{\text{Moles of } O_2 \text{ in exhaust gas}}{\text{Weight of fuel}} = \frac{2.5}{114}$$
$$= 0.0219$$

EXAMPLE 5.11 Determine the flue gas analysis and air fuel ratio by weight when a medium fuel oil having the following composition:

C = 85.7%

H = 10.3%
S = 3.4%
O = 0.5%
Ash = 0.1% (by weight)

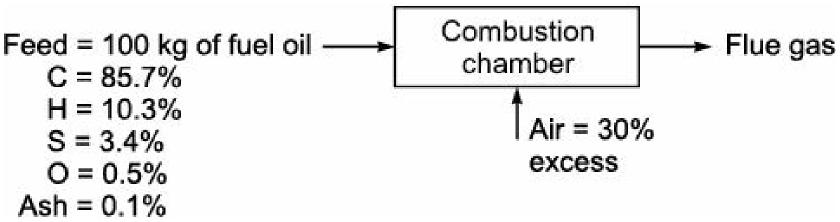
is burnt with 30% excess air. Assume that complete combustion takes place.

Solution: Basis: 100 kg of medium fuel oil.

Reaction: $C + O_2 \rightleftarrows CO_2$

$S + O_2 \rightleftarrows SO_2$

$H_2 + \frac{1}{2}O_2 \rightleftarrows H_2O$



Oxygen balance:

O_2 required for combustion = $85.7 \times \left(\frac{32}{12}\right) + 10.3 \times \left(\frac{16}{2}\right) + 3.4 \times \left(\frac{32}{32}\right)$ = 228.53 + 82.40 + 3.4

= 314.33 kg

O_2 present in fuel = 0.50 kg

Therefore, O_2 theoretically required = 314.33 – 0.50 = 313.83 kg

O_2 supplied = $313.83 \times \left(1 + \frac{30}{100}\right)$ = 407.98 kg

O_2 excess = 407.98 – 313.83 = 94.15 kg

Air supplied = $407.98 \times \left(\frac{100}{23}\right)$ = 1773.83 kg

Air fuel ratio (by weight) = $\frac{1773.83}{100}$ = 17.74

Amount of N_2 supplied = $1773.83 \times \left(\frac{77}{100}\right)$ = 1365.85 kg

Amount of CO_2 formed = $85.7 \times \left(\frac{44}{12}\right)$ = 314.23 kg

Amount of SO_2 formed = $3.4 \times \left(\frac{64}{32}\right)$ = 6.8 kg

Amount of H_2O formed = $10.3 \times \left(\frac{18}{2}\right)$ = 92.7 kg

Flue gas analysis (wet basis)

Components	*Amount* (kgmol)	*Mole%*
O_2	2.942	4.59
N_2	48.780	76.08
CO_2	7.142	11.14
SO_2	0.106	0.17
H_2O	5.150	8.02
	Total = 64.120 kgmol	

EXAMPLE 5.12 The dry flue gases from a oil fired furnace has composition of

CO_2 = 12.1%

O_2 = 5.7%

and N_2 = 82.2%

when analysed by an Orsat apparatus. Calculate:

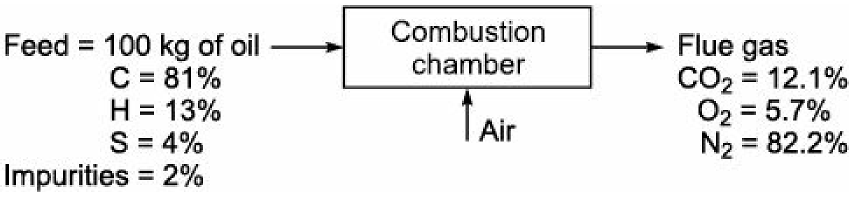
(i) The percentage of excess air

(ii) The weight of combustion air used per kg of oil fired.

Assume oil fuel contains 81% C, 13% H, 4% S and rest impurities. The molecular weight of dry gas is 29.

Solution: Basis: 100 kg of fuel oil fired.

Reaction: $C + O_2 \rightarrow CO_2$



Oxygen balance:

$$\text{Amount of } O_2 \text{ required for combustion} = 81 \times \left(\frac{32}{12}\right) + 13 \times \left(\frac{16}{2}\right) + 4 \times \left(\frac{32}{32}\right)$$

= 216 + 104 + 4

= 324 kg

= 10.125 kgmol

Let ‘x’ be the dry flue gas in kgmol.

Material balance for carbon:

$$x \times \left(\frac{12.1}{100}\right) = 6.75$$

$\therefore\ x$ = 55.785 kgmol

$$\text{Amount of } N_2 \text{ in flue gas} = 55.785 \times \left(\frac{82.2}{100}\right) = 45.86 \text{ kg mol}$$

$$\text{Amount of } O_2 \text{ supplied} = 45.86 \times \left(\frac{21}{79}\right) = 12.19 \text{ kgmol}$$

(i) The percentage of excess air $= \dfrac{O_2 \text{ supplied} - O_2 \text{ theoretically required}}{O_2 \text{ theoretically required}} \times 100$ =

$\dfrac{12.19 - 10.125}{10.125} \times 100$ = 20.4%

(ii) Amount of air used = 45.86 × $\left(\dfrac{100}{79}\right)$ = 58.05 kgmol = 1683.46 kg

$$\frac{\text{Weight of combustion air}}{\text{Weight of oil}} = \frac{1683.46}{100}$$
$$= 16.83$$

EXAMPLE 5.13 Calculate the excess air used in a furnace when the flue gas Orsat analysis is

CO_2 = 8.3%

O_2 = 9.7%

CO = 0.3%

H_2 = 0.3%

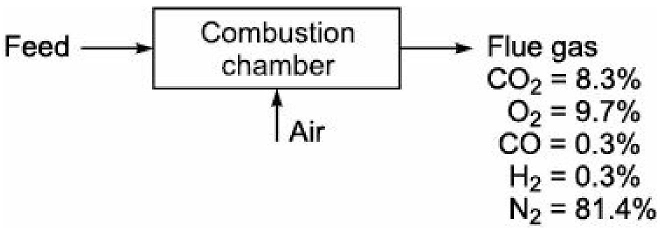
and N_2 = 81.4%.

Solution: Basis: 100 kgmol of flue gas.

Reaction: $C + O_2 = CO_2$

$C + \frac{1}{2}O_2 = CO$

$H_2 + \frac{1}{2}O_2 = H_2O$



Oxygen balance:

Amount of N_2 in flue gas = 81.4 kgmol

Amount of O_2 supplied = 81.4 × $\left(\dfrac{21}{79}\right)$ = 21.637 kgmol

O_2 accounted = 8.3 + 9.7 + 0.15 = 18.15 kg mol

O_2 unaccounted = 21.637 – 18.15 = 3.487 kgmol

O_2 used for the formation of water = 3.487 kgmol

O_2 theoretically required = 8.3 + 0.15 + 3.487 + 0.15 kgmol = 12.087 kgmol

The percentage of excess air $= \dfrac{O_2 \text{ supplied} - O_2 \text{ theoretically required}}{O_2 \text{ theoretically required}} \times 100$ =

$$\frac{21.637 - 12.087}{12.087} \times 100 = 79\%$$

EXAMPLE 5.14 The flue gas from a furnace using a hydrocarbon fuel oil analyses as follows by volume.

CO_2 = 15.5%

CO = 0.3%

O_2 = 2.5%

and N_2 = 81.7%.

Calculate:

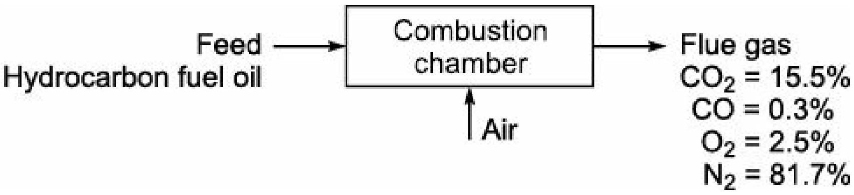
(i) The percentage of excess air used

(ii) The percentage composition of fuel burnt (by weight).

Solution: Basis: 100 kgmol of flue gas

Reaction: $C + O_2 \rightleftharpoons CO_2$

$H_2 + \frac{1}{2}O_2 \rightleftharpoons H_2O$



Amount of N_2 in flue gas = 81.7 kgmol

Oxygen balance:

O_2 supplied from air $= 81.7 \times \left(\frac{21}{79}\right) = 21.71$ kgmol

O_2 accounted = 15.5 + 0.15 + 2.5 = 18.15 kgmol

O_2 unaccounted = 21.71 – 18.15 = 3.56 kgmol

Unaccounted O_2 used for the formation of water:

H_2 reacted = 3.56 × 2 = 7.12 kgmol

= 14.24 kg

Carbon in flue gas = 15.5 + 0.3 = 15.8 kgatom

= 189.6 kg

O_2 required for C $= 189.6 \times \left(\frac{32}{12}\right) = 505.6$ kg

= 15.8 kgmol

O_2 required for H $= 14.24 \times \left(\frac{16}{2}\right) = 113.92$ kg

= 3.56 kgmol

Therefore, O_2 theoretically required = 15.8 + 3.56 = 19.36 kgmol

(a) Percentage of excess air $= \dfrac{O_2 \text{ supplied} - O_2 \text{ theoretically required}}{O_2 \text{ theoretically required}} \times 100 = \dfrac{21.71 - 19.36}{19.36} \times 100 = 12.14\%$

(b) Composition of fuel:

Components	*Amount* (kg)	*Weight*%
C	189.6	93.01
H	14.24	6.99
	Total = 203.84 kg	

EXAMPLE 5.15 Coal for fuel containing

C = 88%
H = 7%
S = 0.4%
O = 2.4%
N = 2.2%

and of gross calorific value of 40,000 kJ/kg and specific gravity 1.1 is burnt with air as the atomizing agent at a rate of 50 kg/h. Assuming that 30% excess air is used and the combustion is complete. Calculate:

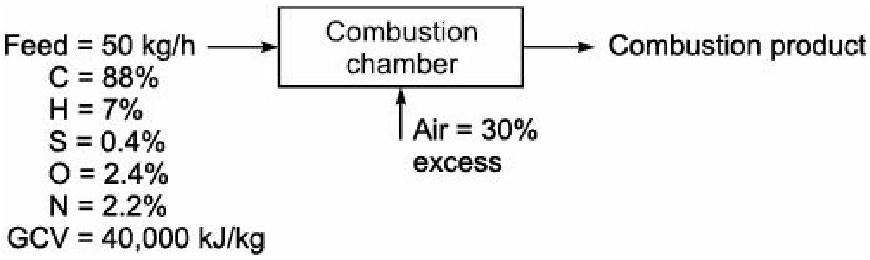
(i) The volume at NTP of air supplied to the burner per hour.
(ii) The volume of the resulting product of combustion per hour at 750°C.
(iii) The volumetric composition of combustion product.

Solution: Basis: 50 kg/h of coal for fuel used.

Reaction: $C + O_2 \rightleftarrows CO_2$

$S + O_2 \rightleftarrows SO_2$

$H_2 + \frac{1}{2}O_2 \rightleftarrows H_2O$



Oxygen balance:

O_2 required for combustion $= 50 \times 0.88 \times \left(\dfrac{32}{12}\right) + 50 \times 0.07 \times \left(\dfrac{16}{2}\right) + 50 \times 0.004 \times \left(\dfrac{32}{32}\right)$

$= 117.33 + 28 + 0.2 = 145.53$ kg

O_2 present in fuel $= 50 \times 0.024 = 1.2$ kg

O_2 theoretically required $= 145.53 - 1.2 = 144.33$ kg $= 4.51$ kgmol

O_2 supplied = $4.51 \times \left(1 + \frac{30}{100}\right) = 5.863$ kgmol

(i) Air supplied = $5.863 \times \left(\frac{100}{21}\right) = 27.919$ kgmol

1 kgmol of air = 22.414 m^3

Therefore, 27.919 kgmol of air = $\frac{22.414 \times 27.919}{1}$

The volume of air supplied at NTP = 625.78 m^3/h
O_2 excess = 5.863 – 4.51 = 1.353 kgmol

(ii) N_2 supplied from air = 27.919 × (0.79) = 22.06 kgmol

N_2 present in fuel = 50 × 0.022 = 1.1 kg

= 0.039 kgmol
Therefore, the amount of N_2 in the product = 22.06 + 0.039 = 22.099 kgmol

CO_2 formed = $(50 \times 0.88) \times \left(\frac{44}{12}\right) = 161.33$ kg

= 3.67 kgmol

H_2O formed = $50 \times (0.07) \times \left(\frac{18}{2}\right) = 31.5$ kg

= 1.75 kgmol

SO_2 formed = $50 \times (0.004) \times \left(\frac{64}{32}\right) = 0.4$ kg

= 0.006 kgmol
Amount of flue gas formed = (1.353) + (22.099) + (3.67) + (1.75) + (0.006) = 28.878 kgmol

1 kgmol of air → 22.414 m^3

Therefore, 28.878 kgmol of air → $\frac{22.414 \times 28.878}{1}$

Amount of combustion product = 647.27 m^3

= $647.27 \times \frac{750 + 273}{273}$

The volume of resulting product = 2425.48 m^3/h.
(iii) Volumetric composition of combustion product:

Components	*Amount* (kgmol)	*Mole*%	*Volume*%
CO_2	3.670	12.70	12.70
O_2	1.353	4.69	4.69
N_2	22.099	76.53	76.53
H_2O	1.750	6.06	6.06

SO_2	0.006 Total = 28.878 kgmol	0.02	0.02

EXAMPLE 5.16 A gas mixture containing 86% methane (CH_4) and 14% ethane (C_2H_6) by volume is burnt with air. Orsat analysis of the flue gas after complete combustion shows 5.4% carbon dioxide by volume. The air enters at 0°C, 1 atm and contains no water vapour. Calculate:

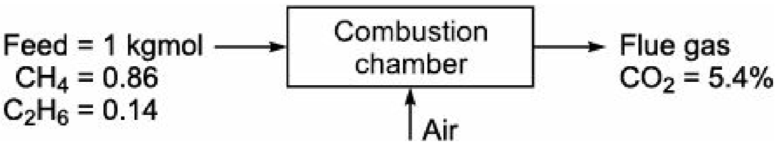
(i) The percentage of excess air used.

(ii) The volume in m^3 of the flue gas produced at 340°C and 760 mmHg per m^3 of fuel gas measured at NTP.

Solution: Basis: 1 kgmol of fuel gas mixture.

Reaction: $CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$

$C_2H_6 + 3.5O_2 \rightarrow 2CO_2 + 3H_2O$



Oxygen balance:

O_2 required for combustion of $CH_4 = 0.86 \times 2 = 1.72$ kgmol

O_2 required for combustion of $C_2H_6 = 0.14 \times 3.5 = 0.49$ kgmol

Amount of O_2 required for complete combustion = 1.72 + 0.49 = 2.21 kgmol

Carbon dioxide formed:

CO_2 formed by first reaction = 0.86 kgmol

CO_2 formed by second reaction = 0.14 × 2 kgmol

Total amount of CO_2 formed = 0.86 + 0.28 = 1.14 kgmol

Let 'x' be the amount of dry flue gas in kgmol. Therefore,

$x \times 0.054 = 1.14$

$\therefore\ x = 21.11$ kgmol

Amount of excess air + N_2 from air = 21.11 – 1.14 = 19.97 kgmol

O_2 theoretically required = 2.21 kgmol

$$N_2 \text{ theoretically supplied} = 2.21 \times \left(\frac{79}{21}\right) = 8.31 \text{ kgmol}$$

$$\text{Air theoretically required} = 8.31 \times \left(\frac{100}{79}\right) = 10.52 \text{ kgmol}$$

Amount of excess air = 19.97 – 8.31 = 11.66 kgmol

$$\text{(i) Percentage of excess air} = \frac{\text{Amount of excess air}}{\text{Air theoretically required}} \times 100 = \frac{11.66}{10.52} \times 100 = 110.8$$

Therefore, dry flue gas = 21.11 kgmol.

(ii) From the chemical reaction, we have

1 kg mol of CH_4 → 2 kgmol of H_2O

Therefore, 0.86 kgmol of CH_4 → $\dfrac{2 \times 0.86}{1}$

Hence the amount of water formed from first reaction = 1.72 kgmol.

From the chemical reaction, we have

1 kgmol of C_2H_6 → 3 kgmol of H_2O

So, 0.14 kgmol of C_2H_6 = $\dfrac{3 \times 0.14}{1}$

That is the amount of water formed from the second reaction = 0.42 kgmol.

Now, Total H_2O fomed = 1.72 + 0.42 = 2.14 kgmol

Total wet flue gas = 21.11 + 2.14 = 23.25 kgmol

Since 1 kgmol of flue gas = 22.414 m^3

Therefore, 23.25 kgmol of flue gas = $\dfrac{22.414 \times 23.25}{1} \times \dfrac{(340 + 273)}{273}$ = 1170.14 m^3

Also, 1 kgmol of fuel gas mixture = 22.414 m^3 (at NTP)

Thus, $$\frac{\text{Flue gas at 340°C and 760 mmHg}}{\text{Fuel gas at NTP}} = \frac{1170.14}{22.414}$$
$$= 52.21$$

EXAMPLE 5.17 A producer gas with the composition by volume

CO = 25.7%

CO_2 = 4.9%

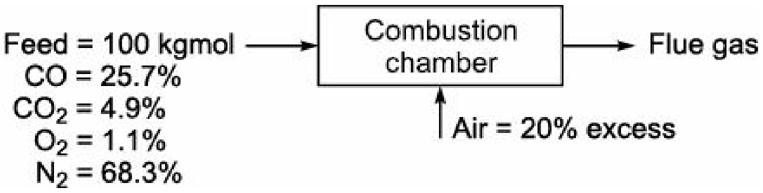
O_2 = 1.1%

and N_2 = 68.3%

is burnt with 20% excess air. If the combustion is 97% complete, calculate the composition by volume of the flue gases.

Solution: Basis: 100 kgmol of producer gas is burnt.

Reaction: $CO + \frac{1}{2}O_2 = CO_2$



Oxygen balance:

Oxygen required for combustion = 25.7 × $\left(\dfrac{1}{2}\right)$ = 12.85 kgmol

Oxygen present in fuel = 1.1 kgmol

Therefore, Oxygen required theoretically = 12.85 – 1.1 = 11.75 kgmol

$$\text{Oxygen supplied 20\% excess} = 11.75 \times \left(1 + \frac{20}{100}\right) = 14.1 \text{ kgmol}$$

Therefore, oxygen required for 97% combustion = 12.85 × 0.97 = 12.47 kgmol

O_2 excess = 14.10 – 12.47 = 1.63 kgmol

Nitrogen balance:

$$\text{Nitrogen from air} = 14.1 \times \left(\frac{79}{21}\right) = 53.04 \text{ kgmol}$$

Nitrogen present in fuel = 68.30 kgmol

Nitrogen present in flue gas = 53.04 + 68.30 = 121.34 kgmol

Carbon dioxide balance:

Carbon dioxide formed from CO = 25.7 × 0.97 = 24.93 kgmol

Carbon dioxide present in fuel = 4.9 kgmol

Corbon dioxide present in flue gas = 24.93 + 4.9 = 29.83 kgmol

Carbon monoxide balance:

Carbon monoxide burnt = 25.7 × 0.97

= 24.93 kgmol

Carbon monoxide unburnt = 25.7 – 24.93

CO present in flue gas = 0.77 kgmol

Flue gas analysis

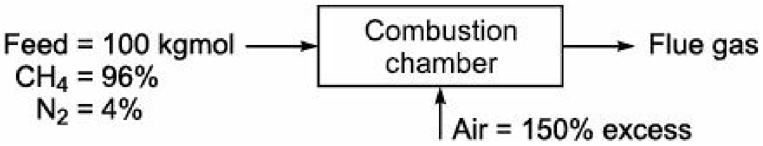
Components	*Amounts* (kgmol)	*Mole%*	*Volume%*
O_2	1.63	1.06	1.06
N_2	121.34	79.01	79.01
CO_2	29.83	19.42	19.42
CO	0.77	0.51	0.51
	Total = 153.57 kgmol		

EXAMPLE 5.18 A fuel gas containing 96% by volume methane (CH_4) and 4% by volume nitrogen (N_2) is burnt in a boiler furnace with 150% excess air. 84% of CH_4 goes to formation of CO_2, 9% to CO and 7% remains unburnt. Determine the composition of stack gas.

Solution: Basis: 100 kgmol of fuel gas.

Reaction: $CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$

$2CH_4 + 3O_2 \rightarrow 2CO + 4H_2O$



Oxygen balance:

O_2 required for complete combustion = 96 × 2 = 192 kgmol

O_2 supplied from 150% excess air = $192 \times \left(1 + \frac{150}{100}\right)$ = 480 kgmol

Reaction one is 84% complete:

CH_4 converted to CO_2 = 96 × 0.84 = 80.64 kgmol

O_2 required to convert CH_4 to CO_2 = 80.64 × 2 = 161.28 kgmol

Reaction two is 9% complete:

CH_4 converted to CO = 96 × 0.09 = 8.64 kgmol

O_2 required to convert CH_4 to CO = $8.64 \times \left(\frac{3}{2}\right)$ = 12.96 kgmol

O_2 actually required = 161.28 + 12.96 = 174.24 kgmol

O_2 excess = 480 – 174.24 = 305.76 kgmol

CO_2 formed = 80.64 kgmol

CO formed = 8.64 kgmol

CH_4 unconverted = 96 × 0.07 = 6.72 kgmol

N_2 supplied from air = $480 \times \left(\frac{79}{21}\right)$ = 1805.7 kgmol

N_2 present in fuel = 4 kgmol

N_2 in flue gas = 1805.7 + 4

ㅅ = 1809.7 kgmol

Therefore, the amount of water vapour formed = $80.64 \times 2 + 8.64 \times \left(\frac{4}{2}\right)$ = 161.28 + 17.28 = 178.56 kgmol

Stack gas analysis:

Components	*Amounts* (kgmol)	*Mole%*
O_2	305.76	12.79
CO_2	80.64	3.37
CO	8.64	0.36
CH_4	6.72	0.28
N_2	1809.7	75.72
H_2O	178.56	7.48
	Total = 2390.02 kgmol	

EXAMPLE 5.19 A producer gas has the following composition by volume:

CO = 27%

CO_2 = 3.5%

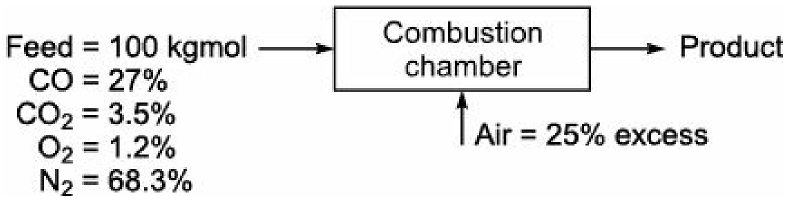
O_2 = 1.2%

and N_2 = 68.3%.

The gas is burnt with 25% excess air. Combustion is only 90% complete. Calculate the composition of the gaseous products formed.

Solution: Basis: 100 kgmol of producer gas burnt

Reaction: $CO + \frac{1}{2}O_2 \rightleftharpoons CO_2$



From the chemical reaction, we have

1 kgmol of CO $\rightarrow \frac{1}{2}$ kgmol of O_2

Therefore, 27 kgmol of CO $\rightarrow \frac{1}{2} \times 27$

O_2 required for combustion = 13.5 kgmol

O_2 present in fuel = 1.2 kgmol

Hence, O_2 required theoretically = 13.5 – 1.2 = 12.3 kgmol

O_2 supplied 25% excess = $12.3 \times \left(1 + \frac{25}{100}\right) = 15.375$ kgmol

Oxygen required for 90% combustion = 13.5 × 0.90 = 12.15 kgmol

Oxygen excess = 15.375 – 12.15 = 3.225 kgmol

Nitrogen balance:

Nitrogen from air = $15.375 \times \left(\frac{79}{21}\right) = 57.839$ kgmol

Nitrogen present in fuel = 68.300 kgmol

So, nitrogen present in product gas = 57.839 + 68.300 = 126.139 kgmol

Carbon dioxide balance:

Carbon dioxide formed from CO = 27.0 × 0.9 = 24.3 kgmol

Carbon dioxide present in fuel = 3.50 kgmol

Therefore, Carbon dioxide present in product gas = 24.3 + 3.50 = 27.80 kgmol

Carbon monoxide balance:

Carbon monoxide burnt = 27 × 0.9 = 24.3 kgmol

Carbon monoxide unburnt = 27.0 – 24.3 = 2.7 kgmol

Carbon monoxide present in product gas = 2.7 kgmol

Composition of gaseous products:

Components	*Amounts* (kgmol)	*Mole*%
O_2	3.225	2.02
N_2	126.139	78.90
CO_2	27.800	17.39
CO	2.700	1.69

Total = 159.864 kgmol

EXAMPLE 5.20 A combustible gas with a composition by volume of

H_2 = 45%

CH_4 = 30%

C_2H_6 = 15%

and N_2 = 10%

is burnt in a combustion chamber in the presence of air. The composition of the dry products of combustion is

CO_2 = 7%

CO = 1%

O_2 = 7%

and N_2 = 85% by volume.

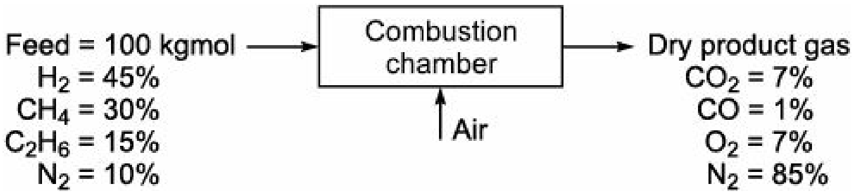
Calculate

(i) The air-fuel ratio on volume basis

(ii) The percentage of excess air.

Solution: Basis: 100 kgmol of combustible gas

Reaction:



Carbon present in combustible gas, C = 27.27% mole.

Carbon present in product gas = 7 + 1 = 8 kgmol.

Let ‘*x*’ be the combustible gas in kgmol and ‘*y*’ be the air used in kgmol.

Carbon balance:

$$x \times \left(\frac{27.27}{100}\right) = 8$$

∴ $x = 29.33$ kgmol

Nitrogen balance:

$x \times 0.10 + y \times 0.79 = 85$

∴ $29.33 \times 0.10 + 0.79y = 85$

∴ $2.933 + 0.79y = 85$

∴ $y = 103.88$ kgmol

(i) Air-fuel ratio = $\dfrac{103.88 \times 22.414}{29.33 \times 22.414} = 3.54$

O_2 supplied by air = 103.88 × 0.21 = 21.81 kgmol

O_2 excess = O_2 in combustion – O_2 required for CO

$$= 7 - 1 \times \left(\frac{1}{2}\right) = 6.5 \text{ kgmol.}$$

(ii) Percentage of excess air = $\dfrac{O_2 \text{ excess}}{O_2 \text{ supplied} - O_2 \text{ excess}} \times 100 = \dfrac{6.5}{21.81 - 6.5} \times 100 = 42.45\%$

EXAMPLE 5.21 A producer gas contains

$CO_2 = 10\%$

$C_2H_4 = 1\%$

$CO = 20\%$

$H_2 = 15\%$

$CH_4 = 2\%$

and $N_2 = 52\%$.

When it is burnt, the products of combustion contains

$CO_2 = 12\%$

$CO = 1\%$

$O_2 = 10\%$

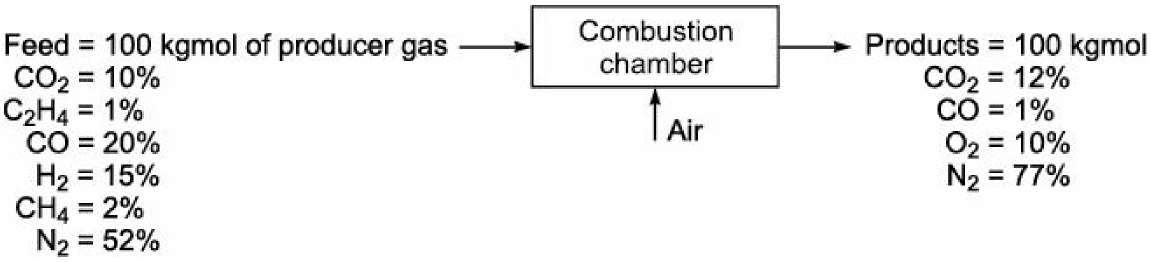
and rest $N_2 = 77\%$.

Calculate:

(i) The volume of air used in the combustion of 1 m^3 of producer gas, both being at the same temperature and pressure.
(ii) The percentage of excess air used in the combustion.
(ii) The percentage of N_2 in the product of combustion which comes from the producer gas.

Solution: Basis: 100 kgmol of producer gas and 100 kgmol of products.

Reaction:



Carbon present in producer gas, C = 26.77% by mole.

Carbon present in product = 12 + 1 = 13 kgmol

Let ‘*x*’ be the producer gas in kgmol and ‘*y*’ be the air used in kgmol.

(i) Carbon balance:

$$x \times \left(\frac{26.77}{100}\right) = 13$$

$$x = 48.56 \text{ kgmol}$$

Nitrogen balance:

$$x \times 0.52 + y \times 0.79 = 77$$

$$48.56 \times 0.52 + y \times 0.79 = 77$$

$$25.25 + 0.79y = 77$$

$$y = 65.51 \text{ kgmol}$$

$$\frac{\text{Moles of air}}{\text{Moles of producer gas}} = \frac{\text{Volume of air at } T, P}{\text{Volume of producer gas at } T, P}$$

$$= \frac{65.51}{48.56}$$

$$= 1.35$$

(ii) Oxygen supplied by air = 65.51 × 0.21 = 13.76 kgmol

O_2 excess = O_2 in combustion gas – O_2 required for CO

$= 10 - 1 \times \left(\frac{1}{2}\right) = 9.5$ kgmol

Now, Percentage of excess air = Percentage of excess O_2

$$= \frac{O_2 \text{ excess}}{O_2 \text{ supplied} - O_2 \text{ excess}} \times 100 = \frac{9.5}{13.76 - 9.5} \times 100 = 223\%$$

(iii) Nitrogen from the producer gas = 48.56 × 0.52 = 25.25 kgmol

Nitrogen from the product of combustion = 77 kgmol

$$\text{Percentage of } N_2 = \frac{\text{Nitrogen from producer gas}}{\text{Nitrogen from the product of combustion}} \times 100 = \frac{25.25}{77} \times 100 = 32.79$$

The percentage of N_2 in the product of combustion which came from the producer gas is 32.79.

Exercises

5.1 A coke contains 80% carbon and 20% non-combustible material by weight.
Calculate:

(i) The amount of oxygen theoretically required to burn 150 kg of coke completely.

(ii) The composition of gases in the product stream if 50% excess air is supplied.

5.2 A coal containing

C = 68%

H = 5%

S = 1%
N = 2%
O = 8%
Ash = 4%
and water = 12% is burnt in a furnace.

The product of combustion dry gas analyses; CO_2 = 14%, O_2 = 5% and rest N_2.

Calculate:

(i) The theoretical volume of air used for the complete combustion of 120 kg of coal.
(ii) The percentage of excess air used.

5.3 A coke contains 87% carbon and 13% non-combustible material by weight.

Calculate:

(i) The amount of oxygen theoretically required to burn 240 kg of coke completely.
(ii) The composition of the gases in the product stream if 40% excess air is supplied.

5.4 A coal sample collected from Mancherial coal mine contains

C = 65%
H = 5%
S = 2%
N = 3%
O = 7%
Ash = 3%

and water = 15% is burnt in a furnace. The product of the combustion dry gas analyses CO_2 = 13%, O_2 = 4% and rest N_2.

Calculate:

(i) The theoretical volume of air used for the complete combustion of 125 kg of coal.
(ii) The percentage of excess air used.

5.5 A sample of coke having the following percentage composition

C = 80%
H = 6%
O = 7%
N = 2%
S = 1%

and the rest is ash. It is gasified in a generator. The gas in the product stream has the percentage composition; CO_2 = 5%, CO = 32%, H_2 = 12% and the rest N_2.

Calculate:

(i) m^3 of gas produced per kg of coke gasified.
(ii) The amount of air used for gasification per m^3 of gas produced.

5.6 A wood sample having an analysis of

C = 46%
O = 23%
Ash = 5%

and rest being moisture and hydrogen. It is burnt in a furnace. An Orsat analysis of the flue gas during a run showed CO_2 = 15%, CO = 2%, O_2 = 4% and rest N_2.

Calculate:

(i) The complete analysis of the wood used.
(ii) The fuel to air ratio.
(iii) The percentage of excess air used.
(iv) The composition of the flue gas.

5.7 A furnace uses coke containing 83% carbon, 1% hydrogen and the rest ash. The furnace operates with 60% excess air. The solid residue contains 1% unburnt carbon of the carbon burnt and 3% goes to form CO. Calculate:

(i) The composition of flue gas.
(ii) The solid residue per 120 kg of coke burnt.
(iii) The kg of carbon lost per 120 kg of coke burnt.

5.8 A coal fired furnace emits 60,000 m^3/h of flue gas at 270°C. The coal used analyses as:

C = 58%
H = 4%
N = 2%
S = 1%
O = 7%
H_2O = 9%
Ash = 19% (by weight).

If the burning rate is 3 tonnes of coal per hour. Calculate:

(i) The Orsat analysis of flue gas.
(ii) The percentage of excess air used.

5.9 A Pulverised coal is burnt in a boiler furnace having the following ultimate, analysis:

C = 69%
H = 5%
O = 18%
N = 2%
and Ash = 6% (by weight of dry sample).

Coal contains 21% moisture. The exist gases carry solid which analyses 8% carbon and 92% ash. Air used is 20% in excess and under these condition, 1% of the total combined carbon in the exit gases pass as CO and rest being as CO_2. Calculate:

(i) What percentage of total carbon of coal is lost in the exit material.
(ii) The exit gas analysis.
(iii) The weight of water vapour accompanies per m^3 of dry gas at 325°C and 1 atmosphere. Air may be considered as dry.

5.10 A fuel oil contains 84% C and 16% H. It is burnt to form flue gas of following composition:

CO_2 = 13%
O_2 = 4%
and N_2 = 83%.

Calculate the percentage of excess air used.

5.11 A combustion reactor is fed with 120 kgmol/h of butane and 2000 kgmol/h of air. Calculate:

(i) The percentage of excess oxygen.

(ii) The composition of gases leaving the combustion reactor. Assume complete combustion of butane.

5.12 A pure hydrocarbon, 320 kg/h is fired in a furnace of the boiler at atmospheric pressure and 25°C. The flue gas analysis on dry basis at atmospheric pressure and 25°C is as given below.

CO_2 = 14%

O_2 = 4%

and N_2 = 82%.

Estimate the formula of the fuel and the volumetric flow rate of the gas.

5.13 In a petrol engine, the dry exhaust analysis gave 2% CO and O_2 was negligible. If the fuel used has an ultimate analysis by weight as

C = 85% and

H = 15%,

calculate, what weight of air was supplied per unit weight of fuel. Assume fuel burnt completely.

5.14 A fuel oil contains 82% C and 18% H. It is burnt to form flue gas of following composition:

CO_2 = 13.5%

O_2 = 3.5%

and N_2 = 83%.

Calculate the percentage of excess air used.

5.15 Octane is burnt with 30% excess air. Calculate:

(i) Air fuel ratio by weight.

(ii) Air fuel ratio by volume.

(iii) Weight of dry exhaust gas formed per unit weight of fuel.

(iv) Moles of O_2 in the exhaust gas per unit weight of fuel (Sp. gr. of Octane is 0.71).

5.16 A flue gas analyses 86% N_2, 9% CO_2 and rest Oxygen on dry basis. It also contains 0.12 moles of water vapour per mole of dry gas. Find the analysis of gas on Nitrogen free basis.

5.17 A coal containing 85% total carbon and 8% unoxidized hydrogen by weight is burnt in air.

(i) If the air is used 30% in excess of that theoretically required, calculate the amount (in kg) of air used per kg of coal burnt.

(ii) Calculate the composition by weight of the gases leaving the furnace.

5.18 In a coal fired boiler test the following data are available.

Coal analysis:

C = 69%

Ash = 31%

Refuse from Ash:

C = 11%

Ash = 89%

Orsat analysis of flue gas:

CO_2 = 14%

CO = 1%
O_2 = 6%
N_2 = 79%.

Calculate on the basis of 100 kg of coal fired:

(i) The weight of refuse drawn from ash pit.
(ii) The weight of CO_2, CO, O_2 and N_2 formed.
(iii) The weight of dry air supplied.
(iv) Average molecular weight of the fuel gas.

5.19 Determine the flue gas analysis and air fuel ratio by weight when a medium fuel oil having the composition

C = 85%
H = 10%
S = 3%
O = 1%
and Ash = 1% (by weight)

is burnt with 20% excess air. Assume that complete combustion takes place.

5.20 The dry flue gases from a oil fired furnace has composition of

CO_2 = 12%
O_2 = 6%
and N_2 = 82%

When analyzed by an orsat apparatus, calculate:

(i) The percentage of excess air.
(ii) The weight of combustion air used per kg of oil fired. Assume oil fuel contains 80% C, 13% H and 4% S and balance impurities. The molecular weight of dry gas is 29.

5.21 Calculate the excess air used in a furnace when the flue gas Orsat analysis is

CO_2 = 8%
O_2 = 10%
CO = 1%
H_2 = 1%
and N_2 = 80%.

5.22 The flue gas from a furnace using a hydrocarbon fuel oil analyses as follows by volume.

CO_2 = 16%
CO = 1%
O_2 = 3%
and N_2 = 80%.

Calculate:

(i) The percentage of excess air used.
(ii) The percentage composition of fuel burnt (by weight).

5.23 The weight composition of a fuel oil is 87% C and 13% H. It is burnt with air which is known to be enriched but the composition of the air is not known, although it is a mixture of N_2 and O_2 only. The Orsat analysis of the flue gases produced is

CO_2 = 14%

O_2 = 4%

and N_2 = 82%.

(i) Determine the percentage of excess oxygen if any.
(ii) What is the composition of air that is being used.
(iii) What would have been the Orsat analysis of the flue gases if air is used and its normal composition and the stoichiometric amount been used. Assume the reaction is 100% complete.

5.24 The purge gas obtained from ammonia synthesis loop has the following composition on mole basis

H_2 = 70%

N_2 = 21%

Ar = 3%

CH_4 = 6%

It is burnt with 30% excess air. Calculate:

(i) The theoretical air required.
(ii) The molar composition of the dry flue gases.

5.25 A furnace is fired with fuel oil, the Orsat analysis of flue gases by volume is as given below:

CO_2 = 11%

O_2 = 7%

and N_2 = 82%

Calculate:

(i) The percentage of excess air
(ii) The C and H ratio in the fuel oil.

Assume that fuel does not contain nitrogen.

5.26 The ultimate analysis of a residual fuel oil (RFO) sample is as given below.

C = 88%
H = 10%
S = 2% (by weight).

It is used as a fuel in a power generating boiler with 30% excess air.

Calculate:

(i) The theoretical dry air requirement
(ii) The actual dry air supplied
(iii) The composition of flue gas.

5.27 A gas mixture containing 83% CH_4 and 17% C_2H_6 by volume is burnt in the presence of air. The Orsat analysis of the flue gas after combustion shows 6% CO_2 by volume. The air enters at 0 °C, 1 atm and contains no water vapours. Calculate:

(i) The percentage of excess air used.

(ii) The volume in m^3 of the flue gas produced at 260 °C and 760 mmHg per m^3 of fuel gas measured at NTP.

5.28 The ultimate analysis of coal sample is given below.

C = 62%
H = 4%
S = 1%
Ash = 15%
N_2 = 2%

and rest is oxygen. Calculate:

(i) Theoretical oxygen requirement per unit weight of coal.
(ii) The theoretical dry air requirement per unit weight of coal.
(iii) The flue gas composition.

Assume that the coal is burnt with 100% excess air.

5.29 The Orsat analysis of the flue gases from a boiler house chimney by volume is as given below:

CO_2 = 12%
O_2 = 4%
and N_2 = 84%.

Assume complete combustion. Calculate:

(i) The percentage of excess air
(ii) The C and H ratio in the fuel.

5.30 In a boiler furnace, pulverised coal having the following ultimate analysis is fired:

C = 69%
H = 5%
O = 18%
N = 2%
and Ash = 6% (by weight % of dry sample).

Coal contains 23% moisture. Exit gases carry solid which analyses 8% carbon and 92% ash. Air used is 20% in excess. Under these conditions, 1% of total combined carbon in the exit gases pass as CO and rest being CO_2. Calculate:

(i) The percentage of total carbon of coal is lost in the exit material.
(ii) The exit gas analysis.
(iii) The weight of water vapour accompanies each cubic metre of dry gas at 280°C and 1 atmosphere. Air may be considered as dry.

5.31 Wood having an analysis of

C = 47%
O = 21%
Ash = 5%

and rest being moisture and hydrogen. It is being burnt in a furnace. An Orsat analysis of the flue gas is given below.

CO_2 = 15%
CO = 2%
O_2 = 5%

and N_2 = 78%

Calculate:

(i) The complete analysis of the wood used
(ii) The fuel to air ratio by weight
(iii) The percentage of excess air used
(iv) The composition of stack gas.

5.32 The gross calorific value of gaseous *n*-propanol at 298 K is 2068 kJ/mol. Calculate the net calorific value (use latent heat of water at 298 K. l_w = 2443 kJ/kg).

Reaction: $C_3H_7OH + 4.5O_2 \rightarrow 3CO_2 + 4H_2O$.

5.33 The GHV of gaseous *n*-butane is 2878 kJ/mol at 298 K. Calculate its NHV in kJ/mol and kJ/kg. l_w = 2443 kJ/kg.

5.34 A sample of fuel oil having C and H ratio 9.3 (by weight) and containing sulfur to the extent of 1.4% (by weight). Calculate the NCV of fuel oil at 298 K.

5.35 A fuel gas containing 95% methane (by volume) and 5% N_2 (by volume) is burnt in a boiler furnace with 150% excess air. 86% of the methane goes to formation of CO_2, 10% to CO and 4% remains unburnt. Calculate the composition of stack gas.

6

Energy Balances

6.1

Introduction

Energy may be defined as the capacity of the system for doing work. It may be generated by various methods. One of the methods of generating energy is by burning of fuels. According to the physical state, the fuels are available in the form of solid, liquid and gas. Some examples of solid, liquid and gaseous fuels are coal and wood, petrol, diesel and kerosene, LPG and natural gas respectively.

There is a possibility of losing energy while it is getting burned for generating energy, which can reduce the profitability of the industry. Hence, accounting of energy for the process is very much essential. The method of accounting of energy for the system is called energy balance. In this process, the amount of energy flowing in and the amount of energy flowing out from the system is recorded. This, in turn, gives the idea of total amount of energy required for the system. There are many forms of energy, among which a few forms are given importance for formulation and calculation of energy balance of the system.

The important forms of energy are:

1. Internal energy
2. Kinetic energy
3. Potential energy.

6.1.1 Internal Energy

Energy possessed by the system by virtue of translation and rotation of molecules is called Internal energy. It is denoted by the symbol U. Its unit is kJ/kg.

6.1.2 Kinetic Energy

Energy possessed by the system by virtue of its motion is called kinetic energy. It is denoted by the symbol E_k. Its unit is kJ/kg.

6.1.3 Potential Energy

Energy possessed by a system by virtue of its position is called potential energy. It is denoted by the symbol E_p. Its unit is kJ/kg. The heat and work are the forms of energy. These are evident only as energy in transition. The usual sign convention is to regard a quantity of heat is positive when it is transferred to the system from the surrounding. On the other hand, a quantity of work is usually regarded as positive when work is done by the system on the surrounding.

Heat is a form of energy. It flows from a high temperature system to a low temperature system. The high temperature system is called hot source and the cold temperature system is called cold receiver. The unit of heat in SI unit is joule and in CGS unit is calorie.

The basis of energy balance of a particular system is the law of conservation of energy. It states that “energy can neither be created nor be destroyed. Whenever it appears in some form, it disappears in some other forms and thus, the total amount of energy remains constant.” This law is also known as the first law of thermodynamics. According to this law, the amount of energy entering into the system minus the amount of energy leaving the system is equal to the amount of energy accumulation within the system.

6.2

General Steady State Energy Balance Equation

A system in which mass as well as energy transfer may take place is called an open system. A system in which no mass transfer but energy transfer may take place is called a closed system. The energy balance equation for closed system is given by

Final energy of the system – Initial energy of the system = Net energy transferred to the system (6.1)

where

Final energy of the system = $U_2 + E_{k2} + E_{p2}$ (6.2)

Initial energy of the system = $U_1 + E_{k1} + E_{p1}$ (6.3)

Net energy transferred = $Q - W$ (6.4)

Substituting Eqs. (6.2), (6.3) and (6.4) in Eq. (6.1), we get

$$(U_2 - U_1) + (E_{k2} - E_{k1}) + (E_{p2} - E_{p1}) = Q - W \qquad (6.5)$$

$$\therefore \Delta U + \Delta E_k + \Delta E_p = Q - W \qquad (6.6)$$

At steady state, there is no accumulation of energy. Therefore,

Input energy – Output energy = 0 (6.7)

∴ Input energy = Output energy (6.8)

6.3

Thermophysics

It is the branch of science which deals with transfer of heat and thermodynamics. It characterizes the transformation of energy. During the transformation of energy, some amount of thermal energy is produced in the form of heat.

For example, consider the rubbing of iron rod on a rough hard surface. In this process transformation of energy takes place, which results in heat and fire.

6.4

Thermochemistry

It is the branch of science which deals with energy changes involved in chemical reactions. Almost all chemical reactions are accompanied by change in energy. This change in energy of chemical reactions is in the form of absorption or evolution of heat. According to thermochemistry, chemical reactions may be classified into two categories; Endothermic and Exothermic chemical reactions.

A chemical reaction that proceeds with the absorption of heat is called an endothermic chemical reaction. For example, consider the photosynthesis reaction.

$$6CO_2 + 6H_2O \xrightarrow{\text{Sunlight}} C_6H_{12}O_6 + 6O_2 \qquad (6.9)$$

In this chemical reaction, 15 MJ of energy is absorbed from the sunlight to produce 1 kgmolof glucose. Hence, it is an endothermic chemical reaction.

A chemical reaction that proceeds with the evolution of heat is called an exothermic chemical reaction. For example, consider the chemical reaction

$$2\text{Na} + \text{Cl}_2 \rightarrow 2\text{NaCl} \qquad (6.10)$$

In this chemical reaction, 411 kJ of energy is produced during the formation of 2 kgmol of NaCl. Hence, it is an exothermic reaction.

The majority of chemical reactions proceed at constant pressure, hence the work performed by chemical reaction is *PV*. Therefore, the heat exchanged during the course of reaction is equal to the change in enthalpy. The heat exchanged for chemical reactions proceed at constant volume is equal to the change in internal energy. The enthalpy and internal energy are related through the equation

$$\Delta H = \Delta U + \Delta (PV) \qquad (6.11)$$

where

ΔH = Change in enthalpy (J/kg)

ΔU = Change in internal energy (J/kg)

$\Delta (PV)$ = Change in work performed (J/kg).

Since $\Delta (PV)$ is very small as compared to ΔH and ΔU. Hence, it may be neglected. In this case, Eq. (6.11) may be written as

$$\Delta H = \Delta U \qquad (6.12)$$

In the case of gaseous reaction, $\Delta (PV)$ may be important due to the number of moles of gas changes as a result of reaction. Then, from the ideal gas equation, we have

$$\Delta (PV) = \Delta (nRT) \qquad (6.13)$$

where,

Δn = Moles of product – Moles of reactant

Substituting Eq. (6.13) in Eq. (6.11), we get

$$\Delta H = \Delta U + \Delta nRT \qquad (6.14)$$

6.5
Heat Capacity

Heat capacity is defined as the amount of heat required to raise the temperature of one kilogram of substance of the system by one degree centigrade. It is generally expressed based on per unit mass or per unit mole. If it is expressed, in per unit mole, it is termed molal heat capacity and it is denoted by the symbol ‘*C*’. Its unit is kJ/kgmol°C. If it is expressed, in per unit mass, it is termed heat capacity. It is also denoted by the symbol ‘*C*’ and its unit is kJ/kg°C. Heat capacity is of two types:

1. Heat capacity at constant pressure
2. Heat capacity at constant volume.

6.5.1 Heat Capacity at Constant Pressure

From the first law of thermodynamics, we know that

$$dU = dQ - dW \qquad (6.15)$$

$$\text{But, } dW = PdV \qquad (6.16)$$

Substituting Eq. (6.16) in Eq. (6.15), we get

$dU = dQ - PdV$

ㅅ $dU = dQ - d(PV)$

ㅅ $dU + d(PV) = dQ$

ㅅ $d(U + PV) = dQ$ (6.17)

But, $H = U + PV$ (6.18)

Substituting Eq. (6.18) in Eq. (6.17), we get

$dH = dQ$ (6.19)

From the heat transfer relation, we know that

$dQ = mC_P\, dT$ (6.20)

$dH = dQ = mC_P\, dT$

Therefore, $dH = mC_P\, dT$ (6.21)

For, $m = 1$

$dH = C_P\, dT$

ㅅ $C_P = \left(\frac{\partial H}{\partial T}\right)_P$ (6.22)

where C_P represents the molal heat capacity at constant pressure.

Heat capacity of gases at constant pressure

The heat capacity of gases at constant pressure is given by

$dQ = mC_P\, dT$ (6.20)

Integrating Eq. (6.20) between the temperature limits T_1 and T_2, we get

$$Q = \int_{T_1}^{T_2} mC_P dT \qquad (6.23)$$

for, $m = 1$

$$Q = \int_{T_1}^{T_2} C_P dT \qquad (6.24)$$

C_P is a function of temperature. For ideal gases at 1 atmosphere, C_P is denoted by $C_P°$ and is given by the equatio

$C_P° = a + bT + cT^2 + dT^3$ (6.25)

where

$C_P°$ = Heat capacity at ideal condition (kJ/kg°C)

T = Temperature (K)

a, b, c, d = Constants

Substituting Eq. (6.25) in Eq. (6.24), we get

$$Q = \int_{T_1}^{T_2} (a + bT + cT^2 + dT^3)\, dT \qquad (6.26)$$

$$\therefore \quad Q = \left[aT + \frac{bT^2}{2} + \frac{cT^3}{3} + \frac{dT^4}{4} \right]_{T_1}^{T_2}$$

$$\therefore \quad Q = \left[a(T_2 - T_1) + \frac{b}{2}(T_2^2 - T_1^2) + \frac{c}{3}(T_2^3 - T_1^3) + \frac{d}{4}(T_2^4 - T_1^4) \right] \qquad (6.27)$$

Mean molal heat capacity

The calculation of heat change of a substance using Eq. (6.27) is lengthy procedure, because it requires a lot of information regarding the substances. Hence, to avoid the lengthy procedure, it is convenient to use mean molal heat capacity.

Let us assume any arbitrary base temperature T_1 and the temperature limit between which the heat change is desired is T_1 and T_2. Then, the mean molal heat capacity is given by the equation

$$C^\circ_{Pm} = \frac{\int_{T_1}^{T_2} C^\circ_P \, dT}{(T_2 - T_1)} \qquad (6.28)$$

Substituting Eq. (6.25) in Eq. (6.28), we get

$$C^\circ_{Pm} = \frac{a(T_2 - T_1) + \frac{b}{2}(T_2^2 - T_1^2) + \frac{c}{3}(T_2^3 - T_1^3) + \frac{d}{4}(T_2^4 - T_1^4)}{T_2 - T_1} \qquad (6.29)$$

$$C^\circ_{Pm} = a + \frac{b}{2}(T_2 + T_1) + \frac{c}{3}(T_2^2 + T_2T_1 + T_1^2) + \frac{d}{4}(T_2 + T_1)(T_2^2 + T_1^2)$$

where

C°_{Pm} = Mean molal heat capacity (J/kgmol °C)

T_1, T_2 = Temperature (K)

a, b, c, d = Constants.

In most of the cases, the arbitrary base temperature T_1 = 298 K.

Heat capacity of gaseous mixture

The calculation of heat capacity of gaseous mixture of known composition in the case of heating or cooling is very much essential in unit operation. This calculation may be performed in a simplified way by the equation

$$C^\circ_{P\text{mix}} = \sum_{i=1}^{n} x_i \cdot C^\circ_{Pi} \qquad (6.30)$$

where

$C^\circ_{P\text{mix}}$ = Heat capacity of gaseous mixture at ideal condition (J/kgmol · °C)

x_i = Mole fraction of ith component of gaseous mixture

C°_{Pi} = Heat capacity of ith component of gaseous mixture (J/kgmol °C)

If $C^\circ_{P\text{mix}}$ is known, then the change of heat for 'm' mole of gaseous mixture may be calculated using the equation

$$Q = \int_{T_1}^{T_2} mC^\circ_{P\text{mix}} dT \qquad (6.31)$$

where

Q = Heat change (J)

m = Moles of gaseous mixture

$C^\circ_{P\text{mix}}$ = Heat capacity of gaseous mixture.

6.5.2 Heat Capacity at Constant Volume

From the first law of thermodynamics, we have

$$dU = dQ - dW \qquad (6.32)$$

We know that,

$$dW = PdV \qquad (6.33)$$

Since volume of the system is constant.

$$\text{Therefore, } dV = 0 \qquad (6.34)$$

Substituting Eq. (6.34) in Eq. (6.33), we get

$$dW = 0 \qquad (6.35)$$

Substituting Eq. (6.35) in Eq. (6.32), we get

$$dU = dQ \qquad (6.36)$$

From the heat transfer relation, we have

$$dQ = mC_V\, dT \qquad (6.37)$$

Comparing Eqs. (6.36) and (6.37), we get

$$dU = dQ = mC_V\, dT$$

$$dU = mC_V\, dT \qquad (6.38)$$

For, $m = 1$

$$dU = C_V\, dT$$

$$\therefore\ C_V = \left(\frac{\partial U}{\partial T}\right)_V \qquad (6.39)$$

where C_V is the molal heat capacity at constant volume.

6.6

Enthalpy

The total heat content of a substance is called enthalpy. Mathematically, it may be expressed by the equation as

$$H = U + PV \qquad (6.40)$$

where

H = Enthalpy (J/kg)
U = Internal energy (J/kg)
P = Absolute pressure (N/m^2)
V = Specific volume (m^3/kg)

During the chemical reaction, heat may be absorbed or evolved. The amount of heat absorbed or evolved during a chemical reaction plays a major role in economics of the process. The enthalpy change of a chemical process may be positive or negative. When the enthalpy change associated with a chemical reaction is positive, then heat must be added to the process to keep the reaction temperature from dropping. When the enthalpy change associated with a chemical reaction is negative, then heat must be removed from the process to keep the reaction temperature from shooting up.

6.6.1 Heat of Formation

It is defined as the change of enthalpy that accompanies during the formation of one mole of compounds from its reactants at a given temperature and pressure. For example, consider the formation of water vapour by the chemical reaction

$$H_2(g) + \tfrac{1}{2}O_2(g) \rightleftharpoons H_2O(g) \qquad (6.41)$$

During this chemical reaction, 241.8 kJ of heat is released when one mole of water vapour is produced. This amount of heat of formation is negative because heat is released during the formation reaction. Eventhough we generally want the coefficient of balanced reaction to be a whole number, the heat of formation specifies for one mole of products only. The heat of formation of element is arbitrarily assigned as zero.

6.6.2 Heat of Reaction

It is defined as the amount of heat that must be added or removed when reactants are fed to the reactor in stoichiometric proportion and the reaction proceed to completion at a given temperature and pressure. In otherwords, we can say that it is the enthalpy change of the substance at the end of the chemical reaction. Heat of reaction is denoted by the symbol ΔH_R. Its unit is J/kgmol. It may be positive or negative. If the heat of reaction is positive, then the reaction is endothermic and if the heat of reaction is negative, then the reaction is exothermic at given temperature and pressure.

Standard heat of reaction

It is defined as the heat of reaction resulting from the change in enthalpy of a chemical reaction that accompanies during the formation of one mole of compounds when all the chemical species are in their standard state. The standard state means the proceeding of chemical reaction at 1 atmosphere and 25°C. It is denoted by ΔH°_R. Its unit is in kJ/kgmol. The standard heat of reaction may be positive or negative. For example, consider the formation of methanol by chemical reaction

$$CO + 2H_2 \rightleftharpoons CH_3OH \qquad (6.42)$$

In this chemical reaction, when carbon monoxide reacts with hydrogen to form methanol, a huge amount of heat is released. Hence, it is an exothermic reaction. The standard heat of reaction accompanying a chemical change is equal to the algebraic sum of the standard heat of formation of the products minus the algebraic sum of the standard heat of formation of the reactants. It may be expressed by the equation

$$\Delta H_R^\circ = \sum \Delta H^\circ_{f(\text{Products})} - \sum \Delta H^\circ_{f(\text{Reactants})} \qquad (6.43)$$

where,

ΔH_R° = Standard heat of reaction (kJ/kgmol)

$\Delta H^\circ_{f(\text{Products})}$ = Heat of formation of the products at standard state (kJ/kgmol)

$\Delta H^\circ_{f(\text{Reactant})}$ = Heat of formation of reactants at standard state (kJ/kgmol).

6.6.3 Heat of Combustion

It is defined as the amount of heat released when one mole of substance is completely burnt in the presence of oxygen at a temperature of 25 °C and pressure 1 atmosphere. During the combustion reaction, the enthalpy of the substance under combustion decreases and becomes zero at the completion of the reaction. Hence, the heat of combustion is assigned with negative sign. It is denoted by ΔH_C. For example, consider the combustion reaction

$$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O \qquad (6.44)$$

In this combustion reaction, methane gets burnt in the presence of oxygen to give rise to carbon dioxide and water. The enthalpy of methane decreases.

Calorific value

It is defined as the total amount of heat generated when a unit mass of substance is completely burnt in the presence of oxygen. The calorific value is also known as heating value. It is the characteristics of any combustible substances. The calorific value of any combustible substance is always positive. Its unit is kJ/kg. For example, the calorific value of coal is 20 MJ/kg.

6.7

Heat of Solution

It is defined as the change in enthalpy when a unit mass of solid or liquid or gaseous substance is completely dissolved in a liquid substance. The heat of solution is also known as heat of dissolution. It is the characteristics of any soluble substances. It is denoted by ΔH_S. Its unit is kJ/kgmol of solution.

6.8

Heat of Mixing

It is defined as the change in enthalpy when two or more liquid substances are mixed together. It is the characteristics of miscible substances. It is denoted by ΔH_m. Its unit is kJ/kgmol of solution.

6.9

Heat of Crystallization

It is defined as the amount of heat that must be removed from the unit mass of liquid substances to freeze it at its freezing point with no change in temperature. It is denoted by ˆ H_{cr} . Its unit is kJ/kgmol. For example, consider the process of manufacturing of sugar. In this process, sugar-cane juice is initially heated to get a desired concentration and then it cools to get sugar crystals.

6.10

Flame Temperature

Consider a fuel is burnt in a reactor in the presence of oxygen. During the burning of fuel, a considerable amount of heat is released. Some amount of this heat is lost due to heat transfer through the wall of the reactor and the remaining heat helps to rise the temperature of the reaction products. If the amount of heat lost due to heat transfer is less, higher will be the products temperature. If the reactor is adiabatic, then the highest temperature is achievable in this process. This highest achievable temperature is known as Adiabatic Flame temperature. It is also called theoretical flame temperature. In process industry, eventhough the fuel is burnt in a well insulated reactor, there will be some amount of heat lost due to the radiation from the reactor surface. The temperature achievable at this condition is called Actual Flame temperature. The actual flame temperature is always less than the adiabatic flame temperature.

6.11

Heat of Condensation

It is defined as the amount of heat that must be removed from the unit mass of vapour to condense with no change in temperature. It is denoted by ˆ H_{con}. The unit of heat of condensation is kJ/kgmol.

6.12

Heat of Vaporisation

It is defined as the amount of heat that must be required to vaporise the unit mass of liquid substance at its boiling point with no change in temperature. It is denoted by ˆ H_{vap}. The unit of heat of vaporisation is kJ/kgmol.

6.13

Hess's Law

Hess's law states that the amount of heat either absorbed or evolved during the course of a chemical reaction is same and does not matter whether the reaction completes in a single step or in multiple steps. This is also known as the law of constant heat summation. For example, consider the formation of corbon dioxide. We can obtain it in a single step as

$$C + O_2 \rightleftharpoons CO_2 \qquad (6.45)$$

We can also obtain it by multiple steps

$$C + \frac{1}{2}O_2 \rightleftharpoons CO \qquad (6.46)$$

$$\text{and } CO + \frac{1}{2}O_2 \rightleftharpoons CO_2 \qquad (6.47)$$

For the preparation of carbon dioxide, either we follow the single step or multiple step, the amount of heat evolved is same.

EXAMPLE 6.1 Calculate the standard heat of reaction of the following reaction.

$C_2H_6(g) \rightleftharpoons C_2H_4(g) + H_2(g)$

Data:

Component	^ H°_C (kJ/mol)
$C_2H_6(g)$	–1561
$C_2H_4(g)$	–1411
$H_2(g)$	–286

Solution: Basis: 1 mole of $C_2H_4(g)$ produced.

Reaction: $C_2H_6(g) \rightleftharpoons C_2H_4(g) + H_2(g)$

$$\Delta H^{\circ}_R = \left[\sum \Delta H^{\circ}_C\right]_{\text{Reactant}} - \left[\sum \Delta H^{\circ}_C\right]_{\text{Product}}$$

$= [1 \times (-1561)] - [1\times(-1411) + 1 \times (-286)]$

$= -1561 - (-1697)$

$= -1561 + 1697$

$= 136$ kJ

EXAMPLE 6.2 Calculate the heat of reaction at 25 °C of the following reaction.

$C_2H_5OH(g) \rightleftharpoons CH_3CHO(g) + H_2(g)$

Data:

Component	^ H°_C (kJ/mol)
$C_2H_5OH(g)$	–1410
$CH_3CHO(g)$	–1193
$H_2(g)$	–286

Solution: Basis: 1 mole of gaseous C_2H_5OH

Reaction: $C_2H_5OH(g) \rightleftharpoons CH_3CHO(g) + H_2(g)$

$$\Delta H^{\circ}_R = \left[\sum \Delta H^{\circ}_C\right]_{\text{Reactants}} - \left[\sum \Delta H^{\circ}_C\right]_{\text{Products}}$$

$= [1 \times (-1410)] - [1 \times (-1193) + 1 \times (-286)]$

$= -1410 - (-1193 - 286)$

$= -1410 + 1479$

$= 69$ kJ

EXAMPLE 6.3 Calculate the standard heat of reaction of the following reaction at 25°C.

$HCl(g) + NH_3(g) = NH_4Cl(s)$

Data:

Component	^ H°_F (kJ/kgmol)
HCl (g)	–92,377.78

NH_3 (g)	–46,224.48
NH_4Cl (g)	–3,15,616.06

Solution: Basis: 1 kgmol of NH_4Cl.

Reaction: $HCl(g) + NH_3(g) = NH_4Cl(s)$

$$\Delta H^\circ_R = \left[\sum \Delta H^\circ_f\right]_{\text{Product}} - \left[\sum \Delta H^\circ_f\right]_{\text{Reactants}}$$

$= [1 \times (–3,15,616.06)] – [1 \times (–92,377.78) + 1 \times (– 46,224.48)]$

$= –3,15,616.06 – (–92,377.78 – 46,224.48)$

$= –3,15,616.06 + 1,38,602.26$

$= –1,77,013.8$ kJ.

EXAMPLE 6.4 Calculate the standard heat of reaction $\Delta H°_R$ of the following reaction.

$C_2H_5OH + CH_3COOH \rightleftharpoons C_2H_5OOCH_3 + H_2O$

Data:

Component	$\Delta H°_C$ (kJ/mol)
C_2H_5OH	–1,367.89
CH_3COOH	–872.32
$C_2H_5OOCH_3$	–2,255.78
H_2O	0

Solution: Basis: 1 mole of C_2H_5OH

Reaction: $C_2H_5OH + CH_3COOH \rightleftharpoons C_2H_5OOCH_3 + H_2O$

$$\Delta H^\circ_R = \left[\sum \Delta H^\circ_C\right]_{\text{Reactants}} - \left[\sum \Delta H^\circ_C\right]_{\text{Products}}$$

$= [1 \times (–1,367.89) + 1 \times (–872.32)] – [1 \times (–2,255.78) + 1 \times 0]$

$= (–1,367.89 – 872.32) – (–2,255.78)$

$= 15.57$ kJ.

EXAMPLE 6.5 Calculate the standard heat of reaction for the reaction

$Na_2CO_3 + Fe_3O_3 \rightleftharpoons Na_2OFe_2O_3 + CO_2$

Data:

Component	$\Delta H°_f$ (kJ/gmol)
Na_2CO_3	–1129.65
Fe_2O_3	–817.30
$Na_2OFe_2O_3$	–1412.27
CO_2	–100.69

Solution: Basis: 1 gmol of Na_2CO_3

Reaction: $Na_2CO_3 + Fe_2O_3 \rightleftharpoons Na_2OFe_2O_3 + CO_2$

$$\Delta H_R^\circ = \left[\sum \Delta H_f^\circ\right]_{\text{Products}} - \left[\sum \Delta H_f^\circ\right]_{\text{Reactants}}$$

= [1 × (–1412.27) + 1 × (–100.69)] – [1 × (–1129.65) + 1(–817.30)]

= (–1412.27 – 100.69) – (–1129.95 – 817.30)

= –1512.96 + 1946.95

= 433.99 kJ.

EXAMPLE 6.6 Calculate the standard heat of reaction ΔH_R^{298} for the reaction

$$2FeS_2 + \frac{11}{2}O_2 \rightleftharpoons Fe_2O_3 + 4SO_2$$

The standard heat of formation of the compounds are

Components	ΔH_f^{298} (kJ/mol)
FeS_2	–178.03
O_2	0
Fe_2O_3	–822.75
SO_2	–297.11

Solution: Basis: 2 moles of FeS_2

Reaction: $2FeS_2 + \frac{11}{2}O_2 \rightleftharpoons Fe_2O_3 + 4SO_2$

$$\Delta H_R^{298} = \left[\sum \Delta H_f^{298}\right]_{\text{Products}} - \left[\sum \Delta H_f^{298}\right]_{\text{Reactants}}$$

= [1 × (–822.75) + 4 × (–297.11)] – [2 × (–178.03) + 5.5 × (0)]

= (–822.75 – 1188.44) – (–356.06 – 0)

= –2011.19 + 356.06

= –1655.13 kJ/mol

EXAMPLE 6.7 Calculate the standard heat of reaction of the following reaction.

$$CH_3OH(l) + \frac{1}{2}O_2(g) \rightleftharpoons HCHO(g) + H_2O(l)$$

Data:

Component	^ H°_f (kcal/mol)
CH_3OH	–57.13
HCHO	–25.94
H_2O	–68.27

Solution: Basis: 1 mole of methanol

Reaction: $CH_3OH(l) + \frac{1}{2}O_2(g) \rightleftharpoons HCHO(g) + H_2O(l)$

$$\Delta H_R^\circ = \left[\sum \Delta H_f^\circ\right]_{\text{Products}} - \left[\sum \Delta H_f^\circ\right]_{\text{Reactants}}$$

= [1 × (–25.94) + 1 × (–68.27)] – [1 × (–57.13) + 1/2(0)]

= (–25.94 – 68.27) – (–57.13 + 0)
= (–94.21) – (–57.13)
= –94.21 + 57.13
= –37.08 kcal

EXAMPLE 6.8 Calculate the heat absorbed for isothermal reaction.

$$C_4H_{10}(g) \rightleftharpoons C_2H_4(g) + C_2H_6(g)$$

At 298 K and 1 atm pressure, the standard heats of combustion (kcal/mol) for all components of the reaction are

Component	ΔH°_C (kcal/mol)
$C_4H_{10}(g)$	– 686.29
$C_2H_4(g)$	–337.21
$C_2H_6(g)$	–372.82

Solution: Basis: 1 mole of C_4H_{10}

Reaction: $C_4H_{10}(g) \rightleftharpoons C_2H_4(g) + C_2H_6(g)$

Heat absorbed = Standard heat of reaction

$$= \left[\sum \Delta H^\circ_C\right]_{\text{Reactant}} - \left[\sum \Delta H^\circ_C\right]_{\text{Products}}$$

= [1 × (–686.29)] – [1 × (–337.21) + 1 × (–372.82)]
= –686.29 – [(–337.21) – (372.82)]
= –686.29 – (–337.21 – 372.82)
= –686.29 + 710.03
= 23.74 kcal.

EXAMPLE 6.9 Calculate the standard heat of reaction ΔH°_R of the following reaction.

$$CH_3Cl(g) + KOH(s) \rightleftharpoons CH_3OH(l) + KCl(s)$$

Data:

Component	ΔH°_f (kcal/mol)
$CH_3Cl(g)$	–24.58
$CH_3OH(s)$	–57.13
$KOH(s)$	–101.45
$KCl(s)$	–104.31

Solution: Basis: 1 mol of CH_3Cl

Reaction: $CH_3Cl(g) + KOH(s) \rightleftharpoons CH_3OH(l) + KCl(s)$

$$\Delta H^\circ_R = \left[\sum \Delta H^\circ_f\right]_{\text{Products}} - \left[\sum \Delta H^\circ_f\right]_{\text{Reactants}}$$

= [1 × (–57.13) + 1 × (–104.31)] – [1 × (–24.58) + 1 × (–101.45)]
= (–57.13 – 104.31) – (–24.58 – 101.45)

$= -161.44 + 126.03$

$= -35.41.$

EXAMPLE 6.10 Calculate the standard heat of reaction ΔH°_R of the following reaction.

$$(COOH)_2(s) \rightarrow HCOOH(l) + CO_2(g)$$

Data:

Component	ΔH°_C (kcal/mol)
$(COOH)_2(s)$	–58.46
$HCOOH(l)$	–60.81
$CO_2(g)$	0

Solution: Basis: 1 mole of oxalic acid

Reaction: $(COOH)_2(s) \rightarrow HCOOH(l) + CO_2(g)$

$$\Delta H^\circ_R = \left[\sum \Delta H^\circ_C\right]_{\text{Reactants}} - \left[\sum \Delta H^\circ_C\right]_{\text{Products}}$$

$= [1 \times (-58.46)] - [1 \times (-60.81) + 1 \times (0)]$

$= -58.46 - (-60.81 + 0)$

$= -58.46 + 60.81$

$= 2.35$ kcal.

EXAMPLE 6.11 Calculate the enthalpy change between the reactants and products at standard condition if 50 mole of CO_2 is produced according to the following reaction.

$$2C_4H_{10}(g) + 13O_2(g) \rightarrow 8CO_2(g) + 10H_2O(l)$$

Data:

Component	ΔH°_f (kcal/mol)
$C_4H_{10}(g)$	–30.04
$CO_2(g)$	–93.98
$H_2O(l)$	–68.27
$O_2(g)$	0.0

Solution: Basis: 8 moles of CO_2.

Reaction: $2C_4H_{10}(g) + 13O_2(g) \rightarrow 8CO_2(g) + 10H_2O(l)$

$$\Delta H^\circ_R = \left[\sum \Delta H^\circ_f\right]_{\text{Products}} - \left[\sum \Delta H^\circ_f\right]_{\text{Reactants}}$$

$= [8 \times (-93.98) + 10 \times (-68.27)] - [2 \times (-30.04) + 13 \times (0)]$

$= (-751.84 - 682.7) - (-60.08 + 0)$

$= -1434.54 + 60.08$

$= -1374.46$ kcal.

Now, 8 moles of $CO_2 \rightarrow -1374.46$ kcal

Therefore, 50 moles of CO_2 = $\frac{-1374.46 \times 50}{8}$

Enthalpy change, ^ H = – 8590.37 kcal.

EXAMPLE 6.12 Calculate the standard heat of formation of *n*-propanol liquid using following data:

$\Delta H^\circ_{f(CO_2)}$ = –93.98 kcal/mol

$\Delta H^\circ_{f(H_2O)}$ = – 68.27 kcal/mol

$\Delta H^\circ_{C(C_3H_7OH)}$ = – 484.40 kcal/mol

Solution: Basis: 1 mole of *n*-propanol.
Reaction:

1. $C(s) + O_2(g) \rightarrow CO_2\ (g)$ $\qquad \Delta H_1 = -93.98$ kcal/mol
2. $H_2(g) + \frac{1}{2} O_2(g) \rightarrow H_2O(l)$ $\qquad \Delta H_2 = -68.27$ kcal/mol
3. $C_3H_7OH(l) + 4.5O_2(g) \rightarrow 3CO_2(g) + 4H_2O(l)$ $\qquad \Delta H^\circ_C = -484.40$ kcal/mol
4. $3C(s) + 4H_2(g) + \frac{1}{2} O_2(g) \rightarrow C_3H_7OH(l)$

$$\begin{aligned}\Delta H^\circ_{f(C_3H_7OH)} &= 3\Delta H_1 + 4\Delta H_2 - \Delta H^\circ_C \\ &= 3 \times (-93.98) + 4 \times (-68.27) - 1 \times (-484.40) \\ &= -281.94 - 273.08 + 484.40 \\ &= -70.62 \text{ kcal.}\end{aligned}$$

EXAMPLE 6.13 Calculate the standard heat of formation of liquid ethyl acetate using following data.

$\Delta H^\circ_{f(CO_2)}$ = –93.98 kcal/mol

$\Delta H^\circ_{f(H_2O)}$ = –68.26 kcal/mol

$\Delta H^\circ_{C(C_4H_8O_2)}$ = –532.82 kcal/mol

Solution: Basis: 1 mole of liquid ethyl acetate.
Reaction:

1. $C(s) + O_2(g) \rightarrow CO_2(g)$ $\qquad \Delta H_1 = -93.98$ kcal/mol
2. $H_2(g) + \frac{1}{2} O_2(g) \rightarrow H_2O(l)$ $\qquad \Delta H_2 = -68.26$ kcal/mol
3. $C_4H_8O_2(l) + 5O_2 \rightarrow 4CO_2(g) + 4H_2O(l)$ $\qquad \Delta H^\circ_C = -532.82$ kcal/mol

4. $4C(s) + 4H_2(g) + O_2(g) \rightarrow C_4H_8O_2(l)$

$$\begin{aligned}\Delta H^\circ_{f(C_4H_8O_2)} &= 4\Delta H_1 + 4\Delta H_2 - \Delta H^\circ_C \\ &= 4 \times (-93.98) + 4\,(-68.26) - (-532.82) \\ &= (-375.22 - 272.04) - (-532.82) \\ &= -648.96 + 532.82 \\ &= -116.14 \text{ kcal.}\end{aligned}$$

EXAMPLE 6.14 Calculate the heat of formation of benzoic acid crystals $C_7H_6O_2$ at 298 K using the following data.

$\Delta H^\circ_{f(CO_2)}$ = –93.98 kcal/mol

$\Delta H^\circ_{f(H_2O)}$ = –68.26 kcal/mol

$\Delta H^\circ_{C(C_7H_6O_2)}$ = –770.71 kcal/mol

Solution: Basis: 1 mole of benzoic acid crystals

Reaction:

1. $C(s) + O_2(g) \rightarrow CO_2(g)$ $\quad \Delta H_1 = -93.98$ kcal/mol
2. $H_2(g) + \frac{1}{2}O_2(g) \rightarrow H_2O(l)$ $\quad \Delta H_2 = -68.26$ kcal/mol
3. $C_7H_6O_2(s) + 7.5O_2(g) \rightarrow 7CO_2(g) + 3H_2O(l)$ $\quad \Delta H^\circ_C = -770.71$ kcal/mol
4. $7C(s) + 3H_2(g) + O_2(g) \rightarrow C_7H_6O_2$

$$\begin{aligned}\Delta H^\circ_{f(C_7H_6O_2)} &= 7\Delta H_1 + 3\Delta H_2 - \Delta H^\circ_C \\ &= [7 \times (-93.98) + 3 \times (-68.26)] - [1 \times (-770.71)] \\ &= (-675.86 - 204.78) - (-770.71) \\ &= -862.64 + 770.71 \\ &= -91.93 \text{ kcal}\end{aligned}$$

EXAMPLE 6.15 Calculate the standard heat of formation of glycerol liquid ($C_3H_8O_3$) using the following data.

$\Delta H^\circ_{f(CO_2)}$ = –93.98 kcal/mol

$\Delta H^\circ_{f(H_2O)}$ = –68.26 kcal/mol

$\Delta H^\circ_{C(C_3H_8O_3)}$ = –396.25 kcal/mol

Solution: Basis: 1 mole of glycerol liquid.

Reaction:

1. $C(s) + O_2(g) \rightarrow CO_2(g)$ $\quad \Delta H_1 = -93.98$ kcal/mol
2. $H_2(g) + \frac{1}{2}O_2(g) \rightarrow H_2O(l)$ $\quad \Delta H_2 = -68.26$ kcal/mol

3. $C_7H_6O_2(s) + 7.5O_2(g) \rightarrow 7CO_2(g) + 3H_2O(l)$ $\Delta H_C^\circ = -770.71$ kcal/mol

4. $7C(s) + 3H_2(g) + O_2(g) \rightarrow C_7H_6O_2$

$$\begin{aligned} \Delta H^\circ_{f(C_7H_6O_2)} &= 7\Delta H_1 + 3\Delta H_2 - \Delta H_C^\circ \\ &= [7 \times (-93.98) + 3 \times (-68.26)] - [1 \times (-770.71)] \\ &= (-675.86 - 204.78) - (-770.71) \\ &= -862.64 + 770.71 \\ &= -91.93 \text{ kcal} \end{aligned}$$

EXAMPLE 6.16 Calculate the heat of formation of gaseous ethyl alcohol at 298 K using following data.

$\Delta H^\circ_{f(CO_2)} = -93.98$ kcal/mol

$\Delta H^\circ_{f(H_2O)} = -68.26$ kcal/mol

$\Delta H^\circ_{C(C_2H_5OH)} = -336.79$ kcal/mol

Solution: Basis: 1 mole of gaseous ethyl alcohol.

Reaction:

1. $C(s) + O_2(g) \rightarrow CO_2(g)$ $\Delta H_1 = -93.98$ kcal/mol
2. $H_2(g) + \frac{1}{2}O_2(g) \rightarrow H_2O(l)$ $\Delta H_2 = -68.26$ kcal/mol
3. $C_2H_5OH(g) + 3O_2(g) \rightarrow 2CO_2(g) + 3H_2O(l)$ $\Delta H_C^\circ = -336.79$ kcal/mol
4. $2C(s) + 3H_2(g) + \frac{1}{2}O_2(g) \rightarrow C_2H_5OH(g)$

$$\begin{aligned} \Delta H^\circ_{f(C_2H_5OH)} &= 2\Delta H_1 + 3\Delta H_2 - \Delta H_C^\circ \\ &= [2 \times (-93.98) + 3 \times (-68.26)] - [1 \times (-336.79)] \\ &= (-187.96 - 204.78) + -336.79 \\ &= -392.74 + 336.79 \\ &= -55.95 \text{ kcal.} \end{aligned}$$

EXAMPLE 6.17 Calculate the standard heat of formation of liquid 1–3 butadiene using following data.

$\Delta H^\circ_{f(CO_2)} = -93.98$ kcal/mol

$\Delta H^\circ_{f(H_2O)} = -68.26$ kcal/mol

$\Delta H^\circ_{C(C_4H_6)} = -601.89$ kcal/mol

Solution: Basis: 1 mole of liquid 1–3 butadiene C_4H_6.

Reaction:

1. $C(s) + O_2(g) \rightarrow CO_2\ (g)$ $\qquad \Delta H_1 = -93.98$ kcal/mol
2. $H_2(g) + \frac{1}{2}O_2(g) \rightarrow H_2O(l)$ $\qquad \Delta H_2 = -68.26$ kcal/mol
3. $C_4H_6(l) + 5.5O_2(g) \rightarrow 4CO_2(g) + 3H_2O(l)$ $\qquad \Delta H_C^\circ = -601.89$ kcal/mol
4. $4C(s) + 3H_2(g) \rightarrow C_4H_6(l)$

$$\begin{aligned}\Delta H^\circ_{f(C_4H_6)} &= 4\Delta H_1 + 3\Delta H_2 - \Delta H_C^\circ \\ &= [4 \times (-93.98) + 3 \times (-68.26)] - [1 \times (-601.89)] \\ &= (-375.92 - 204.78) + 601.89 \\ &= -580.7 + 601.89 \\ &= 21.19 \text{ kcal.}\end{aligned}$$

EXAMPLE 6.18 Calculate the change in enthalpy between reactants and products at standard condition if 6 mole of ethylene oxide is produced as per the following reaction.

$$C_2H_4(g) + \tfrac{1}{2}O_2(g) \rightleftharpoons C_2H_4O(g)$$

Data:

Component	^ $H^\circ{}_f$ (kcal/mol)
$C_2H_4(g)$	12.53
$C_2H_4O(g)$	–12.56
$O_2(g)$	0

Solution: Basis: 1 mole of C_2H_4 gas.

Reaction: $\qquad C_2H_4(g) + \frac{1}{2}O_2(g) \rightarrow C_2H_4O(g)$

$$\begin{aligned}\Delta H_R^\circ &= \left[\sum \Delta H_f^\circ\right]_{\text{Products}} - \left[\sum \Delta H_f^\circ\right]_{\text{Reactants}} \\ &= 1 \times (-12.56) - \left[1 \times (12.53) + \frac{1}{2} \times (0)\right] \\ &= -12.56 - 12.53 \\ &= -25.09 \text{ kcal}\end{aligned}$$

Now, $\qquad$ 1 mole of $C_2H_4O \equiv -25.09$ kcal

Therefore, $\qquad$ 6 mole of $C_2H_4O \equiv \dfrac{-25.09 \times 6}{1}$

Thus, change in enthalpy (ΔH) = –150.54 kcal.

EXAMPLE 6.19 Calculate the standard heat of reaction when gaseous NH_3 is dissolved in water to form 3% by weight of its solution.

Data:

Component	^ H°_f (kcal/mol)
$NH_3(g)$	– 11.93
$NH_4OH(l)$	– 86.26
$H_2O(l)$	– 68.26

Solution: Basis: 100 kg of 3% NH_3 solution

Reaction: $NH_3(g) + H_2O(l) \rightarrow NH_4OH(l)$

$$\Delta H_R^\circ = \left[\sum \Delta H_f^\circ\right]_{\text{Products}} - \left[\sum \Delta H_f^\circ\right]_{\text{Reactants}}$$

$$= [1 \times (-86.26)] - [1 \times (-11.93) + 1 \times (-68.26)]$$

$$= -86.26 - (-11.93 - 68.26)$$

$$= -86.26 + 80.19$$

$$= -6.07 \text{ kcal}$$

$$NH_3 \text{ present in solution} = \frac{3}{17}$$

$$= 0.176 \text{ kgmol}$$

$$= 176 \text{ mole}$$

Now, $1 \text{ mole of } NH_3 \equiv 6.07 \text{ kcal}$

Therefore, $176 \text{ mole of } NH_3 \equiv \dfrac{6.07 \times 176}{1} = 1068.32 \text{ kcal}$

Hence, $\text{the heat of dissolution} = \dfrac{1068.32 \text{ kcal}}{100 \text{ kg of solution}}$

EXAMPLE 6.20 Calculate the changes in enthalpy between reactants and products at standard condition if 20 mole of formaldehyde is produced according to the following reaction.

$CH_4(g) + O_2(g) \rightleftharpoons HCHO(g) + H_2O(g)$

Data:

Component	^ H°_C (kcal/mol)
$CH_4(g)$	–212.71
$HCHO(g)$	–134.57

Solution: Basis: 1 mole of HCHO.

Reaction: $CH_4(g) + O_2(g) \rightleftharpoons HCHO(g) + H_2O(g)$

$$\Delta H_R^\circ = \left[\sum \Delta H_C^\circ\right]_{\text{Reactants}} - \left[\sum \Delta H_C^\circ\right]_{\text{Products}}$$

$= 1 \times (-212.71) - 1 \times (-134.57)$
$= -212.71 + 134.57$
$= -78.13$ kcal.

EXAMPLE 6.21 Calculate the heat that must be added to 5 kgmol of air to heat from 298 K to 573 K using mean molal heat capacity data for air given below.

C°_{Pm} = 29.40 kJ/kgmol · K for air between temperature range 298 K to 573 K.

Solution: Basis: 5 kgmol of air.

$$Q = mC^{\circ}_{Pm}(T - T_0)$$

where

Q = Amount of heat added (kJ)
m = 5 kgmol of air
C°_{Pm} = 29.40 kJ/kgmol · K for air
T = 573 K
T_0 = 298 K

Therefore, $Q = 5 \times 29.40 \times (573 - 298) = 40{,}425$ kJ.

EXAMPLE 6.22 Calculate the heat needed to raise the temperature of 2 kgmol of NH_3 for 350 K to 450 K using mean molal heat capacity.

Data:

$C^{\circ}_{Pm_1}$ for NH_3 between 298 K to 350 K = 36.86 kJ/kgmol · K

$C^{\circ}_{Pm_2}$ for NH_3 between 298 K to 450 K = 38.71 kJ/kgmol · K

Solution: Basis: 2 kgmol of NH_3.

$$Q = m[C^{\circ}_{Pm_2}(T_2 - T_0) - C^{\circ}_{Pm_1}(T_1 - T_0)]$$

where

Q = Amount of heat needed
m = 2 kgmol of NH_3
$C^{\circ}_{Pm_2}$ = Mean molal heat capacity (kJ/kgmol · K)
$C^{\circ}_{Pm_1}$ = Mean molal heat capacity (kJ/kgmol · K)
T_2 = 450 K
T_1 = 350 K
T_0 = 298 K

$Q = 2[38.71(450 - 298) - 36.86(350 - 298)]$
$= 2[38.71 \times 152 - 36.86 \times 52]$
$= 2\,[5{,}883.92 - 1{,}916.72]$
$= 2 \times 3967.2$
$= 7934.4$ kJ

EXAMPLE 6.23 Chlorinated diphenyl is heated from 303 K to 503 K in an indirectly fired heater at a rate of 3500 kg/h. Calculate the heat to be supplied to the fluid in the heater. The heat capacity of the fluid in this temperature range is given by the equation

$$C_P = 0.751 + 1.465 \times 10^{-3} T, \text{ kJ/kg} \cdot \text{K}$$

Solution: Basis: 3500 kg/h of chlorinated diphenyl.

$$
\begin{aligned}
Q &= m\left(\int_{T_1}^{T_2} C_P dT\right) \\
&= \left[\int_{T_1}^{T_2} (0.751 + 1.465 \times 10^{-3} T)\, dT\right] \\
&= m\left[0.751T + \frac{1.465 \times 10^{-3} \times T^2}{2}\right]_{T_1}^{T_2} \\
&= m\left[0.751(T_2 - T_1) + \frac{1.465 \times 10^{-3}}{2} \times (T_2^2 - T_1^2)\right] \\
&= 3500\left[0.751(503 - 303) + \frac{1.465 \times 10^{-3}}{2} \times (503^2 - 303^2)\right] \\
&= 3500\left[0.751 \times 200 + \frac{1.465 \times 10^{-3}}{2} \times 161200\right] \\
&= 938976.5 \text{ kJ/h} \\
&= 260.82 \text{ kW}
\end{aligned}
$$

EXAMPLE 6.24 A mixture of isomeric Diphenyl and Dichloro Tetrachloroethane is used as a thermic fluid in a liquid phase heating system. The thermic fluid enters an indirect fired heater at a temperature of 450 K and leaves the heater at a temperature of 550 K. Calculate the supply of heat to the heater per kg of the liquid heated. The heat capacity of the fluid is given by the equation

$$C_P = 1.435 + 2.19 \times 10^{-3} T, \text{ kJ/(kg} \cdot \text{K)}$$

where

$T = K$

Solution: Basis: 1 kg of DDT.

$$Q = m\int_{T_1}^{T_2} C_P dT$$

$$= m\left[\int_{T_1}^{T_2} (1.435 + 2.19 \times 10^{-3}T)\, dT\right]$$

$$= m\left[1.435T + \frac{2.19 \times 10^{-3}T^2}{2}\right]_{T_1}^{T_2}$$

$$= m\left[1.435(T_2 - T_1) + \frac{2.19 \times 10^{-3}}{2}(T_2^2 - T_1^2)\right]$$

$$= 1 \times \left[1.435(550 - 450) + \frac{2.19 \times 10^{-3}}{2}(550^2 - 450^2)\right]$$

$$= 1 \times (143.5 + 109.5)$$

$$= 253 \text{ kJ/kg}$$

EXAMPLE 6.25 Flue gases leaving the stack of a boiler at 520 K have the following molar composition.

CO_2 = 11.4%

H_2O = 13.0%

O_2 = 2.3%

and N_2 = 73.3%.

Calculate the heat lost in 1 kgmol of gas mixture above 298 K.

Data:

Component	(kJ/kgmol ⊣ K)
CO_2	41.62
H_2O	34.33
O_2	30.14
N_2	29.31

Solution: Basis: 1 kgmol of gas mixture.

$$C^{\circ}_{Pm\,(\text{mix})} = \sum x_i \cdot C^{\circ}_{Pm_i}$$

= 0.114 × 41.62 + 0.130 × 34.33 + 0.023 × 30.14 + 0.733 × 29.31

= 4.745 + 4.463 + 0.693 + 21.484

= 31.385 kJ/kgmol ⊣ K

$$Q = m \dashv C^{\circ}_{Pm\,(\text{mix})}\,(T - T_0)$$

where

Q = Amount of heat lost (kJ)

m = 1 kgmol

$C^{\circ}_{Pm\,(\text{mix})}$ = Mean molal heat capacity (kJ/kgmol ⊣ K)

T = 520 K

T_0 = 298 K

Therefore, $Q = 1 \times 31.385 \times (520 - 298) = 6967.47$ kJ.

EXAMPLE 6.26 A stream of nitrogen flowing at a rate of 150 kgmol/h is heated from 298 Kto 373 K. Calculate the heat that must be transferred.

Data:

$$C^{\circ}_{PN_2} = 29.49 - 5.14 \times 10^{-3}T + 13.18 \times 10^{-6}T^{2} - 4.95 \times 10^{-9}T^{3}, \text{ kJ/kgmol.K}$$

Solution: Basis: 150 kgmol/h of nitrogen gas.

$$Q = m\int_{T_1}^{T_2} C^{\circ}_{P}\,dT$$

$$= m\left[\int_{T_1}^{T_2} (29.49 - 5.14 \times 10^{-3}T + 13.18 \times 10^{-6}T^{2} - 4.95 \times 10^{-9}T^{3})\,dT\right]$$

$$= m\left[29.49T - \frac{5.14 \times 10^{-3}}{2}T^{2} + \frac{13.18 \times 10^{-6}}{3}T^{3} - \frac{4.95 \times 10^{-9}}{4}T^{4}\right]_{T_1}^{T_2}$$

$$= 150\left[\begin{array}{l} 29.49(373 - 298) - \dfrac{5.14 \times 10^{-3}}{2}(373^{2} - 298^{2}) + \dfrac{13.18 \times 10^{-6}}{3}(373^{3} - 298^{3}) \\ \qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad - \dfrac{4.95 \times 10^{-9}}{4}(373^{4} - 298^{4}) \end{array}\right]$$

$$= 150\,[2211.75 - 129.33 + 111.73 - 14.19]$$

$$= 150 \times (2179.96)$$

$$= 326994 \text{ kJ/h}$$

$$= 90.83 \text{ kW.}$$

EXAMPLE 6.27 Pure ethylene is heated from 298 K to 523 K at atmospheric pressure. Calculate the heat added per kgmol of ethylene using the data given below.

$$C^{\circ}_{PC_2H_2} = a + bT + cT^{2} + dT^{3}, \text{ kJ/kgmol} \dashv \text{K}$$

Data:

Component	*a*	$b \times 10^3$	$c \times 10^6$	$d \times 10^9$
C_2H_2	4.13	155.01	–81.53	17.0

Solution: Basis: 1 kgmol of pure C_2H_2.

$$
\begin{aligned}
Q &= m\int_{T_1}^{T_2} C_P^\circ \, dT \\
&= m\left[\int_{T_1}^{T_2} (4.13 + 155.01 \times 10^{-3} T - 81.53 \times 10^{-6} T^2 + 17.0 \times 10^{-9} T^3)\, dT\right] \\
&= m\left[4.13T + \frac{155.01 \times 10^{-3}}{2} T^2 - \frac{81.53 \times 10^{-6}}{3} T^3 + \frac{17.0 \times 10^{-9}}{4} T^4\right]_{T_1}^{T_2} \\
&= 1\left[\begin{aligned} &4.13(523 - 298) + \frac{155.01 \times 10^{-3}}{2}(523^2 - 298^2) - \frac{81.53 \times 10^{-6}}{3}(523^3 - 298^3) \\ &\qquad + \frac{17.0 \times 10^{-9}}{4}(523^4 - 298^4)\end{aligned}\right] \\
&= 929.25 + 14317.11 - 3168.58 + 284.46 \\
&= 12362.24 \text{ kJ}
\end{aligned}
$$

EXAMPLE 6.28 A stream of CO_2 flowing at a rate of 100 kgmol/h is heated from 298 K to 383 K. Calculate the heat that must be transferred.

Data:

$$C_{P\,CO_2}^\circ = 21.35 + 64.27 \times 10^{-3} T - 41.01 \times 10^{-6} T^2$$

Solution: Basis: 100 kgmol/h of CO_2.

$$
\begin{aligned}
Q &= m\int_{T_1}^{T_2} C_P^\circ\, dT \\
&= m\left[\int_{T_1}^{T_2} (21.35 + 64.27 \times 10^{-3}T - 41.01 \times 10^{-6}T^2)\, dT\right] \\
&= m\left[21.35T + \frac{64.27 \times 10^{-3}}{2}T^2 - \frac{41.01 \times 10^{-6}}{3}T^3\right]_{T_1}^{T_2} \\
&= 100\left[21.35(383 - 298) + \frac{64.27 \times 10^{-3}}{2}(383^2 - 298^2) - \frac{41.01 \times 10^{-6}}{3}(383^3 - 298^3)\right] \\
&= 100[1814.75 + 1860.13 - 406.24] \\
&= 100(3268.64) \\
&= 326864 \text{ kJ/h}
\end{aligned}
$$

EXAMPLE 6.29 Calculate the heat that must be removed in cooling 1 kgmol of O_2 from 480 K to 300 K using C_P° data given below.

$$C_{PO_2}^\circ = 26.01 + 11.76 \times 10^{-3}T - 2.35 \times 10^{-6}T^2$$

Solution: Basis: 1 kgmol of O_2 gas.

$$
\begin{aligned}
Q &= m\int_{T_1}^{T_2} C_P^\circ\, dT \\
&= m\left[\int_{T_1}^{T_2} (26.01 + 11.76 \times 10^{-3}T - 2.35 \times 10^{-6}T^2)\, dT\right] \\
&= m\left[26.01T + \frac{11.76 \times 10^{-3}}{2}T^2 - \frac{2.35 \times 10^{-6}}{3}T^3\right] \\
&= 1\left[26.01(300 - 480) + \frac{11.76 \times 10^{-3}}{2}(300^2 - 480^2) - \frac{2.35 \times 10^{-6}}{3}(300^3 - 480^3)\right] \\
&= 1[-4681.80 - 825.55 + 65.48] \\
&= -\,5441.87 \text{ kJ.}
\end{aligned}
$$

EXAMPLE 6.30 Calculate the heat to be added in heating 34 kg of CH_4 from 303 K to 523 K using C_P° data given below.

Data:

$$C^{\circ}_{P\text{CH}_4} = 19.26 + 52.13 \times 10^{-3}T + 11.95 \times 10^{-6}T^2,\ \text{kJ/kgmol} \cdot \text{K}$$

Solution: Basis: 34 kg of CH_4.

$$Q = m\int_{T_1}^{T_2} C^{\circ}_P\, dT$$

$$= m\left[\int_{T_1}^{T_2} (19.26 + 52.13 \times 10^{-3}T + 11.95 \times 10^{-6}T^2)\, dT\right]$$

$$= m\left[19.26T + \frac{52.13 \times 10^{-3}}{2}T^2 + \frac{11.95 \times 10^{-6}}{3}T^3\right]_{T_1}^{T_2}$$

$$= 2\left[19.26(523 - 303) + \frac{52.13 \times 10^{-3}}{2}(523^2 - 303^2) + \frac{11.95 \times 10^{-6}}{3}(523^3 - 303^3)\right]$$

$$= 2[4237.2 + 4736.53 + 459.02]$$

$$= 2(9432.75)$$

$$= 18865.5 \text{ kJ.}$$

EXAMPLE 6.31 Calculate the amount of heat to be supplied for raising temperature from 300 K to 1400 K of 1 kgmol of O_2 using the C°_P data given below.

Data:

$$C^{\circ}_{PO_2} = 26.01 + 11.76 \times 10^{-3}T$$

Solution: Basis: 1 kgmol of O_2.

$$Q = m\int_{T_1}^{T_2} C_P^\circ \, dT$$

$$= m\left[\int_{T_1}^{T_2} (26.01 + 11.76 \times 10^{-3} T)\, dT\right]$$

$$= m\left[26.01T + \frac{11.76 \times 10^{-3}}{2} T^2\right]_{T_1}^{T_2}$$

$$= 1\left[26.01(1400 - 300) + \frac{11.76 \times 10^{-3}}{2}(1400^2 - 300^2)\right]$$

$$= 1[28611 + 10995.6]$$

$$= 39606.6 \text{ kJ.}$$

EXAMPLE 6.32 Calculate the heat required to raise the temperature of 1 kgmol of pure SO_2 from 300 K to 1000 K. Heat capacity data for gaseous SO_2 is given by the following equation.

$$C^\circ_{PSO_2} = 43.46 + 10.64 \times 10^{-3} T - 5.95 \times 10^5 T^{-2}$$

Solution:

$$Q = m\int_{T_1}^{T_2} C_P^\circ \, dT$$

$$= m\left[\int_{T_1}^{T_2} (43.46 + 10.64 \times 10^{-3} T - 5.95 \times 10^5 T^{-2})\, dT\right]$$

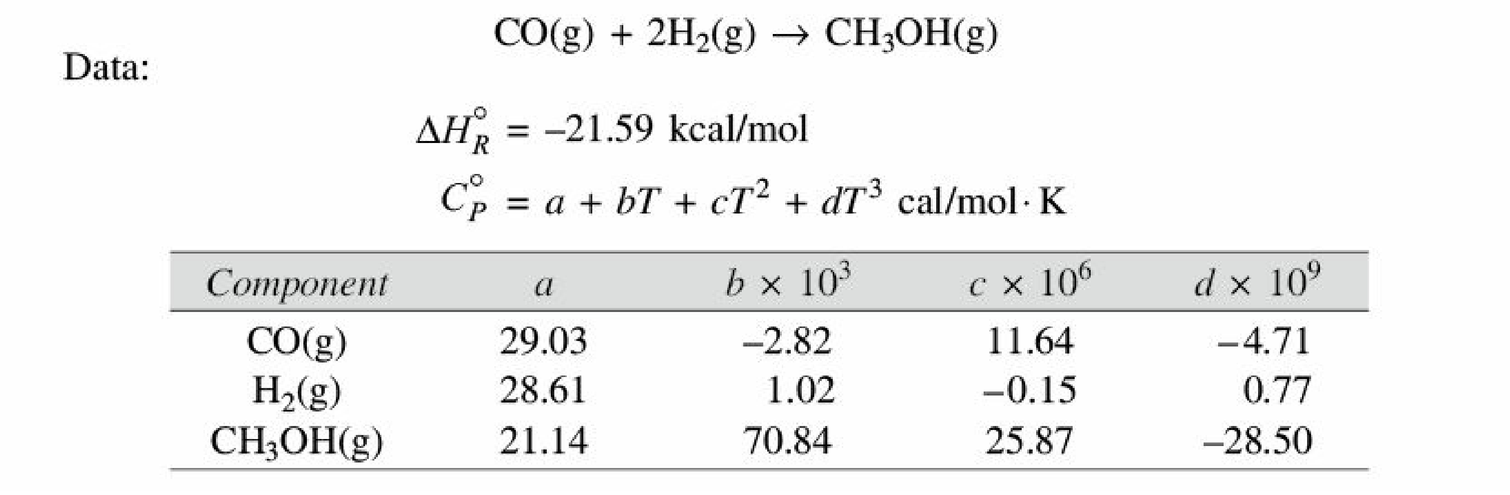
$$= m\left[43.46T + \frac{10.64 \times 10^{-3}}{2} T^2 + 5.95 \times 10^5 T^{-1}\right]_{T_1}^{T_2}$$

$$= 1\left[43.46(1000 - 300) + \frac{10.64 \times 10^{-3}}{2}(1000^2 - 300^2) + \frac{5.95 \times 10^5}{1}\left(\frac{1}{1000} - \frac{1}{300}\right)\right]$$

$$= 1[30422 + 4841.2 - 1388.33]$$

$$= 33874.87 \text{ kJ.}$$

EXAMPLE 6.33 Obtain an empirical equation for calculating the heat of reaction at any temperature ‘T’ for the following reaction.



Data:

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

$$\Delta H_R^\circ = -21.59 \text{ kcal/mol}$$

$$C_P^\circ = a + bT + cT^2 + dT^3 \text{ cal/mol}\cdot\text{K}$$

Component	*a*	*b* × 10^3	*c* × 10^6	*d* × 10^9
CO(g)	29.03	–2.82	11.64	–4.71
H_2(g)	28.61	1.02	–0.15	0.77
CH_3OH(g)	21.14	70.84	25.87	–28.50

Solution: Basis: 1 mol of CO gas.

Reaction: $CO(g) + 2H_2(g) \rightleftharpoons CH_3OH(g)$

^ H_R = Heat of reaction at any temperature T

Now, ^ H_R = $\Delta H_0 + \Delta aT + \frac{\Delta bT^2}{2} + \frac{\Delta cT^3}{3} + \frac{\Delta dT^4}{4}$

$\Delta a = \left[\sum(a)\right]_{\text{Product}} - \left[\sum(a)\right]_{\text{Reactant}}$

= [1 × (21.14)] – [1 × (29.03) + 2 × (28.61)]

= – 65.11

$\Delta b = \left[\sum(b)\right]_{\text{Product}} - \left[\sum(b)\right]_{\text{Reactant}}$

= $[(1 \times 70.84)] \times 10^{-3} - [1 \times (-2.82) + 2 \times (1.02)] \times 10^{-3}$

= 0.07

$\Delta c = \left[\sum(c)\right]_{\text{Product}} - \left[\sum(c)\right]_{\text{Reactant}}$

= $[1 \times (25.87)] \times 10^{-6} - [1 \times 11.64 + 2 \times (-0.15)] \times 10^{-6}$

= 14.53×10^{-6}

$\Delta d = \left[\sum(d)\right]_{\text{Product}} - \left[\sum(d)\right]_{\text{Reactant}}$

= $[1 \times (-28.50)] \times 10^{-9} - [1 \times (-4.71) + 2 \times 0.77] \times 10^{-9}$

= -25.33×10^{-9}

Also, ΔH_R° = –21.59 kcal/mol

= –21590 cal/mol

Therefore, –21590 = $\Delta H_0 + (-65.11) \times 298 + \left(\frac{0.07}{2}\right) \times 298^2 + \left(\frac{14.53 \times 10^{-6}}{3}\right) \times 298^3 + \left(\frac{-25.33 \times 10^{-9}}{4}\right) \times 298^4$

–21590 = ^ H_0 – 19402.78 + 3108.14 + 128.17 – 49.94

$$\hat{H}_0 = -5373.59 \text{ cal/mol}$$

$$\hat{H}_R = -5373.59 - 65.11T + 0.035T^2 + 4.84 \times 10^{-6}T^3 - 6.33 \times 10^{-9}T^4, \text{ cal/mol.}$$

EXAMPLE 6.34 A stream flowing at a rate of 30 kgmol/h containing 30% (mole) N_2 and 70% (mole) H_2. This is to be heated from 300 K to 470 K. Calculate the amount of heat transferred using the C_P° data given below.

$$C_{PN_2}^\circ = 29.57 - 5.43 \times 10^{-3}T + 13.17 \times 10^{-6}T^2, \text{ kJ/kgmol ⊣ K}$$

$$C_{PH_2}^\circ = 28.65 + 1.02 \times 10^{-3}T - 0.15 \times 10^{-6}T^2, \text{ kJ/kgmol ⊣ K}$$

Solution: Basis: 30 kgmol/h of N_2 and H_2 gas mixture.

$$x_{N2} = 0.30$$

$$x_{H2} = 0.70$$

$$C_{P\text{mix}}^\circ = \sum C_{Pi}^\circ \cdot x_i$$

$$= x_{N_2} \cdot C_{PN_2}^\circ + x_{H_2} \cdot C_{PH_2}^\circ$$

$$= 0.30 \times (29.57 - 5.43 \times 10^{-3}T + 13.17 \times 10^{-6}T^2) + 0.70 \times (28.63 + 1.02 \times 10^{-3}T - 0.15 \times 10^{-6}T^2)$$

$$= (8.87 - 1.63 \times 10^{-3}T + 3.95 \times 10^{-6}T^2) + (20.04 + 0.71 \times 10^{-3}T - 0.11 \times 10^{-6}T^2)$$

$$= 28.91 - 0.92 \times 10^{-3}T + 3.84 \times 10^{-6}T^2$$

$$Q = m\int_{T_1}^{T_2} C_{P\text{mix}}^\circ \, dT$$

$$= m\left[\int_{T_1}^{T_2} (28.91 - 0.92 \times 10^{-3}T + 3.84 \times 10^{-6}T^2)\, dT\right]$$

$$= m\left[28.91T - \frac{0.92 \times 10^{-3}}{2}T^2 + \frac{3.84 \times 10^{-6}}{3}T^3\right]_{T_1}^{T_2}$$

$$= 30\left[28.91(470 - 300) - \frac{0.92 \times 10^{-3}}{2}(470^2 - 300^2) + \frac{3.84 \times 10^{-6}}{3}(470^3 - 300^3)\right]$$

$$= 30[4914.70 - 60.21 + 98.33]$$

$$= 30 \times 4952.82$$

$$= 148584.6 \text{ kJ/h}$$

$$= 41.27 \text{ kW.}$$

EXAMPLE 6.35 Calculate the heat required to raise the temperature of 128 kg of pure SO_2 from 350

K to 1100 K. Heat capacity data for gaseous SO_2 is given by the following equation.

$$C^{\circ}_{P\,SO_2} = 43.46 + 10.64 \times 10^{-3}T - \frac{5.95 \times 10^5}{T^2}$$

Solution: Basis: 128 kg of SO_2 gas.

$$\begin{aligned}
Q &= \int_{T_1}^{T_2} C^{\circ}_P\, dT \\
&= m\left[\int_{T_1}^{T_2}\left(43.46 + 10.64 \times 10^{-3}T - \frac{5.95 \times 10^5}{T^2}\right) dT\right] \\
&= m\left[43.46T + \frac{10.64 \times 10^{-3}}{2}T^2 + \frac{5.95 \times 10^5}{T}\right]_{T_1}^{T_2} \\
&= 2\left[43.46(1100 - 350) + \frac{10.64 \times 10^{-3}}{2}(1100^2 - 350^2) + \frac{5.95 \times 10^5}{1}\left(\frac{1}{1100} - \frac{1}{350}\right)\right] \\
&= 2[32595 + 5785.5 - 1159.09] \\
&= 2 \times (37221.41) \\
&= 74442.82 \text{ kJ.}
\end{aligned}$$

EXAMPLE 6.36 A natural gas has the following composition on mole basis.

CH_4 = 83%

C_2H_6 = 15%

and N_2 = 2%.

Calculate the heat to be added to heat 20 kgmol of natural gas from 300 K to 520 K using the heat capacity data given below.

$C^{\circ}_P = a + bT + cT^2$ kJ/kgmol –˥ K

Component	*a*	*b* × 10^3	*c* × 10^6
CH_4(g)	19.26	52.12	11.98
C_2H_6(g)	5.41	178.09	–67.38
N_2(g)	29.60	–5.15	13.19

Solution: Basis: 20 kgmol of natural gas.

$x_{CH_4} = 0.83$

$x_{C_2H_6} = 0.15$

$x_{N_2} = 0.02$

$$C^{\circ}_{P\,\text{mix}} = \sum x_i \cdot C^{\circ}_{Pi}$$

$$= x_{CH_4} \cdot C^{\circ}_{P\,CH_4} + x_{C_2H_6} \cdot C^{\circ}_{P\,C_2H_6} + x_{N_2} \cdot C^{\circ}_{P\,N_2}$$

$= 0.83(19.26 + 52.12 \times 10^{-3}T + 11.98 \times 10^{-6}T^2) + 0.15(5.41 + 178.09 \times 10^{-3}T$
$- 67.38 \times 10^{-6}T^2) + 0.02(29.60 - 5.15 \times 10^{-3}T + 13.19 \times 10^{-6}T^2)$
$= (15.99 + 43.26 \times 10^{-3}T + 9.94 \times 10^{-6}T^2) + (0.81 + 26.71 \times 10^{-3}T$
$- 10.11 \times 10^{-6}T^2) + (0.59 - 0.10 \times 10^{-3}T + 0.26 \times 10^{-6}T^2)$
$C^{\circ}_{P\,\text{mix}} = 17.39 + 69.87 \times 10^{-3}T + 0.09 \times 10^{-6}T^2$

Q = Amount of heat added.

$$Q = m\int_{T_1}^{T_2} C^{\circ}_{P\,\text{mix}}\, dT$$

$$= m\left[\int_{T_1}^{T_2} (17.39 + 69.87 \times 10^{-3}T + 0.09 \times 10^{-6}T^2)\, dT\right]$$

$$= m\left[17.39T + \frac{69.87 \times 10^{-3}}{2}T^2 + \frac{0.09 \times 10^{-6}}{3}T^3\right]_{T_1}^{T_2}$$

$$= 20\left[17.39(520 - 300) + \frac{69.87 \times 10^{-3}}{2}(520^2 - 300^2) + \frac{0.09 \times 10^{-6}}{3}(520^3 - 300^3)\right]$$

$$= 20(3825.80 + 6302.27 + 3.41)$$

$$= 20 \times 10131.48$$

$$= 202629.68 \text{ kJ.}$$

EXAMPLE 6.37 The gas having the following composition is at temperature of 750 K.

SO_2 = 7%
O_2 = 11%
SO_3 = 1%
and N_2 = 81%.

Calculate the heat content of 2 kgmol of gas mixture over 300 K using heat capacity data given below.

$$C^{\circ}_P = a + bT + cT^2$$

Component	*a*	*b* × 10^3	*c* × 10^6
SO_2	43.46	10.64	–5.95
O_2	26.01	11.76	–2.34
SO_3	22.03	121.63	–91.87

N_2	29.60	–5.15	–13.19

Solution: Basis: 2 kgmol of gas mixture.

$$Q = m\int_{T_1}^{T_2} C^{\circ}_{P\,\text{mix}}\,dT$$

$x_{SO_2} = 0.07$

$x_{O_2} = 0.11$

$x_{SO_3} = 0.01$

$x_{N_2} = 0.81$

$$\begin{aligned} C^{\circ}_{P\,\text{mix}} &= \sum x_i \cdot C^{\circ}_{Pi} \\ &= x_{SO_2}\cdot C^{\circ}_{P\,SO_2} + x_{O_2}\cdot C^{\circ}_{P\,O_2} + x_{SO_3}\cdot C^{\circ}_{P\,SO_3} + x_{N_2}\cdot C^{\circ}_{P\,N_2} \end{aligned}$$

$= 0.07 \times (43.46 + 10.64 \times 10^{-3}T - 5.95 \times 10^{-6}T^2)$

$+ 0.11 \times (26.01 + 11.76 \times 10^{-3}T - 2.34 \times 10^{-6}T^2)$

$+ 0.01 \times (22.03 + 121.63 \times 10^{-3}T - 91.87 \times 10^{-6}T^2)$

$+ 0.81 \times (29.60 - 5.15 \times 10^{-3}T - 13.19 \times 10^{-6}T^2)$

$= (3.04 + 0.75 \times 10^{-3}T - 0.42 \times 10^{-6}T^2)$

$+ (2.86 + 1.29 \times 10^{-3}T - 0.26 \times 10^{-6}T^2)$

$+ (0.22 + 1.22 \times 10^{-3}T - 0.92 \times 10^{-6}T^2)$

$+ (23.97 - 4.17 \times 10^{-3}T - 10.68 \times 10^{-6}T^2)$

$= 30.09 - 0.91 \times 10^{-3}T - 12.28 \times 10^{-6}T^2$

$$\begin{aligned} Q &= m\int_{T_1}^{T_2} (30.09 - 0.91\times 10^{-3}T - 12.28\times 10^{-6}T^2)\,dT \\ &= m\left[30.09T - \frac{0.91\times 10^{-3}}{2}T^2 - \frac{12.28\times 10^{-6}}{3}T^3\right]_{T_1}^{T_2} \\ &= 2\left[30.09(750-300) - \frac{0.91\times 10^{-3}}{2}(750^2 - 300^2) - \frac{12.28\times 10^{-6}}{3}(750^3 - 300^3)\right] \\ &= 2[13540.5 - 214.99 - 1616.36] \\ &= 2\times(11709.15) \\ &= 23418.3\ \text{kJ.} \end{aligned}$$

EXAMPLE 6.38 A stream of SO_2 flowing at a rate of 150 kgmol/h is heated from 300 K to 450 K. Calculate the heat that must be transferred.

Data:

$C^\circ_{P\,SO_2} = 43.46 + 10.64 \times 10^{-3}T - 5.95 \times 10^{-6}T^2$, kJ/kgmol ⊣ K

Solution: Basis: 150 kgmol/h of SO_2.

$$Q = m\int_{T_1}^{T_2} C^\circ_P\, dT$$

$$= m\left[\int_{T_1}^{T_2} (43.46 + 10.64 \times 10^{-3}T - 5.95 \times 10^{-6}T^2)\, dT\right]$$

$$= m\left[43.46T + \frac{10.64 \times 10^{-3}}{2}T^2 - \frac{5.95 \times 10^{-6}}{3}T^3\right]_{T_1}^{T_2}$$

$$= 150\left[43.46(450 - 300) + \frac{10.64 \times 10^{-3}}{2}(450^2 - 300^2) - \frac{5.95 \times 10^{-6}}{3}(450^3 - 300^3)\right]$$

$= 150\ (6519 + 598.5 - 127.18)$

$= 150 \times (6990.32)$

$= 1048548$ kJ/h

$= 291.26$ kW

EXAMPLE 6.39 Flue gas leaving the boiler stack at 650 K has the following composition on mole basis.

$CO_2 = 12\%$

$H_2O = 13\%$

$O_2 = 2\%$

and $N_2 = 73\%$.

Calculate the heat lost in 10 kgmol of gas mixture above 300 K using heat capacity data given below.

$C^\circ_P = a + bT + cT^2$, kJ/kgmol ⊣ K

Component	*a*	$b \times 10^3$	$c \times 10^6$
CO_2(g)	21.35	64.27	– 41.01
H_2O(g)	32.49	0.08	13.21
O_2(g)	26.01	11.76	–2.35
N_2(g)	29.60	–5.15	13.19

Solution: Basis: 10 kgmol of gas mixture.

$x_{CO_2} = 0.12$

$x_{H_2O} = 0.13$

$x_{O_2} = 0.02$

$x_{N_2} = 0.73$

$$C^\circ_{P\,\text{mix}} = \sum x_i \cdot C^\circ_{Pi}$$

$$= x_{CO_2} \cdot C^\circ_{P\,CO_2} + x_{H_2O} \cdot C^\circ_{P\,H_2O} + x_{O_2} \cdot C^\circ_{P\,O_2} + x_{N_2} \cdot C^\circ_{P\,N_2}$$

$= 0.12\,(21.35 + 64.27 \times 10^{-3}T - 41.01 \times 10^{-6}T^2)$

$+ 0.13\,(32.49 + 0.08 \times 10^{-3}T + 13.21 \times 10^{-6}T^2)$

$+ 0.02\,(26.01 + 11.76 \times 10^{-3}T - 2.35 \times 10^{-6}T^2)$

$+ 0.73(29.60 - 5.15 \times 10^{-3}T + 13.19 \times 10^{-6}T^2)$

$= (2.56 + 7.71 \times 10^{-3}T - 4.92 \times 10^{-6}T^2)$

$+ (4.22 + 0.01 \times 10^{-3}T + 1.71 \times 10^{-6}T^2)$

$+ (0.52 + 0.24 \times 10^{-3}T - 0.05 \times 10^{-6}T^2)$

$+ (21.61 - 3.76 \times 10^{-3}T + 9.63 \times 10^{-6}T^2)$

$C^\circ_{P\,\text{mix}} = 28.91 + 4.2 \times 10^{-3}T + 6.37 \times 10^{-6}T^2$

$$Q = m\int_{T_1}^{T_2} C^\circ_{P\,\text{mix}}\,dT$$

$$= m\left[\int_{T_1}^{T_2} (28.91 + 4.2 \times 10^{-3}\,T + 6.37 \times 10^{-6}\,T^2)\,dT\right]$$

$$= m\left[28.91T + \frac{4.2 \times 10^{-3}}{2}T^2 + \frac{6.37 \times 10^{-6}}{3}T^3\right]_{T_1}^{T_2}$$

$$= 10\left[28.91(650 - 300) + \frac{4.2 \times 10^{-3}}{2}(650^2 - 300^2) + \frac{6.37 \times 10^{-6}}{3}(650^3 - 300^3)\right]$$

$$= 10[10118.5 + 698.25 + 525.79]$$

$$= 10 \times (11342.54)$$

$$= 113425.4 \text{ kJ}$$

EXAMPLE 6.40 Toluene is heated from 300 K to 340 K at the rate of 46 kg/s. Calculate the heat required to be added to toluene using the heat capacity data given below.

$C^\circ_P = 1.80 + 812.21 \times 10^{-3}T - 1512.67 \times 10^{-6}T^2$, kJ/kgmol ⊣ K.

The molecular weight of toluene = 92.

Solution: Basis: 46 kg/s of toluene.

Flow rate of toluene, $m = \frac{46}{92}$

= 0.5 kgmol/s.

$$Q = m\int_{T_1}^{T_2} C_P^\circ \, dT$$

$$= m\left[\int_{T_1}^{T_2} (1.80 + 812.21 \times 10^{-3} T - 1512.67 \times 10^{-6} T^2)\, dT\right]$$

$$= m\left[1.80T + \frac{812.21 \times 10^{-3}}{2} T^2 - \frac{1512.67 \times 10^{-6}}{3} T^3\right]_{T_1}^{T_2}$$

$$= 0.5\left[1.80\,(340 - 300) + \frac{812.21 \times 10^{-3}}{2}(340^2 - 300^2) - \frac{1512.67 \times 10^{-6}}{3}(340^3 - 300^3)\right]$$

= 0.5 × (72.0 + 10396.29 – 6203.96)
= 0.5 × (4264.33)
= 2132.17 kJ/s
= 2132.17 kW.

EXAMPLE 6.41 Air containing 21% (mole) O_2 and 79% (mole) N_2 is to be heated from 300 Kto 450 K. Calculate the heat required to be added if the air flow rate is 5 m^3 per minute using data given below.

$C_{PO_2}^\circ = 26.01 + 11.76 \times 10^{-3}T - 2.35 \times 10^{-6}T^2$, kJ/kgmol ⏌ K

$C_{PN_2}^\circ = 29.60 - 5.15 \times 10^{-3}T + 13.19 \times 10^{-6}T^2$, kJ/kgmol ⏌ K

Solution: Basis: 5 m^3 per minute air flow.

Molal flow rate of air, $m = \frac{5}{22.4}$

= 0.223 kgmol/min

$x_{O2} = 0.21$

$x_{N2} = 0.79$

$$C_{P\,\text{mix}}^\circ = \sum x_i \cdot C_{Pi}^\circ$$
$$= x_{O_2} \cdot C_{PO_2}^\circ + x_{N_2} \cdot C_{PN_2}^\circ$$

$= 0.21\,(26.01 + 11.76 \times 10^{-3}T - 2.35 \times 10^{-6}T^2)$

$+ 0.79\,(29.60 - 5.15 \times 10^{-3}T + 13.19 \times 10^{-6}T^2)$

$= (5.46 + 2.47 \times 10^{-3}T - 0.49 \times 10^{-6}T^2)$

$+ (23.38 - 4.07 \times 10^{-3}T + 10.42 \times 10^{-6}T^2)$

$C_{P\,\text{mix}}^\circ = 28.84 - 1.6 \times 10^{-3}T + 9.93 \times 10^{-6}T^2$

$$Q = m\int_{T_1}^{T_2} C^{\circ}_{P\,\text{mix}}\, dT$$

$$= m\left[\int_{T_1}^{T_2} (28.84 - 1.6 \times 10^{-3}T + 9.93 \times 10^{-6}T^2)\, dT\right]$$

$$= m\left[28.84T - \frac{1.6 \times 10^{-3}}{2}T^2 + \frac{9.93 \times 10^{-6}}{3}T^3\right]_{T_1}^{T_2}$$

$$= 0.223\left[28.84\,(450 - 300) - \frac{1.6 \times 10^{-3}}{2}(450^2 - 300^2) + \frac{9.93 \times 10^{-6}}{3}(450^3 - 300^3)\right]$$

= 0.223 [4326 – 90 + 212.25]

= 0.223 (4448.25)

= 991.96 kJ/min.

= 16.53 kW.

EXAMPLE 6.42 The gas having the following composition by volume is at the temperature of 770 K.

SO_2 = 6%

O_2 = 11%

SO_3 = 1%

and N_2 = 82%.

Calculate the heat content of 5 kgmol gas mixture over 300 K using mean molal heat capacity data given below.

Component	(kJ/kgmol ⅃ K)
SO_2	46.89
O_2	31.46
SO_3	66.28
N_2	29.93

Solution: Basis: 5 kgmol

$x_{SO_2} = 0.06$

$x_{O_2} = 0.11$

$x_{SO_3} = 0.01$

$x_{N_2} = 0.82$

$$C^{\circ}_{P\,\text{mix}} = \sum x_i \cdot C^{\circ}_{Pi}$$

$$= x_{SO_2} \cdot C^{\circ}_{P\,SO_2} + x_{O_2} \cdot C^{\circ}_{P\,O_2} + x_{SO_3} \cdot C^{\circ}_{P\,SO_3} + x_{N_2} \cdot C^{\circ}_{P\,N_2}$$

= 0.06 × 46.89 + 0.11 × 31.46 + 0.01 × 66.28 + 0.82 × 29.93

= 2.81 + 3.46 + 0.66 + 24.54

= 31.47 kJ/kgmol ⊣ K

Now, $Q = \mathrm{m}\, C^{\circ}_{P\,\mathrm{mix}} (T - T_0)$

where

Q = Amount of heat (kJ)

m = 5 kgmol of gas mixture

$C^{\circ}_{P\,\mathrm{mix}}$ = 31.47 kJ/kgmol ⊣ K

T = 770 K

T_0 = 300 K

Therefore, $Q = 5 \times 31.47 \times (770 - 300) = 73954.5$ kJ.

EXAMPLE 6.43 An approximate equation for C_P of gaseous HCl is

$C^{\circ}_{P\,\mathrm{HCl}} = 6.6 + 0.96 \times 10^{-3} T$, cal/mol ⊣ K

Calculate the heat required to raise the temperature of 100 gmol of gas from 350 K to 550 K.

Solution: Basis: 100 gmol of HCl gas.

Now,

$$Q = m \int_{T_1}^{T_2} C^{\circ}_P \, dT$$

$$= m \left[\int_{T_1}^{T_2} (6.6 + 0.96 \times 10^{-3} T)\, dT \right]$$

$$= m \left[6.6T + \frac{0.96 \times 10^{-3}}{2} T^2 \right]_{T_1}^{T_2}$$

$$= 100 \left[6.6(550 - 350) + \frac{0.96 \times 10^{-3}}{2} (550^2 - 350^2) \right]$$

= 100 × [1320 + 86.4]

= 100 × (1406.4)

= 140640 cal

= 140.64 kcal

EXAMPLE 6.44 The heat capacity of air is given by

$C_P = a + bT + cT^2$, cal/mol ⊣ K

where, $a = 6.39$, $b = 1.76 \times 10^{-3}$ and $c = -0.27 \times 10^{-6}$.

Calculate the mean molal heat capacity in the range 298 K to 530 K. What is the quantity of heat required for 20 kgmol of air to heat from 298 K to 530 K?

Solution: Basis: 20 kgmol of air.

$$\begin{aligned} C^{\circ}_{Pm} &= a + \frac{b}{2}(T + T_0) + \frac{c}{3}(T^2 + TT_0 + T_0^2) \\ &= 6.39 + \frac{1.76 \times 10^{-3}}{2}(530 + 298) + \left(\frac{-0.27 \times 10^{-6}}{3}\right)(530^2 + 530 \times 298 + 298^2) \\ &= 6.39 + 0.73 - 0.05 \\ &= 7.07 \text{ cal/mol} \cdot \text{K} \end{aligned}$$

Now, $Q = m C^{\circ}_{Pm} (T - T_0)$

where

Q = Amount of heat (cal)

C°_{Pm} = 7.07 cal/mol ⋅ K

T = 530 K

T_0 = 298 K

m = 20 kgmol

Therefore, $Q = (20 \times 10^3) \times (7.07) \times (530 - 298)$

Q = 32804.8 kcal.

EXAMPLE 6.45 Calculate the standard heat of reaction of the following reaction

$$C_5H_{12}(l) + 8O_2(g) \rightleftharpoons 5CO_2(g) + 6H_2O(l)$$

Data:

Component	(kJ/mol)
C_5H_{12} (l)	–173.49
CO_2 (g)	–393.51
H_2O(l)	–285.83
O_2 (g)	0

Solution: Basis: 1 mole of C_5H_{12}.

Reaction: $C_5H_{12}(l) + 8O_2(g) \rightleftharpoons 5CO_2(g) + 6H_2O(l)$

$$\Delta H^{\circ}_R = \left[\sum \Delta H^{\circ}_f\right]_{\text{Product}} - \left[\sum \Delta H^{\circ}_f\right]_{\text{Reactant}}$$

$= [5 \times (-393.51) + 6 \times (-285.83)] - [1 \times (-173.49) + 8(0)]$

$= -3509.04$ kJ/mol

Exercises

6.1 Calculate the standard heat of reaction of the following reaction.

$$C_2H_5OH(g) \rightleftharpoons CH_3CHO(g) + H_2(g)$$

Data:

Component	(kJ/mol)
$C_2H_5OH(g)$	–1409
$CH_3CHO(g)$	–1192
$H_2(g)$	–286

6.2 Calculate the heat of reaction at 25°C of the following reaction.

$$C_2H_6(g) \rightleftharpoons C_2H_4(g) + H_2(g)$$

Data:

Component	(kJ/mol)
$C_2H_6(g)$	–1562
$C_2H_4(g)$	–1413
$H_2(g)$	–285

6.3 Calculate the standard heat of reaction ΔH_R° of the following reaction.

$$4NH_3(g) + 5O_2(g) \rightleftharpoons 4NO(g) + 6H_2O(g)$$

Data:

Component	(kJ/mol)
$NH_3(g)$	–10.97
$O_2(g)$	0
$NO(g)$	21.55
H_2O	–57.75

6.4 Calculate the standard heat of reaction ΔH_R° of the following reaction.

$$3CaSO_4(s) + SiO_2(s) \rightleftharpoons 3CaO \dashv SiO_2(s) + 3SO_2(g) + 1.5O_2(g)$$

Data:

Component	(kJ/mol)
$CaSO_4$ (s)	–342.17
$SiO_2(s)$	–215.79
$CaO \dashv SiO_2(s)$	–687.60
$SO_2(g)$	–70.88
$O_2(g)$	0.0

6.5 Obtain an empirical equation for calculating the heat of reaction at any temperature '*T*' for the following reaction

$$CH_4(g) + C_2H_4(g) \rightleftharpoons C_3H_8(g)$$

Data:

$\Delta H_R^\circ = -19.74$ kcal/mol

$C_p^\circ = a + bT + cT^2 + dT^3$ cal/mol · K

Component	*a*	$b \times 10^3$	$c \times 10^6$	$d \times 10^9$
$CH_4(g)$	19.25	52.11	11.95	–11.33
$C_2H_4(g)$	4.13	156.01	– 81.55	16.99
$C_3H_8(g)$	– 4.22	305.25	– 157.93	32.15

6.6 Calculate the amount of heat to be supplied for raising temperature from 300 K to 1500 K of 10 kgmol of O_2 using the C_p° data given below.

Data:

$$C_{PO_2}^\circ = 26.01 + 11.76 \times 10^{-3}T - 2.34 \times 10^{-6}T^2.$$

6.7 Obtain an empirical equation for calculating the heat of reaction at any temperature '*T*' for the following reaction:

$$CO(g) + H_2O(g) \rightleftharpoons CO_2(g) + H_2(g)$$

Data:

$\Delta H_R^\circ = -9.83$ kcal/mol

$C_p^\circ = a + bT + cT^2 + dT^3$ cal/mol · K

Component	*a*	$b \times 10^3$	$c \times 10^6$	$d \times 10^9$
$CO(g)$	28.02	–2.83	12.65	–4.71
$H_2O(g)$	33.49	0.09	11.23	–5.57
$CO_2(g)$	21.33	65.29	– 43.03	9.69
$H_2(g)$	28.63	2.01	– 0.17	0.77

6.8 Calculate the heat required to raise the temperature of 64 kg of pure SO_2 from 298 K to 1200 K. Heat capacity data for gaseous SO_2 is given by the following equation.

$$C_{PSO_2}^\circ = 43.46 + 10.64 \times 10^{-3}T - \frac{5.95 \times 10^5}{T^2}$$

6.9 Calculate the heat needed to raise the temperature of 8 kgmol of NH_3 from 360 K to 520 K using mean molal heat capacity.

Data:

$C_{Pm_1}^\circ$ for NH_3 between 298 K to 360 K = 36.98 kJ/kgmol · K

$C_{Pm_2}^\circ$ for NH_3 between 298 K to 520 K = 39.26 kJ/kgmol · K

6.10 Calculate the heat that must be added to 15 kgmol of air to heat from 298 K to 570 K using mean molal heat capacity data for air given below.

C_{Pm}° = 29.40 kJ/kgmol · K for air

between temperature range 298 K to 570 K.

6.11 A stream of Nitrogen flowing at a rate of 120 kgmol/h is heated from 300 K to 380 K. Calculate the heat that must be transferred.

Data

$$C^{\circ}_{PN_2} = 29.49 - 5.14 \times 10^{-3}T - 13.18 \times 10^{-6}T^2 - 4.95 \times 10^{-9}T^3.$$

6.12 Calculate the heat required to raise the temperature of 10 kgmol of oxygen from 300 K to 425 K using the heat capacity data given below.

$$C^{\circ}_{PO_2} = 26.01 + 11.76 \times 10^{-3}T - 2.35 \times 10^{-6}T^2.$$

6.13 Calculate the standard heat of formation of glycerol liquid using the following data

$$\Delta H^{\circ}_{f(CO_2)} = -93.98 \text{ kcal/mol}$$

$$\Delta H^{\circ}_{f(H_2O)} = -68.26 \text{ kcal/mol}$$

$$\Delta H^{\circ}_{C(C_3H_8O_3)} = -396.25 \text{ kcal/mol.}$$

6.14 Calculate the heat of formation of gaseous ethyl alcohol at 298 K using the following data.

$$\Delta H^{\circ}_{f(CO_2)} = -93.98 \text{ kcal/mol}$$

$$\Delta H^{\circ}_{f(H_2O)} = -68.26 \text{ kcal/mol}$$

$$\Delta H^{\circ}_{C(C_2H_5OH)} = -336.79 \text{ kcal/mol.}$$

6.15 Calculate the standard heat of formation of liquid 1–3 butadiene using the following data

$$\Delta H^{\circ}_{f(CO_2)} = -93.98 \text{ kcal/mol}$$

$$\Delta H^{\circ}_{f(H_2O)} = -68.26 \text{ kcal/mol}$$

$$\Delta H^{\circ}_{C(C_4H_6)} = -601.89 \text{ kcal/mol.}$$

6.16 Calculate the change in enthalpy between reactants and products at standard condition if 10 mole of ethylene oxide is produced as per the following reaction.

$$C_2H_4(g) + \frac{1}{2}O_2(g) \rightleftharpoons C_2H_4O(g)$$

Data:

Component	(kcal/mol)
$C_2H_4(g)$	12.53
$C_2H_4O(g)$	–12.56
$O_2(g)$	0

6.17 Calculate the standard heat of reaction when gaseous NH_3 is dissolved in water to form 5% by weight of its solution.

Data:

Component	(kcal/mol)
$NH_3(g)$	–11.93

$NH_4OH(l)$	–86.26
$H_2O(l)$	–68.26

6.18 Calculate the change in enthalpy between reactants and products at standard condition if 25 moles of formaldehyde is produced according to the following reaction.

$$CH_4(g) + O_2(g) \rightleftharpoons HCHO(g) + H_2O(g)$$

Data:

Component	(kcal/mol)
$CH_4(g)$	–212.71
$HCHO(g)$	–134.57

6.19 The heat of dilution of one mole $KClO_3$ in 5.6 mole of water at 292 K is –37.3 kJ per mole of $KClO_3$. Calculate the heat absorbed when 2000 kg of solution is to be prepared at 292 K having the above composition.

6.20 Methane is oxidised with air to produce formaldehyde as per the following equation:

$$CH_4(g) + O_2(g) \rightleftharpoons HCHO(g) + H_2O(g).$$

200 moles of methane is fed to the reactor at 310 K. Air is used 20% in excess and is supplied at 370 K. If the percentage conversion is 70, calculate the heat that must be removed from the product stream to emerge at 470 K.

Data:

Component	(310 – 298) K	(470 – 298) K
CH_4	36.04	40.19
N_2	–	29.29
O_2	–	30.08
HCHO	–	41.29
H_2O	–	34.24

where C°_{Pm} is in kJ/kgmol.K.

6.21 Obtain an empirical equation for calculating the heat of reaction at any temperature '*T*' for the reaction

$$CO(g) + 2H_2(g) \rightleftharpoons CH_3OH(g)$$

Data:

$$\Delta H^{\circ}_R = -90.41 \text{ kJ/kgmol}$$

$$C^{\circ}_P = a + bT + cT^2 \text{ kJ/kgmol} \dashv \text{ K}$$

Component	*a*	$b \times 10^3$	$c \times 10^6$
$CO(g)$	28.02	–2.83	12.65
$H_2(g)$	28.63	2.01	–0.17
$CH_3OH(g)$	21.14	70.84	25.86

6.22 For the reaction

$$SO_2(g) + \frac{1}{2}O_2(g) \rightleftharpoons SO_3(g)$$

Calculate the heat of reaction at 1000 K using the data given.

$C_p = a + bT$, cal/mol ⊣ K

Data:

Component	DH_f (cal/mol)	*a*	$b \times 10^3$
$SO_2(g)$	–70944	6.14	13.84
$O_2(g)$	0	6.73	1.51
$SO_3(g)$	–94580	6.08	23.54

6.23 The molal heat capacity of oxygen is given by

$C_P = 6.12 + 3.17 \times 10^{-3}T - 1.01 \times 10^{-6}T^2$, cal/mol ⊣ K

Express C_P in cal/mol°C.

6.24 Calculate the theoretical flame temperature of a gas containing 20% CO and 80% N_2 when burnt with 60% excess air. Both air and gas initially being at 298 K.

Data:

$C_P = a + bT + cT^2$, kJ/kgmol ⊣ K

Component	*a*	$b \times 10^3$	$c \times 10^6$
CO	6.34	10.14	3.15
O_2	6.12	3.17	1.01
N_2	6.46	1.39	0.07

6.25 Dry methane is burnt with dry air, both being initially at 298 K. The flame temperature is 1670 K. If complete combustion is assumed, how much excess air is to be used? C_P data mean values are given.

Data:

ΔH_R° = –801550 J/gmol ⊣ K

$C_{P(CO_2)}$ = 51.79 J/gmol ⊣ K

$C_{P(H_2O)}$ = 40.19 J/gmol ⊣ K

$C_{P(N_2)}$ = 32.15 J/gmol ⊣ K

$C_{P(O_2)}$ = 32.41 J/gmol ⊣ K

6.26 Calculate the theoretical flame temperature of a gas containing 30% CO and 70% N_2 when burnt with 120% excess air, both air and gas being at 298 K. Use the data given below:

$\Delta H^\circ_{f(CO_2)}$ = –393137 J/gmol

$\Delta H^\circ_{f(CO)}$ = –110402 J/gmol

$C_{P(CO_2)}$ = 50.16 J/gmol ⊣ K

$C_{P(O_2)}$ = 32.02 J/gmol ⊣ K

$C_{P(N_2)}$ = 31.56 J/gmol ⊣ K.

6.27 Chlorinated diphenyl is heated from 310 K to 552 K at the rate of 4,500 kg/h in an indirectly fired heater. The specific heat of the fluid in the temperature range studies is given by

$C_P = 0.28 + 0.35 \times 10^{-3}T$, kcal/kg°C

Calculate the heat to be supplied to the fluid in the heater.

6.28 If $C_P = a + bT$, where C_P is the specific heat at constant pressure, a and b are the constants. T is the absolute temperature. Show that the mean specific heat C_{Pm} from T_1 to T_2 is the average of the heat capacities at T_1 and T_2.

6.29 Calculate the theoretical flame temperature of a gas containing 25% CO and 75% N_2 when burnt with 100% excess air, both air and gas initially being at 298 K. Use the data given.

$C_{P(CO_2)} = 6.34 + 10.14 \times 10^{-3}T - 3.42 \times 10^{-6}T^2$, cal/gmol ⊣ K

$C_{P(O_2)} = 6.12 + 3.17 \times 10^{-3}T - 1.01 \times 10^{-6}T^3$, cal/gmol ⊣ K

$C_{P(N_2)} = 6.46 + 1.39 \times 10^{-3}T - 0.07 \times 10^{-6}T^3$, cal/gmol ⊣ K

ΔH_R° = –67636 cal/gmol.

6.30 Calculate the standard heat of reaction for the following reaction

$CO(g) + H_2O(g) \rightleftharpoons CO_2(g) + H_2(g)$

Data:

Component	$\hat{H}_f$ (kJ/gmol)
CO	–110.6
H_2O	–242.0
CO_2	–394.0
H_2	0

6.31 Calculate the heat of reaction at 780 K and 1 atm for the following reaction

$CO_2 + 4H_2 \rightleftharpoons CH_4 + 2H_2O$

which goes to completion.

Data:

Component	$\hat{H}_f^\circ$ (kJ/gmol)
CO_2	–393.65
H_2O	–241.90
CH_4	–74.89

$C_{P(CO_2)}$ = 50.85 kJ/kmol°C

$C_{P(H_2)}$ = 30.0 kJ/kmol°C

$C_{P(CH_4)}$ = 61.78 kJ/kmol°C

$C_{P(H_2O)}$ = 39.18 kJ/kmol°C

6.32 The heat capacity equation for SiC is expressed as

$$C_P = 8.89 + 2.91 \times 10^{-3}T - \frac{0.28 \times 10^5}{T^2}, \text{ cal/gmol} \dashv \text{ K}$$

for the temperature range of 298 K to 1600 K. What is the mean heat capacity at 1400 K?

6.33 Ethyl alcohol C_2H_5OH is to be burnt with 50% excess air in a furnace. Calculate the maximum temperature that the furnace walls have to withstand assuming that air and ethyl alcohol enters the furnace at 298 K. Use the data given.

Data:

Component	$\hat{H}_f^\circ$ (kJ/kgmol)
C_2H_5OH	–277700
CO_2	–393700
H_2O	–242200

Temperature (K)	$C_{P(N_2)}$ (kJ/kgmol ⊣ K)	$C_{P(O_2)}$ (kJ/kgmol ⊣ K)	$C_{P(H_2O)}$ (kJ/kgmol ⊣ K)	$C_{P(CO_2)}$ (kJ/kgmol ⊣ K)
1000	30.64	32.37	37.08	47.56
1200	31.22	33.02	38.29	49.35
1400	31.77	33.60	39.45	50.82
1600	32.25	34.05	40.56	51.99
1800	32.67	34.40	41.17	53.13

6.34 State Hess's law and check whether the following set of reactions satisfies the law.

1. $Ca(s) + \frac{1}{2}O_2(g) \rightleftarrows CaO(s)$ + 635.77, kJ

2. $C(s) + O_2(g) \rightleftarrows CO_2(g)$ + 393.77, kJ

3. $CaO(s) + CO_2(g) \rightleftarrows CaCO_3(s)$ + 178.15, kJ

6.35 Calculate the theoretical flame temperature of a gas mixture containing 20% CO and 80% N_2, when burnt with 100% excess air. Both air and gas are initially supplied at 298 K. Mean heat capacities in the temperature range considered in J/gmol °C are

$C_{P(CO_2)}$ = 53.2 J/gmol °C

$C_{P(CO)}$ = 29.2 J/gmol °C

$C_{P(O_2)}$ = 34.8 J/gmol °C

$C_{P(N_2)}$ = 33.0 J/gmol °C.

6.36 The standard heat of reaction at 25 °C and 1 atm for the reaction

$$4NH_3 + 5O_2 \rightleftarrows 4NO + 6H_2O$$

is –904.6 kJ/mol. 200 moles of Ammonia and 400 moles of Oxygen is fed into the reactor in which NH_3 is completely consumed. The product stream emerges at 292 °C. Calculate the heat transferred to or from the reactor. Assume that no pressure change takes place. C_P values at 290°C are as follows.

$C_{P(O_2)} = 30.80$ J/mol°C

$C_{P(NO)} = 29 + 8 \times 10^{-3}T + 3 \times 10^{-6}T^2$, J/mol °C

$C_{P(H_2O)} = 30.48$ J/gmol °C

6.37 CH_4 is burnt in a poorly designed combustion chamber. 4000 mol/h of CH_4 is fed to reactor at 298 K along with theoretical required amount of air at 450 K. Calculate the heat transferred from the reactor if 80% of CH_4 is burnt. The mole ratio of CO_2 to CO in the product gas is 10 : 1 and the combustion gases leave the furnace at 650 K. If the ratio of CO_2 : CO is 15 : 1. What is the heat transferred. Use the data given.

Data:

$^\wedge\ H_{(CH_4)} = -69.95$ kJ/mol

$C_{P(CO)} = 6.7$ cal/gmol°C

$C_{P(CO_2)} = 5.3$ cal/gmol°C

$C_{P(air)} = 6.7$ cal/gmol°C

6.38 Calculate the theoretical flame temperature of gas containing 20% CO and 80% N_2 when burnt with 200% excess air. Both air and gas are at 298 K. Heat of formation of data is:

$CO_2 = -391337$ J/gmol

$CO = -110402$ J/gmol

Average specific heat values,

$CO_2 = 50.16$ J/gmol $\dashv$ K

$O_2 = 32.02$ J/gmol $\dashv$ K

$N_2 = 31.56$ J/gmol $\dashv$ K.

6.39 For the hypothetical reaction

$A + B \rightleftharpoons C$

The heat of reaction at 298 K is –1000 cal/mol of C formed. At what temperature does the reaction change from exothermic to endothermic? The specific heat values in cal/mol °C are

$C_{P(A)} = 6.0 + 50 \times 10^{-3}T$ cal/mol °C

$C_{P(B)} = 6.5 + 20 \times 10^{-3}T$ cal/mol °C

$C_{P(C)} = 1.5 + 60 \times 10^{-3}T$ cal/mol °C

6.40 Dry methane and dry air at 298 K and 1 atm are burnt with 120% excess air. The standard heat of reaction is –802 kJ/mole of methane. Determine the final temperature attained by the gaseous products if

(i) The combustion process is adiabatic

(ii) 10% of the heat produced is lost to the surroundings when 1 mole of methane is burnt. Use the data given.

Mean heat capacity data:

$C_{P(O_2)}$ = 31.90 J/gmol K

$C_{P(N_2)}$ = 32.15 J/gmol K

$C_{P(H_2O)}$ = 40.19 J/gmol K

$C_{P(CO_2)}$ = 51.79 J/gmol K.

6.41 Dry methane is burnt with dry air both are initially at 298 K. The flame temperature is 1580 K. If complete combustion is assumed, then how much excess air is to be used?

Data:

ΔH_R° = –801556 J/gmol

$C_{Pm(CO_2)}$ = 51.79 J/gmol K

$C_{Pm(H_2O)}$ = 40.19 J/gmol K

$C_{Pm(N_2)}$ = 32.15 J/gmol K

$C_{Pm(O_2)}$ = 32.40 J/gmol K.

6.42 Determine the adiabatic reaction temperature for the combustion of 10 kg of CH_4 using 25 kgmol of air. The reactants may be assumed to be at 370 K.

Data:

Component	ˆ H_f (kJ/kgmol)
CO_2	–393900
H_2O	–286200
CH_4	–74900

6.43 Calculate the theoretical temperature of a gas containing 18% CO and 82% N_2 when burnt with 60% excess air and gas initially at 298 K.

Data: $C_P = a + bT + cT^2$, kJ/kgmol ⅃ K

Component	*a*	$b \times 10^3$	$c \times 10^6$
CO_2	6.34	10.14	3.15
O_2	6.12	3.17	1.00
N_2	6.46	1.39	0.01

6.44 Calculate the heat of reaction at 298 K for the following reaction.

$Na_2CO_3(s) + Fe_2O_3(s)$ ㄹ Na_2O ⅃ $Fe_2O_3(s) + CO_2(g)$

Data:

Component	ˆ H_f° (kcal/gmol)
$Na_2CO_3(s)$	–269.6
$Fe_2O_3(s)$	–195.3

Na_2O ⊣ $FeO_3(s)$	–337.5
$CO_2(g)$	–94.03

6.45 Find an expression to determine the heat of reaction at unknown temperature

$$A + B \rightleftharpoons C + D$$

for which standard heat of reaction of 298 K is known.

6.46 Find the heat liberated with roasting of 1000 kg of pyrite containing 36% sulfur if the degree of combustion of sulfur is 0.96. The combustion of pyrite is given by the following equation:

$$4FeS_2 + 11O_2 \rightleftharpoons 2Fe_2O_3 + 8SO_2 + Q$$

where

$$Q = 3413.2 \text{ kJ}$$

Pure FeS_2 contains 54.35% sulfur and 45.65% Iron.

6.47 The standard heat of hydrogenation of gaseous propylene (C_3H_6) to propane is –29.6 kcal.The heat of combustion of propane is –530.6 kcal at 298 K. Utilizing the known heat of combustion of CO_2 = – 94.0 kcal and liquid water H_2O = – 68.3 kcal, determine the heat of combustion and the standard heat of formation of propylene.

6.48 Calculate the heat balance of the reactor for producing H_2 by catalytic conversion of CH_4 for 1000 m^3 of Hydrogen. The heat loss to the environment account to 5% of the total. The conversion reaction is

$$CH_4 + H_2O \rightleftharpoons CO + 3H_2, –206200 \text{ kJ}$$

The composition of the starting mixture is $CH_4 : H_2O = 1 : 2$. The initial temperature of the mixture is 370 K and the temperature at the reaction zone is 1170 K.

Data:

Temperature (K)	$C_P(CH_4)$ (kJ/kgmol ⊣ K)	$C_P(H_2O)$ (kJ/kgmol ⊣ K)	$C_P(CO)$ (kJ/kgmol ⊣ K)	$C_P(H_2)$ (kJ/kgmol ⊣ K)
370	36.72	33.29	28.97	29.10
1170	–	38.14	31.36	29.90

6.49 Write the short notes on

(i) Theoretical flame temperature

(ii) Specific heat

(iii) Latent heat of vaporization

(iv) Heat of combustion

6.50 What is meant by ‘Heat of Reaction’? Explain how will you calculate the heat of reaction at a temperature different from standard conditions.

6.51 Calculate the heat of reaction of the following reaction.

$$CO_2 + 4H_2 \rightleftharpoons 2H_2O + CH_4$$

at 490°C using the data given.

Data:

$$\Delta H_R^\circ = –39432 \text{ kcal/kgmol}$$

Temperature (°C)	$\hat{H}(CO_2)$ (kcal/kgmol)	$\hat{H}(H_2)$ (kcal/kgmol)	$\hat{H}(H_2O)$ (kcal/kgmol)	$\hat{H}(CH_4)$ (kcal/kgmol)
25	218	172	200	210
490	5340	3409	4254	5730

6.52 Derive a relation to find the heat of reaction as a function of temperature.

6.53 Calculate the heat of reaction at 1100 K and 1 atm of the reaction

$$\frac{1}{2}H_2 + \frac{1}{2}Cl_2 \rightleftharpoons HCl$$

Data:

$C_{P(H_2)}$ = 29.46 kJ/kgmol · K

$C_{P(Cl_2)}$ = 36.45 kJ/kgmol · K

$C_{P(HCl)}$ = 30.00 kJ/kgmol · K

$\Delta H^\circ_{f(HCl)}$ = –92,300 kJ/kgmol

6.54 Calculate the theoretical flame temperature of carbon monoxide burnt at constant pressure with 150% excess air when the reactants enter at 360 K.

Data:

$\hat{H}_R$ = – 67,600 kcal/kgmol

$C_{P(CO_2)} = 6.34 + 10.14 \times 10^{-3}T - 3.42 \times 10^{-6}T^2$, kcal/kgmol · K

$C_{P(O_2)} = 6.12 + 3.17 \times 10^{-3}T - 1.01 \times 10^{-6}T^2$, kcal/kgmol · K

$C_{P(N_2)} = 6.46 + 1.39 \times 10^{-3}T - 0.07 \times 10^{-6}T^2$, kcal/kgmol · K

6.55 Calculate the theoretical flame temperature for CO burnt at constant pressure with 120% excess air when the reactants enter at 96°C.

Data:

ΔH°_R = – 67,636 cal/mol.

Component	*Mean heat capacity* (C_{Pm}) (cal/gmol°C)
CO	6.98
Air	6.99
CO_2	12.70
O_2	8.30
N_2	7.90

6.56 Chlorinated diphenyl is heated from 45°C to 290°C at the rate of 2000 kg/h in an indirectly fired heater. The specific heat of the fluid in the temperature range studied is given by the equation

$C_P = 0.28 + 0.35 \times 10^{-3}T$, kcal/kg°C

Calculate the heat to be supplied to the fluid in the heater.

6.57 Carbon monoxide at 370 K is burnt under atmospheric condition with dry air at 770 K in 100% excess of that theoretically required. The products of combustion leave the reaction chamber at

1220 K. Assuming complete combustion, calculate the heat evolved in the reaction chamber in kcal per kgmol of carbon monoxide burnt. The heat of combustion of carbon monoxide is 67645 kcal/kgmol. The following average values of specific heat in kcal/kgmol °C may be used.

Temperature (K)	*Component*	*Average specific heat* (kcal/kgmol°C)
370	CO	7.00
770	Air	7.25
1220	CO_2	11.80
1220	Air	7.50

6.58 Calculate the energy required in kcal to heat 5 kgmol of hydrogen from 298 to 410 K. Using the C_p° data given by the equation

$$C_{P(H_2)} = 6.95 - 0.20 \times 10^{-3} T + 0.48 \times 10^{-6} T^2, \text{ kcal/kgmol } \dashv \text{ K}$$

where T is in K.

6.59 Calculate the standard heat of reaction of the following reaction at 298 K.

$$HCl(g) + NH_3(g) \rightleftharpoons NH_4Cl(s)$$

Data:

Component	⌃ H_f° (kcal/kgmol)
HCl(g)	–22063
NH_3(g)	–11040
NH_4Cl(s)	–75380

$$\left\{ \begin{aligned} \text{kgmol of } CH_4 &= \frac{\text{kg of } CH_4}{\text{M.W. of } CH_4} \\ &= \frac{34}{17} = 2 \end{aligned} \right\}$$

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