

**Eastern
Economy
Edition**

Revised Edition

Rate Processes in Metallurgy

A.K. Mohanty



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A.K. Mohanty

Former Principal
National Institute of Technology
Rourkela, Orissa

PHI Learning Private Limited

New Delhi-110001
2009

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A.K. Mohanty

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ISBN-978-81-203-3591-2

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Third Printing (Revised Edition)

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July, 2009

Published by Asoke K. Ghosh, PHI Learning Private Limited, M-97, Connaught Circus, New Delhi-110001 and Printed by Meenakshi Art Printers, Delhi-110006.

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Preface

The initial development of metallurgical processes started on singular or piecemeal basis as it was then assumed that there was little common ground among the different processes or process-steps. However, with the development of science and technology of metal extraction, refining and processing, it was realized that the various processes could be grouped in a series of unit operations or unit processes, each based on some common basic concepts. This realization opened up a new field for the experimental and analytical research in the thermodynamic and kinetic principles of the different unit operations and unit processes employed. These studies led to a significant improvement in both the design of equipment and process-flowsheets as well as in their performance. With the development of computers and automation techniques, the present trend in metallurgical industry is towards building of large-capacity, high-productivity, automated reactors. This objective demands putting more emphasis on the understanding of the basic scientific principles of the different processes at the metallurgical education stage itself. The purpose of this book, therefore, is to provide a firm foundation to students, pursuing undergraduate courses in metallurgical engineering, in the study of the fundamental principles of rate phenomena or kinetic aspects of various metallurgical processes. Although such courses are offered in some institutions in this country and abroad, there are only a few general books dealing with this subject. And these books do not cut across the entire cross-section of the kinetic aspects of metallurgical processes. This thoroughly **revised** edition is aimed at providing a comprehensive treatment of the subject matter.

Chapter 1 highlights the importance of the subject, its subdivision into different topics, and outlines their underlying principles. Chapter 2 deals with the kinetic properties of fluids, the derivation of fluid-dynamic equations and their application to the development of fluid flow instruments as well as to the packed beds, fluidized beds, and high speed flow of compressible fluids. Chapter 3 is on heat transfer, starting with the derivation of conduction equation

and its applications. It analyzes convection and radiation problems with examples pertinent to industrial processes. Chapter 4 presents the mass transport—the major part of which is devoted to diffusion in solids with some simple applications. The other section of this chapter discusses various aspects of convective mass transfer along with the existing theoretical approaches available for interpretation of experimental and industrial data. Chapter 5 explains the techniques of dimensional analysis and illustrates their use for dependent variables involved in metallurgical systems. Dimensional analysis is an important tool for arriving at functional relationships for empirical analysis of any process. As such, this technique leads to several dimensionless relationships of general nature, which become universally applicable to systems of different sizes but similar geometries, and therefore, form the basis of up- or down-scaling of processes. Keeping this in view, the procedure for normalization of differential equations has also been illustrated in this chapter. Chapter 6 deals with an important simplification of the transport problems by means of the boundary layer theory. In Chapter 7, the basic principles of reaction kinetics are discussed and parameters such as “order of a reaction” and “activation energy” are explained. Further, the methods of determination of these parameters are briefly reviewed and their use to arrive at the mechanism of reactions is illustrated. The reaction rate theories are elucidated in this chapter, and their application to the interpretation of some extensively studied metallurgical reactions is also described. Chapter 8 is devoted to the study of simultaneous transfer of heat, mass and momentum for various metallurgical phenomena. It is a new and upcoming field in process engineering and is very helpful in mathematical formulation of systems involving multiple reactions.

Application of the derived relationships in the text material of each chapter is illustrated with the help of suitable solved examples. At the end of each chapter, review questions and problems are included for the student to test his understanding of the subject.

It is hoped that the book in its revised form will be equally useful and appreciated by the readers.

I would gratefully receive constructive criticism of this work and suggestions for its improvement.

A.K. Mohanty

Acknowledgements

This thoroughly revised text is a revised version of an Educational Monograph which was sponsored by the Curriculum Development Centre, University of Roorkee (U.P.). The work was undertaken by me in collaboration with Prof. M.L. Kapoor and Prof. V.N.S. Mathur, both of the Department of Metallurgical Engineering, University of Roorkee, Roorkee. I take this opportunity to thank my earlier collaborators for their untiring efforts in assisting me in this work. The financial assistance received from the University of Roorkee and the encouragement and support from Prof. S.C. Handa, the then coordinator of the QIP Centre, University of Roorkee, are also gratefully acknowledged.

For the writing of this book, a vast amount of literature available on related subjects has been extensively utilized. Reference to these literature has been indicated in the text and also compiled at the end of the book. As it is difficult to acknowledge each one individually, I wish to put on record my gratitude to the authors and publishers of these works.

Finally, I wish to thank the Publishers, PHI Learning, for the meticulous care they took, both during the editorial and production stages of this book.

A.K. Mohanty

Introduction

Metallurgical processes, in general, involve interactions between one or more substances, in the same or different phases, in the form of chemical reactions or physical changes. As a result, one or more components of a phase are transferred to other phases. For example, in the case of sulphur removal in an iron blast furnace, the following reaction occurs:



where the square brackets indicate the metal phase and the parentheses, the slag phase. In other words, Eq. (1.1) states that sulphur dissolved in the metal phase reacts with oxygen ions present in the slag phase to form sulphur ions which pass into the slag phase and oxygen atoms which dissolve in the metal phase. Similarly, during solidification in eutectic alloy systems from a liquid state, the components of the liquid phase get transferred to different solid phases through a physical change.

All such processes involve a number of consecutive steps which may be broadly grouped into the following three categories:

- (i) Transfer of the reactants from the interior or bulk of the phase to the reaction zone or reaction sites.
- (ii) The chemical or physical change at the reaction zone or sites.
- (iii) Transfer of the products from the reaction zone or sites to the interior or bulk of the respective phases.

As an example, for the desulphurization reaction represented by Eq. (1.1), these three steps will include: (i) transfer of sulphur and oxygen ions from the bulk of metal and slag phases respectively to the slag metal interface, (ii) chemical reaction at the interface as described by Eq. (1.1),¹ and (iii) transfer of reaction products, namely sulphur ions and oxygen to bulk slag and metal phases respectively from the reaction zone.

¹ There are a number of other simultaneous reactions which take place at the interface, but these will be considered for detailed treatment in Chapter 7 on reaction kinetics.

Of the three steps mentioned above, the first and the third, which involve the transfer of materials between bulk phases and the reaction zone, form a part of the study of what is called the *transport phenomenon*, whereas the second step is related to *reaction kinetics*. Thus an understanding of the overall kinetics of Eq. (1.1), and other similar chemical reactions or physical changes, will involve a study of the mass transport process and reaction kinetics, such as chemical kinetics or the kinetics of physical changes.

It is also known that chemical reactions and physical changes are accompanied by either absorption or evolution of heat causing temperature gradients in the system. This effect will invariably result in flow of heat through the phases around the reaction zone. Further, temperature gradients will induce convection currents in case there are fluid phases involved in the reaction. In a number of metallurgical processes, forced convection is also introduced in order to enhance the overall reaction rate. Hence, a detailed mathematical analysis of such processes, necessarily involves the study of heat transfer as well as fluid flow. A combined study of the three aspects, namely mass transfer, heat transfer and fluid flow, forms the subject matter of transport phenomena. The study of the rate processes, therefore, includes that of the two broad subjects—transport phenomena and reaction kinetics. The basic principles of these two subjects are briefly discussed in the next two sections.

I.I BASIC PRINCIPLES OF TRANSPORT PHENOMENA

The first principle on which transport processes are based involves striking a balance between momentum, mass and energy. According to this principle, based wholly on experimental facts, all these quantities are conserved during any process. This means that any change in any of them in a system or its part will be equal to the amount exchanged by it with its surroundings. For example, let us consider a shaft furnace in which gaseous reduction of iron ore is going on. Let the reducing gas be hydrogen. According to this principle, the amount of hydrogen let into the system will be equal to the amount of hydrogen leaving the system plus that consumed in reduction and that retained in the system. Similarly, one can strike a balance for energy. In the case of momentum, one has to take ‘force’ into consideration as well since it is equal to the rate of change of momentum. The usefulness of the application of this principle is illustrated with the help of the following example which considers mass balance, also known as material balance, in industrial practice.

EXAMPLE 1.1 A blast furnace produces 2000 tonnes of pig iron per day. The composition of pig iron is as follows: C (4.0%), P (93%), Mn (1.0%), Si (1.7%), S (0.04%) and Fe (rest). The raw materials used and their compositions are as follows:

Iron ore: Fe_2O_3 (88.5%), SiO_2 (3.0%), Al_2O_3 (4%), P_2O_5 (0.5%), H_2O (4.0%)

Flux: CaCO_3 (75%), MgCO_3 (16.8%), SiO_2 (5%), Al_2O_3 (3.2%)

Manganese ore: MnO_2 (52%), Fe_2O_3 (41%), SiO_2 (5%), Al_2O_3 (2%)

Coke: C (72%), SiO_2 (1.5%), Al_2O_3 (8%), FeS (2%), Fe_2O_3 (3%)

The amounts of flux, manganese ore, coke, and quartz (assuming it to contain only silica) used per tonne of pig iron are 350 kg, 60 kg, 850 kg and 80 kg, respectively. Calculate the (a) amount of iron ore used per day assuming that 99.80% of the iron charged goes to pig iron and the rest to slag, (b) weight of the slag phase, (c) volume of air at NTP required per day, and (d) amount of flue gases assuming CO/CO₂ ratio to be 2.

The atomic weights of various elements are: Fe (56), P (31), S (32), Mn (55), Ca (40), C (12), Mg (24), Al (27), Si (28), H (1) and O (16).

Solution The input materials are iron ore, manganese ore, limestone, coke and blast, whereas the materials produced are pig iron, slag and flue gases. In all, there are 11 elements, namely Fe, O, P, S, Mn, Ca, Mg, Al, Si, H, C involved in this process. Thus we require that mass balance for each of these elements be drawn to assess the required quantities. We, therefore, strike these balances as follows:

(i) Mass balance for iron on per day basis yields

$$\begin{aligned} & \left[\left(\frac{88.5}{100} \times W_o \times \frac{112}{160} \right) + \left(2000 \times \frac{60}{1000} \times \frac{41}{100} \times \frac{112}{160} \right) \right. \\ & \quad \left. + 2000 \times \frac{850}{1000} \left(\frac{2}{100} \times \frac{56}{88} + \frac{3}{100} \times \frac{112}{160} \right) \right] \frac{99.8}{100} \\ & = 2000 \times \left[1 - \frac{1}{100} (4 + 0.3 + 1.0 + 1.7 + 0.04) \right] \end{aligned}$$

where W_o is the weight of the iron ore used per day and is found to be 2859 tonnes on solving the above equation. Further, 0.2% of iron from incoming materials goes to slag and forms either FeO or FeS. Thus slag contains 3.73 tonnes of iron.

(ii) Mass balance for phosphorus yields

$$\frac{0.5W_o}{100} \times \frac{62}{142} = \frac{2000 \times 0.3}{100} + W_p$$

(phosphorus in iron ore) (phosphorus in pig iron)

where W_p is the weight of phosphorus in the slag phase and is found to be 0.240 tonne. As the slag phase will contain phosphorus in the form of P_2O_5 (which reacts with other oxides to form phosphates), so the weight of P_2O_5 in slag will be 0.55 tonne.

- ### (iii) Mass balance for sulphur yields

where W_S is the weight of sulphur in slag and is calculated to be 11.56 tonnes. This sulphur is present in slag as sulphide of either calcium, manganese, magnesium or iron.

- (iv) Mass balance for manganese yields

where W_{Mn} is the weight of manganese in slag and is calculated to be 19.45 tonnes. This manganese in slag is present either as MnS or as MnO.

- (v) Calcium balance in the system yields

$$2000 \times \frac{350}{1000} \times \frac{75}{100} \times \frac{40}{100} + W_{\text{Ca}} = W_{\text{Ca}}$$

(calcium from flux)

where W_{Ca} is the weight of calcium in the slag phase and is found to be 210 tonnes. This calcium goes to slag as CaO or CaS which may in turn react with other oxides.

- (vi) Magnesium balance similarly yields

$$2000 \times \frac{350}{1000} \times \frac{16.8}{100} \times \frac{24}{84} = W_{\text{Mg}} \\ (\text{magnesium from flux})$$

where W_{Mg} is the weight of magnesium in the slag phase and is found to be 33.6 tonnes. This goes to slag as oxide or sulphide and where it may react further.

- #### (vii) Aluminium balance yields

where W_{Al} , which is calculated to be 145.67 tonnes, is the amount of aluminium in the slag phase entering it in the form of Al_2O_3 .

- (viii) Silicon balance can be drawn as follows:

$$\begin{aligned}
 & + 2000 \times \frac{60}{1000} \times \frac{5}{100} \times \frac{28}{60} + 2000 \times \frac{850}{1000} \times \frac{1.5}{100} \times \frac{28}{60} \\
 & \quad (\text{silicon from manganese ore}) \qquad \qquad \qquad (\text{silicon from coke}) \\
 & + 2000 \times \frac{80}{1000} \times \frac{28}{60} = 2000 \times \frac{1.7}{100} + W_{\text{Si}} \\
 & \quad (\text{silicon from quartz}) \qquad \qquad \qquad (\text{silicon in pig iron})
 \end{aligned}$$

where W_{Si} is the amount of silicon in slag and is found to be 111.73 tonnes. This silicon goes to slag as SiO_2 where it reacts with other oxides to form silicates.

With this we have calculated the amount of various elements, except oxygen, going to slag. Therefore, we now calculate the amount of slag as well as the oxygen present in it. As we have already indicated, various elements go to slag as oxides or sulphides. Therefore, we will first calculate the total amount as oxide and then correct for sulphide by replacing some oxygen by an equivalent amount of sulphur which is present in slag. Thus,

$$\begin{aligned}
 \text{Weight of slag} &= \left(3.73 \times \frac{72}{56} \right) + \left(0.240 \times \frac{142}{62} \right) + \left(11.56 \right) \\
 &\quad (\text{FeO}) \qquad \qquad \qquad (\text{P}_2\text{O}_5) \qquad \qquad \qquad (\text{Sulphur}) \\
 &+ \left(19.45 \times \frac{71}{55} \right) + \left(210 \times \frac{56}{40} \right) + \left(33.6 \times \frac{40}{24} \right) + \left(145.67 \times \frac{102}{54} \right) \\
 &\quad (\text{M}_n\text{O}) \qquad \qquad \qquad (\text{C}_a\text{O}) \qquad \qquad \qquad (\text{MgO}) \qquad \qquad \qquad (\text{Al}_2\text{O}_3) \\
 &+ \left(111.73 \times \frac{60}{28} \right) - \left(11.56 \times \frac{16}{32} \right) = 900.80 \text{ tonnes} \qquad \qquad \qquad \text{Ans.} \\
 &\quad (\text{SiO}_2) \qquad \qquad \qquad (\text{oxygen equivalent of sulphur})
 \end{aligned}$$

(Note: For every 32 tonnes of S joining the slag, 16 tonnes of O do not form oxides.)

$$\begin{aligned}
 \text{Oxygen in this slag} &= 900.80 - (3.73 + 0.24 + 11.56 + 19.45 + 210 + \\
 &33.6 + 145.67 + 111.73) \\
 &= 364.82 \text{ tonnes}
 \end{aligned}$$

We now come to the balance of those elements which, among others, are present in the gas phase too. These elements are H, C and O.

- (ix) Hydrogen balance: Hydrogen is present in ore as moisture and will go to flue gases in the form of water vapour. Thus

$$2859 \times \frac{4}{100} \times \frac{2}{18} = W_H$$

(hydrogen in ore)

where W_H is the weight of hydrogen present in the form of water vapour in the flue gases and is found to be 12.71 tonnes.

(x) Carbon balance yields

$$\begin{aligned}
 2000 \times \frac{350}{1000} \times \left(\frac{12}{100} \times \frac{75}{100} + \frac{16.8}{100} \times \frac{12}{84} \right) &+ 2000 \times \frac{850}{1000} \times \frac{72}{100} \\
 &\quad \text{(carbon in flux)} \qquad \qquad \qquad \text{(carbon in coke)} \\
 &= 2000 \times \frac{4}{100} + W_C \\
 &\quad \text{(carbon in pig iron)}
 \end{aligned}$$

where W_C is the weight of carbon in flue gases and is found to be 1223.8 tonnes. As flue gas contains CO and CO_2 in the ratio 2:1, $2/3$ weight of this carbon (i.e. 815.867 tonnes) is present as CO and $1/3$ weight, i.e. 407.933 tonnes as CO_2 .

(xi) Finally, we have the oxygen balance as

$$\begin{aligned}
 2859 \left(\frac{88.5}{100} \times \frac{48}{160} + \frac{3}{100} \times \frac{32}{60} + \frac{4}{100} \times \frac{48}{102} \times \frac{0.5}{100} \times \frac{80}{142} + \frac{4}{100} \times \frac{16}{18} \right) \\
 + 2000 \times \frac{350}{1000} \left(\frac{75}{100} \times \frac{48}{100} + \frac{16.8}{100} \times \frac{48}{84} + \frac{5}{100} \times \frac{32}{60} + \frac{3.2}{100} \times \frac{48}{102} \right) \\
 + 2000 \times \frac{60}{1000} \left(\frac{52}{100} \times \frac{32}{87} + \frac{41}{100} \times \frac{48}{160} + \frac{5}{100} \times \frac{32}{60} + \frac{2}{100} \times \frac{48}{102} \right) \\
 &+ \left(2000 \times \frac{80}{1000} \times \frac{32}{60} \right) + W_{OB} \\
 &= \left(12.71 \times \frac{16}{2} + 815.867 \times \frac{16}{12} + 407.933 \times \frac{32}{12} \right) + \frac{364.82}{\text{(oxygen in slag)}} \\
 &\quad \text{(oxygen in flue gases)}
 \end{aligned}$$

where W_{OB} is the weight of oxygen supplied by the blast and is found to be 1197.87 tonnes by solving the above equation. As blast consists of air which contains N_2 (77%) and O_2 (23%) by weight, so this amount of oxygen will be accompanied by 4010.26 tonnes of N_2 . Further, as carbon is burnt to CO at the tuyere level, 1197.87 tonnes of oxygen shall burn 898.40 tonnes of carbon which forms 73.4% of the carbon of coke. To calculate the volume of blast as well as that of flue gases, we substitute the weight of gases by their volume.

(a) For blast volume:

$$\begin{aligned}
 1197.87 \text{ tonnes of oxygen} &= \frac{1172.62}{32} \times 22.4 \times 10^3 \\
 &= 8.38 \times 10^5 \text{ m}^3 \text{ at NTP}
 \end{aligned}$$

$$\begin{aligned}
 4010.26 \text{ tonnes of nitrogen} &= \frac{4010.26}{28} \times 22.4 \times 10^3 \\
 &= 3.21 \times 10^6 \text{ m}^3 \text{ at NTP}
 \end{aligned}$$

Thus,

$$\begin{aligned}\text{Total volume of the blast} &= 8.38 \times 10^5 + 3.21 \times 10^6 \\ &= 4.05 \times 10^6 \text{ m}^3 \text{ at NTP} \quad \text{Ans.}\end{aligned}$$

(b) For flue gases:

$$\begin{aligned}\text{Volume of water vapour} &= \frac{12.71}{2} \times 22.4 \times 10^3 \\ &= 1.42 \times 10^5 \text{ m}^3 \text{ at NTP}\end{aligned}$$

$$\begin{aligned}\text{Volume of CO} &= \frac{815.867}{12} \times 22.4 \times 10^3 \\ &= 1.52 \times 10^6 \text{ m}^3 \text{ at NTP}\end{aligned}$$

$$\text{Volume of CO}_2 = \frac{407.933}{12} \times 22.4 \times 10^3 = 7.61 \times 10^5 \text{ m}^3 \text{ at NTP}$$

$$\text{Volume of blast} = 4.05 \times 10^6 \text{ m}^3 \text{ at NTP}$$

Total volume of flue gases

$$\begin{aligned}&= 1.42 \times 10^5 + 1.52 \times 10^6 + 7.61 \times 10^5 + 4.05 \times 10^6 \\ &= 6.473 \times 10^6 \text{ m}^3 \text{ at NTP} \quad \text{Ans.}\end{aligned}$$

The above example shows how the law of conservation of mass helps in the calculation of requirement or production of certain quantities when the others are known.

Whereas the first principle is concerned with the accounting of basic quantities, there is a second principle devoted to the rate and the direction towards which a process will proceed under a given set of conditions. According to this phenomenological relationship, the rate of flow of a quantity per unit area¹ per unit time is proportional to the gradient or potential. Mathematically, we can express this by the equation

$$J_i \propto \left(-\frac{\partial \psi_i}{\partial X} \right) \quad (1.2)$$

where J_i is the flux or rate of flow of quantity i per unit area per unit time, ψ , its potential, and X denotes the direction of flow. The negative sign in the above equation signifies that the flow will take place from higher to lower potential. For example, for flow of heat q , the potential is temperature, T . Hence, Eq. (1.2) takes the form

$$J_q \propto \left(-\frac{\partial T}{\partial X} \right) \quad (1.3)$$

which states that the rate of flow of heat per unit time per unit area, in the X -direction is proportional to the gradient of temperature in that direction. Obviously, the heat flow will be in the direction of decreasing temperature as indicated by the negative sign. Further, Eq. (1.3) implies that the rate of heat

¹ This area is taken on a plane perpendicular to the direction of flow.

flow in a bar will increase with increase in the temperature difference at its two ends and the direction of flow will be from higher to lower temperature. Similarly, for molecular diffusion of a component in the X -direction, Eq. (1.2) takes the form

$$J_i \propto \left(-\frac{\partial C_i}{\partial X} \right) \quad (1.4)$$

where C_i denotes the concentration of component i . In the following three chapters of the present text, these principles will be applied to derive relations of practical utility of transport phenomena to various processes with simple illustrations.

1.2 BASIC PRINCIPLES OF REACTION KINETICS

As exemplified earlier by the case of sulphur removal in the iron blast furnace, the second step is related to the study of reaction kinetics in the concerned reaction. In this particular case, a chemical reaction is involved, but similar kinetic considerations have to be made even for physical changes such as solidification of liquid metal, phase transformation, etc.

In all such cases, one has to study the factors which affect the rate of the concerned reaction. A reaction generally involves constituents known as *reactants* which take part in the reaction to form the products. The rate of the reaction may refer to the rate of change of the concentrations of either the reactants or the products with respect to time. Thus, the parameter ‘time’ is of fundamental importance in reaction kinetics. The study of reaction rate assumes great significance in metallurgical industries since it is linked with the productivity of any process (which is also a function of time) as well as process analysis and design of units.

The role of reaction kinetics should also be considered in relation to that of reaction thermodynamics since both these disciplines form part of the subject of physical chemistry of reactions. Thermodynamics mainly deals with the most stable or equilibrium state of a reaction. It also considers the condition of feasibility of a reaction. On the other hand, kinetics deals with the situation much before the equilibrium and gives information about the rate at which the equilibrium state is approached. At equilibrium, the overall reaction rate is zero as the rate of the forward reaction equals that of the reverse reaction. Many reactions which are thermodynamically feasible may not take place at any appreciable rate, particularly at lower temperatures. But the rate can be increased by increasing the temperature or in some cases by using a catalyst. However, if a reaction is thermodynamically not feasible, the study of kinetics is meaningless. This explains why thermodynamics is fundamentally of greater significance than kinetics.

For the study of reaction kinetics, the reactions have to be classified first. Although there are various ways of classifying the reactions as will be discussed

in detail in Chapter 7 on reaction kinetics, it may be pertinent to mention here the most important way of classification from a kinetic point of view, based on the nature of phases involved in a reaction. The simplest type of reaction is called a *homogeneous reaction*, and involves only one type of phase in its reactants and products. On the other hand, reactions involving more than one type of phase are known as *heterogeneous reactions* which are in general more complex than the former type. The guiding principle in the study of reaction kinetics of heterogeneous complex reactions is to break up these reactions into simpler steps which may be homogeneous in nature. Kinetic studies of these simpler reaction steps are then carried out based on the principles which will be discussed in detail in Chapter 7 and the rate of each of the steps is obtained. The slowest of these steps would then govern the rate of the overall reaction and is thus known as the *rate controlling step*. Therefore, in order to increase the rate of the overall reaction, the rate of the slowest step has to be accelerated first. The details of these principles with suitable applications will be discussed in Chapter 7.

1.3 UNITS AND DIMENSIONS

In this section, a general feature of all mathematical equations which forms the basis of dimensional analysis is briefly explained. This is discussed in detail in Chapter 5.

Every physical quantity has some dimension by virtue of either its definition or its relationship with other quantities. For example, velocity, which is defined as distance travelled per unit time, will have the dimensions of length per unit time (by virtue of its definition). From this definition it is seen that velocity is expressed in terms of dimensions of length and time. Thus, one can divide physical quantities into two categories. First, those whose units are expressed in terms of certain others. Such quantities are called *derived* quantities. Second, we have those quantities in terms of which all derived quantities can be expressed. Only four quantities, namely mass, length, time and temperature, come under this category. These four quantities are therefore called *basic* quantities. Dimensions of these basic quantities are represented respectively by the symbols M, L, t and T. Thus, velocity will have the dimensions Lt^{-1} and acceleration Lt^{-2} . Determination of dimensions of any physical quantity from its relationship with other quantities is based on the principle of dimensional homogeneity. According to this principle, all terms in an expression, correlating different physical quantities, separated by the signs of equality, addition and subtraction must have the same dimensions. For example, force F is related to mass m and acceleration a by the relation

$$F = ma \quad (1.5)$$

According to the principle of dimensional homogeneity, both right- and left-hand sides of the above equation must have the same dimensions. As acceleration

has the dimensions Lt^{-2} and mass M, force will have the dimensions MLt^{-2} . Thus, Eq. (1.5) has been helpful in determining the dimensions of force in terms of those of the basic quantities. We now consider another example in which the dimensions of a proportionality constant are to be determined. For this purpose, we consider the phenomenon of molecular diffusion expressed by Eq. (1.4), written in the following alternative form by incorporating D_i as the constant of proportionality, where D_i is known as the *diffusion coefficient* of component i

$$J_i = -D_i \frac{\partial C_i}{\partial X} \quad (1.6)$$

The flux J_i is the mass of component i diffusing per unit time per unit area and will thus have the dimensions $ML^{-2}t^{-1}$. The concentration C_i is the mass of component i per unit volume and will thus have the dimensions ML^{-3} . The concentration gradient $\partial C_i / \partial X$ will thus have the dimensions ML^{-4} . According to the principle of dimensional homogeneity, the dimensions of D_i will be equal to the dimensions of J_i divided by dimensions of $\partial C_i / \partial X$, i.e. $ML^{-2}t^{-1}/ML^{-4}$ or L^2t^{-1} . In Table 1.1, the dimensions of some important physical quantities are summarized.

Apart from the dimensions, every physical quantity has a ‘unit’ in which it is measured. For example, mass is measured in terms of either grams, kilograms, pounds, tonnes, etc. and length in terms of metres, feet, miles, etc. Similarly, time can be measured in terms of seconds, minutes, hours, years, etc. and temperature in degrees Celsius, Fahrenheit or Kelvin. Once one assigns the units in which these basic quantities are measured, one can evaluate the ‘derived units’ for other physical quantities from their dimensions. As an example, if length is measured in centimetres and time in seconds, D_i in Eq. (1.6) will be measured in $cm^2 s^{-1}$. Thus by selecting a set of units for length, mass, time and temperature, one can arrive at a system of units in which various physical quantities can be measured or reported. Though these sets may be made in several ways, the systems given in Table 1.2 are commonly employed in scientific work. The most recent system of units accepted internationally is the SI system which is shown in both Tables 1.1 and 1.2. In this book, the SI system of units is used throughout, emphasizing basic concepts, definitions or relationships. Even if data on a certain quantity is reported in some other system, we can convert it to SI unit by taking the help of the dimensions of the quantity and the relationship between the basic quantities in the two systems, as illustrated in Example 1.2. Table 1.2 gives the conversion factors between the SI units and the cgs units which were earlier used in scientific work.

In a number of cases, the units of common physical quantities are given a specific name. For example, dimensions of force are MLt^{-2} . If M is measured in grams, L in centimetres and t in seconds, instead of writing force as $g cm s^{-2}$, one commonly uses the term ‘dyne’. Though these terms are helpful in briefly representing units, yet the importance of dimensions lies in conversion of units from one system to the other.

TABLE 1.1 Dimensions of important physical quantity

	<i>Relation with other basic quantities</i>	<i>Dimensions</i>	<i>SI units</i>
ity	—	M	kilogram (kg)
ture	—	L	metre (m)
s	—	t	second (s)
—	—	T	kelvin (K)
gravity	(length) ²	L^2	m^2
—	(length) ³	L^3	m^3
—	mass/volume	$ML^{-3}t^0$ or ML^{-3}	$kg\ m^{-3}$
ratio of density of a substance to that of water	—	$M^0L^0t^0$	—
tion	distance/time	M^0Lt^{-1}	$m\ s^{-1}$
um	velocity/time	M^0Lt^{-2}	$m\ s^{-2}$
nergy	mass × velocity	MLt^{-1}	$kg\ m\ s^{-1}$
, stress	mass × acceleration	MLt^{-2}	newton (N) or kg
of elasticity	force × distance	ML^2t^{-2}	joule (J)
of inertia	work/time	ML^2t^{-3}	$J\ s^{-1}$ (W)
—	force/area	$ML^{-1}t^{-2}$	pascal (Pa) or N m ⁻²
—	stress/strain	$ML^{-1}t^{-2}$	$kg\ m^{-1}\ s^{-2}$
—	mass × (distance) ²	ML^2t^0	$kg\ m^2$
—	force × distance	ML^2t^{-2}	$kg\ m^2\ s^{-2}$
—	force/length	Mt^{-2} or ML^0t^{-2}	newton/metre (N m ⁻¹)
— (dynamic)	shear stress/velocity gradient	$ML^{-1}t^{-1}$	pascal-second (Pa s) or $kg\ m^{-1}\ s^{-1} = 10$

TABLE 1.1 Dimensions of important physical quantity (*Contd.*)

<i>ity</i>	<i>Relation with other basic quantities</i>	<i>Dimensions</i>	<i>SI units</i>
ic viscosity	dynamic viscosity/density	$L^2 t^{-1}$ or $M^0 L^2 t^{-1}$	$m^2 s^{-1}$
energy, heat	—	Q	joule (or J)
capacity (specific heat)	heat/mass/temperature change	—	$J kg^{-1} K^{-1}$
heat capacity	heat/mole/temperature change	—	$J mol^{-1} K^{-1}$
per unit mass	heat/temperature/mass	$L^2 t^{-2} T^{-1}$	$J kg^{-1} K^{-1}$
cal equivalent of heat	mechanical work done/heat produced	$L^2 t^{-2} T^{-1}$	$J kg^{-1} K^{-1}$
conductivity	heat/area/temperature gradient/time	$QL^{-1} t^{-1} T^{-1}$	$J m^{-1} s^{-1} K^{-1}$ or $W m^{-1} K^{-1}$
ty	mass/area/concentration gradient/time	$L^2 t^{-1}$	$m^2 s^{-1}$
nsfer coefficient	heat/area/time/temperature gradient	$QL^{-2} t^{-1} T^{-1}$	$J m^{-2} s^{-1} K^{-1}$ or $W m^{-2} K^{-1}$
nsfer coefficient	mass/area/time/concentration gradient	$L t^{-1}$	$m s^{-1}$

TABLE 1.2 Systems of units and conversion factors

<i>s symbol</i>	<i>CGS unit</i>	<i>SI unit</i>	<i>Conversion</i>
	gram (g)	kilogram (kg)	$1 \text{ kg} = 10^3 \text{ g}$
	centimetre (cm)	metre (m)	$1 \text{ m} = 10^2 \text{ cm}$
	second (s)	second (s)	—
	sq. cm (cm^2)	sq. m (m^2)	$1 \text{ sq. m} = 10^4 \text{ sq. cm}$
	cubic centimetre (cc)	cubic metre (m^3)	$1 \text{ m}^3 = 10^6 \text{ cc}$
	g/cc	kg m^{-3}	$1 \text{ kg m}^{-3} = 10^{-3} \text{ g/cc}$
<i>f</i>	cm s^{-1}	m s^{-1}	$1 \text{ m s}^{-1} = 10^2 \text{ cm s}^{-1}$
<i>tia, I</i>	cm s^{-2}	m s^{-2}	$1 \text{ m s}^{-2} = 10^2 \text{ cm s}^{-2}$
	g cm^2	kg m^2	$1 \text{ kg m}^2 = 10^7 \text{ g cm}^2$
	g cm s^{-1}	kg m s^{-1}	$1 \text{ kg m s}^{-1} = 10^5 \text{ g cm s}^{-1}$
<i>E or W</i>	dyne (dyn)	newton (N)	$1 \text{ N} = 10^5 \text{ dyn}$
	erg	joule (J)	$1 \text{ J} = 10^7 \text{ erg}$
	erg s^{-1}	watt (W)	$1 \text{ W} = 10^7 \text{ erg s}^{-1}$
<i>ss, P or p</i>	dyne/cm ²	pascal (Pa)	$1 \text{ Pa} = 1 \text{ N m}^{-2} = 1 \text{ dyne/cm}^2$
	atmospheres (atm)		$1 \text{ atm} = 1.013 \times 10^5 \text{ N m}^{-2}$
	bar		$1 \text{ bar} = 10^5 \text{ N m}^{-2}$
<i>γ</i> dynamic viscosity)	dyne/cm or erg/cm^2	newton/metre (N m^{-1}) (or J m^{-2})	$1 \text{ N m}^{-1} = 10^3 \text{ dyne/cm}$
<i>Q</i>	poise	$\text{kg m}^{-1} \text{ s}^{-1}$	$1 \text{ kg m}^{-1} \text{ s}^{-1} = 10 \text{ poise}$
<i>cient, D</i>	thermo-chemical calorie (cal)	joule	$1 \text{ cal} = 4.184 \text{ J}$
<i>osity</i>	$\text{cm}^2 \text{ s}^{-1}$	$\text{m}^2 \text{ s}^{-1}$	$1 \text{ m}^2 \text{ s}^{-1} = 10^4 \text{ cm}^2 \text{ s}^{-1}$
<i>oefficient, K_M</i>	$\text{cm}^2 \text{ s}^{-1}$ (stokes)	$\text{m}^2 \text{ s}^{-1}$	$1 \text{ stoke} = 10^{-4} \text{ m}^2 \text{ s}^{-1}$
<i>C</i>	cm s^{-1}	m s^{-1}	$1 \text{ cm s}^{-1} = 10^{-2} \text{ m s}^{-1}$
	mole/litre	mole/cu. m	$1 \text{ mole/litre} = 10^3 \text{ mole/m}^3$

EXAMPLE 1.2 Find the conversion factor for pound (lbf) to newton (N).

Solution One pound is the force required for movement of 453.6 g (one pound) in the FPS system at an acceleration of 32.2 ft s^{-2} .

$$\begin{aligned}\text{Thus, one pound} &= \left(\frac{453.6}{1000}\right) \left(\frac{32.2 \times 12 \times 2.54}{100}\right) \text{ newton} \\ &= 4.45 \text{ Newton}\end{aligned}$$

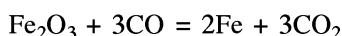
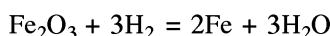
Various names commonly employed in the SI system, are also given in Table 1.2 along with the dimensions. Sometimes the magnitudes of different quantities are either too small or too large for representing them in a process. In such cases, certain prefixes are used, which are given in Table 1.3.

TABLE 1.3 Decimals, multiples and submultiples of units

Multiples			Submultiples		
Prefix	Symbol	Multiple	Prefix	Symbol	Submultiple
tera	T	10^{12}	unit	—	1
giga	G	10^9	deci	d	10^{-1}
mega	M	10^6	centi	c	10^{-2}
kilo	k	10^3	milli	m	10^{-3}
hecto	h	10^2	micro	μ	10^{-6}
deca	da	10	nano	n	10^{-9}
unit	—	1	pico	p	10^{-12}

1.4 IMPORTANCE OF THE SUBJECT

In the early stages of the development of the science of metallurgy, the results of the study of different metallurgical processes were interpreted qualitatively in terms of effects of different process variables. With improved understanding of these processes, different research workers started investigating the mechanism and thermodynamics of these processes and tried to explain the end results of the processes studied in terms of these two fundamental considerations. Such explanations could only account for time-independent functions. However, for the complete conceptual development of these processes, one has also to study their progress as a function of time. For this purpose, one needs knowledge of both transport phenomena and reaction kinetics. For example, the gaseous reduction of haematite in the iron blast furnace takes place according to the following overall reactions:



The conditions under which the above reactions will proceed in the forward direction can be assessed by means of thermodynamics. But under given

conditions of temperature and gas flow rate, how fast these reactions will proceed can only be analysed with the help of transport phenomena and reaction kinetics, and it is this analysis which is necessary for the quantitative evaluation of the progress of a reaction over time.

A systematic study of this subject, therefore, forms a prerequisite for mathematical modelling of metallurgical processes. Many of these processes are complicated and their experimental studies are not only difficult, time-consuming and costly but also hazardous. Therefore, application of mathematical modelling techniques is required for the optimization of existing processes and development of new techniques.

Another important area in which these studies will be helpful include simulation of metallurgical processes. Various ‘similarity criteria’ are used for ‘scaling-up’ of the laboratory bench scale experimentation or pilot plant scale results to semi-commercial or commercial plant data for use in the design of the process—flowsheets, equipment or plants. These make extensive use of a large number of dimensionless parameters related to mass, heat or momentum transfer as also data on chemical systems. A study of the rate processes of metallurgical systems will help in obtaining these parameters, and this will ultimately contribute to simulation studies.

REVIEW QUESTIONS

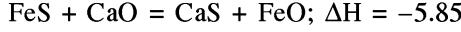
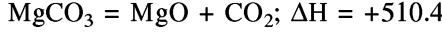
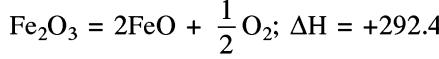
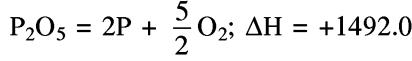
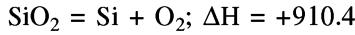
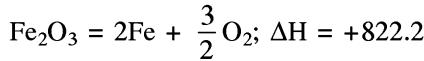
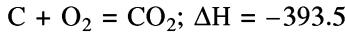
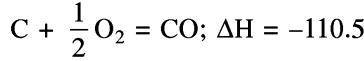
1. With the help of suitable examples, explain the basic principles of transport phenomena.
2. Explain the terms ‘fundamental’ and ‘derived’ quantities. Give typical examples.
3. Explain and differentiate between the terms ‘units’ and ‘dimensions’. Give typical examples of these in the different systems used.
4. Discuss the subject matter and importance of transport phenomena and reaction kinetics.
5. Illustrate how different aspects of transport phenomena and reaction kinetics play their role in mathematical analysis of gas-solid reactions.

PROBLEMS

1. An iron ore, containing Fe_2O_3 (88%), SiO_2 (3.5%), Al_2O_3 (4%), P_2O_5 (0.6%) and the rest moisture, is smelted in a blast furnace to produce pig iron containing C (4.1%), Si (1.75%), P (0.36%), Mn (1.1%) and S (0.4%). 800 kg of coke, having C (72.5%), SiO_2 (15%), Al_2O_3 (7.8%) FeS (2.1%) and rest Fe_2O_3 , is consumed for production of one tonne of pig iron.

For per tonne of pig iron produced, calculate

- (i) the amount of iron ore required (assume all Fe joins pig iron),
 - (ii) the amount of limestone and quartz (pure SiO_2) required for maintaining the CaO/SiO_2 ratio at 1.2 and Al_2O_3 content of slag at 18%; assume limestone to contain CaCO_3 (76%), MgCO_3 (16.5%), Al_2O_3 (3%) and the rest silica,
 - (iii) the amount of slag produced, assuming that 50 kg of manganese ore having MnO_2 (55%), Fe_2O_3 (40%), SiO_2 (4%) and Al_2O_3 (1%) is used per tonne of pig iron produced, and
 - (iv) the volume of air required assuming CO/CO_2 ratio of flue gases to be 1.8.
2. Draw a heat-balance sheet for Problem 1, using the following data:
- (a) Standard heats of formation in kJ/mol for different compounds are:
 $\text{SiO}_2 = -910.4$; $\text{MnO} = -384.9$, $\text{FeO} = -264.4$; $\text{Fe}_2\text{O}_3 = -821.3$;
 $\text{CO} = -118.4$; $\text{CO}_2 = -393.5$; $\text{P}_2\text{O}_5 = -1492.0$; $\text{CaCO}_3 = -1207.1$;
 $\text{CaO} = -634.3$; $\text{MgCO}_3 = -1111.7$; $\text{MgO} = -601.2$; $\text{FeS} = -100.4$;
 $\text{CaS} = -476.1$
Assume sulphur in slag to be present as CaS .
 - (b) Heats of reaction in kJ:



- (c) Molar specific heats at constant pressure, C_p , for different constituents, in joules per mole are as follows:

$$C_p, \text{Ca} = 28.4 + 4.10T - 0.46T^{-2}$$

$$C_p, \text{CO}_2 = 44.14 + 9.03T - 8.53T^{-2}$$

$$C_p, \text{H}_2 = 75.43$$

$$C_p, \text{N}_2 = 27.86 + 4.26T$$

$$C_p, \text{O}_2 = 29.95 + 4.18T - 1.67T^{-2}$$

- (d) Temperature of different phases:
 Blast preheat temperature = 600°C,
 Exit gas temperature = 210°C
 Pig iron and slag temperature = 1600°C
 Rise in temperature of cooling water = 50°C
- (e) Cooling water used = 2000 litres per tonne of pig iron
- (f) Sensible heats in pig iron and slag are respectively, 1255 and 2092 kJ/kg. Neglect all other heat effects of dissolution of C, S, Mn, P and Si in iron.
- 3.** A copper concentrate analyses as follows:
- Cu (28%), S (20%), Fe (35%) and SiO_2 (rest)
- On matte smelting this concentrate, 8% S is lost by volatilization. On converting the matte produced in this operation, the converter slag analyses as Cu (3.5%), Fe (as FeO) (48.0%) and SiO_2 (25%).
- The converter slag is returned to the matte smelting furnace and contains all the iron present in matte. Pure quartz (SiO_2 = 100%) and pure limestone (CaCO_3 = 100%) are used as fluxes in the smelting process. The smelting furnace slag contains SiO_2 , CaO and FeO in the ratio $\text{SiO}_2/\text{CaO}/\text{FeO} = 2:1:2$.
- Assuming no loss of copper in smelting furnace slag and also that other oxides do not interfere with the smelting process, calculate:
- the weight and grade of matte (% Cu content) per tonne of concentrate used,
 - the weight of converter slag returned to the smelting furnace per 1000 kg of concentrate, and
 - the amount of fluxes needed per tonne of concentrate to produce the required smelting slag.
- 4.** A sample of pig iron has the following composition:

C (4.2%), Si (1.2%), Mn (1.5%), P (0.35%), and S (0.045%)

It is converted into steel in an LD converter. The blown metal analysis reveals the following composition:

Si (0.01%), Mn (0.20%), C (0.05%), P (0.02%)

If 10% of iron ore (pure haematite) is used for cooling, calculate the amount of oxygen required for refining one tonne of pig iron at NTP, assuming that 90% of carbon burnt escapes as CO in the gases and 2% of iron joins slag as FeO.

CHAPTER 2

Flow of Fluids

The study of the flow of fluids constitutes the most significant part of the analytical study of transport phenomena in metallurgical systems, particularly in reactors. This is because such flow affects, to a great extent, the overall kinetics of the reactions through its effects on the heat and mass transport steps. The main aim of the study of the flow of fluids in metallurgical processes is either to obtain the velocity or pressure profiles inside metallurgical reactors or liquid metal flow systems as a function of time or to find the pressure drop across a reactor for a given mass or volume flow rate. Mathematically, these aims can be expressed in two ways:

$$(i) \bar{v} = \bar{v}(x, y, z, t) \quad (2.1)$$

$$P = P(x, y, z, t) \quad (2.2)$$

$$(ii) Q = Q(P) \quad (2.3)$$

where the symbol \bar{v} represents the velocity vector having three components v_x , v_y and v_z in the rectangular coordinate system, P denotes the pressure and Q the mass or volume flow rate. Equations (2.1) and (2.2) which correlate the components of velocity and pressure, respectively as functions of position and time, require for their solution four simultaneous equations as these involve four dependent variables. These four relations are obtained by drawing differential mass and momentum balances as will be shown in Section 2.3. For the estimation of the pressure drop across a reactor for predetermined flow rates, one takes the help of expressions for overall mass, momentum and mechanical energy balances which will be derived in Section 2.4. However, before considering these balances, we require a good knowledge of the nature of fluid flow, and this is discussed in the next section.

2.1 NATURE OF FLUID FLOW

Though the nature of fluid flow has been the subject of several theoretical and experimental studies by many eminent workers in the areas of applied

mathematics and hydraulics, the most illustrative experiment, which is considered classical in this context, was performed by Osborne Reynolds in 1883. He used transparent pipes through which water was allowed to flow with different velocities, and a stream of coloured dye was injected parallel to the path of water flow. At low water velocities, it was observed that the dye flowed in parallel straight lines. However, when the velocity of water increased, at some stage the flow became erratic and the entire mass of water became coloured with the dye.

The first type of flow above is called the *laminar* or *streamline* flow. In this case, the fluid flows, on a macroscopic scale, due to the movement of fine laminations relative to adjacent fluid layers in a parallel manner and fluid particles in each layer move in regular paths known as streamlines. At higher velocities, the flow is known as *turbulent* flow. Here, the fluid particles, move in irregular manner breaking down the streamlines and get intimately mixed. More details of these two types of fluid flow will be discussed later. It is, however, necessary to discuss some more experimental work carried out by Reynolds which has helped to form the basis of the classification of the flow of fluids into the above two types.

Reynolds studied the flow of fluids of different physical properties, namely the density and the viscosity, at different velocities through smooth horizontal pipes of different diameters. Based on these studies, he concluded that, whether a fluid flow was laminar or turbulent would depend on the magnitude of the parameter $\rho v d / \mu$, where ρ and μ are the density and viscosity of the fluid respectively, v its average velocity and d the diameter of the pipe. The actual magnitude for the demarcation between the two types of flow was found to depend on the type of channel used for the flow and the roughness of the channel surface.

In the case of smooth pipes, the flow was found to be laminar when $\rho v d / \mu$ was less than 2100, and turbulent for values greater than 2100. For other channels such as packed beds, different values are applicable.

The parameter $\rho v d / \mu$, which is dimensionless with a consistent set of units for individual terms, is known as the Reynolds number and is denoted by N_{Re} . Thus,

$$N_{\text{Re}} = \frac{\rho v d}{\mu} \quad (2.4)$$

As the above two types of fluid flow will be considered hereafter in different contexts, it is necessary to point out some more of their characteristics. In the case of laminar flow, the velocity of the fluid at a given position does not fluctuate with time but remains constant. But in the case of turbulent flow, the streamlines are broken, causing the flow of a macroscopic amount of fluid across the direction of flow. Hence, the velocity of the fluid will fluctuate with time at a given position. There would therefore be two variables for each component of velocity, namely the average velocity and a variable describing the

fluctuation of velocity with time, which is irregular in nature. A typical velocity profile at a fixed position for turbulent flow in the x -direction is shown in Fig. 2.1.

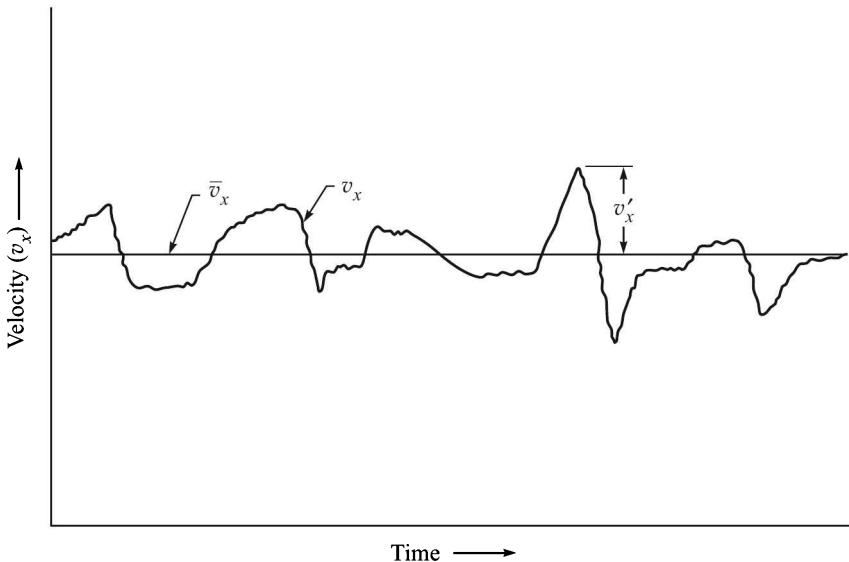


Fig. 2.1 Velocity profile at a fixed point for turbulent flow in x -direction.

The time average velocity component along the x -direction, \bar{v}_x , is given by the equation

$$\bar{v}_x = \frac{1}{t_0} \int_0^{t_0} v_x dt \quad (2.5)$$

where t_0 is the time for which the average value is considered. This average velocity is also sometimes called the *temporal mean velocity*. Since v_x is an irregular function of time, one can determine the value of \bar{v}_x by graphical integration of the v_x vs. time profile. The fluctuating component, v_x' , at any instant in the x -direction (Fig. 2.1) is defined by the equation

$$v_x' = v_x - \bar{v}_x \quad (2.6)$$

Similar terms like v_y , \bar{v}_y , v_y' and v_z , \bar{v}_z and v_z' can be obtained for y -and z -directions, respectively. Some more details about turbulent flow will be discussed in a later section.

However, before considering other details of fluid flow, it is necessary to discuss a basic physical property of fluids—viscosity. This is done in the Section 2.2.

2.2 VISCOSITY

Consider a fluid in laminar flow. The adjacent layers of this fluid will move with different velocities. The layer nearer to the solid surface will have the lowest or zero velocity, whereas, as one moves away from it, the velocity would progressively increase. This difference in velocity causes an exertion of shearing force by one layer on the other adjacent to it. The magnitude of this force is directly proportional to the area of contact between the two layers and the velocity difference between the two and inversely proportional to the distance between them. This statement is mathematically formulated as follows:

$$\tau_{yx} = -\mu \frac{\partial v_x}{\partial y} \quad (2.7)$$

where τ_{yx} is the shearing force per unit area, $\partial v_x / \partial y$ is the gradient of x -component of velocity in the y -direction, and μ is the constant of proportionality called the *viscosity*. The negative sign in the above equation signifies that the shearing force is such that it acts in the direction opposite to that of flow on the layer having higher velocity. This equation can be derived, as will be shown in a subsequent section, on the basis of momentum transfer. The relation expressed by Eq. (2.7) is called Newton's law of viscosity. All those fluids for which μ is independent of v and can be taken as constant, are called *Newtonian fluids*. For a number of fluids, viscosity varies with shearing stress. These fluids are termed *non-Newtonian fluids* and are classified as follows:

- (i) Ideal fluids or Bingham plastics are those which follow the relationship

$$\tau_{yx} = -\mu \frac{\partial v_x}{\partial y} + \tau_0$$

where τ_0 is a constant and signifies the threshold stress for the start of viscous flow.

- (ii) Dilatant fluids are those whose viscosity increases with increase in shear stress.
- (iii) Pseudoplastics are materials whose viscosity decreases with increase in shear stress. Real plastics show a behaviour in between those of ideal fluids and pseudoplastics.
- (iv) Thixotropic fluids are those whose viscosity depends upon the shearing stress.

In the field of metallurgy, one is concerned mainly with Newtonian fluids as all gaseous, metallic and slag systems follow Newton's law under normal process conditions. We can also formulate equations for viscosity similar to Eq. (2.7) for flow in other directions, viz.

$$\tau_{zy} = -\mu \frac{\partial v_y}{\partial z} \quad (2.8)$$

$$\tau_{xz} = -\mu \frac{\partial v_z}{\partial x} \quad (2.9)$$

If the viscosity of a fluid is independent of the direction of flow, it is known as an *isotropic fluid*. It will be seen later that viscosity plays an important role in determining the velocity profile of a flowing fluid. It is, therefore, essential to know about the viscosity of fluids of common metallurgical interest. In the following part of this section, we briefly discuss about the viscosity of gases, metallic melts and slags.

2.2.1 Viscosity of Gases

Viscosities of gases have been studied both experimentally and theoretically. The simplest theoretical approach for the calculation of viscosity at low densities is based on kinetic theory which leads to the relation

$$\mu = \frac{2}{3d^2} \left(\frac{mk_B T}{\pi^3} \right)^{1/2} \quad (2.10)$$

where d and m are the diameter and mass of the molecules, respectively, k_B is Boltzmann's constant and T is the absolute temperature. This expression was modified by Chapman-Enskog to take into account the interaction among particles. They obtained the relation

$$\mu = 2.6693 \times 10^{-5} (MT)^{1/2} / \sigma^2 \Omega_\mu \quad (2.11)$$

where M is the molecular weight of the gas, σ the characteristic diameter of gas particles and Ω_μ , a function called dimensionless temperature. Values of the constants σ and Ω_μ for a gas are given later in Tables 4.1 and 4.2, respectively.

The viscosity of a gas at a desired temperature and pressure can also be calculated from its critical data and by making use of standard graphs (Figs. 2.2 and 2.3) which give the correlation between reduced viscosity μ_r , reduced temperature T_r and reduced pressure P_r . μ_c , the critical viscosity of a gas, is empirically given as

$$\mu_c = 7.70 M^{1/2} P_c^{2/3} T_c^{-1/6} \quad (2.12)$$

where μ_c is in micropoise, P_c the critical pressure in atmospheres and T_c the critical temperature in kelvin. The viscosity of the gas is then given by the equation

$$\mu = \mu_r \mu_c \quad (2.13)$$

EXAMPLE 2.1 Calculate the viscosity of nitrogen at 27°C and 100 atm pressure. The molecular weight of the gas is 28 and its critical temperature and pressure are 126 K and 34 atm respectively.

Solution The critical viscosity μ_c of the gas according to Eq. (2.12) is given as

$$\begin{aligned} \mu_c &= 7.7 \times (28)^{1/2} \times (34)^{2/3} \times (126)^{-1/6} \\ &= 191.2 \text{ micropoise} \end{aligned}$$

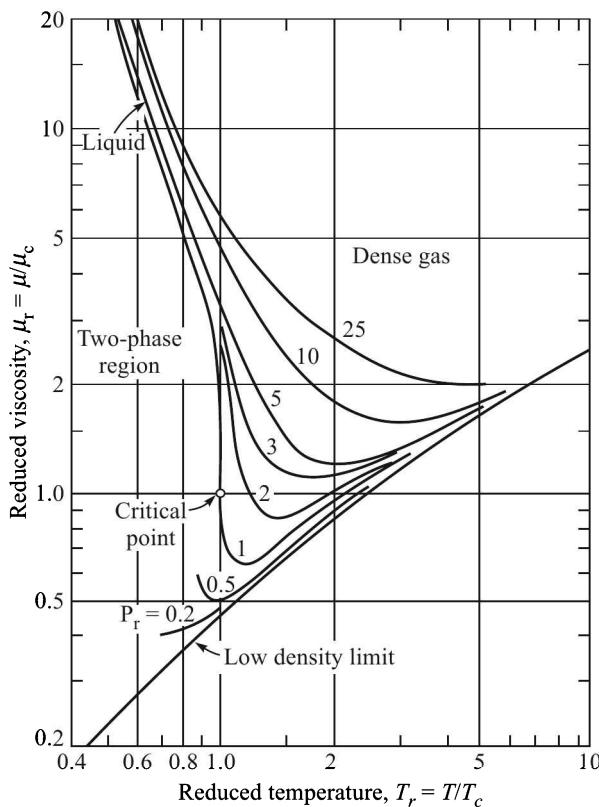


Fig. 2.2 Relationship between reduced viscosity and reduced temperature at different reduced pressures for gases.

$$\begin{aligned}\text{Reduced temperature } T_r &= \frac{273 + 27}{126} \\ &= 2.38\end{aligned}$$

$$\text{Reduced pressure } P_r = \frac{100}{34} = 2.94$$

From Fig. 2.2, we get $\mu_r = 1.1$.

$$\begin{aligned}\text{Hence, from Eq. (2.13), we have } \mu &= \mu_r \mu_c = 1.1 \times 191.2 \\ &= 210 \text{ micropoise} \quad \text{Ans.}\end{aligned}$$

In the case of gas mixtures, we make use of values of average critical pressure, temperature and viscosity calculated, using additive-law as follows, and subsequently Figs. 2.2 and 2.3 are used to estimate viscosity at the desired temperature and pressure.

$$\begin{aligned}P_c &= \sum (N_i P_{ci}), \quad T_c = \sum (N_i T_{ci}) \\ \mu_c &= \sum (N_i \mu_{ci})\end{aligned}$$

where N_i refers to the mole fraction of component i .

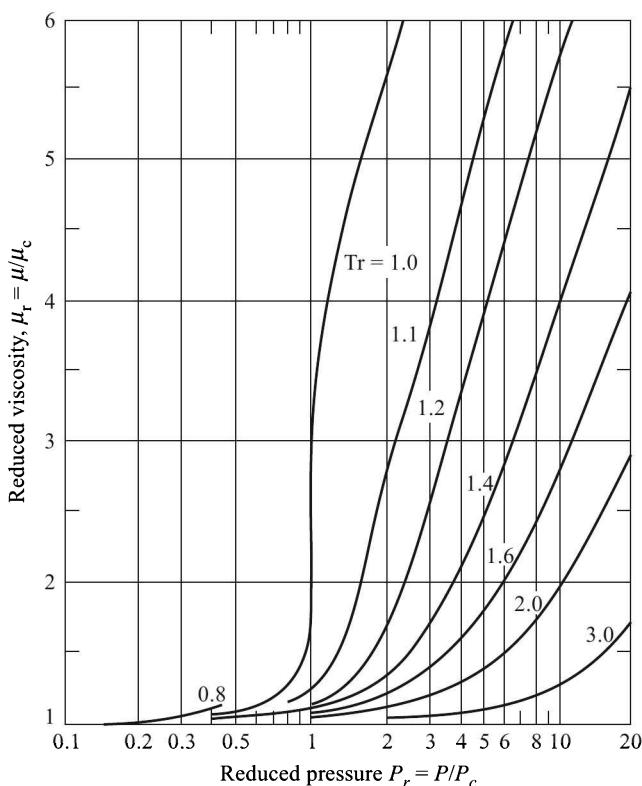


Fig. 2.3 Relationship between reduced viscosity and reduced pressure at different reduced temperatures for gases.

Viscosity of a gas can also be found out at one atmosphere pressure and at the desired temperature with the help of nomograms shown in Fig. 2.4. In this figure, each gas has a pivot point as shown in the middle of the figure. The temperature is plotted on the left vertical axis and viscosity on the right. To find the viscosity at a desired temperature, one has to join the temperature point with the pivot point for the gas and extend it to the viscosity scale and thus obtain the viscosity. For example, viscosity of air at 50°C is about 0.019 cP as seen from Fig. 2.4.

2.2.2 Viscosity of Liquid Metals and Alloys

The viscosity of liquid metals and alloys, like that of any other liquid, can be related to their structure. However, since there is no generalized principle which is applicable to explain the structure of all metals and alloys, a generalized theory on the viscosity of all liquid metals and alloys could not be developed. The most satisfactory theory has been put forward by Chapman,¹ who has proposed a model for the viscosity of pure liquid metals on the basis of the presence of

¹ Thomas W. Chapman, A.I. Ch. E. Journal, 12: 2, 395 (1966).

spherical atoms and has suggested that the potential difference between neighbouring atoms would be a function of the distance $\phi(r)$ between the atoms (r) and an energy parameter (ε), characteristic of the metal given by the relation

$$\phi(r) = 4\varepsilon \left[\left(\frac{\delta}{r} \right)^{12} - \left(\frac{\delta}{r} \right)^6 \right] \quad (2.14)$$

where δ is the interatomic distance in the close-packed metal crystal at 0 K in Å.

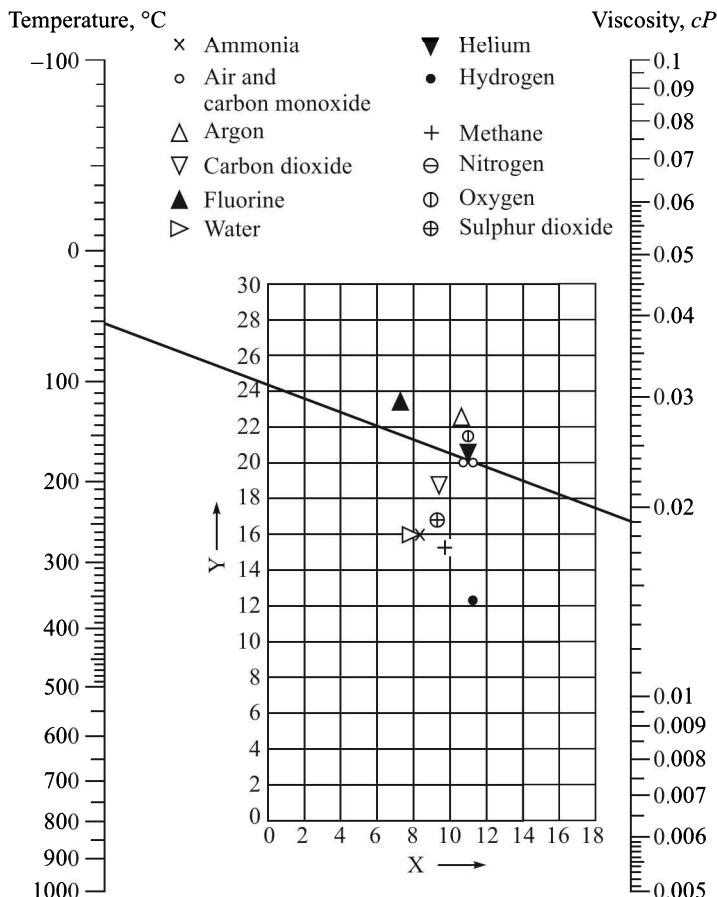


Fig. 2.4 Graphical representation of viscosity of gases as a function of temperature.

Chapman then assumed that all liquid metals obey the same function $\phi(r)$ and that all of them have a reduced viscosity μ^* , which is a function of a reduced temperature T^* and a reduced volume V^* , where the functional relationship is given by

$$\mu^*(V^*)^2 = f(T^*) \quad (2.15)$$

and μ^* , V^* and T^* are given by

$$\mu^* = \frac{\mu\delta^2 N_0}{\sqrt{MRT}} \quad (2.16)$$

$$T^* = \frac{k_B T}{\varepsilon} \quad (2.17)$$

$$V^* = \frac{1}{n\delta^3} \quad (2.18)$$

where

μ = viscosity of the liquid metal, poise

δ = interatomic distance, Å

N_0 = Avogadro's number

M = atomic weight

R = universal gas constant, erg mol⁻¹ K⁻¹

T = absolute temperature, K

k_B = Boltzmann constant

ε = energy parameter characteristic of specific metal

η = number of atoms per unit volume

Of all the above parameters, the energy parameter ε is the most difficult to obtain. Ling¹ had determined these parameters for sodium and potassium from experimental X-ray scattering curves. Chapman used these data to plot a graph between $\mu^*(V^*)^2$ and $1/T^*$ for sodium and potassium for different temperatures and found that all the data fall on a smooth curve as shown in Fig. 2.5.

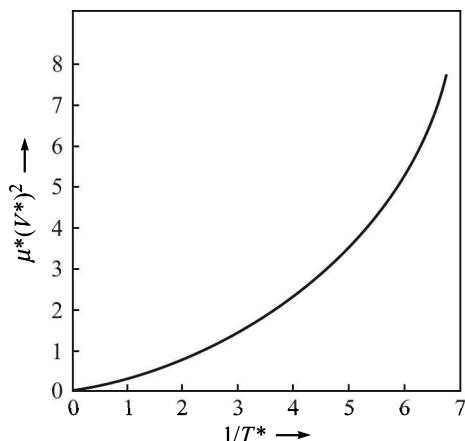


Fig. 2.5 Relationship between function $\mu^*(V^*)^2$ and $1/T^*$ for liquid sodium and potassium.

¹ R.C. Ling, *J. Chern. Phys.*, **25**: 609 (1956).

Chapman further assumed that the viscosities of all the available liquid metals obey the same functional relationship and that their data can be fitted into the empirical curve in Fig. 2.5 by adjusting the value of ϵ for different metals. This way the values of ϵ/k_B for all the metals can be obtained. As per the suggestion of Lennard-Jones and Devonshire,¹ Chapman correlated the ϵ/k_B values with the melting points of the metals and found that for all metals, an excellent relationship of the form

$$\frac{\epsilon}{k_B} = 5.20T_m \quad (2.19)$$

exists, where T_m is the melting point of the metals in K. Chapman's theory is considered to be the most satisfactory theory on the viscosity of liquid metals.

Another relationship between the viscosities and the melting points of the metals has been proposed by Andrade,² which is given by the equation

$$\mu_m = C(T_m M)^{1/2} V^{-2/3} \quad (2.20)$$

where

μ_m = viscosity, poise

T_m = melting point, K

M = atomic weight

V = atomic volume, cm³

C = a constant = 6.12×10^{-4}

This relationship is based on the assumption that the oscillation of the atoms is responsible for the transfer of momentum from one layer of a fluid to another which is subjected to shear stress. Reasonably good agreement was observed by Andrade between the experimental and the calculated values for many liquid metals around their melting points.

Viscosity of all metals is found to decrease with increase in temperature, and the effect can be expressed quantitatively in the form of an Arrhenius type of equation, as follows:

$$\mu_T = \mu_0[\exp(E_\mu/RT)] \quad (2.21)$$

where

μ_T = viscosity at T K

μ_0 = a constant

E_μ = activation energy for viscous flow

R = universal gas constant

T = temperature, K

The values of E_μ are found to be usually low, ranging from 5 to 50 kJ/mole.

From the available data, which is rather limited, it is found that the composition of an alloy has a significant effect on its viscosity. Also, viscosity

¹ J.E. Lennard-Jones and A.F. Devonshire, *Proc. Roy. Soc. (London)*, **A169**: 319 (1939) and **A170**: 464 (1939).

² E.N. Dac Andrade. *Phil. Mag.*, **19**: 497, 698 (1934) and *Endeavour XIII*, **47**: 117 (1954).

is found to depend on the nature of the atomic interaction in the alloys as reflected in the phase diagrams. For example, in many binary alloy systems, it is observed that

- (i) the viscosity tends to have a maximum value at the composition where a congruently melting compound is formed; and
- (ii) the viscosity has a minimum value at the composition where a eutectic is formed.

The first situation relates to strong interatomic interaction between the opposite types of atoms leading to ordering whereas the second indicates strong interaction between the same types of atoms, leading to the clustering phenomenon.

EXAMPLE 2.2 Calculate the viscosity of liquid copper at 1100°C with the help of the following data:

Melting point of copper = 1083°C

Atomic weight of copper = 63.5

Density of copper = 8.9 g cm⁻³

Solution We can determine the viscosity by the application of Eq. (2.20) considering 1100°C as close to the melting point. According to this equation, we have

$$\begin{aligned}\mu &= C(T_m M)^{1/2} V^{-2/3} \\ &= 6.12 \times 10^{-4} [(1083 + 273) \times 63.5]^{1/2} \times (63.5/8.9)^{-2/3} \\ &= 4.85 \times 10^{-2} \text{ poise} \\ &= 4.85 \times 10^{-3} \text{ kg m}^{-1} \text{ s}^{-1} \quad \text{Ans.}\end{aligned}$$

2.2.3 Viscosity of Slags

Most of the common slags are derived from oxides, although of late a few fluoride-based slags have found application in secondary refining processes. The liquid oxide slags consist of cations and anions formed by acid-base reactions among the constituents. An oxide is considered to be acidic, if, when dissolved in the molten slag, it acquires additional oxygen ions to form complex anions whereas a basic oxide ionises to contribute oxygen ions to the melt. The most common acidic constituent in oxide slags is silica (SiO_2), and the viscosity of the liquid oxide slag may be discussed by taking into account the viscosity of pure liquid SiO_2 and its variation with the addition of basic oxides like lime (CaO), magnesia (MgO), sodium oxide (Na_2O), etc.

The viscosity of pure liquid silica is very high, of the order of 10^5 poise. This may be attributed to the silica network structure involving strong Si—O covalent bonds, very similar to the structure of pure solid silica except that the long range order may be somewhat broken in the liquid. Such a structure is shown in Fig. 2.6, which illustrates the nature of SiO_4^{4-} tetrahedral groups.

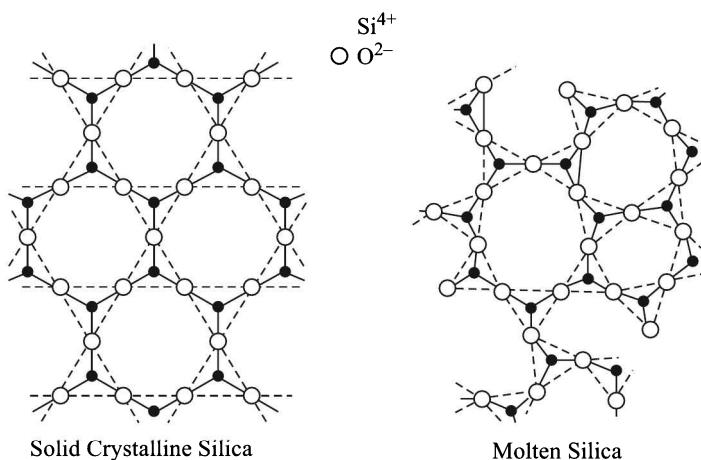


Fig. 2.6 Structure of silica.

The high viscosity is due to the strong resistance to viscous flow because of the high energy Si—O bonds shown in the figure. When a basic oxide like CaO is added to the liquid silica, the former dissociates to form Ca^{2+} and O^{2-} ions. The O^{2-} ion enters the silica network and each O^{2-} ion causes two of the SiO_4^{4-} tetrahedra to separate whereas the Ca^{2+} ion is accommodated in the interstices of the silicate structure. This is shown in Fig. 2.7. Increasing addition of CaO

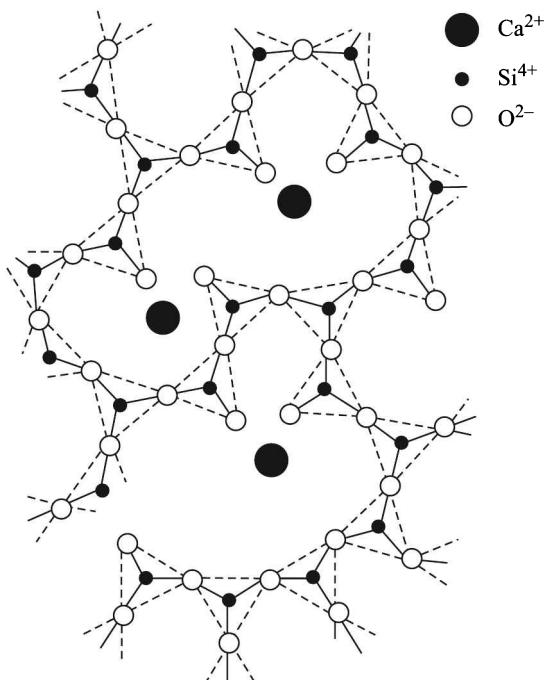


Fig. 2.7 Effect of calcium oxide additions on structure of molten silica.

causes progressive breakdown of the three-dimensional silica network. The amount of breakdown may be related to the number of broken links per silicate tetrahedron which is a function of the composition of the binary oxide solution and the oxygen/silicon ratio in the melt. Moreover, the silica network when breaking down forms smaller discrete complex ions which are characteristic of the composition. This is shown in Table 2.1. Finally, at the orthosilicate composition of $2\text{CaO} \cdot \text{SiO}_2$, having an oxygen/silicon ratio of 4:1, all the four links of each silica tetrahedron are broken and the melt consists of discrete SiO_4^{4-} ions and Ca^{2+} ions. Beyond this, further addition of CaO does not have any effect on the structure of the melt.

TABLE 2.1 Structural relationship in $\text{CaO}-\text{SiO}_2$ melts

Molecular formula	O/Si	Structure	Equivalent silicate ion
SiO_2	2:1	All corners of tetrahedra shared	Infinite network
$\text{CaO} \cdot 2\text{SiO}_2$	5:2	One broken link per tetrahedron	$(\text{Si}_6\text{O}_{15})^{6-}$ or $(\text{Si}_8\text{O}_{20})^{8-}$
$\text{CaO} \cdot \text{SiO}_2$	3:1	Two broken links per tetrahedron	$(\text{Si}_3\text{O}_9)^{6-}$ or $(\text{Si}_4\text{O}_{12})^{8-}$
$3\text{CaO} \cdot 2\text{SiO}_2$	7:2	Three broken links per tetrahedron	$(\text{Si}_2\text{O}_7)^{6-}$
$2\text{CaO} \cdot \text{SiO}_2$ (orthosilicate)	4:1	All four links broken	Discrete SiO_4^{4-} tetrahedra

The case with any other divalent basic metal oxide is similar to what happens with CaO. The change in viscosity in the binary oxide follows the change in its structure. As the network is progressively broken down, the resistance to viscous flow also decreases progressively and the shear process becomes easier. Also, the activation energy for viscous flow, therefore, decreases from a high value of about 140 kcal/mole for pure SiO_2 to about 30 kcal/mole at the orthosilicate ($2\text{MO} \cdot \text{SiO}_2$) composition. Figure 2.8¹ shows the decrease in the activation energy of viscous flow for monovalent and divalent basic silicates.

Industrial slags are, however, rarely composed of binary silicates. Various other components such as Al_2O_3 , MgO , FeO , Fe_2O_3 , P_2O_5 , etc. are always present in these slags. Out of these, all the divalent basic oxides such as MgO , FeO or MnO may be expected to behave as CaO which would modify the silica network, whereas acidic oxides such as TiO_2 , P_2O_5 would act as network formers. Therefore, the former category should reduce the silicate viscosity whereas the latter should increase it.

Al_2O_3 , however, cannot strictly be classified as an acidic or a basic oxide as it can behave both ways, depending on the overall composition. In metallurgical slags, Al_2O_3 is important in blast furnace slags where the basicity

¹ J.D. Mackenzie, *Chem. Rev.*, **56**: 455 (1956).

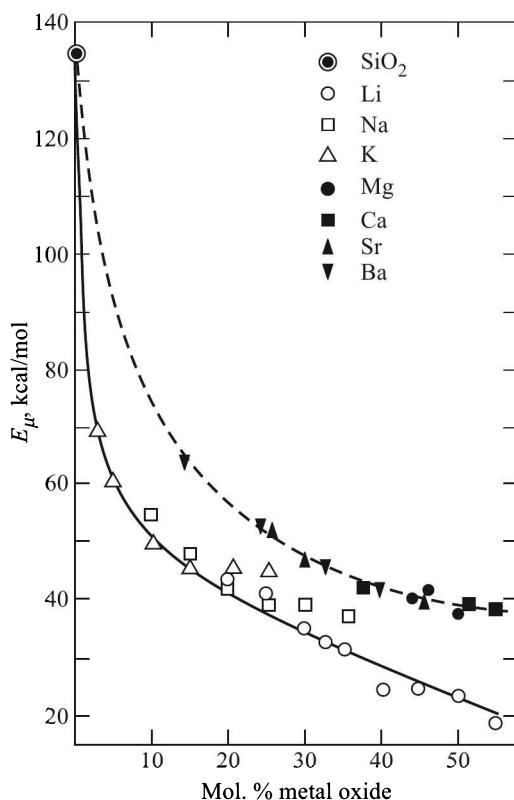


Fig. 2.8 Effect of metal oxide additions on activation energy of viscous flow of silicate melts.

is low. Therefore, it behaves as an acidic constituent and may form $(\text{AlO}_3)^{3-}$ anions in the melt. In general, Al_2O_3 is found to slightly increase the viscosity when added to a binary silicate.

A discussion on slag viscosity would be incomplete without considering the effect of CaF_2 which is added in the form of the well-known flux, fluorspar, to decrease the viscosity of oxide slags. The reason for this decrease is, however, not fully understood. It is thought that this may be due to the breaking up of CaF_2 to CaF^+ cations which tend to decrease the electrostatic bonds between the silicate anion and the previously present Ca^{2+} cations in the melt. This decrease may help in lowering the viscosity of the melt. The effect of CaF_2 is found to be more pronounced in acidic rather than basic slags.

The viscosity of a slag decreases as the temperature increases. This is due to the fact that, in liquid slags, the ions become more mobile when the temperature increases. Therefore, the resistance to flow decreases causing a decrease in the viscosity. However, quantitative data in this regard is not very exhaustive in the literature.

2.3 DIFFERENTIAL MASS AND MOMENTUM BALANCES

These balances may be considered as basic in the formulation of various aspects of fluid flow. In general, the expressions for these balances which may be considered microscopic in nature are derived by considering a small volume element fixed in space in the flowing fluid. This volume element is usually known as *control volume*. The change in any variable in this control volume can be either due to its interaction with the surroundings or due to some reaction inside the control volume or due to changes in the value of this variable in the control volume. In this section, only non-reacting systems, i.e. those in which there is no change because of chemical reactions, will be considered for the sake of simplicity. Further, as an illustration, the balances have been worked out by considering control volumes in the rectangular coordinate system.

2.3.1 Differential Mass Balance: Continuity Equation

The continuity equation is the mathematical expression for the law of conservation of mass for flowing fluids. This is universally applicable to all types of fluid flow, such as laminar or turbulent with only slight variation, as long as the fluid forms a continuum. To derive this equation, we consider a differential volume element as shown in Fig. 2.9, in which fluid enters from the faces touching the point $P(x, y, z)$ and leaves from the faces touching the point $Q(x + \delta x, y + \mu y, z + \delta z)$.

According to the law of conservation of mass, we can write the following general relation for a non-reacting fluid:

$$\begin{aligned} & [(\text{Mass of fluid entering the volume element per unit time}) \\ & - (\text{Mass of fluid leaving the volume element per unit time})] \\ & = [\text{Rate of change in mass of fluid in the volume element}] \end{aligned} \quad (2.22)$$

Mass of fluid entering the volume element per unit time

$$= (\rho v_x)_{x=x} \delta y \delta z + (\rho v_y)_{y=y} \delta x \delta z + (\rho v_z)_{z=z} \delta x \delta y \quad (2.23)$$

where ρ is the density and v_x , v_y and v_z are the components of the fluid velocity in x -, y -, and z -directions, respectively at the positions indicated by the appropriate suffices. Thus $(\rho v_x)_{x=x}$, $(\rho v_y)_{y=y}$ and $(\rho v_z)_{z=z}$ are the mass flow rates per unit cross-sectional area in x -, y -, and z -directions, respectively at the entrance faces of the volume element for the respective directions. Similarly, we get the following expression for the fluid leaving the volume element:

Mass of fluid leaving the volume element per unit time

$$= (\rho v_x)_{x=x+\delta x} \delta y \delta z + (\rho v_y)_{y=y+\delta y} \delta x \delta z + (\rho v_z)_{z=z+\delta z} \delta x \delta y \quad (2.24)$$

For the change in mass of fluid in the volume element per unit time, we can write the following relation:

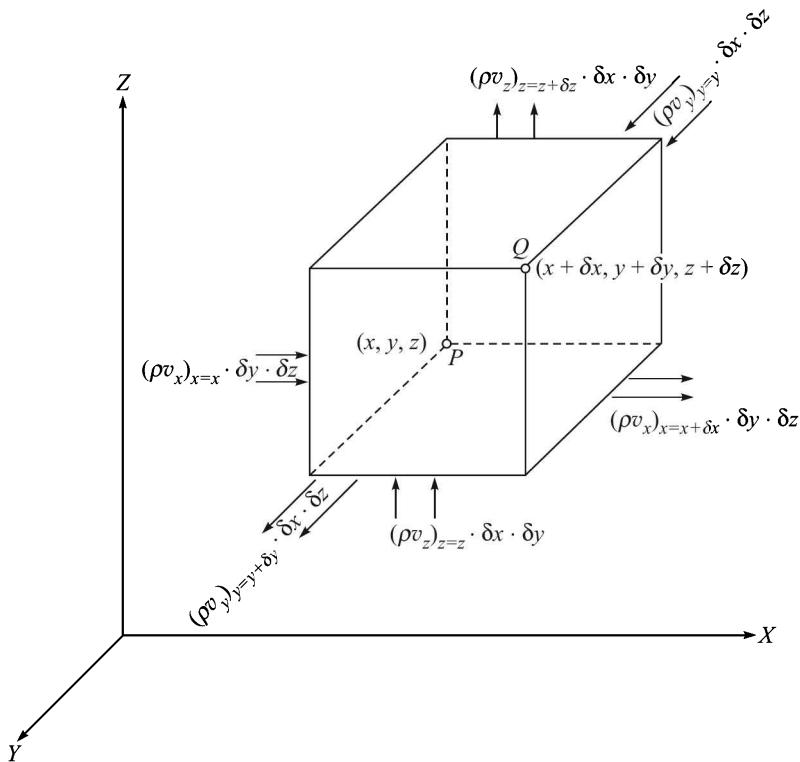


Fig. 2.9 Differential volume element for derivation of continuity equation in rectangular coordinate system.

Change in mass per unit time in the volume element

$$\frac{\partial}{\partial t} (\rho \delta x \delta y \delta z) = \delta x \delta y \delta z \left(\frac{\partial \rho}{\partial t} \right) \quad (2.25)$$

Substitution of Eqs. (2.23) to (2.25) in Eq. (2.22) and division of both sides by $\delta x \delta y \delta z$ lead to the equation

$$\begin{aligned} \frac{\partial \rho}{\partial t} = - & \left[\frac{(\rho v_x)_{x=x+\delta x} - (\rho v_x)_{x=x}}{\delta x} + \frac{(\rho v_y)_{y=y+\delta y} - (\rho v_y)_{y=y}}{\delta y} \right. \\ & \left. + \frac{(\rho v_z)_{z=z+\delta z} - (\rho v_z)_{z=z}}{\delta z} \right] \end{aligned} \quad (2.26)$$

If we consider the dimensions of the volume element to be infinitesimal, the above equation can be expressed in the form of the following partial differential equation:

$$\frac{\partial \rho}{\partial t} = - \left[\frac{\partial (\rho v_x)}{\partial x} + \frac{\partial (\rho v_y)}{\partial y} + \frac{\partial (\rho v_z)}{\partial z} \right] \quad (2.27)$$

In vectorial notations, Eq. (2.27) can be written as

$$\frac{\partial \rho}{\partial t} + \nabla(\rho \mathbf{v}) = 0 \quad (2.28)$$

Equations (2.27) and (2.28) form the generalized statements of the continuity equation. The continuity equation for turbulent flow can similarly be obtained from the above equation by substitution of expressions for v_x , v_y , v_z in terms of \bar{v}_x , \bar{v}_y and \bar{v}_z . Thus, for turbulent flow, we get the continuity equation as follows:

$$\frac{\partial \rho}{\partial t} = - \left[\frac{\partial(\rho \bar{v}_x)}{\partial x} + \frac{\partial(\rho \bar{v}_y)}{\partial y} + \frac{\partial(\rho \bar{v}_z)}{\partial z} \right] \quad (2.29)$$

Or using vectorial notation, we have

$$\frac{\partial \rho}{\partial t} \nabla(\rho \mathbf{v}) = 0 \quad (2.30)$$

Thus, the continuity equation for turbulent flow is similar to that for laminar flow Eq. (2.28).

In a number of practical applications, we require the statement of continuity equation either for steady state conditions or for incompressible fluids, for example, for the flow of a liquid. In what follows, in this section, these two cases are considered.

Continuity equation for steady state

The steady state is defined as that state in which the density of the fluid in any differential element fixed in space does not change with time. In fact, the general definition of steady state includes the time independence of all intensive properties of the system. The concept of steady state, as already mentioned, is important in the case of "continuous" type of reactors, e.g. a blast furnace used for metal extraction. According to the definition of steady state, we have

$$\frac{\partial \rho}{\partial t} = 0 \quad (2.31)$$

Substitution of the above equation in Eqs. (2.27) and (2.28) leads to the following continuity equations for this case:

$$\frac{\partial(\rho v_x)}{\partial x} + \frac{\partial(\rho v_y)}{\partial y} + \frac{\partial(\rho v_z)}{\partial z} = 0 \quad (2.32)$$

Or in vectorial notation, we have

$$\nabla(\rho \mathbf{v}) = 0 \quad (2.33)$$

Continuity equation for an incompressible fluid

A fluid is said to be incompressible if the density of the same chunk of fluid in a flowing system does not change with time in spite of change in external pressure. We arrive at the mathematical formulation of this statement as below.

In general, the density of a flowing fluid can be assumed to be a function of time and position, i.e.

$$\rho = \rho(x, y, z, t) \quad (2.34)$$

In the differential form, we have

$$d\rho = \frac{\partial \rho}{\partial t} dt + \frac{\partial \rho}{\partial x} dx + \frac{\partial \rho}{\partial y} dy + \frac{\partial \rho}{\partial z} dz \quad (2.35)$$

Thus

$$\frac{d\rho}{dt} = \frac{\partial \rho}{\partial t} + \frac{\partial \rho}{\partial x} \frac{dx}{dt} + \frac{\partial \rho}{\partial y} \frac{dy}{dt} + \frac{\partial \rho}{\partial z} \frac{dz}{dt} \quad (2.36)$$

Substitution of $\partial \rho / \partial t$ from Eq. (2.27) and simplification of the resulting expression lead to the relation

$$\begin{aligned} \frac{d\rho}{dt} = & - \left[(v_x - v_{x0}) \frac{\partial \rho}{\partial x} + (v_y - v_{y0}) \frac{\partial \rho}{\partial y} + (v_z - v_{z0}) \frac{\partial \rho}{\partial z} \right] \\ & - \rho \left[\frac{\partial v_x}{\partial x} + \frac{\partial v_y}{\partial y} + \frac{\partial v_z}{\partial z} \right] \end{aligned} \quad (2.37)$$

where

$$v_{x0} = \frac{\partial x}{\partial t}, v_{y0} = \frac{\partial y}{\partial t}, v_{z0} = \frac{\partial z}{\partial t}$$

Equation (2.37) is helpful in calculating the change in density with time in a volume frame supposed to be moving with a velocity having v_{x0} , v_{y0} , and v_{z0} as its components in the x -, y -, and z -directions, respectively. An interesting special case of Eq. (2.37) arises in which the volume frame has the same velocity components as the flowing fluid. For this case, we get from Eq. (2.37), the equation

$$\frac{D\rho}{Dt} = - \rho \left[\frac{\partial v_x}{\partial x} \frac{\partial v_y}{\partial y} + \frac{\partial v_z}{\partial z} \right] \quad (2.38)$$

where $d\rho/dt$ has been replaced by $D\rho/Dt$ and is called the “substantial derivative of density”, and can be proved with the help of Eq. (2.27) to be defined by the relation

$$\frac{D\rho}{Dt} = \frac{\partial \rho}{\partial t} + v_x \frac{\partial \rho}{\partial x} + v_y \frac{\partial \rho}{\partial y} + v_z \frac{\partial \rho}{\partial z} \quad (2.39)$$

Equations (2.38) and (2.39) can be expressed in the following alternative forms respectively in vectorial notation

$$\frac{D\rho}{Dt} + \rho \nabla \cdot \mathbf{v} = 0 \quad (2.40)$$

$$\frac{D\rho}{Dt} = \frac{\partial \rho}{\partial t} + \mathbf{v} \cdot \nabla \rho \quad (2.41)$$

According to the definition of an incompressible fluid, which requires us to concentrate on the same chunk of fluid, we have

$$\frac{D\rho}{Dt} = 0 \quad (2.42)$$

This relation on substitution in Eq. (2.38) leads to

$$\frac{\partial v_x}{\partial x} + \frac{\partial v_y}{\partial y} + \frac{\partial v_z}{\partial z} = 0 \quad (2.43)$$

Or, in vectorial form, for an incompressible liquid, we have

$$\nabla \cdot \mathbf{v} = 0 \quad (2.44)$$

Continuity equation in other coordinate systems

Though the above derivations in this section have been made in respect of the rectangular coordinate system, these relations cause many complications in solving problems with cylindrical and spherical symmetries. For such cases, it is more convenient to use the continuity equation in terms of cylindrical or spherical coordinate systems. We can transform the equations in rectangular coordinate system to these systems by using standard work of Pipes,¹ Lamb² and Schlichting.³ The final expressions of the continuity equation in cylindrical and spherical coordinates, as a result of such transformations, are as follows:

- (i) For cylindrical coordinates (r, θ, z) , the general equation is

$$\frac{\partial \rho}{\partial t} + \frac{1}{r} \frac{\partial}{\partial r} (\rho v_r) + \frac{1}{r} \frac{\partial}{\partial \theta} (\rho v_\theta) + \frac{\partial}{\partial z} (\rho v_z) = 0 \quad (2.45)$$

- (ii) For spherical coordinates (r, θ, ϕ) , the general equation is

$$\frac{\partial \rho}{\partial t} + \frac{1}{r^2} \frac{\partial}{\partial r} (\rho r^2 v_r) + \frac{1}{r \sin \theta} (\rho v_\theta \sin \theta) + \frac{1}{r \sin \theta} \frac{\partial}{\partial \phi} (\rho v_\phi) = 0 \quad (2.46)$$

The significance of the continuity equation is illustrated by the following example.

EXAMPLE 2.3 The velocity distribution for two-dimensional flow of an incompressible fluid is given by

$$v_x = 5 - x \quad \text{and} \quad v_y = 4 + y$$

Show that the requirements of the continuity equation are satisfied.

Solution For two-dimensional flow of an incompressible fluid, the continuity Eq. (2.43) is modified to—

¹ L. Pipes, *Applied Mathematics for Engineers and Physicists*, McGraw-Hill, New York (1958).

² H. Lamb, *Hydrodynamics*, Dover, New York (1945).

³ H. Schlichting, *Boundary Layer Theory*, McGraw-Hill, New York (1955).

$$\frac{\partial v_x}{\partial x} + \frac{\partial v_y}{\partial y} = 0$$

Given $v_x = 5 - x$ and $v_y = 4 + y$, we have

$$\frac{\partial v_x}{\partial x} = -1, \quad \frac{\partial v_y}{\partial y} = +1$$

So

$$\frac{\partial v_x}{\partial x} + \frac{\partial v_y}{\partial y} = -1 + 1 = 0$$

This satisfies the requirement of the above continuity equation.

2.3.2 Differential Momentum Balance: The Equation of Motion

The concept of a differential momentum balance on a control volume in a flowing fluid is based on Newton's second law of motion which states that the rate of change of momentum is equal to the force acting on the system. For deriving this equation of motion, consider again the control volume in rectangular coordinates shown in Fig. 2.10. According to Newton's law of motion, we have the following relation for momentum balance on this volume element:

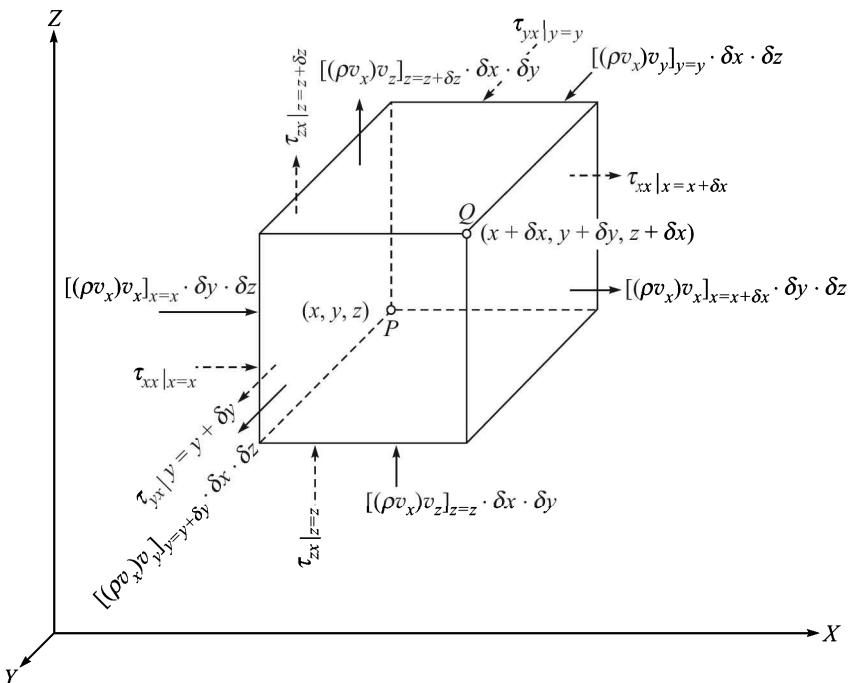


Fig. 2.10 Differential volume element for derivation of equation of motion in rectangular coordinate system.

$$[(\text{Rate of momentum input}) - (\text{Rate of momentum output})] = [(\text{Rate of change of momentum on the volume element}) - (\text{Sum of net forces acting on the element})] \quad (2.47)$$

As both momentum and force are vectors, the above balance is to be considered separately for each of the three directions which will ultimately lead to three momentum balance equations. In the following part of this subsection, a relation for momentum balance for its component in the x -direction will be derived and the relations for momentum components in the y - and z -directions will be written considering the symmetry properties.

The x -component of momentum which is equal to ρv_x for unit volume, where ρ is fluid density and v_x is the velocity component in the x -direction, can enter the volume element under consideration, as shown in Fig. 2.10, from all the three faces through which the fluid enters and can leave this element from the rest of the faces. Hence, the amount of x -component of momentum entering this volume element will be expressed by the relation.

[x -component of momentum accompanying the fluid entering volume element per unit time]

$$= [\{(\rho v_x) v_x\}_{x=x}] \delta y \delta z + [\{(\rho v_x) v_y\}_{y=y}] \delta x \delta z + [\{(\rho v_x) v_z\}_{z=z}] \delta x \delta y \quad (2.48)$$

since $\rho v_x \delta y \delta z$ is the mass of the fluid entering per unit time at $x = x$ and so on. Similarly, for other directions

[x -component of momentum accompanying the fluid leaving volume element per unit time]

$$= [\{(\rho v_x) v_x\}_{x=x+\delta x}] \delta y \delta z + [\{(\rho v_x) v_y\}_{y=y+\delta y}] \delta x \delta z + [\{(\rho v_x) v_z\}_{z=z+\delta z}] \delta x \delta y \quad (2.49)$$

Rate of change of x -component of momentum in volume element

$$= \frac{\partial(\rho v_x)}{\partial t} \delta x \delta y \delta z \quad (2.50)$$

In the present derivation, the effects of electrical and magnetic fields are not considered.

The force acting in the x -direction on the volume element can be classified broadly into two categories—*bulk forces* and *superficial forces*. Bulk forces, which may be defined as those acting on the whole volume of the element, can be further subdivided into two categories—gravitational forces and those due to the pressure of the matter inside the volume element. The superficial forces can also be classified into two categories—normal and tangential stresses.

For gravitational force, F_g , in the x -direction, we can formulate the relation

$$F_g = \rho g_x \delta x \delta y \delta z \quad (2.51)$$

where g_x is the component of acceleration due to gravity g in the x -direction.

The force F_p due to pressure is equal to the difference in pressure P on two faces of the element whose normal lies in the x -direction. Thus, we have

$$\begin{aligned}
F_P &= (P_{x=x}) \delta y \delta z - (P_{x=x+\delta x}) \delta y \delta z = \left[P_{x=x} - \left\{ P_{x=x} + \left(\frac{\partial P}{\partial x} \right) \delta x \right\} \right] \delta y \delta z \\
&= - \frac{\partial P}{\partial x} \delta x \delta y \delta z
\end{aligned} \tag{2.52}$$

The net force F_{xx} acting due to normal component of stress on the yz -plane¹ is expressed as

$$\begin{aligned}
F_{xx} &= (\tau_{xx})_{x=x} \delta y \delta z - (\tau_{xx})_{x=x+\delta x} \delta y \delta z \\
&= \left[(\tau_{xx})_{x=x} - \left\{ (\tau_{xx})_{x=x} + \left(\frac{\partial \tau_{xx}}{\partial x} \right) \delta x \right\} \right] \delta y \delta z \\
&= - \frac{\partial \tau_{xx}}{\partial x} \delta x \delta y \delta z
\end{aligned} \tag{2.53}$$

where τ_{xx} is the normal stress per unit area in the x -direction.

Similarly, the net force F_{yx} acting due to tangential component of stress on the xz -plane is obtained as

$$\begin{aligned}
F_{yx} &= (\tau_{yx})_{y=y} \delta x \delta z - (\tau_{yx})_{y=y+\delta y} \delta x \delta z \\
&= \left[(\tau_{yx})_{y=y} - \left\{ (\tau_{yx})_{y=y} + \left(\frac{\partial \tau_{yx}}{\partial y} \right) \delta y \right\} \right] \delta x \delta z \\
&= - \frac{\partial \tau_{yx}}{\partial y} \delta x \delta y \delta z
\end{aligned} \tag{2.54}$$

and the net force F_{zx} acting due to the tangential component of stress on the xy -plane is

$$\begin{aligned}
F_{zx} &= (\tau_{zx})_{z=z} \delta x \delta y - (\tau_{zx})_{z=z+\delta z} \delta x \delta y \\
&= - \frac{\partial \tau_{zx}}{\partial z} \delta x \delta y \delta z
\end{aligned} \tag{2.55}$$

Thus, the sum F_x of total forces, obtained from Eqs. (2.51) to (2.55), is given by the equation

$$\begin{aligned}
F_x &= F_g + F_P + F_{xx} + F_{yx} + F_{zx} \\
&= \left(\rho g_x - \frac{\partial P}{\partial x} - \frac{\partial \tau_{xx}}{\partial x} - \frac{\partial \tau_{yx}}{\partial y} - \frac{\partial \tau_{zx}}{\partial z} \right) \delta x \delta y \delta z
\end{aligned} \tag{2.56}$$

¹ In symbols F_{xx} , etc., the first subscript denotes the direction of the normal to the plane on which the stress is acting. The second subscript denotes the direction in which the stress acts.

Substitution of Eqs. (2.48) to (2.50) and (2.56) in Eq. (2.47) leads to

$$\begin{aligned} \frac{\partial(\rho v_x)}{\partial t} \delta x \delta y \delta z &= \left[\left\{ (\rho v_x v_x)_{x=x} - (\rho v_x v_x)_{x=x+\delta x} \right\} \delta y \delta z \right] \\ &+ \left[\left\{ (\rho v_x v_y)_{y=y} - (\rho v_x v_y)_{y=y+\delta y} \right\} \delta x \delta z \right] + \left[\left\{ (\rho v_x v_z)_{z=z} - (\rho v_x v_z)_{z=z+\delta z} \right\} \delta x \delta y \right] \\ &+ \left[\left(\rho g_x - \frac{\partial P}{\partial x} - \frac{\partial \tau_{xx}}{\partial x} - \frac{\partial \tau_{yx}}{\partial y} - \frac{\partial \tau_{zx}}{\partial z} \right) \delta x \delta y \delta z \right] \end{aligned}$$

or

$$\begin{aligned} \delta x \delta y \delta z \left\{ \frac{\partial(\rho v_x)}{\partial t} \right\} &= \left[(\rho v_x v_x)_{x=x} - \left\{ (\rho v_x v_x)_{x=x} + \frac{\partial(\rho v_x v_x)}{\partial x} \delta x \right\} \right] \delta y \delta z \\ &+ \left[(\rho v_x v_y)_{y=y} - \left\{ (\rho v_x v_y)_{y=y} + \frac{\partial(\rho v_x v_y)}{\partial y} \delta y \right\} \right] \delta x \delta z \\ &+ \left[(\rho v_x v_z)_{z=z} - \left\{ (\rho v_x v_z)_{z=z} + \frac{\partial(\rho v_x v_z)}{\partial z} \delta z \right\} \right] \delta x \delta y \\ &+ \left[\left(\rho g_x - \frac{\partial P}{\partial x} - \frac{\partial \tau_{xx}}{\partial x} - \frac{\partial \tau_{yx}}{\partial y} - \frac{\partial \tau_{zx}}{\partial z} \right) \delta x \delta y \delta z \right] \end{aligned}$$

which on simplification yields

$$\begin{aligned} \frac{\partial(\rho v_x)}{\partial t} &= - \left[\frac{\partial(\rho v_x v_x)}{\partial x} + \frac{\partial(\rho v_x v_y)}{\partial y} + \frac{\partial(\rho v_x v_z)}{\partial z} \right] \\ &+ \left[\rho g_x - \frac{\partial P}{\partial x} \right] - \left[\frac{\partial \tau_{xx}}{\partial x} + \frac{\partial \tau_{yx}}{\partial y} + \frac{\partial \tau_{zx}}{\partial z} \right] \quad (2.57) \end{aligned}$$

On the basis of symmetry, we can arrive at the following equations respectively for components of momentum balance in the y- and z-directions.

$$\begin{aligned} \frac{\partial(\rho v_y)}{\partial t} &= - \left[\frac{\partial(\rho v_y v_x)}{\partial x} + \frac{\partial(\rho v_y v_y)}{\partial y} + \frac{\partial(\rho v_y v_z)}{\partial z} \right] \\ &- \left[\frac{\partial \tau_{xy}}{\partial x} + \frac{\partial \tau_{yy}}{\partial y} + \frac{\partial \tau_{zy}}{\partial z} \right] + \left[\rho g_y - \frac{\partial P}{\partial y} \right] \quad (2.58) \end{aligned}$$

$$\begin{aligned} \frac{\partial(\rho v_z)}{\partial t} &= - \left[\frac{\partial(\rho v_z v_x)}{\partial x} + \frac{\partial(\rho v_z v_y)}{\partial y} + \frac{\partial(\rho v_z v_z)}{\partial z} \right] \\ &- \left[\frac{\partial \tau_{xz}}{\partial x} + \frac{\partial \tau_{yz}}{\partial y} + \frac{\partial \tau_{zz}}{\partial z} \right] + \left[\rho g_z - \frac{\partial P}{\partial z} \right] \quad (2.59) \end{aligned}$$

Equations (2.57) to (2.59) are the equations of motion and can be written in the following vectorial form:

$$\frac{\partial(v)}{\partial t} = -\nabla(\rho\mathbf{v}\mathbf{v}) - \nabla P - \nabla\tau + \rho\mathbf{g} \quad (2.60)$$

where $\mathbf{v}\mathbf{v}$ is a dyadic product of the velocity vector. Equation (2.60) can also be written in the following substantial derivative form:

$$\rho \frac{D\mathbf{v}}{Dt} = -\nabla P - \nabla\tau + \rho\mathbf{g} \quad (2.61)$$

The above set of equations contains thirteen dependent variables,¹ namely pressure, P , three velocity vectors, v_x , v_y and v_z , and nine stress variables, i.e. τ_{xx} , τ_{yy} , τ_{zz} , τ_{yx} , τ_{zx} , τ_{xy} , τ_{zy} , τ_{xz} and τ_{yz} . Thus, in order to arrive at a solution, we must have, in all, thirteen simultaneous equations. But we have as yet only four equations—one continuity equation and three equations of motion. In order to arrive at the remaining nine equations, we have to resort to the second principle (Section 1.1) on which the transport phenomenon is based. According to it, the momentum flux or the rate of transfer of momentum from one point to the other is proportional to the momentum concentration or the momentum per unit volume. For example, let us consider the x -direction momentum flux along the y -direction. According to the second principle

$$\frac{\partial(\rho v_x)}{\partial t} \propto \frac{\partial(\rho v_x)}{\partial y} \quad (2.62)$$

or

$$\frac{\partial(\rho v_x)}{\partial t} = \alpha \rho \frac{\partial(v_x)}{\partial y} \quad (2.63)$$

where α is the constant of proportionality and ρ is considered to be constant and the minus sign signifies that the flux will be down the gradient. According to the second law of motion, the rate of change of momentum is equal to the force. As in the present case, the change is in the x -direction but the gradient of change is considered along the y -direction, i.e. on the xz -plane. So this force will be a shear force, i.e. τ_{yx} . Further, the value of the term $\alpha\rho$ depends upon the type of fluid and forms the most important kinetic property of the fluid called the viscosity which is denoted by the symbol μ . Hence, Eq. (2.63) can be rewritten as

$$\tau_{yx} = -\mu \frac{\partial v_x}{\partial y} \quad (2.64)$$

This equation has the same form as Eq. (2.7), which described the Newton's law of viscosity. Equation (2.64) correlates the shearing force with the velocity gradient in a two-dimensional system. This equation can be

¹ It may be mentioned that in the case of compressible fluids, density will also be a function of position and time. But with the help of the equation of state, one can calculate it, once $p(x, y, z, t)$ is known.

extended to three-dimensional cases as well, and the resultant equations obtained for various shearing forces will be as follows:

$$\tau_{xx} = -2\mu \frac{\partial v_x}{\partial x} + \frac{2\mu}{3} \left(\frac{\partial v_x}{\partial x} + \frac{\partial v_y}{\partial y} + \frac{\partial v_z}{\partial z} \right) \quad (2.65)$$

$$\tau_{yy} = -2\mu \frac{\partial v_y}{\partial y} + \frac{2\mu}{3} \left(\frac{\partial v_x}{\partial x} + \frac{\partial v_y}{\partial y} + \frac{\partial v_z}{\partial z} \right) \quad (2.66)$$

$$\tau_{zz} = -2\mu \frac{\partial v_z}{\partial z} + \frac{2\mu}{3} \left(\frac{\partial v_x}{\partial x} + \frac{\partial v_y}{\partial y} + \frac{\partial v_z}{\partial z} \right) \quad (2.67)$$

$$\tau_{xy} = \tau_{yx} = -\mu \left(\frac{\partial v_x}{\partial y} + \frac{\partial v_y}{\partial x} \right) \quad (2.68)$$

$$\tau_{xz} = \tau_{zx} = -\mu \left(\frac{\partial v_x}{\partial z} + \frac{\partial v_z}{\partial x} \right) \quad (2.69)$$

$$\tau_{yz} = \tau_{zy} = -\mu \left(\frac{\partial v_y}{\partial z} + \frac{\partial v_z}{\partial y} \right) \quad (2.70)$$

For detailed derivation of these equations, the inquisitive reader may refer to the work of Knudsen and Katz.¹

With the help of the above nine equations, we can eliminate the stress terms from Eqs. (2.57) to (2.61), and assuming viscosity μ to be constant (Newtonian fluids), we get the following equations:

For the x -component of momentum, we get

$$\rho \frac{Dv_x}{Dt} = -\frac{\partial P}{\partial x} + \rho g_x + \mu \left(\frac{\partial^2 v_x}{\partial x^2} + \frac{\partial^2 v_x}{\partial y^2} + \frac{\partial^2 v_x}{\partial z^2} \right) + \frac{\mu}{3} \left(\frac{\partial v_x}{\partial x} + \frac{\partial v_y}{\partial y} + \frac{\partial v_z}{\partial z} \right) \quad (2.71)$$

Similarly, for the y - and z -directions, we get

$$\rho \frac{Dv_y}{Dt} = -\frac{\partial P}{\partial y} + \mu \left(\frac{\partial^2 v_y}{\partial x^2} + \frac{\partial^2 v_y}{\partial y^2} + \frac{\partial^2 v_y}{\partial z^2} \right) + \frac{\mu}{3} \left(\frac{\partial v_x}{\partial x} + \frac{\partial v_y}{\partial y} + \frac{\partial v_z}{\partial z} \right) + \rho g_y \quad (2.72)$$

$$\rho \frac{Dv_z}{Dt} = -\frac{\partial P}{\partial z} + \mu \left(\frac{\partial^2 v_z}{\partial x^2} + \frac{\partial^2 v_z}{\partial y^2} + \frac{\partial^2 v_z}{\partial z^2} \right) + \frac{\mu}{3} \left(\frac{\partial v_x}{\partial x} + \frac{\partial v_y}{\partial y} + \frac{\partial v_z}{\partial z} \right) + \rho g_z \quad (2.73)$$

¹ J.K. Knudsen and D.L. Katz, *Fluid Dynamics and Heat Transfer*, McGraw-Hill, New York (1958).

In vectorial form, this may be expressed as

$$\rho \frac{D\mathbf{v}}{Dt} = - \nabla P + \mu \nabla^2 \mathbf{v} + \frac{\mu}{3} \nabla \cdot \mathbf{v} + \rho \mathbf{g} \quad (2.74)$$

For an incompressible fluid, therefore, with the help of Eq. (2.44), we can arrive at the equation

$$\rho \frac{D\mathbf{v}}{Dt} = - \nabla P + \mu \nabla^2 \mathbf{v} + \rho \mathbf{g} \quad (2.75)$$

The above equations are known as “Navier–Stokes equations” which represent the equations of motion in the rectangular coordinate system.

Equation of motion in other coordinate systems

In many practical applications such as in the case of pipes or some spherical reactors, the equation of motion has to be applied in the cylindrical or the spherical coordinate system. The transformation of the equation of motion from the rectangular to the cylindrical or spherical coordinate system follows standard mathematical techniques which need not be considered here. The transformed forms in these two systems are given below:

(a) Equations of motion in cylindrical coordinates

(i) The radial component in terms of stresses is given by the equation

$$\begin{aligned} & \frac{\partial v_r}{\partial r} + v_r \frac{\partial v_r}{\partial r} + \frac{v_\theta}{r} \frac{\partial v_r}{\partial \theta} - \frac{v_\theta^2}{r} + v_z \frac{\partial v_r}{\partial z} \\ &= gr - \frac{1}{\rho} \frac{\partial \rho}{\partial r} - \frac{1}{\rho} \left[\frac{1}{r} \frac{\partial}{\partial r} (r \tau_{rr}) + \frac{1}{r} \frac{\partial \tau_{r\theta}}{\partial \theta} - \frac{\tau_{\theta\theta}}{r} + \frac{\partial \tau_{rz}}{\partial z} \right] \end{aligned} \quad (\text{A})$$

The radial component in terms of velocity gradients for Newtonian fluids with constant density is given by the equation

$$\begin{aligned} & \frac{\partial v_r}{\partial r} + v_r \frac{\partial v_r}{\partial r} + \frac{v_\theta}{r} \frac{\partial v_r}{\partial \theta} - \frac{v_\theta^2}{r} + v_z \frac{\partial v_r}{\partial z} \\ &= gr - \frac{1}{\rho} \frac{\partial \rho}{\partial r} + \frac{\mu}{\rho} \left[\frac{\partial}{\partial r} \left\{ \frac{1}{r} \frac{\partial}{\partial r} (rv_r) \right\} + \frac{1}{r^2} \frac{\partial^2 v_r}{\partial \theta^2} + \frac{\partial^2 v_r}{\partial z^2} - \frac{2}{r^2} \frac{\partial v_\theta}{\partial \theta} \right] \end{aligned} \quad (\text{B})$$

(ii) The angular component in terms of stresses is given by the equation

$$\begin{aligned} & \frac{\partial v_\theta}{\partial t} + v_r \frac{\partial v_\theta}{\partial r} + \frac{v_\theta}{r} \frac{\partial v_\theta}{\partial \theta} + \frac{v_r v_\theta}{r} + v_z \frac{\partial v_\theta}{\partial z} \\ &= g\theta - \frac{\rho}{r} \frac{\partial \rho}{\partial \theta} - \frac{1}{\rho} \left\{ \frac{1}{r^2} \frac{\partial}{\partial r} (r^2 \tau_{r\theta}) + \frac{1}{r} \frac{\partial \tau_{\theta\theta}}{\partial \theta} + \frac{\partial \tau_{\theta z}}{\partial z} \right\} \end{aligned} \quad (\text{C})$$

The angular component in terms of velocity gradients for Newtonian fluids with constant density is given by the equation

$$\frac{\partial v_\theta}{\partial t} + v_r \frac{\partial v_\theta}{\partial r} + \frac{v_\theta}{r} \frac{\partial v_\theta}{\partial \theta} + \frac{v_r v_\theta}{r} + v_z \frac{\partial v_\theta}{\partial z} \\ = g\theta - \frac{1}{\rho r} \frac{\partial \rho}{\partial \theta} + \frac{\mu}{\rho} \left[\frac{\partial}{\partial r} \left\{ \frac{1}{r} \frac{\partial}{\partial r} (rv_\theta) \right\} + \frac{1}{r^2} \frac{\partial^2 v_\theta}{\partial \theta^2} + \frac{2}{r^2} \frac{\partial v_r}{\partial \theta} + \frac{\partial^2 v_\theta}{\partial z^2} \right] \quad (\text{D})$$

(iii) The axial component in terms of stresses is given by the equation

$$\frac{\partial v_z}{\partial t} + v_r \frac{\partial v_z}{\partial r} + \frac{v_\theta}{r} \frac{\partial v_z}{\partial \theta} + v_z \frac{\partial v_z}{\partial z} \\ = gz - \frac{1}{\rho} \frac{\partial \rho}{\partial z} - \frac{1}{\rho} \left\{ \frac{1}{r} \frac{\partial}{\partial r} (r\tau_{rz}) + \frac{1}{r} \frac{\partial \tau_{\theta z}}{\partial \theta} + \frac{\partial \tau_{zz}}{\partial z} \right\} \quad (\text{E})$$

The axial component in terms of velocity gradients for Newtonian fluids with constant density is given by the equation

$$\frac{\partial v_z}{\partial t} + v_r \frac{\partial v_z}{\partial r} + \frac{v_\theta}{r} \frac{\partial v_z}{\partial \theta} + v_z \frac{\partial v_z}{\partial z} \\ = gz - \frac{1}{\rho} \frac{\partial \rho}{\partial z} + \frac{\mu}{\rho} \left\{ \frac{1}{r} \frac{\partial}{\partial r} \left(r \frac{\partial v_z}{\partial r} \right) + \frac{1}{r^2} \frac{\partial^2 v_z}{\partial \theta^2} + \frac{\partial^2 v_z}{\partial z^2} \right\} \quad (\text{F})$$

(b) *Equations of motion in spherical coordinates*

The equations of motion in this system for various components are as follows:

(i) The radial component in terms of stresses is given by the equation

$$\frac{\partial v_r}{\partial t} + v_r \frac{\partial v_r}{\partial r} + \frac{v_\theta}{r} \frac{\partial v_r}{\partial \theta} + \frac{v_\phi}{r \sin \phi} \frac{\partial v_r}{\partial \phi} - \frac{v_\theta^2 + v_\phi^2}{r} \\ = gr - \frac{1}{\rho} \frac{d\rho}{dr} - \frac{1}{\rho} \left\{ \frac{1}{r^2} \frac{\partial}{\partial r} (r^2 \tau_{rr}) + \frac{1}{r \sin \theta} \frac{\partial}{\partial \theta} (\tau_{r\theta} \sin \theta) \right. \\ \left. + \frac{1}{r \sin \theta} \frac{r \tau_{r\phi}}{\partial \phi} - \frac{\tau_{\theta\theta} + \tau_{\phi\phi}}{r} \right\} \quad (\text{G})$$

The radial component in terms of velocity gradients for Newtonian fluids with constant density is given by the equation

$$\frac{\partial v_r}{\partial t} + v_r \frac{\partial v_r}{\partial r} + \frac{v_\theta}{r} \frac{\partial v_r}{\partial \theta} + \frac{v_\phi}{r \sin \theta} \frac{\partial v_r}{\partial \phi} - \frac{v_\theta^2 + v_\phi^2}{r} \\ = gr - \frac{1}{\rho} \frac{d\rho}{dr} + \frac{\mu}{\rho} \left\{ \frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial v_r}{\partial r} \right) + \frac{1}{r^2 \sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial v_r}{\partial \theta} \right) \right. \\ \left. + \frac{1}{r^2 \sin^2 \theta} \frac{\partial^2 v_r}{\partial \phi^2} - \frac{2}{r^2} v_r - \frac{2}{r^2} \frac{\partial v_\theta}{\partial \theta} - \frac{2}{r^2} v_\theta \cot \theta - \frac{2}{r^2 \sin \theta} \frac{\partial v_\phi}{\partial \phi} \right\} \quad (\text{H})$$

(ii) The θ -component in terms of stresses is given by the equation

$$\begin{aligned} \frac{\partial v_\theta}{\partial t} + v_r \frac{\partial v_\theta}{\partial r} + \frac{v_\theta}{r} \frac{\partial v_\theta}{\partial \theta} + \frac{v_\phi}{r \sin \theta} \frac{\partial v_\theta}{\partial \phi} \frac{v_r v_\theta}{r} - \frac{v_\theta^2 \cot \theta}{r} \\ = - \frac{1}{r \rho} \frac{\partial \rho}{\partial \theta} - \frac{1}{r^2 \rho} \frac{\partial}{\partial r} (r^2 \tau_{r\theta}) - \frac{1}{\rho r \sin \theta} \left(\frac{\partial}{\partial \phi} (\tau_{\theta\theta} \sin \theta) \right) \\ - \frac{1}{r \rho \sin \theta} \frac{\partial \tau_{\theta\theta}}{\partial \phi} - \frac{\tau_{r\theta} \cot \theta}{r \rho} \tau_{\phi\phi} + g \theta \end{aligned} \quad (\text{I})$$

Also, the θ -component in terms of velocity gradients for Newtonian fluids with constant density is given by the equation

$$\begin{aligned} \frac{\partial v_\theta}{\partial t} v_r \frac{\partial v_\theta}{\partial r} + \frac{v_\theta}{r} \frac{\partial v_\theta}{\partial \theta} + \frac{v_\theta}{r \sin \theta} \frac{\partial v_\theta}{\partial \phi} + \frac{v_r v_\theta}{r} - \frac{v_\theta^2 \cot \theta}{r} \\ = g \theta - \frac{1}{\rho r} \frac{\partial \rho}{\partial \theta} + \frac{\mu}{\rho} \left\{ \frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial v_\theta}{\partial r} \right) \right. \\ \left. + \frac{1}{r^2 \sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial v_\theta}{\partial \theta} \right) + \frac{1}{r^2 \sin \theta} \frac{\partial^2 v_\theta}{\partial \phi^2} \right. \\ \left. + \frac{2}{r^2} \frac{\partial v_r}{\partial \theta} - \frac{v_\theta}{r^2 \sin^2 \theta} - \frac{2 \cos \theta}{r^2 \sin^2 \theta} \frac{\partial v_\phi}{\partial \phi} \right\} \end{aligned} \quad (\text{J})$$

(iii) The ϕ -component in terms of stresses is given by the equation

$$\begin{aligned} \frac{\partial v_\phi}{\partial t} + v_r \frac{\partial v_\phi}{\partial r} + \frac{v_\theta}{r} \frac{\partial v_\phi}{\partial \theta} + \frac{v_\phi}{r \sin \theta} \frac{\partial v_\phi}{\partial \phi} + \frac{v_\phi v_r}{r} + \frac{v_\theta v_\phi \cot \theta}{r} \\ = g \phi - \frac{1}{r \rho \sin \theta} \frac{\partial \rho}{\partial \phi} - \frac{1}{\rho r^2} \frac{\partial}{\partial r} (r^2 \tau_{r\phi}) \\ - \frac{1}{r \rho} \frac{\partial \tau_{\theta\phi}}{\partial \theta} - \frac{1}{r \rho \sin \theta} \frac{\partial \tau_{\phi\phi}}{\partial \phi} - \frac{\tau_{r\phi}}{r \rho} - \frac{2 \cot \phi}{r \rho} \tau_{\theta\phi} \end{aligned} \quad (\text{K})$$

The ϕ -component in terms of velocity gradients for Newtonian fluids with constant density is given by the equation

$$\begin{aligned} \frac{\partial v_\phi}{\partial t} + v_r \frac{\partial v_\phi}{\partial r} + \frac{v_\theta}{r} \frac{\partial v_\phi}{\partial \theta} + \frac{v_\phi}{r \sin \theta} \frac{\partial v_\phi}{\partial \phi} + \frac{v_\phi v_r}{r} + \frac{v_\theta v_\phi \cot \theta}{r} \\ = g \phi - \frac{1}{r \rho \sin \theta} \frac{\partial \rho}{\partial \phi} + \frac{\mu}{\rho} \left\{ \frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial v_\phi}{\partial r} \right) + \frac{1}{r^2 \sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial v_\phi}{\partial \theta} \right) \right. \\ \left. + \frac{1}{r^2 \sin \theta} \frac{\partial^2 v_\phi}{\partial \phi^2} - \frac{v_\phi}{r^2 \sin^2 \theta} + \frac{2}{r^2 \sin \theta} \frac{\partial v_r}{\partial \phi} + \frac{2 \cot \theta}{r^2 \sin \theta} \frac{\partial v_\phi}{\partial \phi} \right\} \end{aligned} \quad (\text{L})$$

Equation of motion for ideal fluids

Very often, the fluids are classified into two categories—ideal and non-ideal. Ideal fluids are those for which viscosity $\mu = 0$. They are also known as *in viscid fluids*. Fluids for which the viscosity is not zero are known as *non-ideal fluids*.

In the case of ideal fluids, where $\mu = 0$, the Navier-Stokes equation in relation (2.74) is modified to

$$\rho \frac{D\mathbf{v}}{Dt} = - \nabla P + \rho \mathbf{g} \quad (2.76)$$

This modified equation of motion is known as *Euler's equation*. Although, strictly speaking, no fluid can be considered to be ideal, yet in some practical cases, particularly while considering fluid flow away from the container or vessel walls, such an assumption may be justified. Examples of such situations in metallurgy can be found in the case of large furnaces like reverberatory furnaces and twin-hearth furnaces or for flow near the tap-holes of large furnaces and ladles. In all these cases, Euler's equation can be applied.

Equation of motion for turbulent flow

The basic parameters of turbulent flow such as the time average velocity \bar{v}_x and the fluctuating component v'_x along the x -direction (Fig. 2.1) were introduced in Section 2.1, to explain the nature of such flow. While considering the equation of motion for turbulent flow, the velocity components v_x , v_y and v_z for streamline flow will not be applicable for turbulent flow since the velocity now will change with time. Thus, the original Navier-Stokes equation has to be modified by substituting the equations for v_x , v_y and v_z in terms of \bar{v}_x , \bar{v}_y , \bar{v}_z and v'_x , v'_y and v'_z . We, therefore, have for the x -component, the following form:

$$\begin{aligned} \rho \frac{D\bar{v}_x}{Dt} &= - \left[\frac{\partial(\rho \bar{v}_x v'_x)}{\partial x} + \frac{\partial(\rho v'_x v'_y)}{\partial y} + \frac{\partial(\rho v'_x v'_z)}{\partial z} \right] \\ &\quad - \frac{\partial P}{\partial x} + \rho g_x + \mu \left[\frac{\partial^2 \bar{v}_x}{\partial x^2} + \frac{\partial^2 \bar{v}_x}{\partial y^2} + \frac{\partial^2 \bar{v}_x}{\partial z^2} \right] \end{aligned} \quad (2.77)$$

where

$$\overline{v'_x v'_x} = \frac{1}{t_0} \int_0^{t_0} (v'_x)^2 dt \quad (2.78)$$

$$\overline{v'_x v'_y} = \frac{1}{t_0} \int_0^{t_0} v'_x v'_y dt \quad (2.79)$$

and

$$\overline{v'_x v'_z} = \frac{1}{t_0} \int_0^{t_0} v'_x v'_z dt \quad (2.80)$$

A comparison of Eq. (2.77) for turbulent flow with Eq. (2.71) for laminar flow shows that, apart from replacement of velocities and pressure by time average velocities and pressure, we get new terms associated with fluctuations in the equation of motion for turbulent flow. These terms, viz. $v'_x v'_x$, $v'_x v'_y$, etc. are usually known as *Reynolds or turbulent stresses* and denoted in general, by the relation

$$\bar{\tau}_{ij} = - \rho \overline{v'_i v'_j} \quad (2.81)$$

where i and j represent any two of the three directions x -, y -, and z -. The nine terms thus obtained constitute the components of turbulent stress tensor.

According to Boussinesq,¹ these stresses can be written in the following form, in analogy to Newton's law of viscosity (Section 2.2)

$$\bar{\tau}_{ij} = - \mu_t \frac{\partial \bar{v}_j}{\partial i} \quad (2.82)$$

where μ_t , is known as the *turbulent coefficient of viscosity* or *eddy viscosity*. Combining Eqs. (2.81) and (2.82) with Eq. (2.77), we get for the x -component the equation

$$\begin{aligned} \rho \frac{D \bar{v}_x}{Dt} &= \mu_t \left(\frac{\partial^2 \bar{v}_x}{\partial x^2} + \frac{\partial^2 \bar{v}_x}{\partial y^2} + \frac{\partial^2 \bar{v}_x}{\partial z^2} \right) - \frac{\partial P}{\partial x} + \rho g_x + \\ &\quad \mu \left(\frac{\partial^2 \bar{v}_x}{\partial x^2} + \frac{\partial^2 \bar{v}_x}{\partial y^2} + \frac{\partial^2 \bar{v}_x}{\partial z^2} \right) \end{aligned} \quad (2.83)$$

Considering the other two directions and combining the terms in Eq. (2.83), we get in vectorial form the relation

$$\rho \frac{D \mathbf{v}}{Dt} = - \nabla P + \rho \mathbf{g} + (\mu + \mu_t) \nabla^2 \mathbf{v} \quad (2.84)$$

This is, therefore, the equation of motion for turbulent flow. Comparing this with the Navier–Stokes Eq. (2.75) for the equation of motion for laminar flow, it can be seen that the term $\mu_t \nabla^2 \mathbf{v}$ is the additional term in the case of turbulent flow.

Different models have been proposed by various authors to calculate the value of μ_t , which help in obtaining the velocity profiles for turbulent flow. Details of such models are beyond the purview of this book. However, a brief outline of the most widely used model suggested by Prandtl² may not be out of place. This is known as *Prandtl's mixing length theory* in which he proposed that the broken streamlines in the case of turbulent flow, which may be called eddies, move about in the fluid in the same way as molecules do in a gas. Thus, a characteristic length, termed as mixing length, l , may play a similar role for the eddies for the transmittance of turbulent stresses as done by the parameter *mean free path* for interpreting the viscosity of gases.

¹ T.V. Boussinesq, *Mem. Pres. Dev. Sev.*, Paris, 23 (1877).

² L. Prandtl, *Z. Angew. Math. Mech.*, 5: 136 (1925).

Prandtl further suggested that the turbulent stress may be given by

$$\tau_{xy} = - \rho \left(l \frac{d\bar{v}}{dy} \right)^2 \quad (2.85)$$

and that

$$l = Ky \quad (2.86)$$

where K is a universal constant. With the help of these two equations, it would be possible to obtain velocity profiles for turbulent flow in different configurations.

2.3.3 Applications of Differential Balance Equations

These equations are commonly applied to systems which have predominantly laminar flow with low values of Reynolds number. Some of the applications, such as in the case of flow through pipes and for viscosity measurements by different methods, have been discussed in the next few sections as illustrative examples. Some more applications have been shown in the chapter on Boundary Layer Theory.

Laminar flow through a pipe

For the sake of simplicity, we may consider the laminar flow of an incompressible fluid of constant viscosity through a horizontal cylindrical pipe of radius R under the steady state condition (Fig. 2.11). A length L of the pipe may be considered, for which the initial and final pressures are P_1 and P_2 ($P_2 > P_1$) respectively. This length of pipe may be assumed to be very far away from the entrance or exit points for the fluid in the pipe, so that the flow may be considered as fully-developed as is explained below. This gives rise to the parabolic velocity profile for the laminar flow as shown in the figure. It may be mentioned that, near the entrance and the exit points, the effect of the viscosity at the wall alters the velocity profile in such a way that it is no longer parabolic in nature. The velocity may rapidly change from zero at the wall to a maximum value a short distance away from it, which is maintained for a larger part of the

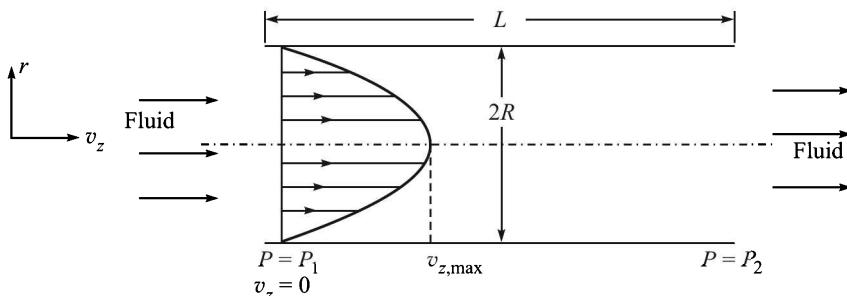


Fig. 2.11 Viscous flow through a capillary.

cross-section. Such terminal flow patterns are not considered fully developed, whereas away from the terminal points, the flow is fully developed. At the entrance end, the flow is sometimes said to be *developing flow*.

If the fluid flow is considered in the z -direction along the pipe and v_z is the velocity of the fluid at a distance r from the centre, then $v_z = 0$ at $r = R$ (at the wall) and $v_z = v_z \text{ max}$ at $r = 0$ (at the centre). The continuity equation in cylindrical coordinates, i.e. Eq. (2.45), for steady state flow in this case reduces to

$$\frac{\partial v_z}{\partial z} = 0 \quad (2.87)$$

and the equation of motion in the axial direction in this case, i.e. Eq. (F) in Section 2.3.2 with the help of Eq. (2.87), takes the form

$$\frac{P_1 - P_2}{L} = \frac{\mu}{\pi r} \frac{\partial}{\partial r} \left(r \frac{\partial v_z}{\partial r} \right) \quad (2.88)$$

where μ is the viscosity of the fluid. Integration of the above equation gives

$$v_z = - \frac{P_1 - P_2}{\mu L} + \frac{r^2}{4} + C_1 \ln r + C_2 \quad (2.89)$$

$$\frac{\partial v_z}{\partial r} = - \frac{P_1 - P_2}{\mu L} \frac{r}{2} + \frac{C_1}{\pi r} \quad (2.90)$$

where C_1 and C_2 are constants of integration. The values of C_1 and C_2 can be obtained by applying the following boundary conditions:

$$(i) \quad v_z = 0 \quad \text{at} \quad r = R \quad (2.91)$$

$$(ii) \quad \frac{\partial v_z}{\partial r} = 0 \quad \text{at} \quad r = 0 \quad (2.92)$$

Substitution of these values in Eqs. (2.89) and (2.90) gives as the following values

$$C_1 = 0 \quad \text{and} \quad C_2 = \frac{P_1 - P_2}{\mu L} \frac{R^2}{4}$$

Hence Eq. (2.89) takes the form

$$v_z = \frac{(P_1 - P_2)}{4\mu L} (R^2 - r^2) \quad (2.93)$$

The volumetric flow rate Q through the pipe will be given by the equation

$$\begin{aligned} Q &= \int_0^R (2\pi r v_z) dr \\ &= \int_0^R \frac{(P_1 - P_2)}{4\mu L} (R^2 - r^2) (2\pi r) dr \\ &= \frac{(P_1 - P_2)\pi R^4}{8\mu L} \end{aligned} \quad (2.94)$$

This equation is generally known as the *Hagen-Poiseuille equation*. It can also be used to determine the viscosity μ of the fluid by rearranging the terms such that

$$\mu = \frac{(P_1 - P_2) \pi R^4}{8 L Q} \quad (2.95)$$

This method of viscosity determination is referred to as the *capillary method*, where μ can be determined when the other parameters are experimentally obtained. The application of Eqs. (2.94) and (2.95) will be shown through some examples. It may be emphasized that these equations are applicable only under the following conditions which are implicit in their derivations.

- (i) The flow should be continuous and laminar.
- (ii) The viscosity of the fluid does not change with velocity or, in other words, the flow is Newtonian.
- (iii) The fully developed steady state flow is maintained in the portion of the pipe under consideration. This has been estimated to hold for pipe lengths above the value of $(0.07 R N_{Re})$ where R is the radius of the pipe.

EXAMPLE 2.4 Calculate the viscosity of a fluid flowing with laminar flow at the rate of 380 cm^3 per minute in a capillary of diameter 75 mm , given that the pressure drop over a length of 300 m of the capillary is $1.41 \times 10^5 \text{ Pa}$.

Solution The given data is

$$\text{Volume flow rate, } Q = \frac{380}{10^6 \times 60} \text{ m}^3 \text{ s}^{-1}$$

$$\text{Radius of the capillary, } R = \frac{75}{2 \times 1000} \text{ m}$$

$$\text{Length of the capillary, } L = 300 \text{ m}$$

$$\text{Pressure drop } (P_1 - P_2) = 1.41 \times 10^5 \text{ Pa}$$

Using Eq. (2.95), the viscosity μ is obtained as

$$\begin{aligned} \mu &= \frac{(P_1 - P_2) \pi R^4}{8 L Q} \\ &= \frac{1.41 \times 10^5 \times \left(\frac{75}{2 \times 1000} \right)^4 \times \frac{22}{7}}{8 \times 300 \times \frac{380}{10^6 \times 60}} \\ &= 57.6 \text{ kg m}^{-1} \text{ s}^{-1} = 5.76 \times 10^2 \text{ poise} \end{aligned} \quad \text{Ans.}$$

Viscosity determination by Stokes' method

In this method, a solid spherical ball is allowed to fall in a fluid, the viscosity of which is to be determined so that the velocity of the fluid dragged adjacent to the moving ball remains laminar. By noting the distance travelled by the ball in a given time, its velocity is determined, from which the viscosity can be calculated by using Stokes' equation which is derived as follows.

Consider a sphere of radius R around which a fluid flows in a streamline motion at a terminal velocity v_∞ . Using the basic concepts, and the mathematical treatment considered beyond the scope of the present work, the shear stress $\tau_{r\theta}$ and the pressure distribution P_r around the sphere can be shown to be given by the equations

$$\tau_{r\theta} = \frac{3}{2} \frac{\mu v_\infty}{R} \left(\frac{R}{r} \right)^4 \sin \theta \quad (2.96)$$

$$P_r = P_0 - \rho_l g z - \frac{3}{2} \mu v_\infty \left(\frac{R}{r} \right)^2 \cos \theta \quad (2.97)$$

where R is the radius of the sphere, r is the radial distance from the centre of the sphere inside the liquid, v_∞ is the terminal velocity, z is the height equal to $R \cos \theta$ above a datum line, θ is the angle the radial direction makes with vertical axis, P_r is the pressure at distance r , P_0 is the pressure far away from the sphere on the plane at $z = 0$, ρ_l is the density of the fluid, and g is the acceleration due to gravity.

Therefore, at the surface of the sphere, i.e. for $r = R$, the equations for these quantities will take the forms

$$\tau_{R\theta} = \frac{3}{2} \frac{\mu v_\infty}{R} \sin \theta \quad (2.98)$$

$$P_R = P_0 - \rho_l g R \cos \theta - \frac{3}{2} \mu v_\infty \cos \theta \quad (2.99)$$

The total tangential force F_T acting on the sphere because of shear stress will be given by the relation

$$\begin{aligned} F_T &= \int_0^{2\pi} \int_0^\pi \tau_{R\theta} R^2 \sin \theta d\theta d\phi \\ &= \int_0^{2\pi} \int_0^\pi \frac{3}{2} \mu v_\infty R^2 \sin^2 \theta d\theta d\phi \\ &= 4\pi \mu R v_\infty \end{aligned} \quad (2.100)$$

where ϕ is the angle which the projection of r on the horizontal plane passing through the centre of the sphere makes with the y -axis. Similarly, the total normal force F_N acting on the sphere will be given by the relation

$$\begin{aligned}
F_N &= \int_0^{2\pi} \int_0^\pi P_R R^2 \sin \theta d\theta d\phi \\
&= \int_0^{2\pi} \int_0^\pi (P_0 - \rho_l g R \cos \theta - \frac{3}{2} \mu v_\infty \cos \theta) R^2 \sin \theta d\theta d\phi \\
&= \frac{4}{3} \pi R^3 \rho_l g + 2\pi \mu R v_\infty
\end{aligned} \tag{2.101}$$

Thus, the total fluid force acting on the sphere is

$$F_f = F_T + F_N = \frac{4}{3} \pi R^3 \rho_l g + 6\pi \mu v_\infty R \tag{2.102}$$

The first term on the right-hand side of Eq. (2.102) represents the buoyant force and the second term the kinetic or frictional or drag force, designated by the symbol F_k . Thus

$$F_k = 6\pi \mu v_\infty R \tag{2.103}$$

The above relation for the drag or viscous resistance of the liquid is referred to as *Stokes' law*.

Apart from the above two forces exerted by the fluid, there is an additional force because of the falling motion of the sphere of density ρ_s , namely the gravitational force F_g given by the equation

$$F_g = \frac{4}{3} \pi R^3 \rho_s g \tag{2.104}$$

Of the different forces, the gravitational and buoyant forces are independent of the velocity of the moving sphere, but the drag or viscous force increases with an increase in the velocity of the sphere and when the sphere has attained the terminal velocity, we get the following relationship from the force balance expression

$$F_g = F_f \tag{2.105}$$

which, on substitution of values from Eqs. (2.97) and (2.104) yields

$$\frac{4}{3} \pi R^3 \rho_s g = \frac{4}{3} \pi R^3 \rho_l g + 6\pi \mu v_\infty R$$

or

$$\mu = \frac{2(\rho_s - \rho_l) R^2 g}{9v_\infty} \tag{2.106}$$

Thus from our knowledge of the radius R of the sphere, the terminal velocity v_∞ , and the densities ρ_s , and ρ_l of the solid sphere and the fluid respectively, we can determine the viscosity. Conversely, the terminal velocity v_∞ of the particle can be calculated when all the other parameters including the viscosity μ of the fluid are known.

EXAMPLE 2.5 During deoxidation of liquid steel in a furnace, the time taken for alumina deoxidation products of radius 10^{-3} cm to rise through 40 cm of the liquid steel bath is 12 minutes. Calculate the viscosity of liquid steel, given that the densities of liquid steel and the deoxidation product are 7000 and 2800 kg m^{-3} respectively and g equals 9.81 m s^{-2} .

Solution Here, since the density of the solid is less than that of the liquid, the former will rise and not fall.

$$\text{Rate of rise, } v_{\infty} = \frac{\text{distance}}{\text{time}} = \frac{40}{100 \times 12 \times 60} \text{ m s}^{-1}$$

$$\text{Radius of the solid, } R = \frac{10^{-3}}{10^2} = 10^{-5} \text{ m}$$

$$\text{Density of the liquid, } \rho_l = 7000 \text{ kg m}^{-3}$$

$$\text{Density of the solid, } \rho_s = 2800 \text{ kg m}^{-3}$$

$$\text{Acceleration due to gravity, } g = 9.81 \text{ m s}^{-2}$$

Using Eq. (2.106) in a slightly modified form, the viscosity of liquid steel is obtained as

$$\begin{aligned} \mu &= \frac{2(\rho_l - \rho_s)R^2g}{9v_{\infty}} \\ &= \frac{2(7000 - 2800)(10^{-5})^2 \times 9.81}{9 \times \frac{40}{100 \times 12 \times 60}} \\ &= \frac{2 \times 4200 \times 10^{-10} \times 9.81 \times 100 \times 12 \times 60}{9 \times 40} \\ &= 1.65 \times 10^{-3} \text{ kg m}^{-1} \text{ s}^{-1} = 1.65 \times 10^{-2} \text{ poise} \quad \text{Ans.} \end{aligned}$$

Viscosity determination by concentric cylinder method

In this method, the fluid, the viscosity of which is to be determined, is filled between two concentric cylinders. One of these cylinders, either the inner or the outer, is made to rotate at a slow speed to generate laminar flow inside the fluid. The value of the viscosity of the fluid is calculated from experimental determination of the torque required to rotate the cylinders at a desired speed. For arriving at the equation used for calculation, we assume that the outer cylinder having a radius R_o is rotated at a speed of W revolutions per unit time and the inner cylinder of radius R_i is kept stationary as shown in Fig. 2.12. We further assume that the rotation causes a laminar angular velocity inside the fluid. If $v_{r\theta}$ is the angular velocity at a radius r from the centre of the inner cylinder, then the liquid will evidently follow the two boundary conditions given below.

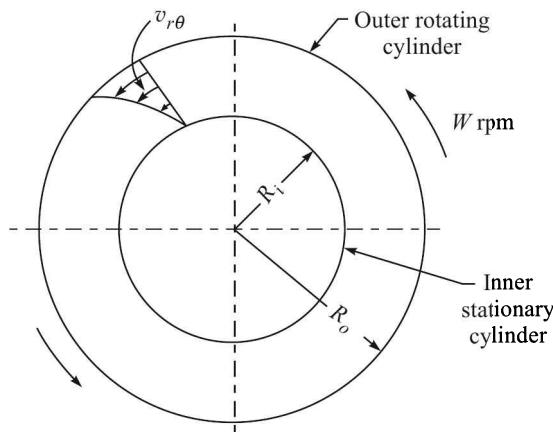


Fig. 2.12 Viscosity determination by concentric cylinder method.

$$\begin{aligned}v_{r\theta} &= 0 \quad \text{at} \quad r = R_i \\v_{r\theta} &= 2\pi WR_o \quad \text{at} \quad r = R_o\end{aligned}$$

Further, the equation of motion in an angular direction for an incompressible fluid under steady state conditions Eq. (D) (Section 2.3.2) will take the form

$$\frac{d}{dr} \left[\frac{1}{r} \frac{\partial}{\partial r} (r v_{r\theta}) \right] = 0 \quad (2.107)$$

This equation on integration and with the help of the boundary conditions specified above will yield

$$v_{r\theta} = \frac{2\pi W R_o^2 (r^2 - R_i^2)}{(R_o^2 - R_i^2)r} \quad (2.108)$$

Further, the shear stress distribution inside the liquid for the present case is given by the equation

$$\begin{aligned}\tau_{r\theta} &= -\mu r \frac{\partial}{\partial r} \left(\frac{v_{r\theta}}{r} \right) \\&= -\mu r \frac{\partial}{\partial r} \left[\frac{2\pi W R_o^2 (r^2 - R_i^2)}{(R_o^2 - R_i^2)r^2} \right] \\&= -\mu \left(\frac{2\pi W R_o^2}{R_o^2 - R_i^2} \right) \left(\frac{2R_i^2}{r^2} \right) \quad (2.109)\end{aligned}$$

Therefore, the shear force $\tau_{R_o\theta}$, at the outer cylinder, will be given by the equation

$$\tau_{R_o\theta} = + \frac{4\pi\mu W R_i^2}{R_o^2 - R_i^2} \quad (2.110)$$

If L be the length of the cylinders, the torque, τ will be given by the equation

$$\tau = \frac{4\pi\mu WR_i^2 L}{R_o^2 - R_i^2} \quad (2.111)$$

Hence

$$\mu = \frac{\tau(R_o^2 - R_i^2)}{4\pi W R_i^2 L} \quad (2.112)$$

Thus, from our knowledge of the radii of the outer and inner cylinders, their lengths, speed of rotation and torque, we can calculate the viscosity of the fluid as illustrated by the following example.

EXAMPLE 2.6 Calculate the viscosity of a liquid blast furnace slag based on the concentric cylinder method, given that the outside and inside radii of the graphite cylinders used are 4 and 3 cm, respectively, the length of the cylinders is 8 cm, the speed of rotation of the outer cylinder is 5 revolutions per second and the torque is 22.5 J.

Solution The outside radius, $R_o = \frac{4}{100}$ m

The inside radius, $R_i = \frac{3}{100}$ m

Length of the cylinders, $L = \frac{8}{100}$ m

Speed of rotation, $W = 5$ rps

Torque involved, $\tau = 22.5$ J

Using Eq. (2.112), we have

$$\begin{aligned} \mu &= \frac{\tau(R_o^2 - R_i^2)}{4\pi W R_i^2 L} \\ &= \frac{22.5 \times \left[\left(\frac{4}{100} \right)^2 - \left(\frac{3}{100} \right)^2 \right]}{4\pi \times 5 \left(\frac{3}{100} \right)^2 \left(\frac{8}{100} \right)} \\ &= \frac{22.5 \times \frac{7}{(100)^2}}{4\pi \times 5 \left(\frac{3}{100} \right)^2 \times \left(\frac{8}{100} \right)} \\ &= \frac{22.5 \times 7 \times 100}{4 \times \pi \times 5 \times 9 \times 8} \\ &= 3.48 \text{ kg m}^{-1} \text{ s}^{-1} = 34.8 \text{ poise} \quad \text{Ans.} \end{aligned}$$

Apart from the types of viscometers described above, there is one more type called the oscillating type. The treatment of such viscometers is beyond the scope of the present text.

2.4 OVERALL OR MACROSCOPIC BALANCE

In Section 2.3, mass and momentum balance relationships were derived by considering an infinitesimal volume element (control volume) of the flowing fluid. Such an analytical approach is referred to as a microscopic approach. The main drawback of such a rigorous approach is that it involves highly complex mathematics. Since the control volume is located away from the boundaries of the flowing fluid, the solution of the differential equations involved, for obtaining parameters such as total flow rate or pressure difference for the entire system, requires accurate specification of the boundary conditions of the system. Apart from this, the microscopic approach is generally valid for laminar flow and for restricted geometries only. In turbulent flow and for complex geometries, the rigorous analytical approach is found to be deficient, since a certain amount of empiricism has to be incorporated in such cases. In many practical cases such as flow of liquid metal in ladles, tundishes or launders or the working of different flow meters, it is much more convenient to consider the macroscopic mass, momentum and energy balances for the entire system by taking into account the conditions at the inlet and outlet ends of the system. Such an approach involves much less mathematical manipulation, but may provide less detailed information about the system. To make these results more meaningful, it is invariably necessary to use empirical relationships which are specific for each of the systems under consideration. In the following sections, equations for overall mass, momentum and energy balances will be derived and a few of their applications illustrated.

2.4.1 Overall Mass Balance

For the derivation of an equation for overall mass balance, we consider a reactor, as shown in Fig. 2.13, having A_e and A_{ex} as the inlet and outlet cross-sectional areas, respectively, normal to the direction of fluid flow. Application of the law of conservation of mass to inlet and outlet streams leads to the following relation.

$$\begin{aligned} & [(\text{Amount of fluid entering reactor per unit time}) \\ & \quad - (\text{Amount of fluid leaving reactor per unit time})] \\ & = [(\text{Amount of fluid reacted inside reactor per unit time}) \\ & \quad + (\text{Amount of fluid retained in reactor per unit time})] \end{aligned} \quad (2.113)$$

Amount of fluid entering reactor per unit time

$$= \rho_e v_e A_e \quad (2.114)$$

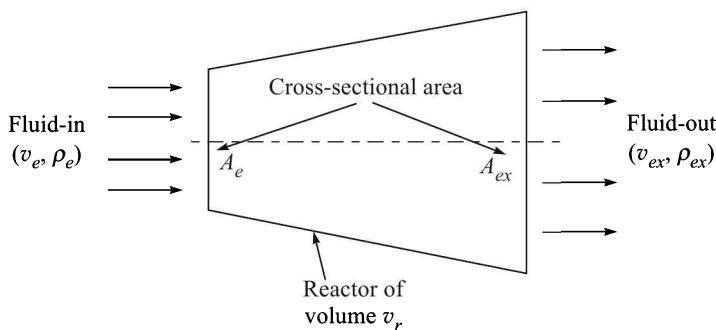


Fig. 2.13 Overall mass balance for a reactor.

Amount of fluid leaving reactor per unit time

$$= \rho_{ex} v_{ex} A_{ex} \quad (2.115)$$

where ρ_e and ρ_{ex} and v_e and v_{ex} are respectively the densities and velocities of the fluid entering and leaving the reactor. Further

$$\text{Amount of fluid retained in reactor} = V_r \frac{\partial \rho}{\partial t} \quad (2.116)$$

where V_r is the volume of the reactor and $\frac{\partial \rho}{\partial t}$ the rate of change of density of the stream with time. If R_f is the amount of fluid reacted per unit time per unit volume of the reactor, then

$$\text{Total fluid reacted per unit time} = V_r R_f \quad (2.117)$$

Substitution of Eqs. (2.114) to (2.117) in Eq. (2.113) leads to the relation

$$\rho_e v_e A_e - \rho_{ex} v_{ex} A_{ex} = V_r \left(\frac{\partial \rho}{\partial t} + R_f \right) \quad (2.118)$$

We can write the above equation in the following alternative form:

$$\delta(\rho v A) + V_r \left(\frac{\partial \rho}{\partial t} + R_f \right) = 0 \quad (2.119)$$

where $\delta(\rho v A)$ represents the difference in mass flow rates of the fluid in the outlet and inlet streams. In the case of a multicomponent fluid, the above equation is applicable to each of the components.

In a number of cases, Eq. (2.119) is applied to a differential element of length along the direction of flow of the fluid considering the entire cross-section of the reactor. This procedure is commonly adopted for modelling fixed-bed type fluid-solid reactors, e.g. for modelling of blast furnace and shaft reactor processes as well as leaching of ion-exchange processes. This type of application is explained by the following example:

EXAMPLE 2.7 Molten steel is teemed from a ladle through a 5 cm diameter nozzle at its bottom. If the volume of the molten steel in the beginning is 2 m³ and the linear velocity of discharge is 90 cm per second, calculate the time required to empty the ladle.

Solution The mass balance relationship as shown in Eq. (2.118) is to be modified in this case as no fluid is entering the ladle, nor is any reacting inside it. Thus

$$P_e v_e A_e = 0, \quad R_f = 0$$

Besides, the density of the fluid may be taken as constant so that the expression for the amount of fluid retained in the reactor per unit time may be given by $(dV_r/dt)\rho$, where V_r is the volume of the fluid and ρ the density. Thus, Eq. (2.118) becomes

$$-\rho v_{ex} A_{ex} = \frac{dV_r}{dt} \rho$$

or

$$dV_r = -v_{ex} A_{ex} dt$$

Integrating between $t = 0$ and $t = t$, where $V_r = V_r$ and $V_r = 0$, respectively, we get

$$V_r = v_{ex} A_{ex} t$$

or

$$t = \frac{V_r}{v_{ex} A_{ex}}$$

From the data given

$$\begin{aligned} V_r &= 2 \text{ m}^3 \\ v_{ex} &= 90 \text{ cm s}^{-1} = 0.9 \text{ m s}^{-1} \end{aligned}$$

$$A_{ex} = \frac{\pi}{4} \left(\frac{5}{100} \right)^2 \text{ m}^2$$

Therefore,

$$\begin{aligned} t &= \frac{2 \times 4 \times 10000}{0.9 \times \pi \times 25} \text{ s} \\ &= 1131.3 \text{ s} \\ &= 18.85 \text{ min} \end{aligned}$$

Ans.

2.4.2 Overall Momentum Balance

As in the case of differential momentum balance, overall momentum balance is based on Newton's second law of motion which can be expressed for a flowing system as follows:

$$[(\text{Amount of momentum input in system per unit time}) - (\text{Amount of momentum output from system per unit time})] = [(\text{Rate of change of momentum in system}) - (\text{Forces acting on system})] \quad (2.120)$$

In order to express the above equation in mathematical form, we consider a reactor having A_i and A_o as the inlet and outlet cross-sectional areas respectively. Let a fluid with densities ρ_i and ρ_o at inlet and outlet ends flow through the reactor at average inlet and outlet velocities \bar{v}_i and \bar{v}_o . If the x -component of the average inlet and outlet velocities are $\bar{v}_{i,x}$ and $\bar{v}_{o,x}$, respectively, then the momentum in the x -direction or the x -momentum entering the reactor will be $(\rho_i \bar{v}_i A_i) \bar{v}_{i,x}$ and that leaving the reactor will be $(\rho_o \bar{v}_o A_o) \bar{v}_{o,x}$. The rate of change of the x -momentum in the reactor can be expressed mathematically as $\partial(\rho_r V_r v_x)/\partial t$, where ρ_r is the average density of the fluid in the reactor and V_r is the volume of the reactor.

Finally, the forces acting on the fluid can be divided into three categories: (i) the force due to fluid pressure difference at the inlet and the outlet, (ii) the force due to gravitational component in the x -direction, and (iii) the frictional force denoted by F_x , in the x -direction, because of the interaction of the fluid with the surface of the reactor or any other surface due to the solids present in the reactor. Details of this frictional force F_x are discussed in the next section. Forces due to tangential and normal stresses in the fluid have been neglected. Thus, the sum of all the forces will be $\{F_x - \rho_r V_r g_x + (P_o A_o - P_i A_i)\}$, where g_x is the x -component of the acceleration due to gravity and P_o and P_i are the pressures at the outlet and inlet of the reactor respectively.

Substitution of the various terms in Eq. (2.120) in mathematical form leads to the following equation for overall momentum balance:

$$\frac{\partial(\rho_r V_r v_x)}{\partial t} = \{(\rho_i v_i A_i) \bar{v}_{i,x} - (\rho_o \bar{v}_o A_o) \bar{v}_{o,x}\} + (P_i A_i - P_o A_o) + \rho_r V_r g_x - F_x \quad (2.121)$$

The above equation can also be written in the following alternative form in terms of mass flow rates:

$$\frac{\partial(m_r v_r)}{\partial t} = \{(G_i \bar{v}_{i,x}) - (G_o \bar{v}_{o,x})\} + (P_i A_i - P_o A_o) + m_r g_x - F_x \quad (2.122)$$

where m_r is the mass of the fluid in the reactor and G_i and G_o are the mass flow rates at the inlet and outlet respectively. For a reactor operating under steady state, we have

$$\frac{\partial(m_r v_r)}{\partial t} = 0 \quad (2.123)$$

Hence, in this case, the momentum balance equation takes the form

$$\{(G_i \bar{v}_{i,x}) - (G_o \bar{v}_{o,x})\} + (P_i A_i - P_o A_o) + m_r g_x - F_x = 0 \quad (2.124)$$

An application of Eq. (2.124) is illustrated by the following example:

EXAMPLE 2.8 Derive an expression for the terminal velocity of a solid sphere falling through a liquid assuming that Stokes' law holds good for the system.

Solution A solid sphere falling through a liquid attains terminal velocity, denoted by v_∞ , when it reaches a steady state. Thus, Eq. (2.124) will hold good for the sphere. Further, as the velocity and mass of the sphere do not change during its fall, there is no change of momentum. Hence, Eq. (2.124) takes the following form for this system:

$$(P_i A_i - P_o A_o) + \frac{4}{3} \pi r^3 \rho_s g - F_x \quad (\text{Ex. 2.8.1})$$

where r is the radius of the sphere and ρ_s its density. According to Stokes' law, Eq. (2.103), the frictional force is

$$F_x = 6\pi r \mu v_\infty \quad (\text{Ex. 2.8.2})$$

and the term $(P_i A_i - P_o A_o)$ is equal to the buoyant force exerted by the fluid on the sphere and is therefore given by the equation

$$(P_i A_i - P_o A_o) = - \frac{4}{3} \pi r^3 \rho_l g \quad (\text{Ex. 2.8.3})$$

where ρ_l is the density of the liquid. Substitution of Eqs. (Ex. 2.8.2) and (Ex. 2.8.3) in Eq. (Ex. 2.8.1), yields

$$\frac{4}{3} \pi r^3 g (\rho_s - \rho_l) = 6\pi r \mu v_\infty$$

Hence

$$v_\infty = \frac{2}{9} \frac{\pi^2 g (\rho_s - \rho_l)}{\mu} \quad \text{Ans.} \quad (\text{Ex. 2.8.4})$$

In the case $\rho_s \gg \rho_l$, we get

$$v_\infty \approx \frac{2}{9} \frac{\pi^2 g \rho_s}{\mu} \quad \text{Ans.} \quad (\text{Ex. 2.8.5})$$

Friction factor

For application of Eqs. (2.122) and (2.124), we require a knowledge of F_x . For most industrial systems, F_x is not amenable to theoretical calculations. Therefore, it is determined from experimental data on the fluid flow under simulated industrial conditions.

An analysis of the available experimental data on fluid flow in various systems has shown that the frictional force F_x acting at the interface between the fluid and the solid surface is directly proportional to the product of the average kinetic energy per unit volume, i.e. $(\bar{\rho} \bar{v}^2)/2$ of the fluid and the solid. Thus, we can write the following equation for frictional force:

$$F_x = f_{fr} \left(\frac{1}{2} \bar{\rho} \bar{v}^2 \right) A \quad (2.125)$$

The constant of proportionality, f_{fr} , in the above equation is known as *friction factor* in cases in which the fluid is surrounded by the solid surface (e.g. for flow through a pipe) and as *drag coefficient* for submerged solids or gas bubbles. It may be pointed out that Eq. (2.125) does not form the statement of a law, but serves as a mathematical statement for the definition of the friction factor or drag coefficient. It has been experimentally observed that in the case of smooth surfaces, which are of interest in metallurgical systems, friction factor is only a function of Reynolds number. In the following subsections, the experimental data on friction factor or drag coefficient is summarized for the systems that are important from the point of view of the study of metallurgical processes.

Friction factor for flow through smooth pipes. Friction factor for flow through smooth pipes is calculated using data found experimentally on pressure drop during flow across a known length under steady state conditions and subsequent application of Eqs. (2.122) and (2.125). For the statement of expressions for friction factors, the flow can be divided into three regions.

Laminar flow region. In this region, signified by a value of Reynolds number below 2100, the friction factor is related to the Reynolds number by the relation

$$f_{fr} = \frac{16}{N_{Re}} \quad (2.126)$$

Transition region. This is signified by Reynolds number varying between 2100 and 3000, and the friction factor in this region is an irregular function of the Reynolds number.

Turbulent flow region. This region is characterized by values of the Reynolds number above 3000 and has been extensively studied. Therefore, a number of relations have been proposed for this region. The important relations often used for such calculations in practice, include the following equations:

(i) The Blasius relation

$$f_{fr} = 0.079 (N_{Re})^{-1/4} \quad (2.127)$$

for $3000 < N_{Re} < 10^5$

(ii) Nikuradse's relation

$$(f_{fr})^{-1/2} = 4.0 \log (N_{Re} f_{fr}^{1/2}) - 0.40 \quad (2.128)$$

(iii) von Karman's relation

$$(f_{fr})^{-1/2} = 4.06 \log (N_{Re} f_{fr}^{1/2}) - 0.6 \quad (2.129)$$

(iv) Drew's relation

$$f_{fr} = 0.0014 + 0.125 (N_{Re})^{-0.32} \quad (2.130)$$

(v) Colburn's relation

$$f_{fr} = 0.023 (N_{Re})^{-1/4} \quad (2.131)$$

All the above relations yield similar results for flows with the Reynolds number varying in the range 3000 to 100,000 but yield slightly different values for the friction factor at higher values of the Reynolds number. The application of the above principle is illustrated by the following example.

EXAMPLE 2.9 Calculate the pressure difference under which 30,000 litres of water flow, under steady state conditions, per hour through a horizontal cylindrical pipe of diameter 20 cm and length 10 m. Assume viscosity of water to be 1 cP, and its density 1 g cm⁻³.

Solution Equation (2.124) for the present case takes the form

$$(P_i - P_o)A - F_x = 0 \quad (\text{Ex. 2.9.1})$$

since

$$G_i = G_o, \quad \bar{v}_{i,x} = \bar{v}_{o,x} \quad \text{and} \quad g_x = 0$$

Here A is the uniform cross-sectional area. Again

$$F_x = f_{fr} \left(\frac{1}{2} \bar{\rho} \bar{v}^2 \right) A_s \quad (\text{Ex. 2.9.2})$$

where A_s = wetted surface. From Eqs. (Ex. 2.9.1) and (Ex. 2.9.2), we have

$$(P_i - P_o)A = f_{fr} \left(\frac{1}{2} \bar{\rho} \bar{v}^2 \right) A_s \quad (\text{Ex. 2.9.3})$$

Now, from the data given

$$\rho = 1 \text{ g cm}^{-3} = 1000 \text{ kg m}^{-3}$$

$$d = 20 \text{ cm} = 0.2 \text{ m}$$

$$v = \frac{30,000 \times 4}{1000 \times 3600 \times \pi \times (0.2)^2} = 0.265 \text{ m s}^{-1}$$

and

$$\mu = 1 \text{ cP} = 10^{-2} \text{ P} = 10^{-3} \text{ kg m}^{-1} \text{ s}^{-1}$$

$$N_{Re} = \frac{\rho v d}{\mu} = \frac{100 \times 0.265 \times 0.2}{10^{-3}} = 53,000$$

$$A_s = 2\pi r l = 2\pi \frac{10}{100} \times 10 = 6.28 \text{ m}^2$$

$$A = \pi r^2 = \pi (0.1)^2 = 0.0314 \text{ m}^2$$

Now, using the Blasius relation of Eq. (2.127), we get

$$f_{fr} = 0.079 (N_{Re})^{-1/4} = 0.079 (53,000)^{-1/4} = 5.2 \times 10^{-3}$$

Substitution of numerical values of various quantities in Eq. (Ex. 2.9.3), yields

$$(P_i - P_o) = \frac{5.2 \times 10^{-3} \times \frac{1}{2} \times 1000 \times (0.265)^2 \times 6.28}{0.0314} = 360 \text{ Pa}$$

Drag coefficient for flow around a sphere. Experimental data on drag coefficient for flow around spheres is expressed graphically in Fig. 2.14. It is seen from this figure that the drag coefficient decreases sharply with increase in values of the Reynolds number in lower ranges and attains a constant value at high values of Reynolds number.

It may be pointed out that a decrease in drag coefficient with increasing Reynolds number does not necessarily mean a decrease in frictional force. In fact, the frictional force increases with an increase in fluid velocity. In order to express the drag coefficient mathematically, the graphical representation depicted in Fig. 2.14 is divided into three regions as follows:

- (i) Stokes' law region—prevailing for values of the Reynolds number below 0.8 and in this range, the drag coefficient C_D is expressed by the relation

$$C_D = \frac{24}{N_{Re}} \quad (2.132)$$

- (ii) The intermediate region—signified by values of the Reynolds number ranging between 0.8 and 500. The drag coefficient in this region is calculated using the relation

$$C_D = \frac{18.5}{(N_{Re})^{3/5}} \quad (2.133)$$

- (iii) Newton's law region—signified by values of the Reynolds number above 500. The drag coefficient in this region can be assumed to be constant and has a value of 0.44. Thus, for this region

$$C_D = 0.44 \quad (2.134)$$

Equations (2.132) to (2.134) are used to calculate the velocities of submerged objects in a fluid. For this purpose, these equations are used in conjunction with Eq. (2.124) or Eq. (2.125), as in the following example.

EXAMPLE 2.10 Prove that, for Stokes' law region, the drag coefficient for flow around a sphere can be calculated using Eq. (2.132) ($C_D = 24/N_{Re}$).

Solution According to Stokes' law

$$F_x = 6\pi r\mu v$$

Also, according to Eq. (2.125)

$$F_x = f_{fr} \left(\frac{1}{2} \bar{\rho} \bar{v}^2 \right) \pi r^2 = C_D \left(\frac{1}{2} \bar{\rho} \bar{v}^2 \right) \pi r^2$$

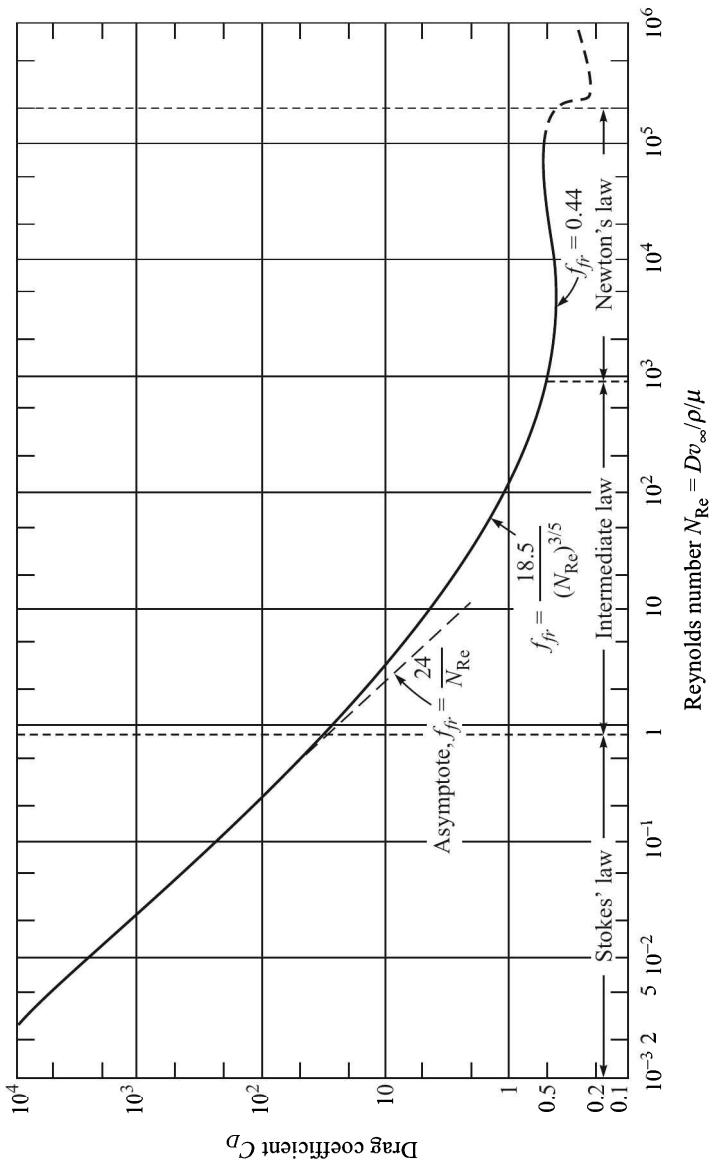


Fig. 2.14 Drag coefficient for flow around spheres.

Hence

$$C_D = \frac{\frac{6\pi r\mu v}{\frac{1}{2}\bar{\rho}\bar{v}^2\pi r^2}}{2} = \frac{12\mu}{\rho v r} = \frac{24\mu}{\rho v d} = \frac{24}{N_{Re}}$$

2.4.3 Overall Mechanical Energy Balance

For deriving the mechanical energy balance equations, we make use of the first law of thermodynamics which, for a system with fluid flow, may be stated as follows:

$$[(\text{Amount of energy entering reactor with fluid per unit time}) - (\text{Amount of energy leaving reactor per unit time})] = [(\text{Rate of change of energy of fluid in reactor}) + (\text{Work done by fluid per unit time on surroundings}) - (\text{Heat absorbed by fluid})] \quad (2.135)$$

In order to arrive at the mathematical formulation of Eq. (2.135) we consider a reactor having A_i and A_o as inlet and outlet cross-sectional areas through which a fluid, with r_i and r_o as inlet and exit densities, is flowing at velocities v_i and v_o at inlet and outlet points. For the present case, the "heat effects" are neglected and the fluid is assumed to have a uniform temperature.

A flowing fluid can carry energy in four forms—potential energy, kinetic energy, internal energy and bulk energy. Thus, for the total specific energy E of the fluid, we have

$$E = \psi + \phi + U + PV \quad (2.136)$$

where ψ is the potential energy, ϕ the kinetic energy and U the internal energy—all per unit mass—and P and V are, as usual, the pressure and specific volume of the fluid.

Hence, for the energy entering the reactor per unit time, we have

$$E_i = (\psi_i + \phi_i + U_i + P_i V_i) \rho_i v_i A_i \quad (2.137)$$

where the subscript 'i' denotes the values of these parameters at the entrance. Similarly, energy leaving the reactor with the fluid per unit time will be

$$E_o = (\psi_o + \phi_o + U_o + P_o V_o) \rho_o v_o A_o \quad (2.138)$$

where the subscript 'o' denotes the corresponding values at the exit end. If W be the work done by the system on the surroundings per unit time per unit mass, we can rewrite Eq. (2.135) in the following alternative form:

$$\begin{aligned} V_r \frac{\partial(E\rho_r)}{\partial t} &= [(\psi_i - \psi_o) + (\phi_i - \phi_o) + (U_i - U_o) \\ &\quad + (P_i V_i - P_o V_o)] \{\rho_o v_o A_o\} - W \rho_o v_o A_o \end{aligned} \quad (2.139)$$

where it has been assumed that no heat is exchanged by the fluid during flow and that the amount of fluid entering the reactor is the same as that leaving it.

Thus, we have

$$\rho_i v_i A_i = \rho_o v_o A_o \quad (2.140)$$

The symbol V_r in Eq. (2.139) refers to the volume of the reactor and ρ_r is the average density of the fluid in the reactor.

We can further simplify Eq. (2.139) with the help of the first law of thermodynamics, which, for a system not involving any heat exchange, can be expressed for finite changes by the following equation:

$$\Delta U = - \int_{V_i}^{V_o} P dV + W_{ir} \quad (2.141)$$

where W_{ir} is the irreversible work done by the fluid.

For an infinitesimal change, Eq. (2.141) can be expressed in the form

$$dU = - P dV + \partial W_{ir} \quad (2.142)$$

Equation (2.139) can now be written as

$$\begin{aligned} \left(\frac{\rho_r V_r}{\rho_o v_o A_o} \right) \left(\frac{\partial E}{\partial T} \right) &= \{ (\psi_i - \psi_o) + (\phi_i - \phi_o) + (U_i - U_o) + (P_i V_i - P_o V_o) - W \} \\ &= [(-\Delta\psi) - (\Delta\phi) - (\Delta U) - \{ \Delta(PV) \} - W] \end{aligned} \quad (2.143)$$

where Δ signifies finite changes of different parameters. In terms of an infinitesimal change, Eq. (2.143) can be written as

$$\begin{aligned} \left(\frac{\rho_r V_r}{\rho_o v_o A_o} \right) \left(\frac{\partial E}{\partial T} \right) &= \{ -d\psi - d\phi - dU - d(PV) - \partial W \} \\ &= \{ -d\psi - d\phi - dU - P dV - V dP - \partial W \} \end{aligned} \quad (2.144)$$

From Eqs. (2.142) and (2.144), we have

$$\left(\frac{\rho_r V_r}{\rho_o v_o A_o} \right) \left(\frac{\partial E}{\partial T} \right) = \{ -d\psi - d\phi + (P dV - \partial W_{ir}) - P dV - V dP - \partial W \}$$

or

$$\left(\frac{\rho_r V_r}{\rho_o v_o A_o} \right) \left(\frac{\partial E}{\partial T} \right) = \{ -d\psi - d\phi - V dP - \partial(W + W_{ir}) \} \quad (2.145)$$

Equation (2.145) is a form of Bernoulli's equation for unsteady state. Under steady state conditions

$$\left(\frac{\partial E}{\partial T} \right) = 0 \quad (2.146)$$

Therefore, for steady state Eq. (2.145) yields Bernoulli's equation

$$d\psi + d\phi + V dP + \partial(W + W_{ir}) = 0 \quad (2.147)$$

In terms of finite changes, this may be expressed as

$$\Delta\psi + \Delta\phi + \int_{P_i}^{P_o} VdP + (W + W_{ir}) = 0 \quad (2.148)$$

Equations (2.147) and (2.148) are widely used in industrial applications such as calculation of pressure drops for fluid flow in reactors. In cases where W , the work done by the system on the surroundings may be taken as zero and W_{ir} may be equated to W_f , the frictional work, we may write Eqs. (2.147) and (2.148) as

$$d\psi + d\phi + VdP + \partial W_f = 0 \quad (2.149)$$

$$\Delta\psi + \Delta\theta + \int_{P_i}^{P_o} VdP + W_f = 0 \quad (2.150)$$

When potential energy (ψ) change is due to only the change in the height h of the fluid, we get

$$dy = gdh \quad (2.151)$$

$$\Delta\psi = g\Delta h \quad (2.152)$$

Again considering the kinetic energy ϕ per unit mass to be $v^2/2$

$$d\phi = \frac{1}{2} d(v^2) = \frac{1}{2} \times 2v dv$$

or

$$d\phi = vdv \quad (2.153)$$

Similarly,

$$\Delta\phi = v\Delta v \quad (2.154)$$

Using Eqs. (2.151) to (2.154), Eqs. (2.149) and (2.150) can be expressed as

$$gdh + vdv + vdP + \partial W_f = 0 \quad (2.155)$$

and

$$g\Delta h + v\Delta v + \int_{P_i}^{P_o} VdP + W_f = 0 \quad (2.156)$$

In order to take into account the variation of velocity from the boundary to the interior of the fluid, a correction factor α is introduced in the kinetic energy term. Hence, Eqs. (2.155) and (2.156) take the form

$$gdh + \frac{1}{\alpha} vdv + VdP + \partial W_f = 0 \quad (2.157)$$

and

$$g\Delta h + \frac{1}{\alpha} v\Delta v + \int_{P_i}^{P_o} VdP + W_f = 0 \quad (2.158)$$

The value of α is 1/2 for laminar flow but approaches 1 for turbulent flow. Equation (2.157) can also be written in the integrated form

$$gh + \frac{v^2}{2\alpha} + VP + W_f = \text{constant} \quad (2.159)$$

Since V , the specific volume, is equal to $1/\rho$, where ρ is the density, we get

$$gh + \frac{v^2}{2\alpha} + \frac{P}{\rho} + W_f = \text{constant} \quad (2.160)$$

Equations (2.158) and (2.160) are useful forms of the energy balance equation which can be applied to different situations as shown by the following examples. Equation (2.160) is the common form of *Bernoulli's equation*.

EXAMPLE 2.11 Derive an expression for overall mechanical energy balance for steady state flow of an incompressible fluid through a smooth cylindrical pipe.

Solution For an infinitesimal volume element across the entire section perpendicular to the direction of flow, we can use Eq. (2.157), i.e.

$$gdh + \frac{1}{\alpha} vdv + VdP + \partial W_f = 0 \quad (\text{Ex. 2.11.1})$$

For turbulent flow, $\alpha = 1$. So, we get

$$gdh + vdv + VdP + \partial W_f = 0 \quad (\text{Ex. 2.11.2})$$

For the case of a pipe in which there is no change in velocity and the axis of the pipe is horizontal, Eq. (Ex. 11.2) takes the form

$$VdP + W_f = 0 \quad \text{or} \quad \frac{dP}{\rho} + W_f = 0 \quad (\text{Ex. 2.11.3})$$

From Eq. (2.125), we can have

$$dF_x = f_{fr} \left(\frac{1}{2} \rho v^2 \right) dA$$

or, in this case

$$-\pi r^2 dP = f_{fr} \times 2\pi r dx \times \frac{1}{2} \rho v^2$$

or

$$dP = f_{fr} \frac{\rho v^2}{r} dx \quad (\text{Ex. 2.11.4})$$

where dx is the thickness of the volume element and dP is the pressure differential over this element. Substitution of Eq. (Ex. 2.11.4) in Eq. (Ex. 2.11.3) yields

$$-f_{fr} \frac{v^2}{r} dx + W_f = 0$$

Hence, frictional work done during flow is given by

$$W_f = f_{fr} \frac{v^2}{r} dx \quad (\text{Ex. 2.11.5})$$

Substitution of Eq. (Ex. 2.11.5) in Eq. (Ex. 2.11.1) yields the required relation as

$$gdh + \frac{1}{2} vdv + VdP + f_{fr} \frac{v^2}{r} dx = 0 \quad \text{Ans.} \quad (\text{Ex. 2.11.6})$$

EXAMPLE 2.12 Derive the mechanical energy balance equation for isothermal turbulent flow of an ideal gas through a smooth horizontal pipe of uniform diameter.

Solution For a volume element of thickness dx and area equal to that of cross-section of the pipe, by using Eq. (Ex. 2.11.5), Eq. (2.157) takes for the present case the form

$$vdv + VdP + F_{fr} \frac{v^2}{r} dx = 0 \quad (\text{Ex. 2.12.1})$$

Under steady state conditions, the mass flow rate G_m will be constant, i.e.

$$G_m = \frac{vA}{V} = \text{constant}$$

or

$$v = \frac{G_m V}{A} \quad (\text{Ex. 2.12.2})$$

since V is the specific volume of the fluid.

Thus, we can express Eq. (Ex. 2.12.1) as follows:

$$\frac{G_m}{A} VdV + VdP + F_{fr} \left(\frac{G_m}{A} \right)^2 V^2 \frac{dx}{r} = 0$$

Dividing throughout by V^2 , we get

$$\frac{G_m}{A} d(\ln V) + \frac{dP}{V} + F_{fr} \left(\frac{G_m}{A} \right)^2 \frac{dx}{r} = 0 \quad (\text{Ex. 2.12.3})$$

Further, for an ideal isothermal gas, we have

$$PV = RT \quad \text{or} \quad V = \frac{RT}{P}$$

Using this, Eq. (Ex. 2.12.3) takes the form

$$\frac{G_m}{A} d(\ln V) + \frac{1}{2RT} d(P)^2 + F_{fr} \left(\frac{G_m}{A} \right)^2 \frac{dx}{r} = 0 \quad \text{Ans.} \quad (\text{Ex. 2.12.4})$$

This is the required equation.

2.4.4 Applications of Overall Balances

Flow meters

The rate of flow through pipes or conduits can be measured with the help of instruments whose working is based on the overall mechanical energy balance, i.e. Bernoulli's equation. In these meters, the fluid is either accelerated or retarded at the section used for measurement and the change in kinetic energy is measured by the pressure difference so produced. Important meters among this group include the:

- (i) Pitot tube
- (ii) Orifice meter
- (iii) Nozzle
- (iv) Venturi meter
- (v) Rotameter

Apart from the above, there are other flow measuring instruments such as the hot wire anemometer, magnetometer, Thomas meter, quantity meter, etc. which are based on other properties of flow. In the following subsections, however, we deal briefly only with the principles of the above five types of meters. The inquisitive reader interested in a detailed treatment of flow measurements should refer to standard texts on this subject.

Pitot tube. In a pitot tube, a small element of fluid is brought to rest at an orifice situated at right angles to the direction of flow. The flow rate is obtained by measuring the difference between the impact and the static pressures. The pitot tube consists of two concentric tubes, arranged parallel to the direction of flow. The impact pressure is measured on the open end of the inner tube. The end of the outer concentric tube is sealed and a series of orifices on the curved surface give an accurate indication of the static pressure as shown in Fig. 2.15.

Neglecting frictional losses, application of Bernoulli's equation [Eq. (2.160)] to positions (1) and (2) in this figure yields

$$\frac{1}{2} v_1^2 + \frac{P_1}{\rho} + g x_1 = \frac{1}{2} v_2^2 + \frac{P_2}{\rho} + g x_2 \quad (2.161)$$

But $x_1 = x_2$ and $v_2 = 0$, we therefore get

$$\frac{P_2 - P_1}{\rho} = \frac{\Delta P}{\rho} = \frac{1}{2} v_1^2 \quad (2.162)$$

or

$$v_1 = \sqrt{\frac{2\Delta P}{\rho}} \quad (2.163)$$

But in general, we use the relation

$$v = C \sqrt{\frac{2\Delta P}{\rho}} \quad (2.164)$$

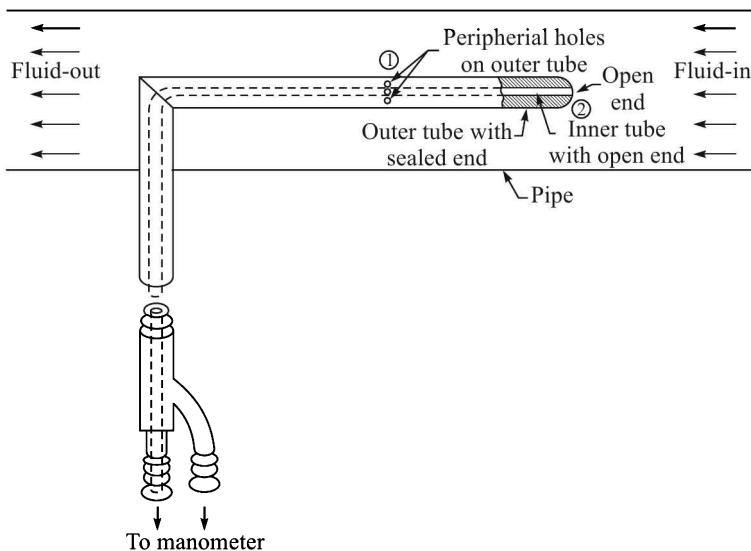


Fig. 2.15 Principle of action of pitot tube.

for calculation of the velocity. In this expression, C is a constant for the instrument and takes care of the frictional losses.

The pitot tube measures the velocity of only a fine filament of liquid and can therefore be used for exploring velocity distribution at various positions in a moving fluid.

Orifice meter, nozzle and venturi meter. In all these measuring devices, the fluid is accelerated by causing it to flow through a construction. Thus, the kinetic energy is increased at the cost of the pressure energy. The flow rate is obtained by measuring the pressure difference between the points at (i) the inlet of the meter, and (ii) a point of reduced pressure. The salient features of all these meters are shown in Fig. 2.16.

Neglecting frictional losses, one can express Bernoulli's equation in the following form for the fluid at the left-hand (Section 1) and right-hand (Section 2) sides of the meters.

$$\frac{v_1^2}{2\alpha_1} - \frac{v_2^2}{2\alpha_2} + g(z_2 - z_1) + \int_1^2 VdP = 0 \quad (2.165)$$

where α_1 and α_2 are the coefficients for laminar flow at these points and subscripts 1 and 2 refer to left and right sides. Further, we can write the mass balance equation as follows:

$$G_m = \frac{v_1 A_1}{V_1} = \frac{v_2 A_2}{V_2} \quad (2.166)$$

where G_m is the mass flow rate.

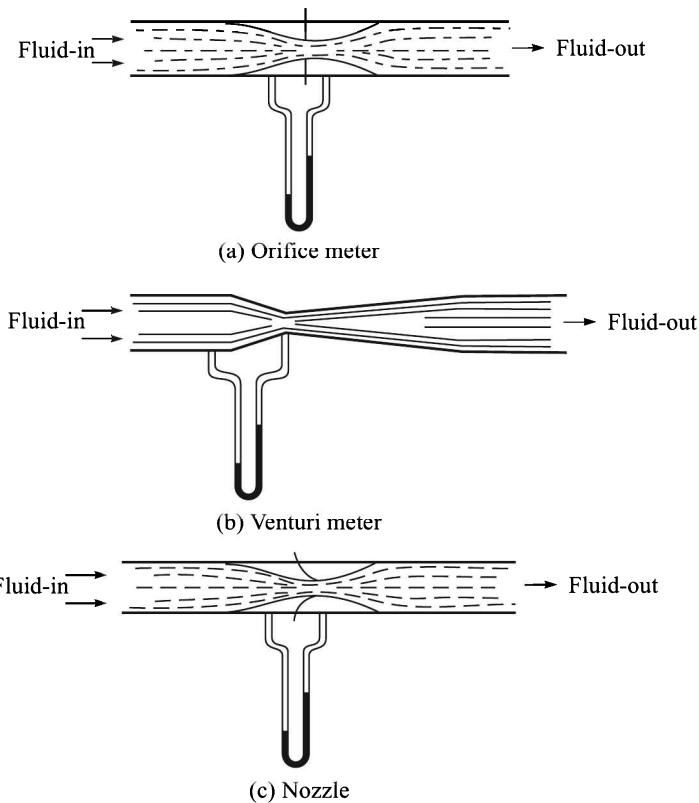


Fig. 2.16 Schematic diagram showing principle of action of orifice meter, venturi meter and nozzle.

From the above equations, we get for an incompressible fluid, the relation

$$G_m \propto \frac{A_2}{V} \left[-\frac{2\alpha_2(z_1 - z_2)g + V(P_1 - P_2)}{1 - \left(\frac{\alpha_2}{\alpha_1}\right)\left(\frac{A_2}{A_1}\right)} \right]^{1/2} \quad (2.167)$$

which can be used for obtaining the mass flow rate when the other parameters in the equation are known.

EXAMPLE 2.13 Derive the energy equation for fluid flow of a gas following the relation $PV^n = C$, where $n \neq 1$ and C is constant.

Solution According to the energy equation [Eq. (2.158)], we have

$$g\Delta h + \frac{1}{2}v\Delta v + \int_{P_i}^{P_o} VdP + W_f = 0$$

The third term in this relation can now be changed on the basis of the equation $PV^n = C$. Thus, we have

$$V^n = \frac{C}{P}$$

or

$$V = \left(\frac{C}{P} \right)^{1/n}$$

So

$$\begin{aligned} \int_{P_i}^{P_o} V dP &= \int_{P_i}^{P_o} \left(\frac{C}{P} \right)^{1/n} dP = C^{1/n} \int_{P_i}^{P_o} P^{-1/n} dP \\ &= C^{1/n} \left[\frac{P^{1-\frac{1}{n}}}{1 - \frac{1}{n}} \right]_{P_i}^{P_o} = \left(\frac{n}{n-1} \right) C^{1/n} \left[P_o^{\frac{n-1}{n}} - P_i^{\frac{n-1}{n}} \right] \end{aligned}$$

So, the required energy equation becomes

$$g\Delta h + \frac{1}{\alpha} v\Delta v + \left(\frac{n}{n-1} \right) C^{1/n} \left[P_o^{\frac{n-1}{n}} - P_i^{\frac{n-1}{n}} \right] + W_f = 0 \quad \text{Ans.}$$

Rotameter. In the meters already described, the area of constriction or orifices is constant and the pressure drop was expressed as a function of flow rate. However, a rotameter is a variable area meter. It consists of a vertical glass tube with a very small taper towards the lower end. The fluid passes upwards and the flow rate is indicated by the position of the float as shown in Fig. 2.17. Analysis of the force balance on the float will give the following relation for pressure difference $-\Delta P$ over the float:

$$-\Delta P = \frac{V_f (\rho_f - \rho) g}{A_f} \quad (2.168)$$

Further, we have

$$G_m = C_D A_2 \left[\frac{2\rho(-\Delta P)}{1 - \left(\frac{A_2}{A_1} \right)^2} \right]^{1/2} \quad (2.169)$$

where V_f is the volume of the float, ρ_f and ρ respectively the densities of the float and the fluid, A_f the maximum cross-sectional area of the float in a horizontal plane, G_m the mass flow rate, C_D is a constant called the *discharge coefficient* for the rotameter, A_2 is the annular area between the float and the tube and A_1 is the cross-sectional area of the tube on the downstream side of the float. Substitution of ΔP in the above equation leads to

$$G_m = C_D A_2 \left[\frac{2g V_f (\rho_f - \rho) \rho}{A_f \left\{ 1 - \left(\frac{A_2}{A_1} \right)^2 \right\}} \right]^{1/2} \quad (2.170)$$

The coefficient of discharge of the rotameter depends on the shape of the float and the Reynolds number. The use of floats of different densities increases the range of the meter.

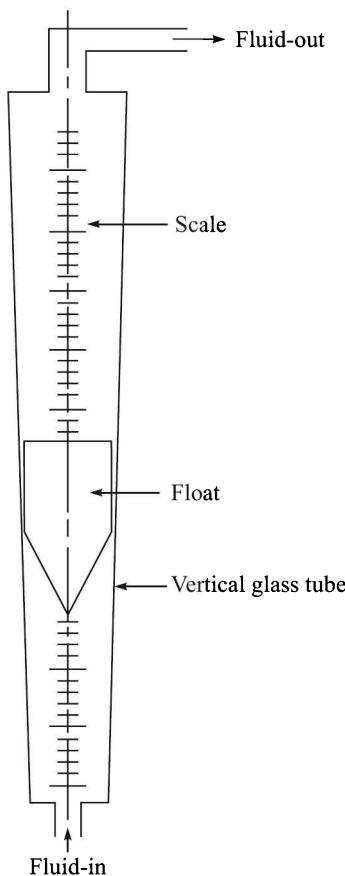


Fig. 2.17 Schematic representation of principle of rotameter.

Chimney draft

In fossil-fuel fired metallurgical furnaces, chimneys are provided to carry away the flue gases. These chimneys also produce a draft, known as chimney draft or natural draft, which helps to draw in atmospheric air into the furnace to assist in the combustion process of the fossil-fuel. The magnitude of this draft is proportional to the pressure drop caused by the chimney and can be calculated by applying the energy balance, i.e. Bernoulli's equation as given in Eq. (2.160).

Consider a chimney of height h as shown in Fig. 2.18, which is connected to the flue of a furnace. Let P_1 and P_2 be the pressures at the bottom and the top of the chimney, and P_0 the pressure at the furnace door. If ρ_a and ρ_g are the density of air at room temperature and that of the hot gas inside the chimney at $t^\circ\text{C}$, by taking the velocity components and the frictional work W_f as zero, we get from Eq. (2.160), the relations

$$\frac{P_0}{\rho_a} = \frac{P_2}{\rho_a} + gh$$

or

$$P_0 = P_2 + \rho_a gh \quad (2.171)$$

Similarly

$$\frac{P_1}{\rho_g} = \frac{P_2}{\rho_g} + gh$$

or

$$P_1 = P_2 + \rho_g gh \quad (2.172)$$

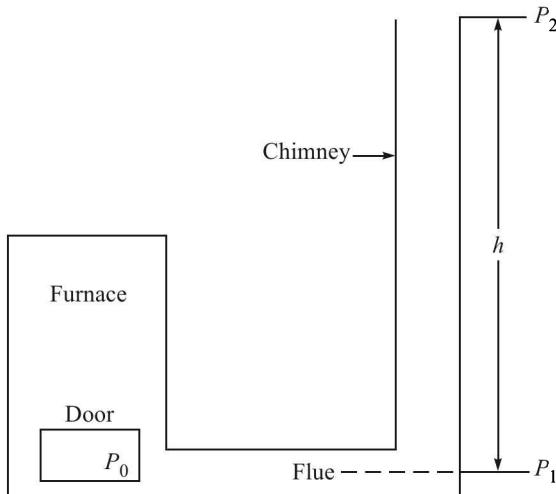


Fig. 2.18 Furnace with chimney.

From Eqs. (2.171) and (2.172), we get

$$P_0 - P_1 = (\rho_a - \rho_g)gh \quad (2.173)$$

In the above equation, $(P_0 - P_1)$, the pressure drop between the furnace and the bottom of the chimney, which generates the chimney draft, is also sometimes known as the buoyancy pressure.

If ρ_g° is the density of the flue gas at room temperature, i.e. 25°C , we can write

$$\frac{\rho_g}{\rho_g^\circ} = \frac{273 + 25}{273 + t} = \frac{298}{273 + t} \quad (2.174)$$

or

$$\rho_g = \rho_g^\circ \left(\frac{298}{273 + t} \right)$$

From Eqs. (2.173) and (2.174), we get

$$(P_0 - P_1) = \Delta P = \left(\rho_a \frac{-298 \rho_g^\circ}{273 + t} \right) gh \quad (2.175)$$

Equation (2.175) can be used to calculate the chimney draft when all the other parameters in the equation are known. However, the draft thus produced is usually of a small magnitude, may be of the order of about 0.003 atm. Since this is insufficient to draw in adequate quantity of combustion air, fans and blowers have to be provided with the furnace system to generate forced draft for combustion.

2.5 HIGH SPEED FLOW OF GASES

In a number of metallurgical processes such as the LD process, flash roasting, blast furnace smelting, we are concerned with the flow of gases or compressible fluids in a reactor. Since these gases enter the reactor at very high speeds, we now discuss the basic concepts involved in the achievement of high speed flow of gases. Such a flow is achieved in practice by the use of tapered nozzles. The shapes of these nozzles can be arrived at from a study of the equations of continuity and motion. These high speeds, generally in the supersonic range, are usually represented by a dimensionless group known as 'Mach number' which is defined as the ratio of the velocity of gas to that of sound at the same temperature. The velocity of sound v_s is related to the properties of the medium in which it travels. Thus, for a gaseous medium, the velocity of sound is expressed by the relation

$$v_s = \left(\frac{\gamma RT}{M_g} \right)^{1/2} = \left(\frac{\gamma PV}{M_g} \right)^{1/2} = \left(\frac{\gamma P}{\rho_g M_g} \right)^{1/2} \quad (2.176)$$

where γ is C_p/C_v , i.e. the ratio of the specific heat of the gas at constant pressure to that at constant volume, R the universal gas constant, T the absolute temperature and M_g the molecular weight of the gas. The Mach number which is represented by the symbol N_{Ma} is therefore given by v/v_s .

We now consider the steady state flow of a gas through a conical nozzle. As the cross-sectional area A of the nozzle will vary with the axial position as well as the density ρ_g of the gas owing to pressure change resulting from

change in area, the continuity equation under steady state conditions will take the following form:

$$d(\rho_g A_z v_z) = 0$$

or

$$\frac{d\rho_g}{\rho_g} + \frac{dA_z}{A_z} + \frac{dv_z}{v_z} = 0 \quad (2.177)$$

where ρ_g , v_z and A_z are respectively, the density, the velocity of the gas and the cross-sectional area at position z in the nozzle, and z denotes the axial distance in the direction of flow of the gas.

As the flow under consideration is a high-speed one, the gas is not able to exchange an appreciable amount of heat with its surroundings and thus for all practical purposes, we can consider the flow to be adiabatic. The energy equation for flow along the axial direction, which if considered to be horizontal, can be formulated in this case, with the help of Eq. (2.157), as

$$v_z dv_z + \frac{1}{\rho_g} dP = 0 \quad (2.178)$$

The frictional work W_f has been neglected in this equation, as such effects in high-speed flow of gases are small. α has been taken as 1 and the specific volume V equals $1/\rho_g$.

As the flow is assumed to be adiabatic under reversible conditions it will follow the relationship, for one mole of gas

$$PV^\gamma = C \quad \text{or} \quad P = \frac{C}{(M_g/\rho_g)^\gamma} \quad (2.179)$$

Hence

$$\rho_g = \left(\frac{P}{C} \right)^{1/\gamma} M_g \quad (2.180)$$

where C is a constant.

Substitution of the above relation for ρ_g in Eq. (2.178) yields

$$v_z dv_z + \left\{ \left(\frac{C}{P} \right)^{1/\gamma} \frac{1}{M_g} \right\} dP = 0 \quad (2.181)$$

On integration, this equation leads to

$$\frac{v_z^2}{2} = \frac{\gamma(C)^{1/\gamma}}{\gamma - 1} \frac{P^{(\gamma-1)/\gamma}}{M_g} + \alpha \quad (2.182)$$

where α is the constant of integration. The above equation helps in correlating pressure and velocity inside the nozzle. Let v_1 and v_2 be the velocities of the gas inside the nozzle at any two different points, and P_1 and P_2 be the corresponding pressures at these points. Thus, we get

$$\frac{v_1^2}{2} - \frac{v_2^2}{2} = - \frac{\gamma}{(\gamma - 1) M_g} C^{1/\gamma} P_1^{(\gamma-1)/\gamma} - C^{1/\gamma} P_2^{(\gamma-1)/\gamma} \quad (2.183)$$

For an adiabatic process for an ideal gas, we have

$$C = P_1 V_1^\gamma = P_2 V_2^\gamma \quad (2.184)$$

Equation (2.183), therefore, becomes

$$\frac{v_1^2}{2} - \frac{v_2^2}{2} = - \left(\frac{\gamma}{\gamma - 1} \right) \left(\frac{P_1 V_1 - P_2 V_2}{M_g} \right)$$

or

$$\frac{v_1^2}{2} + \frac{\gamma P_1 V_1}{(\gamma - 1) M_g} = \frac{v_2^2}{2} + \frac{\gamma P_2 V_2}{(\gamma - 1) M_g} \quad (2.185)$$

Hence, along the nozzle

$$\frac{v_z^2}{2} + \frac{\gamma P V}{(\gamma - 1) M_g} = \text{constant} \quad (2.186)$$

i.e. the sum of kinetic and potential energies of the gas remains constant.

We can also incorporate v_s , the velocity of sound, in the above relation from Eq. (2.176) and state it in the following alternative form:

$$\frac{v_z^2}{2} + \frac{v_s^2}{\gamma - 1} = \text{constant} \quad (2.187)$$

In order to arrive at the relation for the variation in velocity of flow with cross-sectional area of the nozzle, we can combine the energy equation and the adiabatic equation of state as follows:

$$v_z dv_z + \frac{dP}{\rho} = 0$$

or

$$v_z dv_z + \frac{dP}{d\rho} \frac{d\rho}{\rho} = 0 \quad (2.188)$$

which, by making use of Eq. (2.179), can be stated as

$$v_z dv_z + \left(\frac{\gamma P}{M_g \rho_g} \right) \frac{d\rho}{\rho} = 0 \quad (2.189)$$

and which on incorporation of the v_s term from Eq. (2.176) can be written as

$$v_z dv_z + v_s^2 \frac{d\rho}{\rho} = 0 \quad (2.190)$$

Substitution for $\frac{d\rho}{\rho}$ from the above equation in the continuity Eq. (2.177), yields

$$\frac{dv_z}{v_z} = \frac{v_z dv_z}{v_s^2} - \frac{dA}{A} \quad (2.191)$$

which on simplification gives

$$\frac{dv_z}{dA} = \frac{v_z v_s^2}{A(v_z^2 - v_s^2)} \quad (2.192)$$

Equation (2.192) shows that for values of $v_z < v_s$, the parameter dv_z/dA will be negative, meaning thereby that the velocity of the gas in this range will increase if the cross-sectional area of the nozzle decreases, i.e. if the nozzle is convergent. But for $v_z > v_s$, the value of dv_z/dA is positive which means that for supersonic velocities of the gas, the cross-sectional area of the nozzle should increase for an increase in velocity, i.e. the nozzle should be divergent. Hence, one requires a "convergent-divergent nozzle" for the attainment of supersonic velocities of a gaseous jet. Such nozzles have minimum cross-sectional area at the point where the gas flowing through them attains sonic velocity. This point is called the "throat" of the nozzle. The ratio of the pressure at sonic velocity to that at the entrance of the nozzle is known as *critical ratio* and can be calculated with the help of Eq. (2.185) under the assumption that the velocity of the gas at the entrance of the nozzle is far less than that of sound. Thus for the attainment of sonic velocity, Eq. (2.185) reduces to

$$\frac{v_s^2}{2} = -\frac{\gamma}{\gamma-1} \left(\frac{P_i V_i - P_s V_s}{M_g} \right) \quad (2.193)$$

Using Eq. (2.176), this becomes

$$\frac{\gamma P_s V_s}{2 M_g} = \frac{\gamma P_s V_s}{(\gamma-1) M_g} \left(1 - \frac{P_i V_i}{P_s V_s} \right) \quad (2.194)$$

or

$$\frac{\gamma-1}{2} = 1 - \frac{P_2 V_2}{P_s V_s} \quad (2.195)$$

where P_i and P_s are the values of pressures at the entrance and at the point where sonic velocity is attained in the nozzle and V_i and V_s are the corresponding volumes. For an adiabatic process, we have

$$P_i V_i^\gamma = P_s V_s^\gamma$$

or

$$\frac{V_i}{V_s} = \left(\frac{P_s}{P_i} \right)^{1/\gamma} \quad (2.196)$$

Substituting this in Eq. (2.195) and simplifying, we get

$$\frac{P_s}{P_i} = \left(\frac{2}{\gamma+1} \right)^{\gamma/(\gamma-1)} \quad (2.197)$$

Again, since $P_i V_i / T_i = P_s V_s / T_s$, we can get for an ideal gas the equation

$$\frac{T_s}{T_i} = \left(\frac{P_s}{P_i} \right)^{(\gamma-1)/\gamma} \quad (2.198)$$

Once the value of pressure at the throat of the nozzle is established by the above equation, we can calculate the velocity of the gas at the exit point by making use of Eq. (2.185). Application of these equations is demonstrated by the following example.

EXAMPLE 2.14 Oxygen (mol. wt. 32, $\gamma = 1.4$) is made to enter a convergent-divergent nozzle at 7 atm pressure and 27°C. Assuming the gas to behave ideally, calculate (i) the critical pressure for the gas, and (ii) the exit temperature and velocity, if the pressure at the exit is 1 atm.

Solution According to Eq. (2.197), the critical pressure P_s is given by the equation

$$P_s = P_i \left(\frac{2}{1+\gamma} \right)^{\gamma/(\gamma-1)} = 7 \times \left(\frac{2}{2.4} \right)^{1.4/0.4} = 3.7 \text{ atm}$$

As the process of flow is adiabatic and the gas is assumed to be ideal, the temperature of the gas at the throat is given by Eq. (2.198).

Now

$$\frac{T_s}{T_i} = \left(\frac{P_s}{P_i} \right)^{(\gamma-1)/\gamma} \quad (\text{Ex. 2.14.1})$$

or

$$T_s = (273 + 27) \times \left[\frac{3.7}{7} \right]^{0.4/1.4} = 250.1 \text{ K}$$

The sonic velocity v_s at this temperature from Eq. (2.176) is

$$v_s = \left(\frac{\gamma_g R T_s}{M_g} \right)^{1/2} = \left(\frac{1.4 \times 8318 \times 250.1}{32} \right)^{1/2} = 301.8 \text{ m s}^{-1}$$

Therefore, T_{ex} , from Eq. (Ex. 2.14.1) is given by

$$\frac{T_{ex}}{T_i} = \left(\frac{P_{ex}}{P_i} \right)^{(\gamma-1)/\gamma}$$

Thus

$$T_{ex} = 300 \left(\frac{1}{7} \right)^{0.4/1.4} = 172.1 \text{ K}$$

According to Eq. (2.185), v_{ex} is given by

$$\begin{aligned} v_{ex}^2 &= v_s^2 + \frac{2\gamma R}{\gamma-1} \left(\frac{T_{ex} - T_s}{M_g} \right) \\ &= (301.8)^2 + \frac{2 \times 1.4 \times 8318}{1.4 - 1} \times \frac{250.1 - 172.1}{32} \end{aligned}$$

or

$$v_{ex} = 482.7 \text{ m s}^{-1}$$

2.5.1 High Velocity Jets

The characteristics of high velocity jets which are used in various metallurgical operations as outlined earlier may now be considered. An important consideration in the development of such jets is that the jet should leave the nozzle at a pressure equal to that of the surroundings; otherwise it may expand or contract, causing a change in its momentum. As the jet leaves the nozzle, it will start interacting with its surroundings resulting in a decrease in its velocity and the development of a radial gradient in the velocity profile. When this velocity profile gets stabilized, the jet is said to be a developed one.

The velocity profile of a radial jet is found experimentally to be given by the function

$$v_{rx} = v_{ax} \exp\left(-\frac{0.694r}{r_{ax/2}}\right) \quad (2.199)$$

where v_{rx} and v_{ax} are the velocities at a radial distance r from the axis and that at the axis of jet, respectively at a distance x from the pole as shown in Fig. 2.19; $r_{ax/2}$ is the radial distance from the axis at which the velocity is equal to half of the axial velocity. The ‘pole’ of the jet is the point at which the tangent to the surfaces of the jet intersects the axis of the jet (Fig. 2.19).

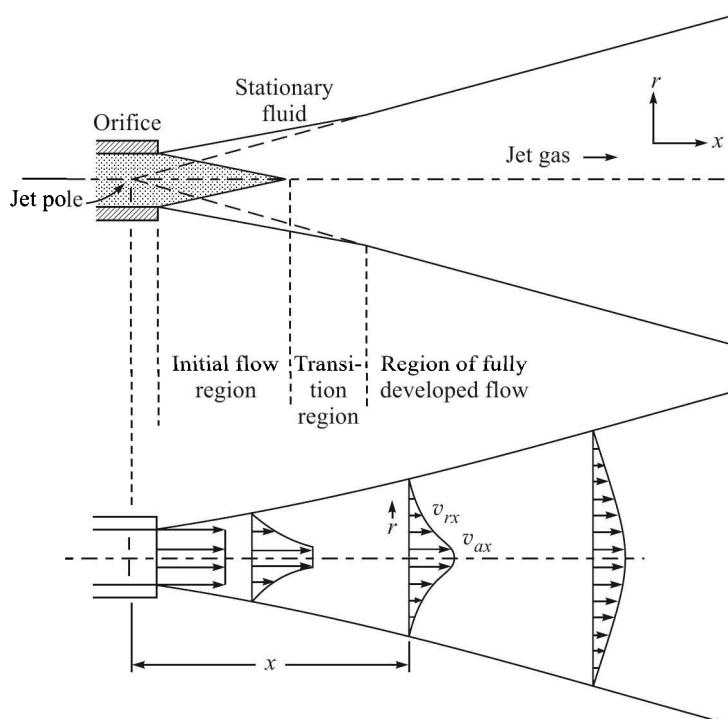


Fig. 2.19 Velocity profile of high-velocity jets.

The axial velocity at any distance x from the pole is given by the equation

$$v_a = \frac{k_j v_{ex} r_{ex}}{x} \quad (2.200)$$

where k_j is the jet constant and is found to be equal to 12.4 for an air jet in air and 12.8 for a water jet in water; v_{ex} and r_{ex} are the velocity and radius at the exit end of the nozzle respectively.

2.6 FLOW THROUGH PACKED BEDS

In a number of metallurgical processes such as blast furnace smelting, shaft type direct reduction processes, shaft type lime kilns or chlorinators, etc. packed columns, through which reacting gases are passed, are used. The different theoretical approaches for the prediction of pressure drops across such beds for given flow rates can be considered by two approaches. In one approach, a packed bed is considered to be a system consisting of a number of particles submerged in a fluid and the pressure drop is calculated by summing up the resistances of submerged particles. In the second approach, a packed bed is considered to consist of a bundle of tangled tubes of weird cross-section. Quantitative analysis of such beds based on the latter approach has been found to be more successful than that based on the former. For low flow rates, we can thus apply the equation derived in Section 2.3.3, to calculate the pressure drop ΔP across the bed for given flow rates. Taking the gravitational effect also into account, we can express Eq. (2.95) in the following modified form:

$$\frac{\Delta P - \rho L g \sin \alpha}{L} = \frac{8\mu v_{av}}{R^2} \quad (2.201)$$

where ρ is the density, L the length of the capillary or bed, R the radius of the capillary or bed, v_{av} the average velocity of flow and α the angle of tilt or inclination for flow. To arrive at an equation for the tube radius R in terms of particle size, we proceed as follows. It is known that for a pipe, its radius R , volume V , and surface area A are related by the equation

$$R = \frac{2V}{A} \quad (2.202)$$

In this approach, since the space or gap between different particles of the packed bed is assumed to be occupied by the cylinders, the volume of the voids in the bed is considered equal to that of the pipe. If ϵ be the void fraction of the bed, Eq. (2.202) can be rewritten as

$$R = \frac{2\epsilon}{a} \quad (2.203)$$

where a is the surface area per unit volume of the bed, which in turn is related to the surface area of the particle as follows:

$$a = (1 - \epsilon) a_p \quad (2.204)$$

where a_p is the average surface area per unit volume of the particle and is given by the equation

$$a_p = \frac{4\pi r_p^2}{\phi \times (4/3)\pi r_p^3} = \frac{6}{\phi D_p} \quad (2.205)$$

where r_p and D_p are respectively the equivalent radius and diameter of the particle and ϕ its shape factor. These parameters are defined by the relations

$$D_p = \left[\frac{6 \times (\text{volume of the particle})}{\pi} \right]^{1/3} \quad (2.206)$$

$$\phi = \frac{\pi D_p^2}{\text{surface area of the particle}} \quad (2.207)$$

With the help of Eqs. (2.203) to (2.207), we can arrive at the following equation for equivalent radius R of the cylindrical pipe:

$$R = \frac{\varepsilon \phi D_p}{3(1-\varepsilon)} \quad (2.208)$$

In connection with the flow through pipes, another term called the *hydraulic radius*, represented by the symbol R_h is used instead of R . By convention, it is related to R by the relation

$$R = 2R_h \quad (2.209)$$

Another term commonly used in this connection is *superficial velocity* \bar{v}_0 of the gas. It is defined as the velocity of the gas through the reactor without particles and is related to the actual average velocity \bar{v} through the bed by the equation

$$\bar{v}_0 = \bar{v} \varepsilon \quad (2.210)$$

Substitution of Eqs. (2.208) and (2.210) in Eq. (2.201) leads to the relation

$$\frac{\Delta P - \rho L g \sin \alpha}{L} = \frac{72\mu(1-\varepsilon)^2 \bar{v}_0}{\phi^2 D_p^2 \varepsilon^3} \quad (2.211)$$

Equation (2.211), although correctly predicting the influence of various parameters on the pressure drop across the bed, yields higher quantitative results because of the following reasons:

- (i) The distance travelled by the gas will be more than the length L of the bed, because of the tortuous or zig-zag path that it would follow.
- (ii) The calculation of tube radius according to Eq. (2.208) usually gives higher values.

Both the above factors result in lower calculated values of the pressure drop ΔP across the bed as compared with the experimental data.

Another empirical relationship was found between velocity and pressure drop in the form

$$\frac{\Delta P - \rho g L \sin \alpha}{L} = \frac{150\mu(1-\varepsilon)^2 \bar{v}_0}{\phi^2 D_p^2 \varepsilon^3} \quad (2.212)$$

The above relation is known as the Blake-Kozeny equation.¹ It differs from Eq. (2.211) only in the constant factor and is applicable to beds with low flow rates in laminar region and void-fractions less than 0.5, and satisfying the condition.

$$\frac{D_p \rho \bar{v}_0}{(1-\varepsilon)\mu} < 10 \quad (2.213)$$

It is also important to note that the Blake-Kozeny equation corresponds to a bed friction factor of

$$f_{fr} = \frac{(1-\varepsilon)^2}{\varepsilon^3} \times \frac{75\mu}{D_p \rho \bar{v}_0} \quad (2.214)$$

Further analysis of experimental data on turbulent flow through isothermal packed beds has shown that the friction factor for these systems is given by

$$f_{fr} = \frac{7}{12} \quad (2.215)$$

We now use the above equation to arrive at a relation for calculation of the pressure drop in respect of high speed flow through a packed bed. From Eq. (2.201), we get for uniform flow under steady state through a packed bed of uniform cross-sectional area A , the relation

$$(P_e - P_{ex})A + \rho ALg \sin \theta = F \quad (2.216)$$

where L is the length of the bed and θ the angle subtended by the direction of flow with the vertical axis pointing downwards. F is the frictional force, and the subscripts "e" and "ex" stand for entry and exit respectively.

According to Eqs. (2.125) and (2.215) the frictional force acting on the fluid is given by the equation

$$F = \frac{7}{12} \left(\frac{1}{2} \rho \bar{v}^2 \right) a A L \quad (2.217)$$

where a is the surface area per unit volume of the bed and can be calculated with the help of Eqs. (2.204) and (2.205). Thus, from Eqs. (2.216) and (2.217) we get the relation

$$\frac{(P_e - P_{ex}) + \rho g L \sin \theta}{L} = 3.5 \frac{1}{\phi D} \left(\frac{1}{2} \rho v_0^2 \right) \times \frac{1-\varepsilon}{\varepsilon^3} \quad (2.218)$$

¹ H. Schlichting, *Boundary Layer Theory*, McGraw-Hill, New York. (1955).

where the different symbols used have already been defined earlier in the text. Equation (2.218) is applicable for the flow rates given by

$$\frac{D_p \rho v_0}{\mu(1-\varepsilon)} > 1000$$

and is known as the *Burke-Plummer equation*.¹

A generalized empirical relationship for pressure drop across isothermal packed beds for all flow rates was obtained by Ergun.² by the addition of Eqs. (2.211) and (2.213). The resulting relation, commonly known as *Ergun's equation*, is as follows:

$$\frac{(P_e - P_{ex}) + \rho g L \sin \theta}{L} = \frac{150 \mu v_0 (1-\varepsilon)^2}{(\phi D_p)^2 \varepsilon^3} + \frac{1.75 \rho v_0^2 (1-\varepsilon)}{D_p \varepsilon^3} \quad (2.219)$$

Equation (2.219) can be rewritten in the following form:

$$\left[\frac{(\Delta P + \rho g L \sin \theta)}{G_m} \right] \times \frac{D_p}{L} \frac{\varepsilon^3}{1-\varepsilon} = 150 \frac{\mu v_0 (1-\varepsilon)}{\phi^2 D_p G_m} + 1.75 \quad (2.220)$$

where G_m is the mass flow rate per unit cross-sectional area of the bed. In Fig. 2.20, the logarithm of the left-hand side of the above equation is plotted against $\log \{D_p G_m / \mu(1-\varepsilon)\}$. It is seen from this plot that in respect of small

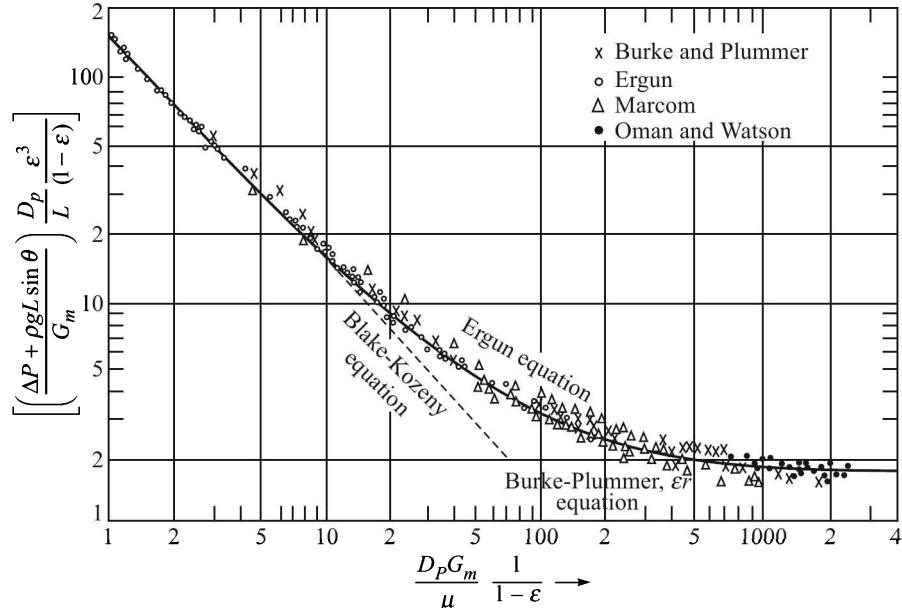


Fig. 2.20 Characteristics of flow through isothermal packed bed.

¹ H. Schlichting, *Boundary Layer Theory*, McGraw-Hill, New York (1955).

² S. Ergun, *Chem. Eng. Prog.*, **48**: 93 (1952).

particles and low velocities, the Blake-Kozeny equation (2.212) is followed whereas for bigger particles and higher velocities the Burke-Plummer equation (2.218) holds good. Certain terms in both these equations are somewhat modified to bring uniformity with Ergun's equation. The applicability of Ergun's equation (2.219) is restricted only to the flow of gases in the isothermal systems in which the pressure drop across the system is small as compared to the absolute pressure so that a gas could be assumed to behave as an incompressible fluid. For the other cases, the Ergun's equation is combined with the overall energy balance equation. For this purpose, we consider a differential element across the reactor having a thickness dz along the direction of flow. According to the overall mechanical energy balance, given by Eq. (2.157), for flow through this element, we can formulate the following relation with gravitational effect included in the δW_f term and α taken as unity:

$$v_z dv_z + VdP + \delta W_f = 0 \quad (2.221)$$

where V is the specific volume, i.e. volume per unit mass, z the axial direction, v_z the velocity of the fluid in this direction and P the pressure. The gas is compressible, but under steady state conditions, the mass flow rate per unit cross-sectional area, G_m , is constant. So we can express the velocity v_z as follows:

$$v_z = \frac{G_m}{\rho} = \frac{G_m V}{\epsilon} \quad (2.222)$$

Further, the work done δW_f against frictional force F_{fr} can be expressed as

$$\delta W_f = F_{fr} dz \quad (2.223)$$

Therefore, with the help of Eq. (2.219), for the total work δW , including the gravitational effect, we get the following relation:

$$\delta W = \left[\frac{150\mu(1-\epsilon)^2 G_m V}{D_p^2 \epsilon^3} + \frac{1.75(1-\epsilon)G_m^2 V}{D_p \epsilon^3} \right] V dz \quad (2.224)$$

Substitution of Eqs. (2.222) and (2.224) in Eq. (2.221) and the division of the resulting expression by V^2 yields

$$\frac{G_m^2}{\epsilon^2} \times \frac{dV}{V} + \frac{dP}{V} + \left[\frac{150\mu(1-\epsilon)^2 G_m}{D_p^2 \epsilon^3} + \frac{1.75(1-\epsilon)G_m^2}{D_p \epsilon^3} \right] dz = 0 \quad (2.225)$$

On integration of the preceding equation, under isothermal conditions, and assuming the gas to be ideal, we get

$$\frac{G_m^2}{\epsilon^2} \ln \left(\frac{P_{ex}}{P_e} \right) + \left(\frac{P_{ex}^2 - P_e^2}{2P_e V_e} \right) + \left[\frac{150\mu(1-\epsilon)^2 G_m}{D_p^2 \epsilon^3} + \frac{1.75(1-\epsilon)G_m^2}{D_p \epsilon^3} \right] z = 0 \quad (2.226)$$

where z is the total height of the bed.

For non-isothermal conditions, Eq. (2.225) can be integrated by taking the temperature profile in the reactor into consideration.

2.7 FLOW THROUGH FLUIDIZED BEDS

In Section 2.6 it was indicated that during the flow of a fluid through a packed bed, the flow rate is relatively low. However, if the rate of flow is increased continuously, a stage will come when the particles remain freely suspended in the fluid stream. The bed under this condition is said to be *fluidized*. If with increase in the velocity of the fluid, the bed expands in such a way as to increase the average distance between the particles, due mainly to the presence of a continuous and large quantity of fluid, the fluidization is said to be *particulate*. If, on the other hand, the fluid passes through the fluidized bed in the form of discontinuous bubbles, the fluidization is called *aggregative*. The former type commonly occurs in liquid-solid as well as finely divided solid-gas systems, whereas the latter is observed in respect of solid-gas systems and sometimes in high-density solid-liquid systems. It has been found that for the dimensionless Froude number, $N_{Fr} (v_{mf}^2/gd)$, less than unity, particulate fluidization results in the bed whereas above this value ‘aggregative fluidization’ occurs. Here v_{mf} is the fluid velocity at the minimum fluidization state, g the acceleration due to gravity and d the average distance between the particles.

Fluidized bed reactors have become important in metallurgical processes particularly for combustion of pulverized coal and for roasting of sulphide concentrates as these reactive systems offer rapid heat and mass transfer.

In order to calculate the minimum fluidization velocity v_{mf} and pressure drop across the bed to effect fluidization, we take the help of the Ergun’s equation. For such calculations, therefore, we assume that the symbols ρ_s and ρ_f represent the densities of the solid and the fluid, respectively. At the instant when fluidization just starts, the bed becomes suspended in the fluid, say a gaseous phase. At this instant, the total buoyancy and the upward force or thrust due to the gas must be equal to the downward force due to the weight of the bed. Mathematically, we write

$$AL_{mf}g(1 - \varepsilon_{mf})\rho_f + A\Delta P_{mf} = AL_{mf}g(1 - \varepsilon_{mf})\rho_s \quad (2.227)$$

or

$$\Delta P_{mf} = L_{mf}g(1 - \varepsilon_{mf})(\rho_s - \rho_f) \quad (2.228)$$

where the symbols A , L_{mf} and ε_{mf} represent respectively the cross-sectional area, the length and the void-fraction of the bed at the minimum fluidization state and ΔP_{mf} is the pressure drop across the bed in this state. Substitution of the expression for ΔP_{mf} from the Ergun’s equation in the above equation and rearrangement of the terms in the resulting equation leads to

$$\frac{\rho_f(\rho_s - \rho_f)gD_p^3}{\mu_f} = 150 \frac{1 - \varepsilon}{\varepsilon_{mf}^3} \frac{v_{mf} D_p \rho_f}{\mu_f} + \frac{1.75}{\varepsilon_{mf}^3} \left(\frac{v_{mf} D_p \rho_f}{\mu_f} \right)^2 \quad (2.229)$$

We can write this expression in the following alternative form, in terms of the dimensionless Galileo number, N_{Ga} , and Reynolds number, $N_{\text{Re, mf}}$, for fluidization.

$$N_{\text{Ga}} = 150 \frac{(1 - \varepsilon_{\text{mf}})}{\varepsilon_{\text{mf}}^2} N_{\text{Re, mf}} + 1.75 \frac{1}{\varepsilon_{\text{mf}}^3} N_{\text{Re, mf}}^2 \quad (2.230)$$

where N_{Ga} and $N_{\text{Re, mf}}$ are defined by the equations

$$N_{\text{Ga}} = \frac{\rho_f(\rho_s - \rho_f)gD_p^3}{\mu_f^2} \quad (2.231)$$

and

$$N_{\text{Re, mf}} = \frac{v_{\text{mf}}\rho_f D_p}{\mu_f} \quad (2.232)$$

As the value of ε_{mf} is generally not known, the above relation has to be further simplified by combining it with experimental data on a number of systems. If the value of ε_{mf} is assumed to be 0.4, Eq. (2.230) takes the following form:

$$N_{\text{Re, mf}}^2 + 51.4 N_{\text{Re, mf}} - 0.0366 N_{\text{Ga}} = 0 \quad (2.233)$$

Wen and Yu¹, based on the results of their studies, however, have suggested an alternative relationship as follows.

$$N_{\text{Re, mf}} = \{(33.7)^2 + 0.0408 N_{\text{Ga}}\}^{1/2} - 33.7 \quad (2.234)$$

EXAMPLE 2.15 Chalcopyrite copper ore of average particle diameter 0.01 cm is roasted in a fluidized bed roaster at 550°C. Calculate the minimum fluidization velocity, given that the densities of the ore and air are 4.5 g cm⁻³ and 0.0003 g cm⁻³, respectively, and the viscosity of air is 0.04 cP at 550°C.

Solution Using Eq. (2.234), we have

$$N_{\text{Re, mf}} = \{(33.7)^2 + 0.0408 N_{\text{Ga}}\}^{1/2} - 33.7$$

Now

$$N_{\text{Re, mf}} = \frac{v_{\text{mf}}\rho_f D_p}{\mu_f}$$

and

$$N_{\text{Ga}} = \frac{\rho_f(\rho_s - \rho_f)gD_p^3}{\mu_f^2}$$

where the symbols have the meanings mentioned in the text. From the above equations, we have

$$\frac{v_{\text{mf}}\rho_f D_p}{\mu_f} = \left\{ (33.7)^2 + 0.0408 \frac{\rho_f(\rho_s - \rho_f)gD_p^3}{\mu_f^2} \right\}^{1/2} - 33.7$$

¹ C.Y. Wen and Y.H. Yu, *A.I.Ch.E.Jl.*, **12**: 610 (1966).

Given

$$\rho_f = 0.0003 \text{ g cm}^{-3} = 0.3 \text{ kg m}^{-3}$$

$$\rho_s = 4.5 \text{ g cm}^{-3} = 4500 \text{ kg m}^{-3}$$

$$D_p = 0.01 \text{ cm} = 1 \times 10^{-4} \text{ m}$$

$$g = 9.81 \text{ m s}^{-2}$$

$$\mu_f = 0.04 \text{ cP} = 4 \times 10^{-4} \text{ P} = 4 \times 10^{-5} \text{ kg m}^{-1} \text{ s}^{-1}$$

Therefore, on substitution of the values in the above relation, we get

$$\frac{v_{mf} \times 0.3 \times 10^{-4}}{4 \times 10^{-5}} = \left\{ (33.7)^2 + 0.0408 \frac{0.3(4500 - 0.3) 9.81 \times (10^{-4})^3}{(4 \times 10^{-5})^2} \right\}^{1/2} - 33.7$$

or

$$\begin{aligned} \frac{v_{mf} \times 3}{4} &= \left\{ 1135.7 + 0.0408 \frac{0.3 \times 4499.7 \times 9.81 \times 10^{-12}}{16 \times 10^{-10}} \right\}^{1/2} - 33.7 \\ &= \{ 1135.7 + 0.3377 \}^{1/2} - 33.7 = 33.71 - 33.7 = 0.01 \end{aligned}$$

or

$$v_{mf} = \frac{0.04}{3} = 0.0133 \text{ m s}^{-1}$$

In the above discussion, we have derived equations for the minimum fluidization velocity. If the velocity of the fluidizing gas in the bed is increased further, the bed will also expand further. Ultimately when the upward thrust and buoyancy effects together become greater than the effect of the terminal velocity of the particles falling under gravity, they are carried away by the stream of the fluid. The minimum velocity of the fluid at which the particles are carried away by the stream is called the *elutriation velocity* denoted by v_E , and the equation used for evaluating its value is dependent upon the particle Reynolds number

$$N_{Re, p} = \frac{\rho_f v_f D_p}{\mu_f}$$

as given below:

(i) For $N_{Re, p} < 0.4$

$$v_E = \frac{(\rho_s - \rho_f) g D_p^2}{18 \mu_f} \quad (2.235)$$

(ii) For $0.4 < N_{Re, p} < 500$

$$v_E = 0.0178 \frac{(\rho_s - \rho_f) g D_p}{(\rho_f \mu_f)^{1/2}} \quad (2.236)$$

(iii) For $500 < N_{Re, p} < 2 \times 10^5$

$$v_E = \left[\frac{3.1 (\rho_s - \rho_f) g D_p}{\rho_f} \right]^{1/2} \quad (2.237)$$

EXAMPLE 2.16 Calculate the elutriation velocity in the problem given in Example 2.15.

Solution The particle Reynolds number

$$N_{Re, p} = \frac{\rho_f v_{mf} D_p}{\mu_f} = \frac{0.3 \times 0.0133 \times 10^{-4}}{4 \times 10^{-5}} = 0.01$$

Since $N_{Re, p} < 0.4$, Eq. (2.235) should be applied. Therefore, elutriation velocity

$$v_E = \frac{(\rho_s - \rho_f) g D_p^2}{18 \mu_f} = \frac{(4500 - 0.3) \times 9.81 (10^{-4})^2}{18 \times 4 \times 10^{-5}} = 0.613 \text{ m s}^{-1} \quad \text{Ans.}$$

2.8 MOTION OF GAS BUBBLES IN LIQUIDS

A large number of metallurgical processes related to extraction and refining of metals involve the interaction of a gas and a liquid phase. Some common examples of such interaction are steel making, precipitation of copper, nickel and cobalt by hydrogen from ammoniacal sulphate solutions, purification of aluminium by chlorine, precipitation of Ag, Cu, Ni(CO)₄, CO(CO)₄ by CO from their solutions and of CuS and CoS from solutions of their salts by H₂S. The gaseous phase is often introduced in these reactive systems as bubbles rising through the liquid. Therefore, the motion and behaviour of gas bubbles in liquids has been studied in detail.

The shape and velocity of a bubble depends upon its volume which in turn also affects its velocity. But the classification of shapes and velocities of bubbles is expressed as a function of bubble Reynolds number

$$N_{Re, p} = \frac{D_b v_b \rho_l}{\mu_l}$$

where D_b is the equivalent spherical bubble diameter for the same volume, v_b the velocity of the bubble and ρ_l and μ_l respectively the density and the viscosity of the liquid phase. The experimental studies on behaviour of gas bubbles of different volumes have led to the following conclusions.

- (i) Very small bubbles with Reynolds number equal to or less than 2 behave like rigid solid spheres. These follow Stokes' law and thus their terminal velocity v_∞ is given by the relation obtained from Eq. (2.106) as

$$v_\infty = \frac{D_b^2 g (\rho_l - \rho_g)}{18 \mu_l} \quad (2.238)$$

Bubbles rising through molten silver usually have a diameter less than 0.2 cm.

- (ii) Bubbles with Reynolds number between 2 and 400 are still spherical in shape but their rising velocity is far greater than that predicted by

- Stokes' law, i.e. Eq. (2.238). This is assumed to be due to circulation of gas inside the bubble which in turn reduces the drag force of the liquid by affecting a convenient movement in the gas liquid interface.
- (iii) Bubbles having Reynolds number between 400 and 5000 are either spheroidal or ellipsoidal and rise in a spiral path through the liquid.
 - (iv) Bubbles having Reynolds number above 5000 are of spherical-cap shape and rise at a terminal velocity v_∞ , given by the equation

$$v_\infty = 1.02 \times \left(\frac{g D_b}{2} \right)^{1/2} \quad (2.239)$$

The angle subtended by these caps at the centre of the sphere is around 50° .

The rise of gas bubbles through liquids is accompanied by another important phenomenon. They expand in volume because of a continuous decrease in the hydrostatic pressure on them as they rise. Such a change in volume adversely affects and reduces the effective gas-liquid interfacial area and therefore the interaction between them. It is important to note that the greater this increase in volume, the more pronounced will be the effect of the reducing area. The change in volume, however, will be a function of the pressure at the surface of the liquid, the height through which the bubble rises and also the density of the liquid. For the sake of mathematical analysis, we consider here a spherical-capped bubble rising through the liquid. (We can similarly analyse the behaviour of bubbles with other shapes.) Let V_0 be the volume of this bubble at a depth H_0 below the surface of the liquid. It is important to note that the bubble may initiate or form at this depth, e.g. in open hearth furnace steel making, a carbon monoxide gas bubble nucleates at the bottom of the metal bath on refractory surface. The velocity of this bubble according to Eq. (2.239) will be given by the equation

$$\begin{aligned} v_\infty &= 1.02 \times \left(\frac{g D_b}{2} \right)^{1/2} = 1.02 \times \left[g \left(\frac{6V_0}{\pi} \right)^{1/3} \right]^{1/2} \\ &= 1.02 \times \left(\frac{6}{\pi} \right)^{1/6} (g)^{1/2} (V_0)^{1/6} \end{aligned} \quad (2.240)$$

Further, the total pressure P_0 at depth H_0 will be

$$P_0 = P_{\text{atm}} + \rho_l g H_0 \quad (2.241)$$

where ρ_l is the density of the liquid in which the bubble is rising. Similarly at any other depth H from the surface of the liquid, the total pressure on the bubble will be

$$P_H = P_{\text{atm}} + \rho_l g H \quad (2.242)$$

Assuming the gas to behave ideally, the volume of the bubble at height H will be given by

$$(P_{\text{atm}} + \rho_l g H_0) V_0 = (P_{\text{atm}} + \rho_l g H) V_b$$

or

$$V_b = \frac{P_{\text{atm}} + \rho_l g H_0}{P_{\text{atm}} + \rho_l g H} V_0 \quad (2.243)$$

Hence the velocity at height H will be given by the relation, obtained from (Eq. 2.240)

$$v_H = 1.02 \times \left(\frac{6}{\pi} \right)^{1/6} (g)^{1/2} (V_0)^{1/6} \left(\frac{P_{\text{atm}} + \rho_l g H_0}{P_{\text{atm}} + \rho_l g H} \right)^{1/6} \quad (2.244)$$

The above relation is based on two implied assumptions: (i) The bubble attains terminal velocity instantaneously, and (ii) the pressure inside the bubble is equal to the static pressure at any depth inside the liquid. Though the first assumption is valid for most gas-liquid systems, the second does not hold good for liquids at moderate depths if kept under low pressure surroundings, e.g. in vacuum degassing of melts in ladles, the bubbles inside the melt at different depths will experience different pressure changes during their rise. For a bubble close to the top layer of metal in the ladle, the pressure change will show major effects but for deep-seated bubbles, the hydrostatic head of the volume of metal will have appreciable effect and therefore a small upward movement of the bubble will not result in any appreciable pressure change inside the bubble.

EXAMPLE 2.17 Argon gas is purged through liquid steel from the bottom at 1600°C. Assuming the bubbles to be of spherical-cap shape of equivalent spherical bubble diameter 1 cm, calculate the residence time of the gas in a bath of depth 50 cm. The density and viscosity of liquid steel at 1600°C are given as 7 g cm^{-3} and $2 \times 10^{-2} \text{ poise}$ respectively.

Solution Since the Reynolds number of the bubble is not known, we assume a value in a certain range to apply in any particular relationship in order to obtain the velocity value, which can then be used to calculate the Reynolds number to check whether the first assumption was correct or not. In the present case, the argon bubbles of spherical-cap shape may be assumed to follow the relationship given in Eq. (2.239). Thus

$$\begin{aligned} D_b &= 1 \text{ cm} \\ g &= 981 \text{ cm s}^{-2} \\ \rho_l &= 7.0 \text{ g cm}^{-3} \\ \mu_l &= 2 \times 10^{-2} \text{ P} \end{aligned}$$

Therefore

$$\text{Terminal velocity, } v_\infty = 1.02 \times \left(\frac{g D_b}{2} \right)^{1/2} = 1.02 \times \left(\frac{9.81 \times 1}{2} \right)^{1/2} = 22.6 \text{ cm s}^{-1}$$

Thus

$$\text{Bubble Reynolds number, } N_{\text{Re, b}} = \frac{D_b v \rho_l}{\mu_l} = \frac{1 \times 22.6 \times 7.0}{2 \times 10^{-2}} = 7910$$

This shows that the first assumption is correct, as $N_{\text{Re, b}}$ is greater than 5000.

$$\text{Residence time} = \frac{\text{distance}}{\text{terminal velocity}} = \frac{50}{22.6} = 2.21 \text{ s} \quad \text{Ans.}$$

REVIEW QUESTIONS

1. Discuss the importance of the study of fluid flow, giving typical examples of such flow in metallurgical systems.
2. Describe different types of fluid flow. Discuss their characteristics.
3. Derive the continuity equation in the rectangular coordinate system. Transform this equation into spherical and cylindrical coordinate systems.
4. State and discuss the continuity equation for a steady state flow.
5. Derive the continuity equation for an incompressible fluid.
6. Derive the equation of motion in the rectangular coordinate system.
7. State the equation of motion in the substantial derivative form.
8. Write an essay on the viscosity of gases.
9. Discuss the methods of estimating the viscosity of metals.
10. Derive the differential mechanical energy balance equation.
11. Discuss the theory of capillary method of determining viscosity.
12. Derive the expression for Stokes' law.
13. With the help of the equation of motion, derive a relation for determining the viscosity of a fluid by the concentric cylinder method.
14. Derive an equation for the overall mass balance for a reacting fluid flowing through a cylindrical reactor.
15. Explain the term "friction factor". Explain how this factor can be determined for flow through a reactor.
16. How is the "drag coefficient" for objects travelling through a fluid determined? Illustrate your answer with the help of a suitable example.
17. Derive an equation for the overall energy balance for steady state flow of an incompressible fluid through a horizontal pipe.
18. Discuss the principles of different types of flow meters.
19. Derive an equation for the reversible adiabatic flow of a gas through a truncated cone.
20. Discuss the theoretical basis of attainment of supersonic flow in gases.
21. Derive an equation for the pressure drop for laminar flow through a packed bed.

22. Derive the Burke-Plummer equation for flow through a packed bed. Discuss the limitations of this equation.
23. Write down the Ergun's equation. How is it applied to isothermal flow of a gas through a packed bed?
24. Explain the terms: particulate fluidization, aggregative fluidization, minimum fluidization velocity, and elutriation velocity. Discuss their significance.
25. Derive equations for calculation of 'minimum fluidization' and elutriation velocities.
26. Discuss the theory of motion of gas bubbles in liquids.

PROBLEMS

1. Water with density 1000 kg m^{-3} is flowing through a smooth tube of 10 cm diameter at a rate of $1.2 \text{ m}^3 \text{ h}^{-1}$. Calculate the Reynolds number for this flow and also comment on the nature of flow. Assume the viscosity of water to be $10^{-3} \text{ kg m}^{-1} \text{ s}^{-1}$.
2. Draw the average velocity profile along the radial direction for Problem 1 assuming the following relationships:

(i) For laminar flow

$$\frac{v_z}{v_{z, \text{max}}} = 1 - \left(\frac{r}{R} \right)^2$$

(ii) For turbulent flow

$$\frac{v_z}{v_{z, \text{max}}} = \left(1 - \frac{r}{R} \right)^{1/7}$$

where z denotes the axial direction and $v_{z, \text{max}}$ is the velocity at the centre of the tube.

3. The following local velocity-time record is obtained with the help of an anemometer for a steady state flow.

Time (s)	1	3	7	9	11	16
Velocity v_x (cm s^{-1})	13.3	16.4	11.8	10.7	12.6	14.2

Calculate: (i) the average velocity (\bar{v}_x), and (ii) the turbulent intensity factor (I_x).

4. Derive, from first principles, the continuity equation for the steady state flow of an incompressible fluid.
5. With the help of Eqs. (2.45) and (2.46), arrive at the continuity equations for flow only in radial directions in spherical and cylindrical bodies.
6. Derive Eq. (2.61) from Eq. (2.59).

7. With the help of the equations of continuity and motion, derive an equation for the prediction of the shape of the surface of a liquid contained in a rotating cylindrical vessel.
8. Derive an equation for the axial flow of an incompressible fluid between two concentric cylinders.
9. Calculate the viscosity of a gas at 150°C and 600 atm pressure from the following data:

Molecular weight = 32

Critical pressure = 41 atm

Critical temperature = 138 K

10. Calculate the viscosity of a liquid metal at its melting point and at 300°C with the help of the following data:

Melting point = 232°C

Atomic weight = 118.7

Density = 7100 kg m⁻³

Activation energy for viscous flow = 12 kJ/mol

11. Derive the differential mechanical energy balance equation from first principles.

12. The following data was obtained on a capillary viscometer.

Diameter of the capillary = 6×10^{-3} m

Rate of flow = 26 litre per hour

Length of the capillary = 0.15 m

Pressure drop across the capillary = 610 Pa

Calculate the viscosity of the liquid.

13. The terminal velocity of a solid sphere is found to be 2.2 cm/s. Calculate the viscosity of the fluid with the help of the following data:

Density of the solid = 7800 kg m⁻³

Density of the fluid = 2450 kg m⁻³

Diameter of the sphere = 1.5×10^{-3} m

Acceleration due to gravity = 9.81 m s⁻²

14. Derive an equation for the volumetric flow rate of an ideal compressible fluid through a horizontal smooth pipe.

15. Air enters a convergent-divergent nozzle at a pressure of 11 atm and temperature of 75°C. Assuming air to behave ideally, calculate the critical pressure for sonic flow. Also calculate the exit velocity and temperature of the gas assuming the exit pressure to be 1 atm. It is given that γ for air is equal to 1.4 and molecular weights of oxygen and nitrogen are 32 and 28, respectively.

16. Calculate the rate of flow of an incompressible fluid per square metre cross-sectional area through a packed bed with the help of the following data:

Viscosity of the fluid	$= 10^{-3} \text{ kg m}^{-1} \text{ s}^{-1}$
Diameter of particles	$= 2 \times 10^{-2} \text{ m}$
Void fraction	$= 0.4$
Length of the bed	$= 5 \text{ m}$
Pressure drop across the bed	$= 3 \text{ atm}$
Shape factor	$= 1$

17. Calculate the pressure drop to be maintained across an isothermal packed bed of length 30 m for maintaining a rate of flow of 50 tonnes of air per square metre per day making use of the following data:

Viscosity of air	$= 4 \times 10^{-5} \text{ kg m}^{-1} \text{ s}^{-1}$
Diameter of particles	$= 5 \times 10^{-2} \text{ m}$
Void fraction	$= 0.35$
Temperature of the bed	$= 300^\circ\text{C}$
Density of air at 300°C	$= 0.635 \text{ kg m}^{-3}$
Exit pressure	$= 1 \text{ atm}$
Shape factor	$= 1$

18. Calculate the minimum fluidization and elutriation velocities for a bed of haematite particles of 0.07 mm diameter with the help of the following data:

Density of haematites	$= 5200 \text{ kg m}^{-3}$
Viscosity of the gas	$= 3.5 \times 10^{-5} \text{ kg m}^{-1} \text{ s}^{-1}$
Molecular weight of the gas	$= 28$
Temperature	$= 400^\circ\text{C}$
Pressure at the top of the bed	$= 1 \text{ atm}$

Assume the bed to behave ideally. Neglect the effect of the change of pressure on the density of the gas.

19. Calculate the terminal rising velocity of spherical-cap-shaped bubbles of volume $5 \times 10^{-6} \text{ m}^3$ through molten iron. Use relevant data from standard tables.

CHAPTER 3

Heat Transfer

All pyrometallurgical processes involve chemical reactions which are accompanied by either absorption or evolution of heat. As a result of these reactions, the system becomes nonisothermal, i.e. different parts of the reactor develop different temperatures. This difference in temperature causes a transfer of heat from one part of the reactor to the other and also from the reactor to the surrounding atmosphere or vice versa. This transfer can occur by one or more of the three elementary heat transfer processes—conduction, convection and radiation.

Conduction is that mode of heat transfer in which heat is transferred from one part of the system to another by the exchange of internal energy of the molecules or the atoms with their neighbours without causing a net macroscopic flow of mass or material. From this statement it is clear that transfer of heat by this mode requires a solid or fluid medium, i.e. one consisting of a continuous array of atoms or molecules. This is the only mode by which heat is transferred through opaque solids such as refractories, solid metals or alloys. Transparent solids involve, in addition, transfer by radiation. A detailed treatment of conductive heat transfer is presented in Section 3.1.

Convection is defined as that mode of heat transfer in which the transfer takes place through macroscopic movement of the material from one part of the system to the other. It is of course implied that these two parts, between which this material exchange occurs, will be at different temperatures. Heat transfer by convection is also referred to as convective heat transfer, which is predominant in the case of fluids. A detailed treatment of this mode of heat transfer is presented in Section 3.2.

Radiation is that mode of heat transfer in which heat energy gets transferred from one part of a system to another by means of electromagnetic waves. It is well known that a body, depending upon its temperature, emits energy in the form of electromagnetic waves or radiations. When these radiations strike another object, a part of these may be absorbed resulting in the transfer of heat from one body to another. This mode of heat transfer does not need any

supporting material or medium for transfer of energy, in contrast to conduction and convection. It is predominant at high temperatures and accounts for a large percentage of heat transferred from luminous flames and also from hot metal bath to the roof of open hearth and reverbratory furnaces. This mode of heat transfer is dealt with in detail in Section 3.3.

The main aims of the study of heat transfer, as far as kinetic aspects of metallurgical processes are concerned, include (i) either arriving at the temperature profiles in the reactor or estimating the temperature in the reaction zone, (ii) calculating the average temperature inside the reactor, and (iii) calculating the heat losses from the bounding surfaces. In all these cases, we require a knowledge of the temperature T as a function of space or location (i.e. x , y and z coordinates) and time t expressed in a functional mathematical form such as

$$T = T(x, y, z, t) \quad (3.1)$$

As the above function contains only one dependent variable, i.e. temperature, it requires only one equation for its solution. However, in the case of convective heat transfer, which involves flow of a fluid, this equation is solved simultaneously with mass- and momentum-balance equations. This equation is, therefore, derived, for various modes of heat transfer in the respective sections. Section 3.4 is devoted to some applications of heat transfer studies in metallurgy.

3.1 CONDUCTION

According to the second law of thermodynamics, heat will flow from any part of a body at a higher temperature to another at a lower temperature. According to the phenomenological approach which assumes the flux to be directly proportional to the potential gradient, the rate of heat transfer, from the part at higher temperature will be directly proportional to the gradient of temperature which also acts as the driving force for heat flow. This statement is expressed mathematically as

$$\dot{q} = -k_x A \frac{\partial T}{\partial x} \quad (3.2)$$

where \dot{q} is the rate of heat transfer per unit time, T the absolute temperature, A the area normal to the direction of flow and k_x is the constant of proportionality known as the thermal conductivity of the material through which heat flow is being considered. In the above equation, the symbol x denotes the direction of flow. The negative sign indicates that the flow will take place in the direction of negative temperature gradient, i.e. it will take place from higher to lower temperature.¹ Equation (3.2) in one-dimensional form is commonly

¹ Another parameter called the *heat flux* denoted by J , is sometimes used to indicate the ratio of q and A , which may be defined as the heat transfer rate per unit time per unit cross-sectional area. The concept of 'heat flux' is similar to 'mass flux' as discussed later.

known as *Fourier's law* of heat conduction. In later sub-sections, this law will be used in conjunction with the law of conservation of energy to arrive at relations that can be used for calculation of temperature profiles in the desired system. But before doing so, we discuss below *thermal conductivity* of materials, a property which influences temperatures profiles.

3.1.1 Thermal Conductivity

As seen from Eq. (3.2), thermal conductivity, in general, can be defined as the amount of heat transferred per unit area of a material under unit temperature gradient. The dimensions of thermal conductivity can be arrived at with the help of Eq. (3.2) which states that

$$\begin{aligned} k_x &= - \frac{\dot{q}}{A} \times \frac{1}{\frac{\partial T}{\partial x}} \\ &= \frac{QL^{-2}}{t TL^{-1}} = QL^{-1} t^{-1} T^{-1} \end{aligned} \quad (3.3)$$

Thus, in the SI system, thermal conductivity is expressed as joules per metre per second per kelvin, i.e. $J m^{-1} s^{-1} K^{-1}$ or watts per metre per kelvin, i.e. $W m^{-1} K^{-1}$. Similarly, in the CGS system it is expressed as calories per centimetre per second per degree Celsius, i.e. $cal cm^{-1} s^{-1} ^\circ C^{-1}$.

Another commonly used property in conjunction with heat conduction is thermal diffusivity (α) which is defined by the relation

$$\alpha = \frac{k}{\rho C_p} \quad (3.4)$$

where k is the thermal conductivity, ρ the density and C_p the heat capacity at constant pressure. It can be shown that thermal diffusivity will have the unit $m^2 s^{-1}$ in the SI system and $cm^2 s^{-1}$ in the CGS system. Because of the complicated experimental techniques used for determination of the thermal conductivity of different materials, the data available on thermal conductivities of solids and fluids, particularly on materials of metallurgical interest, is scarce except in the case of some standard refractory materials. Therefore, in general, one is required to calculate values of thermal conductivity of materials using certain relations arrived at either on some theoretical or on some empirical basis. The most commonly used relationships for fluids and metals are summarized below.

Thermal conductivity of gases

Theoretical approaches to the prediction of thermal conductivity are based on the kinetic theory of gases. On the basis of this theory, we can arrive at the following relation for conductivity (k) of a monatomic ideal gas,¹

¹ J.O. Hirschfelder, C.F. Curtis and R.B. Bird, *Molecular Theory of Gases and Liquids*, Wiley, New York, p. 534 (1954).

$$k = \frac{C_v V \lambda}{3} \quad (3.5)$$

which, for dilute gases can be modified to

$$k = \frac{1}{d^2} \left(\frac{k_B^3 T}{\pi^3 m} \right)^{1/2} \quad (3.6)$$

where C_v is the heat capacity of the gas at constant volume, V the specific volume, λ the mean free path of the gas, d and m its atomic diameter and mass respectively, k_B the Boltzmann constant, and T the absolute temperature.

In order to take into account the interaction among various atoms, Chapman and Gowling¹ suggested the following semi-empirical relationship.

$$k = 1.989 \times 10^{-4} \left(\frac{T}{M} \right)^{1/2} \frac{1}{\sigma^2 \Omega_k} \quad (3.7)$$

where k is in cal cm⁻¹ s⁻¹ K⁻¹, M the molecular weight, σ the collision diameter in Å and Ω_k which is equal to Ω_μ , is a function identical to the collision function in the theory of viscosity and is calculated using the dimensionless temperature $k_B T / \varepsilon$. Values of σ and Ω_k are given in Tables 4.1 and 4.2. Equation (3.7) is very similar to Eq. (2.11) and, therefore, permits the deduction of the following relation between viscosity μ and thermal conductivity k of the monatomic gas.

$$k = \frac{15 R \mu}{4 M} \quad (3.8)$$

For polyatomic gases, we use the following semi-empirical relation due to Eucken²

$$k = \left(C_p + \frac{5R}{4M} \right) \mu \quad (3.9)$$

where C_p is the heat capacity at constant pressure. In the case of mixtures of gases, the relation generally used is given by the equation

$$k = \sum_{i=1}^n \frac{N_i k_i}{\sum_{j=1}^n N_j \phi_{ij}} \quad (3.10)$$

where N_i is the mole fraction and k_i the conductivity of the i th component and ϕ_{ij} is defined as

$$\phi_{ij} = \frac{1}{8} \left(1 + \frac{M_i}{M_j} \right)^{-1/2} \left[1 + \left(\frac{\mu_i}{\mu_j} \right)^{1/2} \left(\frac{M_j}{M_i} \right)^{1/4} \right]^2 \quad (3.11)$$

Equations (3.10) and (3.11) are applicable only at low densities.

¹ S. Chapman and T.G. Gowling, *Mathematical Theory of Non-Uniform Gases*. 2nd ed., Cambridge, New York (1951).

² A. Eucken, *Physik. z.*, **14**: 325 (1914).

EXAMPLE 3.1 Calculate the thermal conductivity and thermal diffusivity of argon at 500°C and 1 atm pressure with the help of (i) Eq. (3.6), and (ii) Eq. (3.7) making use of the following data:

Molecular weight	= 40
Atomic diameter	= 3.82 Å
Collision diameter (σ)	= 3.418 Å
Ω_k	= 0.8963
C_v	= 1.5 R
R	= $8.3 \times 10^3 \text{ kg m}^2 \text{ s}^{-2} \text{ kg-mol}^{-1} \text{ K}^{-1}$
N	= 6.02×10^{23}

Solution (i) According to Eq. (3.6), we have

$$\begin{aligned} k &= \frac{1}{d^2} \left(\frac{k_B^3 T}{\pi^3 m} \right)^{1/2} = \frac{1}{d^2} \left(\frac{R^3 T N}{\pi^3 N^3 M} \right)^{1/2} \\ &= \frac{1}{(3.82 \times 10^{-10})^2} \left[\frac{(8.3 \times 10^3)^3 \times (500 + 273)}{\left(\frac{22}{7} \right)^3 (6.02 \times 10^{23})^2 \times 40} \right]^{1/2} (\because 1 \text{ Å} = 10^{-10} \text{ m}) \\ &= 6.8 \text{ J m}^{-1} \text{ s}^{-1} \text{ K}^{-1} \end{aligned} \quad \text{Ans.}$$

$$\begin{aligned} \text{Density } (\rho) \text{ of the gas} &= \left(\frac{RT}{MP} \right)^{-1} \\ &= \left[\frac{8.3 \times 10^3 \times (500 + 273)}{40 \times 1.01 \times 10^5} \right]^{-1} = 0.64 \text{ kg m}^{-3} \end{aligned}$$

$$\text{Thermal diffusivity, } \alpha = \frac{k}{\rho C_v} = \frac{6.8}{0.64 \times 1.5 \times 8.3 \times 10^3} = 8.5 \times 10^{-4} \text{ m}^2 \text{ s}^{-1}$$

Ans.

(ii) According to Eq. (3.7), we have

$$\begin{aligned} k &= 1.989 \times 10^{-4} \frac{1}{\sigma^2 \Omega_k} \left(\frac{T}{M} \right)^{1/2} \\ &= 1.989 \times 10^{-4} \frac{1}{(3.418)^2 \times 0.8963} \times \left(\frac{500 + 273}{40} \right)^{1/2} \\ &= 8.35 \times 10^{-5} \text{ cal cm}^{-1} \text{ s}^{-1} \text{ K}^{-1} \\ &= 3.5 \times 10^{-2} \text{ J m}^{-1} \text{ s}^{-1} \text{ K}^{-1} \end{aligned} \quad \text{Ans.}$$

$$\text{Thermal diffusivity, } \alpha = \frac{k}{\rho C_v} = \frac{3.5 \times 10^{-2}}{0.64 \times 1.5 \times 8.3 \times 10^3} = 4.4 \times 10^{-6} \text{ m}^2 \text{ s}^{-1}$$

Ans.

It is seen that Eqs. (3.6) and (3.7) lead to widely different results. Equation (3.7) leads to results which are quite close to the experimental data and are hence frequently used for prediction of thermal conductivities of monatomic gases. Another approach to estimating thermal conductivity of gases at a desired temperature and pressure is based on critical data of gases. In Fig. 3.1 reduced thermal conductivity (defined as the ratio of thermal conductivity at any temperature and pressure to that at critical values of temperature and pressure) is plotted against reduced temperature for different values of reduced pressure.

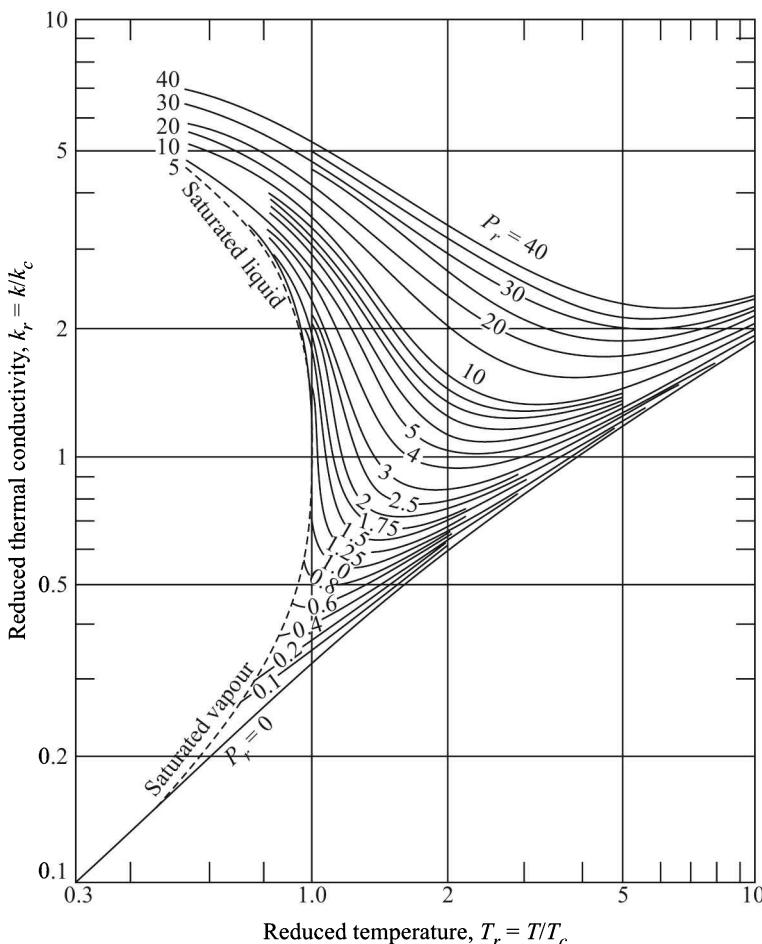


Fig. 3.1 Relationship between reduced thermal conductivity and reduced temperature at different reduced pressures.

This figure gives the value of reduced thermal conductivity. The thermal conductivity of the gas can then be obtained by knowing the critical thermal conductivity k_c and using the equation

$$k = k_c k_r \quad (3.12)$$

This is similar to Eq. 2.13 applicable in the case of viscosity.

EXAMPLE 3.2 Calculate the thermal conductivity of nitrogen, oxygen and air at 150°C and 10 atm pressure by making use of (i) Eq. (3.9), and (ii) Fig. 3.1, and with the following data:

$$T_{c, N_2} = 126.2 \text{ K} \quad T_{c, O_2} = 154.4 \text{ K}$$

$$P_{c, N_2} = 33.5 \text{ atm} \quad P_{c, O_2} = 49.7 \text{ atm}$$

$$k_{c, N_2} = 3.63 \times 10^{-2} \text{ J m}^{-1} \text{ s}^{-1} \text{ K}^{-1} \quad k_{c, O_2} = 5.05 \times 10^{-2} \text{ J m}^{-1} \text{ s}^{-1} \text{ K}^{-1}$$

$$C_{p, N_2} = 1064 \text{ J kg}^{-1} \text{ K}^{-1} \quad C_{p, O_2} = 912 \text{ J kg}^{-1} \text{ K}^{-1}$$

Solution (i) For using Eq. (3.9), μ values are required. This is done as follows. According to Eq. (2.12), we have

$$\begin{aligned} \mu_{c, N_2} &= 7.70 (M_{N_2})^{1/2} (P_{c, N_2})^{2/3} (T_{c, N_2})^{-1/6} \\ &= 7.70 \times (28)^{1/2} (33.5)^{2/3} (126.2)^{-1/6} \\ &= 188.8 \text{ micropoise} \\ &= 1.89 \times 10^{-5} \text{ kg m}^{-1} \text{ s}^{-1} \end{aligned}$$

Similarly

$$\begin{aligned} \mu_{c, O_2} &= 7.7 \times (32)^{1/2} \times (49.7)^{2/3} \times (154.4)^{-1/6} \\ &= 253.7 \text{ micropoise} \\ &= 2.54 \times 10^{-5} \text{ kg m}^{-1} \text{ s}^{-1} \end{aligned}$$

$$T_{r, N_2} = \frac{T}{T_{c, N_2}} = \frac{150 + 273}{126.2} = 3.35$$

$$T_{r, O_2} = \frac{T}{T_{c, O_2}} = \frac{150 + 273}{154.4} = 2.74$$

$$P_{r, N_2} = \frac{10}{33.5} = 0.3$$

$$P_{r, O_2} = \frac{10}{49.7} = 0.2$$

From Fig. 2.2 for $P_r = 0.3$ and $T_r = 3.35$, $\mu_r = 1.35$ for nitrogen;
for $P_r = 0.2$ and $T_r = 2.74$, $\mu_r = 1.1$ for oxygen.

Hence

$$\begin{aligned} \mu_{N_2} &= \mu_r \mu_{c, N_2} \text{ from Eq. (2.13)} \\ &= 1.35 \times 188.8 = 255 \text{ micropoise} = 2.55 \times 10^{-5} \text{ kg m}^{-1} \text{ s}^{-1} \end{aligned}$$

and

$$\begin{aligned}\mu_{O_2} &= \mu_r \mu_{c, O_2} = 1.1 \times 253.7 = 279 \text{ micropoise} \\ &= 2.79 \times 10^{-5} \text{ kg m}^{-1} \text{ s}^{-1}\end{aligned}$$

For air,

$$\begin{aligned}T_r &= 0.79 \times T_{r, N_2} + 0.21 \times T_{r, O_2} \\ &= 0.79 \times 3.35 + 0.21 \times 2.74 \\ &= 3.22 \\ P_r &= 0.79 \times P_{r, N_2} + 0.21 \times P_{r, O_2} \\ &= 0.79 \times 0.3 + 0.21 \times 0.2 \\ &= 0.28\end{aligned}$$

Hence

$$\begin{aligned}\mu_c &= 7.7 \times (0.79 \times 28 + 0.21 \times 32)^{1/2} \times (0.79 \times 33.5 + 0.21 \times 49.7)^{2/3} \\ &\quad \times (0.79 \times 126.2 + 0.21 \times 154.4)^{-1/6} \\ &= 203 \text{ micropoise} \\ &= 2.03 \times 10^{-5} \text{ kg m}^{-1} \text{ s}^{-1}\end{aligned}$$

From Fig. (2.2), we have for $T_r = 3.22$ and $P_r = 0.28$, $\mu_r = 1.25$. Thus

$$\begin{aligned}\mu_{air} &= \mu_r \mu_c = 1.25 \times 203 \\ &= 254 \text{ micropoise} = 2.54 \times 10^{-5} \text{ kg m}^{-1} \text{ s}^{-1}\end{aligned}$$

Now using Eq. (3.9), we have

$$\begin{aligned}k_{N_2} &= \left(C_{p, N_2} + \frac{5}{4} \times \frac{R}{M_{N_2}} \right) \mu_{N_2} \\ &= \left(1064 + \frac{5}{4} \times \frac{8.3 \times 10^3}{28} \right) \times 2.55 \times 10^{-5} \quad \text{Ans.} \\ &= 3.7 \times 10^{-2} \text{ J m}^{-1} \text{ s}^{-1} \text{ K}^{-1} \\ k_{O_2} &= \left(912 + \frac{5}{4} \times \frac{8.3 \times 10^3}{32} \right) \times 2.79 \times 10^{-5} \\ &= 3.5 \times 10^{-2} \text{ J m}^{-1} \text{ s}^{-1} \text{ K}^{-1} \quad \text{Ans.}\end{aligned}$$

For finding the thermal conductivity of air, we can use Eq. (3.10) which requires calculating ϕ_{ij} . This is done as follows by using Eq. (3.11).

i	j	M_i/M_j	μ_i/μ_j	ϕ_{ij}	N_j	$\Sigma N_j \phi_{ij}$
O_2	O_2	1	1	1	0.21	0.98
	N_2	$32/28$	$279/255$	0.977	0.79	
N_2	O_2	$28/32$	$255/279$	1.02	0.21	1.00
	N_2	1	1	1	0.79	

Substitution of ϕ_{ij} in Eq. (3.10) leads to

$$\begin{aligned} k_{\text{air}} &= \frac{0.21 \times 3.5 \times 10^{-2}}{0.98} + \frac{0.79 \times 3.7 \times 10^{-2}}{1.00} \\ &= 3.67 \times 10^{-2} \text{ J m}^{-1} \text{ s}^{-1} \text{ K}^{-1} \end{aligned} \quad \text{Ans.}$$

(ii) From Fig. 3.1, we have

(a) For $T_r = 3.35$ and $P_r = 0.3$, $k_r = 0.9$.

Hence, using Eq. (3.12), we have

$$\begin{aligned} k_{\text{N}_2} &= k_r k_{c, \text{N}_2} = 0.9 \times 3.63 \times 10^{-2} \\ &= 3.3 \times 10^{-2} \text{ J m}^{-1} \text{ s}^{-1} \text{ K}^{-1} \end{aligned} \quad \text{Ans.}$$

(b) For $T_r = 2.74$ and $P_r = 0.2$, $k_r = 0.75$. Therefore, we have

$$\begin{aligned} k_{\text{O}_2} &= k_r k_{c, \text{O}_2} = 0.75 \times 5.05 \times 10^{-2} \\ &= 3.8 \times 10^{-2} \text{ J m}^{-1} \text{ s}^{-1} \text{ K}^{-1} \end{aligned} \quad \text{Ans.}$$

(c) For $T_r = 3.22$ and $P_r = 0.28$, $k_r = 0.86$. Therefore, we have

$$k_{\text{air}} = k_r k_{c, \text{air}}$$

Again using (Eq. 3.10), we have

$$\begin{aligned} k_{\text{air}} &= 0.86 \left[\frac{0.21 \times 5.05 \times 10^{-2}}{0.98} + \frac{0.79 \times 3.63 \times 10^{-2}}{1.00} \right] \\ &= 3.4 \times 10^{-2} \text{ J m}^{-1} \text{ s}^{-1} \text{ K}^{-1} \end{aligned} \quad \text{Ans.}$$

Thermal conductivity of liquids

In the case of monatomic liquids, Bridgeman's equation¹ given below is generally used for calculation of thermal conductivity.

$$k = 2.8 \left(\frac{N}{V} \right)^{2/3} k_B v_s \quad (3.13)$$

where N is Avogadro's number, k_B the Boltzmann constant, and V the volume per mole. The parameter v_s in this equation is the velocity of sound in the liquid expressed by the relation

$$v_s = \left[\gamma \left(\frac{\partial P}{\partial \rho} \right)_T \right]^{1/2} \quad (3.14)$$

where $\gamma = (C_p/C_v)$ and the quantity $(\partial P/\partial \rho)$ is readily obtainable from the isothermal compressibility measurements.

EXAMPLE 3.3 Calculate the thermal conductivity of a monatomic liquid having the following properties:

Density of the liquid = $3.9 \times 10^3 \text{ kg m}^{-3}$

¹ P.W. Bridgeman, *Proc. Am. Acad. Arts. Sci.*, **59**: 141 (1923).

$$\text{Isothermal compressibility, } \beta = -\frac{1}{V} \left(\frac{\partial V}{\partial P} \right)_T = 2.7 \times 10^{-8} \text{ Pa}^{-1}$$

Boltzmann's constant, $k_B = 1.38 \times 10^{-23} \text{ J mol}^{-1} \text{ K}^{-1}$, $\gamma = 1$

Molecular weight = 47

Solution $v_s = \left[\gamma \left(\frac{\partial P}{\partial \rho} \right) \right]^{1/2}$ from Eq. (3.14)

$$= \gamma^{1/2} \left[\frac{1}{\rho} \left(\frac{1}{\rho} \frac{\partial \rho}{\partial P} \right)_T^{-1} \right]^{1/2}$$

$$= \gamma^{1/2} \rho^{-1/2} \left(-\frac{1}{V} \times \frac{\partial V}{\partial P} \right)^{-1/2}$$

$$= \gamma^{1/2} \rho^{-1/2} \beta^{-1/2}$$

$$= 1 \times (3.9 \times 10^3)^{-1/2} (2.7 \times 10^{-8})^{-1/2} = 97 \text{ m s}^{-1}$$

Therefore, from (Eq. 3.13), we get

$$k = 2.8 \times \left[\frac{\frac{6.02 \times 10^{23}}{47}}{\frac{3.9 \times 10^3}{97}} \right]^{2/3} \times (1.38 \times 10^{-23}) \times 97$$

$$= 5.08 \times 10^{-4} \text{ J m}^{-1} \text{ s}^{-1} \text{ K}^{-1} \quad \text{Ans.}$$

Thermal conductivity of solids

Because of the complicated mechanism of conduction in solids, thermal conductivity in them is generally measured experimentally and no reliable relationship is available to theoretically predict their thermal conductivities, k , except the one given below, used in the case of pure metals.

$$k = L k_e T \quad (3.15)$$

where k_e is the electrical conductivity of metal, L is a constant known as Lorenz number, weakly dependent upon temperature and varying between 22 and $29 \times 10^{-9} \text{ V}^2 \text{ K}^{-2}$ at 0°C and T the absolute temperature. Data on conductivity of metals is presented in *Metals Handbook*.¹ However, typical values for metals and some materials of interest to metallurgical systems are presented in Table 3.1 (a), (b), (c) and (d).

In a number of pyrometallurgical processes involving gas-solid reactions, a knowledge of conductivity of porous materials is required. No rigorous treatment or any exact empirical relation is available for this purpose. For approximate calculations, however, we use the following relation

$$k_{\text{eff}} = k_f^\varepsilon k_s^{1-\varepsilon} \quad (3.16)$$

¹ American Society for Metals, *Metals Handbook*, 2nd ed., Cleveland, Ohio (1979).

TABLE 3.1(a) Thermal properties of metals at 250°C*

Metal	Density (g cm ⁻³)	M. pt. (°C)	Sp. heat (cal g ⁻¹ °C ⁻¹)	Thermal conductivity (cal cm ⁻¹ s ⁻¹ K ⁻¹)	Electrical conductance (μ Ω ⁻¹)	Lorenz number (V ² K ⁻²)
Lithium	0.53	108.5	0.79	0.17	0.108	22.10 × 10 ⁻⁹
Sodium	0.97	97.8	0.295	0.32	0.218	20.4 × 10 ⁻⁹
Potassium	0.86	63.7	0.177	0.23	0.143	22.58 × 10 ⁻⁹
Beryllium	1.85	1277	0.45	0.38	0.25	21.34 × 10 ⁻⁹
Magnesium	1.74	650	0.25	0.38	0.224	19.32 × 10 ⁻⁹
Calcium	1.55	838	0.149	0.30	0.218	19.32 × 10 ⁻⁹
Titanium	4.51	1668	0.126	—	0.024	—
Zirconium	6.49	1852	0.066	—	0.024	—
Vanadium	6.1	1900	0.120	—	0.04	—
Chromium	7.19	1875	0.11	0.16	0.078	28.79 × 10 ⁻⁹
Molybdenum	10.2	2610	0.061	0.35	0.19	25.86 × 10 ⁻⁹
Tungsten	19.3	3410	0.032	0.40	0.181	31.02 × 10 ⁻⁹
Manganese	7.43	1245	0.115	—	0.054	—
Iron	7.86	1536	0.11	0.18	0.10	25.27 × 10 ⁻⁹
Cobalt	8.9	1495	0.099	0.16	0.16	14.04 × 10 ⁻⁹
Nickel	8.9	1453	0.105	0.22	0.145	21.30 × 10 ⁻⁹
Palladium	12.0	1552	0.058	0.17	0.093	25.66 × 10 ⁻⁹
Platinum	21.4	1769	0.032	0.17	0.095	25.12 × 10 ⁻⁹
Rhodium	12.4	1966	0.059	0.21	0.22	—
Copper	8.96	1083	0.092	0.94	0.593	22.26 × 10 ⁻⁹
Silver	10.5	960.8	0.056	0.98	0.616	22.34 × 10 ⁻⁹
Gold	19.3	1063	0.031	0.71	0.42	23.73 × 10 ⁻⁹
Zinc	7.14	419.5	0.0915	0.27	0.167	22.69 × 10 ⁻⁹
Cadmium	8.65	320.9	0.055	0.22	0.146	21.16 × 10 ⁻⁹

TABLE 3.1(a) Thermal properties of metals at 250°C¹ (Contd.)

Metal	Density (g cm ⁻³)	M. pt. (°C)	Sp. heat (cal g ⁻¹ °C ⁻¹)	Thermal conductivity (cal cm ⁻¹ s ⁻¹ K ⁻¹)	Electrical conductance (μ Ω ⁻¹)	Lorenz number (V ² K ⁻²)
Mercury	13.6	-38.4	0.033	0.02	0.011	25.53 × 10 ⁻⁹
Aluminum	2.70	660	0.215	0.50	0.382	18.34 × 10 ⁻⁹
Gallium	5.91	29.8	0.079	—	0.058	—
Silicon	2.33	1410	0.162	0.20	0.10	28.08 × 10 ⁻⁹
Germanium	5.32	937.4	0.073	0.14	0.022	8.94 × 10 ⁻²
Tin	7.30	231.9	0.054	0.16	0.088	25.53 × 10 ⁻⁹
Lead	11.4	327.4	0.031	0.083	0.046	25.33 × 10 ⁻⁹
Arsenic	5.72	817	0.082	—	0.029	—
Antimony	6.62	630.5	0.049	0.05	0.026	27.00 × 10 ⁻⁹
Bismuth	9.8	271.3	0.034	0.02	0.009	31.20 × 10 ⁻⁹
Selenium	4.79	217	0.084	1 × 10 ⁻⁵	0.08	17.55 × 10 ⁻⁶
Tellurium	6.24	449.5	0.047	0.014	10 ⁻⁶	19.66 × 10 ⁻⁹
Cerium	6.67	795	0.042	0.026	0.013	28.08 × 10 ⁻⁹
Thorium	11.7	1750	0.034	—	0.055	—
Uranium	19.07	1132	0.028	0.064	0.034	26.43 × 10 ⁻⁹
Indium	7.31	156.2	0.057	0.057	0.111	9.21 × 10 ⁻³
Thallium	11.85	303	0.031	0.093	0.055	2.37 × 10 ⁻²
Lanthanum	6.17	920	0.045	0.033	—	—
Hafnium	13.1	2222	0.035	0.22	0.031	0.99 × 10 ⁻⁹
Niobium						
(Columbium)	8.4	2415	0.065	0.125	0.080	21.94 × 10 ⁻⁹
Tantalum	16.6	2996	0.036	0.131	0.081	22.53 × 10 ⁻⁹

* Groupwise as per Periodic Table.

TABLE 3.1(b) Thermal conductivity of common metals at different temperatures

<i>Metal</i>	<i>Temperature</i> (°C)	<i>Thermal conductivity</i> (cal cm ⁻¹ s ⁻¹ K ⁻¹)
Aluminium	100	0.492
	300	0.64
	600	1.01
	700	0.247*
	790	0.290*
Cadmium	0	0.220
	100	0.216
	355	0.106*
	435	0.119*
Copper	18	0.918
	100	0.908
Steel	18	0.112
	100	0.107
Tin	0	0.153
	100	0.143
Lead	330	0.039*
	700	0.037*
	700	0.036*
Mercury	0	0.0196*
	120	0.0261*
	222	0.0303*
Potassium	200	0.1073*
	400	0.0956*
	600	0.0846*
Sodium	100	0.2055*
	300	0.1809*
	500	0.1596*
Na-K alloy (56/44)	100	0.0617*
	300	0.0648*
	500	0.0675*
Brass (Cu-Zn as 70/30)	-50	0.2275
	0.0	0.2482
	200	0.3102
	400	0.3309
Chromel A (Ni-Cr as 80/20)	200	0.0372
	400	0.0455
Chromel P (Ni-Cr as 90/10)	200	0.0496
	400	0.0579
Gun Bronze (Cu-Sn-Zn as 86/9/4)	200	0.1572
	400	0.1820
Monel (Ni-Cr as 67/29)	200	0.0745
	400	0.0827

* Values for liquid metal/alloy.

TABLE 3.1(c) Thermal conductivity of some gases at 1 atm pressure

Temperature K	Thermal conductivity of gas ($\times 10^3$ W m $^{-1}$ K $^{-1}$)						
	H ₂	O ₂	Air	CO ₂	CO	CH ₄	NO
100	67.99	9.04	—	—	—	10.63	—
200	128.19	18.33	—	9.49	—	21.84	17.78
300	181.72	—	26.31	16.62	25.27	34.27	25.89
450	250.95	—	37.04	29.08	43.61	—	—
800	384.22	—	57.80	—	—	—	—
1100	463.83	—	72.34	—	—	—	—
1333	519.21	—	—	—	—	—	—
1700	—	—	96.05	—	—	—	—

where k_{eff} , k_f and k_s are respectively the effective thermal conductivity of the porous material, the thermal conductivity of fluid filling the pores and that of the solid material, respectively, and ε is the void-fraction.

EXAMPLE 3.4 Calculate the thermal conductivity of a porous reduced iron layer formed by the gaseous reduction of dense ferric oxide ($\rho = 5300$ kg m $^{-3}$), assuming that reduction leads to a change in volume. Density and thermal conductivity of iron may respectively be taken as 7800 kg m $^{-3}$ and 65 J m $^{-1}$ s $^{-1}$ K $^{-1}$. The thermal conductivity of the gaseous medium may be assumed to be 3.2×10^{-2} J m $^{-1}$ s $^{-1}$ K $^{-1}$.

Solution To calculate the void-fraction ε of the porous iron layer, we assume the volume of ferric oxide to be V m 3 . Therefore, we get

$$\text{Mass of ferric oxide} = 5300V \text{ kg}$$

$$\begin{aligned}\text{Mass of iron formed} &= 5300V \times \frac{112}{160} \\ &= 3710V \text{ kg}\end{aligned}$$

$$\text{Volume of iron} = \frac{3710V}{7800} = 0.476V \text{ m}^3$$

Therefore

$$\text{Void-fraction, } \varepsilon = \left(\frac{V - 0.476V}{V} \right) = 0.524$$

According to Eq. (3.16), thermal conductivity k of the porous layer will be given by

$$\begin{aligned}k &= (k_g)^{0.524} (k_{\text{Fe}})^{0.476} \\ &= (3.2 \times 10^{-2})^{0.524} \times (65)^{0.476} \\ &= 1.13 \text{ J m}^{-1} \text{ s}^{-1} \text{ K}^{-1} \quad \text{Ans.}\end{aligned}$$

TABLE 3.1(d) Thermal conductivity of refractory materials

Refractory	Apparent Bulk density (g cm ⁻³)	Porosity (%)	Composition (%)	Thermal conductivity (× 10 ³ cal cm ⁻¹ s ⁻¹ K ⁻¹)		
				200°C	600°C	1000°C
Fire brick	2.65	18.4	SiO ₂ (53.1), Al ₂ O ₃ (43.3), MgO (0.5), CaO (0.6), Fe ₂ O ₃ (2.5)	2.40	3.47	3.89
Fire brick	2.59	26.7	SiO ₂ (54.2), Al ₂ O ₃ (38.8), MgO (1.1), CaO (0.1), Fe ₂ O ₃ (2.7), TiO (2.7)	2.40	2.98	3.39
Kaolin brick	2.66	10.8	SiO ₂ (52.0), Al ₂ O ₃ (45.9), Fe ₂ O ₅ (1.5), TiO (0.4)	4.67	5.58	6.37
	2.69	23.2	SiO ₂ (97.0), impurities-rest	3.39	4.10	4.47
	2.5	49.1	SiO ₂ (5), Al ₂ O ₃ + Cr ₂ O ₃ (60), MgO (15), FeO (15)	1.12	1.78	2.19
Silica brick	2.24	30.4	SiO ₂ (97.0), impurities-rest	2.81	3.97	4.80
Chrome brick	3.94	30.5	SiO ₂ (5), Al ₂ O ₃ + Cr ₂ O ₃ (60), MgO (15), FeO (15)	3.39	3.80	3.97
Magnesite brick	3.54	31.6	MgO + CaO (90), Fe ₂ O ₂ (5)	13.65	10.26	8.98
Spinel brick	3.64	36.3	Al ₂ O ₃ (65), MgO + CaO (26)	3.60	4.34	4.67
Fused alumina brick	3.67	21.3	Al ₂ O ₃ ≈ (100)	6.16	8.15	9.47
Zirconia brick	4.87	29.5	SiO ₂ (27.3), Al ₂ O ₃ (7.8), ZrO ₂ (60.4), Fe ₂ O ₃ (1.6)	3.47	4.34	4.59
Bonded silicon carbide	2.53	16	SiC (89), impurities-rest	—	36.53	37.23

3.1.2 Heat Conduction Equation

Heat conduction equation is derived in a similar way as the mass and momentum balance equations in Chapter 2 by considering a differential volume element in a solid stagnant material as shown in Fig. 3.2. Consider that heat is flowing into this element through the faces touching the point $P(x, y, z)$ and leaving from the other three faces, i.e. those touching the point $Q(x + \delta x, y + \delta y, z + \delta z)$. If heat is the only form of energy which this element is exchanging with the surroundings and if there is a chemical or physical reaction taking place in the element leading to evolution or absorption of heat, then according to the law of conservation of energy, we have the following relation.

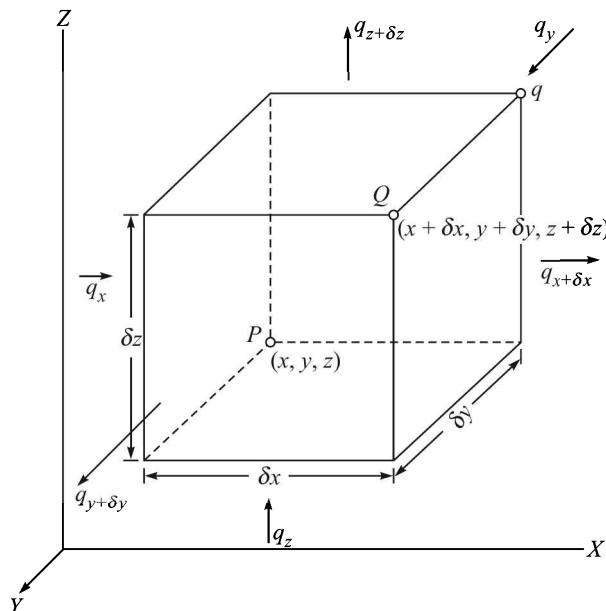


Fig. 3.2 Differential volume element for derivation of heat-conduction equation in rectangular coordinates.

Rate of flow of heat into the volume element – Rate of flow of heat out of the volume element

$$= \text{Rate of change of heat in the volume element} - \text{Rate of heat production due to the reaction} \quad (3.17)$$

If \dot{q}_x , \dot{q}_y and \dot{q}_z be the amounts of heat entering the differential volume element under consideration per unit time from the x -, y - and z -directions, respectively from the face touching the point P , then using Eq. (3.2), we get

$$\dot{q}_x = - kx\delta y\delta z \left(\frac{\partial T}{\partial x} \right)_{x=x} \quad (3.18)$$

$$\dot{q}_y = -k_y \delta x \delta z \left(\frac{\partial T}{\partial y} \right)_{y=y} \quad (3.19)$$

$$\dot{q}_y = -k_z \delta x \delta y \left(\frac{\partial T}{\partial x} \right)_{z=z} \quad (3.20)$$

where k_x , k_y and k_z are the thermal conductivities of the material in the x -, y - and z -directions respectively.

For the amounts of heat leaving this volume element in the x -, y -, and z -directions from the other three faces touching the point Q, we can similarly write the following relations:

$$\dot{q}_{x=\delta x} = -k_x \delta y \delta z \left(\frac{\partial T}{\partial x} \right)_{x=x+\delta x} \quad (3.21)$$

$$\dot{q}_{y+\delta y} = -k_y \delta x \delta z \left(\frac{\partial T}{\partial y} \right)_{y=y+\delta y} \quad (3.22)$$

$$\dot{q}_{z+\delta z} = -k_z \delta x \delta y \left(\frac{\partial T}{\partial z} \right)_{z=z+\delta z} \quad (3.23)$$

The amount of heat retained per unit time in the volume element is

$$\frac{\partial q}{\partial t} \delta x \delta y \delta z \quad (3.24)$$

Further if C_p and ρ be respectively, the specific heat at constant pressure and density of the material of the volume element, then

$$\frac{\partial q}{\partial t} = C_p \rho \frac{\partial T}{\partial t} \quad (3.25)$$

Also, let the amount of heat produced due to reaction per unit time = \dot{q}_r

Substitution of Eqs. (3.18) to (3.26) in Eq. (3.17) and division of both sides by the term $\delta x \delta y \delta z$ leads to the relation

$$\begin{aligned} & \frac{k_x}{\delta x} \left[\left(\frac{\partial T}{\partial x} \right)_{x=x+\delta x} - \left(\frac{\partial T}{\partial x} \right)_{x=x} \right] + \frac{k_y}{\delta y} \left[\left(\frac{\partial T}{\partial y} \right)_{y=y+\delta y} - \left(\frac{\partial T}{\partial y} \right)_{y=y} \right] \\ & + \frac{k_z}{\delta z} \left[\left(\frac{\partial T}{\partial z} \right)_{z=z+\delta z} - \left(\frac{\partial T}{\partial z} \right)_{z=z} \right] = C_p \rho \frac{\partial T}{\partial t} - \frac{\dot{q}_r}{\delta x \delta y \delta z} \end{aligned} \quad (3.27)$$

Taking the dimensions of the volume element to be infinitesimal and denoting by σ the amount of heat produced due to the reaction per unit time per unit volume, we can write the above relation in the following alternative form.

$$C_p \rho \frac{\partial T}{\partial t} = \frac{\partial}{\partial x} \left(k_x \frac{\partial T}{\partial x} \right) + \frac{\partial}{\partial y} \left(k_y \frac{\partial T}{\partial y} \right) + \frac{\partial}{\partial z} \left(k_z \frac{\partial T}{\partial z} \right) + \sigma \quad (3.28)$$

If the material is isotropic, i.e. $k_x = k_y = k_z = k$, we have

$$\frac{\partial T}{\partial t} = \frac{\partial}{\partial x} \left(\frac{k}{C_p \rho} \frac{\partial T}{\partial x} \right) + \frac{\partial}{\partial y} \left(\frac{k}{C_p \rho} \frac{\partial T}{\partial y} \right) + \frac{\partial}{\partial z} \left(\frac{k}{C_p \rho} \frac{\partial T}{\partial z} \right) + \frac{\sigma}{C_p \rho} \quad (3.29)$$

If k , C_p and ρ are assumed to be independent of temperature, and we use the parameter "thermal diffusivity", α which is defined as $\alpha = k/C_p\rho$, we can now write Eq. (3.29) as

$$\frac{\partial T}{\partial t} = \alpha \left(\frac{\partial^2 T}{\partial x^2} + \frac{\partial^2 T}{\partial y^2} + \frac{\partial^2 T}{\partial z^2} \right) + \frac{\sigma}{C_p \rho} \quad (3.30)$$

Two important simplified cases of heat conduction related to the above relation are as follows:

- (i) *Heat conduction without any heat producing/consuming/reaction.* In this case, the heat produced or consumed per unit time per unit volume will be equal to zero. Hence

$$\sigma = 0 \quad (3.31)$$

Therefore, Eq. (3.30) is simplified to

$$\frac{\partial T}{\partial t} = \alpha \left(\frac{\partial^2 T}{\partial x^2} + \frac{\partial^2 T}{\partial y^2} + \frac{\partial^2 T}{\partial z^2} \right) = \alpha \nabla^2 T \quad (3.32)$$

where ∇^2 is the Laplace operator.

- (ii) *Heat conduction under steady state.* In this case, the temperature profile in the conducting medium does not change with time. In other words, at any position in the reactor, the temperature is not a function of time. Hence

$$\frac{\partial T}{\partial t} = 0 \quad (3.33)$$

So, the heat conduction equation for this case without heat source or sink in the system, i.e. $\sigma = 0$, takes the form

$$\nabla^2 T = 0 \quad (3.34)$$

For study of a number of practical cases, one requires the heat conduction equation in cylindrical or spherical coordinate systems. Equation (3.32) can be transformed to these coordinate systems by using a standard transformation method. The transformed relations in these coordinate systems are given below:

- (a) Heat conduction equation in the cylindrical coordinate system is given by

$$\frac{\partial T}{\partial t} = \alpha \left[\frac{1}{r} \frac{\partial}{\partial r} \left(r \frac{\partial T}{\partial r} \right) + \frac{1}{r^2} \frac{\partial^2 T}{\partial \theta^2} + \frac{\partial^2 T}{\partial z^2} \right] \quad (3.35)$$

- (b) Heat conduction equation in the spherical coordinate system is given by

$$\frac{\partial T}{\partial t} = \frac{\alpha}{r^2} \left[\frac{\partial}{\partial r} \left(r^2 \frac{\partial T}{\partial r} \right) + \frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial T}{\partial \theta} \right) + \frac{1}{\sin^2 \phi} \frac{\partial^2 T}{\partial \phi^2} \right] \quad (3.36)$$

3.1.3 Applications of the Heat Conduction Equation

In this subsection, the application of heat conduction equation to simple cases of metallurgical importance will be discussed. These cases are broadly grouped into two categories of ‘steady-state’ and ‘transient-state’ heat conduction and subclassified as follows.

Steady state heat conduction. Three cases, which are important for metallurgists, are considered in this group:

1. Steady state heat conduction to a spherical pellet from an infinite stagnant fluid medium.
2. Steady state heat conduction through composite walls.
3. Steady state conduction in two-dimensional systems.

Transient or unsteady state heat conduction. Three cases are considered in this group too.

1. Unsteady state heat conduction from a unidimensional plate.
2. Heat conduction with moving interfaces.
3. Heat conduction with a moving heat source.

A detailed treatment of various heat conduction problems has been presented by Carslaw and Jaeger,¹ and Jakob.² The reader may refer to their works for a further study of the methods of solving problems related to heat conduction and for the solution of problems under given sets of conditions.

Steady state heat conduction to a spherical pellet from an infinite stagnant fluid medium

A number of metallurgical processes such as roasting and solid state reduction, involve gas-solid reactions. Laboratory kinetic studies of these reactions involve measurement of the change in weight with time of a pellet suspended in a flowing gas medium. This medium affects both heat- and mass-transfer to the surface of the pellet and therefore requires a careful consideration in the analysis of solid-gas reactions. For the present, a limiting case of a stagnant fluid shall be considered.

¹ H.S. Carslaw and J.C. Jaeger, *Conduction of Heat in Solids*, Clarendon, Oxford (1959).

² M. Jakob, *Heat Transfer*, Wiley, New York (1959).

We consider a spherical pellet of radius R_0 as shown in Fig. 3.3. Let its surface temperature be T_s and that of the gas at a very large distance from the pellet be T_g . From Eq. (3.36), we get the following relation for radial heat transfer in the pellet under steady state:

$$\frac{\partial}{\partial r} \left(r^2 \frac{\partial T}{\partial r} \right) = 0 \quad (3.37)$$

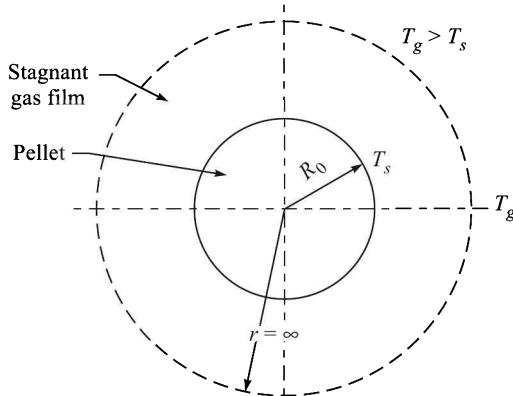


Fig. 3.3 Steady state heat conduction to a spherical pellet from an infinite stagnant fluid medium ($T_g > T_s$).

Integration of the above equation yields

$$T = - \frac{C_1}{r} + C_2 \quad (3.38)$$

where C_1 and C_2 are the constants of integration, values of which are obtained using the following boundary conditions:

- (i) $T = T_s$ at $r = R_0$
- (ii) $T = T_g$ at $r = \infty$

Substitution of these conditions in Eq. (3.38) leads to the relation

$$T = T_g - \frac{(T_g - T_s) R_0}{r} \quad (3.39)$$

Using this relation, we can arrive at the following equation for the heat transfer per unit time to the pellet:

$$q = - A k \left(\frac{\partial T}{\partial r} \right)_{r=R_0}$$

or

$$q = + 4\pi R_0^2 k \left(\frac{\partial T}{\partial r} \right)_{r=R_0}$$

or

$$q = 4\pi R_0 k (T_g - T_s) \quad (3.40)$$

We can apply similar treatment to the radial flow of heat through a system consisting of concentric spheres. An application of Eq. (3.40) is shown in Example 3.5.

Steady state heat conduction through composite walls

In this case, a system with cylindrical symmetry and having heat conduction only in the radial direction is considered as this situation occurs commonly in industrial processes, e.g. in recuperators, heat flow from the walls of Cowper stoves, cupolas, etc. In nuclear reactors too, using rod type bonded fuel elements, heat generated in the central fuel element is radially transferred through the bond metal and cladding to the flowing coolant surrounding such elements or fuel bundles. In the case of muffle furnaces with parallel composite walls, one-dimensional steady state heat flow can be considered by using Eq. (3.2).

Under steady state conditions with heat flow only in the radial direction, Eq. (3.35) can be simplified to the form

$$\frac{\partial}{\partial r} \left(r \frac{\partial T}{\partial r} \right) = 0 \quad (3.41)$$

We now consider a composite cylindrical refractory shell consisting of concentric layers of different materials as shown in Fig. 3.4. Let r_0, r_1, r_2, r_3, r_4 be the radii at various interfaces and let T_0, T_1, T_2, T_3, T_4 be the temperatures at these interfaces respectively. Let k_1, k_2, k_3 and k_4 be the conductivities of these materials. As, in general, the temperature at the inner and outer surfaces of the wall are measured, so the aim of the analysis in the present section is to derive an equation for the temperature profiles as well as the amount of heat flowing through the wall in terms of properties of these layers and the temperature of the inner and outer surfaces, i.e. T_0 and T_4 .

Integration of Eq. (3.41) yields

$$T = C_1 \ln r + C_2 \quad (3.42)$$

where C_1 and C_2 are constants of integration and are determined by the temperatures at the two ends of a layer. Thus, for the first layer temperature,

$$\begin{aligned} T &= T_0, \quad \text{at } r = r_0, \quad \text{and} \\ T &= T_1, \quad \text{at } r = r_1 \end{aligned}$$

Hence Eq. (3.2) can be expressed in the form

$$T = \frac{T_0 - T_1}{\ln r_0 - \ln r_1} \ln \frac{r}{r_0} + T_1 \quad (3.43)$$

and the amount of heat transferred per unit axial length of this layer per unit time can be expressed as

$$q = -2\pi r_0 k_1 \left(\frac{\partial T}{\partial r} \right)_{r=r_0}$$

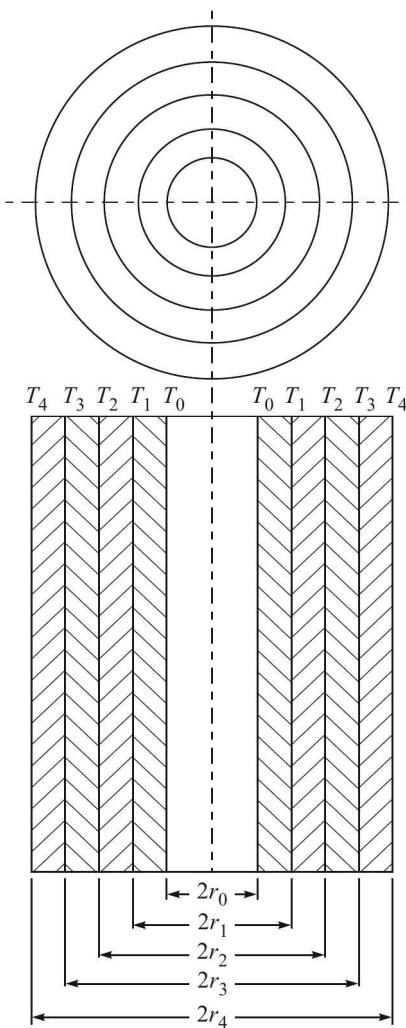


Fig. 3.4 Heat conduction through composite walls.

$$= - \frac{T_0 - T_1}{\frac{1}{2\pi k_1} (\ln r_0 - \ln r_1)} \quad (3.44)$$

We can formulate similar equations for the other layers too.

As the heat flow through the composite refractory wall is considered to be under steady state, whatever heat enters into a layer at one end, must also leave it at the other. Hence

$$q = - \frac{T_0 - T_1}{\frac{1}{2\pi k_1} \ln \left(\frac{r_0}{r_1} \right)} = - \frac{T_1 - T_2}{\frac{1}{2\pi k_2} \ln \left(\frac{r_1}{r_2} \right)} = - \frac{T_2 - T_3}{\frac{1}{2\pi k_3} \ln \left(\frac{r_2}{r_3} \right)} = - \frac{T_3 - T_4}{\frac{1}{2\pi k_4} \ln \left(\frac{r_3}{r_4} \right)}$$

$$\equiv - \frac{T_0 - T_4}{\frac{1}{2\pi k_1} \ln\left(\frac{r_0}{r_1}\right) + \frac{1}{2\pi k_2} \ln\left(\frac{r_1}{r_2}\right) + \frac{1}{2\pi k_3} \ln\left(\frac{r_2}{r_3}\right) + \frac{1}{2\pi k_4} \ln\left(\frac{r_3}{r_4}\right)} \quad (3.45)$$

The last equality in the above equation is the required result. With the help of the above equation, we can also calculate the temperatures at the different interfaces of the composite wall.

EXAMPLE 3.5 In a laboratory experiment on the study of the mechanism of roasting of sulphide ores, pellets of ores of diameter 1.5 cm were heated at 900°C in an atmosphere of hot air. Calculate the rate of heat transfer by conduction inside the pellet. The thermal conductivity of the ore may be taken as 2 W m⁻¹ K⁻¹ and the initial surface temperature of the ore as 25°C.

Solution R_0 , radius of the ore pellet = 1.5 cm = 0.015 m

k , thermal conductivity of the pellet = 2 W m⁻¹ K⁻¹.

T_s , surface temperature of the pellet = 25 + 273 = 298 K

T_g , gas temperature = 900 + 273 = 1173 K

Using Eq. (3.40), the rate of heat transfer is

$$\begin{aligned} q &= + 4\pi R_0 k (T_g - T_s) \\ &= + 4\pi \times 0.015 \times 2 \times (1173 - 298) \\ &= 4\pi \times 0.015 \times 2 \times 875 \\ &= 330 \text{ W} \end{aligned} \quad \text{Ans.}$$

Two-dimensional steady state heat conduction

So far, we have considered the flow of heat in one direction only. A number of industrial problems can be reduced to one-dimensional systems by making use of the properties of symmetry. But for cases involving heat conduction in systems of irregular geometries, a multi-dimensional approach is needed. In this section, we consider the techniques for solving two-dimensional steady-state problems. The extension of these techniques to three-dimensional systems is considered to be out of the scope of the present text and the reader may refer to some standard text on numerical techniques for solutions of such problems. For two-dimensional steady-state conduction, the equation for heat conduction, viz. Eq. (3.34), reduces to

$$\frac{\partial^2 T}{\partial x^2} + \frac{\partial^2 T}{\partial y^2} = 0 \quad (3.46)$$

This equation is generally called the *Laplace equation*. It can be solved under a given set of boundary conditions by computational methods. Alternatively, an analytical solution may be obtained through the application of either the method of separation of variables or the Laplace transforms. In this section, we will discuss one of the computational methods, namely flux-plotting or flow-net

technique, and defer the use of application of analytical techniques on similar equations to some other sections. Other methods of computational techniques, namely

- (i) the finite differences method, and
- (ii) the finite element method

are discussed in detail in many standard textbooks.

We now briefly discuss the flux-plotting or flow-net technique and illustrate its use with the help of simple examples, under the condition that the temperatures at the boundaries are known. Such a condition is referred to as the Dirichlettype boundary condition.

Flux-plotting or flow-net technique. This technique is based on the properties of complex functions. We consider a complex function, $f(z)$ which can be separated into real and imaginary parts and hence expressed as follows:

$$f(z) \equiv f(x + iy) = \phi(x, y) + i\psi(x, y) \quad (3.47)$$

where ϕ and ψ are two real functions of coordinates x and y . Differentiation of the above equation with respect to x yields

$$\frac{\partial f(z)}{\partial x} = \frac{df(z)}{dz} \frac{\partial z}{\partial x} = i \frac{df(z)}{dz} = \frac{\partial \phi}{\partial x} + i \frac{\partial \psi}{\partial x} \quad (3.48)$$

as

$$\frac{\partial z}{\partial x} = 1$$

Similarly, differentiation of this function with respect to y yields

$$\frac{\partial f(z)}{\partial y} = \frac{df(z)}{dz} \frac{\partial z}{\partial y} = i \frac{df(z)}{dz} = \frac{\partial \phi}{\partial y} + i \frac{\partial \psi}{\partial y} \quad (3.49)$$

Comparison of Eqs. (3.48) and (3.49) shows that

$$\frac{\partial \phi}{\partial x} = \frac{\partial \psi}{\partial y} \quad (3.50)$$

and

$$\frac{\partial \psi}{\partial x} = - \frac{\partial \phi}{\partial y} \quad (3.51)$$

These relations lead to the conclusion that the functions ϕ and ψ are orthogonal. This means that if we draw the “iso- ϕ ” and “iso- ψ ” lines at arbitrarily selected values of ϕ and ψ on a rectangular coordinate system, the tangents to these lines at the points of intersection of the two functions will be at right angles to each other. We now take the partial derivatives of Eqs. (3.50) and (3.51), first with respect to x and then with respect to y . We will then obtain the following four equations:

$$\frac{\partial^2 \phi}{\partial x^2} = \frac{\partial^2 \psi}{\partial x \partial y} \quad (3.52)$$

$$\frac{\partial^2 \psi}{\partial x^2} = - \frac{\partial^2 \phi}{\partial x \partial y} \quad (3.53)$$

$$\frac{\partial^2 \phi}{\partial y \partial x} = \frac{\partial^2 \psi}{\partial y^2} \quad (3.54)$$

$$\frac{\partial^2 \psi}{\partial y \partial x} = - \frac{\partial^2 \phi}{\partial y^2} \quad (3.55)$$

From Eqs. (3.52) and (3.55), we get

$$\frac{\partial^2 \phi}{\partial x^2} + \frac{\partial^2 \phi}{\partial y^2} = 0 \quad (3.56)$$

Similarly, Eqs. (3.53) and (3.54) lead to

$$\frac{\partial^2 \psi}{\partial x^2} + \frac{\partial^2 \psi}{\partial y^2} = 0 \quad (3.57)$$

The above equations show that both the functions ϕ and ψ follow the Laplace equation which is also followed by the temperature as expressed by Eq. (3.46). If we identify the function ϕ with temperature T , we can proceed to determine what the function ψ represents. For this purpose, we consider the flow of heat in the x -direction across a rectangular cross-sectional area of breadth δy and height h . The heat flow rate through this area will be expressed as

$$q = - \int_0^y kh \frac{\partial T}{\partial x} dy \quad (3.58)$$

where k is the thermal conductivity.

According to Eq. (3.50), we have

$$\frac{\partial \phi}{\partial x} \equiv \frac{\partial T}{\partial x} = + \frac{\partial \psi}{\partial y} \quad (3.59)$$

Thus

$$q = \int_y^{y+\delta y} kh \frac{\partial \psi}{\partial y} dy = kh (\psi_{y+\delta y} - \psi_y) \quad (3.60)$$

or

$$\Delta \psi \equiv \psi_{y+\delta y} - \psi_y = \frac{q}{kh} \quad (3.61)$$

i.e. the difference, $\Delta \psi$, in the values of the two iso- ψ lines, one at $y = y$ and the other at $y = y + \Delta \psi$ when multiplied by thermal conductivity k , and height h , gives the value of heat flow rate q . The function ψ , therefore, represents the heat-flow rate. It is also called the *stream function*, more about which will be discussed in Chapter 6. Further, the iso- ψ lines along which no heat flows are called *adiabatics* whereas the iso- ϕ lines, i.e. those representing constant

temperature, are termed *isotherms*. It is obvious that the flow of heat takes place down the temperature gradient. Therefore, the heat flow and temperature functions will be orthogonal to each other.

This treatment clearly illustrates that if the temperature distribution, also called *potential function*, in any system is known, the corresponding *stream function* can be determined. The temperature function for a system can easily be found by making an electrical analogue of the system, and thus calculating the heat flow rate. This is illustrated by the following example.

EXAMPLE 3.6 The temperature function T of a two-dimensional slab is given by the equation

$$T = Ax + By + Cxy + D$$

Derive the equation for the heat flow rate q .

Solution The first step in solving this problem is to verify if the temperature function follows the Laplace equation, i.e. Eq. (3.46). From the given relationship for T , we have

$$\frac{\partial T}{\partial x} = A + Cy$$

and therefore

$$\frac{\partial^2 T}{\partial x^2} = 0 \quad (\text{Ex. 3.6.1})$$

Similarly

$$\frac{\partial T}{\partial y} = B + Cx$$

or

$$\frac{\partial^2 T}{\partial y^2} = 0 \quad (\text{Ex. 3.6.2})$$

From Eqs. (Ex. 3.6.1) and (Ex. 3.6.2), we get

$$\frac{\partial^2 T}{\partial x^2} + \frac{\partial^2 T}{\partial y^2} = 0 \quad (\text{Ex. 3.6.3})$$

i.e. the temperature T follows the Laplace equation, Eq. (3.46). Further, using Eq. (3.50), we have

$$\frac{\partial \phi}{\partial x} \equiv \frac{\partial T}{\partial x} \equiv \frac{\partial \psi}{\partial y} = A + Cy$$

Hence

$$\psi = Ay + \frac{Cy^2}{2} + f(x) \quad (\text{Ex. 3.6.4})$$

Similarly, using Eq. (3.51), we have

$$\frac{\partial \phi}{\partial y} \equiv \frac{\partial T}{\partial y} = - \frac{\partial \psi}{\partial x} = B + Cx$$

Hence

$$\psi = -Bx - \frac{Cx^2}{2} + f(y) \quad (\text{Ex. 3.6.5})$$

Taking functions $f(y)$ and $f(x)$ from Eqs. (6.4) and (6.5) above respectively, we can write

$$\psi = Ay - Bx + \frac{C}{2} (y^2 - x^2) \quad (\text{Ex. 3.6.6})$$

In Fig. 3.5, the isotherms and adiabatics for $A = 40$, $B = 30$, $C = 20$ and $D = 100$ are drawn. These are seen to show orthogonal behaviour. Once the function ψ is known, we can calculate the heat flow rate by making use of Eq. (3.61).

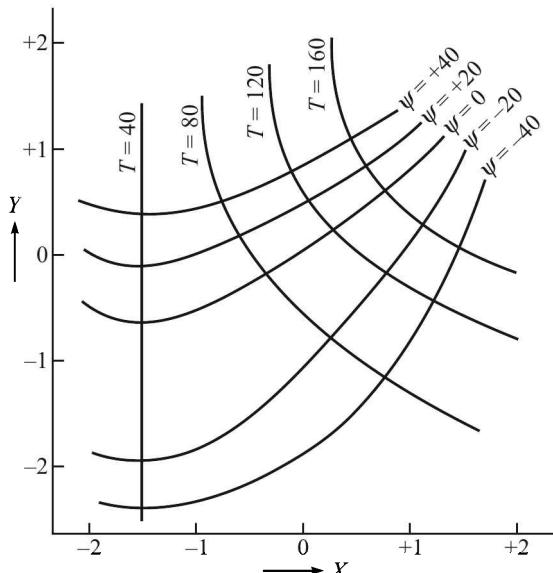


Fig. 3.5 Plot of orthogonal isotherms and adiabatics for a two-dimensional slab.

In case the analytical form of the potential function for a system is not known, we can make use of the graphical technique to arrive at the amount of heat conducted. As an example, we consider the flow of flue gases through a rectangular duct which is schematically shown in Fig. 3.6. Under steady state conduction, the inner and outer surfaces of this duct attain constant temperatures, say T_i and T_o respectively. Let the temperature isotherms be drawn on this wall at temperature intervals of ΔT which correspond to distances Δx . The amount of heat flowing through the length L of the duct will be given by the equation

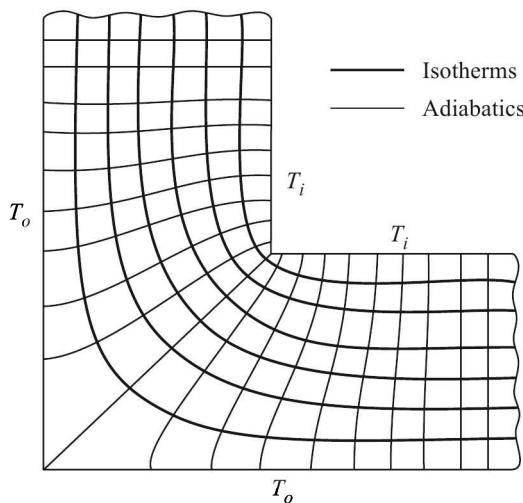


Fig. 3.6 Steady state heat conduction through a rectangular duct—use of graphical technique.

$$\Delta q = - kL \Delta y \frac{\Delta T}{\Delta x} \quad (3.62)$$

or

$$\frac{\Delta q}{kL} = - \Delta y \frac{\Delta T}{\Delta x} \quad (3.63)$$

From considerations of simplicity, if Δy be kept equal to Δx , then

$$\frac{\Delta q}{kL} = - \Delta T \quad (3.64)$$

Thus, we draw adiabatics on the duct at distances Δy , keeping them equal to Δx , and also adhering to the condition that the adiabatics are orthogonal to the isotherms. Thus, if there are N_a adiabatics and N_i isotherms drawn to cover the whole thickness of the wall, the total amount of heat transferred can be proved to be expressed by the relation

$$q = kL \frac{N_a}{N_i} (T_i - T_o) \quad (3.65)$$

The factor N_a/N_i is generally known as the *shape factor* of the body. An application of this method is illustrated by the following example.

EXAMPLE 3.7 Calculate the temperature of the outer surface of a rectangular flue duct through which hot gases at a temperature of 500°C are flowing. The length of the duct, the average thermal conductivity of the duct wall material and the shape factor are 20 m, $0.9 \text{ W m}^{-1} \text{ K}^{-1}$ and 4 respectively. The rate of heat flow may be taken as 32,000 W.

Solution Thermal conductivity of duct material, $k = 0.9 \text{ W m}^{-1} \text{ K}^{-1}$

$$\text{Shape factor, } \frac{N_a}{N_i} = 4$$

Length of the duct, $L = 20 \text{ m}$

Inside wall temperature, $T_i = 500 + 273 = 773 \text{ K}$

Heat transfer rate, $q = 32,000 \text{ W}$

Using Eq. (3.65), we have

$$q = kL \frac{N_a}{N_i} (T_i - T_o)$$

or

$$32,000 = 0.9 \times 20 \times 4 (773 - T_o)$$

or

$$773 - T_o = \frac{32,000}{0.9 \times 20 \times 4} = \frac{32,000}{72} = 444$$

or

$$T_o = 773 - 444 = 329 \text{ K} = 56^\circ\text{C}$$

Thus, the outside wall temperature is 56°C .

Ans.

Unsteady state heat conduction

In the previous three subsections, the heat conduction equations were applied to different steady state conditions, where the temperature of a system was only a function of space, not of time. However, most metallurgical processes involve heating or cooling of substances where the temperature distribution is not only a function of space but also a function of time. Heat conduction in such cases is known as *unsteady state heat conduction* or *transient heat conduction*.

From the point of view of transient heat conduction, different processes can be broadly divided into three categories: (i) those which are primarily controlled by transient heat conduction such as heat treatment or solidification processes, (ii) those in which transient heat conduction plays a significant role such as welding, zone-refining, etc., and (iii) those in which transient heat conduction plays a relatively minor role such as gas-solid and slag-metal reactions. In the following subsections, we consider the simplified versions of some of the processes in the first two categories as illustrative examples. We can, however, extend this method of analysis with slight modifications to industrial practices as well.

Heating or cooling of plates, cylinders and spheres, etc. The above phenomena are encountered in many metallurgical processes such as heat treatment processes and heating and cooling during hot working of metals. These processes are primarily controlled by transient heat conduction.

In all the above cases, the temperature distribution can be determined by solving the heat conduction equation in the respective coordinate systems. We may take up the case of the heating or cooling of a plate as an illustration, where the heat conduction equation in the rectangular coordinate system may be considered.

Even in the case of the heating or cooling of a plate, two different situations may arise depending on the thermal conductivity of the material. If it is extremely high, there will be negligible thermal resistance by the material and no temperature gradient inside the plate. The temperature distribution during heating or cooling will therefore be independent of space, depending only on time. Such heating or cooling is known as *Newtonian heating or cooling*. However, with finite but lower thermal conductivity, there will be internal temperature gradients and the temperature distribution will be a function of both space and time. Both these cases will now be considered separately.

(i) **Newtonian heating or cooling of a plate.** For the sake of convenience, we may consider the cooling of a plate of thickness $2L$ whose length and width are much larger than the thickness. Such a plate is known as an *infinite plate* in which heat flow is considered in a one-dimensional manner in a direction normal to the thickness. Here L is known as the *semi-thickness* of the plate. This is shown in Fig. 3.7(a).

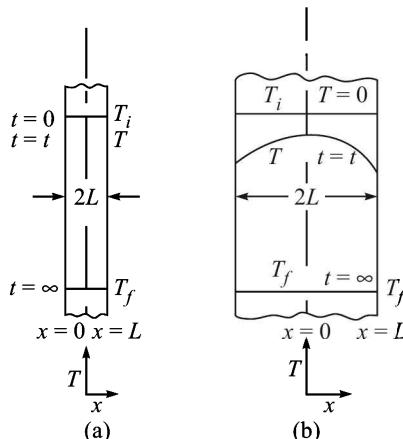


Fig. 3.7 (a) Newtonian cooling; (b) Cooling with low k value.

Let the plate be initially at a uniform temperature T_i and let it be cooled by a fluid at temperature T_f . Since the temperature is only a function of time, the rate of heat lost by the plate is equal to the rate of heat transferred to the fluid. Thus

$$-V\rho C_p \frac{dT}{dt} = hA (T - T_f) \quad (3.66)$$

where V = volume of the plate

ρ = density of the plate

C_p = heat capacity of the plate at constant pressure

T = absolute temperature at any time t

h = heat transfer coefficient from plate to fluid

A = surface area of the plate.

Rearranging Eq. (3.66), we get

$$\frac{dT}{T - T_f} = - \left(\frac{hA}{V\rho C_p} \right) dt$$

or

$$d[\ln(T - T_f)] = - \left(\frac{hA}{V\rho C_p} \right) dt$$

Integrating the above equation, we have

$$\ln(T - T_f) = - \left(\frac{hA}{V\rho C_p} \right) t + I$$

where I is the integration constant.

At $t = 0$, $T = T_i$. Therefore, we have

$$I = \ln(T_i - T_f)$$

Hence

$$\ln(T - T_f) = - \frac{hA}{V\rho C_p} t + \ln(T_i - T_f)$$

or

$$\ln\left(\frac{T - T_f}{T_i - T_f}\right) = - \left(\frac{hA}{V\rho C_p} \right) t$$

or

$$\frac{T - T_f}{T_i - T_f} = \exp\left[-\left(\frac{hA}{V\rho C_p}\right)t\right] \quad (3.67)$$

Equation 3.67 gives the dimensionless temperature history of the plate. It shows that during Newtonian cooling (or heating), the temperature falls (or rises) exponentially with time. Application of Eq. (3.67) will be demonstrated later by an illustrative example.

Equation (3.67) can also be expressed in terms of four dimensionless groups. The left-hand side of this equation is already a dimensionless temperature term. The right-hand side term $(hA/V\rho C_p)t$ can be expressed as

$$\left(\frac{hA}{V\rho C_p}\right)t = \left(\frac{hL}{k}\right)\left(\frac{k}{\rho C_p}\right)\left(\frac{AL}{V}\right)\left(\frac{t}{L^2}\right) = \left(\frac{hL}{k}\right)\left(\frac{\alpha t}{L^2}\right)\left(\frac{AL}{V}\right)$$

where $\alpha = k/\rho C_p$ is the thermal diffusivity of the plate. We now introduce three dimensionless groups as follows:

- (i) Dimensionless heat transfer coefficient known as Biot's number

$$N_{Bi} = \frac{hL}{k}$$

- (ii) Dimensionless time known as Fourier's number

$$N_{Fo} = \frac{\alpha t}{L^2}$$

- (iii) Dimensionless position, $G = \frac{AL}{V}$

The value of G depends on the geometry of the object. G is 1 for infinite plates, 2 for infinite cylinders and 3 for cubes and spheres.

With the introduction of these dimensionless groups, Eq. (3.67) can be expressed as

$$\frac{T - T_f}{T_i - T_f} = \exp [- (N_{Bi}, N_{Fo}, G)] \quad (3.68)$$

Equation (3.68) helps to plot dimensionless temperature profiles for objects of different geometries, for various (N_{Bi} , N_{Fo} , G) values. These profiles can be used to depict the temperature history during Newtonian cooling or heating.

EXAMPLE 3.8 A steel plate of 2 mm thickness and 1 m² surface area is quenched from a temperature of 800°C in water at 30°C. Assuming Newtonian cooling, calculate the time required to bring down the temperature of the plate to 400°C. Given:

$$\rho = 7600 \text{ kg m}^{-3}$$

$$h = 60 \text{ W m}^{-2} \text{ K}^{-1}$$

$$C_p = 500 \text{ J kg}^{-1} \text{ K}^{-1}$$

Solution Volume of the plate, $V = \text{area} \times \text{thickness} = 1 \times (2/1000) = 0.002 \text{ m}^3$

$$T_i = 800 + 273 = 1073 \text{ K}$$

$$T_f = 30 + 273 = 303 \text{ K}$$

$$T = 400 + 273 = 673 \text{ K}$$

Using Eq. (3.67), we have

$$\frac{673 - 303}{1073 - 303} = \exp \left[- \left(\frac{60 \times 1}{0.002 \times 7600 \times 500} \right) t \right]$$

or

$$0.48 = \exp (- 7.89 \times 10^{-3} t)$$

or

$$\ln (0.48) = - (7.89 \times 10^{-3}) t$$

or

$$t = 93.02 \text{ s}$$

Ans.

(ii) *Heating or cooling of a plate with finite thermal resistance.* This is a situation more commonly encountered in practice. Here, the thermal conductivity of the material is finite and the temperature of the plate, as mentioned earlier, is a function of both space and time. In this case, there are also two possibilities depending on the magnitude of the surface thermal resistance. If the surface resistance is negligible, the surface temperature of the plate reaches the ambient temperature instantaneously. But in most practical cases, the surface resistance is finite and the heating or cooling of an object with finite surface and internal resistance should be considered in such cases. This is for instance the case of a hot steel plate quenched in a liquid bath during heat treatment.

Once again we may consider the cooling of an infinite plate with thickness $2L$ where heat flows in a one-dimensional manner in a direction normal to the thickness. Let the plate be at a uniform initial temperature of T_i and be quenched in a fluid at a temperature T_f . Let the thermal conductivity of the plate be k and the heat transfer coefficient for flow of heat from the plate to the fluid be h . The situation is shown in Fig. 3.7(b).

For the sake of convenience, the origin of the x -axis is selected at the centre of the plate so that we can take the advantage of temperature symmetry about $x = 0$. The heat conduction equation, Eq. (3.27), in this case is reduced to

$$\frac{dT}{dt} = \alpha \frac{d^2T}{dx^2} \quad (3.69)$$

where α is the diffusivity, and T is the absolute temperature of the plate as a function of time t and distance x from the origin.

Equation (3.69) yields the temperature history of the plate, $T = T(x, t)$, when solved with the following initial and boundary conditions:

$$(i) \text{ At } t = 0, \quad T = T_i$$

$$(ii) \text{ At } x = 0, \quad \frac{\partial T}{\partial x} = 0$$

$$(iii) \text{ At } x = \pm L, \quad k \frac{\partial T}{\partial x} = \mp h (T - T_f)$$

Boundary condition (iii) shows that the rate at which heat is given by the plate is equal to the rate at which heat is taken up by the fluid.

We now introduce the terms θ and θ_1 defined by

$$\theta = T - T_f$$

and

$$\theta_1 = T_i - T_f$$

Thus, Eq. (3.69) becomes

$$\frac{\partial \theta}{\partial t} = \alpha \frac{\partial^2 \theta}{\partial x^2} \quad (3.70)$$

The above boundary conditions now become

(i) At $t = 0$, $\theta = \theta_1$

(ii) At $x = 0$, $\frac{\partial \theta}{\partial x} = 0$

(iii) At $x = \pm L$, $\mp k \frac{\partial \theta}{\partial x} = \pm h\theta$

Equation (3.70) can be solved with the above boundary conditions by the separation of variables method. We assume that

$$\theta = X(x) Y(t) \quad (3.71)$$

where X is a function of x alone and Y is a function of t alone. Then

$$\frac{\partial \theta}{\partial t} = X \frac{\partial Y}{\partial t}$$

and

$$\frac{\partial^2 \theta}{\partial x^2} = Y \frac{\partial^2 X}{\partial x^2}$$

Thus, Eq. (3.70) becomes

$$X \frac{\partial Y}{\partial t} = \alpha Y \frac{\partial^2 X}{\partial x^2}$$

or

$$\frac{1}{\alpha} \times \frac{1}{Y} \frac{\partial Y}{\partial t} = \frac{1}{X} \frac{\partial^2 X}{\partial x^2}$$

The two sides of the above equation are functions of different independent variables, so that they can be equal only if each side is equal to some constant. Let this constant, which may be known as a separation constant, be equal to $-\lambda^2$. Thus

$$\frac{1}{\alpha} \times \frac{1}{Y} \frac{\partial Y}{\partial t} = -\lambda^2 \quad (3.72)$$

and

$$\frac{1}{X} \frac{\partial^2 X}{\partial x^2} = -\lambda^2 \quad (3.73)$$

The solution of Eq. (3.72) is

$$Y = A e^{-\lambda^2 \alpha t}$$

and the solution of Eq. (3.73) is

$$X = B \cos \lambda x + C \sin \lambda x$$

where A , B and C are constants.

Thus, Eq. (3.71) becomes

$$\theta = XY = Ae^{-\lambda^2 \alpha t} (B \cos \lambda x + C \sin \lambda x)$$

which may be expressed as

$$\theta = e^{-\lambda^2 \alpha t} (B^1 \cos \lambda x + C^1 \sin \lambda x) \quad (3.74)$$

where B^1 and C^1 are constants given by $B^1 = AB$ and $C^1 = AC$.

Differentiating Eq. (3.74) with respect to x , we have

$$\frac{\partial \theta}{\partial x} = e^{-\lambda^2 \alpha t} (B^1 \lambda \sin \lambda x + C^1 \lambda \cos \lambda x) \quad (3.75)$$

Therefore

$$\left(\frac{\partial \theta}{\partial x} \right)_{x=0} = e^{-\lambda^2 \alpha t} (C^1 \lambda)$$

However, to satisfy the boundary condition (ii), at $x = 0$, we have $\partial \theta / \partial x = 0$. Therefore, we get

$$0 = e^{-\lambda^2 \alpha t} (C^1 \lambda)$$

This is satisfied only when $C^1 = 0$. Substituting $C^1 = 0$ in Eq. (3.74), we get

$$\theta = e^{-\lambda^2 \alpha t} (B^1 \cos \lambda x) \quad (3.76)$$

This gives

$$\frac{\partial \theta}{\partial x} = -e^{-\lambda^2 \alpha t} (B^1 \lambda \sin \lambda x)$$

Therefore

$$\left(\frac{\partial \theta}{\partial x} \right)_{x=L} = e^{-\lambda^2 \alpha t} (B^1 \lambda \sin \lambda L) \quad (3.77)$$

But from boundary condition (iii) and Eq. (3.76), we get

$$\begin{aligned} \left(\frac{\partial \theta}{\partial x} \right)_{x=L} &= -\frac{h}{k} \theta \\ &= -\frac{h}{k} e^{-\lambda^2 \alpha t} (B^1 \cos \lambda L) \end{aligned} \quad (3.78)$$

From Eqs. (3.77) and (3.78), we get

$$-e^{-\lambda^2 \alpha t} B^1 \lambda \sin \lambda L = -\frac{h}{k} e^{-\lambda^2 \alpha t} B^1 \cos \lambda L$$

This gives

$$\cot \lambda L = \frac{k}{h} \lambda \quad (3.79)$$

The right-hand side of the above equation can also be expressed as

$$\frac{k}{hL} \times \lambda L = \frac{1}{N_{Bi}} \times \lambda L$$

since in the previous subsection, the dimensionless group known as Biot's number, $N_{Bi} = \frac{hL}{k}$ was introduced. Thus, Eq. (3.79) becomes

$$\cot \lambda L = \frac{k}{h} \lambda = \frac{1}{N_{Bi}} \times \lambda L \quad (3.80)$$

Equation (3.80) is known as a *transcendental equation* and there are an infinite number of values of λ which will satisfy it. These values are known as *eigenvalues* which may be designated as $\lambda_1, \lambda_2, \lambda_3, \dots, \lambda_n$. The complete solution of Eq. (3.80) is the sum of the solutions corresponding to each eigenvalue. Thus, from Eq. (3.76), we have

$$\theta = \sum_{n=1}^{\infty} e^{-\lambda_n^2 \alpha t} B_n^1 \cos \lambda_n x \quad (3.81)$$

in which $\lambda_1, \lambda_2, \lambda_3, \dots, \lambda_n$ have the values determined from Eq. (3.80) and $B_1^1, B_2^1, \dots, B_n^1$ are selected to satisfy the condition that $\theta = \theta_1$ at $t = 0$, i.e. boundary condition (i).

With this boundary condition, Eq. (3.81) can be expressed as

$$\theta_1 = \sum_{n=1}^{\infty} B_n^1 \cos \lambda_n x \quad (3.82)$$

For getting the value of B_n^1 , we multiply both the sides of Eq. (3.82) by $\cos \lambda_n x dx$ and integrate between $x = 0$ and $x = L$. Thus

$$\theta_1 \int_0^L \cos \lambda_n x dx = \int_0^L \sum_{n=1}^{\infty} B_n^1 \cos^2 \lambda_n x dx$$

This gives

$$\theta_1 \frac{1}{\lambda_n} \sin \lambda_n L = B_n^1 \left[\frac{L}{2} + \frac{1}{2\lambda_n} \sin \lambda_n L \cos \lambda_n L \right]$$

On simplification, we get

$$B_n^1 = \frac{2\theta_1 \sin \lambda_n L}{\lambda_n L + \sin \lambda_n L \cos \lambda_n L}$$

Putting this value of B_n^1 in Eq. (3.81), we get

$$\frac{\theta}{\theta_1} = \frac{T - T_f}{T_i - T_f} = 2 \sum_{n=1}^{\infty} \frac{\sin \lambda_n L}{\lambda_n L + 2\lambda_n L \cos \lambda_n L} e^{-\lambda_n^2 \alpha t} \cos \lambda_n x \quad (3.83)$$

Equation (3.83) is the analytical expression which helps to determine the value of T as a function of time t and distance x . Here, the λ_n 's are the roots

of Eq. (3.80), the first three of which for different Biot numbers are given below.¹

N_{Bi}	$\lambda_1 L$	$\lambda_2 L$	$\lambda_3 L$
0.1	0.3111	3.1731	6.2991
1.0	0.8603	3.4256	6.4373
10.0	1.4289	4.3058	7.2281
100.0	1.5552	4.6658	7.7764

However, the nature of Eq. (3.83) is such that a certain amount of trial and error is required to solve for any one unknown parameter such as T , x , or t . On the other hand, graphical evaluation of this equation has been found more convenient. For this, we use transient heat conduction charts which have been suggested by several scientists.

Transient heat conduction charts. These charts are also known as *temperature-time charts*. They are given in terms of four dimensionless groups which are similar to those mentioned in the previous subsection on Newtonian heating or cooling. These are as follows:

1. Dimensionless temperature = $\frac{T - T_f}{T_i - T_f}$
2. Dimensionless time, the Fourier number, $N_{Fo} = \frac{\alpha t}{L^2}$
3. Dimensionless heat transfer coefficient, the Biot number, $N_{Bi} = \frac{hL}{k}$
4. Dimensionless position, $G = \frac{x}{L}$

We have, therefore, as before, from Eq. (3.68)

$$\frac{T - T_f}{T_i - T_f} = f(N_{Fo}, N_{Bi}, G)$$

The temperature-time charts are then plotted between $(T - T_f)/(T_i - T_f)$ and N_{Fo} for different $1/N_{Bi}$ and G values. Among the earliest such charts were the Gurney-Lurie² charts which are still referred to. However, these charts are restricted to only a small range of N_{Fo} and N_{Bi} values. Other charts more commonly used are those of Hottel, Schack, Heisler, etc. The Heisler³ charts which are quite useful are valid for N_{Bi} from 0 to ∞ and for large N_{Fo} values. Figure 3.8 shows the Heisler chart for an infinite plate where $(T - T_f)/(T_i - T_f)$ has been plotted against N_{Fo} values for different $1/N_{Bi}$ values with $x/L = 0$. This

¹ H.S. Carslaw and J.C. Jaeger, *Conduction of Heat in Solids*, Oxford University Press, London (1959), p. 491.

² H.P. Gurney and J. Lurie, *Ind. Engg. Chem.*, **15**: 1170 (1923).

³ M.P. Heisler, *Trans. ASME* **69**: 227 (1947).

means that T refers to the point where $x = 0$, i.e. T is the mid-point temperature of the plate. Temperatures at other positions with different x/L values are determined by using correction factors which are obtained from companion Heisler charts. In the Heisler chart shown in Fig. 3.8, $1/N_{Bi}$ ranges from 0 to 100.

The first line refers to $1/N_{Bi}$ value of zero which corresponds to $h = \infty$, i.e. zero surface resistance. Similar charts are available for other geometrical shapes. The use of the Heisler chart is explained with the help of the following example.

EXAMPLE 3.9 A steel plate of 20 mm thickness and 1 m^2 surface area is quenched from a temperature of 800°C in water at 30°C . Calculate the time required to obtain the mid-point temperature of 400°C . Given:

$$h = 60 \text{ W m}^{-2} \text{ K}^{-1}$$

$$k = 30 \text{ W m}^{-1} \text{ K}^{-1}$$

$$\alpha = 0.023 \text{ m}^2 \text{ h}^{-1}$$

$$\text{Solution} \quad \text{Semi-thickness, } L = \frac{20}{2} \text{ mm} = \frac{20}{2 \times 1000} \text{ m} = 0.01 \text{ m}$$

$$\text{Initial temperature, } T_i = 800 + 273 = 1073 \text{ K}$$

$$\text{Final temperature, } T_f = 30 + 273 = 303 \text{ K}$$

$$\text{Mid-point temperature, } T = 400 + 273 = 673 \text{ K}$$

Thus

$$\frac{T - T_f}{T_i - T_f} = \frac{673 - 303}{1073 - 303} = \frac{370}{770} = 0.48$$

$$\frac{1}{N_{Bi}} = \frac{k}{hL} = \frac{30}{60 \times 0.01} = 50$$

Referring to the Heisler chart in Fig. 3.8, which is valid for $x/L = 0$, i.e. the mid-point temperature, for the $(T - T_f)/(T_i - T_f)$ value of 0.48 and $1/N_{Bi}$ value of 50, we get the Fourier number, $N_{Fo} = 37$. Now

$$N_{Fo} = \frac{\alpha t}{L^2}$$

Given

$$\alpha = 0.023 \text{ m}^2 \text{ h}^{-1} = \frac{0.023}{3600} \text{ m}^2 \text{ s}^{-1}$$

Therefore

$$37 = \frac{0.023 \times t}{3600 \times (0.01)^2}$$

or

$$t = \frac{37 \times 3600 \times (0.01)^2}{0.023} = 579.13 \text{ s} \quad \text{Ans.}$$

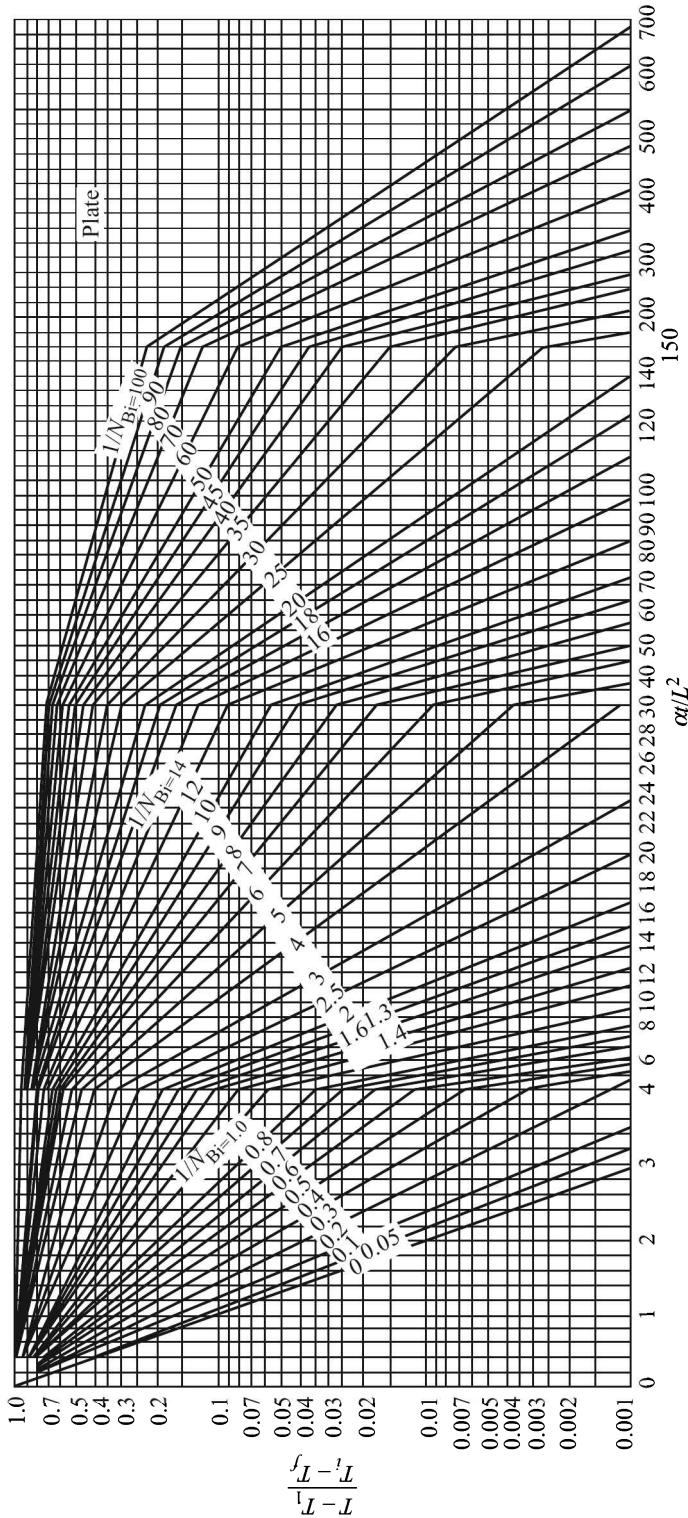


Fig. 3.8 Heisler chart for an infinite plate with $x/L = 0$.

Therefore, the time required to get the mid-point temperature of 400°C in the above case is 579.13 s. Comparing this value with that of Example 3.10, it may be seen that much more time is required in this case because of lower thermal conductivity and greater thickness of the plate.

EXAMPLE 3.10 The steel plate in Example 3.9 is to be austempered by quenching it in a molten salt bath at 300°C from the austenitizing temperature of 950°C. If the “nose” of the T-T-T diagram for the steel is at 500°C corresponding to a time of 400 s, determine if the steel sample can be satisfactorily austempered. Use the data of Example 3.9.

Solution Once again, we have

$$\text{Semi-thickness, } L = 0.01 \text{ m}$$

$$\text{Initial temperature, } T_i = 950 + 273 = 1223 \text{ K}$$

$$\text{Final temperature, } T_f = 300 + 273 = 573 \text{ K}$$

$$\text{Mid-point temperature, } T = 500 + 273 = 773 \text{ K}$$

Thus

$$\frac{T - T_f}{T_i - T_f} = \frac{773 - 573}{1223 - 573} = \frac{200}{650} = 0.308$$

As before

$$\frac{1}{N_{Bi}} = 50$$

Referring to the Heisler chart in Fig. 3.8, valid for $x/L = 0$, i.e. for the mid-point temperature, for the $(T - T_f)/(T_i - T_f)$ value of 0.308 and $1/N_{Bi}$ value of 50, we get Fourier number $N_{Fo} = 60$. Now

$$N_{Fo} = \frac{\alpha t}{L^2}$$

or

$$\begin{aligned} t &= \frac{N_{Fo} \times L^2}{\alpha} = \frac{60 \times (0.01)^2}{0.023} \text{ h} \\ &= \frac{60 \times (0.01)^2 \times 3600}{0.023} \text{ s} \\ &= 939.1 \text{ s} \end{aligned}$$

However, since the nose of the T-T-T diagram corresponds to 400 s, with the above time the transformation of austenite to ferrite and cementite cannot be prevented. Thus, the steel sample cannot be satisfactorily austempered. The situation can be understood by referring to Fig. 3.9, where A, B and P stand for austenite, bainite and pearlite respectively.

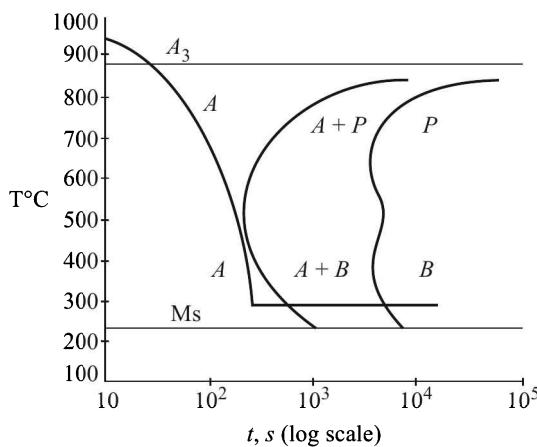


Fig. 3.9 Austempering of steel.

Heat conduction with moving phase boundaries. In a number of metallurgical problems, such as solidification of metals and alloys, reduction of dense solid lumps of ores and oxidation of metals in solid state, heat conduction is accompanied by a change of phase of the conducting medium. This change takes place progressively with time and is accompanied by either release or absorption of heat at the reaction interface. Thus in such systems transfer of heat will be accompanied by a moving phase boundary. Such problems are solved by considering heat conduction through each of the phases taking into account the heat absorbed or liberated at the interface. As a simple example of heat conduction with moving phase boundary, we consider here the case of solidification of a pure metal. To simplify the problem further, we also assume that heat conduction is unidimensional and that the convection effects in the liquid phase are negligible.

We further assume the position of the solid/liquid interface to be at a distance x_s from the heat conducting wall maintained at a temperature T_1 as shown in Fig. 3.10. Let the temperature of the liquid at an infinite distance from the interface be T'_2 . The heat conduction equation for the solid phase can be expressed as

$$\frac{\partial T_s}{\partial t} = \alpha_s \frac{\partial^2 T_s}{\partial x_s^2} \quad (3.84)$$

with boundary condition as

$$T_s = T_1 \text{ at } x_s = 0 \quad \text{for } t > 0 \quad (3.85)$$

and

$$T_s = T_m \text{ at } x_s = x_{sm} \quad \text{for } t > 0 \quad (3.86)$$

where T_m is the melting point of the liquid, x_{sm} the distance of the solid-liquid interface from the heat conducting surface and α_s the thermal diffusivity of the solid.

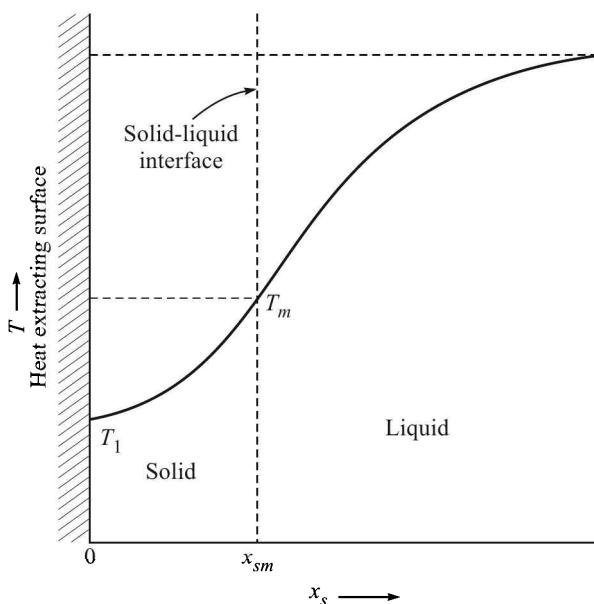


Fig. 3.10 Movement of solidification interface by heat-conduction.

For the liquid phase, we similarly have the equation

$$\frac{\partial T_l}{\partial t} = \alpha_l \frac{\partial^2 T_l}{\partial x_s^2} \quad (3.87)$$

with boundary conditions

$$T_l = T_2 \text{ at } x_s = \infty \text{ for } t > 0 \quad (3.88)$$

$$T_l = T_m \text{ at } x_s = x_{sm} \text{ for } t > 0 \quad (3.89)$$

In the formulation of boundary conditions, it has been assumed that the solidification front moves parallel to the heat conducting surface, i.e. the conduction conditions are such that no dendrite formation during solidification takes place. In other words, only a solidification plane exists and not a solidification zone.

The heat balance at the interface will yield the equation

$$k_s \left(\frac{\partial T_s}{\partial x_s} \right)_{x_s=x_{sm}} - k_l \left(\frac{\partial T_l}{\partial x_s} \right)_{x_s=x_{sm}} = -\rho_s H_s \frac{\partial x_s}{\partial t} \quad (3.90)$$

where k_s and k_l are the thermal conductivities of the solid and liquid phases, respectively and H_s is the enthalpy of solidification per unit mass.

The following solutions for Eqs. (3.84) and (3.87) have been suggested:

$$T_s = A_s + B_s \operatorname{erf} \left(\frac{x_s}{2\sqrt{\alpha_s t}} \right) \quad (3.91)$$

$$T_l = A + B_l \operatorname{erfc} \left(\frac{x_s}{2\sqrt{\alpha_s t}} \right) \quad (3.92)$$

where A_s , A_l , B_s and B_l are constants to be evaluated from boundary conditions. Other functions are defined as

$$\operatorname{erf} \left(\frac{x_s}{2\sqrt{\alpha_s t}} \right) = \frac{1}{\pi} \int_0^{x_s/2\sqrt{\alpha_s t}} \exp(-\beta^2) d\beta \quad (3.93)$$

and

$$\operatorname{erfc} \left(\frac{x_s}{2\sqrt{\alpha_s t}} \right) = 1 - \operatorname{erf} \frac{x_s}{2\sqrt{\alpha_s t}} \quad (3.94)$$

where the symbols “erf” and “erfc” represent respectively the error and complementary error functions. First, we verify whether Eqs. (3.91) and (3.92) satisfy Eqs. (3.84) and (3.87) respectively. For this we arrive at the required derivatives. From Eq. (3.91), we get

$$\begin{aligned} \frac{\partial T_s^*}{\partial x} &= \frac{\partial}{\partial x} \left[A_s + B_s \operatorname{erf} \left(\frac{x_s}{2\sqrt{\alpha_s t}} \right) \right] \\ &= B_s \frac{\partial}{\partial x} \left[\frac{1}{\pi} \int_0^{x_s/2\sqrt{\alpha_s t}} \exp(-\beta^2) d\beta \right] \\ &= B_s \left[\exp \left(-\frac{x_s^2}{4\sqrt{\alpha_s t}} \right) \frac{1}{2\sqrt{\alpha_s t}} \right] \end{aligned} \quad (3.95)$$

Further

$$\frac{\partial^2 T_s}{\partial x^2} = - \left[\frac{B_s x_s}{4(\alpha_s t)^{3/2}} \exp \left(-\frac{x_s^2}{4\alpha_s t} \right) \right] \quad (3.96)$$

and

$$\frac{\partial T_s}{\partial t} = - \left[\frac{B_s x_s}{4\alpha_s (\alpha_s t)^{3/2}} \exp \left(-\frac{x_s^2}{4\alpha_s t} \right) \right] \quad (3.97)$$

Substitution of Eqs. (3.96) and (3.97) in Eq. (3.84) shows that the latter is satisfied by Eq. (3.91). Similarly, we can prove that Eq. (3.92) satisfies Eq. (3.87).

* According to the Leibnitz theorem,

$$\frac{\partial}{\partial x} \left[\int_{f_1(x)}^{f_2(x)} \exp(-\beta^2) d\beta \right] = \left[\left\{ \exp(-f_2^2) \right\} \frac{\partial f_2}{\partial x} - \left\{ \exp(-f_1^2) \right\} \frac{\partial f_1}{\partial x} \right]$$

We now proceed to determine the constants in Eqs. (3.91) and (3.92). According to the conditions expressed by Eqs. (3.85) and (3.88), we get

$$A_s = T_1 \quad (3.98)$$

and

$$A_l = T_2 \quad (3.99)$$

Using the conditions expressed by Eqs. (3.86) and (3.89) and also Eqs. (3.98) and (3.99), we get from Eqs. (3.91) and (3.92), respectively the following relations:

$$T_m = T_1 + B_s \operatorname{erf} \left(\frac{x_{sm}}{2\sqrt{\alpha_s t}} \right) \quad (3.100)$$

and

$$T_m = T_2 + B_l \operatorname{erfc} \left(\frac{x_{sm}}{2\sqrt{\alpha_l t}} \right) \quad (3.101)$$

As T_m , T_l , T_2 , B_s and B_l are independent of t , so the arguments of error and complementary error functions must also be independent of time, Hence

$$x_{sm} = k \sqrt{t} \quad (3.102)$$

where k is a constant.

Using Eq. (3.102) we get from Eqs. (3.100) and (3.101), respectively the following equations for the constants B_s and B_l ,

$$B_s = \frac{T_m - T_1}{\operatorname{erf}(k/2\sqrt{\alpha_s})} \quad (3.103)$$

and

$$B_l = \frac{T_m - T_2}{\operatorname{erfc}(k/2\sqrt{\alpha_l})} \quad (3.104)$$

Substitution of the above equations for B_s and B_l and also using values of A_s and A_l from Eqs. (3.98) and (3.99) in Eqs. (3.91) and (3.92), respectively yields

$$\frac{T_s - T_1}{T_m - T_1} = \operatorname{erf} \left(\frac{x_s}{2\sqrt{\alpha_s t}} \right) \left\{ \operatorname{erf} \left(\frac{k}{2\alpha_s} \right) \right\}^{-1} \quad (3.105)$$

and

$$\frac{T_l - T_2}{T_m - T_2} = \operatorname{erfc} \left(\frac{x_l}{2\sqrt{\alpha_l t}} \right) \left\{ \operatorname{erfc} \left(\frac{k}{2\alpha_l} \right) \right\}^{-1} \quad (3.106)$$

The above equations indicate that if k is determined, we can obtain the temperature distribution. In order to obtain the value of k , we make use of

Eq. (3.90), which with the help of Eqs. (3.102), (3.105) and (3.106) leads to the following equation:

$$\frac{(T_m - T_l) k_s \exp(-k^2/4\alpha_s)}{\sqrt{\pi\alpha_s} \operatorname{erf}(k/2\sqrt{\alpha_s})} - \frac{(T_2 - T_m) k_l \exp(-k^2/4\alpha_\lambda)}{\sqrt{\pi\alpha_\lambda} \operatorname{erfc}(k/2\sqrt{\alpha_l})} = \frac{H_m k \rho_s}{2} \quad (3.107)$$

where H_m ($= H_s$) is the enthalpy of melting per unit mass. The above equation is solved numerically to obtain the value of k for a system. Substitution of the value of k obtained from the above equation in Eqs. (3.105), (3.106) and (3.102) will yield T_s and T_l profiles as functions of time and distance and also the position of the solid-liquid interface.

This treatment is helpful in the design of continuous casting plants. Application of the above equations will now be demonstrated below by an example.

EXAMPLE 3.11 A water-cooled plate maintained at 80°C is brought in contact with pure molten copper at its melting point. Derive an equation for the rate of advancement of the solidification front. Also calculate the thickness of the solid phase after 30 seconds. The properties of copper are as follows:

Melting point = 1356.16 K

Thermal conductivity of solid copper, $k_s = 397 \text{ W m}^{-1} \text{ K}^{-1}$

Density of solid copper, $\rho_s = 8.96 \times 10^3 \text{ kg m}^{-3}$

Specific heat of solid copper, $C_p = 385 \text{ J kg}^{-1} \text{ K}^{-1}$

Heat of fusion of copper, $H_m = 1.3 \times 10^7 \text{ J kg mol}^{-1}$

Atomic weight of copper = 63.54

Solution As in the present case $T_m = T_2$, so Eq. (3.107) assumes the form

$$\frac{(T_m - T_l) k_s \exp(-k^2/4\alpha_s)}{\sqrt{\pi\alpha_s} \operatorname{erfc}(k/2\sqrt{\alpha_s})} = \frac{H_m k \rho_s}{2}$$

That is

$$\begin{aligned} \frac{k}{2\sqrt{\alpha_s}} \left[\operatorname{erf}\left(\frac{k}{2\sqrt{\alpha_s}}\right) \right] \exp\left(\frac{k^2}{4\alpha_s}\right) &= \frac{C_p (T_m - T_l)}{(\pi)^{1/2} H_m} \quad \left(\because \alpha_s = \frac{k_s}{\rho_s C_p} \right) \\ &= \frac{385 [1356.16 - (80 + 273)]}{(3.142)^{1/2} \frac{1.3 \times 10^7}{63.54}} \end{aligned}$$

Solution of the above equation by trial and error using the error function graph yields

$$\frac{k}{2\sqrt{\alpha_s}} = 0.78$$

Thus

$$\begin{aligned} k &= 2 \times 0.78 (\alpha_s)^{1/2} \\ &= 2 \times 0.78 \times \left(\frac{k_s}{\rho_s C_p} \right)^{1/2} \\ &= 1.56 \times \left(\frac{397}{8.96 \times 10^3 \times 385} \right)^{1/2} = 0.0167 \end{aligned}$$

According to Eq. (3.102), the thickness x of the solidified metal is given by the relation

$$x = k \sqrt{t}$$

Thus, the rate of advancement of solidification front is given as

$$\frac{dx}{dt} = \frac{k}{2t^{1/2}} = 0.0084 t^{-1/2} \text{ m s}^{-1}$$

Further, after 30 seconds

$$x = 0.0167 \sqrt{30} = 0.0914 \text{ m} \quad \text{Ans.}$$

Heat conduction with moving heat source. The simplest metallurgical system involving heat conduction with a moving heat source is represented in welding processes. Several common techniques using flame heating by a melting torch, electric arc heating with fluxed electrodes, etc. are in use for this purpose. The "filler material" is provided either by the consumable electrode or by a separate rod or wire, melted by the heat of the torch. These rods are cooled with suitable fluxes to obtain a sound flawless weld.

From a theoretical point of view, a moving heat source, namely the welding electrode or torch, imparts heat to the job being welded in which heat flow occurs by conduction. If we consider the heat losses from the surface of the job to be small, it becomes a case of transient heat conduction whose basic equation, as already pointed out in Section 1.2, will be

$$\frac{\partial T}{\partial t} = \alpha \left(\frac{\partial^2 T}{\partial x^2} + \frac{\partial^2 T}{\partial y^2} + \frac{\partial^2 T}{\partial z^2} \right) \quad (3.108)$$

where T is the excess temperature over the initial temperature of the job.

In order to take into account the movement of the heat source, we can proceed as follows. The temperature at any point in the job can be expressed in terms of three distance coordinates and time by the functional relation

$$T = T(x, y, z, t) \quad (3.109)$$

Hence

$$dT = \frac{\partial T}{\partial x} dx + \frac{\partial T}{\partial y} dy + \frac{\partial T}{\partial z} dz + \frac{\partial T}{\partial t} dt \quad (3.110)$$

or

$$\frac{\partial T}{\partial t} = \frac{\partial T}{\partial x} \frac{\partial x}{\partial t} + \frac{\partial T}{\partial y} \frac{\partial y}{\partial t} + \frac{\partial T}{\partial z} \frac{\partial z}{\partial t} + \frac{\partial T}{\partial t} \quad (3.111)$$

If we transform Eq. (3.111), by considering the heat source to travel with a velocity v_z in the z -direction as shown in Fig. 3.11, we have

$$\frac{\partial x}{\partial t} = 0, \quad \frac{\partial y}{\partial t} = 0, \quad \frac{\partial z}{\partial t} = v_z$$

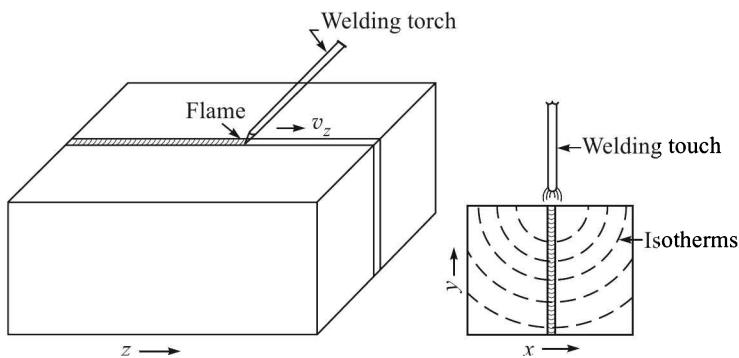


Fig. 3.11 Transient state heat conduction with moving heat source during welding.

Thus, Eq. (3.111) takes the following alternative form for this case:

$$\frac{dT}{dt} = v_z \frac{\partial T}{\partial z} + \frac{\partial T}{\partial t} \quad (3.112)$$

Here dT/dt is the total derivative of temperature T with respect to time t , whereas $\partial T/\partial t$ is the partial derivative between the two parameters with the distance coordinates x , y , and z constant.

Using Eq. (3.108), Eq. (3.112) changes to the following form:

$$\frac{dT}{dt} = \alpha \left[\frac{\partial^2 T}{\partial x^2} + \frac{\partial^2 T}{\partial y^2} + \frac{\partial^2 T}{\partial z^2} \right] + v_z \frac{\partial T}{\partial z} \quad (3.113)$$

If the rate of heat supply by the electrode or welding torch is constant and the velocity v_z is also considered constant, the temperature at a fixed distance from the welding electrode as a function of time will be constant. Thus, for this case

$$\frac{\partial T}{\partial t} = 0 \quad (3.114)$$

Hence, Eq. (3.113) takes the quasi-steady state form

$$\alpha \frac{\partial^2 T}{\partial x^2} + \frac{\partial^2 T}{\partial y^2} + \frac{\partial^2 T}{\partial z^2} + v_z \frac{\partial T}{\partial z} = 0 \quad (3.115)$$

This equation is known to have a solution of the form

$$T = \left[\exp\left(-\frac{v_z z}{2\alpha}\right) \right] f(x, y, z) \quad (3.116)$$

where $f(x, y, z)$ is an unknown function. With the above expression for T , Eq. (3.115) takes the form

$$\frac{\partial^2 f}{\partial x^2} + \frac{\partial^2 f}{\partial y^2} + \frac{\partial^2 f}{\partial z^2} - \left(\frac{v_z}{2\alpha}\right)^2 f = 0 \quad (3.117)$$

Equation (3.117) can be simplified further by considering the symmetry in the system. If we consider any point on the weld, the isotherms around it will form semicircles as shown in Fig. 3.11. Thus, there will be a temperature gradient only along radial and axial directions and not along the angular directions. If Eq. (3.117) is transformed to the cylindrical coordinate system, we get the following relation:

$$\frac{d^2 f}{dr^2} + \frac{2}{r} \frac{df}{dr} - \left(\frac{v_z}{2\alpha}\right)^2 f = 0 \quad (3.118)$$

or

$$r \frac{d^2 f}{dr^2} + 2 \frac{df}{dr} - \left(\frac{v_z}{2\alpha}\right) fr = 0 \quad (3.119)$$

where r is the distance from the welding zone. Equation (3.119) can be transformed further by introducing another function, σ such that

$$\sigma = fr \quad (3.120)$$

Hence, Eq. (3.119) takes the following form of a homogeneous linear equation with constant coefficients:

$$\frac{d^2 \sigma}{dr^2} - \left(\frac{v_z}{2\alpha}\right)^2 \sigma = 0 \quad (3.121)$$

This equation has the following general solution:

$$\sigma = A \exp\left(\frac{v_z r}{2\alpha}\right) + B \exp\left(-\frac{v_z r}{2\alpha}\right) \quad (3.122)$$

Substitution of the above solution for σ in Eq. (3.120) and of the resulting equation in Eq. (3.116) yields the relation

$$T = \frac{1}{r} \left[A \exp\left\{\frac{v_z(r-z)}{2\alpha}\right\} + B \exp\left\{-\frac{v_z(r+z)}{2\alpha}\right\} \right] \quad (3.123)$$

The constants A and B can be evaluated by considering the job to have infinite thickness and, therefore, by the application of the following boundary conditions:

$$(i) \quad T = 0, \quad \text{at} \quad r \rightarrow \infty \quad (3.124)$$

and

$$(ii) \quad 4\pi r^2 k \frac{\partial T}{\partial r} \Big|_{z=0} = Q_0 \quad \text{at} \quad r \rightarrow 0 \quad (3.125)$$

where Q_0 is the rate of heat supply to the job from the torch. Application of the first condition yields

$$A = 0 \quad (3.126)$$

Similarly, application of Eq. (3.125) yields

$$B = \frac{Q_0}{4\pi k} \quad (3.127)$$

By substituting values of A and B in Eq. (3.123), we get

$$T = \frac{Q_0}{4\pi kr} \exp \left\{ -\frac{v_z(r+z)}{2\alpha} \right\} \quad (3.128)$$

This equation yields approximate results because of the following simplifications incorporated in its derivation:

- (i) It ignores the heat losses from the surface of the job being welded.
- (ii) It neglects the thermal effect of fusion and phase transformation which invariably accompany the process of welding.

Application of the above analysis is demonstrated by the following example.

EXAMPLE 3.12 In an electric arc welding operation, two thick steel plates are welded together with the help of an arc moving at the speed of 5 mm/s. If the rate of heat supply is 24,000 W, calculate the temperature at a point 5 cm from the welding zone after 20 seconds of the start of welding. The average thermal conductivity and thermal diffusivity for steel may be taken as $60 \text{ W m}^{-1} \text{ K}^{-1}$ and $1.5 \times 10^{-4} \text{ m}^2 \text{ s}^{-1}$ respectively.

Solution Rate of heat supply, $Q_0 = 24,000 \text{ W}$

Distance from the welding zone, $r = 5 \text{ cm} = 0.05 \text{ m}$

Velocity of welding electrode, $v_z = 5 \text{ mm/s} = 0.005 \text{ m s}^{-1}$

Distance travelled in 20 s, $z = 0.005 \times 20 = 0.1 \text{ m}$

Thermal conductivity of steel, $k = 60 \text{ W m}^{-1} \text{ K}^{-1}$

Thermal diffusivity of steel, $\alpha = 1.5 \times 10^{-4} \text{ m}^2 \text{ s}^{-1}$

Therefore, using Eq. (3.128), we get

$$T = \frac{Q_0}{4\pi kr} \exp \left\{ -\frac{v_z(r+z)}{2\alpha} \right\}$$

On substitution of the relevant values, we have

$$\begin{aligned} T &= \frac{24000}{4\pi \times 60 \times 0.05} \exp \left\{ -\frac{0.005(0.05 + 0.1)}{2 \times 15 \times 10^{-4}} \right\} \\ &= 636.9 \exp(-2.5) = 325.4 \text{ K} \\ &= 52.4^\circ\text{C} \end{aligned}$$

Hence, the required temperature is 52.4°C .

Ans.

3.2 CONVECTION

A number of extractive metallurgical reactors involve fluids under stirred conditions or those flowing through a bed of solid particles. In such reactors, the dominant mode of heat energy transfer is convection. For example, in a blast furnace, the ascending gases heat the charge; in case of Cowper stoves and regenerators, the flowing gases exchange energy with the refractories; in LD converters the heat produced as a result of metal-oxygen reaction is distributed to the bath by stirring caused by the momentum of the impinging gas. We can cite numerous similar examples of convective heat transfer in metallurgical processes. This section is devoted to the principles involved in the quantitative analysis of convective heat transfer in such processes.

The first step in such an analysis is to develop an equation for the system under consideration by striking a total energy balance. This is followed by the solution of this equation under the prevailing initial and boundary conditions to arrive at the amount of heat transferred. In the following subsections, we will first derive equations for differential total energy balance, followed by some illustrative applications such as in the case of convective heat transfer during fluid flow in a pipe. The overall energy balance for a reactor will be taken up thereafter.

3.2.1 Differential Equation for Total Energy Balance

Consider a differential volume element in a rectangular coordinate system as shown in Fig. 3.12. Let the arrows indicate the direction of flow of the fluid, i.e. the fluid enters the element from the faces touching the point $P(x, y, z)$ and leaves the faces touching the point $Q(x + \delta x, y + \delta y, z + \delta z)$.

According to the first law of thermodynamics or the law of conservation of energy, we have the following energy balance statement for this volume element:

Total energy of the fluid entering the element + Amount of energy produced in the element through reactions, if any = Total energy of the fluid leaving the element + Amount of energy retained by the fluid in the element + Work done by the fluid while passing through the volume element

(3.129)

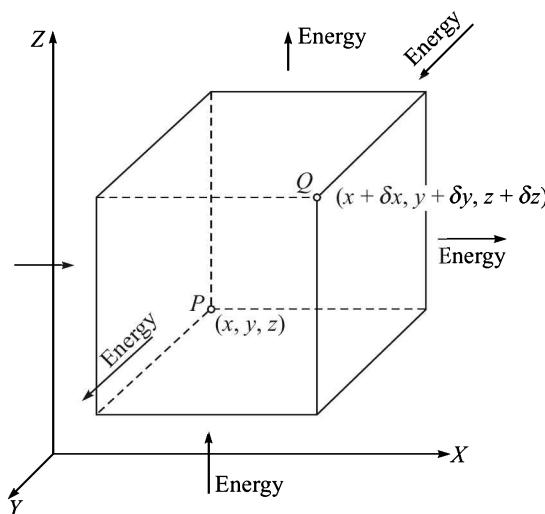


Fig. 3.12 Analysis of convective heat transfer through a differential Volume element.

All the quantities in the above statement may be taken on unit time basis. We now proceed to express each of the terms in the statement in a mathematical form. For the first term on the left-hand side, we can say that energy can enter or leave the volume element under consideration in the following two ways.

- (1) Energy accompanying the flowing fluid in the form of:
 - (a) internal energy, which is the energy associated with the translational, vibrational and rotational movements of the atoms or molecules constituting the fluid and is, therefore, a function of temperature and molar volume or density of the fluid,
 - (b) kinetic energy, which is due to the motion of the fluid,
 - (c) potential energy, which is due to the position and configuration of the fluid.

Thus, the total energy per unit volume of the fluid is given by

$$e = \rho \left(u + \frac{1}{2} \langle v^2 \rangle + \psi \right) \quad (3.130)$$

where u and ψ are the internal energy and potential energy per unit mass and ρ is the density of the fluid.

- (2) Heat exchanged by the fluid inside the volume element by conduction. Thus, the energy entering the volume element per unit time may be expressed as

$$E_{\text{ent}} = (\rho ev_x + J_{q,x})_{x=x} \delta y \delta z + (\rho ev_y + J_{q,y})_{y=y} \delta x \delta z + (\rho ev_z + J_{q,z})_{z=z} \delta x \delta y \quad (3.131)$$

where v_x , v_y and v_z are the velocities in the three directions and $J_{q,x}$, etc. are the heat fluxes in the three directions. Similarly, the energy leaving the volume element may be expressed as

$$E_{ex} = (\rho ev_x + J_{q,x})_{x=x+\delta x} \delta y \delta z + (\rho ev_y + J_{q,y})_{y=y+\delta y} \delta x \delta z + (\rho ev_z + J_{q,z})_{z=z+\delta z} \delta x \delta y \quad (3.132)$$

The amount of heat produced inside the volume element may be expressed as

$$q_s = \sigma \delta x \delta y \delta z \quad (3.133)$$

where σ is the amount of heat produced per unit time per unit volume. It may be mentioned that σ will be positive for exothermic reactions and negative for endothermic reactions. Energy retained by the fluid in the volume element per unit time may be expressed as

$$E_r = \frac{\partial(\rho e)}{\partial t} \delta x \delta y \delta z = \frac{\partial(\rho u + 1/2 \rho <v^2> + \rho \psi)}{\partial t} \delta x \delta y \delta z \quad (3.134)$$

Further, work done by the fluid inside the volume element can be due to viscous stresses, and pressure P . For example, the frictional work done due to the viscous stresses is given as

$$\begin{aligned} \delta W_f = & - \left[(\tau_{xx} v_x)_{x=x} - (\tau_{xx} v_x)_{x=x+\delta x} \right] \delta y \delta z \\ & - \left[(\tau_{xy} v_y)_{y=y} - (\tau_{xy} v_y)_{y=y+\delta y} \right] \delta x \delta z \\ & - \left[(\tau_{xz} v_z)_{z=z} - (\tau_{xz} v_z)_{z=z+\delta z} \right] \delta x \delta y \\ & - \left[(\tau_{yx} v_x)_{x=x} - (\tau_{yx} v_x)_{x=x+\delta x} \right] \delta y \delta z \\ & - \left[(\tau_{yy} v_y)_{y=y} - (\tau_{yy} v_y)_{y=y+\delta y} \right] \delta x \delta z \\ & - \left[(\tau_{yz} v_z)_{z=z} - (\tau_{yz} v_z)_{z=z+\delta z} \right] \delta x \delta y \\ & - \left[(\tau_{zx} v_x)_{x=x} - (\tau_{zx} v_x)_{x=x+\delta x} \right] \delta y \delta z \\ & - \left[(\tau_{zy} v_y)_{y=y} - (\tau_{zy} v_y)_{y=y+\delta y} \right] \delta x \delta z \\ & - \left[(\tau_{zz} v_z)_{z=z} - (\tau_{zz} v_z)_{z=z+\delta z} \right] \delta x \delta y \end{aligned} \quad (3.135)$$

This, on analysis in a manner similar to that presented earlier in Section 2.3.2, can be expressed as

$$\begin{aligned} \delta W_f = & \left[\frac{\partial \tau_{xx} v_x}{\partial x} + \frac{\partial \tau_{xy} v_y}{\partial y} + \frac{\partial \tau_{xz} v_z}{\partial z} + \frac{\partial \tau_{yx} v_x}{\partial x} + \frac{\partial \tau_{yy} v_y}{\partial y} + \frac{\partial \tau_{yz} v_z}{\partial z} \right. \\ & \left. + \alpha \frac{\partial \tau_{zx} v_x}{\partial x} + \frac{\partial \tau_{zy} v_y}{\partial y} + \frac{\partial \tau_{zz} v_z}{\partial z} \right] \delta x \delta y \delta z \end{aligned} \quad (3.136)$$

Similarly, we get the following equation for work done due to change in pressure:

$$\begin{aligned}\delta W_p = & - \left[(Pv_x)_{x=x} - (Pv_x)_{x=x+\delta x} \right] \delta y \delta z \\ & - \left[(Pv_y)_{y=y} - (Pv_y)_{y=y+\delta y} \right] \delta x \delta z \\ & - \left[(Pv_z)_{z=z} - (Pv_z)_{z=z+\delta z} \right] \delta x \delta y \\ & + \left[\frac{\partial(Pv_x)}{\partial x} + \frac{\partial(Pv_y)}{\partial y} + \frac{\partial(Pv_z)}{\partial z} \right] \delta x \delta y \delta z\end{aligned}\quad (3.137)$$

With the help of Eqs. (3.130) to (3.137), Eq. (3.129) yields the following energy balance:

$$\begin{aligned}\frac{\partial(\rho u + (1/2)\rho v^2 + \rho \psi)}{\partial t} = & - \left[\frac{\partial(\rho u + (1/2)\rho v^2 + \rho \psi) v_x}{\partial t} \right. \\ & \left. + \frac{\partial(\rho u + (1/2)\rho v^2 + \rho \psi) v_y}{\partial y} - \frac{\partial(\rho u + (1/2)\rho v^2 + \rho \psi) v_z}{\partial z} \right] \\ & + \left[\frac{\partial[k_x(\partial T/\partial x)]}{\partial x} + \frac{\partial[k_y(\partial T/\partial y)]}{\partial y} + \frac{\partial[k_z(\partial T/\partial z)]}{\partial z} \right] \\ & - \left[\frac{\partial \tau_{xx} v_x}{\partial x} + \frac{\partial \tau_{xy} v_y}{\partial y} + \frac{\partial \tau_{xz} v_z}{\partial z} \frac{\partial \tau_{yx} v_x}{\partial x} + \frac{\partial \tau_{yy} v_y}{\partial y} + \frac{\partial \tau_{yz} v_z}{\partial z} \right. \\ & \left. + \frac{\partial \tau_{zx} v_z}{\partial x} + \frac{\partial \tau_{zy} v_y}{\partial y} + \frac{\partial \tau_{zz} v_z}{\partial z} \right] - \left[\frac{\partial Pv_x}{\partial x} + \frac{\partial Pv_y}{\partial y} + \frac{\partial Pv_z}{\partial z} \right] + \sigma\end{aligned}\quad (3.138)$$

With the help of momentum balance equation and continuity equation applied to this system, it can be shown that

$$\begin{aligned}\frac{\partial \{(1/2)\rho v^2\}}{\partial t} = & - \left\{ \frac{\partial \{(1/2)\rho v^2\} v_x}{\partial x} \right. \\ & \left. + \frac{\partial \{(1/2)\rho v^2\} v_y}{\partial y} + \frac{\partial \{(1/2)\rho v^2\} v_z}{\partial z} \right\} \\ & - \left\{ \frac{\partial(\rho v_x)}{\partial x} \frac{\partial(\rho v_y)}{\partial y} + \frac{\partial(\rho v_z)}{\partial z} \right\} + \rho \left\{ \frac{\partial v_x}{\partial x} \frac{\partial v_y}{\partial y} + \frac{\partial v_z}{\partial z} \right\} \\ & - \left[\left\{ \frac{\partial(\tau_{xx} v_x)}{\partial x} + \frac{\partial(\tau_{yx} v_x)}{\partial y} + \frac{\partial(\tau_{zx} v_x)}{\partial z} \right\} + \right. \\ & \left. \left\{ \frac{\partial(\tau_{xy} v_y)}{\partial x} + \frac{\partial(\tau_{yy} v_y)}{\partial y} + \frac{\partial(\tau_{zy} v_y)}{\partial z} \right\} \right.\end{aligned}$$

$$\begin{aligned}
& + \left[\frac{\partial(\tau_{xz}v_z)}{\partial x} + \frac{\partial(\tau_{yz}v_z)}{\partial y} + \frac{\partial(\tau_{zz}v_z)}{\partial z} \right] \\
& + \left[\left\{ \tau_{xx} \left(\frac{\partial v_x}{\partial x} \right) + \tau_{yx} \left(\frac{\partial v_x}{\partial y} \right) + \tau_{zx} \left(\frac{\partial v_x}{\partial z} \right) \right\} + \right. \\
& \quad \left. \left\{ \tau_{xy} \left(\frac{\partial v_y}{\partial x} \right) + \tau_{yy} \left(\frac{\partial v_y}{\partial y} \right) + \tau_{zy} \left(\frac{\partial v_y}{\partial z} \right) \right\} \right. \\
& \quad \left. + \left\{ \tau_{xz} \left(\frac{\partial v_z}{\partial x} \right) + \tau_{yz} \left(\frac{\partial v_z}{\partial y} \right) + \tau_{zz} \left(\frac{\partial v_z}{\partial z} \right) \right\} \right] \\
& \quad + \{ \rho(v_x g_x + v_y g_y + v_z g_z) \} \tag{3.139}
\end{aligned}$$

where

$$\langle v^2 \rangle = (v_x^2 + v_y^2 + v_z^2) \tag{3.140}$$

Substituting the value of $\frac{\partial \{(1/2)\rho \langle v^2 \rangle\}}{\partial t}$ from Eq. (3.139) in Eq. (3.138),

we get

$$\begin{aligned}
\frac{\partial(\rho u + \rho \psi)}{\partial t} &= - \left\{ \frac{\partial(\rho u v_x)}{\partial x} + \frac{\partial(\rho u v_y)}{\partial y} + \frac{\partial(\rho u v_z)}{\partial z} \right\} \\
&\quad - \left\{ \frac{\partial(\rho \psi v_x)}{\partial x} + \frac{\partial(\rho \psi v_y)}{\partial y} + \frac{\partial(\rho \psi v_z)}{\partial z} \right\} \\
&\quad + \left[\frac{\partial \{k_x (\partial T / \partial x)\}}{\partial x} + \frac{\partial \{k_y (\partial T / \partial y)\}}{\partial y} + \frac{\partial \{k_z (\partial T / \partial z)\}}{\partial z} \right] \\
&\quad - \left[\left\{ \tau_{xx} \left(\frac{\partial v_x}{\partial x} \right) + \tau_{yx} \left(\frac{\partial v_x}{\partial y} \right) + \tau_{zx} \left(\frac{\partial v_x}{\partial z} \right) \right\} \right. \\
&\quad + \left\{ \tau_{xy} \left(\frac{\partial v_y}{\partial x} \right) + \tau_{yy} \left(\frac{\partial v_y}{\partial y} \right) + \tau_{zy} \left(\frac{\partial v_y}{\partial z} \right) \right\} \\
&\quad + \left\{ \tau_{xz} \left(\frac{\partial v_z}{\partial x} \right) + \tau_{yz} \left(\frac{\partial v_z}{\partial y} \right) + \tau_{zz} \left(\frac{\partial v_z}{\partial z} \right) \right\} \\
&\quad + \left\{ P \left(\frac{\partial v_x}{\partial x} \right) + \left(\frac{\partial v_y}{\partial y} \right) + \left(\frac{\partial v_z}{\partial z} \right) \right\} \\
&\quad \left. + \rho (v_x g_x + v_y g_y + v_z g_z) + \sigma \right] \tag{3.141}
\end{aligned}$$

Assuming that the potential energy of the fluid is due only to gravitational forces, we get

$$\frac{\partial(\rho\psi)}{\partial t} = - \left[\frac{\partial(\rho\psi v_x)}{\partial x} + \frac{\partial(\rho\psi v_y)}{\partial y} + \frac{\partial(\rho\psi v_z)}{\partial z} \right] - \rho(v_x g_x + v_y g_y + v_z g_z) \quad (3.142)$$

Using this, Eq. (3.141) is simplified to

$$\begin{aligned} \frac{\partial(\rho u)}{\partial t} - & \left[\frac{\partial(\rho u v_x)}{\partial x} + \frac{\partial(\rho u v_y)}{\partial y} + \frac{\partial(\rho u v_z)}{\partial z} \right] + k \left(\frac{\partial^2 T}{\partial x^2} + \frac{\partial^2 T}{\partial y^2} + \frac{\partial^2 T}{\partial z^2} \right) \\ & - \left[\tau_{xx} \frac{\partial v_x}{\partial x} + \tau_{xy} \frac{\partial v_y}{\partial y} + \tau_{xz} \frac{\partial v_z}{\partial z} \right. \\ & + \tau_{yx} \frac{\partial v_y}{\partial x} + \tau_{yy} \frac{\partial v_y}{\partial y} + \tau_{yz} \frac{\partial v_y}{\partial z} + \tau_{zx} \frac{\partial v_x}{\partial x} + \tau_{zy} \frac{\partial v_y}{\partial y} + \tau_{zz} \frac{\partial v_z}{\partial z} \\ & \left. - P \left(\frac{\partial v_x}{\partial x} + \frac{\partial v_y}{\partial y} + \frac{\partial v_z}{\partial z} \right) + \sigma \right] \end{aligned} \quad (3.143)$$

In the above relation, Fourier's first law of heat conduction has been made use of for expressing conductive heat transfer and the thermal conductivity is assumed to be isotropic. With the help of the continuity equation, the above equation may be expressed in the following substantial derivative form:

$$\begin{aligned} \rho \frac{DU}{Dt} &= k \left(\frac{\partial^2 T}{\partial x^2} + \frac{\partial^2 T}{\partial y^2} + \frac{\partial^2 T}{\partial z^2} \right) - \left[\tau_{xx} \frac{\partial v_x}{\partial x} + \tau_{xy} \frac{\partial v_y}{\partial y} + \tau_{xz} \frac{\partial v_z}{\partial z} \right. \\ &+ \tau_{yx} \frac{\partial v_y}{\partial x} + \tau_{yy} \frac{\partial v_y}{\partial y} + \tau_{yz} \frac{\partial v_y}{\partial z} + \tau_{zx} \frac{\partial v_z}{\partial x} + \tau_{zy} \frac{\partial v_z}{\partial y} + \tau_{zz} \frac{\partial v_z}{\partial z} \\ & \left. - \left(\frac{\partial v_x}{\partial x} + \frac{\partial v_y}{\partial y} + \frac{\partial v_z}{\partial z} \right) + \sigma \right] \end{aligned} \quad (3.144)$$

For the purpose of application, this equation is expressed in terms of temperature and heat capacity instead of internal energy. In order to eliminate the internal energy term and incorporate the temperature term in its place, we take the help of the following thermodynamic relationship:

$$dU = \left(\frac{\partial U}{\partial T} \right)_V dT + \left(\frac{\partial U}{\partial V} \right)_T dV = C_V dT - \left[P - T \left(\frac{\partial P}{\partial T} \right)_V \right] dV \quad (3.145)$$

where C_V is the molar heat capacity of the fluid at constant volume.

Then ρ times the substantial derivative of U with respect to t becomes

$$\rho \frac{DU}{Dt} = C_V \rho \frac{dT}{Dt} - \left[P - T \left(\frac{\partial P}{\partial T} \right)_V \right] \rho \frac{dV}{Dt} \quad (3.146)$$

Further, molar volume is given by $V = 1/\rho$, so that

$$\frac{DV}{Dt} = \frac{D(1/\rho)}{Dt} = -\frac{1}{\rho^2} \frac{D\rho}{Dt}$$

and from Eq. (2.38)

$$\frac{D\rho}{Dt} = -\rho \left(\frac{\partial v_x}{\partial x} + \frac{\partial v_y}{\partial y} + \frac{\partial v_z}{\partial z} \right) \quad (3.147)$$

Therefore

$$\frac{DV}{Dt} = \frac{1}{\rho} \left(\frac{\partial v_x}{\partial x} + \frac{\partial v_y}{\partial y} + \frac{\partial v_z}{\partial z} \right)$$

From Eqs. (3.146) and (3.147), we get

$$\rho \frac{DU}{Dt} = \rho C_V \frac{DT}{Dt} - \left[P - T \left(\frac{\partial P}{\partial T} \right)_V \right] \left(\frac{\partial v_x}{\partial x} + \frac{\partial v_y}{\partial y} + \frac{\partial v_z}{\partial z} \right) \quad (3.148)$$

Substitution of the above relation in Eq. (3.144) yields

$$\begin{aligned} \rho C_V \frac{DT}{Dt} &= k \left(\frac{\partial^2 T}{\partial x^2} + \frac{\partial^2 T}{\partial y^2} + \frac{\partial^2 T}{\partial z^2} \right) - \left[\tau_{xx} \frac{\partial v_x}{\partial x} + \tau_{xy} \frac{\partial v_y}{\partial y} + \tau_{xz} \frac{\partial v_z}{\partial z} \right. \\ &\quad \left. + \tau_{yx} \frac{\partial v_y}{\partial x} + \tau_{yy} \frac{\partial v_y}{\partial y} + \tau_{yz} \frac{\partial v_z}{\partial z} + \tau_{zx} \frac{\partial v_z}{\partial x} + \tau_{zy} \frac{\partial v_y}{\partial y} + \tau_{zz} \frac{\partial v_z}{\partial z} \right] \\ &\quad - T \left(\frac{\partial P}{\partial T} \right)_V \left(\frac{\partial v_x}{\partial x} + \frac{\partial v_y}{\partial y} + \frac{\partial v_z}{\partial z} \right) + \sigma \end{aligned} \quad (3.149)$$

This is the general differential total energy balance equation. It may be pointed out here that, in this equation, the potential energy owing to electric, magnetic and other similar fields has not been considered. This equation is generally used in practice after simplifying it further by taking into consideration the properties of the fluid, its rate of flow and other external conditions. Typical simplifications of this equation for some common applications are listed below.

- (i) For fluid flowing at moderate and low velocities, the effect of shearing and normal stresses can be neglected. Hence, Eq. (3.149) takes the form

$$\begin{aligned} \rho C_V \frac{DT}{Dt} &= k \left(\frac{\partial^2 T}{\partial x^2} + \frac{\partial^2 T}{\partial y^2} + \frac{\partial^2 T}{\partial z^2} \right) \\ &\quad - T \left(\frac{\partial P}{\partial T} \right)_V \left(\frac{\partial v_x}{\partial x} + \frac{\partial v_y}{\partial y} + \frac{\partial v_z}{\partial z} \right) + \sigma \end{aligned} \quad (3.150)$$

- (ii) Using additional simplifications in this case for an isotropic incompressible nonreacting fluid, the above equation further reduces to the form

$$\rho C_V \frac{DT}{Dt} = k \left(\frac{\partial^2 T}{\partial x^2} + \frac{\partial^2 T}{\partial y^2} + \frac{\partial^2 T}{\partial z^2} \right) \quad (3.151)$$

- (iii) For an ideal nonreacting gas for which $(\partial P/\partial T)_V = R/V$, and with $\sigma = 0$, Eq. (3.149) takes the form

$$\rho C_V \frac{DT}{Dt} = k \left(\frac{\partial^2 T}{\partial x^2} + \frac{\partial^2 T}{\partial y^2} + \frac{\partial^2 T}{\partial z^2} \right) - P \left(\frac{\partial v_x}{\partial x} + \frac{\partial v_y}{\partial y} + \frac{\partial v_z}{\partial z} \right) \quad (3.152)$$

In the case of flow through tubes and around cylinders, it is convenient to work with the energy balance equation in cylindrical and spherical coordinate systems respectively. This equation in these systems can be obtained by following the standard coordinate transformation procedure. The energy equations in these coordinate systems are given now, without going into the details of the transformation procedure.

- (a) Energy balance equation in cylindrical coordinate system:

$$\begin{aligned} \rho C_v \frac{DT}{Dt} &= \rho C_v \left(\frac{\partial T}{\partial t} + v_r \frac{\partial T}{\partial r} + \frac{v_\theta}{r} \frac{\partial T}{\partial \theta} + v_z \frac{\partial T}{\partial z} \right) \\ &= -k \left[\frac{1}{r} \frac{\partial}{\partial r} \left(r \frac{\partial T}{\partial x} + \frac{1}{r^2} \frac{\partial^2 T}{\partial \theta^2} + \frac{\partial^2 T}{\partial z^2} \right) \right] \\ &\quad - T \left(\frac{\partial \rho}{\partial T} \right)_v \left[\frac{1}{r} \frac{\partial}{\partial r} (rv_r) + \frac{1}{r} \frac{\partial v_\theta}{\partial \theta} + \frac{\partial v_z}{\partial z} \right] \\ &\quad - \left[\tau_{rr} \frac{\partial v_r}{\partial r} + \tau_{\theta\theta} \frac{1}{r} \left(\frac{\partial v_\theta}{\partial \theta} + v_r \right) \right. \\ &\quad \left. + \tau_{zz} \frac{\partial v_z}{\partial z} + \tau_{r\theta} r \frac{\partial}{\partial r} \left(\frac{v}{r} + \frac{1}{r} + \frac{\partial v_r}{\partial r} \right) \right. \\ &\quad \left. + \tau_{rz} \left(\frac{\partial v_z}{\partial r} + \frac{\partial v_r}{\partial z} \right) + \tau_{\theta z} \left(\frac{1}{r} \frac{\partial v_z}{\partial r} + \frac{\partial v_z}{\partial z} \right) \right] \end{aligned} \quad (A)$$

- (b) Energy balance in spherical coordinate system:

$$\begin{aligned} \rho C_V \frac{DT}{Dt} &= \rho C_v \left(\frac{\partial T}{\partial t} + v_r \frac{\partial T}{\partial r} + \frac{v_\theta}{r} \frac{\partial T}{\partial \theta} + \frac{v_\phi}{r \sin \theta} \frac{\partial T}{\partial \phi} \right) \\ &= -k \left[\frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial T}{\partial r} \right) + \frac{1}{r^2 \sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial T}{\partial \theta} \right) \right] \end{aligned}$$

$$\begin{aligned}
& + \frac{1}{r^2 \sin^2 \theta} \frac{\partial^2 T}{\partial \phi^2} \Big] - T \left(\frac{\partial P}{\partial T} \right)_v \left[\frac{1}{r^2} \frac{\partial}{\partial r} (r^2 v_r) \right. \\
& \quad \left. + \frac{1}{r \sin \theta} \frac{\partial}{\partial \theta} (v_\theta \sin \theta) + \frac{1}{r \sin \theta} \frac{\partial v_\phi}{\partial \phi} \right] \\
& - \left[\tau_{rr} \frac{\partial v_r}{\partial r} + \tau_{\theta\theta} \left(\frac{1}{r} \frac{\partial v_\theta}{\partial \theta} + \frac{v_r}{r} \right) + \tau_{\phi\phi} \left(\frac{1}{r \sin \theta} \frac{\partial v_\phi}{\partial \phi} \frac{v_r}{r} + \frac{v_\theta \cos \theta}{r} \right) \right. \\
& \quad + \tau_{r\theta} \left(\frac{\partial v_\theta}{\partial r} + \frac{1}{r} \frac{\partial v_r}{\partial \theta} - \frac{v_\theta}{r} \right) + \tau_{r\phi} \left(\frac{\partial v_\phi}{\partial r} + \frac{1}{r \sin \theta} \frac{\partial v_r}{\partial \phi} - \frac{v_\phi}{r} \right) \\
& \quad \left. + \tau_{\theta\phi} \left(\frac{1}{r} \frac{\partial v_\phi}{\partial \theta} + \frac{1}{r \sin \theta} \frac{\partial v_\theta}{\partial \phi} - \frac{\cos \theta}{r} v_\phi \right) \right] \tag{B}
\end{aligned}$$

3.2.2 Applications of Differential Total Energy Balance Equation

Convective heat transfer problems can be classified into two categories, depending upon the mode by which pressure gradient for fluid flow is achieved. If heat transfer studies are made on systems in which this gradient is controlled externally, such studies are classified under forced convection. However, for systems in which fluid flow takes place under the pressure gradient produced internally by the system because of density differences arising out of temperature differences within the system, the phenomenon is termed as *free* or *natural convection*. Application of the total energy balance equation to both these categories of convection is illustrated in the following subsections.

Forced convection in fully developed laminar flow through tubes

We have selected this example for illustration of the application of the energy balance equation as it affords an approximate solution to a number of problems of heat transfer encountered in industrial practice. In this subsection, we deal with the analysis of the convective heat transfer in the region of fully developed flow. The concept of this type of flow has been explained in Section 2.3.3.

In order to simplify this problem, we incorporate the following two conditions:

- (i) The fluid is incompressible.
- (ii) The flux of heat exchanged by the fluid with the surroundings is constant.

As a tube exhibits cylindrical symmetry, the energy balance equation should be written in cylindrical coordinates. Thus, we can write the following equations for fully developed flow of an incompressible fluid for the situation shown in Fig. 3.13. Here r is the distance from the centre and z the direction of flow.

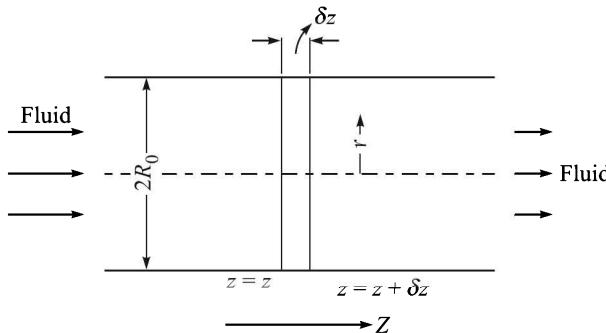


Fig. 3.13 Forced convective heat flow through a volume element in a tube.

- (a) From Eq. (2.45), the continuity equation for the flow takes the form

$$\frac{\partial v_z}{\partial z} = 0 \quad (3.153)$$

as v_r and v_θ are equal to zero.

- (b) From Eq. (F) in Section 2.3.2 and with the help of Eq. (B) in Section 3.2.1, the equation of motion for this system is reduced to

$$-\frac{\Delta P}{\Delta z} = \mu \left[\frac{1}{r} \frac{\partial}{\partial r} \left(r \frac{\partial v_z}{\partial r} \right) \right] \quad (3.154)$$

where it has been assumed that the axis of the pipe through which flow takes place is horizontal. Also, for the flow under consideration, $(\partial^2 v_z / \partial \theta^2)$ and $(\partial^2 v_z / \partial z^2)$ are equal to zero.

- (c) Similarly Eq. (A) in Section 3.2.1 for total energy balance, reduces to

$$\rho C_v \frac{DT}{Dt} = k \left[\frac{1}{r} \frac{\partial}{\partial r} \left(r \frac{\partial T}{\partial r} \right) + \frac{1}{r^2} \frac{\partial^2 T}{\partial \theta^2} + \frac{\partial^2 T}{\partial z^2} \right] \quad (3.155)$$

In the writing of the above equation, the effect of shearing and normal stresses has been neglected because the flow is of low velocity. As the flow is fully developed, we get

$$\frac{\partial T}{\partial \theta} = 0, \quad \frac{\partial T}{\partial t} = 0, \quad \frac{\partial^2 T}{\partial z^2} \approx 0, \quad \text{and} \quad v_r = 0$$

Hence

$$\begin{aligned} \frac{DT}{Dt} &= \frac{\partial T}{\partial t} + v_r \frac{\partial T}{\partial r} + \frac{v_\theta}{r} \frac{\partial T}{\partial \theta} + v_z \frac{\partial T}{\partial z} \\ &= v_z \frac{\partial T}{\partial z} \end{aligned} \quad (3.156)$$

Therefore, Eq. (3.155) takes the following alternative simplified form:

$$v_z \frac{\partial T}{\partial z} = \frac{\alpha}{r} \left\{ \frac{\partial}{\partial r} \left(r \frac{\partial T}{\partial r} \right) \right\} \quad (3.157)$$

where

$$\alpha = \frac{k}{\rho C_v}, \text{ the thermal diffusivity} \quad (3.158)$$

On integration, Eq. (3.154) yields, from $r = 0$ to $r = R_0$

$$v_z = - \frac{\Delta P R_0^2}{4\mu\Delta z} (1 - r^2/R_0^2) \quad (3.159)$$

where R_0 is the radius of tube.

Substitution of v_z from the above equation in Eq. (3.157) yields

$$\frac{\Delta P(R_0^2 - r^2)}{4\mu\Delta z} \frac{\partial T}{\partial z} = - \frac{\alpha}{r} \frac{\partial}{\partial r} \left(r \frac{\partial T}{\partial r} \right) \quad (3.160)$$

It is this partial differential equation which leads to the calculation of temperature of the fluid inside the tube. We consider here a particular case of the application of this equation for which an analytical solution can be arrived at. For this case we assume, apart from constant heat flux from tube surface to the fluid, that the flow has a fully developed thermal profile.

Just as the fully developed velocity profile implies that it is independent of position in axial direction, a fully developed temperature profile will imply that the function $(T_s - T)/(T_s - T_m)$ is independent of the position along the axial direction. Thus, for such a flow, we have

$$\frac{\partial}{\partial z} \left(\frac{T_s - T}{T_s - T_m} \right) = 0 \quad (3.161)$$

where T_s is the surface absolute temperature, T the local fluid absolute temperature, and T_m the mean absolute temperature of the fluid over a cross-section of the tube, which in turn is given by the equation

$$GC_v T_m = C_v \rho v_z T dA \quad (3.162)$$

where G is the mass flow rate of the fluid.

For an incompressible fluid

$$G = \pi R_0^2 v_{av} \rho \quad (3.163)$$

where v_{av} is the mean velocity of the fluid. Hence, the mean absolute temperature T_m can be expressed by the relation

$$T_m = \frac{\int_0^{R_0} \rho v_z T r dr}{v_{av} R_0^2} \quad (3.164)$$

According to Newton's law of cooling, heat transfer rate q , i.e. the amount of heat flowing per unit time to a system is proportional to the difference between the surface temperature and the mean temperature of the system. Thus

$$q \propto (T_s - T_m) \quad (3.165)$$

As q is constant in the present case, the difference $(T_s - T_m)$ along the tube is also constant.

Thus

$$\frac{\partial T_s}{\partial z} - \frac{\partial T_m}{\partial z} = 0$$

or

$$\frac{\partial T_s}{\partial z} = \frac{\partial T_m}{\partial z} \quad (3.166)$$

for a fully developed flow with constant surface heat flux.

Equation (3.161) with the help of Eq. (3.166) yields the relation

$$\frac{\partial T}{\partial z} = \frac{\partial T_s}{\partial z} = \frac{\partial T_m}{\partial z} \quad (3.167)$$

From the above relation, it is clear that the axial temperature gradient in the fluid is independent of the radial position. In order to arrive at the value of the gradient, we consider a small volume element of the tube shown in Fig. 3.13. Striking the heat balance on this element of fluid, we get

$$[G C_p T_m]_{z=z} + q \times 2\pi R_0 \delta z = [G C_p T_m]_{z=z+\delta z} \quad (3.168)$$

or, in the differential form

$$\frac{\partial (G C_p T_m)}{\partial z} = 2\pi R_0 q \quad (3.169)$$

Assuming C_p to be independent of temperature, we get

$$\frac{\partial T_m}{\partial z} = \frac{2\pi R_0 q}{G C_p} \quad (3.170)$$

Integration of this expression yields

$$T_m - T_{m,0} = \frac{2\pi R_0 q}{G C_p} (z - z_0) \quad (3.171)$$

where $T_{m,0}$ is the mean absolute temperature at the position z_0 along the axis of the tube.

From Eq. (3.171), it is clear that temperature T_m varies linearly with distance along the axis of the tube and so does the surface temperature T_s . With the help of Eqs. (3.167) and (3.170), we get the following relation from Eq. (3.160):

$$\frac{\alpha}{r} \left\{ \frac{\partial}{\partial r} \left(r \frac{\partial T}{\partial r} \right) \right\} = \frac{\pi R_0^3 q}{2 G C_p \mu} \left(\frac{\Delta P}{\Delta z} \right) \left(1 - \frac{r^2}{R_0^2} \right) \quad (3.172)$$

On integration, this expression yields

$$T = \frac{\pi R_0^3 q}{\alpha G C_p} \left(\frac{\Delta P}{\Delta z} \right) \left(\frac{r^2}{4} - \frac{r^4}{16} \right) + C_1 \ln r + C_2 \quad (3.173)$$

The values of constants C_1 and C_2 can be determined by using the following boundary conditions:

$$\text{At } r = 0, \quad \frac{\partial T}{\partial r} = 0 \quad (3.174)$$

$$\text{At } r = R_0, \quad T = T_s \quad (3.175)$$

Thus, Eq. (3.173) takes the following form, to show the temperature distribution:

$$T = T_s - \frac{\pi R_0^3 q}{\alpha G C_p} \left(\frac{\Delta P}{\Delta z} \right) \left[\frac{3}{16} + \frac{1}{16} \left(\frac{r}{R_0} \right)^4 - \frac{1}{4} \left(\frac{r}{R_0} \right)^2 \right] \quad (3.176)$$

Free or natural convection

In the preceding section, we analysed the heat transfer in fluids which were made to flow under external forces. Many a time in actual practice, situations arise in which a fluid flows under forces generated *in situ*. Such situations are referred to as free or natural convection. The simplest example of such a case is the heating of a liquid in any container. In this case, the temperature of the liquid will be the highest at the point or surface of heat supply and therefore the density will be the lowest at the said point or surface. Flow of liquid will therefore start under a density gradient. Such density gradients can also occur because of the existence of concentration gradients within the fluid mass. Problems involving natural convection are generally complex and are solved by making use of numerical methods. However, in this work we will introduce a simple problem in which free convection in a system will be analysed. For this purpose, let a semi-finite vertical plate perpendicular to the plane of the paper be in contact with a fluid with both the plate and the fluid having different temperatures T_s and T_∞ respectively as shown in Fig. 3.14, where $T_s > T_\infty$.

The fluid near the wall and in contact with it will be at a temperature higher than that of the bulk fluid and thus have lower density and therefore rise up. Consequently, the fluid will flow from the bulk towards the lower end of the plate and thus have two-dimensional flow, i.e. in the x - and z -directions as shown in the figure. Consider further that the system attains steady state instantaneously.

The relevant relations depicting flows of fluid and heat for such a system can be expressed as follows:

- (i) *Continuity equation:* Equation (2.43) may be modified for this situation as

$$\frac{\partial v_x}{\partial x} + \frac{\partial v_z}{\partial z} = 0 \quad (3.177)$$

- (ii) *Equation of motion:* Equation (2.75) may be modified as

$$v_x \frac{\partial v_z}{\partial x} + v_z \frac{\partial v_z}{\partial z} = \nu \frac{\partial^2 v_z}{\partial x^2} - \frac{1}{\rho} \frac{\partial P}{\partial z} - g_z \quad (3.178)$$

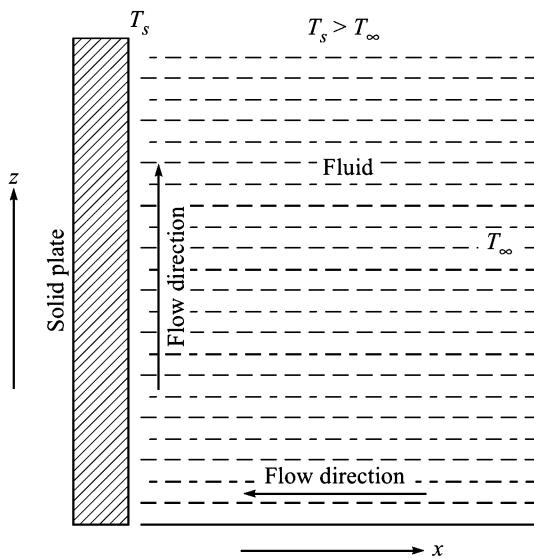


Fig. 3.14 Natural convection due to a hot vertical solid plate.

where $\nu (= \mu/\rho)$ represents the kinematic viscosity of the fluid and g_z is the acceleration due to gravity in the z -direction. The equation of motion may be further modified as follows.

A comparison of Eqs. (3.154) and (3.178) shows that in forced convection, the value of the pressure gradient, $\partial P/\partial z$, is fixed by external forces, but in natural convection it has to be expressed in terms of variation in the density of the fluid, caused by variation in temperature. It can easily be concluded that, for this system, pressure variation along the x -direction at a very large distance from the plate where the temperature difference is negligible, is zero. Therefore, $\partial P/\partial z$ will be independent of the position on the x -axis at that point. Thus, for a vertical plane at an appreciable distance in the x -direction from the plate, where there is no flow of liquid in either the x - or the z -direction, the equation of motion takes the following simple form:

$$-\frac{1}{\rho_\infty} \frac{\partial P}{\partial z} - g_z = 0$$

or

$$\frac{\partial P}{\partial z} = -\rho_\infty g_z \quad (3.179)$$

where ρ_∞ is the density of the fluid at a plane far away from the plate. Substitution of Eq. (3.179) in Eq. (3.178) yields

$$v_x \frac{\partial v_x}{\partial x} + v_z \frac{\partial v_z}{\partial z} = \frac{g_z}{\rho} (\rho_\infty - \rho) + \nu \frac{\partial^2 v_z}{\partial x^2} \quad (3.180)$$

It should, however, be noted that in free convection the flow originates because of the density difference ($\rho_{\infty} - \rho$), which in turn, is a function of the temperature difference and the properties of the fluid, namely the thermal coefficient of volumetric expansion. It is, therefore, proper to express this density difference in terms of these parameters. According to the definition, the coefficient of volumetric thermal expansion β is expressed by the relation

$$\beta = \frac{1}{V} \left(-\frac{\partial V}{\partial T} \right)_P = -\frac{1}{\rho} \left(-\frac{\partial \rho}{\partial T} \right)_P \quad (3.181)$$

Further, we have

$$\frac{\partial \rho}{\partial T} \approx \frac{\rho_{\infty} - \rho}{T_{\infty} - T} \quad (3.182)$$

where T_{∞} is the temperature of the fluid at an appreciable distance from the plate.

With the help of Eqs. (3.181) and (3.182), we may express the equation of motion, Eq. (3.180), in the following form:

$$v_x \frac{\partial v_x}{\partial x} + v_z \frac{\partial v_z}{\partial z} = g_z \beta (T_{\infty} - T) + \nu \frac{\partial^2 v_z}{\partial x^2} \quad (3.183)$$

- (iii) The differential total energy balance equation is the third equation governing the flow of fluid and heat. From Eq. (3.149), we can arrive at the following form for this equation:

$$v_x \frac{\partial T}{\partial x} + v_z \frac{\partial T}{\partial z} = \alpha \frac{\partial^2 T}{\partial x^2} \quad (3.184)$$

In arriving at the above equation from Eq. (3.149), the terms containing the stresses have been neglected. It may be mentioned here that in the preceding subsection on forced convection for flow through a tube, we could solve the equation of motion independently, but in the present case, this equation contains temperature-related terms and hence has to be solved simultaneously with the total energy balance equation taking into account the relevant boundary conditions. It is this fact that makes such problems complex, making an analytical solution elusive. Therefore, such problems can only be solved by computational methods. In the present case, the boundary conditions are quite evident and can be expressed as follows:

$$(i) \text{ at } x = 0, v_x = v_z = 0 \text{ and } T = T_s \quad (3.185)$$

$$(ii) \text{ at } x = \infty, v_x = 0 \text{ and } T = T_{\infty} \quad (3.186)$$

Pohlhausen¹ introduced a stream function ψ and a dimensionless temperature function θ to simplify the set of differential equations governing this system.

¹ K.Z. Pohlhausen, *Angew. Math. Mech.*, 1: 252 (1921).

These functions are defined as follows:

$$\psi = 4\nu C z^{3/4} \xi(\eta) \quad (3.187)$$

and

$$\theta = \frac{T - T_{\infty}}{T_s - T_{\infty}} \quad (3.188)$$

where the functions C , $\xi(\eta)$ and η in Eq. (3.187) are defined by the following relations:

$$C = \left[\frac{g_z \beta (T_s - T_{\infty})}{4\nu^2} \right]^{1/4} \quad (3.189)$$

where $\xi(\eta)$ or ξ is an unknown function of η .

$$\eta = C \frac{x}{z^{1/4}} \quad (3.190)$$

and ν = kinematic viscosity of the fluid.

According to the definition of stream function, we have

$$v_x = - \frac{\partial \psi}{\partial z} \quad (3.191)$$

and

$$v_z = + \frac{\partial \psi}{\partial x} \quad (3.192)$$

With the help of Eqs. (3.187) to (3.192), we can arrive at the following equations for velocities:

$$v_z = 4\nu(z)^{1/2} C^2 \frac{\partial \xi}{\partial \eta} \quad (3.193)$$

and

$$v_x = \nu C(z)^{-1/4} \left(\eta \frac{\partial \xi}{\partial \eta} - 3\xi \right) \quad (3.194)$$

Substitution of the above relations in Eqs. (3.183) and (3.184) yields the equations

$$\frac{d^3 \xi}{d^3 \eta} + 3\xi \frac{d^2 \xi}{d\eta^2} - 2 \left(\frac{d\xi}{d\eta} \right)^2 + \theta = 0 \quad (3.195)$$

and

$$\frac{d^2 \theta}{d\eta^2} + 3 \left(\frac{\nu}{\alpha} \right) \xi \frac{d\theta}{d\eta} = 0 \quad (3.196)$$

The boundary conditions now take the form:

$$(i) \text{ At } \eta = 0, \xi = \frac{d\xi}{d\eta} = 0 \text{ and } \theta = 1 \quad (3.197)$$

$$(ii) \text{ At } \eta \rightarrow \infty, \frac{d\xi}{d\eta} \rightarrow 0 \text{ and } \theta \rightarrow 0 \quad (3.198)$$

Now from Eqs. (3.189) and (3.190), we have

$$\eta = \left[\frac{g_z \beta (T_s - T_\infty)}{4v^2} \right]^{1/4} \frac{x}{z^{1/4}}$$

or

$$\eta = \left[\frac{g_z \beta z^3 (T_s - T_\infty)}{4v^2} \right]^{1/4} \frac{x}{z} = \left(\frac{N_{Gr}}{4} \right)^{1/4} \frac{x}{z} \quad (3.199)$$

where

$$N_{Gr} = \frac{g_z \beta z^3 (T_s - T_\infty)}{v^2} \quad (3.200)$$

which is a dimensionless number known as the *Grahoft number*. The Grahoft number is an important dimensionless group which is obtained when differential equations describing natural convection are made dimensionless. Its physical significance lies in the fact that it represents the ratio of the buoyancy forces and the viscous forces in the system. We will discuss more about this number in Chapter 5.

Equations (3.195) and (3.196) with the boundary conditions given in Eqs. (3.197) and (3.198) are nonlinear equations and can be solved by numerical techniques. Results of such solutions are shown Figs. 3.15(a) and (b) which depict plots of ξ vs. η and θ vs. η for different values of v/α . With the help of these figures we can get ideas about the velocity and temperature profiles in natural convection. The v/α is known as the *Prandtl number*, N_{Pr} which is a dimensionless group. This number can also be simplified to $C_p \mu / k$ where C_p is the heat capacity at constant pressure, μ the viscosity and k the thermal conductivity of the fluid. It may be seen that all these parameters are intrinsic fluid properties.

As noted above, the Prandtl number is the ratio of the kinematic viscosity to the thermal diffusivity of a fluid, and plays an important role in convective heat transfer. It may be also considered as a ratio of the rate coefficient of viscous momentum transfer to that of heat conduction. Thus, when the Prandtl number is very small, much smaller than unity, as in the case of liquid metals, the ability of the fluid to transport momentum is much less than the ability to transport thermal energy. The dimensionless velocity profile will be much smaller than the dimensionless temperature profile in this case. Similarly for large values of the Prandtl number, the velocity profile will be much larger than the temperature profile. This is the case with liquid slags. Finally, when the Prandtl number is close to unity, as in the case of most gases, the two profiles are identical.

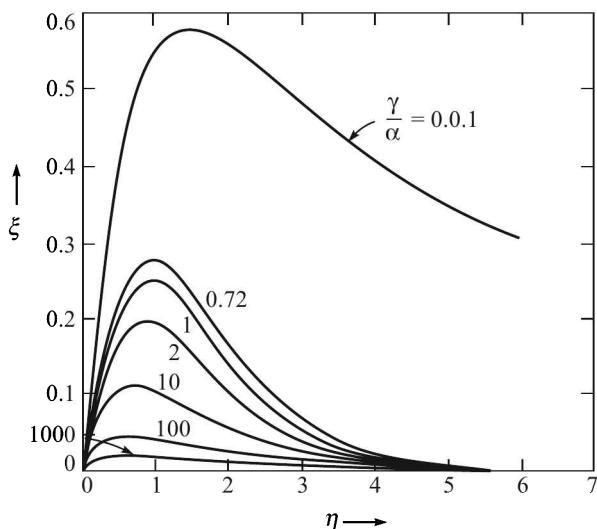


Fig. 3.15(a) Relationship between functions ξ and η for natural convection at different (γ/α) ratios.

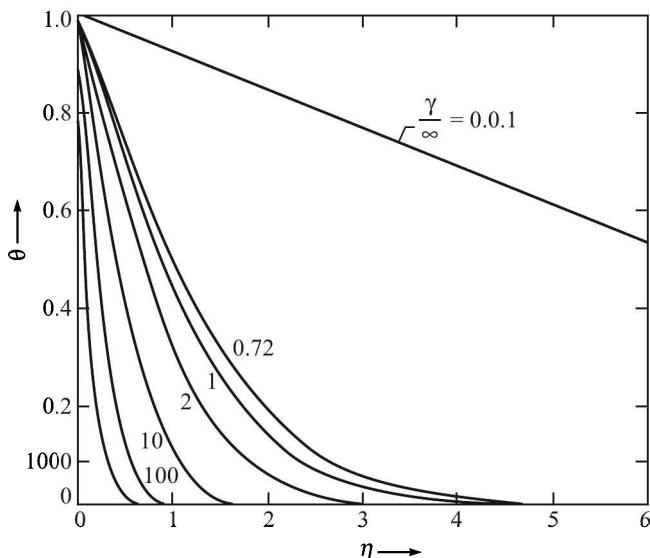


Fig. 3.15(b) Relationship between functions θ and η for natural convection at different (γ/α) ratios.

Convective heat transfer in turbulent flow

In the earlier two subsections, the differential total energy balance equation was applied to the two cases of forced convection and natural convection. In both cases the fluid flow was in the laminar region, where velocity and temperature distribution could be obtained with reasonable accuracy. In turbulent flow,

however, application of the differential balance equation does not give accurate results because of the complexity of the system. The situation is similar to the use of overall or macroscopic balance for fluid flow discussed in Section 2.4, where a certain amount of empiricism is involved. It is, therefore, necessary now to consider the overall thermal energy balance for the whole system.

3.2.3 Overall Thermal Energy Balance—Concept of Heat Transfer Coefficient

This balance is based on the following expression:

$$\text{(Heat input to the system or reactor with the inflowing fluid)} - \text{(Heat output from the reactor with the outflowing fluid)} + \text{(Heat produced inside the reactor through physical changes or chemical reactions, if any)} - \text{(Heat retained inside the reactor)} + \text{(Heat flowing in the reactor from surrounding surfaces)} = 0 \quad (3.201)$$

The first two terms of the above relation can be written in mathematical forms as functions of mass flow rate, specific heat and temperature of the fluid. The third term can be evaluated from the thermodynamic data on the basis of reactions taking place inside the reactor. The fourth term can be expressed as a function of the temperature rise of reactor ingredients and their specific heats and masses. The fifth term can be evaluated by the application of Fourier's first law of heat conduction. However, the application of this relation requires a knowledge of the temperature gradient inside the fluid and at the surface of the reactor. It is rarely possible to assess this term in many practical cases. We, therefore, proceed empirically to express this term. It is well known from experience that the heat flow per unit area per unit time, J , to any system is directly proportional to the difference between the temperature T_b of the bulk and the temperature T_s at the surface of the reactor. Hence, we have

$$J = h (T_b - T_s) \quad (3.202)$$

where h is called the *heat transfer coefficient*. This empirical equation was first suggested by Newton in connection with the cooling phenomenon. Although it is uniformly applicable to both heating and cooling, it is, however, referred to as *Newton's law of cooling*. The evaluation of heat transfer coefficient, h , can follow only from experimental data. Obviously, h will be a function of (i) physical properties of the fluid, namely its density, viscosity, thermal conductivity and specific heat, (ii) the fluid dynamic conditions inside the reactor, namely the temperature and flow rate of fluid and convective conditions, i.e. whether the convection is free or forced, and (iii) the geometry and the dimensions of the reactor. The heat transfer coefficient is, in general, expressed in terms of a dimensionless number called Nusselt's number, defined by the equation

$$N_{\text{Nu}} = \frac{hd}{k} \quad (3.203)$$

where k is the thermal conductivity and d a “characteristic length” or diameter of the particle. In order to take into account the effect of the above mentioned variables, Nusselt's number is also expressed as a function of other dimensionless numbers. Some common relationships between Nusselt's number and other dimensionless numbers for different situations in convective heat transfer and for common reactor geometries are presented in Table 3.2. More about these dimensionless numbers will be discussed in Chapter 5.

In case of heat transfer involving composite walls, in which both conduction and convection play significant roles, we make use of the concept of overall heat transfer coefficient. For example, consider heat dissipation from the stack surface of a blast furnace or that from Cowper stoves or the roof of an open-hearth furnace. In all these cases, the heat conducted through the refractories and metallic shell or casting is lost to the atmosphere by convection. So in such cases, we make use of the overall heat transfer coefficient, the equation for which can be derived as follows.

Let T_h and T_c be the absolute bulk temperature of the hot fluid and the cold fluid respectively. Let T_1 , T_2 , T_3 and T_4 be the absolute boundary temperatures of various (three in this case) conducting or insulating layers between these two fluids. Further, let k_1 , k_2 and k_3 be their respective thermal conductivities and x_1 , x_2 , and x_3 their respective thicknesses. Under steady state conditions, the heat flux J transferred per unit area per unit time will be expressed as

$$\begin{aligned} J &= h_h(T_h - T_1) = k_1 \frac{T_1 - T_2}{x_1} = k_2 \frac{T_2 - T_3}{x_2} \\ &= k_3 \frac{T_3 - T_4}{x_3} = h_c(T_4 - T_c) \end{aligned} \quad (3.204)$$

where h_h and h_c represent respectively the heat transfer coefficients in the hot fluid and the cold fluid. Rearranging, we have

$$\begin{aligned} \frac{T_h - T_1}{1/h_h} &= \frac{T_1 - T_2}{x_1/k_1} = \frac{T_2 - T_3}{x_2/k_2} = \frac{T_3 - T_4}{x_3/k_3} = \frac{T_4 - T_c}{1/h_c} \\ &= \frac{T_h - T_c}{\frac{1}{h_h} + \frac{x_1}{k_1} + \frac{x_2}{k_2} + \frac{x_3}{k_3} + \frac{1}{h_c}} \end{aligned} \quad (3.205)$$

or

$$J = \left[\frac{1}{\frac{1}{h_h} + \frac{x_1}{k_1} + \frac{x_2}{k_2} + \frac{x_3}{k_3} + \frac{1}{h_c}} \right] (T_h - T_c) \quad (3.206)$$

The term within the square brackets is known as the *overall heat transfer coefficient* and is denoted by h_{ov} .

The use of this equation is demonstrated by the following example:

TABLE 3.2 Some common relationships for Nusselt number

<i>Relationship for Nusselt number</i>	<i>Geometry</i>	<i>Conditions of applicability</i>
A. General correlation for forced convection $N_{\text{Nu}} = f(N_{\text{Re}}, N_{\text{Pr}})$		
B. General correlation for natural convection $N_{\text{Nu}} = f(N_{\text{Gr}}, N_{\text{Pr}})$		
C. Convection-heat transfer correlations for internal flow:		
1. $N_{\text{Nu},D} = \frac{hD}{k} = 4.36$	Circular tubes	Laminar fully-developed flow with constant q_s , $N_{\text{Pr}} \geq 0.6$
2. $N_{\text{Nu},D} = 3.66$	Circular tubes	Laminar fully-developed flow, constant T_s , $N_{\text{Pr}} \geq 0.6$
3. $\bar{N}_{\text{Nu},D} = 3.66 + \frac{0.0668(D/L)N_{\text{Re},D}N_{\text{Pr}}}{1 + 0.04((D/L)N_{\text{Re},D}N_{\text{Pr}})^{2/3}}$	Circular tubes	Laminar flow, thermal entry length or an unheated starting length, constant T_s
4. $\bar{N}_{\text{Nu},D} = 1.86 \left(\frac{N_{\text{Re},D}N_{\text{Pr}}}{L/D} \right)^{1/3} \left(\frac{\mu_\infty}{\mu_s} \right)^{0.14}$	Circular tubes	Laminar flow, constant T_s , $F \geq 2$, $0.48 \leq N_{\text{Pr}} < 16,700$ and $0.0044 < \mu_\infty/\mu_s < 9.75$
5. $N_{\text{Nu},D} = 0.023 (N_{\text{Re},D})^{4/5} (N_{\text{Pr}})^{1/3}$	Circular tubes	Turbulent fully developed flow, $0.6 \leq N_{\text{Pr}} \leq 160$, $N_{\text{Re},D} \geq 10,000$ and $(L/D) \geq 60$
6. $N_{\text{Nu},D} = 0.023 (N_{\text{Re},D})^{4/5} (N_{\text{Pr}})^n$	Circular tubes	Turbulent fully-developed flow, $0.6 \leq N_{\text{Pr}} \leq 160$, $N_{\text{Re},D} \geq 10,000$, $(L/D) \geq 60$, $n = 0.4$ for $T_s > T_m$ on heating and $n = 0.3$ for $T_s < T_m$ on cooling.
7. $N_{\text{Nu},D} = 0.027 (N_{\text{Re},D})^{4/5} (N_{\text{Pr}})^{1/3} (\mu_\infty/\mu_s)^{0.14}$	Circular tubes	Turbulent fully-developed flow, $0.7 \leq N_{\text{Pr}} < 16,700$, $N_{\text{Re},D} \geq 10,000$, $(L/D) \geq 60$
8. $N_{\text{Nu},D} = 4.82 + 0.0185 (N_{\text{Re},D}N_{\text{Pr}})^{0.827}$	Circular tubes	Liquid metals in turbulent fully-developed flow, constant q_s^n , $3.6 \times 10^3 < N_{\text{Re},D} < 9.05 \times 10^5$, $10^2 < N_{\text{Re},D} < 10^4$.

9.	$N_{Nu,D} = 5.0 + 0.025 (N_{Re,D} N_{Pr})^{0.8}$	Circular tubes	Liquid metals in turbulent fully-developed flow, constant $T_s, N_{Re,D} > 100$ for liquid metals, $3 \times 10^{-3} \leq N_{Pr} \leq 5 \times 10^{-2}$
D. Convection-heat transfer correlation for external flow			
1.	$N_{Nu,x} = 0.332(N_{Re,x})^{1/2} (N_{Pr})^{1/3}$	Flat plate	Laminar flow, local value $N_{Pr} \geq 0.6$
2.	$N_{Nu,x} = 0.565(N_{Re,x})^{1/2}$	Flat plate	Laminar flow, local value $N_{Pr} \leq 0.05$
3.	$N_{Nu,x} = 0.0296(N_{Re,x})^{4/5} (N_{Pr})^{1/3}$	Flat plate	Turbulent flow, local value $N_{Re,x} \leq 10^8, 0.6 \leq N_{Pr} \leq 60$
4.	$\bar{N}_{Nu,x} = 0.664(N_{Re,x})^{1/2} (N_{Pr})^{1/3}$	Flat plate	Laminar flow, average value
5.	$\bar{N}_{Nu,L} = \{0.037(N_{Re,L})^{4/5} - 871\} (N_{Pr})^{1/3}$	Flat Plate	Mixed flow, average value $5 \times 10^5 = N_{Re,L} \leq 10^8, 0.6 < N_{Pr} < 60$
6.	$\bar{N}_{Nu,L} = 0.036 \{(N_{Re,L})^{4/5} - 9200\} (N_{Pr})^{0.43} (\mu_\infty / \mu_s)^{1/4}$	Flat Plate	Mixed flow, average value $10^5 - 9200\} (N_{Pr})^{0.43} (\mu_\infty / \mu_s)^{1/4} < N_{Re,L} < 5.5 \times 10^6, 0.7 < N_{Pr} < 380, 0.26 < \mu_\infty / \mu_s < 3.5$
7.	$\bar{N}_{Nu,D} = C(N_{Re,D})^m (N_{Pr})^{1/3}$	Cylinder	Average value, $0.4 < N_{Re,D} < 4 \times 10^5, N_{Pr} \geq 0.7$
8.	$\bar{N}_{Nu,D} = 0.4(N_{Re,D})^{1/2} + 0.06(N_{Re,D})^{2/3}(N_{Pr})^{0.4} (\mu_\infty / \mu_s)^{1/4}$	Cylinder	Average value, $10 < N_{Re,D} < 10^5, 0.67 < N_{Pr} < 300, 0.25 < (\mu_\infty / \mu_s) < 5.2$
9.	$\bar{N}_{Nu,D} = 2 + \{0.4(N_{Re,D})^{1/2} + 0.06(N_{Re,D})^{2/3}\} \times (N_{Pr})^{0.4} (\mu_\infty / \mu_s)^{1/4}$	Sphere	Average value, $3.5 < N_{Re,D} < 7.6 \times 10^4, 0.71 < N_{Pr} < 380, 1.0 < \mu_\infty / \mu_s < 3.2$
10.	$\bar{N}_{Nu,D} = 2 + 0.6(N_{Re,D})^{1/2} (N_{Pr})^{1/3} \times 25(x/D)^{-0.7}$	Falling drop	Average value
11.	$\varepsilon \bar{j}_H = 2.06(N_{Re,D})^{-0.575}$	Packed bed	Average value, $90 \leq N_{Re,D} \leq$ of spheres 4000, $N_{Pr} = 0.7$

EXAMPLE 3.13 A furnace is lined with an outer steel shell, 1 cm thick and a refractory lining 5 cm thick. Calculate the overall heat transfer coefficient and the heat flux if the furnace temperature is 1000°C and the outside air temperature is 40°C. The heat transfer coefficients for flowing gases on the hot side and air on the cold side are 5×10^{-3} and 4×10^{-4} cal s⁻¹ cm⁻² K⁻¹ respectively. Assume thermal conductivity of steel and refractory as 60 and 2 W m⁻¹ K⁻¹ respectively.

Solution Heat transfer coefficient on the hot side, h_h

$$\begin{aligned} &= 5 \times 10^{-3} \text{ cal s}^{-1} \text{ cm}^{-2} \text{ K}^{-1} \\ &= 5 \times 10^{-3} \times 4.18 \times 10^4 \text{ W m}^{-2} \text{ K}^{-1} \\ &= 2.09 \times 10^2 \text{ W m}^{-2} \text{ K}^{-1} \end{aligned}$$

Heat transfer coefficient on the cold side, h_c

$$\begin{aligned} &= 4 \times 10^{-4} \text{ cal s}^{-1} \text{ cm}^{-2} \text{ K}^{-1} \\ &= 4 \times 10^{-4} \times 4.18 \times 10^4 \text{ W m}^{-2} \text{ K}^{-1} \\ &= 16.72 \text{ W m}^{-2} \text{ K}^{-1} \end{aligned}$$

Thickness of the steel shell, $x_1 = 1 \text{ cm} = 0.01 \text{ m}$

Thickness of the refractory lining, $x_2 = 5 \text{ cm} = 0.05 \text{ m}$

Thermal conductivity of steel, $k_1 = 60 \text{ W m}^{-1} \text{ K}^{-1}$

Thermal conductivity of refractory, $k_2 = 2 \text{ W m}^{-1} \text{ K}^{-1}$

Temperature on the hot side, $T_h = 1000 + 273 = 1273 \text{ K}$

Temperature on the cold side, $T_c = 40 + 273 = 313 \text{ K}$

(i) Now, the overall heat transfer coefficient, h_{ov} , as given by Eq. (3.206)

$$\begin{aligned} &= \frac{1}{\frac{1}{h_h} + \frac{x_1}{k_1} + \frac{x_2}{k_2} + \frac{1}{h_c}} \\ &= \frac{1}{\frac{1}{2.09 \times 10^2} + \frac{0.01}{60} + \frac{0.05}{2} + \frac{1}{16.72}} \\ &= \frac{1}{0.0048 + 0.00017 + 0.025 + 0.0598} \\ &= \frac{1}{0.08977} = 11.14 \text{ W m}^{-2} \text{ K}^{-1} \quad \text{Ans.} \end{aligned}$$

(ii) Heat flux, $J = h_{ov} (T_h - T_c) = 11.14(1273 - 313)$
 $= 11.14 \times 960 = 1.069 \times 10^4 \text{ W m}^2$ Ans.

3.3 RADIATIVE HEAT TRANSFER

Heat transfer by radiation also called the *radiative* or *radiant heat transfer* is the predominant mode of exchange of energy at elevated temperatures. This mode

involves heat transfer from one body called *source* to the other body called *sink*, by the agency of electromagnetic waves. Thus, we require a knowledge of the nature of thermal radiations before we can discuss the heat exchanges by this mode.

3.3.1 Thermal Radiations and Related Basic Properties of Materials

On heating, a body emits thermal radiations. The wavelengths of these radiations form a continuous spectrum. The energy emitted per unit surface area per unit time of a body of a particular wavelength is called the *monochromatic emissive power*. This power of a body will depend upon the nature of the body, its temperature, and the wavelengths of its radiations. A body having maximum possible or unity emissive power is called a *black body*. We will discuss the characteristics and behaviour of such a body in greater detail at a later stage in this section. For a black body, the monochromatic emissive power at a particular wavelength shall only be a function of its temperature. If $W_{B\lambda}$ be the black body emissive power at wavelength λ , i.e. if $W_{B\lambda}$ be the energy emitted per unit area of the body per unit time in the wavelength range λ to $\lambda + \delta\lambda$, then according to Planck's law, we have

$$W_{B\lambda} = \frac{2\pi hc^2 \lambda^{-5}}{\exp(ch/k_B T\lambda) - 1} \quad (3.207)$$

where c is the velocity of light, h and k_B are Planck's and Boltzmann constants respectively and T is the absolute temperature. For graphical representation this relation is written in the following convenient functional form:

$$W_{B\lambda} T^{-5} = \frac{2\pi hc^2 (\lambda T)^{-5}}{\exp(ch/k_B \lambda T) - 1} = f(\lambda T) \quad (3.208)$$

In Fig. 3.16, the function $W_{B\lambda} T^{-5}$ is plotted against λT . We can draw the following inferences from this plot:

- (i) The monochromatic emissive power of a black body, $W_{B\lambda}$, increases with rise in its temperature.
- (ii) This increase is not uniform for all wavelengths. The rate of increase with temperature is faster for radiations of lower wavelengths than those of higher wavelengths.
- (iii) As a consequence of (ii), the maxima in the plot for $W_{B\lambda}$ shifts to lower wavelengths. This shift in wavelength for maximum $W_{B\lambda}$ with temperature is expressed mathematically by the relation

$$\lambda_{\max} T = \text{constant} \quad (3.209)$$

where the constant is equal to 0.2898 in cgs units (cm K). This statement is referred to as *Wien's displacement law*.

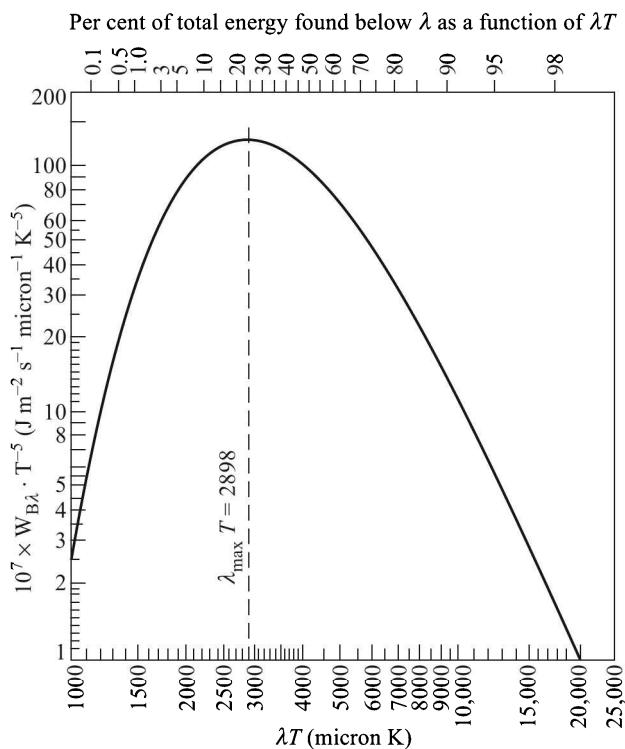


Fig. 3.16 Monochromatc emissive power of a black body as a function of temperature.

Till now, our study was confined to monochromatic radiations only but for analysis of industrial processes, we have to consider the total energy emitted from a hot body. The amount of total radiant energy emitted can also be calculated by integrating the value of $W_{B\lambda}$ with respect to wavelength λ over the whole spectrum of wavelength of radiations. According to the *Stefan-Boltzmann law*, the total energy W_B radiated from a hot black body source per unit area per unit time is proportional to the fourth power of its absolute temperature T . Mathematically, this statement can be expressed by the equation

$$W_B = \sigma T^4 \quad (3.210)$$

where σ is a constant known as the Stefan-Boltzmann constant, having value of 5.67×10^{-8} in SI units, viz. $J m^2 s^{-1} K^{-4}$. The above equation clearly illustrates that with an increase in the temperature of the black body source, the energy emitted increases sharply. Therefore, this mode of heat transfer plays a predominant role especially in systems at high temperatures. We can derive an equation for σ as well as derive Wein's displacement law using *Planck's law*.

Using Planck's law, we can prove the following relations:

$$\sigma = \frac{2\pi^5 k^4}{15c^2 h^3}$$

and

$$\lambda_{\max} T = \text{constant}$$

Till now, we have considered briefly the emission of heat energy from a source. However, transfer of heat also involves another body called the *sink* which acts as the recipient of this energy. We, therefore, consider now the behaviour of a body when heat radiations fall on it. As shown in Fig. 3.17, the incident radiations, which are in fact electromagnetic waves also referred to as *photo-gas*, can behave in three different ways.

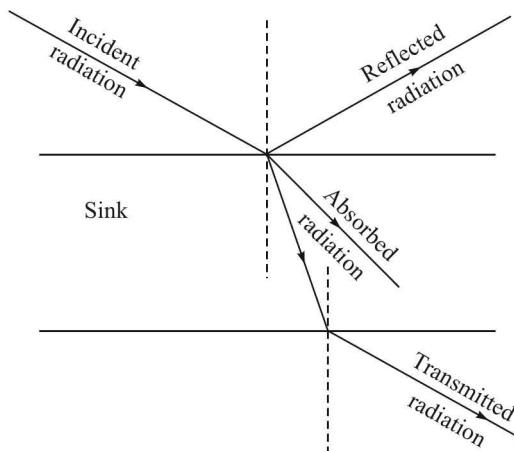


Fig. 3.17 Behaviour of radiations falling on a body.

They may be (i) partly absorbed thereby increasing the energy of the body, (ii) partly reflected, and (iii) partly transmitted through the body. Our main concern in the present treatment is the amount of heat absorbed by the body. The fraction of incident radiant energy absorbed by a body is referred to as its *absorptivity* and is commonly represented by the Greek letter, α . In order to arrive at the relationship between absorptivity α and emissive power W , we consider a perfectly insulated container in which two small bodies A and B of area A_a and A_b are placed. Further, we assume that the bodies are under the state of thermal equilibrium. Hence, the temperatures of these bodies do not change with time. Thus, the amount of heat absorbed by each of these bodies must be equal to that emitted. Let W_c be this incident radiation energy per unit area per unit time on each of the bodies from the container walls. If W_a and W_b be the respective emissive powers of the bodies A and B and α_a and α_b , their absorptivities respectively, we have the following heat balance equations for each of these two bodies.

$$\alpha_a A_a W_c = A_a W_a$$

or

$$\alpha_a W_c = W_a \quad (3.211)$$

and

$$\alpha_b A_b W_c = A_b W_b$$

or

$$\alpha_b W_c = W_b \quad (3.212)$$

The above equations lead to the following two important inferences:

- (i) As the absorptivities of the bodies cannot be greater than unity, these relationships impose a restriction on the emissive power of the bodies. Only the bodies having absorptivities equal to unity will have the highest emissive power. Such bodies of unit absorptivities are called *black bodies*.
- (ii) From Eqs. (3.211) and (3.212), we also get

$$\frac{W_a}{\alpha_a} = \frac{W_b}{\alpha_b} = W_c \quad (3.213)$$

i.e. the ratio of emissive power to absorptivity of all bodies under the state of thermal equilibrium is the same. This statement is known as the *Kirchhoff's law*. It is also evident from Eq. (3.213) that the maximum emissive power of a body can be W_c . The ratio of the emissive power of a body to maximum possible emissive power is called emissivity which is denoted by the symbol ε . Equation (3.213) may be expressed, in terms of emissivities ε_a and ε_b of the two bodies as follows:

$$\frac{W_a/W_c}{\alpha_a} = \frac{W_b/W_c}{\alpha_b}$$

or

$$\frac{\varepsilon_a}{\alpha_a} = \frac{\varepsilon_b}{\alpha_b} = 1 \quad (3.214)$$

In other words, for any substance i under thermal equilibrium

$$\varepsilon_i = \alpha_i \quad (3.215)$$

The above relation provides the following alternative statement of Kirchhoff's law:

“Under the state of thermal equilibrium, the emissivity of a body is equal to its absorptivity”.

3.3.2 Emissivity and Absorptivity of Substances

Both emissivity and absorptivity are surface-sensitive properties. Therefore, apart from the temperature, the material of the body and the wavelength of incident radiations, these properties are also strongly dependent on the characteristics of the surface of the body under study. Some common features of the emissivity and absorptivity of materials are as follows:

- (i) Metallic materials have low emissivity and absorptivity and their values are known to increase with increase in temperature. Absorptivity of these materials is also affected by the temperature of the emitting surface and is found to be directly proportional to the geometric mean of the temperature of the source and that of the absorbing materials. Surface oxidation of these materials strongly enhances these properties.
- (ii) Nonmetallic materials have much higher values of emissivity and absorptivity which decrease with increase in temperature. Typical data on emissivity of important metallic materials and refractories are presented in Table 3.3.

Though both these properties depend upon the wavelength of incident radiations, for approximate solutions of a number of actual industrial heat transfer problems, we may assume these to be independent of wavelength, thereby considerably simplifying these problems. Bodies for which this assumption of constant values of emissivity ε and absorptivity α are made, are known as *grey bodies*.

TABLE 3.3 Emissivity of important metallic materials and refractories

	<i>Material</i>	<i>Temperaure, °C</i>	<i>Emissivity</i>
Aluminum:	98.3% pure, highly polished	225–575	0.039–0.057
	oxidized at 590°C	200–600	0.11–0.19
	Al-coated roofing	35	0.216
	Al-paint	100	0.20–0.40
	silumin—cast and polished	150	0.186
Bismuth:	bright	80	0.340
Copper:	bright polished, electrolytic Cu	80	0.018
	polished fire-refined Cu	115	0.023
	molten Cu	1075–1275	0.16–0.13
	lightly oxidized	20	0.037
	black oxidized	20	0.78
Brass:	black oxidized	200–500	0.57
	highly polished 70–30 brass	250–300	0.028–0.031
	dull plate	50–350	0.22
Gold:	oxidized at 590°C	200–600	0.61–0.59
	pure, highly polished	225–625	0.018–0.035
Iron and steel:	electrolytic iron, highly polished	175–225	0.052–0.064
	wrought iron, highly polished	35–250	0.28
	cast iron, polished	200	0.21
	cast iron, rough, oxidized at 600°C	200	0.64
	cast iron, strongly oxidized	35–250	0.95
	iron plate, completely red-rusted	20	0.685
	rolled sheet steel	20	0.657
Steel plate, rough		37–370	0.94–0.97

Contd.

TABLE 3.3 Emissivity of important metallic materials and refractories (*Contd.*)

	<i>Material</i>	<i>Temperaure, °C</i>	<i>Emissivity</i>
Lead:	molten cast iron	1300–1400	0.29
	molten mild steel	1600–1800	0.28
	iron oxide	500–1200	0.85–0.89
Mercury:	pure (99.96%), unoxidized	125–225	0.057–0.075
	oxidized at 200°C	200	0.63
	Grey oxidized	20	0.28
Manganin:		0–100	0.09–0.12
Nickel:	bright rolled alloy	120	0.048
Nickel:	polished	100	0.045
	technically pure (58.9%)		
	polished	225–375	0.07–0.087
	wire	200–1000	0.096–0.186
Platinum:	nickel oxide	650–1250	0.59–0.86
	pure polished plate	225–625	0.054–0.104
	filament	25–1225	0.036–0.192
	wire	225–1375	0.073–0.182
Silver:	strip	925–1625	0.12–0.17
	polished	20	0.020
Tantalum:	filament	1325–3000	0.194–0.31
Tin:	bright tinned iron sheet	25	0.043–0.064
Tungsten:	filament	3300	0.39
	aged filament	25–3300	0.032–0.35
Zinc:	commercial (99.9%) polished	240–325	0.045–0.053
	oxidized at 400°C	400	0.11
	grey oxidized	20	0.23–0.28
	galvanized sheet, fairly bright	25	0.228
	galvanized sheet, grey oxidized	25	0.276
Refractories:	poor radiators	600	0.65–0.70
	poor radiators	1000	0.75
	good radiators	600	0.80–0.85
	good radiators	100	0.85–0.90
	clay, fired	70	0.91
	corundum, energy rough	80	0.855
Brick:	red, rough	20–25	0.93
	Silica, unglazed, rough	1000	0.80
	Silica, glazed, rough	1100	0.85
	grog brick, glazed	1100	0.75
Enamel:	white, fused on iron	20	0.897
Glass:	smooth	20	0.93
Porcelain:	glazed	20	0.92
Quartz:	rough, fused	20	0.92
Serpentine:	polished	25	0.90
Water:	thick layer (for comparison)	0–100	0.95–0.963

Having discussed briefly the nature of radiations, emissivity and absorptivity or the properties connected with radiative heat transfer, we now proceed to consider some simple cases followed by analysis of some practical cases, involving heat exchanged by radiation, in industrial processes.

3.3.3 Heat Exchange between Two Infinitely Long and Wide Parallel Plates

Consider two parallel plates A and B, as shown in Fig. 3.18 having infinite dimensions along x - and y -axes and separated by a nonabsorbing medium. Let ε_a and ε_b be their respective emissivities, and α_a and α_b the corresponding absorptivities. In a state of thermal equilibrium, we can write the following equations based on Kirchhoff's law,

$$\varepsilon_a = \alpha_a \quad (3.216)$$

$$\varepsilon_b = \alpha_b \quad (3.217)$$

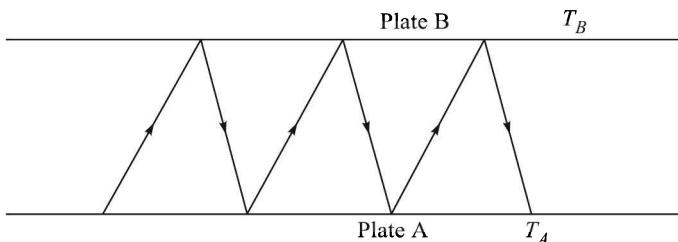


Fig. 3.18 Heat exchange between infinitely long and wide parallel plates.

Further, let T_a and T_b be the absolute temperatures at which these plates are respectively maintained, and A_a and A_b be their respective surface areas. Assuming the plates to behave as "Grey bodies", the amount of radiant energy q_a , emitted per unit time by plate A will be expressed as

$$q_a = \sigma T_a^4 \varepsilon_a A_a \quad (3.218)$$

Of this energy falling on plate B, a fraction α_b will be absorbed and the rest, i.e. fraction $(1 - \alpha_b)$, reflected back towards the plate A, which in turn will absorb a fraction α_a of this amount, i.e. fraction $\alpha_a(1 - \alpha_b)$ of the original amount of radiant energy and reflect back the rest, i.e. the fraction $\alpha_a(1 - \alpha_b)(1 - \alpha_a)$ of the original amount. This process will continue infinitely leading to the following equation for the amount of net radiant energy, $q_{a \rightarrow b}$, transferred from plate A to plate B:

$$\begin{aligned} q_{a \rightarrow b} &= (\sigma T_a^4 \varepsilon_a A_a \alpha_b) + \{\sigma T_a^4 \varepsilon_a A_a (1 - \alpha_b) (1 - \alpha_a) \alpha_b\} \\ &\quad + \{\sigma T_a^4 \varepsilon_a A_a (1 - \alpha_b)^2 (1 - \alpha_a)^2 \alpha_b\} \\ &\quad + \{\sigma T_a^4 \varepsilon_a A_a (1 - \alpha_b)^3 (1 - \alpha_a)^3 \alpha_b\} + \dots \\ &= \sigma T_a^4 \varepsilon_a A_a \alpha_b [1 + (1 - \alpha_a) (1 - \alpha_b) + (1 - \alpha_a)^2 (1 - \alpha_b)^2 + \dots] \end{aligned}$$

$$= \frac{\sigma T_a^4 \varepsilon_a \alpha_b A_a}{1 - (1 - \alpha_a)(1 - \alpha_b)} \quad (3.219)$$

Making use of Eqs. (3.216) and (3.217), this equation will yield

$$q_{a \rightarrow b} = \sigma T_a^4 A_a \left(\frac{1}{\varepsilon_a} + \frac{1}{\varepsilon_b} - 1 \right)^{-1} \quad (3.220)$$

Similarly, we can arrive at the following equation for the radiant energy $q_{b \rightarrow a}$ transferred from plate B to plate A:

$$q_{b \rightarrow a} = \sigma T_b^4 A_b \left(\frac{1}{\varepsilon_a} + \frac{1}{\varepsilon_b} - 1 \right)^{-1} \quad (3.221)$$

Hence, the net amount of heat transferred q from plate A to plate B will be

$$\begin{aligned} q &= q_{a \rightarrow b} - q_{b \rightarrow a} \\ &= \sigma (A_a T_a^4 - A_b T_b^4) \left(\frac{1}{\varepsilon_a} + \frac{1}{\varepsilon_b} - 1 \right)^{-1} \end{aligned} \quad (3.222)$$

As both the plates are of infinite area, we can assume $A_a = A_b$, and arrive at the following relation for the net energy transferred from plate A to plate B, per unit area per unit time.

$$q'' = q/\text{area} = \sigma (T_a^4 - T_b^4) \left(\frac{1}{\varepsilon_a} + \frac{1}{\varepsilon_b} - 1 \right)^{-1} \quad (3.223)$$

Though the above analysis illustrates the method of calculation of the net radiative heat transfer from one body to another, it is of little practical value since we have surfaces of only finite dimensions in actual cases. We, therefore, consider such a system in the following sections.

3.3.4 Heat Exchange between Surfaces of Finite Area: The View Factor

In the preceding section, we dealt with the laws governing the energy emitted in the form of electromagnetic radiation from black bodies. In this section, we will discuss the energy transferred by radiations between two black bodies of arbitrary geometry and orientation. We, therefore, need to know how the energy emitted by a black body is distributed with respect to angle. Because of black body radiations being isotropic, we have the following equation, also known as *Lambert's cosine law*, for the energy radiated in a particular direction:

$$q_{b\theta} = \frac{q_b}{T_1} \cos \theta = \frac{\sigma T^4}{\pi} \cos \theta \quad (3.224)$$

where $q_{b\theta}$ is the energy emitted per unit area per unit time per unit solid angle in the direction of solid angle θ and q_b the energy emitted by the black body in all directions.

We now consider a point source A on a black surface as shown in Fig. 3.19. Let this source emit radiations. The amount of radiation q falling on or intercepted by the surface element X will be expressed in terms of solid angles θ and ϕ as

$$q = q_{b\theta} \sin \theta d\theta d\phi \quad (3.225)$$

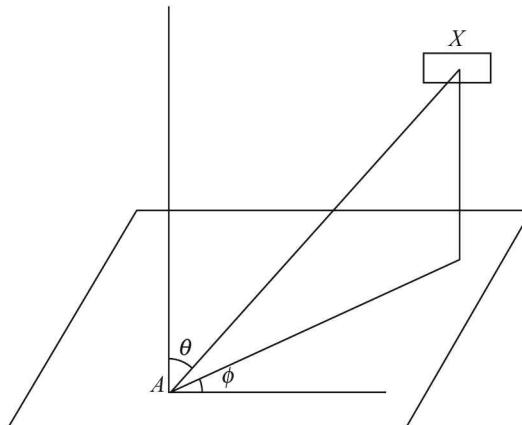


Fig. 3.19 Radiant energy exchange between a point source and a black surface.

It is evident that integration of the above equation over the hemisphere will yield the total energy q_t radiated by the source. Mathematically, we have

$$\begin{aligned} q_t &= \int_0^{\pi} \int_0^{\pi/2} q_{b\theta} \sin \theta d\theta d\phi \\ q_t &= \int_0^{\pi} \int_0^{\pi/2} \left[\frac{\sigma T^4}{\pi} \cos \theta \sin \theta d\theta d\phi \right] = \sigma T^4 \end{aligned} \quad (3.226)$$

Finally consider two black bodies 1 and 2, as shown in Fig. 3.20, facing each other and exchanging heat only by radiation. Let the bodies be at temperatures T_1 and T_2 respectively. Consider surface elements dA_1 and dA_2 on the two bodies which can exchange radiation directly with each other. Let θ_1 and θ_2 be the angles subtended by the line joining the centres of these elements with the normals to the surface elements dA_1 and dA_2 respectively. Energy radiated, q_1 , from the surface element dA_1 into a solid angle in the direction of dA_2 will be expressed by the relation

$$\begin{aligned} q_1 &= q_{b\theta} \sin \theta_1 d\theta_1 d\phi_1 \\ &= \frac{\sigma T_1^4}{\pi} \cos \theta_1 \sin \theta_1 d\theta_1 d\phi_1 \end{aligned} \quad (3.227)$$

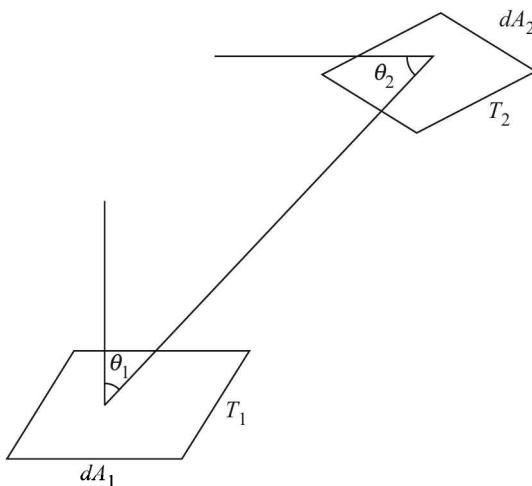


Fig. 3.20 Radiant energy exchange between two black surfaces of finite area.

Solid angle W_1 subtended by the surface element dA_2 is equal to the area formed by the intersection of the solid angle ($\sin \theta_1 d\theta_1 d\phi_1$) with a sphere of radius r_{12} with centre at dA_1 . Thus, we get the following relation for this solid angle:

$$W_1 = \text{area of } dA_2 \text{ projected on a plane perpendicular to } r_{12}$$

or

$$W_1 = \frac{dA_2 \cos \theta_2}{r_{12}^2 \sin \theta_1 d\theta_1 d\phi_1} \quad (3.228)$$

Hence, the net amount of energy $\delta q_{1 \rightarrow 2}$ received by the surface element dA_2 will be expressed as

$$\delta q_{1 \rightarrow 2} = \frac{\sigma T_1^4}{\pi} \frac{\cos \theta_1 \cos \theta_2}{r_{12}^2} dA_1 dA_2 \quad (3.229)$$

Similarly, the net amount of energy, $\delta q_{2 \rightarrow 1}$, received by the surface element dA_1 will be

$$\delta q_{2 \rightarrow 1} = \frac{\sigma T_2^4}{\pi} \frac{\cos \theta_1 \cos \theta_2}{r_{12}^2} dA_1 dA_2 \quad (3.230)$$

Therefore, the net energy exchanged between the surface elements dA_1 and dA_2 will be

$$\begin{aligned} \delta q_{12} &= \delta q_{1 \rightarrow 2} - \delta q_{2 \rightarrow 1} \\ &= \frac{\sigma}{\pi} (T_1^4 - T_2^4) \frac{\cos \theta_1 \cos \theta_2}{r_{12}^2} dA_1 dA_2 \end{aligned} \quad (3.231)$$

The total energy exchanged between bodies 1 and 2 will then be expressed by the relation

$$q = \frac{\sigma}{\pi} (T_1^4 - T_2^4) \left[\int_{A_1 A_2} \int \frac{\cos \theta_1 \cos \theta_2}{r_{12}^2} dA_1 dA_2 \right] \quad (3.232)$$

It should be noted that this integration is restricted only to those pairs of areas which get radiations directly from each other, i.e. those which can see each other. The above relation can also be stated in the following alternative form:

$$q = \sigma(T_1^4 - T_2^4)A_1F_{12} = \sigma(T_1^4 - T_2^4)A_2F_{21} \quad (3.233)$$

where F_{12} and F_{21} are called *view factors* and are defined by the equations

$$F_{12} = \frac{1}{\pi A_1} \left[\iint \frac{\cos \theta_1 \cos \theta_2}{r_{12}^2} dA_1 dA_2 \right] \quad (3.234)$$

and

$$F_{21} = \frac{1}{\pi A_2} \left[\iint \frac{\cos \theta_1 \cos \theta_2}{r_{12}^2} dA_1 dA_2 \right] \quad (3.235)$$

Thus, view factor F_{12} may also be defined as the fraction of the total radiation leaving the black surface A_1 in all directions which are intercepted by the surface A_2 .

From Eqs. (3.234) and (3.235) it is also clear that

$$A_1F_{12} = A_2F_{21} \quad (3.236)$$

The usefulness of these equations is demonstrated by the following example.

EXAMPLE 3.14 Calculate the rate of heat transfer from a furnace floor of area 8 m^2 to a side wall of area 12 m^2 with a common edge with the floor and standing perpendicular on it. The temperatures of the floor and side wall are 600 and 200°C respectively. Assume a view factor of 0.2 .

Solution The given data is:

Temperature of the floor, $T_1 = 600 + 273 = 873 \text{ K}$

Temperature of the side wall, $T_2 = 200 + 273 = 473 \text{ K}$

Area of the floor, $A_1 = 8 \text{ m}^2$

View factor, $F_{12} = 0.2$

Stefan-Boltzmann constant, $\sigma = 5.67 \times 10^{-8} \text{ W m}^{-2} \text{ K}^{-4}$

Thus, from Eq. (3.233), the rate of heat transfer from the floor to the side wall,

$$\begin{aligned} q &= \sigma(T_1^4 - T_2^4)A_1F_{12} \\ &= 5.67 \times 10^{-8} \times (873^4 - 473^4) \times 8 \times 0.2 \\ &= 4870 \text{ W} \end{aligned} \quad \text{Ans.}$$

Further, if a black body heat radiating source is completely surrounded by n black bodies, all the radiations emitted by the source will be absorbed by one or the other surrounding bodies or "sinks". Thus, we have the following equation for view factors:

$$F_{11} + F_{12} + \dots + F_{1n} = 1$$

or

$$\sum_{i=1}^n F_{1i} = 1 \quad (3.237)$$

In the above equation, the term F_{11} represents the fraction of radiations emitted by a part of the heat radiating body which is absorbed by its other part. Technically, it is expressed by the extent by which a body can see itself. If, however, it cannot do so, then $F_{11} = 0$.

Though we have developed the concept of view factor by considering black body radiations, it is in fact only a geometric concept and therefore can be applied to anybody, irrespective of whether it is a black, grey or even a nongrey body, with only a partial modification in its definition as follows: View factor, F_{ij} , may be defined as the fraction of total radiations emitted by a body i which is intercepted directly by a body j .

3.3.5 Calculation of Radiant Heat Transfer for Black Surfaces

In the calculation of radiant heat transfer, although the basic concept of view factor is retained, to facilitate these calculations certain simplifying concepts are used. These shall be briefly reviewed and illustrated with the help of simple examples in the subsequent discussion.

Equivalent surfaces

Consider a black surface X of total area A_1 and having an irregular geometric section as shown in Fig. 3.21. This surface extends with this cross-section in the direction perpendicular to the plane of the paper. Our aim is to determine its view factor. Let us stretch a string from one end of the surface to the other across this cross-section. The path of the string is shown by the dotted line. In case of a two-dimensional surface, this string will take the form of a stretched membrane. Further, let this stretched surface be designated by Y and let its area be $A_{1'}$. We now totally enclose the radiating side or the side on which the string is stretched, by another black surface Z of area A_2 and only at an infinitesimal distance from it, so that all radiations leaving the surface X are absorbed either by surface Y or by surface Z. Thus, according to the definition of view factor, we get the following equation:

$$A_1(F_{11} + F_{12}) = A_1 \quad (3.238)$$

and

$$A_2(F_{21} + F_{22}) = A_2 \quad (3.239)$$

We now consider the radiant energy exchanged between the surfaces Y and Z for which we get the following relations involving view factors:

$$A_{1'}(F_{1'1'} + F_{1'2}) = A_{1'} \quad (3.240)$$

$$A_2(F_{21'} + F_{22}) = A_2 \quad (3.241)$$

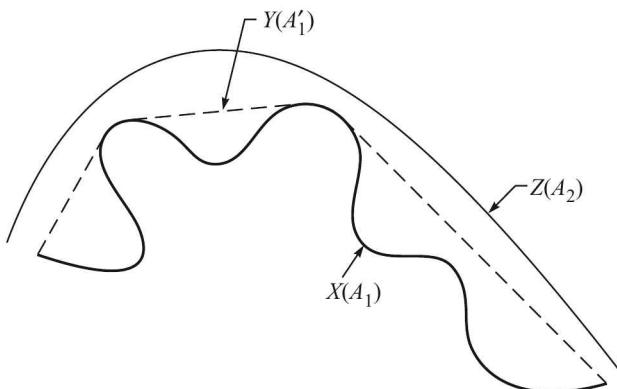


Fig. 3.21 Equivalent black body surfaces.

It is clear from Fig. 3.21 that because of being stretched, the surface Y cannot see itself whereas surface X can do so because of undulations on itself. Hence

$$F_{1'1'} = 0 \quad (3.242)$$

and

$$F_{1'2} = 1 \quad (3.243)$$

Therefore, from Eqs. (3.240) to (3.243) and Eq. (3.236), we get

$$A_2 F_{22} = A_2 - A_2 F_{21'} = A_2 - A_{1'} F_{1'2} = A_2 - A_{1'} \quad (3.244)$$

Substitution of the above equation in Eq. (3.239) leads to the relation

$$A_2 F_{21} = A_1 F_{12} = A_2 - A_2 F_{22} = A_2 - (A_2 - A_{1'}) = A_{1'} \quad (3.245)$$

which with the help of Eq. (3.238) yields

$$A_1 F_{11} = A_1 - A_1 F_{12} = A_1 - A_{1'} \quad (3.246)$$

Equation (3.245) shows that the product $A_1 F_{12}$ can be replaced by an equivalent surface of area $A_{1'}$, which cannot see itself. The area of such surface, in case of two-dimensional surface of irregular geometry, or its length, in case of a surface of regular geometry, can be easily measured by a simple experiment.

Until now we have considered the equivalence of an irregular surface. With its help, one can further simplify the radiant energy transfer from one black surface to another. We shall illustrate this, first by taking a simple case and then another considering a more complicated irregular shape.

Consider first a configuration obtained by the method of stretched strings as shown in Fig. 3.22.

Our aim is to obtain the relations for view factors of the surfaces A_1 , A_2 , and A_3 which are represented in this figure by stretched string surfaces $A_{1'}$, $A_{2'}$ and $A_{3'}$ respectively. For the set of original and string stretched surfaces, we have the following equations:

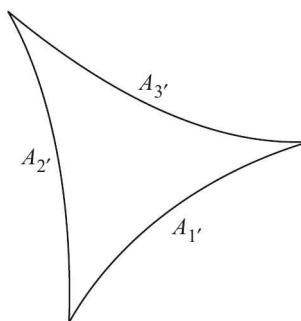


Fig. 3.22 Radiant energy exchanged between black surfaces.

$$A_1 F_{11} + A_1 F_{12} + A_1 F_{13} = A_1 = A_1 F_{11} + A_{1'} \quad (3.247)$$

$$A_2 F_{21} + A_2 F_{22} + A_2 F_{23} = A_2 = A_2 F_{22} + A_{2'} \quad (3.248)$$

$$A_3 F_{31} + A_3 F_{32} + A_3 F_{33} = A_3 = A_3 F_{33} + A_{3'} \quad (3.249)$$

and also the equations

$$A_{1'} F_{12} + A_{1'} F_{13} = A_{1'} \quad (3.250)$$

$$A_{2'} F_{21} + A_{2'} F_{23} = A_{2'} \quad (3.251)$$

$$A_{3'} F_{31} + A_{3'} F_{32} = A_{3'} \quad (3.252)$$

Further, since

$$A_{1'} F_{1'2'} = A_{2'} F_{2'1'} \quad (3.253)$$

$$A_{2'} F_{2'3'} = A_{3'} F_{3'2'} \quad (3.254)$$

and

$$A_{1'} F_{1'3'} = A_{3'} F_{3'1'} \quad (3.255)$$

Equations (3.247) to (3.255), on simplification, yield

$$A_{1'} F_{1'2'} = A_{2'} F_{2'1'} = \frac{A_1 + A_2 - A_3}{2} \quad (3.256)$$

$$A_{2'} F_{2'3'} = A_{3'} F_{3'2'} = \frac{A_2 + A_3 - A_1}{2} \quad (3.257)$$

$$A_{3'} F_{3'1'} = A_{1'} F_{1'3'} = \frac{A_1 + A_3 - A_2}{2} \quad (3.258)$$

From these expressions, we can also calculate the view factors for both the original and the equivalent surfaces.

No-flux surfaces

In order to simplify calculations on radiant heat transfer in furnaces, we make the assumption that under steady state conditions, the conductive heat loss by

the refractory walls to the surroundings is balanced by the convective heat transferred from the heat source to these walls. Thus, as far as radiative energy is concerned, the net exchange between the walls and the other heat sources and sinks is zero. Therefore, these surfaces are referred to as “no-flux surfaces”. Though the above mentioned assumption considerably simplifies the radiant heat transfer calculations, it is only approximate. However, it leads to satisfactory results for many practical purposes. With this assumption, we can modify the equation for the view factor. This modified view factor for the heat exchanged between two black bodies 1 and 2, denoted by the symbol \bar{F}_{12} , in an enclosure having no-flux surfaces, may be defined in analogy to Eq. (3.233) by the relation.

$$\begin{aligned} q_{1=2} &= \sigma A_1 \bar{F}_{12} (T_1^4 - T_2^4) \\ &= \sigma A_1 \bar{F}_{12} (T_1^4 - T_2^4) + q_r \end{aligned} \quad (3.259)$$

where $q_{1=2}$ represents the net heat exchanged between bodies 1 and 2, both being non-black bodies, and q_r the heat reradiated from the no-flux surfaces. The numerical value of the modified view factor, F_{12} , therefore, depends on q_r . Its value can be calculated easily for cases involving simple geometries but for others with more complicated geometry it can only be approximated. As an example, we consider an enclosure consisting of three surfaces, namely a source designated by the symbol 1, a no-flux refractory surface R and a sink designated by the symbol 2, as shown in Fig. 3.23. Under steady state conditions, the net heat exchanged by R with source 1 and sink 2 is zero. Mathematically, we can write

$$\sigma A_1 F_{1R} (T_1^4 - T_R^4) + \sigma A_2 F_{2R} (T_2^4 - T_R^4) = 0 \quad (3.260)$$

which on simplification yields the following equation for the temperature of the no-flux refractory surface:

$$T_R^4 = \frac{A_1 F_{1R} T_1^4 + A_2 F_{2R} T_2^4}{A_1 F_{1R} + A_2 F_{2R}} \quad (3.261)$$

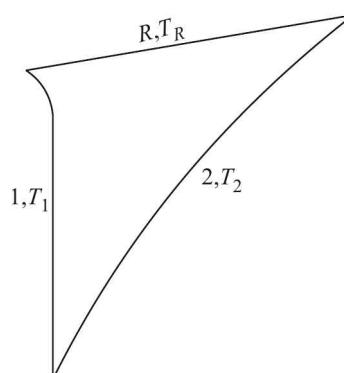


Fig. 3.23 An enclosure having no-flux surface.

Further, the total heat $q_{1 \rightarrow 2}$ received by the sink is equal to the sum of the direct heat from 1 to 2 and the heat reradiated by the no-flux surface R. Thus, we have

$$\begin{aligned} q_{1 \rightarrow 2} &= \sigma A_1 F_{12}(T_1^4 - T_2^4) + \sigma A_R F_{R2}(T_R^4 - T_2^4) \\ &= \sigma A_1 F_{12}(T_1^4 - T_2^4) + \sigma A_1 F_{1R}(T_1^4 - T_R^4) \end{aligned} \quad (3.262)$$

Substituting for T_R^4 from Eq. (3.261) and simplifying the resulting expression, we get

$$q_{1 \rightarrow 2} = \sigma \left(A_1 F_{12} + \frac{A_1 A_2 F_{1R} F_{2R}}{A_1 F_{1R} + A_2 F_{2R}} \right) (T_1^4 - T_2^4) \quad (3.263)$$

A comparison of Eqs. (3.259) and (3.263) leads to the following relation for the modified view factor:

$$\bar{F}_{12} = F_{12} + \frac{1}{\frac{1}{A_1 F_{1R}} + \frac{1}{A_2 F_{2R}}} \quad (3.264)$$

It may be pointed out here that the above equation holds good if the surface R cannot see itself. However, if it can do so, the equation \bar{F}_{12} would take the following form:

$$\bar{F}_{12} = F_{12} + F_{1R} \left(\frac{F_{R2}}{1 - F_{RR}} \right) \quad (3.265)$$

For application of the above analysis, in respect of the modified view factor, to the actual industrial furnaces, we can divide the chamber of the furnace too, into a source, a sink and a no-flux surface, provided it has a uniform temperature. This simple analysis leads to useful results in many industrial practices involving black bodies.

Grey surfaces

In this case, along with the radiations emitted from a surface, we also consider the reradiated flux and thus the problem becomes more complicated than that involving only black surfaces. To deal with a system with grey and no-flux surfaces, we proceed in the following two different ways:

- (i) build up a flux balance for a particular surface, or
- (ii) formulate mathematically the heat exchanged between the two surfaces.

In both these cases, we get a set of linear algebraic equations which can be solved simultaneously to arrive at the expressions for unknown parameters. As we adopted the second method in analysis of the black surfaces, we will use the same technique for the sake of continuity, in this case too.

We consider an enclosure containing n surfaces designated by the numbers 1, 2, 3, ..., $n-1$ and n , of which m surfaces may be grey. Let the absolute

temperatures of all these surfaces be designated as T_1, T_2, \dots, T_n respectively. The radiative heat exchange between surfaces 1 and 2 can be expressed as

$$\begin{aligned} q_{1=2} &= \sigma A_1 f_{12} (T_1^4 - T_2^4) \\ &= \sigma A_2 f_{21} (T_1^4 - T_2^4) \end{aligned} \quad (3.266)$$

where f stands for "grey body view factor".

In comparison to view factors F_{12} and \bar{F}_{12} , the grey body view factor f_{12} includes the effect of direct radiations received from body 1 and also that of indirect radiations received through multiple reflections by body 2. In order to arrive at an expression for f_{12} , which will also depend on the geometry of the system, we simplify the system further by assuming that surface 1 only emits radiations and that all other surfaces are maintained at absolute zero temperature and are, therefore, capable of only reflecting the incident radiations as scatter or diffuse reflections. Thus, Eq. (3.266) takes the form

$$q_{1=2} = A_1 f_{12} \sigma T_1^4 = A_2 f_{21} \sigma T_1^4 \quad (3.267)$$

We denote the flux densities reflected from surfaces 1, 2, ..., n , respectively by the symbols $R_{11}, R_{12}, \dots, R_{1n}$. It should be noted that in these symbols, the first suffix, namely 1, is common to all surfaces because of the fact that the original source of radiations is only surface 1. Thus, the heat flux emitted away from surface 2 will be $A_2 R_{12}$. Also, since for any surface, the heat flux reflected and that absorbed will be in the ratio $(1 - \varepsilon)/\varepsilon$ where ε is the emissivity, heat absorbed by surface 2 will be $A_2 R_{12} \varepsilon_2 / (1 - \varepsilon_2)$. Thus, we have the following equation for the exchange of radiant energy:

$$q_{1=2} = A_1 f_{12} \sigma T_1^4 = A_2 f_{21} \sigma T_1^4 = \frac{A_2 R_{12} \varepsilon_2}{1 - \varepsilon_2} \quad (3.268)$$

or

$$A_1 f_{12} = \frac{A_2 R_{12}}{\sigma T_1^4} \frac{\varepsilon_2}{1 - \varepsilon_2} \quad (3.269)$$

In other words, evaluation of the grey body view factor f_{12} requires the calculation of flux density, R_{12} . For this, we strike a flux balance on surface 2 by considering the incident and reflected radiant energy. Radiations are incident on surface 2 from all surfaces which are seen by it. Thus, the total incident radiation flux q_2 on surface 2 will be

$$q_2 = A_1 F_{12} (\varepsilon_1 \sigma T_1^4 + R_{11}) + A_2 F_{22} R_{12} + A_3 F_{12} R_{13} + A_4 F_{42} R_{14} + \dots + A_n F_{n2} R_{1n} \quad (3.270)$$

From this incident radiation flux, a fraction $(1 - \varepsilon_2)$ is reflected. Therefore, we have

$$[A_1 F_{12} (\varepsilon_1 \sigma T_1^4 + R_{11}) + A_2 F_{22} R_{12} + A_3 F_{32} R_{13} + \dots + A_n F_{n2} R_{1n}] (1 - \varepsilon_2) = A_2 R_{12} \quad (3.271)$$

or on rearranging the terms, we have

$$A_1 F_{12} R_{11} + \left(A_2 F_{22} - \frac{A_2}{1 - \varepsilon_2} \right) R_{12} + A_3 F_{32} R_{13} + \dots + A_n F_{n2} R_{1n} = -A_1 F_{12} \sigma T_1^4 \varepsilon_1 \quad (3.272)$$

We can develop similar relations for all other surfaces. Thus, we will get n simultaneous equations with n unknown terms, namely R_{11}, \dots, R_{1n} , the values of which can be evaluated by solving these equations. In matrix notation, these equations may be expressed in the following manner:

$$\begin{bmatrix} A_1 F_{11} - \frac{A_1}{1 - \varepsilon_1} A_2 F_{12} A_n F_{n1} \\ A_1 F_{12} \left(A_2 F_{22} - \frac{A_2}{1 - \varepsilon_2} \right) A_n F_{n2} \\ \vdots \\ A_1 F_{1n} A_2 F_{2n} \left(A_n F_{nn} - \frac{A_n}{1 - \varepsilon_n} \right) \end{bmatrix} \begin{bmatrix} R_{11} \\ R_{12} \\ \vdots \\ R_{1n} \end{bmatrix} = \begin{bmatrix} F_{11} \\ F_{12} \\ \vdots \\ F_{1n} \end{bmatrix} \sigma T_1^4 \quad (3.273)$$

Thus, we arrive at

$$R_{12} = \frac{D_2}{D} \quad (3.274)$$

where D_2 is the determinant obtained by replacing the second column of the matrix on the left-hand side of Eq. (3.273) by the term on the right-hand side, and D is the determinant obtained from the left-hand side matrix. Similarly, we can obtain relations for all other R_{ij} terms. From Eq. (3.269), we thus, get

$$A_1 f_{12} = A_2 f_{21} = \frac{A_2 \varepsilon_2}{\sigma T_1^4 (1 - \varepsilon_2)} \left(\frac{D_2}{D} \right) \quad (3.275)$$

In case of non-grey enclosures, the problem becomes still more complicated as one has to consider the whole spectrum of wavelengths along with the emissivities of surfaces for these wavelengths. This problem can be solved only in the case of simple geometries. In fact, for most industrial cases, the results obtained by assuming the systems to form a “grey enclosure” lead to sufficiently accurate analysis. We can, therefore, avoid complications resulting from inclusion of non-grey enclosures.

3.3.6 Flames and Furnaces

From the point of view of analysis of radiant heat energy, furnaces can be classified into three different categories as follows:

- (i) On the basis of their dimensions
- (ii) On the basis of their operation
- (iii) On the basis of heat source.

From the dimensional point of view, we can further divide furnaces into two types, namely:

- (a) Furnaces, in which the distance between the heat source and sink is small. In such cases, the source-sink heat exchange can be considered to be limited only to sink area covered by the source directly under it and simple radiation exchange equations can be developed on this basis.
- (b) Furnaces, in which all dimensions are comparable to each other. In this case, the furnace is divided into a number of zones of constant temperature and then the analysis is conducted by making use of the concept of grey body view factor.

From the operational point of view, we can also divide furnaces into two types, namely (a) continuous, and (b) batch type of furnaces. Continuous furnaces can be assumed to work always under steady state, whereas in case of batch type furnaces, this assumption does not hold good. We have to make the necessary allowance for a certain variation in the analytical treatment of such furnaces.

From the point of view of heat supply, we can classify furnaces into, (a) electrical furnaces, (b) fluid-fuel fired furnaces, and (c) solid fuel, e.g. coal fired furnaces. In all these furnaces there will be a gaseous atmosphere. This may consist of natural air or some inert gas in the case of electric furnaces and flue gases in the case of gas, oil or solid-fuel fired furnaces. The radiant energy in such furnaces will travel from the source to the sink through this atmosphere. Hence, we require a knowledge of the effect of such atmospheres on the radiative heat transfer. It has been found that monatomic and diatomic gas molecules such as argon, helium, hydrogen, nitrogen, oxygen, etc. do not affect radiations from source to sink and no correction need be made for the medium in such cases. However, in the case of complex gaseous molecules such as H_2O , CO_2 , SO_2 and also in fluidized-particulate bed systems, the radiative energy transfer is strongly affected and is found to be a strong function of the wavelength of radiation and temperature.

For the calculation of the effect on radiative heat transfer through gaseous phases, we make use of the concept of monochromatic absorbance, α_λ , of a gas which is defined by the equation

$$\alpha_\lambda = 1 - \exp(-k_\lambda L) \quad (3.276)$$

where k_λ is the monochromatic absorption coefficient for radiations of wavelength λ defined as the “ratio of monochromatic absorption of energy per unit time per unit volume” and the “monochromatic beam intensity”; L is the length or thickness of the gaseous medium. If both scattering and absorption processes affect the movement of radiations through the gaseous phase, we use a modified relation in the following form:

$$\rho_\lambda = 1 - \exp(1 - \beta_\lambda L) \quad (3.277)$$

where ρ_λ is the monochromatic extinction fraction, and β_λ the monochromatic extinction coefficient calculated from the following equation:

$$\beta_\lambda = k_\lambda + \sigma_\lambda \quad (3.278)$$

The term σ_λ in this equation is the monochromatic scattering coefficient defined as the ratio of “radiant energy scattered per unit volume per unit time” to the “incident energy of wavelength λ ”.

In order to take all these effects into account, we make use of the concepts of emissivity and absorptivity along with the general assumption of the gas being grey. Thus, for such gas filled furnaces, the net heat flux exchanged is expressed by the relation

$$\dot{q} = \left(\frac{\varepsilon_s + 1}{2} \right) \sigma (\varepsilon_g T_g^4 - \alpha_g T_s^4) \quad (3.279)$$

where ε_s is the emissivity of the solid surface, and ε_g and α_g are the emissivity and absorptivity of the gaseous phase, respectively and are both functions of temperature, pressure and composition of the gas and also the geometry of the system under study.

In Figs. 3.24, 3.25, and 3.26, the emissivity and absorptivity of H_2O vapours and CO and SO_2 gases are shown as functions of the temperature and pressure of the gas.

The analytical treatment of radiation from a flame which is generated by the combustion of atomized oils or powdered coal, requires a study of radiations emerging out of clouds of particles. Experimental investigations for such cases

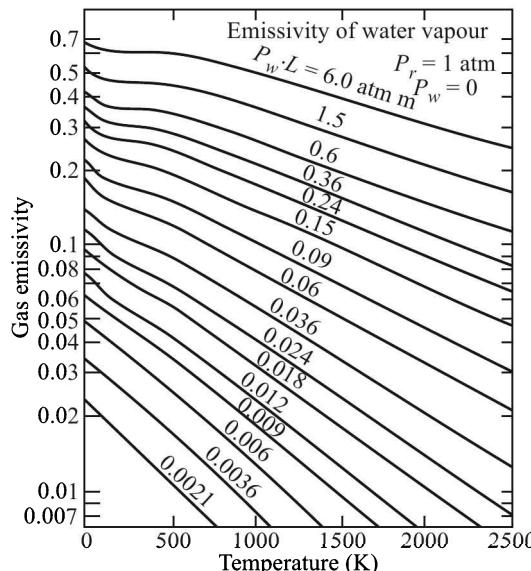


Fig. 3.24 Emissivity of water vapour.

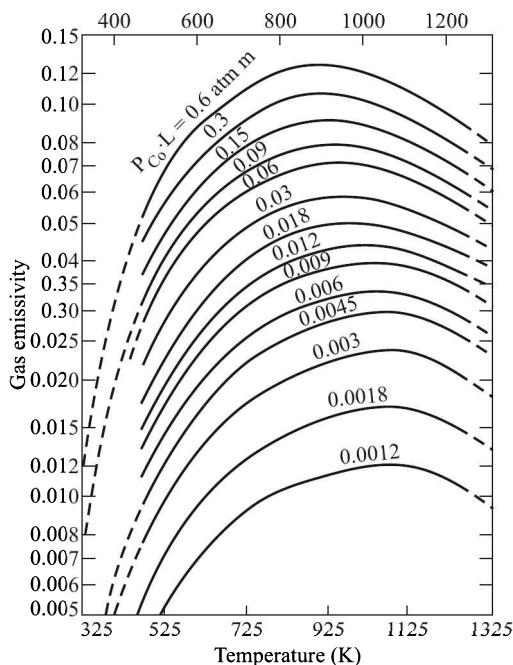


Fig. 3.25 Emissivity of carbon monoxide.

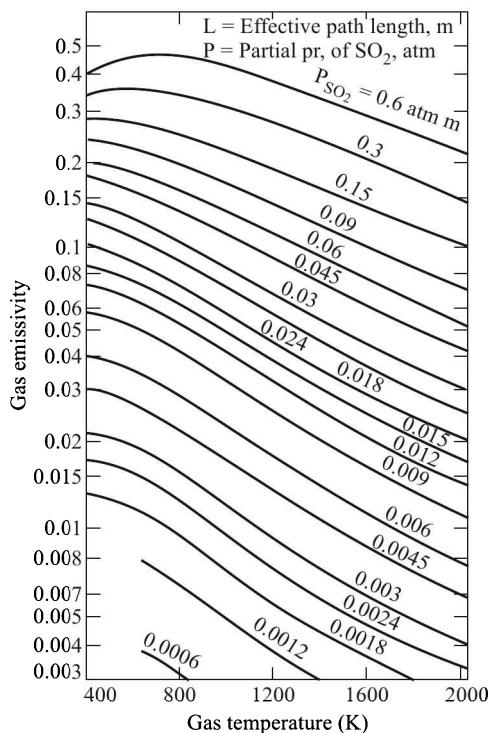


Fig. 3.26 Emissivity of sulphur dioxide.

have shown that the monochromatic emissivity of a flame is given by the relation

$$\varepsilon_\lambda = 1 - \exp \{-CLf(\lambda)\} \quad (3.280)$$

where C is the soot concentration, L the length of the flame and $f(\lambda)$ a function dependent on the wavelength of radiation. In the case of visible range, the function is

$$CLf(\lambda) = kL\lambda^{-1.39} \quad (3.281)$$

whereas, for the infrared range, it is found to be

$$CLf(\lambda) = kL\lambda^{-0.95} \quad (3.282)$$

The product kL is called the *absorption strength* of the flame and is found to be a function of *true* and *red brightness* temperature of the flame—the latter being defined as the temperature of a black body having the same intensity of emission at the mean wavelength of the red screen in an optical pyrometer as the object viewed. In Figs. 3.27 and 3.28, the absorption strength and total emissivity are represented as functions of different variables on which they depend.

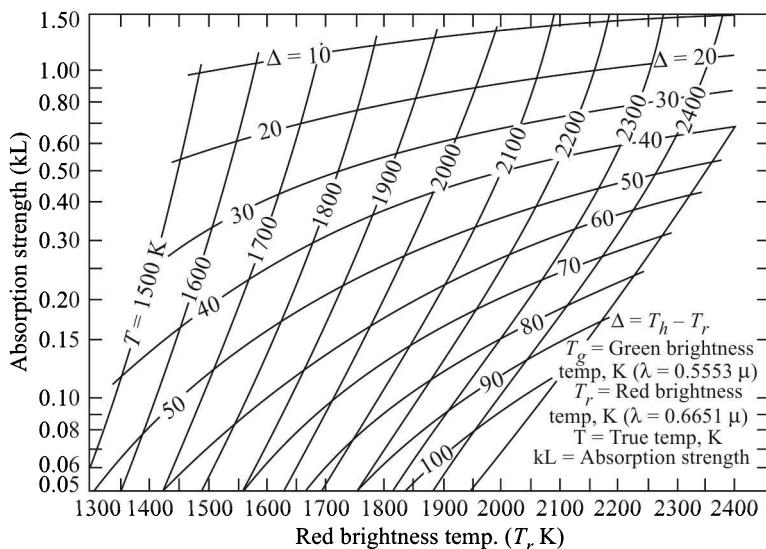


Fig. 3.27 Absorption strength of luminous flames.

In the case of pulverized solid fuel-fired furnaces, the experimental studies are known to conform to the relation

$$\varepsilon_f = 1 - \exp (-\varepsilon_p k_p A_p L) \quad (3.283)$$

where ε_f is the flame emissivity, ε_p the particle emissivity, k_p the number of particles per cubic centimetre, A_p the average particle cross-sectional area, and L the cloud thickness in centimetres.

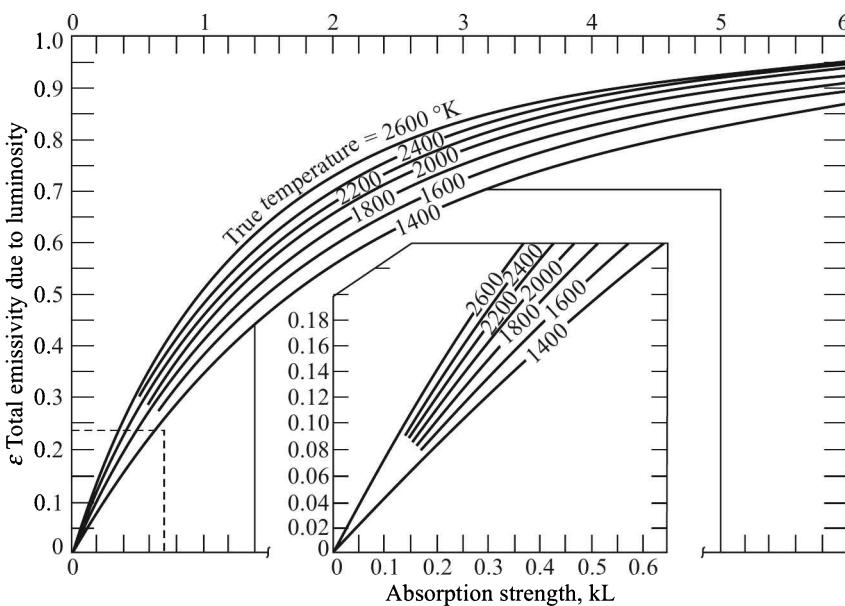


Fig. 3.28 Total emissivity of luminous flames.

REVIEW QUESTIONS

1. Describe the various modes of heat transfer. Give examples of their applications.
2. Enunciate and explain Fourier's first law of heat conduction.
3. State various equations used for the calculation of thermal conductivity of gases, liquids, solids and porous materials.
4. Derive an equation for Fourier's second law of heat conduction in the rectangular coordinate system. Give its equivalent equations in cylindrical and spherical coordinate systems.
5. Derive an equation for steady state heat conduction to a spherical particle from a stagnant fluid medium of infinite dimensions.
6. Derive the steady state, radial heat conduction equation from the interior of a composite cylindrical wall to its surface.
7. Illustrate how steady state heat conduction equation can be applied to rectangular ducts.
8. Discuss the basis of flow-net technique for the solution of two-dimensional steady-state conduction problems.
9. Derive an equation for the temperature of a uniformly heated plate as a function of position and time when it is quenched in a liquid at ambient temperature.

10. Develop a unidimensional plane front solidification model.
11. Derive an equation for the temperature distribution of a solid which is heated by means of a moving source.
12. Derive an equation for convective heat transfer.
13. Derive an equation for the temperature distribution in a hot fluid which is forced to flow through a tube.
14. Analyse the problem of heat transfer in free convection of a fluid.
15. Develop a mathematical model for heat transfer in zone-refining processes.
16. Discuss the laws of heat radiation.
17. Explain the terms: (i) black body, (ii) grey body, (iii) view factor, (iv) emissivity, (v) absorptivity, and (vi) no-flux surface.
18. Develop an equation for heat exchanged between two infinitely long and wide parallel plates.
19. Discuss the methods for the calculation of radiant heat transfer for black surfaces.
20. State and comment on the equations used for the calculation of radiant-heat transfer through gaseous phases.

PROBLEMS

1. Derive the relations between units of thermal conductivity in cgs and SI systems.
2. Calculate the thermal conductivity and thermal diffusivity of helium at 400°C from the following data, making use of (a) Eq. (3.6), and (b) Eq. (3.7).

Molecular weight = 4.0

Atomic diameter = 2.44 Å

Collision diameter = 2.576 Å

$$\Omega_k = 0.6254$$

$$C_v = 1.5 R$$

3. Calculate the thermal conductivity of hydrogen, making use of Eq. (3.9), at 300°C and 15 atmospheres.

Given:

$$T_{c,H_2} = 133.3 \text{ K}; \quad P_{c,H_2} = 12.80 \text{ atm}$$
$$C_{p,H_2} = 14400 \text{ J kg}^{-1} \text{ K}^{-1}; \quad \text{mol. wt.} = 2.00$$

4. Calculate the thermal conductivity of a mixture of gases containing, in terms of mole fraction N , $N_{CO_2} = 0.2$, $N_{O_2} = 0.5$, $N_{N_2} = 0.3$ from the following data:

$$C_{p,\text{CO}_2} = 950 \text{ J kg}^{-1} \text{ K}^{-1}, \quad C_{p,\text{N}_2} = 1064 \text{ J kg}^{-1} \text{ K}^{-1}, \quad C_{p,\text{O}_2} = 912 \text{ J kg}^{-1} \text{ K}^{-1}$$

$$\mu_{\text{CO}_2} = 1.5 \times 10^{-5} \text{ kg m}^{-1} \text{ s}^{-1}, \quad \mu_{\text{N}_2} = 2.6 \times 10^{-5} \text{ kg m}^{-1} \text{ s}^{-1},$$

$$\mu_{\text{O}_2} = 2.8 \text{ kg m}^{-1} \text{ s}^{-1}$$

$$M_{\text{CO}_2} = 44, \quad M_{\text{N}_2} = 28, \quad M_{\text{O}_2} = 32$$

5. Calculate the thermal conductivity of a monatomic liquid having the following properties:

$$\text{Density of the liquid} = 4.5 \times 10^3 \text{ kg m}^{-3}$$

$$\text{Isothermal compressibility} = 4.7 \times 10^{-8} \text{ Pa}^{-1}$$

$$\text{Molecular weight} = 83$$

Assume γ to be unity.

6. A furnace wall consists of three layers—first, a layer of refractory bricks followed by one of insulating bricks and finally a steel shell of 8 mm thickness. The thermal conductivities of the three layers are as follows:

$$\text{Refractory brick} = 4.67 \text{ W m}^{-1} \text{ K}^{-1}$$

$$\text{Insulating brick} = 2.25 \text{ W m}^{-1} \text{ K}^{-1}$$

$$\text{Steel} = 45.15 \text{ W m}^{-1} \text{ K}^{-1}$$

Calculate the minimum thickness of the brick layer to give a heat loss of $5.6 \times 10^4 \text{ kJ m}^{-2} \text{ h}^{-1}$ under the condition that the temperature does not go beyond 1400 K for the insulating brick. The temperature at the surface of the refractory wall is maintained at 1700 K and that of the steel surface at 300 K.

7. The temperature distribution in a two-dimensional steel slab is given by the equation

$$T = 1.3x + 1.5y + 0.3xy + 1000$$

where T is expressed in kelvin and distance x and y in centimetres.

Calculate the heat flux at $x = 3 \text{ cm}$ and $y = 5 \text{ cm}$ from the corner of the slab, assuming thermal conductivity of steel to be $40 \text{ W m}^{-1} \text{ K}^{-1}$.

8. The inner and outer walls of a rectangular duct are maintained at 1000 and 300 K respectively. Find the temperature distribution inside the refractory and calculate the heat flux if the refractory wall thickness is 0.25 m. The thermal conductivity of the brick is $1.47 \text{ W m}^{-1} \text{ K}^{-1}$.
9. A rectangular steel slab of thickness 0.1 m and maintained at 1400 K is quenched in an oil bath maintained at 500 K. Calculate the temperature at the midpoint of the slab after 120 s. The thermal conductivity, density and specific heat of steel may be respectively taken as $45.0 \text{ W m}^{-1} \text{ K}^{-1}$, $7.8 \times 10^3 \text{ kg m}^{-3}$, $0.6 \text{ kJ K}^{-1} \text{ kg}^{-1}$. The heat transfer coefficient for flow of heat from the slab to the oil is $40 \text{ W m}^{-2} \text{ K}^{-1}$.

10. A water-cooled plate maintained at 50°C is brought in contact with molten iron maintained at 1808 K. Calculate the thickness of the solid phase after one minute. The relevant properties of solid and liquid iron are as follows:

$$\text{Melting point} = 1808 \text{ K}$$

$$\text{Thermal conductivity of solid iron} = 63 \text{ W m}^{-1} \text{ K}^{-1}$$

$$\text{Thermal conductivity of liquid iron} = 50 \text{ W m}^{-1} \text{ K}^{-1}$$

$$\text{Density of solid iron} = 7.6 \times 10^3 \text{ kg m}^{-3}$$

$$\text{Density of liquid iron} = 7.4 \times 10^3 \text{ kg m}^{-3}$$

$$\text{Specific heat of solid iron} = 0.6 \text{ kJ kg}^{-1} \text{ K}^{-1}$$

$$\text{Specific heat of liquid iron} = 0.54 \text{ kJ kg}^{-1} \text{ K}^{-1}$$

$$\text{Heat of fusion} = 15000 \text{ kJ kg}^{-1} \text{ mol}^{-1}$$

$$\text{Atomic weight} = 56.0$$

11. A liquid at 350 K is flowing through a pipe of 0.15 m internal diameter 0.005 m wall thickness and 10 m length at a rate of 800 kg per hour. The ambient temperature is 300 K. Calculate the heat lost during the flow. Thermal conductivity of the material of pipe is $25 \text{ W m}^{-1} \text{ K}^{-1}$.
12. Two black discs each of 3 m diameter are placed opposite to one another at a distance of 1.3 m. One disc is maintained at 1000 K and the other at 300 K. Calculate the heat exchanged between the two discs when no other surfaces are present. Assume $\sigma = 5.67 \times 10^{-8} \text{ W m}^{-2} \text{ K}^{-4}$.
13. A cylindrical furnace has a diameter of 1.5 m. Located at the top of the furnace, 1 m away from the job, are heating elements which maintain the top at 1500 K. If the emissivity of the top and the job are 0.75 and 0.5 respectively, calculate the amount of heat transferred to the job assuming that furnace walls are no-flux surfaces, using the standard σ value.

Mass Transfer

Mass transfer is by far the most important aspect of transport phenomenon in the study of metallurgical processes. These processes invariably involve transfer of one or more components from one phase to another phase or other phases. The rates of these processes are thus predominantly controlled by the mass transfer alone. Therefore, most of the initial research work on the kinetics of metallurgical processes was confined only to the study of mass transport, and the effects accompanying energy transport were generally neglected by making simplifying assumptions. For example, for interpretation of experimental data on gaseous reduction of iron ore, earlier attempts made use of the principles of chemical kinetics only. Since this approach could not explain these data over the whole range of reduction, it had to be modified by taking into account the role of mass-transport steps involved in reduction. Though the resulting equations yielded much better results in respect of dense pellets under high rates of flow of gas, they still required further modification particularly in case of studies involving porous pellets and those conducted at slow gas flow rates by taking into consideration the accompanying heat and momentum transfer. This simple example clearly emphasizes the predominant role played by mass transfer in metallurgical processes. In fact in a number of processes involving phase transformations, particularly those involving heat treatment of metals and alloys, as for example carburizing of steels, it is the mass transfer alone which is considered to affect the kinetics of the process along with nucleation which is also controlled by diffusion.

Nowadays, mass transfer along with heat and momentum transfer is considered for the complete mathematical formulation of several extractive metallurgical processes. Such formulations, in which all these aspects are considered simultaneously along with the thermodynamics and chemical kinetics of the involved reactions, are called *mathematical models*. These models find extensive applications in present day process-analysis for assessing the role of different variables on a process or for the analysis of the performance of a reactor and its optimization.

Though mass transfer plays a more important role in chemical and metallurgical reactors than that played by heat and momentum transfers, its development has lagged behind that of both the other aspects of transport phenomenon. This is due to varied applications of momentum and heat transfer. The theory of momentum transfer has developed at a much faster rate because it concerns fluid flow, which is of great importance in tapping the enormous hydrodynamic natural sources of energy as well as in the development of optimum aerodynamic systems for aeroplanes, satellites, missiles, rockets and other outer space vehicles. Close on heels of the development of the theory of momentum transfer is that of heat transfer because of its application to the development of combustion devices and nuclear reactors for exploiting these energy sources. Mass transfer theory has developed mainly through its analogous nature to momentum and heat transfer. Thus, though mass transfer has been of prime importance to metallurgical and other process industries, its development has followed only after that of momentum and heat transfer.

Mass transfer in any system may take place by two different modes.

- (i) **Diffusion.** This is a microscopic mode of mass transfer similar to heat conduction and involves movement of mass on atomic scale. In other words, the movement of molecules of components occurs from one lattice position to a neighbouring one inside the solid or the fluid phases of the system. This mode of mass transfer becomes predominant in systems involving solids and stagnant sections of fluids, i.e. those regions or sections which are not affected by stirring or fluid flow. This is also known as *molecular mass transfer*.
- (ii) **Convection.** This mode of mass transfer, also referred to as *convective mass transfer*, is the macroscopic mode of mass transport similar to heat convection and is predominant in both flowing- and stirred-fluid systems. In this case, the transport of the component under consideration takes place by the transfer of chunks of fluid from one part of the system to the other either because of its flow or because of the stirring effects caused by natural means such as density differences (owing to fluctuations in concentration or temperature or both) or by external forces acting on the system.

A detailed treatment of these modes of mass transfer along with their simple applications will now be presented in this chapter.

4.1 DIFFUSION

Diffusion of a component in a system is governed by Fick's first law, according to which the rate of transfer J_i also known as 'flux' of any component i per unit area per unit time across an interface in a medium having a continuous concentration gradient for this component is expressed by the relation

$$J_i = -D_i \frac{\partial C_i}{\partial x} \quad (4.1)$$

where D_i is a constant, characteristic of the component i and the system under study, and is called the *diffusion coefficient* of component i ; C_i is the concentration of component i expressed as mass or number of moles per unit volume, and $\partial C_i / \partial x$, is the concentration gradient in the direction normal to the interface across which flow or diffusion of the component i is considered. It may be mentioned that the flux J_i is actually a function of the activity gradient, rather than the concentration gradient. However, in many systems, the activity values are not readily available. So, the activity gradient is substituted by the concentration gradient assuming ideal solution behaviour and applying Raoult's law. In this connection, we may mention the phenomenon of *uphill diffusion*, where diffusion actually takes place up the concentration gradient, although correctly, down the activity gradient, as in the case of diffusion of carbon from the austenite region to the cementite region in steels. It may be noted that Eq. (4.1) is similar to Eqs. (3.2) and (2.7) and forms one of the phenomenological principles on which the treatment of transport phenomena is based.

It is important, however, to note that the application of Eq. (4.1) is not as straightforward as of similar equations for momentum and heat transfer. This is due to the fact that the terms C_i and J_i in Eq. (4.1) can be defined in a number of ways. Further, the term D_i is a strong function of composition, apart from being a function of pressure and temperature, which is known to affect the viscosity and thermal conductivity as well.

The differences between applications of Eq. (4.1) and those corresponding to momentum and heat transfer arise out of the fact that in this case, we have to deal with solutions having concentration gradients for various components present in them. The concentration of any component in a solution can be expressed in a number of ways. In metallurgical systems, however, the following four ways are commonly employed.

- (i) *Mass of the concerned component per unit volume.* This form of expression of concentration is denoted by the symbol ρ_i , where the subscript i denotes the component and ρ_i equals the ratio of mass m_i of the component i to volume V of the system. In SI units, it is expressed as kg m^{-3} . This is sometimes called the *mass density*.
- (ii) *Moles of the concerned component per unit volume.* It is generally denoted by the symbol C_i which equals $m_i/M_i V$ or ρ_i/M_i , where M_i is the molecular weight of the component i . In SI units, it is expressed as kg moles m^{-3} .
- (iii) *Mass fraction of the concerned component.* It is generally denoted by the symbol X_i and defined as

$$X_i = \rho_i/\rho = \frac{\rho_i}{\sum \rho_i}$$

$$= \frac{m_i/V}{\sum(m_i/V)} = \frac{m_i}{\sum m_i} \quad (4.2)$$

where $\rho = m/V$, is the mass per unit volume of the system, and m is the total mass of the system.

- (iv) *Mole fraction of the component under consideration.* It is denoted by the symbol N_i and defined as

$$N_i = \frac{C_i}{C} = \frac{C_i}{\sum C_i} = \frac{m_i/M_i}{\sum(m_i/M_i)} \quad (4.3)$$

where C is the sum of the number of moles of all components present in the system per unit volume.

Relationships between all these four different ways of expressing concentration can be easily derived from our knowledge of molecular weights of the different components present in the system. This is illustrated by the following example.

EXAMPLE 4.1 Calculate the values of ρ_i , C_i , X_i and N_i for oxygen and nitrogen in air at NTP assuming these gases to behave ideally. Molecular wt. of $O_2 = 32$ and that of $N_2 = 28$, $R = 8.314 \times 10^3 \text{ kg m}^2 \text{ s}^{-2} \text{ kg-mol}^{-1} \text{ K}^{-1}$ and $1 \text{ atm} = 1.0133 \times 10^5 \text{ kg m}^{-1} \text{ s}^{-2}$.

Solution Air is known to contain 79% N_2 and 21% O_2 by volume. Therefore, one cubic metre of air at NTP will contain 0.79 m^3 and 0.21 m^3 of N_2 and O_2 respectively. According to the ideal gas law, we have

$$PV = nRT$$

or

$$C_i = \frac{n_i}{V} = \frac{P_i}{RT}$$

Further

$$P_i = \text{volumetric fraction of the component } i \times \text{total pressure} = PV_i$$

For this example, the volumetric fraction of N_2 , V_{N_2} is 0.79 and that of O_2 , V_{O_2} is 0.21. Hence

$$\begin{aligned} C_{N_2} &= \frac{P \cdot V_{N_2}}{RT} = \frac{1.0133 \times 10^5 \times 0.79}{8.314 \times 10^3 \times 273} \\ &= 3.53 \times 10^{-2} \text{ kg-mol m}^{-3} \end{aligned} \quad \text{Ans.}$$

and mass concentration ρ_{N_2} is calculated from the value of C_{N_2} and its molecular weights M_{N_2} as

$$\rho_{N_2} = M_{N_2} C_{N_2} = 28 \times 3.53 \times 10^{-2} = 0.99 \text{ kg m}^{-3} \quad \text{Ans.}$$

Similarly

$$\begin{aligned} C_{O_2} &= \frac{P V_{O_2}}{RT} = \frac{1.0133 \times 10^5 \times 0.21}{8.314 \times 10^3 \times 273} \\ &= 9.4 \times 10^{-3} \text{ kg-mol m}^{-3} \end{aligned} \quad \text{Ans.}$$

and

$$\rho_{O_2} = M_{O_2} C_{O_2} = 32 \times 9.4 \times 10^{-3} = 0.3 \text{ kg m}^{-3} \quad \text{Ans.}$$

Further, mass fractions are calculated as

$$X_{N_2} = \frac{\rho_{N_2}}{\rho_{N_2} + \rho_{O_2}} = \frac{0.99}{0.99 + 0.3} = 0.77 \quad \text{Ans.}$$

and

$$X_{O_2} = 1 - 0.77 = 0.23 \quad \text{Ans.}$$

and the mole fractions are calculated as

$$N_{N_2} = \frac{C_{N_2}}{C_{N_2} + C_{O_2}} = \frac{3.53 \times 10^{-2}}{3.53 \times 10^{-2} + 9.4 \times 10^{-3}} = 0.79 \quad \text{Ans.}$$

and

$$N_{O_2} = 1 - 0.79 = 0.21 \quad \text{Ans.}$$

We will now derive different relations for the flux J_i . For this purpose, we consider an n component flowing-fluid consisting of components 1, 2, 3, ..., n . Further, we assume that all these components have concentration gradients in solution and hence simultaneously diffuse in solution in the direction prescribed by Eq. (4.1). Consider the movement of these components along a particular direction, say in the direction of the x -axis. Let v_1, v_2, \dots, v_n be respectively the velocities of the different components 1, 2, ..., n with respect to a stationary coordinate axis. As a result of movements of these species, the local rate v at which the fluid mass passes per unit time through a unit cross-sectional area normal to the direction of flow, which may be considered as the average velocity of the fluid, shall be given by the relation

$$v \Sigma \rho_i = \Sigma \rho_i v_i \quad (4.4)$$

or

$$v = \frac{\Sigma \rho_i v_i}{\Sigma \rho_i} \quad (4.5)$$

The preferential movement of the different components is measured with respect to this velocity and not with respect to the stationary coordinates. The rate of this preferential movement is termed as *diffusion velocity*. Thus, the diffusion velocity, $v_{D,i}$ of the component i is expressed as

$$v_{D,i} = v_i - v \quad (4.6)$$

We can similarly define the *molar average velocity*, v^* , and the *molar diffusion velocity*, $v_{D,i}^*$, and write the following equations:

$$v^* = \frac{\Sigma C_i v_i^*}{\Sigma C_i} \quad (4.7)$$

and

$$v_{D,i}^* = v_i^* - v^* \quad (4.8)$$

where v_i^* is the molar velocity of the component i .

With the help of the above equations for component velocities, we can write the following equations for diffusional and total fluxes for any component i :

- (i) Total mass flux, \dot{m}_i per unit time per unit cross-sectional area with respect to a stationary coordinate

$$\dot{m}_i = \rho_i v_i^* \quad (4.9)$$

- (ii) Total molar flux \dot{M}_i per unit time per unit cross-sectional area with respect to a stationary coordinate

$$\dot{M}_i = C_i v_i^* \quad (4.10)$$

- (iii) Diffusional mass flux J_i

$$J_i = \rho_i v_{D,i} = \rho_i (v_i - v) \quad (4.11)$$

- (iv) Diffusional molar flux J_i^*

$$J_i^* = C_i V_{D,i}^* = C_i (v_i^* - v^*) \quad (4.12)$$

With the help of Eqs. (4.2) and (4.3), equations for Fick's first law of diffusion can be written in the following four alternative forms:

- (i) In terms of mass-concentration

$$J_i = -D_i \frac{\partial \rho_i}{\partial x} \quad (4.13)$$

- (ii) In terms of molar-concentration

$$J_i^* = -D_i \frac{\partial C_i}{\partial x} \quad (4.14)$$

- (iii) In terms of mass-fraction

$$J_i = -\rho D_i \frac{\partial X_i}{\partial x} \quad (4.15)$$

- (iv) In terms of mole-fraction

$$J_i^* = -CD_i \frac{\partial N_i}{\partial x} \quad (4.16)$$

where, J_i and J_i^* are diffusional flux expressed in corresponding units. It may be noted that the diffusion coefficient D_i does not depend upon the units used for mass, because its dimensions are independent of unit of mass as shown below. According to Eq. (4.1), we have

$$\begin{aligned} \text{Dimensions of } D_i &= \frac{\text{dimensions of } (J)}{\text{dimensions of concentration gradient}} \\ &= \frac{ML^{-2}t^{-1}}{ML^{-3}/L} = L^2 t^{-1} \end{aligned} \quad (4.17)$$

Thus, diffusion coefficient D_i shall be expressed in $\text{m}^2 \text{ s}^{-1}$ in SI units and $\text{cm}^2 \text{ s}^{-1}$ in cgs units.

It is interesting to note that the value of diffusion coefficient is independent of the mass units, although by definition, as clearly indicated by Eq. (4.1), the diffusion coefficient of a component is the amount in mass or moles of the component, diffusing per unit area per unit time under its unit concentration gradient. In writing Eqs. (4.13) and (4.16), it has been assumed that mass and molar density of the system do not change during the flow.

With the help of Eqs. (4.4) to (4.16), we can easily derive the following relations for fluxes with respect to a stationary coordinate:

$$\dot{m}_i = -D_i \frac{\partial \rho_i}{\partial x} + X_i(\Sigma \rho_i v_i) \quad (4.18)$$

$$= -D_i \rho \frac{\partial X_i}{\partial x} + X_i(\Sigma \rho_i v_i) \quad (4.19)$$

and

$$\dot{M}_i = -D_i \frac{\partial C_i}{\partial x} + N_i(\Sigma C_i v_i^*) \quad (4.20)$$

$$= -CD_i \frac{\partial N_i}{\partial x} + N_i(\Sigma C_i v_i^*) \quad (4.21)$$

For a stationary fluid, where the average velocities v and v^* are zero, it can be seen that $\dot{m}_i = J_i$ and $\dot{M}_i = J_i^*$

All the above equations for the flux are used in the interpretation of experimental data on mass transfer as well as for the analysis of mass transfer problems of industrial reactors. These applications are possible only if accurate and reliable data on diffusion coefficients of the concerned components are known. In the following section, we will briefly review the available literature on diffusion coefficients in gaseous, liquid and solid phases.

4.1.1 Diffusion in Gases

The initial attempts for prediction of diffusion coefficients in gases and gas mixtures were based on kinetic theory of ideal gases. According to this theory, the diffusion coefficient, D_{AB} of a species A at low gas density in a mixture of gases A and B of equal molecular weights and sizes is expressed by the relation

$$D_{AB} = \frac{1}{3} \bar{v} \lambda_A \quad (4.22)$$

where \bar{v} is the root mean square velocity of the gas molecules expressed by the relation

$$\bar{v} = \left(\frac{8RT}{\pi M_A} \right)^{1/2} \quad (4.23)$$

and λ_A , for component A, is the mean free path of the gas molecules, expressed by the relation

$$\lambda_A = -\frac{1}{\sqrt{2}\pi n d_A^2} \quad (4.24)$$

where d_A is the diameter of the molecules of gas A, n the number of molecules per unit volume and M_A is the molecular weight of gas A. Substituting for \bar{v} and λ_A from Eqs. (4.23) and (4.24) and for n from the ideal gas equation in terms of C , P and T , in Eq. (4.22), we have

$$D_{AB} = \frac{2}{3} \left(\frac{R^3 T^3}{\pi^3 M_A N^3} \right)^{1/2} \left(\frac{1}{P d_A^2} \right) \quad (4.25)$$

Calculation of values of D_{AB} using the above equation yields results for molecules of same molecular weights and diameters for nonpolar gases, i.e. for the isotopes of nonpolar gases, within about 5% of the experimental data. Extension of this approach to nonpolar gases of different molecular weights and sizes leads to the equation

$$D_{AB} = \left(\frac{RT}{\pi N} \right)^{3/2} \left(\frac{2}{M_A} + \frac{2}{M_B} \right) \frac{4}{3P(d_A + d_B)^2} \quad (4.26)$$

where N is the Avogadro's number, d_A and d_B are the diameters of atoms or molecules of gases A and B, respectively and M_A and M_B their respective atomic or molecular weights.

Typical characteristics of gases used for making calculations on diffusion coefficients are presented in Table 4.1.

Chapman and Enskog developed more accurate relations for diffusion coefficients, by taking into account the interactions among various molecules. Their equation for diffusion coefficient of gas A in a binary mixture of gases A and B at low density is as follows:

$$D_{AB} = \frac{2.2646 \times 10^{-5}}{C \sigma_{AB}^2 \Omega_{D,AB}} = \left\{ T \left(\frac{1}{M_A} + \frac{1}{M_B} \right) \right\}^{1/2} \quad (4.27)$$

where the concentration C is expressed in g-mol cm⁻³, temperature T in K, function σ_{AB} in Å, and function $\Omega_{D,AB}$ is a dimensionless function. Its values as a function of kT/ϵ_{AB} are given in Table 4.2. Functions σ_{AB} and ϵ_{AB} , which are called *Lennard-Jones parameters* for the gas mixture, may be evaluated from the standard values of these for the constituent gases from Table 4.1 by making use of the following equations:

$$\sigma_{AB} = 0.5 (\sigma_A + \sigma_B) \quad (4.28)$$

and

$$\epsilon_{AB} = (\epsilon_A \epsilon_B)^{1/2} \quad (4.29)$$

TABLE 4.1 Characteristics of gases

Gas	Molecular weight M_i	Lennard-Jones parameters		Critical constants		
		σ_A	ε/k (K)	T_c (K)	P_c (atm)	V_c (cm ³ /g-mol)
Air	28.97	3.617	97.0	132.0	36.4	86.6
Argon	39.944	3.418	124.0	151.0	48.0	75.2
Bromine	159.83	4.268	520.0	584.0	102.0	144.0
Carbon monoxide	28.01	3.590	110.0	133.0	34.5	93.1
Carbon dioxide	44.01	3.996	190.0	304.2	72.9	94.0
Chlorine	70.91	4.115	357.0	417.0	76.1	124.0
Fluorine	38.0	3.653	112.0	—	—	—
Hydrogen	2.016	2.915	38.0	35.3	12.80	65.0
Helium	4.003	2.576	10.2	5.26	2.26	57.8
Iodine	253.82	4.982	550.0	800.0	—	—
Krypton	83.80	3.498	225.0	209.4	54.3	92.2
Neon	20.183	2.789	35.7	44.5	26.9	41.7
Nitrogen	28.02	3.681	91.5	126.2	33.5	90.1
Nitric oxide	30.01	3.470	119.0	180.0	64.0	57.0
Oxygen	32.00	3.433	113.0	154.4	49.7	74.4
Sulphur dioxide	64.07	4.290	252.0	430.7	77.8	122.0

In the case of vapours of metals, the value of σ_A can be taken as equal to the atomic diameter of the metal. This approach is similar to that on viscosity in Section 2.2.1 and on thermal conductivity in Section 3.1.1.

Apart from the above, another relation is frequently used for the calculation of diffusion coefficients in a binary gas mixture at low pressures. This relation is based on the concept of *corresponding states* and is written as

$$D_{AB} = \frac{a}{P} \left\{ \frac{T}{(T_{c,A} T_{c,B})^{1/2}} \right\}^b (P_{c,A} P_{c,B})^{1/3} (T_{c,A} T_{c,B})^{5/12} \left(\frac{1}{M_A} + \frac{1}{M_B} \right)^{1/2} \quad (4.30)$$

where the symbols $P_{c,A}$ and $T_{c,A}$ represent the critical pressure and temperature, respectively for gas A and $P_{c,B}$ and $T_{c,B}$, respectively those for gas B; a and b are constants whose values are given as follows:

(i) For nonpolar gas-pairs

$$a = 2.745 \times 10^{-4} \quad \text{and} \quad b = 1.823$$

(ii) For water vapour with a nonpolar gas

$$a = 3.64 \times 10^{-4} \quad \text{and} \quad b = 2.334$$

Values of self-diffusion coefficients at other temperatures and pressures can be calculated with the help of a graphical relationship between $PD_A/(PD_A)_0$ and P_r as shown in Fig. 4.1. In this figure $(PD_A)_0$ refers to the diffusion coefficient at low pressure for the temperature under consideration. T_r and P_r are the

TABLE 4.2 Transport characteristic function of gases

kT/ϵ or kT/ϵ_{AB}	$\Omega_\mu = \Omega_k$ (for viscosity And thermal conductivity)	Ω_D, AB (for mass diffusivity)	kT/ϵ or kT/ϵ_{AB}	$\Omega_\mu = \Omega_k$ (for viscosity and thermal conductivity)	Ω_D, AB (for mass diffusivity)
0.30	2.785	2.662	2.60	1.081	0.9878
0.35	2.628	2.476	2.70	1.069	0.9770
0.40	2.492	2.318	2.80	1.058	0.9672
0.45	2.368	2.184	2.90	1.048	0.9576
0.50	2.257	2.066	3.00	1.039	0.9490
0.55	2.156	1.966	3.10	1.030	0.9406
0.60	2.065	1.877	3.20	1.022	0.9328
0.65	1.982	1.798	3.30	1.014	0.9256
0.70	1.908	1.729	3.40	1.007	0.9186
0.75	1.841	1.667	3.50	0.9999	0.9120
0.80	1.780	1.612	3.60	0.9932	0.9058
0.85	1.725	1.562	3.70	0.9870	0.8998
0.90	1.675	1.517	3.80	0.9811	0.8942
0.95	1.629	1.476	3.90	0.9755	0.8888
1.00	1.587	1.439	4.00	0.9700	0.8788
1.05	1.549	1.406	4.10	0.9649	0.8740
1.10	1.514	1.375	4.20	0.9600	0.8652
1.15	1.482	1.346	4.30	0.9553	0.8610
1.20	1.452	1.320	4.40	0.9507	0.8568
1.25	1.424	1.296	4.50	0.9464	0.8530
1.30	1.399	1.273	4.60	0.9422	0.8456
1.35	1.375	1.253	4.70	0.9382	0.8422
1.40	1.353	1.233	4.80	0.9343	0.8124
1.45	1.333	1.215	4.90	0.9305	0.7896
1.50	1.310	1.198	5.0	0.9269	0.7712
1.55	1.296	1.182	6.0	0.8963	0.7556
1.60	1.279	1.167	7.0	0.8721	0.7424
1.65	1.264	1.153	8.0	0.8538	0.7712
1.70	1.248	1.140	9.0	0.8379	0.7556
1.75	1.234	1.128	10.0	0.8242	0.7424
1.80	1.221	1.116	20.0	0.7432	0.6640
1.85	1.209	1.105	30.0	0.7005	0.6232
1.90	1.197	1.094	40.0	0.6712	0.5960
1.95	1.186	1.084	50.0	0.6504	0.5756
2.00	1.175	1.075	60.0	0.6335	0.5596
2.10	1.156	1.057	70.0	0.6194	0.5464
2.20	1.138	1.041	80.0	0.6076	0.5352
2.30	1.122	1.026	90.0	0.5973	0.5256
2.40	1.107	1.012	100	0.5882	0.5170
2.50	1.093	0.9996			

reduced temperature and pressure respectively and are calculated as the ratio of the concerned temperature and pressure to the critical values of these variables for the gas under consideration.

In the absence of any other data, Fig. 4.1 can be used to calculate values of diffusion coefficient for binary gas mixtures by approximating the critical data for the mixture, with the help of the following relationship.

$$P_c = \sum_{i=1}^n N_i P_{c_i} \quad (4.31a)$$

and

$$T_c = \sum_{i=1}^n N_i T_{c_i} \quad (4.31b)$$

where the subscript i refers to the component i and N_i to its mole-fraction.

Application of these relations is now demonstrated by the following examples.

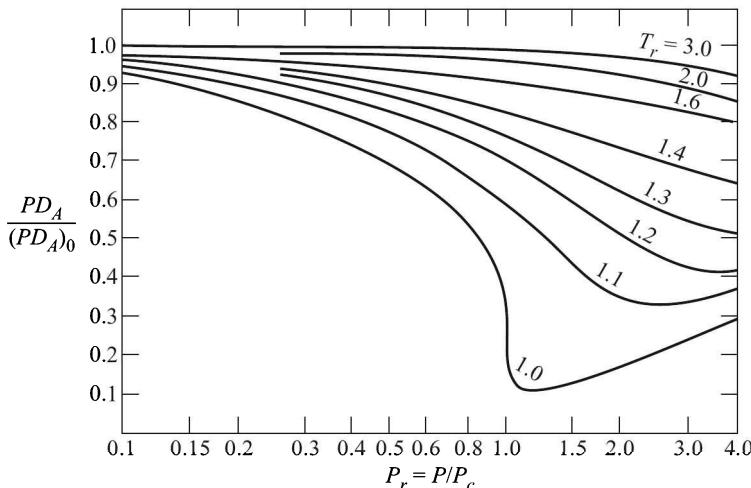


Fig. 4.1 Relationship between function $(PD_A)/(PD_A)_0$ and reduced pressure P_r at different reduced temperatures for gases.

EXAMPLE 4.2 Calculate the self-diffusion coefficient of argon under 0.2 atmosphere pressure and at 298 K (i) by making use of kinetic theory of ideal gases, and (ii) with the help of Chapman-Enskog equation. The relevant data for argon and other constants are as follows:

$$\text{Atomic weight} = 40$$

$$\text{Atomic diameter} = 3.82 \text{ \AA}$$

$$\sigma = 3.418 \text{ \AA}$$

$$\varepsilon/k = 124 \text{ K}$$

$$R = 8.314 \times 10^3 \text{ J kg-mol}^{-1} \text{ K}^{-1}$$

$$N = 6.02 \times 10^{23}$$

Solution (i) According to Eq. (4.25), we have

$$\begin{aligned}
 D_{AA} &= \frac{2}{3} \left(\frac{R^3 T^3}{\pi^3 N^3 M_A} \right)^{1/2} \frac{1}{P d_A^2} \\
 &= \frac{2}{3} \left[\frac{(8.314 \times 10^3)^3 \times (298)^3}{\left(\frac{22}{7}\right)^3 \times (6.02 \times 10^{23})^3 \times 40} \right]^{1/2} \\
 &\quad \times \left[\frac{1}{(0.2 \times 1.01 \times 10^5) \times (3.82 \times 10^{-10})^2} \right] = 6.23 \times 10^{-5} \text{ m}^2 \text{ s}^{-1}
 \end{aligned}$$

(ii) According to Eq. (4.27), for argon, we have

$$D_{AA} = \frac{2.2646 \times 10^{-5}}{C \sigma_{AA}^2 \cdot \Omega_{D,AA}} \left(\frac{2T}{M_A} \right)^{1/2}$$

Under the assumption of ideal gas law, we can also write

$$C = \frac{n}{v} = \frac{P}{RT} = \frac{0.2}{82.05 \times 298} = 8.18 \times 10^{-6} \text{ g-mol cm}^{-3}$$

Also

$$\frac{kT}{\epsilon} = \frac{298}{124} = 2.4$$

From Table 4.2

$$\Omega_{D,AA} = 1.012$$

Therefore

$$\begin{aligned}
 D_{AA} &= \left[\frac{2.2646 \times 10^{-5}}{8.18 \times 10^{-6} \times (3.418)^2 \times 1.012} \right] \left(\frac{2 \times 298}{40} \right)^{1/2} \\
 &= 0.9 \text{ cm}^2 \text{ s}^{-1} = 9 \times 10^{-5} \text{ m}^2 \text{ s}^{-1}
 \end{aligned}$$

A comparison of this result with that calculated using the equation based on the kinetic theory shows that the two values differ by about 30%. It has also been observed that the calculated value obtained, by the second method approximates the experimental data. This anomaly is due to the fact that derivation of the expression based on the kinetic theory of gases does not take into account the interaction between different gas molecules. Thus, this calculation shows that non-consideration of mutual interaction between different gas molecules can lead to results which deviate considerably from experimental data.

EXAMPLE 4.3 Calculate the diffusion coefficient of oxygen in air at one atmosphere pressure and 25°C using the relevant critical data from Table 4.1. Also, calculate the diffusion coefficient of oxygen at 100 atm pressure, the temperature remaining unchanged.

Solution From Table 4.1, the values of critical parameters for oxygen and nitrogen are

$$\begin{aligned} T_{c,O_2} &= 154.4 \text{ K} & P_{c,O_2} &= 33.5 \text{ atm} \\ T_{c,N_2} &= 126.2 \text{ K} & P_{c,N_2} &= 49.7 \text{ atm} \end{aligned}$$

Thus, from Eq. (4.30), we have

$$\begin{aligned} D_{O_2} &= \frac{2.745 \times 10^{-4}}{1} \times \left\{ \frac{298}{(154.4 \times 126.2)^{1/2}} \right\}^{1.823} \times (33.5 \times 49.7)^{1/3} \\ &\quad \times (154.4 \times 126.2)^{5/12} \times \left(\frac{1}{32} + \frac{1}{28} \right)^{1/2} \\ &= 0.207 \text{ cm}^2 \text{ s}^{-1} = 2.07 \times 10^{-5} \text{ m}^2 \text{ s}^{-1} \qquad \text{Ans.} \end{aligned}$$

Further

$$P_{r,O_2} = \frac{100}{33.5} = 2.99 \text{ and } T_{r,O_2} = \frac{298}{154.4} = 1.93$$

Also, from Fig. 4.1, we have

$$\left\{ \frac{PD}{(PD)_0} \right\} = 0.9$$

Thus, at 100 atm pressure

$$\begin{aligned} D_{O_2, 100 \text{ atm}} &= \frac{0.9}{100} (1 \times 0.207 \times 10^{-4}) \\ &= 1.86 \times 10^{-7} \text{ m}^2 \text{ s}^{-1} \qquad \text{Ans.} \end{aligned}$$

4.1.2 Diffusion in Liquids

Theories on prediction of diffusion coefficients in liquids are based either on the hydrodynamics of fluid-flow or on the absolute reaction rate theory. There are two basic approaches in theories based on hydrodynamics. The first approach assumes no slip between the diffusing particle and the surrounding fluid. According to this approach, the diffusion coefficient D_{AB} of component A in solvent B at temperature T is calculated from the equation

$$D_{AB} = \frac{kT}{6\pi\mu_B R_A} \qquad (4.32)$$

where k is the Boltzmann constant, μ_B the viscosity of solvent B and R_A the radius of molecules of component A. The above equation is known as *Stokes Einstein equation*.

In the second hydrodynamic approach, we also take into account the slip between the particle and the fluid and hence arrive at the following equation:

$$D_{AB} = \frac{kT}{4\pi\mu_B R_A} \qquad (4.33)$$

where the symbols have the same meaning as in Eq. (4.32).

Both of these expressions give approximate values of the diffusion coefficient. In order to obtain a more accurate result within ± 10 per cent of the experimental values, the following empirical equation was suggested by Wilke and Chang as an extension of the Stokes-Einstein equation:

$$D_{AB} = 7.4 \times 10^{-8} \times \frac{(\psi_B M_B)^{1/2}}{\mu V_A^{0.6}} \text{ cm}^2 \text{ s}^{-1} \quad (4.34)$$

where ψ_B is called the *association parameter* for the solvent B and has a value of 2.6 for water, V_A is the molar volume of component A in $\text{cm}^3 \text{ g-mol}^{-1}$, μ is the viscosity of the solution in centipoise and M_B the molecular weight of solute component B in solvent A.

On the basis of absolute reaction rate theory, Eyring arrived at the following equation for self-diffusion coefficient of component A:

$$D_{AA} = \frac{kT}{\mu_A} \times \left(\frac{N}{-V_A} \right)^{1/3} \quad (4.35)$$

where N is the Avogadro's number and the other parameters have already been defined. This equation gives less accurate results as compared to Eq. (4.33). In fact, none of the theories yield results which are accurate enough to be used for practical applications. Therefore, the diffusion coefficients of components of interest in a given system are determined experimentally. Values of diffusion coefficients of a few components in some metallurgical systems of common interest are summarized in Table 4.3.

Application of the above equations is demonstrated by the following example.

EXAMPLE 4.4 Calculate the diffusion coefficient at 25°C of a component A, having $M_A = 178$ and $\rho_A = 1280 \text{ kg m}^{-3}$, in water.

Assume viscosity of water as 1 centipoise.

Solution Specific volume V_A of component A is

$$\begin{aligned} V_A &= \frac{178}{1280} = 0.139 \text{ m}^3 \text{ kg-mol}^{-1} \\ &= 139 \text{ cm}^3 \text{ g-mol}^{-1} \end{aligned}$$

Substitution of the relevant value in Eq. (4.34) yields

$$\begin{aligned} D_{A,H_2O} &= 7.4 \times 10^{-8} \left\{ \frac{(2.6 \times 18)^{1/2} \times 298}{0.01 \times (139)^{0.6}} \right\} \\ &= 7.8 \times 10^{-4} \text{ cm}^2 \text{ s}^{-1} \\ &= 7.8 \times 10^{-8} \text{ m}^2 \text{ s}^{-1} \quad \text{Ans.} \end{aligned}$$

4.1.3 Diffusion in Solids

Fick's first law of diffusion is applied to experimental determination of diffusion coefficients of solid components having concentration gradient in the direction

TABLE 4.3 Diffusivity of some components in systems of metallurgical interest

<i>Diffusing component (diffusate)</i>	<i>Diffusion medium or melt</i>	<i>Temperature (°C)</i>	<i>Diffusion coefficient (m² s⁻¹)</i>	<i>Activation energy of diffusion (kJ mol⁻¹)</i>
A. Diffusion of ions in crystalline solids				
Ni ⁺	NiO	—	1.83×10^{-7}	192.04
O ⁻²	NiO	—	1.0×10^{-9}	225.94
Cr ⁺³	Cr ₂ O ₃	—	1.37×10^{-5}	255.64
Pb ⁺²	PbCl ₂	—	7.8×10^{-4}	149.79
O ⁻²	Fe ₂ O ₃	—	1.0×10^7	610.86
Fe ⁺³	Fe ₂ O ₃	—	40	468.61
Co ⁺²	CoO	—	2.15×10^{-7}	144.35
Ag ⁺	α-Cu ₂ S	—	3.8×10^{-8}	19.12
Cu ⁺	α-Ag ₂ S	—	1.2×10^{-8}	13.30
B. Diffusion in metals in solid state				
Aluminium	Copper	20	1.3×10^{-34}	—
Bismuth	Lead	20	1.1×10^{-20}	—
Tin	Iron	900	8.3×10^{-15}	—
Carbon	Iron	800	2.7×10^{-12}	—
Carbon	Iron	1000	32.7×10^{-12}	—
C. Diffusion in liquid metals				
Lead	Lead melt	333–657	9.15×10^{-8}	18.62
Silver	Silver melt	1000–1100	7.1×10^{-8}	34.10
Iron	Iron melt with 2% carbon	1400	9.0×10^{-9}	—
Carbon	Iron melt with 3.5% carbon	1550	6.0×10^{-9}	—
Sulphur	Iron with 0.96–1.24% sulphur	1560	4.9×10^{-8}	35.98
Phosphorous	Iron with 1.5% phosphorous	1256–1412	3.1×10^{-8}	46.02
Sulphur	Carbon saturated iron with 0.64% sulphur	1390–1560	2.8×10^{-8}	31.38
D. Diffusion in molten salts				
Sodium	Sodium chloride	906	14.2×10^{-9}	16.56
Chlorine	Sodium chloride	933	8.8×10^{-9}	29.68
Zinc	Zinc bromide	500	0.22×10^{-9}	67.19
Thallium	Thallium chloride	500	3.89×10^{-9}	19.24

TABLE 4.3 Diffusivity of some components in systems of metallurgical interest
(Contd.)

<i>Diffusing component (diffusate)</i>	<i>Diffusion medium or melt</i>	<i>Temperature (°C)</i>	<i>Diffusion coefficient (m² s⁻¹)</i>	<i>Activation energy of diffusion (kJ mol⁻¹)</i>
E. Diffusion in sulphide melts				
Copper	Cu–S melt (19.8% S)	1160	74.9×10^{-8}	53.55
Copper	Fe–Cu–S melt (32.0/40.0/28.0)	1160	55.2×10^{-8}	82.48
Iron	FeS + Cu ₂ S melt (50/50)	1168–1226	35.7×10^{-8}	57.32
Iron	Fe–S melt (33.5%)	1152	5.22×10^{-9}	56.90
Iron	Fe–S melt (31.0%)	1180	6.39×10^{-9}	71.13
Iron	Fe–S melt (29.0%)	1158	11.91×10^{-9}	115.89
Iron	Fe–Cu–S melt (48.1/20.5/31.9)	1160	7.57×10^{-9}	89.96
Iron	Fe–Cu–S melt (32/40/28)	1168	2.94×10^{-9}	57.32
F. Diffusion in silicate melts				
Calcium	CaO + Al ₂ O ₃ + SiO ₂ (40/20/40)	1400	0.062×10^{-9}	292.88
Calcium	CaO + Al ₂ O ₃ + SiO ₂ (39/21/40)	1400	0.067×10^{-9}	292.88
Silicon	CaO + Al ₂ O ₃ + SiO ₂ (40/20/40)	1430	0.01×10^{-9}	292.88
Oxygen	CaO + Al ₂ O ₃ + SiO ₂ (40/20/40)	1430	0.40×10^{-9}	397.48
Iron	CaO + Al ₂ O ₃ + SiO ₂ (30/15/55)	1500	$0.24\text{--}0.31 \times 10^{-9}$	—
Iron	CaO + Al ₂ O ₃ + SiO ₂ (43/22/35)	1500	$0.21\text{--}0.50 \times 10^{-9}$	—
Iron	FeO + SiO ₂ (61/39)	1275	9.6×10^{-9}	167.36
Phosphorous	CaO + Al ₂ O ₃ + SiO ₂ (40/21/39)	1400	0.2×10^{-9}	194.97
G. Diffusion of gases/vapours at 1 atm pressure				
Oxygen	Air	25	2.06×10^{-5}	—
Hydrogen	Air	25	4.10×10^{-5}	—

(Contd.)

TABLE 4.3 Diffusivity of some components in systems of metallurgical interest
(Contd.)

Diffusing component (diffusate)	Diffusion medium or melt	Temperature (°C)	Diffusion coefficient (m ² s ⁻¹)	Activation energy of diffusion (kJ mol ⁻¹)
Carbon dioxide	Air	25	1.64×10^{-5}	—
Ammonia	Air	25	2.36×10^{-5}	—
Water vapour	Air	25	2.56×10^{-5}	—
Water vapour	Nitrogen	25	2.6×10^{-5}	—
Water vapour	Oxygen	450	13.0×10^{-5}	—
Carbon dioxide	Oxygen	500	9.0×10^{-5}	—
Hydrogen	Oxygen	25	7.0×10^{-5}	—
Hydrogen	Oxygen	500	42.0×10^{-5}	—
Hydrogen	Water vapour	500	51.5×10^{-5}	—
Hydrogen	Water vapour	900	114.0×10^{-5}	—
H. Diffusion of gases in dilute aqueous solutions				
Oxygen	Water	20	1.89×10^{-9}	—
Carbon dioxide	Water	20	11.50×10^{-9}	—
Ammonia	Water	20	1.76×10^{-9}	—
Hydrogen	Water	20	5.13×10^{-9}	—
Nitrogen	Water	20	1.64×10^{-9}	—

of movement in a homogeneous system composed of solids and called a *solid solution*. Further, the actual mechanism of diffusion or mode of transfer in solids should also be known or studied. From the view point of study of the mode or mechanism of diffusion, the solids can be classified into the following three categories:

- (i) Interstitial solutions
- (ii) Substitutional solutions
- (iii) Ionic compounds

Diffusion in interstitial solutions

In such systems, the diffusing component occupies interstitial positions. Diffusion of the component proceeds by a series of jumps of the atoms of this component from the original interstitial sites occupied by them to one of the neighbouring sites. For example, carbon occupies octahedral interstitial position or site in γ -iron and its diffusion proceeds by the jump of carbon atoms from one such site to the other. Diffusion coefficient for such a component i can be calculated using the equation

$$D_i = \alpha a^2 p \gamma \exp\left(-\frac{\Delta G}{RT}\right) \quad (4.36)$$

which can also be written as

$$D_i = \alpha a^2 p \gamma \exp\left(\frac{\Delta S}{R}\right) \exp\left(-\frac{\Delta H}{RT}\right) \quad (4.37)$$

or

$$D_i = D_0 \exp\left(-\frac{\Delta H}{RT}\right) \quad (4.38)$$

where

ΔH = activation energy for diffusion

and

$$D_0 = \alpha a^2 p \gamma \exp\left(\frac{\Delta S}{R}\right), \text{ the frequency factor} \quad (4.39)$$

In these equations, α is a geometric factor, the value of which depends upon the type of crystal and is equal to 1/12 for FCC and 1/24 for BCC lattices; a is the lattice parameter of the solvent; p is the number of neighbouring interstitial sites to any specific site from which the component is diffusing; γ is the vibrational frequency of an atom in an interstitial site, and ΔG is the free energy change for an atom to jump from an interstitial site to the neighbouring one.

For experimental determination of diffusion coefficients of interstitial components, Eq. (4.36) is rewritten in the following alternative form:

$$D = \frac{\alpha a^2}{\tau} \quad (4.40)$$

where τ is the mean time of stay of the solute atom in an interstitial site. Diffusion coefficients of interstitial components are usually determined by the internal friction method which yields the value of relaxation time τ_σ for inelastic strain. This relaxation time is related to τ for a BCC lattice by the equation

$$\tau = \frac{3}{2} \tau_\sigma \quad (4.41)$$

Thus, Eq. (4.40) assumes the form

$$D = \left(\frac{1}{24\tau}\right) a^2 = \frac{a^2}{36\tau_\sigma} \quad (4.42)$$

This equation is commonly used for the calculation of diffusion coefficients of interstitial solutes.

EXAMPLE 4.5 Calculate the diffusion coefficient of carbon in α -iron at 500°C from the following data:

Lattice constant of iron = 2.85 Å

Inelastic strain relaxation time (τ_σ) = 4.7×10^{-10} s

Also, calculate (i) the activation energy ΔH , and frequency factor D_0 for diffusion if the value of τ_σ changes to 4.28×10^{-8} s at 300°C, and (ii) the mean time of stay of a carbon atom at an interstitial site. Neglect the effect of change in lattice parameter caused by temperature variation.

Solution According to Eq. (4.42), value of diffusion coefficients, D_{773} and D_{573} at 500°C and 300°C are respectively calculated as

$$\begin{aligned} D_{773} &= \frac{a^2}{36\tau_\sigma} = \frac{(2.85 \times 10^{-8})^2}{36 \times 4.7 \times 10^{-10}} \text{ cm}^2 \text{ s}^{-1} \\ &= 4.8 \times 10^{-8} \text{ cm}^2 \text{ s}^{-1} = 4.8 \times 10^{-12} \text{ m}^2 \text{ s}^{-1} \end{aligned}$$

and

$$D_{573} = \frac{(2.85 \times 10^{-10})^2}{36 \times 4.28 \times 10^{-8}} = 5.3 \times 10^{-14} \text{ m}^2 \text{ s}^{-1}$$

Further, according to Eq. (4.38), we have

$$\ln D = \ln D_0 - \frac{\Delta H}{RT}$$

Substituting the relevant values of D_{773} and D_{573} , we get

$$\ln (4.8 \times 10^{-12}) = \ln D_0 - \frac{\Delta H}{8.3 \times 773}$$

or

$$-26.06 = \ln D_0 - 1.56 \times 10^{-4} \times \Delta H$$

and similarly

$$-30.57 = \ln D_0 - 2.10 \times 10^{-14} \times \Delta H$$

which on simplification yield the required values as

$$\begin{aligned} \Delta H &= 82.0 \text{ kJ} & \text{Ans.} \\ \ln D_0 &= 13.268 \end{aligned}$$

or

$$D_0 = 1.73 \times 10^{-6} \text{ m}^2 \text{ s}^{-1} \quad \text{Ans.}$$

Further, using Eq. (4.41) for mean time, its value at the two temperatures can be calculated as

$$\tau = \frac{3}{2} \tau_\sigma$$

At 773 K

$$\tau_{773} = \frac{3}{2} \times 4.7 \times 10^{-10} = 7.05 \times 10^{-10} \text{ s}$$

and at 573 K

$$\tau_{573} = \frac{3}{2} \times 4.28 \times 10^{-8} = 6.42 \times 10^{-8} \text{ s} \quad \text{Ans.}$$

Diffusion in substitutional solid solutions

Experimental investigations have revealed that diffusion in these systems also takes place by the jumps of atoms from one lattice site to the adjacent or neighbouring sites in the direction of concentration gradient. An atomistic

analysis on this basis leads to the following equation for the self-diffusion coefficient:

$$D = a^2 V \exp \left\{ \left(\frac{\Delta S_m + \Delta S_f}{R} \right) \right\} \exp \left\{ - \left(\frac{Q_m + Q_f}{RT} \right) \right\} \quad (4.43)$$

where

ΔS_f and Q_f , are the entropy and enthalpy changes respectively to form one mole of vacancies, and

ΔS_m and Q_m , are respectively the entropy and enthalpy that must be spent to move a mole of solute into these vacancies.

The term self-diffusion coefficient will be explained in a later subsection. Although the above equation is similar to one used in the case of interstitial diffusion, the experimental determination of diffusion coefficients in this case, i.e. in substitutional solutions, is not as simple as that in the case of interstitial diffusion. To explain this difference in the behaviour of components diffusing in interstitial and in substitutional solutions, we proceed as follows.

We consider a cylindrical rod made up of a substitutional solid solution alloy consisting of components A and B. Let the concentration in moles per unit volume of the component A decrease uniformly in this rod in a direction from left to right as shown in Fig. 4.2. If the total number of atoms ($n_A + n_B$) of components A and B per unit volume of the rod is assumed to be constant throughout the rod, then the concentration of component B must increase from left to right. Now, if diffusion of component A takes place from left to right, then simultaneous diffusion of the component B must take place from right to left. Hence any experimental investigation will register the effect of two counterdiffusing components in which each of these shall follow Fick's first law of diffusion. Thus, the diffusion of components A and B can be expressed mathematically, in accordance with Eq. (4.1), by the following relations:

$$J_A = -D_A \cdot \frac{\partial C_A}{\partial x} \quad (4.44)$$

$$J_B = -D_B \cdot \frac{\partial C_B}{\partial x} \quad (4.45)$$

These equations show that any variation in concentration along the axial direction x of the bar, in which diffusion is taking place, will result from the diffusion of both these components. Strictly speaking, there will also be a flow of vacancies accompanying the diffusion of components and an exact analysis will require their consideration too. But this effect owing to flow of vacancies, in general, is small and therefore not considered.

In the case of multicomponent systems, such changes in concentration will similarly be caused by the diffusion of all components constituting such solid solutions. Thus, experimental determination of diffusion coefficients will not be as simple a problem as determination of thermal conductivity. This simultaneous diffusion of both the components in a binary system will also bring in another

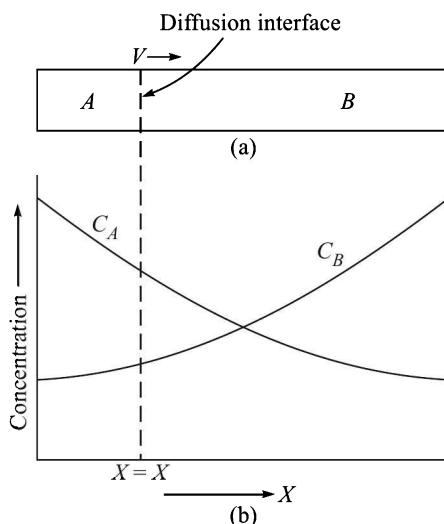


Fig. 4.2 Diffusion in cylindrical rod of substitutional solid solution (A + B): (a) Cylindrical rod of substitutional alloy (A + B); (b) Concentration profile along the rod.

effect which can be illustrated by considering an interface at a distance x from the left-hand end of the same bar, as shown in Fig. 4.2, in which diffusion is taking place. We now consider three possible cases, namely $D_A > D_B$, $D_A < D_B$, and $D_A = D_B$. As the total number of moles of components A and B in any volume element should remain constant, the concentration gradients for the two components A and B must follow the relation

$$\frac{\partial C_A}{\partial x} = \frac{\partial C_B}{\partial x} \quad (4.46)$$

Now consider the components diffusing across the interface x . From Fig. 4.2, it is clear that component A will diffuse from left to right whereas component B will diffuse from right to left. Assuming in the first case, $D_A > D_B$, obviously the number of moles of component A diffusing to the right of the interface x will be greater than those of B diffusing towards the left. Thus, the volume of the solid on the left of the interface under consideration must decrease. If the cross-sectional area of the bar does not change with time, then the position of the interface must change or, in other words, it will move towards the left. Similarly, in the second case with $D_A < D_B$, the interface will move towards the right and in the third case with $D_A = D_B$, which is rarely observed in actual systems, the interface will remain stationary. Kirkendall was the first to observe such an effect experimentally when $D_A \neq D_B$ and hence this effect is called the *Kirkendall effect*.

The rate of movement v of the interface per unit time which is its mass average velocity, as pointed out above, owing to different values of diffusion

coefficients of components A and B, can be expressed, using notations used earlier, as

$$v = \frac{D_A - D_B}{C_A + C_B} \frac{\partial C_A}{\partial x} \quad (4.47)$$

In their classic experiments, Smigelskas and Kirkendall¹ studied the diffusion of copper and zinc in α -brass by forming a diffusion couple and marking the boundary between the two alloys of different compositions by means of wires of a non-reacting refractory metal such as molybdenum. Since Kirkendall's work, a number of other systems have also been studied. In these systems, two alloys of different compositions are welded together with fine refractory metal wires placed at the weld interface. The distance of these wires from one end of this couple is measured as a function of time and this data, along with the concentration profile in a direction perpendicular to the weld, is made use of to estimate data on diffusion of the components by applying the following mass transfer analysis.

Consider an infinitesimal element of width δx in the bar in which diffusion takes place in the axial direction designated as the x -direction, as shown in Fig. 4.3. We now derive an expression for the change in concentration of component A with time in the element δx situated at a distance x from the lefthand end of the bar. Mass balance for this element yields the relation:

$$\begin{aligned} & (\text{Rate of change of the concentration of component A per unit time}) \\ & \times (\text{Volume of the element}) = (\text{Amount of component A entering the element per unit time at interface } x = x) - (\text{Amount of this component A leaving the element per unit time at interface } x = x + \delta x) \end{aligned} \quad (4.48)$$

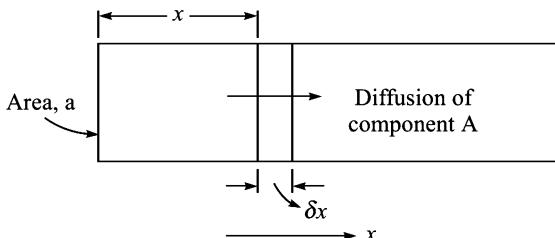


Fig. 4.3 Diffusion along axial direction in a bar.

Assuming a to be the cross-sectional area of the rod, the rate of change of the amount ∂m_A of component A per unit time in the volume element is expressed as

$$\partial m_A = a \left(\frac{\partial C_A}{\partial t} \right) \delta x \quad (4.49)$$

¹ Smigelskas, A.D. and Kirkendall, E.O., *Trans. AlME*, **171** (1947), 130.

The total amount $(m_A)_{x=x}$ of the component A entering at the interface $x = x$, will be due to the following two modes of transfer: (i) Due to Kirkendall effect, i.e. due to the movement of the interface. This amount represented by the symbol $(m_A)_k$ will be

$$(m_A)_k = (C_A v a)_{x=x} \quad (4.50)$$

where v is the average velocity at which the interface moves. (ii) Due to the diffusion across the interface. This amount, represented by the symbol $(m_A)_D$ will be

$$(m_A)_D = -D_A \left(\frac{\partial C_A}{\partial x} \right)_{x=x} a \quad (4.51)$$

Thus

$$\begin{aligned} (m_A)_{x=x} &= (m_A)_k + (m_A)_D \\ &= \left\{ (C_A v a)_{x=x} - D_A \left(\frac{\partial C_A}{\partial x} \right)_{x=x} a \right\} \end{aligned} \quad (4.52)$$

Similarly, the amount $(m_A)_{x=x+\delta x}$ of the component A leaving the volume element at $x = x + \delta x$ will be

$$(m_A)_{x=x+\delta x} = \left\{ (C_A v a)_{x=x+\delta x} - D_A \left(\frac{\partial C_A}{\partial x} \right)_{x=x+\delta x} a \right\} \quad (4.53)$$

Substitution of Eqs. (4.49), (4.52) and (4.53) in Eq. (4.48), representing the mass balance of component A yields

$$\partial m_A = \{(m_A)_{x=x} - (m_A)_{x=x+\delta x}\}$$

or

$$a \left(\frac{\partial C_A}{\partial t} \right) \delta x = \left[a \left\{ C_A v - D_A \left(\frac{\partial C_A}{\partial x} \right)_{x=x} \right\} \right] - \left[a \left\{ C_A v - D_A \left(\frac{\partial C_A}{\partial x} \right)_{x=x+\delta x} \right\} \right] \quad (4.54)$$

Using Taylor's expansion and neglecting the second and higher order terms, we get

$$\frac{\partial C_A}{\partial t} = - \frac{\partial}{\partial x} \left\{ C_A v - D_A \left(\frac{\partial C_A}{\partial x} \right) \right\} \quad (4.55)$$

Substitution of the relation for v from Eq. (4.47) in Eq. (4.55), leads to

$$\begin{aligned} \frac{\partial C_A}{\partial t} &= - \frac{\partial}{\partial x} \left[\frac{C_A (D_A - D_B)}{C_A + C_B} \left(\frac{\partial C_A}{\partial x} \right) - D_A \left(\frac{\partial C_A}{\partial x} \right) \right] \\ &= \frac{\partial}{\partial x} \left[\frac{C_B D_A + C_A D_B}{C_A + C_B} \left(\frac{\partial C_A}{\partial x} \right) \right] \end{aligned} \quad (4.56)$$

Further, mole fractions N_A and N_B of the components A and B respectively of the solution are defined as per Eq. (4.3) by the relations

$$N_A = \frac{C_A}{C_A + C_B} \quad (4.57a)$$

and

$$N_B = \frac{C_B}{C_A + C_B} \quad (4.57b)$$

Making use of these, Eq. (4.56) can be written in the form

$$\frac{\partial C_A}{\partial t} = \frac{\partial}{\partial x} \left[\tilde{D} \left(\frac{\partial C_A}{\partial x} \right) \right] \quad (4.58)$$

where the function \tilde{D} , defined by the equation

$$\tilde{D} = (D_A N_B + D_B N_A) \quad (4.59)$$

is called the *interdiffusion* or *mutual* or *chemical diffusion* coefficient and D_A and D_B are known as *intrinsic diffusion coefficients* of components A and B respectively. Equation (4.59), known as *Darken's equation*, is used for experimental determination of the diffusion coefficient. For this purpose, two methods are commonly adopted. In the next subsection, we will briefly discuss the principles of these two methods.

Determination of diffusion coefficients in substitutional solutions. Two methods have been used for experimental determination of interdiffusion coefficient \tilde{D} and hence the intrinsic diffusion coefficients, D_A and D_B . These methods, namely the Matano method and the Grube method will be discussed briefly along with their limitations.

Matano method. In this method, the concentration profile along the direction of diffusion is determined as a function of time by taking samples at different distances along the diffusion path and the data so obtained are analysed mathematically to obtain diffusion coefficients. For the mathematical analysis, Eq. (4.58) is transformed to a new coordinate system by the introduction of a new function λ such that

$$\lambda = \frac{x}{\sqrt{t}} \quad (4.60)$$

Thus

$$\frac{\partial \lambda}{\partial x} = \frac{1}{\sqrt{t}} \quad (4.61)$$

and

$$\frac{\partial \lambda}{\partial t} = -\frac{x}{2(t)^{3/2}} \quad (4.62)$$

With the help of Eqs. (4.60) to (4.62), Eq. (4.58) assumes the form

$$-\frac{1}{2} \lambda \frac{\partial C_A}{\partial \lambda} = \frac{\partial}{\partial \lambda} \left\{ \left(\tilde{D} \frac{\partial C_A}{\partial \lambda} \right) \right\}$$

or

$$\tilde{D} = \frac{-\frac{1}{2} \int_{C_{A1}}^{C_{A2}} \lambda dC_A}{\frac{dC_A}{d\lambda}} \quad (4.63)$$

If the concentration profiles are determined for a fixed time, then Eq. (4.63) can be expressed in the form

$$\tilde{D} = -\frac{1}{2t} \left(\frac{\partial x}{\partial C_A} \right) \left[\int_{C_{A1}}^{C_{A2}} x \cdot dC_A \right] \quad (4.64)$$

Equation (4.64) is used to calculate the value of \tilde{D} from experimental data which is obtained in the form of concentration profile of a component at a fixed time as shown in Fig. 4.4. For evaluating the integral in the above equation, one should first draw the concentration (C) and distance (x) axes. The x -axis is drawn at a position such that the two shaded areas in Fig. 4.4 are equal. The weld surface at this axis is known as Matano interface. Now suppose, we want to determine the diffusion coefficient at a concentration corresponding to the point O . Firstly, we draw a tangent at the point O and then calculate $\partial C_A / \partial x$ and hence $\partial x / \partial C_A$. We then determine the cross-hatched area which will obviously be equal to the integral $\int_O^{C_A} x \cdot dC_A$ at the point O . Substitution of these

values in Eq. (4.64) leads to determination of the value of \tilde{D} . It should, however, be noted that this method is of general applicability. But the other method, namely the Grube method, described later, is applicable only to the systems for which \tilde{D} is constant.

We now demonstrate the application of the Matano method by the following example.

EXAMPLE 4.6 A gold-nickel diffusion couple of limiting composition 10 and 50 At per cent nickel is heated at 925°C for 25 days. Thin slices 0.03 cm thick and parallel to the original interface are machined and analysed, giving the following data:

Slice no.	Distance from one end (cm)	At % Ni	Slice no.	Distance from one end (cm)	At % Ni
1	0.00	10.0	6	0.15	24.0
2	0.03	10.5	7	0.18	31.5
3	0.06	12.5	8	0.21	38.0
4	0.09	15.5	9	0.24	46.0
5	0.12	19.0	10	0.27	50.0

Calculate the interdiffusion coefficient at 20 At % nickel.

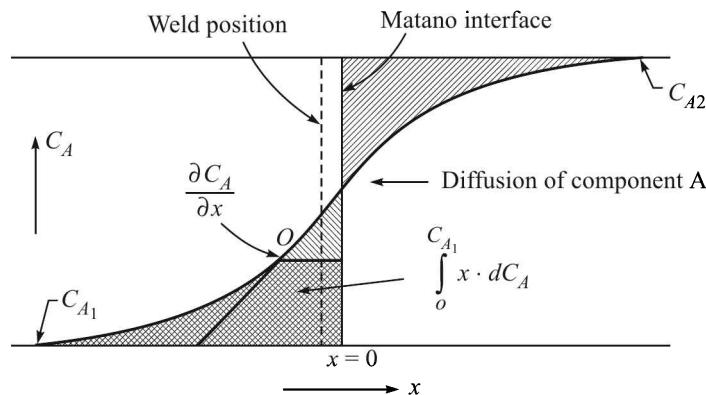


Fig. 4.4 Matano method for determination of diffusion coefficient in substitutional solutions.

Solution The concentration profile as a function of distance is shown in Fig. 4.5. A tangent has been drawn to the curve at the point P corresponding to 20 At % nickel.

$$\text{At } 20 \text{ At \% Ni, } \frac{dC}{dx} = \frac{10}{0.066} = 151.5 \text{ At \% cm}$$

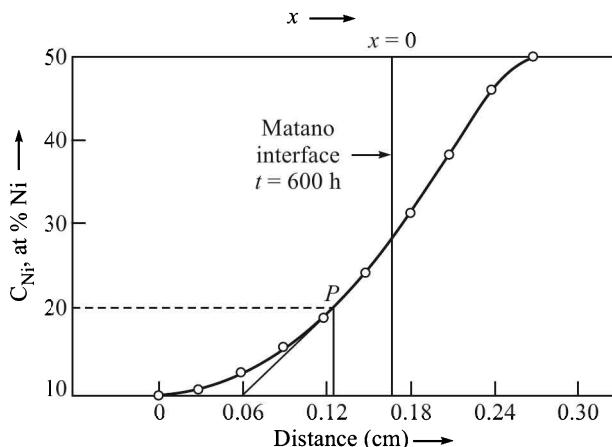


Fig. 4.5 Concentration profiles as a function of distance in Au-Ni diffusion couple.

Area under the curve from 10 to 20 At % Ni is

$$\int_{C_{Ni}=10}^{C_{Ni}=20} x dC = -0.426 \text{ cm At \%}$$

Time, $t = 25 \times 24 \times 3600 \text{ s} = 2.16 \times 10^6 \text{ s}$

Thus, \tilde{D} from Eq. (4.64) will be

$$\begin{aligned}
 \tilde{D} &= -\frac{1}{2t} \left(\frac{\partial x}{\partial C_{\text{Ni}}} \right) \left\{ \int_{C_{\text{Ni}}=10}^{C_{\text{Ni}}=20} x \cdot dC_{\text{Ni}} \right\} \\
 &= -\frac{1}{2 \times 2.16 \times 10^6} \frac{1}{151.5} (-0.426) \text{ cm}^2 \text{ s}^{-1} \\
 &= \frac{0.426 \times 10^{-4}}{2 \times 2.16 \times 10^6 \times 151.5} \text{ m}^2 \text{ s}^{-1} \\
 &= 6.49 \times 10^{-14} \text{ m}^2 \text{ s}^{-1} \quad \text{Ans.}
 \end{aligned}$$

Grube method. In this method, the value of \tilde{D} is assumed to be constant, i.e. independent of composition and hence this method is applicable only to the following three special cases:

- (i) Those in which a radioactive isotope diffuses in the matrix of its own element.
- (ii) For diffusion in dilute solutions of solute B, i.e., with $N_B \rightarrow 0$, in solvent A for which the term $(D_A N_B + N_A D_B)$ is approximately equal to D_B .
- (iii) For diffusion in systems in which the composition does not change appreciably and thus \tilde{D} becomes practically constant.

When \tilde{D} is constant, Eq. (4.58) on division of both sides by the total number of moles per unit volume, takes the following modified form

$$\frac{\partial N_A}{\partial t} = \tilde{D} \left(\frac{\partial^2 N_A}{\partial x^2} \right) \quad (4.65)$$

This equation can be written in a more commonly used alternative form by replacing the mole fraction terms by the corresponding concentration terms, as given below:

$$\frac{\partial C_A}{\partial t} = D \left(\frac{\partial^2 C_A}{\partial x^2} \right) \quad (4.66)$$

This equation can also be obtained directly from Eq. (4.58) with the assumption of constant D value and is also known as *Fick's second law of diffusion*. It is used for solution of problems related to unsteady state diffusion. A general form of this equation which is applicable to diffusion in all three directions will be derived later.

The boundary conditions for solution of Eq. (4.65) will be

$$N_A = N_{A1} \quad \text{for } t = 0 \quad \text{at } 0 < x < \infty \quad (4.67\text{a})$$

$$N_A = N_{A2} \quad \text{for } t = 0 \quad \text{at } -\infty < x < 0 \quad (4.67\text{b})$$

These conditions are based on the fact that the initial concentration of component A is constant on either side of the diffusion couple and is equal to N_{A1} and N_{A2} in the two pieces. Hence, the solution of Eq. (4.65) will be

$$N_A = N_{A1} + \left(\frac{N_{A2} - N_{A1}}{2} \right) \left\{ 1 - \operatorname{erf} \left(\frac{x}{2\sqrt{Dt}} \right) \right\} \quad (4.68)$$

where

$$\operatorname{erf} \left(\frac{x}{2\sqrt{Dt}} \right) \equiv \frac{2}{\sqrt{\pi}} \left\{ \int_0^{x/(2\sqrt{Dt})} \exp(-\xi^2) d\xi \right\} \quad (4.69)$$

and the notation erf represents the Gauss error function.

For application of the above equation, the concentration of component A is determined experimentally directly or indirectly along the direction of diffusion at various values of x . Substitution of these values in Eq. (4.68) yields the value of $\operatorname{erf} x/2\sqrt{Dt}$. Making use of the standard tables for error functions as given in Table 4.4, the value of the argument $x/2\sqrt{Dt}$ is found for these values of the error function. Substitution of relevant values of x and t in these arguments yields the value of the diffusion coefficient.

Application of the above method is demonstrated below by an example.

EXAMPLE 4.7 During an experiment on the case carburization of a 0.2% C steel under a gaseous atmosphere having carbon potential equivalent to 1% C in steel, the concentration of carbon at a distance of 0.1 cm from the surface after 10 hours was found to be 0.52%. Calculate the interdiffusion coefficient of carbon in iron using the Grube method.

Solution From the given data, we have

$$\text{Time, } t = 10 \times 3600 = 36000 \text{ s}$$

$$\text{Distance, } x = 0.1 \text{ cm} = 0.001 \text{ m}$$

If the concentration is taken in % C, using Eq. (4.68), we have

$$0.52 = 0.2 + \frac{1.0 - 0.2}{2} \left[1 - \operatorname{erf} \left(\frac{x}{2\sqrt{Dt}} \right) \right]$$

or

$$\left[1 - \operatorname{erf} \left(\frac{x}{2\sqrt{Dt}} \right) \right] = \frac{0.52 - 0.2}{0.4} = 0.8$$

or

$$\operatorname{erf} \left(\frac{x}{2\sqrt{Dt}} \right) = 0.20$$

From the table of error functions (Table 4.4), we have

$$\frac{x}{2\sqrt{Dt}} = 0.18$$

TABLE 4.4 Error functions

<i>x</i>	<i>erf x</i>	<i>erfc x</i>	<i>x</i>	<i>erf x</i>	<i>erfc x</i>
0.00	0.000000	$1.000000 \cdot 10^0$	1.65	0.980376	$0.196244 \cdot 10^{-1}$
0.05	0.056372	$0.943628 \cdot 10^0$	1.70	0.983790	$0.162095 \cdot 10^{-1}$
0.10	0.112463	$0.887537 \cdot 10^0$	1.75	0.986672	$0.133283 \cdot 10^{-1}$
0.15	0.167996	$0.832004 \cdot 10^0$	1.80	0.989090	$0.109095 \cdot 10^{-1}$
0.20	0.222703	$0.777297 \cdot 10^0$	1.85	0.991111	$0.888897 \cdot 10^{-2}$
0.25	0.276326	$0.723674 \cdot 10^0$	1.90	0.992790	$0.720957 \cdot 10^{-2}$
0.30	0.328627	$0.671373 \cdot 10^0$	1.95	0.994179	$0.582066 \cdot 10^{-2}$
0.35	0.379382	$0.620618 \cdot 10^0$	2.00	0.995322	$0.467773 \cdot 10^{-2}$
0.40	0.428392	$0.571608 \cdot 10^0$	2.05	0.996258	$0.374190 \cdot 10^{-2}$
0.45	0.475482	$0.524518 \cdot 10^0$	2.10	0.997021	$0.297946 \cdot 10^{-2}$
0.50	0.520500	$0.479500 \cdot 10^0$	2.15	0.997639	$0.236139 \cdot 10^{-2}$
0.55	0.563323	$0.436677 \cdot 10^0$	2.20	0.998137	$0.186284 \cdot 10^{-2}$
0.60	0.603856	$0.396144 \cdot 10^0$	2.25	0.998537	$0.146271 \cdot 10^{-2}$
0.65	0.642029	$0.357971 \cdot 10^0$	2.30	0.998857	$0.114317 \cdot 10^{-2}$
0.70	0.677801	$0.322199 \cdot 10^0$	2.35	0.999111	$0.889265 \cdot 10^{-3}$
0.75	0.711156	$0.288844 \cdot 10^0$	2.40	0.999312	$0.688512 \cdot 10^{-3}$
0.80	0.742101	$0.257899 \cdot 10^0$	2.45	0.999469	$0.530578 \cdot 10^{-3}$
0.85	0.770668	$0.229332 \cdot 10^0$	2.50	0.999593	$0.406950 \cdot 10^{-3}$
0.90	0.796908	$0.203092 \cdot 10^0$	2.55	0.999689	$0.310660 \cdot 10^{-3}$
0.95	0.820891	$0.179109 \cdot 10^0$	2.60	0.999764	$0.236034 \cdot 10^{-3}$
1.00	0.842701	$0.157299 \cdot 10^0$	2.65	0.999822	$0.178487 \cdot 10^{-3}$
1.05	0.862436	$0.137564 \cdot 10^0$	2.70	0.999866	$0.134332 \cdot 10^{-3}$
1.10	0.880205	$0.119795 \cdot 10^0$	2.75	0.999899	$0.100621 \cdot 10^{-3}$
1.15	0.896124	$0.103876 \cdot 10^0$	2.80	0.999926	$0.750126 \cdot 10^{-4}$
1.20	0.910314	$0.896860 \cdot 10^{-1}$	2.85	0.999944	$0.556557 \cdot 10^{-4}$
1.25	0.922900	$0.770999 \cdot 10^{-1}$	2.90	0.999959	$0.410973 \cdot 10^{-4}$
1.30	0.934008	$0.659921 \cdot 10^{-1}$	2.95	0.999970	$0.302024 \cdot 10^{-4}$
1.35	0.943762	$0.562378 \cdot 10^{-1}$	3.00	0.999979	$0.220899 \cdot 10^{-4}$
1.40	0.952285	$0.477149 \cdot 10^{-1}$	3.05	0.999984	$0.160792 \cdot 10^{-4}$
1.45	0.959695	$0.403050 \cdot 10^{-1}$	3.10	0.999988	$0.116481 \cdot 10^{-4}$
1.50	0.961051	$0.338949 \cdot 10^{-1}$	3.15	0.999992	$0.830760 \cdot 10^{-5}$
1.55	0.971623	$0.283773 \cdot 10^{-1}$	3.20	0.999994	$0.602513 \cdot 10^{-5}$
1.60	0.976348	$0.236516 \cdot 10^{-1}$			

and, therefore, substituting the value of *t*, we get

$$\frac{0.001}{2\sqrt{D \times 36000}} = 0.18$$

or

$$\sqrt{D} = \frac{0.001}{2 \times 0.18 \times \sqrt{36000}}$$

Hence

$$D = 2.15 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$$

Ans.

Intrinsic diffusion coefficients and atomic mobilities. Though the diffusion of any component takes place in the direction of its decreasing concentration, i.e. in the direction of negative concentration gradient, the true driving force from the thermodynamic point of view as mentioned earlier will be its chemical potential or the activity gradient. Thus we can express the driving force F_A acting on an atom of species A, by the equation

$$F_A = -\frac{1}{N} \left(\frac{\partial \bar{G}_A}{\partial x} \right) \quad (4.70)$$

where N is the Avogadro's number and \bar{G}_A the partial molar free energy of component A expressed by the following thermodynamic relation

$$\begin{aligned} \bar{G}_A &= G_A^0 + RT \ln a_A \\ &= G_A^0 + RT \ln \gamma_A + RT \ln N_A \end{aligned} \quad (4.71)$$

where a_A and γ_A are respectively the Raoultian activity and activity coefficient of component A. With this, Eq. (4.70) takes the form

$$F_A = -\left(\frac{RT}{N} \right) \left[\frac{\partial \ln \gamma_A}{\partial x} + \frac{\partial \ln N_A}{\partial x} \right] \quad (4.72)$$

If B_A be the atomic mobility of atoms of component A or their velocity under the influence of unit force, then the velocity v_{Ax} of A atoms in the x -direction under the force defined by Eq. (4.72) will be expressed as

$$\begin{aligned} v_{Ax} &= B_A F_A = -B_A \left(\frac{RT}{N} \right) \left[\frac{\partial \ln \gamma_A}{\partial x} + \frac{\partial \ln N_A}{\partial x} \right] \\ &= -k B_A T \left[\frac{\partial \ln \gamma_A}{\partial x} + \frac{\partial \ln N_A}{\partial x} \right] \end{aligned} \quad (4.73)$$

where $k (= R/N)$ is the Boltzmann's constant.

If C_A be the concentration of A atoms per unit volume expressed as moles \cdot vol $^{-1}$, the flux J_A of the atoms of component A, i.e. the number of atoms of component A crossing per unit cross-sectional area per unit time, will be expressed as

$$J_A = -B_A C_A k T \left[\frac{\partial \ln \gamma_A}{\partial x} + \frac{\partial \ln N_A}{\partial x} \right] \quad (4.74)$$

From Eqs. (4.1) and (4.74), we get

$$D_A = \frac{\partial \ln C_A}{\partial x} = B_A k T \left[\frac{\partial \ln \gamma_A}{\partial x} + \frac{\partial \ln N_A}{\partial x} \right] \quad (4.75)$$

Further, the mole fraction N_A of the component A is related to concentration by the equation

$$N_A = \frac{C_A}{\sum C_A} \quad (4.76)$$

Thus, assuming that the total moles of solution per unit volume, i.e. $\sum C_A$ remain unchanged, we can write

$$\frac{\partial \ln C_A}{\partial x} = \frac{\partial \ln N_A}{\partial x} \quad (4.77)$$

Hence, Eq. (4.75) becomes

$$D_A = B_A kT \left[1 + \frac{\partial \ln \gamma_A}{\partial \ln N_A} \right] \quad (4.78)$$

We can write a similar equation for D_B , too. For diffusion occurring in an ideal solution, for example, the diffusion of a radioactive element in its own matrix, $\gamma_A = 1$. Therefore, for such cases

$$D_A^* = B_A kT \quad (4.79)$$

where D_A^* is called the self-diffusion coefficient of component A. This relation, called the *Nernst-Einstein equation*, correlates the self-diffusion coefficients, also known as tracer-diffusion coefficients with atomic mobilities. From our knowledge of the values of these diffusion coefficients and other relevant thermodynamic data on concerned systems, we can calculate with the help of Eq. (4.78), the intrinsic diffusion coefficients D_A and D_B at any desired composition and from these, the inter-diffusion coefficient \tilde{D} . To calculate self-diffusion coefficients from our knowledge of the inter-diffusion coefficients and vice-versa, we make use of an alternative expression which can be derived as follows. From Eqs. (4.59) and (4.78), we get

$$\tilde{D} = N_B B_A kT \left[1 + \frac{\partial \ln \gamma_A}{\partial \ln N_A} \right] + N_A B_B kT \left[1 + \frac{\partial \ln \gamma_B}{\partial \ln N_B} \right] \quad (4.80)$$

According to Gibbs-Duhem equation

$$N_A \partial \ln \gamma_A + N_B \partial \ln \gamma_B = 0 \quad (4.81)$$

Hence

$$N_A \frac{\partial \ln \gamma_A}{\partial N_A} + N_B \frac{\partial \ln \gamma_B}{\partial N_B} = 0 \quad (4.82)$$

or

$$\frac{\partial \ln \gamma_A}{\partial \ln N_A} - \frac{\partial \ln \gamma_B}{\partial \ln N_B} = 0 \quad (4.83)$$

With this, Eq. (4.80) assumes the following alternative form:

$$\begin{aligned} \tilde{D} &= (N_B B_A kT + N_A B_B kT) \left(1 + \frac{\partial \ln \gamma_A}{\partial \ln N_A} \right) \\ &= (N_B D_A^* + N_A D_B^*) \left(1 + \frac{\partial \ln \gamma_A}{\partial \ln N_A} \right) = (N_B D_A^* + N_A D_B^*) \left(1 + \frac{\partial \ln \gamma_A}{\partial \ln N_A} \right) \end{aligned} \quad (4.84)$$

where according to Eq. (4.79), $D_B^* = B_B kT$.

Equation (4.84) can be used to calculate intrinsic and self-diffusion coefficients for experimentally determined values of \tilde{D} as a function of composition.

The use of the above equations is demonstrated by the following example.

EXAMPLE 4.8 The activity coefficient of lead in Pb–Cd alloys is calculated using the following equation:

$$\frac{\ln \gamma_{\text{Pb}}}{(1 - N_{\text{Pb}})^2} = 1.5$$

where N_{Pb} is the atomic fraction of lead in the alloy. If the self-diffusion coefficient of lead and cadmium at 482°C are respectively $2 \times 10^{-7} \text{ m}^2 \text{ s}^{-1}$ and $4 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$, calculate the inter-diffusion coefficient of alloy of this system containing 25 atomic per cent of lead.

Solution The given equation for calculation of γ_{Pb}

$$\frac{\ln \gamma_{\text{Pb}}}{(1 - N_{\text{Pb}})^2} = 1.5$$

yields the following relation

$$\frac{\partial \ln \gamma_{\text{Pb}}}{\partial \ln N_{\text{Pb}}} = 3.0N_{\text{pb}}^2 - 3.0N_{\text{pb}}$$

For the given alloy

$$N_{\text{pb}} = 0.25$$

and therefore

$$N_{\text{Cd}} = 0.75$$

Further, self-diffusion coefficient of Pb, $D_{\text{Pb}}^* = 2 \times 10^{-7} \text{ m}^2 \text{ s}^{-1}$ and, self-diffusion coefficient of Cd, $D_{\text{Cd}}^* = 4 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$.

Therefore, using Eq. (4.84), the inter-diffusion coefficient \tilde{D} is calculated as follows for the alloy of given composition.

$$\begin{aligned}\tilde{D} &= (N_{\text{Cd}} D_{\text{Pb}}^* + N_{\text{Pb}} D_{\text{Cd}}^*) \left(1 + \frac{\partial \ln \gamma_{\text{Pb}}}{\partial \ln N_{\text{Pb}}} \right) \\ &= (0.75 \times 2 \times 10^{-7} + 0.25 \times 4 \times 10^{-10}) [1 + 3.0(0.25)^2 - 3.0 \times 0.25] \\ &= (1.5 \times 10^{-7} + 1.0 \times 10^{-10})(0.4375) \\ &= 6.56 \times 10^{-8} \text{ m}^2 \text{ s}^{-1}\end{aligned}\quad \text{Ans.}$$

Diffusion in ionic compounds

In ionic compounds, diffusion takes place by the movement of ions through jumps on vacant sites. An ionic compound is considered to consist of two sublattices, namely an anionic sub lattice and a cationic sublattice. The number of vacancies on these two sublattices may be different, depending upon the type of defects present in such compounds. So, the mobility of different ionic species will be different. Hence, contributions to the process of overall diffusion by the different ionic species in a particular compound will be different, i.e. the value of mobility B and hence velocity v and also the value of diffusion co-efficient D will be different. Further, as diffusion in ionic compounds involves

the movement of charged particles, namely the ions, it will simultaneously involve flow of electric current owing to each type of ions present, i.e. the different cations and anions present in the crystalline compound. Hence, for such compounds the diffusion coefficient will also be related to the electrical conductivity. Such a relation can be derived as follows.

Using Eq. (4.73), the velocity v_i of an ionic species i may be linked to the electrical potential gradient and the ionic mobility by the following relation

$$v_i = B_i F_i = -B_i Z_i e \left(\frac{\partial E}{\partial x} \right) \quad (4.85)$$

Thus

$$J_i = +n_i v_i = -n_i B_i Z_i e \left(\frac{\partial E}{\partial x} \right) \quad (4.86)$$

where the symbols B_i , J_i and n_i represent respectively the mobility, flux and concentration, in number of ions per unit volume of the i th ion, E is the electrical potential measured along the x -direction and $Z_i e$ is the charge on the i th ion. Thus, the current I_i owing to the movement of the i th ion will be

$$I_i = z_i e J_i = -z_i^2 n_i e^2 B_i \left(\frac{\partial E}{\partial x} \right) \quad (4.87)$$

Hence, ionic conductivity σ_i owing to the i th ionic species, is expressed by the relation

$$\sigma_i = -\frac{I_i}{\partial E / \partial x} = +z_i^2 e^2 n_i B_i \quad (4.88)$$

Further, according to Eq. (4.79), for a single component system, self-diffusion coefficient D^* and intrinsic diffusion coefficient D will be

$$D = D_i^* = k T B_i \quad (4.89)$$

Comparison of Eqs. (4.88) and (4.89) leads to the equation

$$D_i = \frac{k T \sigma_i}{z_i^2 e^2 n_i} \quad (4.90)$$

This equation is called the *Extended Nernst-Einstein equation*. Thus, from Eq. (4.90), it follows that for calculation of the value of diffusion coefficient D_i of the i th ionic species, we must know the value of its conductivity σ_i . The numerical value of σ_i will be equal to the total conductivity of the ionic compound multiplied by the fraction of the current conducted by the i th ionic species, called its *transference number* and represented by the symbol t_i . It is obvious that the sum of the transference numbers for all the current carrying species in the crystal will be unity. Thus

$$\sum_i (t_i + t_e) = 1 \quad (4.91)$$

where t_e is the fraction of the total current carried by electrons. The transference numbers for various ionic species of crystals can be determined experimentally and therefore the value of the diffusion coefficients of ionic species.

A case of immense practical importance in ionic conduction of compounds is the one in which one particular species is the dominant current carrier, i.e. its transference number is almost equal to unity. For example, in a NaCl crystal, the transference number of Na^+ ion is close to unity. For such cases, we can write Eq. (4.90) in the form

$$D_i = \frac{kT\sigma}{(z_i e)^2 n_i} \quad (4.92)$$

where σ is the specific conductivity of the compound. Such systems are of enormous value in determining the thermodynamic and kinetic data of various systems. In 1957, Kiukkola and Wagner¹ found that if ZrO_2 crystal is stabilized with 15% CaO, its structure changes from monoclinic to cubic and the transference number of oxygen-ions O^{2-} becomes unity in a certain range of surrounding oxygen partial pressure, p_{O_2} . This ionic conductor has found extensive applications in the experimental determinations of thermodynamic and kinetic data on systems involving oxygen either in the combined form, e.g. in oxides and silicates or in the dissolved form in metals. This ionic conductor, frequently called a solid electrolyte, has also been used in fuel cells.

The transference number of oxygen-ions $t_{\text{O}^{2-}}$ in such cases is dependent upon the oxygen partial pressure p_{O_2} in the surrounding atmosphere and therefore it remains unity only for a certain specific oxygen partial pressure depending upon temperature. For example, calcia-stabilized zirconia has transference number for oxygen-ions equal to unity for a pressure range of 10^{-15} to 1 atm at 1000°C. In fact, in all such crystals, which may be designated as defect-crystals, because of the presence of anionic or cationic vacancies, the transference number becomes dependent on the partial pressure of the component present in the gas-phase.

Application of some of the equations derived above is illustrated with the help of the following example.

EXAMPLE 4.9 CoO is known to have transference number equal to unity for Co^{2+} ions. The value of inter-diffusion coefficient \tilde{D} at 1000°C is found to be $2.2 \times 10^{-11} \text{ m}^2 \text{ s}^{-1}$. Calculate the self-diffusion coefficient for cobalt-ions (Co^{2+}) at this temperature. The logarithm of the ionic fraction of Co^{2+} in the crystal is directly proportional to the logarithm of oxygen partial pressure. Further, the concentration of Co^{2+} ions has been found to have the following values at the indicated partial pressures of oxygen.

- (i) At $p_{\text{O}_2} = 0.047 \text{ atm}$ $N_{\text{Co}^{2+}} = 0.4963$
- (ii) At $p_{\text{O}_2} = 0.51 \text{ atm}$ $N_{\text{Co}^{2+}} = 0.4936$

Solution According to Eq. (4.83), we have

$$\frac{\partial(\ln a_{\text{Co}^{2+}})}{\partial(\ln N_{\text{Co}^{2+}})} = \frac{\partial(\ln a_{\text{O}^{2-}})}{\partial(\ln N_{\text{O}^{2-}})} = \frac{1}{2} \left(\frac{\partial(\ln p_{\text{O}_2})}{\partial(\ln N_{\text{O}^{2-}})} \right) \quad (\text{since } \text{O}_2 = 2\text{O}^{2-})$$

¹K. Kiukkola and C. Wagner, J. of Electrochem. Soc., **104**, 379 (1957).

$$\begin{aligned}
 &= -\frac{1}{2} \frac{\partial(\ln p_{O_2})}{\partial(\ln N_{O^{2+}})} \quad (\text{since } N_{O^{2-}} + N_{Co^{2+}} = 1) \\
 &= \frac{1}{2} \left[\frac{\ln(0.047) - \ln(0.51)}{\ln(0.4963) - \ln(0.4936)} \right] = 218.5
 \end{aligned}$$

According to Eq. (4.84), we have

$$\begin{aligned}
 \tilde{D} &= (N_{CO^{2+}} D_{O^{2-}}^* + N_{O^{2-}} D_{Co^{2+}}^*) \left(\frac{\partial(\ln a_{Co^{2+}})}{\partial(\ln N_{Co^{2+}})} \right) \\
 &= N_{O^{2-}} D_{Co^{2+}}^* \left(\frac{\partial(\ln a_{Co^{2+}})}{\partial(\ln N_{Co^{2+}})} \right)
 \end{aligned}$$

As the transference number of Co^{2+} is unity, hence on substitution of the relevant values in the equation for \tilde{D} we get

$$2.2 \times 10^{-11} \approx 0.5 D_{Co^{2+}}^* (218.5)$$

or

$$D_{Co^{2+}}^* = 2 \times 10^{-13} \text{ m}^2 \text{ s}^{-1} \quad \text{Ans.}$$

Diffusion of gases through porous solids

In a number of metallurgical reactions involving solids and gases as, for example, in the gaseous reduction of iron ore, we require a knowledge of the diffusion coefficients of the gas through porous reacted solids. Diffusion of gases in these solids can take place by three different modes as follows:

(i) *Bulk diffusion.* This is the normal mode of diffusion of gases. It is predominant, in case the diameter of pores is much larger than the mean free path of the gas. Such a condition will, in general, prevail in gases under high pressures and high temperatures, because under these conditions the mean free path of the gas molecules will become very small.

(ii) *Knudsen diffusion.* In this case, the diffusion of gas proceeds by repeated collisions with the surface of the pores or the pore-walls. Such a condition exists under low pressures of gas and for small pore-size, because the smaller diameter of pores will lead to more frequent collisions of the gas molecules with the solid surface as compared to collisions among themselves. Knudsen diffusion coefficient D_K at low pressures is related to the pore-diameter and temperature by the equation

$$D_K = \left[97r \left(\frac{T}{M_g} \right)^{1/2} \right] \text{ m}^2 \text{ s}^{-1} \quad (4.93a)$$

where r is the radius of the pore in metres, T the absolute temperature in °K and M_g , the molecular weight of the gas. In order to determine the relative roles of bulk and Knudsen diffusions in a porous solid, we compare the mean free path

of the gas as indicated by Eq. (4.24) with the pore-radius. If the pore-radius is far greater than the mean free path, then the effect of D_K , is neglected in calculations for the diffusion coefficient and vice versa. However, when both these parameters are of the same order, they have to be taken into account in such calculations for the diffusion coefficient.

Thus, taking into account the bulk diffusion coefficient D_B and the Knudsen diffusion coefficient D_K , the overall diffusion coefficient D is expressed by the relation.

$$\frac{1}{D} = \frac{1}{D_B} + \frac{1}{D_K} \quad (4.93b)$$

(iii) *Surface diffusion.* This mode plays an effective role at low temperatures and is due to the adsorption of the gas at the surface followed by subsequent diffusion from one vacant position to the other on the surface. To take into account the effect of surface diffusion, which in metallurgical systems is generally negligible, its effect is added to that of the bulk diffusion.

Apart from the above three major modes of diffusion in porous solids, the diffusing gas may also take a zig-zag path depending upon the pore geometry. To take this effect into account as well, the calculated value of diffusion coefficient D is further modified by a factor called the *tortuosity factor* represented by the symbol τ . Thus, for porous solids, the equation for the effective diffusion coefficient D_e takes the form

$$D_e = \frac{D\omega}{\tau} \quad (4.94)$$

where ω is the void-fraction.

Application of the above equations is illustrated with the help of the following example.

EXAMPLE 4.10 Calculate the diffusion coefficient of oxygen at 25°C and 1 atm pressure, for its diffusion through a porous solid having the following properties:

$$\begin{aligned} \text{Void-fraction} &= 0.37 \\ \text{Radius of pores} &= 7 \times 10^{-5} \text{ m} \\ \text{Tortuosity factor} &= 2.1 \end{aligned}$$

Solution In Example 4.3, we calculated

$$D_{O_2,B} = 2.07 \times 10^{-5} \text{ m}^2 \text{ s}^{-1}$$

for the bulk phase diffusion of oxygen.

According to Eq. (4.93a), Knudsen diffusion coefficient D_K for O₂ will be

$$\begin{aligned} D_K &= 97 \times 7 \times 10^{-5} \times \left(\frac{298}{32} \right)^{1/2} \\ &= 2.07 \times 10^{-6} \text{ m}^2 \text{ s}^{-1} \end{aligned}$$

Further, according to Eq. (4.93b), we have

$$\frac{1}{D_{O_2}} = \frac{1}{2.07 \times 10^{-5}} + \frac{1}{2.07 \times 10^{-6}}$$

or

$$D_{O_2} = 1.88 \times 10^{-6} \text{ m}^2 \text{ s}^{-1}$$

Therefore, the effective diffusion coefficient D_{e,O_2} is calculated using Eq. (4.94), as below:

$$\begin{aligned} D_{e,O_2} &= \frac{D_{O_2} \omega}{\tau} \\ &= \frac{1.88 \times 10^{-6} \times 0.37}{2.1} = 3.3 \times 10^{-7} \text{ m}^2 \text{ s}^{-1} \quad \text{Ans.} \end{aligned}$$

4.1.4 Applications

Several reactive and nonreactive systems involve either steady state or unsteady state mass transfer by diffusion. Kinetics of different processes occurring in such heterogeneous systems is mostly controlled by diffusion rates, especially at elevated temperatures. In several instances, the effect of diffusion of a component is also coupled with phase transformations or chemical reactions occurring in such systems. Typical examples of these include case-hardening of steels using either liquid or gaseous phase carburization, cyanidation, nitriding or carbonitriding, gaseous oxidation of metals, topo-chemical gaseous reduction of oxides or physical processes of refining such as zone-refining and vacuumdegassing. In this section, we will briefly discuss some important metallurgical systems involving simple diffusion with fixed and moving boundaries and diffusion coupled with phase transformations and chemical reactions.

Permeability of gases through metallic membranes

As an example of application of interstitial diffusion, we consider the diffusion of gases such as hydrogen and nitrogen through thin metallic foils, generally referred to as the metallic membranes. The two sides of these membranes are maintained at different partial pressures of the gas whose diffusion is to be studied. Assuming that the dissolution of gas at the surface of the membrane follows Sievert's law, we can write the following equations for the concentration of the gas on the two sides of the membrane:

$$X_1 = K_S (P_1)^{1/2} \quad (4.95)$$

and

$$X_2 = K_S (P_2)^{1/2} \quad (4.96)$$

where K_S is the Sievert's law constant; X_1 and X_2 are the surface gas concentrations in terms of mass fractions on the two sides of the membrane and P_1

and P_2 are the respective partial pressures of the gas on these two sides. In writing these equations, it has been assumed that the rate of dissolution of the gas is so high, that the surface attains equilibrium concentration as soon as it comes in contact with the gas. As P_1 and P_2 have different values, so the concentration X_1 and X_2 will also be different. Thus, there will be a concentration gradient in the membrane which will become constant once the membrane achieves steady state. Thus, under these conditions, the amount J of the gas diffusing per unit time through the membrane from surface 1 to surface 2, with the implied assumption of $P_1 > P_2$, will be expressed by the equation

$$J = \rho D_g A \left(\frac{X_1 - X_2}{\delta} \right) \quad (4.97)$$

where D_g is the diffusion coefficient of the gas, ρ the density of the solid material of the membrane, δ the thickness of the membrane and A its surface area. With the help of Eqs., (4.95) and (4.96), we can write Eq. (4.97) in the following modified form:

$$J = D_g \rho K_S A \left(\frac{\sqrt{P_1} - \sqrt{P_2}}{\delta} \right) \quad (4.98)$$

The product $D_g K_S$ is generally referred to as permeability of the membrane. It is clear from the above equation that if J is determined experimentally, as a function of P_1 and P_2 , we can calculate the value of the permeability $D_g K_S$ and from our knowledge of the value of the Sievert's law constant K_S for the gas, we can determine the diffusion coefficient D_g . This method is commonly employed for experimental determination of permeability of gases and also their diffusion coefficients. The use of these relations is demonstrated by the following example.

EXAMPLE 4.11 Hydrogen gas diffuses at the rate of $22 \text{ cm}^3 \text{ s}^{-1}$ (volume specified at NTP) from a pressure of 16 atm through an iron foil of thickness 0.01 cm and cross-sectional area 25 cm^2 to a pressure of 1 atm. Calculate the permeability of the foil for the gas and also its diffusion coefficient in iron when the Sievert's law constant is $8.9 \times 10^{-4} \text{ atm}^{-1/2}$. Density of iron may be taken as 7.8 g cm^{-3} .

Solution The given data is:

$$\text{Initial pressure } P_1 = 16 \text{ atm}$$

$$\text{Final pressure } P_2 = 1 \text{ atm}$$

$$\text{Cross-sectional area } A = 25 \text{ cm}^2 = 25 \times 10^{-4} \text{ m}^2$$

$$\text{Foil thickness } \delta = 0.01 \text{ cm} = 10^{-4} \text{ m}$$

$$\text{Amount of gas diffusing per unit time, } J = 22 \text{ cm}^3 \text{ s}^{-1} = 22 \times 10^{-6} \text{ m}^3 \text{ s}^{-1}$$

$$\text{Density of iron, } \rho = 7.8 \text{ g cm}^{-3} = 7.8 \times 10^3 \text{ kg m}^{-3}$$

$$\text{Sievert's law constant, } K_S = 8.9 \times 10^{-4} \text{ atm}^{-1/2}$$

Using Eq. (4.98), we have

$$J = \rho D_g K_S A \left(\frac{\sqrt{P_1} - \sqrt{P_2}}{\delta} \right)$$

or

$$\frac{2 \times (22 \times 10^{-6})}{22.4} = D_g K_S (25 \times 10^{-4}) \left(\frac{\sqrt{16} - \sqrt{1}}{10^{-4}} \right) (7.8 \times 10^3)$$

Hence

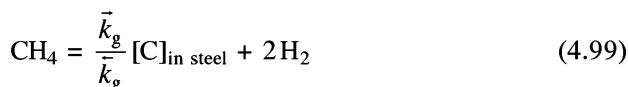
$$\text{Permeability} = D_g K_S = 3.35 \times 10^{-8} \text{ m}^2 \text{ s}^{-1} \text{ atm}^{-1/2} \quad \text{Ans.}$$

Therefore

$$\begin{aligned} \text{Diffusion coefficient } D_g &= \frac{\text{Permeability}}{K_S} \\ &= \frac{3.35 \times 10^{-8}}{8.9 \times 10^{-4}} = 3.76 \times 10^{-5} \text{ m}^2 \text{ s}^{-1} \quad \text{Ans.} \end{aligned}$$

Carburization of steels

In this process, a workpiece of steel is heated to the austenitic range in an environment of high carbon activity. Such environments are provided either by mixtures of gases, viz. CH₄-H₂ mixture or by a solid medium containing carbon, e.g. charcoal, or by a liquid salt bath containing the mixture of cyanide and other salts. During the process of carburization, carbon from the environment gets adsorbed at the surface of the workpiece of steel. This adsorption is associated with a number of chemical reactions. The adsorbed carbon then diffuses into the bulk of the workpiece to be carburized. This diffusion of carbon in steel occurs as interstitial diffusion. As indicated from the above description, the whole process of carburizing of steel, therefore, involves a coupling of chemical reaction with diffusion in series. In case of carburization with gaseous CH₄-H₂ mixtures, the chemical reaction occurring at the surface is known to be



This reaction is reversible in nature and known to follow the rate equation

$$\frac{dn_C}{dt} = \vec{k}_g \left[\frac{P_{\text{CH}_4}}{(P_{\text{H}_2})^r} \right] - \vec{k}_b \{(P_{\text{H}_2})^{(2-r)} C_{\text{CS}}\} \quad (4.100)$$

where \vec{k}_g and \vec{k}_b are respectively the forward and backward specific reaction rates and r is a constant which can assume values between 0 and 2. The differential term dn_C/dt represents the number of moles of carbon entering the steel workpiece per unit time per unit surface area. When the concentration of carbon at the surface of the workpiece C_{CS} attains equilibrium with the surrounding gaseous phase, the differential term, dn_C/dt will become equal to

zero. If C_{Ce} be the surface carbon concentration under the equilibrium condition, we can write the following relation from Eq. (4.100), by putting $C_{Cs} = C_{Ce}$, and $dn_C/dt = 0$:

$$\frac{\bar{k}_g(P_{CH_4})}{\bar{k}_g(P_{H_2})^2} = C_{Ce} \quad (4.101)$$

Substitution of this relation in Eq. (4.100) yields

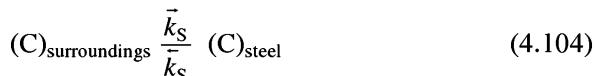
$$\begin{aligned} \frac{dn_C}{dt} &= \bar{k}_g(P_{H_2})^{(2-r)} (C_{Ce} - C_{Cs}) \\ &= k_C(C_{Ce} - C_{Cs}), \text{ say} \end{aligned} \quad (4.102)$$

where

$$k_C = \bar{k}_g(P_{H_2})^{(2-r)} \quad (4.103)$$

This equation can be used to calculate the amount of carbon entering the workpiece per unit time per unit surface area from the gas phase.

In case of a condensed phase reaction, we can write the following reaction for the transfer of carbon from the surrounding phase into the steel workpiece



where $(C)_{\text{steel}}$ refers to the carbon at the surface of the workpiece. If the above reaction is also considered to be a first order reversible reaction (the term ‘order’ will be explained in Chapter 7 on ‘reaction kinetics’), we can then write the following equation

$$\frac{dn_C}{dt} = \bar{k}_S a_C - \bar{k}_S C_{Cs} \quad (4.105)$$

where the symbol a_C represents the activity of carbon in the surrounding phase and C_{Cs} the concentration of carbon at the surface of the steel workpiece. Under the state of equilibrium between the surface of the workpiece and the surrounding phase, we again get from Eq. (4.105), the relation

$$C_{Cs} = C_{Ce} = \frac{\bar{k}_S a_C}{\bar{k}_S} \quad (4.106)$$

where as stated earlier C_{Ce} is the equilibrium surface carbon concentration. Thus, Eq. (4.105) will assume the form

$$\frac{dn_C}{dt} = \bar{k}_S (C_{Ce} - C_{Cs}) \quad (4.107)$$

On comparison of the rate equations, we find that Eqs. (4.102) and (4.107) are similar with the only difference that k_C in the former is substituted by \bar{k}_S in the latter. Thus, we can make use of either of these equations for further analytical treatment of the next step, namely the diffusion of carbon. As is evident, this will take place under unsteady state conditions. But before going

into the complicated unsteady state treatment, we consider first a simplified case which is based on Fick's first law of diffusion.

In this simplified treatment, one assumes that the concentration profile of carbon inside the workpiece remains linear throughout the process and the surface is always in equilibrium with the surroundings. Thus, we assume that at any instant of time t the concentration profile in the workpiece is described by straight line 1 as shown in Fig. 4.6. Let this profile change to line 2 after a lapse of time δt . Thus, the amount of carbon which has diffused into the sample per unit cross-sectional area normal to the plane of the paper (assuming the sample to be kept on the paper and diffusion occurring in directions along the planes parallel to the paper) will be equal to the area of the shaded portion in Fig. 4.6. This area A can be expressed by the relation

$$A = \frac{1}{2} (C_{Ce} - C_{Ci}) \delta x = \text{amount of carbon diffused, } m_C \quad (4.108)$$

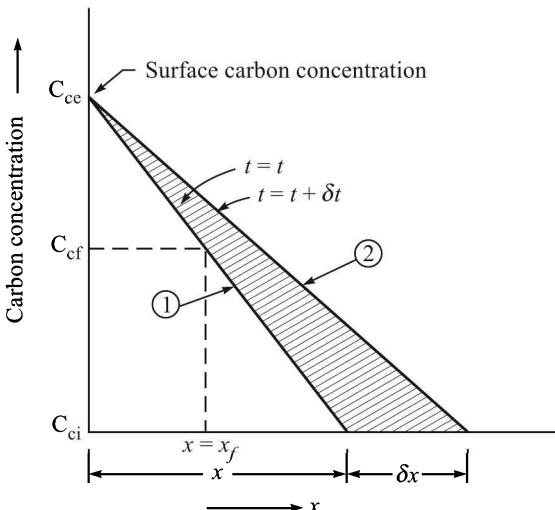


Fig. 4.6 Assumed carbon concentration profiles in a workpiece during carburization of steel.

where C_{Ce} and C_{Ci} are equilibrium carbon concentration and initial carbon concentration respectively at the surface of the workpiece. According to Eq. (4.108), the amount of carbon m_C diffusing per unit area from the surface into the workpiece in time δt , will be

$$m_C = -J_C \delta t = +D_C \left(\frac{\partial C_C}{\partial x} \right)_{x=0} \delta t \quad (4.109)$$

where J_C and D_C are respectively the carbon flux and carbon diffusion coefficients and $(\partial C_C / \partial x)$ the gradient of carbon concentration in the sample along the direction of its diffusion. From Eqs. (4.108) and (4.109), we get

$$\frac{1}{2} (C_{Ce} - C_{Ci}) \delta x = D_C \left(\frac{C_{Ce} - C_{Ci}}{x} \right) \delta t \quad (4.110)$$

which on simplification and integration yields

$$x^2 = 4D_C t \quad (4.111)$$

In the above equation, the constant of integration has been taken to be equal to zero as at $t = 0$ at $x = 0$, i.e. the surface has initial concentration C_{Ci} at the start of the carburization process. The above equation also shows that the plane at which the carbon concentration has the initial value, moves to a distance from the surface of the workpiece which is proportional to the square root of time. During carburization, we are in general, interested in a desired ‘case-thickness’. This amounts to stating that the carbon content in this case-thickness, say x_f should not be below a certain desired or specified level, say C_{Cf} , as shown in Fig. 4.6. From this, we can write the following equation between x_f and x

$$\frac{x_f}{x} = \frac{C_{Ce} - C_{Cf}}{C_{Ce} - C_{Ci}} \quad (4.112)$$

Eliminating x from Eq. (4.112), with the help of Eq. (4.111), we get

$$x_f = 2 \left(\frac{C_{Ce} - C_{Cf}}{C_{Ce} - C_{Ci}} \right) (D_C t)^{1/2} \quad (4.113)$$

This parabolic equation is of immense help in carburizing and other casehardening processes as it allows the approximate calculation of the time for attainment of the desired case-thickness. The use of this relation is illustrated with the help of the following example.

EXAMPLE 4.12 A rectangular piece of γ -iron containing initially 0.20% carbon is placed in a carburizing atmosphere at 1000°C for 4 hours. The equilibrium surface carbon content of iron was calculated to be 1.1%. If the diffusion coefficient of carbon in γ -iron at 1000°C is $1.89 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$, calculate the case-thickness up to which the carbon content is above or equal to 0.8%.

Solution According to Eq. (4.113), we have

$$\begin{aligned} x_f &= 2 \left(\frac{C_{Ce} - C_{Cf}}{C_{Ce} - C_{Ci}} \right) (D_C t)^{1/2} \\ &= 2 \left(\frac{1.1 - 0.8}{1.1 - 0.2} \right) [1.89 \times 10^{-10} \times 4 \times 3600]^{1/2} \\ &= 1.09 \times 10^{-3} \text{ m} \end{aligned} \quad \text{Ans.}$$

For analysis of unsteady state diffusion, we can make use of a suitable expression depending upon the shape of the workpiece, by the method of finite system solution. For a simple illustration, we consider the carburization of a steel plate of thickness $2L$, the surface of which is exposed to the surroundings having high chemical potential for carbon. For small values of thickness $2L$, compared to the length and breadth of the workpiece, we can consider this problem to be a one-dimensional diffusion problem under unsteady state, along

the thickness of the workpiece. The solution is similar to one discussed in Section 3.4.3 for unsteady state heat conduction. Considering the x -direction to be along the thickness of the workpiece, the following equation can be written for the unsteady state diffusion, according to Fick's second law, using Eq. (4.66)

$$\left(\frac{\partial C_C}{\partial t} \right) = D_C \left(\frac{\partial^2 C_C}{\partial x^2} \right) \quad (4.114)$$

The solution of the above equation should observe the following initial and boundary conditions, if the position of the origin for measurement of distance x is considered to lie at the middle of the plate as shown in Fig. 4.7.

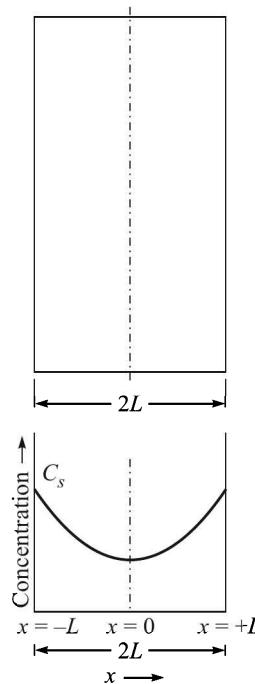


Fig. 4.7 Diffusion of carbon during carburization of γ -iron plate.

- (i) Initially the carbon concentration in the plate is uniform. Therefore, representing it by the symbol C_{Ci} , we can write the following initial condition

$$C_C = C_{Ci} \quad \text{for } -L < x < +L \quad \text{at } t = 0 \quad (4.115)$$

- (ii) Further, considering the symmetrical profile the carbon concentration shall be minimum at the middle of the plate throughout the carburization process, since the diffusion proceeds from the surface of the workpiece. Therefore, the second condition becomes

$$\frac{\partial C_C}{\partial x} = 0 \quad \text{for } x = 0 \quad \text{at } t > 0 \quad (4.116)$$

- (iii) The amount of carbon entering the plate, as a result of the carburizing process, will obviously diffuse into the plate from the surface. Therefore, we get the following equation as the third condition:

$$\begin{aligned}\frac{dn_C}{dt} &= k_m (C_{Ce} - C_{Cs}) \\ &= -D_C \left\{ \left(\frac{\partial C_C}{\partial x} \right)_{x=\pm L} \right\} \quad \text{for } t > 0 \quad (4.117)\end{aligned}$$

where $k_m = k_C$ for gas-phase carburizing [Eq. (4.102)] and $k_m = k_S$ for salt-bath or liquid-phase carburizing [Eq. (4.107)].

In order to apply the above set of equations to plates of different dimensions, it is better to express them in dimensionless forms, for which we introduce the following dimensionless variables.

- (i) The dimensionless concentration C_C^* , defined by the equation

$$C_C^* \equiv \frac{C_{Ce} - C_C}{C_{Ce} - C_{Ci}} \quad (4.118)$$

- (ii) Similarly, the dimensionless length x^* is defined by

$$x^* \equiv \frac{x}{L} \quad (4.119)$$

Substituting the above relations in Eq. (4.114), we get

$$\frac{\partial C_C^*}{\partial t^*} = \frac{\partial^2 C_C^*}{\partial x^{*2}} \quad (4.120)$$

where

$$t^* = \frac{D_C t}{L^2} \quad (4.121)$$

The parameter t^* can be considered as dimensionless time.

Further, the three boundary conditions expressed by Eqs. (4.115) to (4.117) will take the following alternative forms, respectively

$$(i) \quad C_C^* = 1 \quad \text{for} \quad -1 < x^* < +1 \quad \text{at} \quad t^* = 0 \quad (4.122)$$

$$(ii) \quad \frac{\partial C_C^*}{\partial x^*} = 0 \quad \text{for} \quad x^* = 1 \quad \text{at} \quad t^* > 0 \quad (4.123)$$

$$(iii) \quad C_C^* = - \left(\frac{D_C}{k_m} \right) \left(\frac{\partial C_C^*}{\partial x^*} \right) \quad \text{for} \quad t^* > 0 \quad (4.124)$$

Equation (4.120) can be solved by making use of the variable separable method as in Section 3.1.3 according to which C_C^* can be expressed as a function of the product of two variables—one containing only t^* and the other only x^* . Thus, we can write the following functional relation for C_C^* :

$$C_C^* = \Psi(t^*) \phi(x^*) \quad (4.125)$$

With the help of the above relation, we can write Eq. (4.120) in the following alternative form.

$$\frac{1}{\psi} \frac{\partial \psi}{\partial t^*} = \frac{1}{\phi} \frac{\partial^2 \phi}{\partial x^{*2}} = \kappa \text{ (say)} \quad (4.126)$$

From this equation it is evident that κ cannot be a function of either Ψ or ϕ . Thus, we get from Eq. (4.126) the following two total differential equations.

$$\frac{d\Psi}{dt^*} + \kappa\Psi = 0 \quad (4.127)$$

and

$$\frac{d^2\phi}{dx^{*2}} + \kappa\phi = 0 \quad (4.128)$$

Solutions of these yield

$$\psi = A_1 \exp(-\kappa t^*) \quad (4.129)$$

and

$$\phi = A_2 \cos(\sqrt{\kappa} x^*) + A_3 \sin(\sqrt{\kappa} x^*) \quad (4.130)$$

where A_1, A_2 and A_3 are constants of integration. Their values can be determined by applying the initial and boundary conditions. In writing the solution of Eq. (4.126) in the above form, it is implied that κ is a positive constant which will only conform to the actual practical situation. Substitution of Eqs. (4.129) and (4.130) in Eq. (4.125) yields

$$C_C^* = [A_4 \cos(\sqrt{\kappa} x^*) + A_5 \sin(\sqrt{\kappa} x^*)] \exp(-\kappa t^*) \quad (4.131)$$

where constants, $A_4 = A_1 A_2$ and $A_5 = A_1 A_3$. The second boundary condition defined by Eq. (4.123) requires that $A_5 = 0$. Thus, Eq. (4.131) takes the following form:

$$C_C^* = A_4 \cos(\sqrt{\kappa} x^*) \exp(-\kappa t^*) \quad (4.132)$$

Substitution of the above relation in Eq. (4.124) yields

$$\cot\sqrt{\kappa} = \sqrt{\kappa} \frac{D_C}{k_m L} \quad (4.133)$$

This equation leads to evaluation of the value of function κ . Values of κ are evaluated graphically by plotting the functions $\cot\sqrt{\kappa}$ and $(D_C/k_m L)\sqrt{\kappa}$ against $\sqrt{\kappa}$ as shown in Fig. 4.8. The points of intersection of these plots will satisfy Eq. (4.133) and because of a ‘cot’ function being involved, this equation will obviously yield a series of n values for κ , which may be denoted by the symbols $\kappa_1, \kappa_2, \dots, \kappa_n$, corresponding to different values of κ separated in different ranges say $0 - \pi, \pi - 2\pi, 2\pi - 3\pi$, etc.

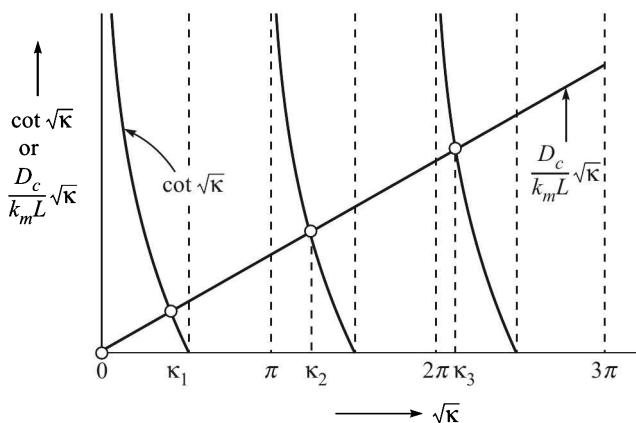


Fig. 4.8 Plots of functions $\cot \sqrt{\kappa}$ and $\frac{D_c \sqrt{\kappa}}{k_m L}$ vs. $\sqrt{\kappa}$ for carburization of steel plate.

Thus, a general solution for C_C^* takes the form

$$C_C^* = [A_{41} \cos(\sqrt{\kappa_1} x^*) + A_{42} \cos(\sqrt{\kappa_2} x^*) + \dots + A_{4n} \cos(\sqrt{\kappa_n} x^*) + \dots] \{ \exp(-\kappa^*) \} \quad (4.134)$$

Values of constants $A_{41}, A_{42}, A_{4n}, \dots$ can be determined by application of the initial condition expressed by Eq. (4.122), which yields

$$1 = \sum_{n=1}^{\infty} A_{4n} \cos(\sqrt{\kappa_n} x^*) \quad (4.135)$$

Evaluation of the constants A_{4n} follows the normal method of determination of Fourier coefficients which requires the multiplication of both sides of Eq. (4.135) by $\cos(\sqrt{\kappa_m} x^*) dx^*$ followed by integration from $x^* = 0$ to 1. Thus, we get

$$\int_0^1 \cos(\sqrt{\kappa_m} x^*) dx^* = \int_0^1 \sum_{n=1}^{\infty} A_{4n} \cos(\sqrt{\kappa_n} x^*) \cos(\sqrt{\kappa_m} x^*) dx^* \quad (4.136)$$

The right-hand side of the above equation is equal to zero for $n \neq m$, but for $n = m$, we get

$$\frac{1}{\sqrt{\kappa_n}} \sin \sqrt{\kappa_n} = A_{4n} \left[\frac{1}{2} + \frac{\cos 2\sqrt{\kappa_n}}{4\sqrt{\kappa_n}} \right] \quad (4.137a)$$

or

$$A_{4n} = \frac{4 \sin \sqrt{\kappa_n}}{2\sqrt{\kappa_n} + \sin 2\sqrt{\kappa_n}} = \frac{2 \sin \sqrt{\kappa_n}}{\sqrt{\kappa_n} + \sin \sqrt{\kappa_n} \cos \sqrt{\kappa_n}} \quad (4.137b)$$

Therefore, a particular solution of Eq. (4.120) takes the form

$$C_C^* = \sum_{n=1}^{\infty} \left[\frac{2 \sin(\sqrt{\kappa_n}) \cos(\sqrt{\kappa_n} x^*) \exp(-\kappa_n t^*)}{(\sqrt{\kappa_n} + \sin \sqrt{\kappa_n} \cos \sqrt{\kappa_n})} \right] \quad (4.138)$$

This solution shows that C_C^* is a function of κ , t^* and x^* .

Further, as κ is a function ($D_C/k_m L$), so C_C^* also becomes a function of three dimensionless quantities, viz. t^* , x^* and $(k_m L/D_C)$. In Figs. 4.9(a-d), C_C^* is plotted as a function of t^* for various values of x^* and $(k_m L/D_C)$. This dimensionless group $(k_m L/D_C)$ is known as Sherwood number, more about which will be discussed later.

Figure 4.9(a) shows that C_C^* approaches zero only for those systems for which the value of the parameter $(k_m L/D_C)$ is very high. This means that only

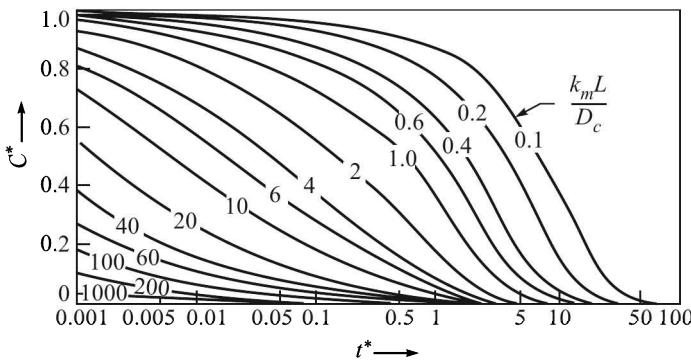


Fig. 4.9(a) Relationship between dimensionless concentration and dimensionless time during carburization, at the surface ($x^* = x/L = 1$).

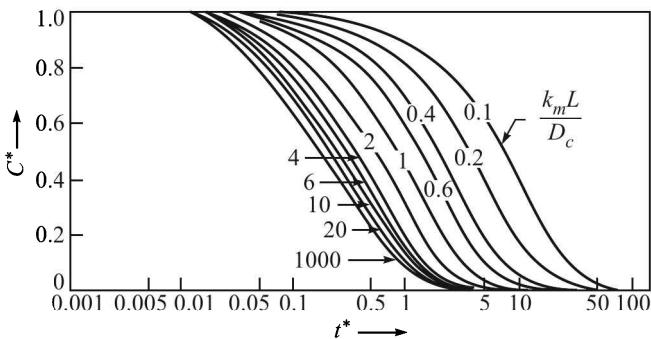


Fig. 4.9(b) Relationship between dimensionless concentration and dimensionless time during carburization (at $x^* = 0.6$).

in systems having $k_m \gg D_C$, the surface concentration will be equal to the equilibrium value and be constant at a given temperature for a fixed carburizing bath composition. Further, Fig. 4.9(d) shows that for $t^* \leq 0.1$, the concentration at the centre of plate will not change. As these are the two basic conditions for

application of the approximate treatment given earlier in this section, they should only be applied under these conditions and for all other cases, the use should be made of Figs. 4.9(a-d) for calculation of the carbon concentration profiles.

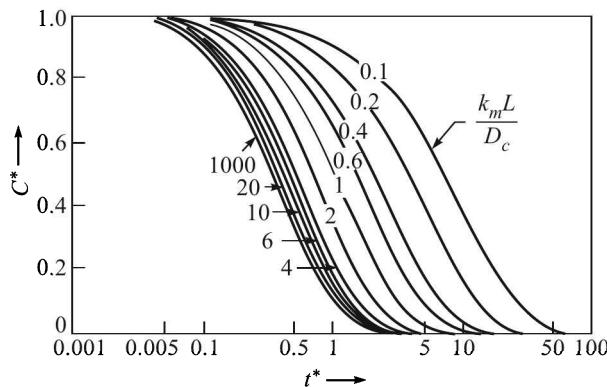


Fig. 4.9(c) Relationship between dimensionless concentration and dimensionless time during carburization (at $x^* = 0.3$).

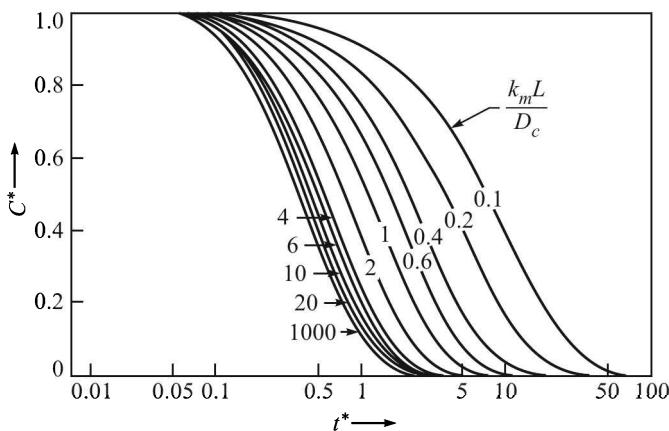


Fig. 4.9(d) Relationship between dimensionless concentration and dimensionless time during carburization (at $x^* = 0$).

It may be stated that the above treatment can also be applied to systems of cylindrical and spherical symmetry by making suitable modifications for changing over to these coordinate systems. Application of these relations is demonstrated below by an example.

EXAMPLE 4.13 A 2 cm thick plate of mild steel containing 0.19% C was suspended in a carburizing bath for 6 hours. Calculate the carbon content at the surface, at 0.7 em and 0.4 ern from the surface and at the centre of the plate with the help of the following data:

$$C_{Ce} = 1.5\%$$

$$k_m = 2 \times 10^{-6} \text{ m s}^{-1}$$

$$D_C = 2.0 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$$

Solution The values of x^* at the given depths will be as follows:

$$x_{\text{surface}}^* = \frac{x}{L} = \frac{1}{1} = 1$$

$$x_{0.7}^* = \frac{0.3}{1} = 0.3$$

$$x_{0.4}^* = \frac{0.6}{1} = 0.6$$

$$x_{\text{centre}}^* = \frac{0}{1} = 0$$

$$L = 1 \text{ cm} = 1 \times 10^{-2} \text{ m}; t = 6 \text{ h} = 6 \times 3600 \text{ s}$$

Further

$$\begin{aligned} t^* &= \frac{D_C t}{L^2} = \frac{2 \times 10^{-10} \times 6 \times 3600}{(1 \times 10^{-2})} \\ &= 4.32 \times 10^{-2} \end{aligned}$$

and

$$\frac{k_m L}{D_C} = \frac{2 \times 10^{-6} \times (1 \times 10^{-2})}{2 \times 10^{-10}} = 100$$

From Figs. 4.9(a-d), we get the following values of C_C^* for the above values of x^* , t^* and k_m/D_C .

$$C_{C, \text{surface}}^* = 0.1 \quad C_{C, 0.7}^* = 1.0$$

$$C_{C, 0.4}^* = 0.9 \quad C_{C, \text{centre}}^* = 1.0$$

Thus, using Eq. (4.118), we get

$$\begin{aligned} C_{C, \text{surface}} &= C_{Ce} - [C_{C, \text{surface}}^* (C_{Ce} - C_{Ci})] \\ &= [1.5 - 0.1 (1.5 - 0.19)] = 1.37\% \quad \text{Ans.} \end{aligned}$$

Similarly, using the same expressions for other cases, we have

$$X_{C, 0.4} = C_{Ce} - 0.9 (C_{Ce} - C_{Ci}) = 1.5 - 0.9 \times 1.31 = 0.32\%$$

$$C_{C, 0.7} = C_{Ce} - 1.0 (C_{Ce} - C_{Ci}) = 0.19\%$$

Similarly, $C_{C, \text{centre}} = 0.19\%$

The above treatment assumes that the surrounding phase or the environment in the neighbourhood of the surface of the workpiece of steel to be carburized has the same composition as the bulk of the surrounding phase or environment. In case, the transport of carbon through the surroundings is also slow, this assumption may not hold good and we will have to accordingly modify the above treatment to take into account the rate of diffusion of carbon

to the surface of the workpiece through the bulk of the surrounding phase or the environment.

A similar analysis may be carried out for the case of alloy homogenization which has been done by Geiger and Poirer.¹

Diffusion with moving phase boundaries

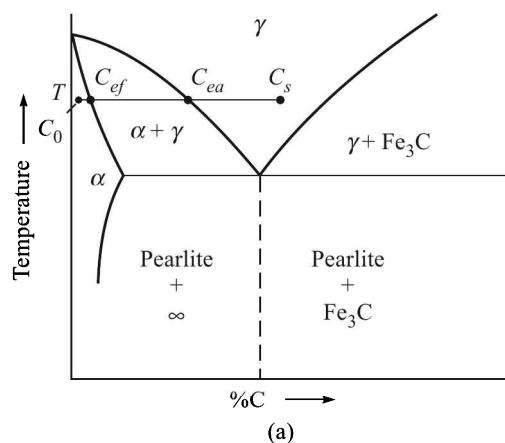
Problems involving diffusion with moving phase boundaries are encountered in metallurgical systems containing solid state phase transformations or oxidation-reduction reactions with solid metals or their compounds and a fluid phase. All such problems can be treated making use of the generalized diffusion equation with minor modifications to take care of other variables in specific cases under study. For arriving at proper mathematical treatments, we will classify these problems into the following four categories:

- (i) Transformation of one phase into another induced by absorption or desorption at the surface followed by its diffusion to or from the phases. Such situations can exist in the systems which involve eutectoid or peritectoid reactions. A common example is the carburization of ferrite above the eutectoid temperature which leads to the formation of austenite. Similarly, the reverse reaction of decarburization of austenite into ferrite represents another example of this type of problem.
- (ii) Transformation of a two phase system into a single phase system owing to some surface reaction followed by diffusion of a component. Such a situation can exist in the above-mentioned systems involving ferrite-austenite transformation for austenization of dual phase, i.e. ferrite-austenite alloy.
- (iii) Gaseous oxidation of metals.
- (iv) Topochemical gaseous reduction of dense oxides.

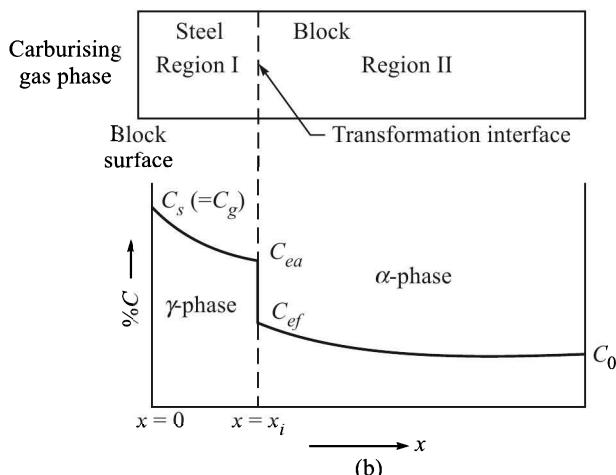
In analysis of the above cases, it will be assumed that the overall process is diffusion-controlled, meaning thereby that the chemical and/or the surface reaction steps involved are much faster than the diffusional step in the process.

Gaseous carburization of ferritic steels. Gaseous carburization of ferritic steels above the eutectoid temperature may be accompanied by simultaneous transformation to austenite. For consideration of this case of gaseous carburization of ferritic steel at temperature T , consider a block of steel as depicted in Fig. 4.10. For the sake of simplicity of treatment, we consider a one-dimensional system only. Figure 4.10(b) shows the schematic concentration profile, with the position of the phase transforming interface at $x = x_i$. Thus, we can schematically divide the whole block into two regions, namely: (i) Region I, for which $0 < x_1 < x_i$, and in which the transformation to austenite has already

¹ G.H. Geiger and D.R. Poirer, *Transport Phenomena in Metallurgy*, Addison Wesley, Reading, Mass. (1974).



(a)



(b)

Fig. 4.10 Gaseous carburization of ferritic steels: (a) Schematic Fe–C diagram; (b) Schematic concentration profile in the steel block.

taken place, and, (ii) Region II for which $x_{II} > x_I$ and in which the transformation is yet to occur.

For each of these regions, using Fick's second law, we can write an unsteady state diffusion equation as follows.

For Region I

$$\frac{\partial C_{CI}}{\partial t} = D_I \left(\frac{\partial^2 C_{CI}}{\partial x_I^2} \right) \quad (4.139)$$

For Region II

$$\frac{\partial C_{CII}}{\partial t} = D_{II} \left(\frac{\partial^2 C_{CII}}{\partial x_{II}^2} \right) \quad (4.140)$$

where D_I and D_{II} are the values of diffusion coefficients in Phase I and Phase II respectively. These equations will follow three boundary conditions as given next.

Initial condition

$$C_{II} = C_0 \quad \text{for } 0 < x < 00 \quad \text{at } t = 0 \quad (4.141)$$

Boundary conditions

$$C_{II} = C_{ef} \quad \text{at } x_{II} = x_i \quad \text{for } t > 0 \quad (4.142)$$

$$C_{II} = C_0 \quad \text{at } x_{II} = \infty \quad \text{for } t > 0 \quad (4.143)$$

$$C_{CI} = C_{ea} \quad \text{at } x_I = x_i \quad \text{for } t > 0 \quad (4.144)$$

$$C_{CI} = C_{ef} \quad \text{at } x_I = 0 \quad \text{for } t > 0 \quad (4.145)$$

Carbon-conservation condition. Mass balance of carbon at the interface, with the assumption of constant values of D_I and D_{II} yields

$$-\left[D_I \frac{\partial C_{CI}}{\partial x} \right]_{x=x_i} = (C_{ea} - C_{ef}) \left(\frac{\partial x_i}{\partial t} \right) - \left[D_{II} \frac{\partial C_{II}}{\partial x} \right]_{x=x_i} \quad (4.146)$$

In these equations, symbols C_0 , C_g , C_{ef} and C_{ea} , respectively represent the initial concentration of carbon in the steel block at temperature T , carbon concentration in austenite in equilibrium with the gas phase, carbon concentration in ferrite under equilibrium with austenite at temperature T and carbon content of austenite under equilibrium with ferrite at temperature T . This is schematically represented in Fig. 4.10(a), depicting the relevant portion of the Fe-C equilibrium diagram. Similarly, the symbols C_{CI} and C_{II} represent instant carbon concentrations in regions I and II respectively, at the time under consideration.

The above problem is similar to one involving heat conduction with moving phase boundary as discussed in Section 3.1.3 and can thus be solved as follows in a similar manner by making use of the solution suggested by Neumann.

$$C_{CI} = A_I + B_I \operatorname{erf} \left(\frac{x_I}{2\sqrt{D_I t}} \right) \quad (4.147)$$

$$C_{II} = A_{II} + B_{II} \operatorname{erf} \left(\frac{x_{II}}{2\sqrt{D_{II} t}} \right) \quad (4.148)$$

Making use of the conditions represented by Eqs. (4.145) and (4.141) respectively, we get

$$A_I = C_g \quad (4.149)$$

and

$$A_{II} = C_0 \quad (4.150)$$

Thus

$$C_{CI} = C_g + B_I \operatorname{erf} \left(\frac{x_I}{2\sqrt{D_I t}} \right) \quad (4.151)$$

and

$$C_{\text{Cl}} = C_0 + B_{\text{II}} \operatorname{erfc} \left(\frac{x_{\text{II}}}{2\sqrt{D_{\text{II}} t}} \right) \quad (4.152)$$

Based on similar arguments as put forward in Section 3.1.3 in relation to the analysis of a problem on heat transfer, we get

$$x_i = k\sqrt{t} \quad (4.153)$$

where k is a constant.

Substituting for x_i and the conditions expressed by Eqs. (4.142) and (4.144) in Eqs. (4.151) and (4.152), we get

$$C_{\text{ea}} = C_g + B_{\text{I}} \operatorname{erf} \left(\frac{k}{2\sqrt{D_{\text{I}}}} \right) \quad (4.154)$$

and

$$C_{\text{ef}} = C_0 + B_{\text{II}} \operatorname{erfc} \left(\frac{k}{2\sqrt{D_{\text{II}}}} \right) \quad (4.155)$$

Values of concentrations C_{ef} and C_{ea} at temperature T can be obtained from the iron-carbon equilibrium diagram. Hence, the above equations can be used to eliminate the constants B_{I} and B_{II} from Eqs. (4.151) and (4.152). Thus, we get

$$\frac{C_{\text{Cl}} - C_g}{C_{\text{ea}} - C_g} = \frac{\operatorname{erf}(x_{\text{I}}/2\sqrt{D_{\text{I}} t})}{\operatorname{erf}(k/2\sqrt{D_{\text{I}}})} \quad (4.156)$$

and

$$\frac{C_{\text{Cl}} - C_0}{C_{\text{ef}} - C_0} = \frac{\operatorname{erfc}(x_{\text{II}}/2\sqrt{D_{\text{II}} t})}{\operatorname{erfc}(k/2\sqrt{D_{\text{II}}})} \quad (4.157)$$

Substitution of the above equations in Eq. (4.146), yields

$$\begin{aligned} C_{\text{ea}} - C_{\text{ef}} &= \frac{C_g - C_{\text{ea}}}{\sqrt{\pi} \left(\frac{k}{2\sqrt{D_{\text{I}}}} \right) \exp \left(\frac{k^2}{4D_{\text{I}}} \right) \operatorname{erf} \left(\frac{k}{2\sqrt{D_{\text{I}}}} \right)} \\ &\quad - \frac{C_{\text{ef}} - C_0}{\sqrt{\pi} \left(\frac{k}{2\sqrt{D_{\text{II}}}} \right) \exp \left(\frac{k^2}{4D_{\text{II}}} \right) \operatorname{erfc} \left(\frac{k}{2\sqrt{D_{\text{II}}}} \right)} \end{aligned} \quad (4.158)$$

We can evaluate k from the above equation by the iterative method and then proceed to evaluate the concentration profiles as well as the position of the interface as illustrated by the following example.

EXAMPLE 4.14 A pure iron plate is exposed at 800°C to a carburizing atmosphere which brings its surface carbon to the equilibrium value of 0.9% C.

Calculate the rate of movement of ferrite-austenite interface and also its position after 20 hours. The austenite phase in equilibrium with ferrite contains 0.4% carbon, and the ferrite phase may be assumed to consist of pure iron. The diffusion coefficient of carbon in austenite is $1.4 \times 10^{-11} \text{ m}^2 \text{ s}^{-1}$.

Solution On substitution of the relevant values Eq. (4.158) may be written in the form

$$0.4 - 0.0 = \frac{0.9 - 0.4}{\left[\sqrt{\pi} \left\{ \frac{k}{2 \times (1.4 \times 10^{-11})^{1/2}} \right\} \exp \left\{ \frac{k^2}{4 \times (1.4 \times 10^{-11})} \right\} \operatorname{erf} \left\{ \frac{k}{2 \times (1.4 \times 10^{-11})^{1/2}} \right\} \right]}$$

Iterative solution of above equation yields

$$k = 5.09 \times 10^{-6} \text{ m s}^{-1/2}$$

According to Eq. (4.153) (since $t = 20 \text{ h}$)

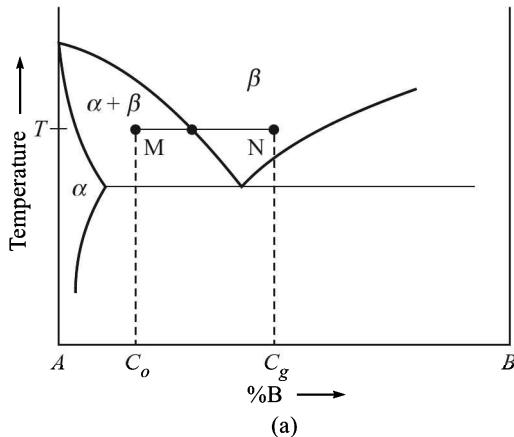
$$x = k\sqrt{t} = 5.09 \times 10^{-6} \times (20 \times 3600)^{1/2} = 1.37 \times 10^{-3} \text{ m} \quad \text{Ans.}$$

Therefore, from Eq. (4.153), by differentiation, the rate of movement of the ferrite-austenite interface is

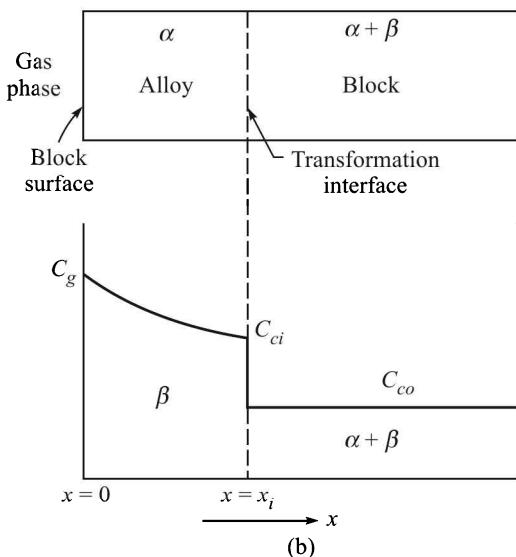
$$\begin{aligned} \frac{dx}{dt} &= \frac{1}{2} k(t)^{-1/2} = \frac{1}{2} \times 5.09 \times 10^{-6} \times (20 \times 3600)^{-1/2} \\ &= 9.5 \times 10^{-9} \text{ m s}^{-1} \end{aligned} \quad \text{Ans.}$$

Gaseous diffusion in dual-phase alloys. This case can be treated in a similar fashion as the earlier one with certain modifications that can be illustrated by considering an alloy of composition represented by the point M in the schematic equilibrium diagram as shown in Fig. 4.11(a). An alloy of this composition will consist of two phases α and β . Let this alloy be brought in contact with a gaseous phase, which has a partial pressure of component B corresponding to composition at the point M in Fig. 4.11(a). As soon as the gaseous phase and the solid alloy come in contact, the surface of the solid will immediately undergo a phase transformation to phase β corresponding to composition at the point N in this figure. The component B will then diffuse into the solid which will first increase the relative amount of β phase in the alloy, finally transforming it totally to β and then allowing component B to diffuse further. The composition of profile at any instant of time t is schematically shown in Fig. 4.11(b). It is seen that diffusion of component B will take place only in the single phase region of phase β . This unsteady state diffusion of the component B will, following Ficks second law, be governed by the equation

$$\frac{\partial C_{B\beta}}{\partial t} = D_{B\beta} \left(\frac{\partial^2 C_{B\beta}}{\partial x^2} \right) \quad (4.159)$$



(a)



(b)

Fig. 4.11 Diffusion in dual-phase alloys: (a) Schematic equilibrium diagram; (b) Concentration profile due to diffusion in the block.

The analytical treatment of this case has, therefore, to be made under the following conditions:

(i) Boundary conditions

$$C_{B\beta} = C_g \quad \text{at} \quad x = 0 \quad \text{for} \quad t > 0 \quad (4.160)$$

$$C_{B\beta} = C_{Ci} \quad \text{at} \quad x = x_i \quad \text{for} \quad t > 0 \quad (4.161)$$

(ii) Mass balance at the interface

This will yield the following relation:

$$\left[-D_{B\beta} \left(\frac{\partial C_{B\beta}}{\partial x} \right) \right]_{x=x_i} = (C_{Ci} - C_{Co}) \left(\frac{\partial x_i}{\partial t} \right) \quad (4.162)$$

A general solution of Eq. (4.159) is expressed by the relation

$$C_{B\beta} = A + B \operatorname{erf} \left(\frac{x}{2\sqrt{D_{B\beta} t}} \right) \quad (4.163)$$

where A and B are constants.

According to the condition expressed by Eq. (4.160), we get

$$A = C_g \quad (4.164)$$

Further on the basis of arguments put forward in Section 3.1.3 dealing with heat transfer under similar conditions, we can express x_i as

$$x_i = k\sqrt{t} \quad (4.165)$$

where k is a constant.

Using this equation and the condition expressed by Eqs. (4.161) and (4.164), we can write the following equation from Eq. (4.163):

$$C_{Ci} = C_g + B \operatorname{erf} \left(\frac{k}{2\sqrt{D_{B\beta}}} \right) \quad (4.166)$$

Substituting for A and B from Eqs. (4.164) and (4.166) respectively in Eq. (4.163) and the resulting equation for $C_{B\beta}$ in Eq. (4.162), we get

$$\frac{C_g - C_{Ci}}{C_{Ci} - C_{Co}} = \frac{\sqrt{\pi} k \exp \left(+ \frac{k^2}{4D_{B\beta}} \right) \operatorname{erf} \left(+ \frac{k}{2\sqrt{D_{B\beta}}} \right)}{2\sqrt{D_{B\beta}}} \quad (4.167)$$

With the help of above relation, we can determine the value of the constant k which in turn can be used to determine concentration profiles as well as the change in x_i with time to solve the problem under study.

Gaseous oxidation of metals. Oxidation of metals is an electrochemical process consisting of two reactions, namely an anodic reaction involving the change of a metal M to its cation, M^{z+} , according to the equation



and a simultaneous cathodic reaction involving oxygen and expressed as



The oxidation reaction represented by Eq. (4.168) proceeds at the metal/oxide interface whereas the reduction reaction represented by Eq. (4.169) occurs at the gas/oxide interface. Further, the oxidation reaction can proceed in any of the following four different ways, once an oxide film is formed on the metal.

- (i) In case the oxide product formed as a result of surface-oxidation has a smaller volume on the basis of per mole of metal oxidized, the oxide film formed will have cracks or pores developed in it. The diffusion of oxygen will take place through these cracks or pores causing the gas/metal oxidation reaction to take place at the metal surface. The rate of oxidation in this case will depend upon the void fraction in the film and also on the structure of cracks or the pores. The rate of increase in thickness of oxide can be calculated from the rate of diffusion of oxygen through the porous layer. This case can be treated in a similar manner as the reduction of dense pellets discussed later in this section.
- (ii) In case a dense film of oxide is formed having vacancies on cationic sites and electronic conductivity, metal cations and electrons will be formed at the oxide/metal interface. These metal cations and electrons will diffuse through the oxide film and lead to the formation of oxygen ions resulting from the reaction of electrons with gaseous oxygen at gas/oxide interface and thus the oxide film will grow at the oxide/gas interface.
- (iii) In case a dense oxide film having oxygen ion vacancies is formed, the oxygen ions formed at the oxide/gas interface through the reaction expressed by Eq. (4.169) will diffuse to the oxide/metal interface resulting in the formation of fresh oxide layer at metal/oxide interface. The electrons participating in this reaction will be released at the oxide/metal interface by the reaction expressed by Eq. (4.168) and diffuse through the oxide film to the gas/oxide interface.
- (iv) Finally, if the film formed is dense and has conductivity for both cations and anions and also for electrons, the growth of film will take place by the diffusion of both the ionic species and the electrons. Thus, in this case, both modes (ii) and (iii) will be effective in the growth of oxide film.

A careful study of the above referred modes shows that the second and the third modes form special case of the fourth one. Therefore, for mathematical analysis of the thickness of oxide layer formed in dense oxides as a function of time, we need to consider only the fourth case. The analytical treatment of the formation of oxide layer is originally due to Wagner¹ and is described here assuming that dense oxide M_xO_y is formed as a result of oxidation. The direction of flow of various ionic species and electrons through this layer is shown in Fig. 4.12.

¹ C. Wagner, *Atom Movements*, American Society for Metals, Cleveland, Ohio (1951), p. 153.

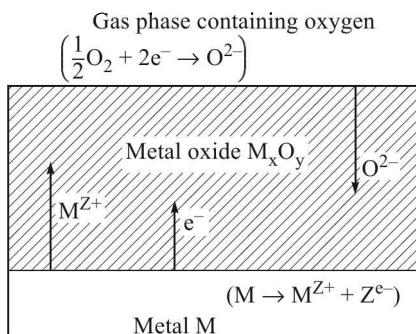


Fig. 4.12 Gaseous oxidation of metals.

Assuming the chemical and electrochemical reactions to be much faster than the diffusion of ions and electrons, we can assume a state of local equilibrium to exist at the interfaces and also inside the oxide system. Thus, for the equilibrium relationship between the oxide, metal and oxygen anywhere in the oxide film and at both the interfaces, we can write the equation

$$\mu_{M_xO_y} = x\mu_M + 0.5 y \mu_{O_2} \quad (4.170)$$

where the different μ terms denote the chemical potentials of species indicated by appropriate suffixes. As the oxide phase contains pure M_xO_y , therefore, its chemical potential throughout the phase will be constant and numerically equal to its standard state chemical potential $\mu_{M_xO_y}^0$. In case the metal phase consists of a pure metal and not an alloy, then at the oxide/metal interface, its chemical potential will also be equal to its standard state chemical potential. However, the chemical potential of oxygen will be equal to one corresponding to its equilibrium value. Thus, at the oxide/metal interface, for the reaction, we have



The equilibrium constant K_{eq} is expressed as

$$K_{eq} = \frac{a_{M_x} O_y}{(a_M)^x (P_{O_2})^{y/2}} = \frac{1}{(P_{O_{2,M}})^{y/2}} \quad (4.172)$$

where $P_{O_{2,M}}$ is the partial pressure of oxygen at the oxide/metal interface under the equilibrium condition.

Besides, if $P_{O_{2,g}}$ be the oxygen partial pressure in the atmosphere, i.e. at the gas/oxide interface, then the necessary condition for oxidation of metal to occur in this atmosphere is

$$P_{O_{2,g}} > P_{O_{2,M}} \quad (4.173)$$

Further, the activity of the metal at the gas/oxide interface can be obtained with the help of Eq. (4.172), by the relation

$$a_M = \left[\frac{1}{K_{eq} (P_{O_{2,M}})^{y/2}} \right]^{1/x} < 1 \quad (4.174)$$

Thus, there will be gradients in chemical potentials of oxygen as well as metal in the oxide phase in the direction normal to the interfaces. The chemical potential of metal will be greater at the metal/oxide interface than that at the gas/oxide interface, whereas that of oxygen will be greater at the gas/oxide interface. Both these potentials will change continuously in the oxide film. Therefore, oxygen gas and oxygen ions will both diffuse towards the metal/oxide interface and the metal cations towards the gas/oxide interface.

But these chemical potentials according to Eq. (4.171) will be related at any point in the oxide phase by the equation

$$xd\mu_M + \frac{y}{2} d\mu_{O_2} = 0 \quad (4.175)$$

or

$$d\mu_M = -\frac{y}{2x} d\mu_{O_2} \quad (4.176)$$

since $\mu_{M_xO_y}$ is constant at a given temperature for systems in which pure oxide is formed.

The oxide phase will, however, contain only ions and electrons. Therefore, chemical potentials of elemental species must be correlated to the potentials of these charged particles or species. These correlations, according to thermodynamic principles are, as follows:

$$\mu_M = \mu_M^{z+} + z\mu_{e-} \quad (4.177)$$

and

$$\mu_{O_2} = 2(\mu_{O^{2-}} - 2\mu_{e-}) \quad (4.178)$$

where z^+ is the charge on the cation formed as a result of the oxidation of the metal. As the oxide phase M_xO_y will be electrically neutral, the net charge on the cations and anions must be equal and opposite. Thus

$$xz - 2y = 0 \quad (4.179)$$

Therefore, Eq. (4.176) can be written in the following alternative form:

$$d\mu_M = -\frac{z}{4} d\mu_{O_2} \quad (4.180)$$

As there is a chemical potential gradient of various elemental species across the oxide phase, there will also be a chemical potential gradient for charged species and their movement will take place under such a gradient and also the electrical potential gradient which may result from the difference in rates of movement of charged species. The total force F_i on a mole of charged particles

denoted by the suffix i under the influence of both these chemical and electrical potential gradients will be expressed by the relation

$$F_i = \frac{\partial \eta_i}{\partial x} \quad (4.181)$$

where η is called the *electrochemical potential* and expressed as

$$\eta_i = \mu_i + z_i F \psi \quad (4.182)$$

where the symbol ψ denotes the electrical potential, F the Faraday's constant, and z_i the charge on the i th ion or charged species.

For the ionic species i , the flux J_i per unit time per unit cross-sectional area, according to Eqs. (4.86), (4.181) and (4.182) will be expressed by the relation

$$\begin{aligned} J_i &= n_i B_i F_i = -n_i B_i \left(\frac{\partial \eta_i}{\partial x} \right) \\ &= -n_i B_i \left[\frac{\partial \mu_i}{\partial x} + z_i F \frac{\partial \psi}{\partial x} \right] \end{aligned} \quad (4.183)$$

where n_i is the concentration of ionic species i and B_i the ionic mobility; also, $\partial \psi / \partial x$ is the electrical potential gradient in the x -direction. For the three charged species involved in the present case, the above relation takes the forms

$$J_{M^{z+}} = - \left[n_{M^{z+}} B_{M^{z+}} \left\{ \frac{\partial \mu_{M^{z+}}}{\partial x} + z F \frac{\partial \psi}{\partial x} \right\} \right] \quad (4.184)$$

$$J_{O^{2-}} = - \left[n_{O^{2-}} B_{O^{2-}} \left\{ \frac{\partial \mu_{O^{2-}}}{\partial x} - 2 F \frac{\partial \psi}{\partial x} \right\} \right] \quad (4.185)$$

and

$$J_{e^-} = - \left[n_{e^-} B_{e^-} \left\{ \frac{\partial \mu_{e^-}}{\partial x} - F \frac{\partial \psi}{\partial x} \right\} \right] \quad (4.186)$$

Further, to maintain electrical neutrality, the transfer of charged species across any interface will follow the relation

$$z(J_{M^{z+}}) - 2(J_{O^{2-}}) - (J_{e^-}) = 0 \quad (4.187)$$

Substitution of Eqs. (4.184) to (4.186) in the above relation yields

$$\frac{\partial \psi}{\partial x} = \frac{- \left[z n_{M^{z+}} B_{M^{z+}} \left(\frac{\partial \mu_{M^{z+}}}{\partial x} \right) + 2 n_{O^{2-}} B_{O^{2-}} \left(\frac{\partial \mu_{O^{2-}}}{\partial x} \right) + n_{e^-} B_{e^-} \left(\frac{\partial \mu_{e^-}}{\partial x} \right) \right]}{F \left(z^2 n_{M^{z+}} B_{M^{z+}} + 4 n_{O^{2-}} B_{O^{2-}} + n_{e^-} B_{e^-} \right)} \quad (4.188)$$

The variables n_{e^-} , $n_{O^{2-}}$ and $n_{M^{z+}}$ can be expressed as follows in terms of the experimentally determinable variables, namely the transport numbers and the

electrical conductivities of the species. Under the influence of only electrical potential gradient, the currents due to various charged species as obtained from Eqs. (4.184) to (4.186) will be

$$I_{M^{z+}} = -zFJ_{M^{z+}} = -(zF)^2 n_{M^{z+}} B_{M^{z+}} \left(\frac{\partial \psi}{\partial x} \right) \quad (4.189)$$

$$I_{O^{2-}} = -2FJ_{O^{2-}} = -(2F)^2 n_{O^{2-}} B_{O^{2-}} \left(\frac{\partial \psi}{\partial x} \right) \quad (4.190)$$

$$I_{e^-} = -FJ_{e^-} = -(F)^2 n_{e^-} B_{e^-} \left(\frac{\partial \psi}{\partial x} \right) \quad (4.191)$$

The total current flowing per unit cross-sectional area through the oxide layer will, thus be

$$\begin{aligned} I &= I_{M^{z+}} + I_{O^{2-}} + I_{e^-} \\ &= [(zF)^2 n_{M^{z+}} B_{M^{z+}} + (2F)^2 n_{O^{2-}} B_{O^{2-}} + F^2 n_{e^-} B_{e^-}] \frac{\partial \psi}{\partial x} \end{aligned} \quad (4.192)$$

Thus, specific conductivity σ of the oxide will be

$$\sigma = -\frac{I}{\frac{\partial \psi}{\partial x}} = (zF)^2 n_{M^{z+}} B_{M^{z+}} + (2F)^2 n_{O^{2-}} B_{O^{2-}} + F^2 n_{e^-} B_{e^-} \quad (4.193)$$

and the transport numbers $t_{M^{z+}}$, $t_{O^{2-}}$ and t_{e^-} of the various charged species M^{z+} , O^{2-} and e^- will be, respectively, expressed by the relations

$$\begin{aligned} t_{M^{z+}} &= -\left(\frac{I_{M^{z+}}}{\frac{\partial \psi}{\partial x}} \right) \frac{1}{\sigma} = \frac{\sigma_{M^{z+}}}{\sigma} \\ &= \frac{z^2 n_{M^{z+}} B_{M^{z+}}}{z^2 n_{M^{z+}} B_{M^{z+}} + 4n_{O^{2-}} B_{O^{2-}} + n_{e^-} B_{e^-}} \end{aligned} \quad (4.194)$$

$$\begin{aligned} t_{O^{2-}} &= -\left(\frac{I_{O^{2-}}}{\frac{\partial \psi}{\partial x}} \right) \frac{1}{\sigma} = \frac{\sigma_{O^{2-}}}{\sigma} \\ &= \frac{4n_{O^{2-}} B_{O^{2-}}}{z^2 n_{M^{z+}} B_{M^{z+}} + 4n_{O^{2-}} B_{O^{2-}} + n_{e^-} B_{e^-}} \end{aligned} \quad (4.195)$$

Similarly

$$\begin{aligned} t_{e^-} &= -\left(\frac{I_{e^-}}{\frac{\partial \psi}{\partial x}} \right) \frac{1}{\sigma} = \frac{\sigma_{e^-}}{\sigma} \\ &= \frac{n_{e^-} B_{e^-}}{z^2 n_{M^{z+}} B_{M^{z+}} + 4n_{O^{2-}} B_{O^{2-}} + n_{e^-} B_{e^-}} \end{aligned} \quad (4.196)$$

Elimination of potential gradient $\partial\psi/\partial x$ from Eq. (4.189) with the help of Eqs. (4.194) to (4.196) yields

$$J_{M^{z+}} = \frac{t_{M^{z+}}\sigma}{(zF)^2} \left[\left(1 - t_{M^{z+}}\right) \left(\frac{\partial\mu_{M^{z+}}}{\partial x} \right) + \left(\frac{zt_{O^{2-}}}{2}\right) \left(\frac{\partial\mu_{O^{2-}}}{\partial x} \right) + \left(zt_{e^-}\right) \left(\frac{\partial\mu_{e^-}}{\partial x} \right) \right] \quad (4.197a)$$

which, using Eq. (4.180), will take the form

$$J_{M^{z+}} = \left[\frac{t_{M^{z+}} t_{e^-} \sigma}{4zF^2} \left(\frac{\partial\mu_{O^{2-}}}{\partial x} \right) \right] \quad (4.197b)$$

Similarly, we can write

$$J_{O^{2-}} = - \left[\frac{t_{O^{2-}} t_{e^-} \sigma}{8F^2} \left(\frac{\partial\mu_{O^{2-}}}{\partial x} \right) \right] \quad (4.198)$$

$$J_{M_xO_y} = \left\{ \frac{J_{M^{z+}}}{x} - \frac{J_{O^{2-}}}{y} \right\} = \left\{ \frac{t_{e^-} (t_{M^{z+}} + t_{O^{2-}}) \sigma}{8yF^2} \right\} \frac{\partial\mu_{O^{2-}}}{\partial x} \quad (4.199)$$

which on integration yields

$$J_{M_xO_y} dx = \int_A^B \frac{t_{e^-} (t_{M^{z+}} + t_{O^{2-}}) \sigma}{8yF^2} d\mu_{O^{2-}} \quad (4.200)$$

where $A = \mu_{O^{2-}}$ at M/M_xO_y interface, and $B = \mu_{O^{2-}}$ at gas- M_xO_y interface.

The parameters t_{e^-} , $t_{M^{z+}}$ and $t_{O^{2-}}$ are known to be functions of $\mu_{O^{2-}}$ and not of x and t . Thus, if $\mu_{O^{2-}}$ at M/M_xO_y interface and at the gas- M_xO_y interface be constant, the integral on the right-hand side of Eq. (4.200) will assume a constant value, say, K_{ox} . The value of K_{ox} can be calculated making use of the available experimental data on transport numbers as a function of $\mu_{O^{2-}}$. We can, therefore, write Eq. (4.200) in the following alternative form:

$$\int_0^{x_{ox}} J_{M_xO_y} dx = K_{ox} \quad (4.201)$$

Under the assumption that the oxide phase attains steady state instantaneously, the above equation yields

$$J_{M_xO_y} x_{ox} = K_{ox} \quad (4.202)$$

where x_{ox} is the instantaneous thickness of the oxide layer, and is related to $J_{M_xO_y}$ by the simple equation

$$J_{M_xO_y} = \frac{dn_{M_xO_y}}{dt} = \frac{d}{dt} \left[\frac{\rho_{M_xO_y} x_{ox}}{M_{M_xO_y}} \right] = \left(\frac{\rho_{M_xO_y}}{M_{M_xO_y}} \right) \left(\frac{dx_{ox}}{dt} \right) \quad (4.203)$$

In this equation $\rho_{M_xO_y}$ and $M_{M_xO_y}$ are the density and molecular weight of the oxide respectively. Substitution of Eq. (4.202) in Eq. (4.203) yields

$$x_{ox} dx_{ox} = \left(\frac{K_{ox} M_{M_xO_y}}{\rho_{M_xO_y}} \right) dt \quad (4.204)$$

This on integration, using the initial condition $x_{ox} = 0$, at $t = 0$ yields

$$x_{ox}^2 = \left(\frac{2M_{M_xO_y} K_{ox}}{\rho_{M_xO_y}} \right) t \quad (4.205)$$

This parabolic relation shows that the thickness of the scale or the oxide layer will grow at a rate directly proportional to the square root of time.

We now consider a limiting case for the calculation of K_{ox} . This case pertains to semiconductors for which K_{ox} is expressed in an alternative form. For this class of semiconductors, t_{e^-} approximates unity.

Thus, from Eqs. (4.200) and (4.201), we can write

$$K_{ox} = \int_A^B \left\{ \left(\frac{t_{M^{z+}} + t_{O^{2-}}}{8yF^2} \right) \sigma \right\} d\mu_{O^{2-}} \quad (4.206)$$

where $A = \mu_{O^{2-}}$ at M/M_xO_y interface and $B = \mu_{O^{2-}}$ in gas phase.

According to Eqs. (4.193) to (4.195), we can write

$$\begin{aligned} \sigma t_{M^{z+}} &= \sigma_{M^{z+}} = (zF)^2 n_{M^{z+}} B_{M^{z+}} \\ &= (zF)^2 n_{M^{z+}} \left(\frac{D_{M^{z+}}^*}{kT} \right) \end{aligned} \quad (4.207)$$

and

$$\begin{aligned} \sigma t_{O^{2-}} &= \sigma_{O^{2-}} = 4F^2 n_{O^{2-}} B_{O^{2-}} \\ &= 4F^2 n_{O^{2-}} \left(\frac{D_{O^{2-}}^*}{kT} \right) \end{aligned} \quad (4.208)$$

where $D_{M^{z+}}^*$ and $D_{O^{2-}}^*$ are, respectively, the self-diffusion coefficients of ions M^{z+} and O^{2-} . Substitution of the above equations in Eq. (4.200) leads to

$$K_{ox} = \int_A^B \left\{ \frac{N \left(z^2 n_{M^{z+}} D_{M^{z+}}^* + 4n_{O^{2-}} D_{O^{2-}}^* \right)}{8y} \right\} (d \ln P_{O_2}) \quad (4.209)$$

where $A = P_{O_2}$ at M/M_xO_y interface, $B = P_{O_2}$ in gas phase and N is the Avogadro's number. The above equation is further simplified depending upon the relative values of $D_{M^{z+}}^*$ and $D_{O^{2-}}^*$. In case, a crystal has cationic vacancies, then $D_{M^{z+}}^* \gg D_{O^{2-}}^*$, and, therefore, the term containing $D_{O^{2-}}^*$ is neglected. If the crystal has anionic vacancies, then $D_{O^{2-}}^* \gg D_{M^{z+}}^*$, and, therefore, the term containing $D_{M^{z+}}^*$ is neglected and thus, the integration gets further simplified.

Application of the above equation is illustrated below with the help of an example.

EXAMPLE 4.15 The free energy change for the oxidation of a metal M to its oxide MO at 800°C is $-1.0 \times 10^5 \text{ kJ kg-mol}^{-1}$ of oxide. This metal is exposed to air at this temperature. The oxide which is predominantly an electronic conductor is related to $D_{M^{z+}}^*$ expressed in $\text{cm}^2 \text{ s}^{-1}$ units and the oxygen partial pressure, P_{O_2} , in atm as follows:

$$\ln D_{M^{z+}}^* = -23.3 - 0.15 \ln P_{O_2}$$

Calculate the (i) value of K_{ox} , and (ii) thickness of the oxide layer formed after exposing the metal for one week.

Given: Molecular weight of metal = 60
Density of the oxide = 4300 kg m^{-3}

Also assume that $D_O^* \ll D_M^*$.

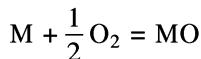
Solution According to the principles of thermodynamics, we have

$$\Delta G^\circ = -RT \ln K_{eq}$$

Hence, using the given value of ΔG° at 800°C, we have

$$K_{eq} = \exp\left(-\frac{\Delta G^\circ}{RT}\right) = 6.8 \times 10^4$$

Further, the formation of oxide takes place according to the equation



Thus

$$K_{eq} = \frac{1}{(P_{O_2})^{1/2}}$$

or

$$P_{O_2} = \left(\frac{1}{K_{eq}}\right)^2 = 2.17 \times 10^{-10} \text{ atm}$$

Thus, the oxygen partial pressure at the metal-metal oxide interface will be 2.17×10^{-10} atm.

According to Eq. (4.209), we have

$$\begin{aligned} K_{ox} &= \int_{2.17 \times 10^{-10}}^{0.21} \frac{Nn_{M^{z+}}}{2} D_{M^{z+}}^* (d \ln P_{O_2}) \\ &= \frac{Nn_{M^{z+}}}{2} \int_{2.17 \times 10^{-10}}^{0.21} [(P_{O_2})^{-0.15} \{\exp (-23.3)\} (d \ln P_{O_2})] \end{aligned}$$

$$\begin{aligned}
 &= - \left[\frac{Nn_{M^{z+}}}{0.3} \right] [\exp(-23.3)] [(0.21)^{-0.15} - (2.17 \times 10^{-10})^{-0.15}] \\
 &= 6.8 \times 10^{-9} (n_{M^{z+}}) = (6.8 \times 10^{-13}) \frac{4300}{76} \\
 &= 3.85 \times 10^{-11} \text{ kg-mol m}^{-1} \text{ s}^{-1} \quad \text{Ans.}
 \end{aligned}$$

According to Eq. (4.205), we have

$$\begin{aligned}
 x_{ox} &= \left[\left(\frac{2M_{M_x O_y}}{\rho_{M_x O_y}} \right) \right]^{1/2} (K_{ox})^{1/2} (t)^{1/2} \\
 &= \left(\frac{2 \times 76}{4300} \right)^{1/2} \times (3.85 \times 10^{-11}) \times (7 \times 24 \times 3600)^{1/2} \\
 &= 9.07 \times 10^{-4} \text{ m} \quad \text{Ans.}
 \end{aligned}$$

Topochemical gaseous reduction of dense spherical pellets. The rates of many solid-gas reactions are of immense industrial significance to metallurgists, since such reactions are involved in numerous roasting, calcination and smelting processes. Therefore, extensive laboratory studies on the kinetics of such reactions have been made. Among these reactions, the most commonly studied reaction on laboratory scale is the reduction kinetics of dense hematite pellets with a gaseous reductant such as hydrogen or carbon monoxide. The reduction in such cases proceeds by the chemical reaction at a well-defined moving interface by the reaction which in case of hydrogen will be



The gaseous reductant reaches the interface from the bulk of the gas phase by diffusion through a gas-film formed around the pellet and the porous reduced shell. Thus, the overall reaction may be considered to involve the following five steps:

- (i) Diffusion of hydrogen from the bulk of the gas phase to the surface of the pellet through the gas film.
- (ii) Diffusion of hydrogen from the surface of the pellet through the reduced layer to the reaction interface.
- (iii) Chemical reaction at the reaction interface.
- (iv) Diffusion of the product, i.e. water vapours, formed as a result of chemical reaction, from the reaction interface to the surface of the pellet.
- (v) Diffusion of water vapours from the surface of the pellet to the bulk of the gas phase, through the gas film.

Such gas-solid reactions which proceed by the movement of a well-defined interface are called *topochemical reactions*. In the present analysis, it will be

assumed that the chemical reaction is much faster than the diffusional steps. Thus, diffusion will control the overall reaction rate. The case in which the chemical reaction is slower than diffusion will be considered in Chapter 7.

Further, if the gas velocity in the bulk phase is high, diffusion of gases through the gas film will be of insignificant importance in the overall reaction. Hence, the rate of reduction will be controlled by diffusion of the gas through the porous reduced-shell. Now, if the total pressure of the gas is the same at every point in the reduced shell, then the amount of hydrogen diffusing into the shell will be equal to that of the water vapours diffusing out. Thus, we need consider the diffusion of only one gaseous component. Further, the above arguments lead to the assumptions that the surface of the pellet will have the same composition of the gas as the bulk and the interface will have the composition corresponding to that for equilibrium of the reaction, expressed by Eq. (4.210).

For mathematical analysis of this problem, we need to consider the diffusion equation in the spherical coordinate system as the pellet shows a spherical symmetry. For this case, under steady state conditions, the diffusion equation shall assume the form

$$\frac{\partial}{\partial r} \left(r^2 \frac{\partial C}{\partial r} \right) = 0 \quad (4.211)$$

which on integration yields

$$C = - \frac{A}{r} + B \quad (4.212)$$

where C is the concentration of diffusing phase at radius r of the spherical pellet, and A and B are constants of integration and their values are determined by using the following boundary conditions.

$$(i) \quad C = C_b \quad \text{at} \quad r = R_o \quad (4.213)$$

$$(ii) \quad C = C_e \quad \text{at} \quad r = R_i \quad (4.214)$$

where C_e is the equilibrium gas concentration for the reaction taking place at the reaction interface situated at a radius R_i and C_b is the bulk concentration of the surface of spherical pellet of radius R_o , as shown in Fig. 4.13. Making use of these two conditions, Eq. (4.212) takes the form

$$\frac{C_b - C}{C_b - C_e} = \frac{R_o - r}{R_o - R_i} \frac{R_i}{r} \quad (4.215)$$

If the overall reaction is controlled by the diffusion in the reacted shell and if α moles of the gas react with β moles of the pellet leading to the formation of the product, then we can write an equation based on mass balance. According to this, the amount of gas m_g diffusing in from the surface of the pellet is equal to the amount of gas reacted. Thus

$$m_g = -4\pi R_o^2 \left(D \frac{\partial C}{\partial r} \right)_{r=R_o} = \left(\frac{\alpha}{\beta} \right) \left(\frac{\rho}{M} \right) (4\pi R_i^2) \left(\frac{dR_i}{dt} \right) \quad (4.216)$$

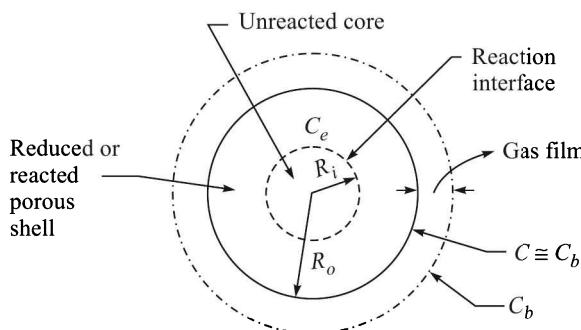


Fig. 4.13 Topochemical gaseous reduction of dense spherical pellets.

where ρ is the density of the solid and M its molecular weight. Substitution of the expression for C in this equation from Eq. (4.215), yields

$$D \left(\frac{R_o R_i}{R_o - R_i} \right) (C_b - C_e) = \left(\frac{\alpha}{\beta} \right) \left(\frac{\rho}{M} R_i^2 \right) \left(\frac{dR_i}{dt} \right)$$

or

$$\frac{dR_i}{dt} = \left(\frac{DR_o(C_b - C_e)}{R_i(R_o - R_i)} \right) \left(\frac{M}{\rho} \right) \left(\frac{\beta}{\alpha} \right) \quad (4.217)$$

Integration of the above equation and then the application of the initial condition, viz. $R_i = R_o$ at $t = 0$, yields

$$\frac{R_i^2}{2} - \frac{R_i^3}{3R_o} E - \frac{R_o^2}{6} = \frac{\beta M (C_b - C_e) Dt}{\alpha \rho} \quad (4.218)$$

This equation can be used to find the position of the radius R_i of the reaction interface at any time t from which we can calculate the degree of fractional reduction f . Let us consider the reduction of a dense Fe_2O_3 pellet. For this case, the fractional reduction f is defined as the amount of oxygen removed at any instant as a fraction of the total oxygen present in the pellet initially.

If ρ be the density of the pellet containing W_o as the initial amount of oxygen present in it, then

$$W_o = \frac{48}{160} \rho \frac{4\pi}{3} R_o^3 \quad (4.219)$$

If R_i be the radius of the reaction interface at any instant, then W_i the amount of oxygen present in the pellet at that instant will be given by the equation

$$W_i = \frac{48}{160} \rho \frac{4\pi}{3} R_i^3 \quad (4.220)$$

With the help of Eqs. (4.219) and (4.220), we can write for f the equation

$$f = \frac{W_o - W_i}{W_o} = \frac{R_o^3 - R_i^3}{R_o^3} = 1 - \left(\frac{R_i}{R_o} \right)^3 \quad (4.221)$$

Hence

$$R_i = R_o (1 - f)^{1/3} \quad (4.222)$$

Substitution of the above equation for R_i in Eq. (4.218) yields

$$(2f - 3) + 3(1 - f)^{2/3} = \frac{6\beta}{\alpha} \frac{M(C_b - C_e)}{\rho R_o^2} Dt \quad (4.223)$$

The above equation shows that if the function on the left-hand side is directly proportional to time, the rate is controlled by diffusion through porous shell. Once this step is found to control the reaction, we can calculate the reaction rate and the extent of reaction at any instant as illustrated by the following example.

EXAMPLE 4.16 A dense hematite pellet 1.5×10^{-2} m in diameter, is reduced isothermally at 700°C with pure hydrogen maintained under one atmosphere pressure. The diffusion coefficient of hydrogen in porous reduced shell is found to be 1.7×10^{-5} m 2 s $^{-1}$. Derive an equation for the rate of movement of the reaction interface. Also, calculate the fractional reduction and the amount of oxygen removed from the pellet in 3 hours. The density of pellet is 5300 kg m $^{-3}$. Atomic weight of iron = 56, and, ΔG° , the standard free energy change of the reaction, $\text{Fe}_2\text{O}_3 + 3\text{H}_2 = 2\text{Fe} + 3\text{H}_2\text{O}$ is 6.7 kJ at 700°C .

Solution Mass of the pellet = $\frac{4}{3} \pi R_o^3 \rho$

$$\begin{aligned} &= \frac{4}{3} \frac{22}{7} \left(\frac{1.5 \times 10^{-2}}{2} \right)^3 5300 \\ &= 9.37 \times 10^{-3} \text{ kg} \end{aligned}$$

Amount of oxygen initially present in the pellet

$$= 9.37 \times 10^{-3} \times \frac{48}{160} = 2.81 \times 10^{-3} \text{ kg}$$

Equilibrium constant K_{eq} for the given reaction will be

$$K_{\text{eq}} = \exp \left(-\frac{\Delta G^\circ}{RT} \right) = \exp \left(\frac{6700}{8.3 \times 973} \right) = 0.436$$

Thus, at the reaction interface, we have

$$\left(\frac{P_{\text{H}_2\text{O}}}{P_{\text{H}_2}} \right)^3 = \left(\frac{1 - P_{\text{H}_2}}{P_{\text{H}_2}} \right)^3 = 0.436 \quad (\text{assuming } P_{\text{H}_2} + P_{\text{H}_2\text{O}} = 1 \text{ atm})$$

or

$$P_{\text{H}_2} = 0.568 \text{ atm}$$

Assuming hydrogen to behave as an ideal gas, the concentration C_b of hydrogen in the bulk phase will be

$$\begin{aligned} C_b &= \frac{P_{H_2}}{RT} = \frac{1}{0.082 \times 973} = 1.25 \times 10^{-2} \text{ kg-mol m}^{-3} \\ &= 12.5 \times 10^{-3} \text{ kg-mol m}^{-3} \end{aligned}$$

The concentration C_e of hydrogen at the reaction interface will be

$$C_e = \frac{0.568 \times 1}{0.082 \times 973} = 7.12 \times 10^{-3} \text{ kg-mol m}^{-3}$$

Thus

$$(C_b - C_e) = (12.5 - 7.12) \times 10^{-3} = 5.38 \times 10^{-3} \text{ kg-mol m}^{-3}$$

According to Eq. (4.217)

$$\begin{aligned} \frac{dR_i}{dt} &= \frac{DR_o(C_b - C_e)}{R_i(R_o - R_i)} \left(\frac{M}{\rho} \right) \left(\frac{\beta}{\alpha} \right) \\ &= \frac{(1.7 \times 10^{-5}) \times (7.5 \times 10^{-3}) \times (5.38 \times 10^{-3})}{R_i \{(7.5 \times 10^{-3}) - R_i\}} \frac{160}{5300} \frac{1}{3} \\ &= \frac{6.9 \times 10^{-12}}{R_i (7.5 \times 10^{-3} - R_i)} \text{ m s}^{-1} \end{aligned}$$

Hence

$$\left\{ \frac{(7.5 \times 10^{-3}) R_i^2}{2} - \frac{R_i^3}{3} \right\} = (6.9 \times 10^{-12}) t \quad \text{Ans.}$$

Thus, for

$$\begin{aligned} t &= 3 \text{ h} \\ R_i &= 5 \times 10^{-3} \text{ m} \end{aligned}$$

and, therefore, $f = 0.7$ by using Eq. (4.222).

Ans.

4.2 CONVECTIVE MASS TRANSFER—NATURAL AND FORCED CONVECTION

In convective mass transfer, transport of a given species is affected by diffusion as well as convection because of motion of the bulk of the fluid. The continuity equation for a single component system has already been derived in Chapter 2, Section 2.3.1. But most of the systems of practical importance to metallurgists consist of a number of components and require the derivation of the mass balance equation for each of the components. Thus, we have to deal with a number of simultaneous differential equations. Therefore, the problems involving

convective mass transfer become more complex than the diffusion problems as these are also coupled with the transfer of momentum.

In the following subsection, we will first deal with the general mass transfer equation in laminar flow followed by its application to some typical examples from metallurgical systems.

4.2.1 General Differential Equation for Convective Mass Transfer

In most of the metallurgical processes such as those occurring in open hearth furnaces, roasters, blast furnaces or even in stoves, we have a multicomponent reactive or nonreactive fluid, flowing through the reactor. In this subsection, therefore, continuity equation for a single-phase multicomponent reacting fluid will be derived. For this purpose, we consider an elemental volume shown in Fig. 4.14 in an n -component fluid flowing in the reactor. Let there be m independent chemical reactions occurring among these components. According to the law of conservation of mass for an arbitrary component i , we can write the relation

$$\begin{aligned} & (\text{Amount of component } i \text{ flowing into the element}) \\ & - (\text{Amount of component } i \text{ flowing out of the element}) \\ & = (\text{Amount of component } i \text{ accumulated}) \\ & \pm (\text{Amount of component } i \text{ consumed or produced}) \quad (4.224) \end{aligned}$$

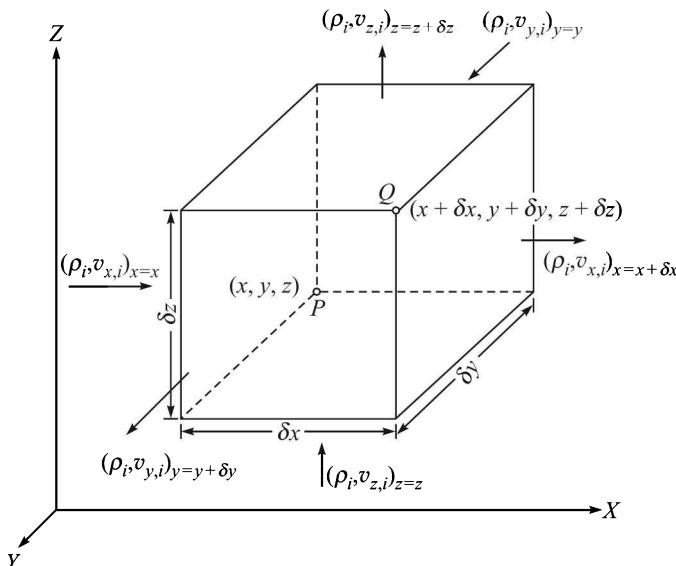


Fig. 4.14 Analysis of convective mass transfer through a differential volume element.

For the last term on the right-hand side of Eq. (4.224), positive sign is used if the component is consumed and negative sign if it is produced in the reactor. If we consider the direction of flow of fluid as shown in Fig. 4.14, we can write the following equations based on a similar analysis as followed for arriving at Eqs. (2.23) and (2.24). The mass of fluid entering the volume element per unit time

$$m_e = (\rho_i v_{xi})_{x=x} \partial y \partial z + (\rho_i v_{yi})_{y=y} \partial x \partial z + (\rho_i v_{zi})_{z=z} \partial x \partial y \quad (4.225)$$

and the mass of fluid leaving the volume element per unit time

$$m_l = (\rho_i v_{xi})_{x=x+\partial x} \partial y \partial z + (\rho_i v_{yi})_{y=y+\partial y} \partial x \partial z + (\rho_i v_{zi})_{z=z+\partial z} \partial x \partial y \quad (4.226)$$

where ρ_i is the density, and v_{xi} , v_{yi} and v_{zi} are, respectively, the components of fluid velocities in x - y - and z -directions for the component i at the positions indicated as suffixes outside brackets. For example, $(\rho_i v_{xi})_{x=x}$, is the mass flowrate of component i per unit cross-sectional area in the x -direction at the entrance face of the volume element. Similarly, for accumulation of the component i , we can write the equation as follows.

Amount of component i accumulated in the volume per unit time

$$q_e = \frac{\partial \rho_i}{\partial t} \partial x \partial y \partial z \quad (4.227)$$

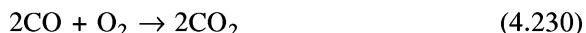
If r_{ij} be the mass rate of production or consumption per unit volume per unit time of the component i in the j th reaction, then, the total amount of this component produced or consumed per unit time

$$q_l = \left(\sum_{j=1}^m r_{ij} \right) \partial x \partial y \partial z \quad (4.228)$$

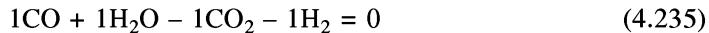
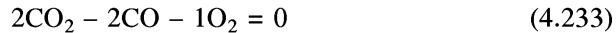
where the sign of r_{ij} is positive if the component is produced and negative if consumed. In general, the rate r_{ij} is expressed in terms of another variable called the *reaction progress variable*, ξ . To define this variable, we consider the j th chemical reaction which can be written in the form

$$\gamma_{1j} B_1 + \gamma_{2j} B_2 + \dots + \gamma_{ij} B_i + \gamma_{nj} B_n = 0 \quad (4.229)$$

where B_1 , B_2 , etc. are respectively the chemical symbols of a total number of n -components 1, 2, etc. including both reactants and products, and γ_{1j} , γ_{2j} , etc. respectively are the numbers of molecules of components 1, 2, etc. taking part in the j th chemical reaction, according to the stoichiometric chemical equation. As a convention, these coefficients are negative for the reactants and positive for the products. For example, in a gaseous mixture consisting of CO, CO₂, H₂O and O₂, the various reactions taking place can be written as



According to the convention represented by Eq. (4.229), the above reactions can be written as



It is easy to prove on the basis of the law of conservation of mass that for all reactions j , the total mass of the reactants equals that of the products, i.e.

$$\sum_{i=1}^n \gamma_{ij} M_i = 0 \quad (4.236)$$

In Eq. (4.236), M_i is the molecular weight of the component i . It should, however, be noted that these reactions occur only among the components of the flowing fluid. Further with the help of chemical equations, we can write for the j th reaction

$$\frac{r_{1j}}{\gamma_{1j} M_1} = \frac{r_{2j}}{\gamma_{2j} M_2} = \dots = \frac{r_{ij}}{\gamma_{ij} M_i} = \dots = \frac{r_{nj}}{\gamma_{nj} M_j} = \frac{\partial \xi_j}{\partial t} \quad (4.237)$$

where ξ_j is the *reaction progress variable* for the j th reaction. Hence, using Eq. (4.237), we can write Eq. (4.228) as

$$\text{Amount of component } i \text{ reacted per unit time} = \left[\sum_{j=1}^m \gamma_{ij} M_i \left(\frac{\partial \xi_j}{\partial t} \right) \right] \partial x \partial y \partial z \quad (4.238)$$

Substitution of Eqs. (4.225) to (4.228) and Eq. (4.238) in Eq. (4.224) and considering the volume element to be infinitesimal, we get the following continuity equation for the component i in the reactive multicomponent system under study.

$$\frac{\partial \rho_i}{\partial t} = - \left[\frac{\partial}{\partial x} (\rho_i v_{xi}) + \frac{\partial}{\partial y} (\rho_i v_{yi}) + \frac{\partial}{\partial z} (\rho_i v_{zi}) \right] + \left[\sum_{j=1}^m \gamma_{ij} M_i \left(\frac{\partial \xi_j}{\partial t} \right) \right] \quad (4.239)$$

Equation (4.239) takes the following form in cylindrical coordinates:

$$\frac{\partial \rho_i}{\partial t} = - \left\{ \frac{1}{\gamma} \frac{\partial}{\partial \gamma} (\rho_i v_{ir}) + \frac{1}{r} \frac{\partial}{\partial \theta} (\rho_i v_{i\theta}) + \frac{\partial}{\partial z} (\rho_i v_{iz}) \right\} + \left\{ \sum_{j=1}^m \gamma_{ij} M_i \left(\frac{\partial \xi_j}{\partial t} \right) \right\} \quad (4.240)$$

In the spherical coordinate system, Eq. (4.239) can be written as

$$\frac{\partial \rho_i}{\partial t} = - \left[\frac{1}{r^2} \frac{\partial}{\partial r} (r^2 \rho_i v_{ir}) + \frac{1}{r \sin \theta} \frac{\partial}{\partial \theta} (\rho_i v_{i\theta} \sin \theta) \right]$$

$$+ \frac{1}{r \sin \theta} \frac{\partial(\rho_i v_{i\phi})}{\partial \phi} \Big] + \left[\sum_{j=1}^m \gamma_{ij} M_i \left(\frac{\partial \xi_j}{\partial t} \right) \right] \quad (4.241)$$

It is, however, to be noted that the velocity components v_{xi} , v_{yi} and v_{zi} in Eq. (4.239) must not be equal to the fluid velocities in x -, y - and z -directions. Though there are a number of different ways of writing the Eq. (4.239), the one which makes use of convectional and molecular flow of fluids is often used. For this purpose, the velocity component v_{xi} of the mass flow rate is split into two components as follows:

$$\rho_i v_{xi} = \rho_i v_x + J_{xi} \quad (4.242)$$

where v_x is the mean fluid velocity and J_{xi} the diffusional flux of component i or the molecular flow rate of component i over and above the fluid flow rate. This is expressed, according to Eq. (4.1) as

$$J_{xi} = -D_{xi} \left(\frac{\partial \rho_i}{\partial x} \right) \quad (4.243)$$

where the symbol D_{xi} is the diffusion coefficient of the component i in the x -direction.

With the help of Eqs. (4.242) and (4.243), we can write Eq. (4.239) in the following form:

$$\begin{aligned} \frac{\partial \rho_i}{\partial t} &= - \left[\frac{\partial}{\partial x} (\rho_i v_x) + \frac{\partial}{\partial y} (\rho_i v_y) + \frac{\partial}{\partial z} (\rho_i v_z) \right] \\ &+ \left[\frac{\partial}{\partial x} \left(D_{xi} \frac{\partial \rho_i}{\partial x} \right) + \frac{\partial}{\partial y} \left(D_{yi} \frac{\partial \rho_i}{\partial y} \right) + \frac{\partial}{\partial z} \left(D_{zi} \frac{\partial \rho_i}{\partial z} \right) \right] + \left[\sum_{j=1}^m \gamma_{ij} M_i \left(\frac{\partial \xi_j}{\partial t} \right) \right] \end{aligned} \quad (4.244)$$

We now consider a commonly used form of the above equation. For the case in which both ρ_i and D_i are constant, we can write Eq. (4.244) in the following substantial derivative form:

$$\frac{D\rho_i}{Dt} = D_i \left(\frac{\partial^2 \rho_i}{\partial x^2} + \frac{\partial^2 \rho_i}{\partial y^2} + \frac{\partial^2 \rho_i}{\partial z^2} \right) + \sum_{j=1}^m \gamma_{ij} M_i \left(\frac{\partial \xi_j}{\partial t} \right) \quad (4.245)$$

In the cylindrical coordinate system, the above equation becomes

$$\begin{aligned} \frac{\partial \rho_i}{\partial t} + \left(v_r \frac{\partial \rho_i}{\partial r} + \frac{v_\theta}{r} \frac{\partial \rho_i}{\partial \theta} + v_z \frac{\partial \rho_i}{\partial z} \right) &= D_i \left\{ \frac{1}{r} \frac{\partial}{\partial r} \left(r \frac{\partial \rho_i}{\partial r} \right) + \frac{1}{r^2} \frac{\partial^2 \rho_i}{\partial \theta^2} + \frac{\partial^2 \rho_i}{\partial z^2} \right\} \\ &+ \sum_{j=1}^m \gamma_{ij} M_i \left(\frac{\partial \xi_j}{\partial t} \right) \end{aligned} \quad (4.246)$$

and in the spherical coordinate system as

$$\begin{aligned} \frac{\partial \rho_i}{\partial t} + & \left(v_r \frac{\partial \rho_i}{\partial r} + \frac{v_\theta}{r} \frac{\partial \rho_i}{\partial \theta} + \frac{v_\phi}{r \sin \theta} \frac{\partial \rho_i}{\partial z} \right) \\ = D_i & \left[\frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial \rho_i}{\partial r} \right) + \frac{1}{r^2 \sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial \rho_i}{\partial \theta} \right) \right. \\ & \left. + \frac{1}{r^2 \sin^2 \theta} \left(\frac{\partial^2 \rho_i}{\partial \phi^2} \right) \right] + \sum_{j=1}^m \gamma_{ij} M_i \left(\frac{\partial \xi_j}{\partial t} \right) \end{aligned} \quad (4.247)$$

In some cases, instead of mass densities, (ρ terms), molar concentrations, (C terms) in the fluid phase may remain constant during the process. For such a case, Eq. (4.245) will assume the form

$$\frac{DC_i}{Dt} = D_i \left(\frac{\partial^2 C_i}{\partial x^2} + \frac{\partial^2 C_i}{\partial y^2} + \frac{\partial^2 C_i}{\partial z^2} \right) + \sum_{j=1}^m \left(\gamma_{ij} \frac{\partial \xi_j}{\partial t} \right) \quad (4.248)$$

Equations (4.244) to (4.247) can also be written in terms of mass- and mole-fractions by making use of Eqs. (4.2) and (4.3). From these equations, we can also obtain the relations for a limiting case by putting the reaction-component equal to zero for the systems in which no chemical reaction takes place.

Further, it may be noted that in the case of a stagnant nonreacting system, Eq. (4.248) will assume the form

$$\frac{\partial C_i}{\partial t} = D_i \left(\frac{\partial^2 C_i}{\partial x^2} + \frac{\partial^2 C_i}{\partial y^2} + \frac{\partial^2 C_i}{\partial z^2} \right) \quad (4.249)$$

This equation is the general form of the Fick's Second Law of Diffusion which was discussed for diffusion in one direction only in Section 4.1.3. This equation is frequently used to calculate concentration profiles in which diffusion is the dominating mode of mass transfer. The use of this equation was illustrated in Section 4.1.3.

4.2.2 Applications

Convective mass transfer equations find extensive applications in arriving at the exact solution of boundary layer problems. Some of these problems shall be discussed in Chapter 6. Apart from these, there are several other cases in which convective mass transfer is involved. Some commonly occurring problems of this type will be discussed in this subsection.

Mass transfer in forced convective laminar flow in a pipe

The importance of the analysis of convective mass transfer lies in its application to the corrosion of pipes containing flowing fluids, monolithic converters or tube wall reactors and the calculation of mass transfer coefficients in packed beds.

In order to illustrate the general principles of the method of analysis in respect of this case, we consider a multicomponent fluid flowing through a pipe of radius r_0 . Let component A of the fluid react with the surface of the pipe. We further assume that the chemical reaction involving this component is very fast and hence a state of chemical equilibrium exists for the fluid in contact with the surface of the pipe. Let the initial concentration of component A in fluid be C_A^0 and that at the wall of the pipe be C_A^w which will be a constant. We now proceed to arrive at the concentration profile in the radial direction, under the assumed condition that the velocity profile of the fluid in the pipe is fully developed. By fully developed flow, we may recall that the velocity profile in the radial direction does not change with position along the axial direction. The continuity equation for this system in cylindrical coordinates can be obtained from Eq. (4.246) by putting the reaction component equal to zero and also by assuming steady state to prevail. Thus, we have

$$v_z \frac{\partial C_A}{\partial z} + v_r \frac{\partial C_A}{\partial r} = D_A \left[\frac{1}{r} \frac{\partial}{\partial r} \left(r \frac{\partial C_A}{\partial r} \right) + \frac{\partial^2 C_A}{\partial z^2} \right] \quad (4.250)$$

where D_A is the diffusion coefficient of A in the fluid.

In the above equation, the concentrations are expressed in terms of moles per unit volume. For fully developed region

$$v_r = 0 \quad (4.251)$$

and

$$\frac{\partial C_A}{\partial r} \gg \frac{\partial^2 C_A}{\partial z^2} \quad (4.252)$$

Hence, the above equation simplifies further to

$$v_z \frac{\partial C_A}{\partial z} = D_A \left[\frac{1}{r} \frac{\partial}{\partial r} \left(r \frac{\partial C_A}{\partial r} \right) \right] \quad (4.253)$$

The boundary conditions for the above equation will be:

$$(i) \text{ at } r = 0 \quad \frac{\partial C_A}{\partial r} = 0 \quad (4.254)$$

$$(ii) \text{ at } r = r_0 \quad C_A = K_{eq} C_A^w \quad (4.255)$$

where K_{eq} is the equilibrium constant and C_A^w as already stated will be constant, if the activity a_{AS} of component A at the pipe-surface is a constant.

Thus, another boundary condition for this case will be

$$(iii) \text{ at } r = r_0 \quad \frac{dC_A^w}{dz} = 0 \quad (4.256)$$

The momentum balance Eq. (2.88) for the system in cylindrical coordinates for fully developed flow reduces to

$$\frac{\partial P}{\partial z} = \mu \left[\frac{\partial^2 v_z}{\partial r^2} + \frac{1}{r} \left(\frac{\partial v_z}{\partial r} \right) \right] \quad (4.257)$$

The above equation on integration under the boundary conditions

$$v_z = 0 \text{ at } r = r_0 \quad (4.258)$$

and

$$\frac{\partial v_z}{\partial r} = 0 \text{ at } r = 0, \text{ i.e. } v_z \text{ is finite at } r = 0 \quad (4.259)$$

yields

$$\begin{aligned} v_z &= \frac{1}{4\mu} \left(\frac{\partial P}{\partial z} \right) (r_0^2 - r^2) \\ &= 2\bar{v}_z \left[1 - \left(\frac{r}{r_0} \right)^2 \right] \end{aligned} \quad (4.260)$$

where \bar{v}_z is the average velocity of the fluid.

Substitution of Eq. (4.260) in Eq. (4.253) leads to

$$2\bar{v}_z \left[1 - \left(\frac{r}{r_0} \right)^2 \right] \left(\frac{\partial C_A}{\partial z} \right) = D_A \left[\frac{1}{r} \frac{\partial}{\partial r} \left(r \frac{\partial C_A}{\partial r} \right) \right] \quad (4.261)$$

The above equation can be solved by numerical methods under the boundary conditions laid down in Eqs. (4.254) to (4.256) in order to obtain the concentration profile of component A in the radial direction. From this concentration profile, we can evaluate the rate of transfer of component A from the surface in the radial direction. In a limiting case of low flow rates, J_A is found to follow the equation

$$J_A = 1.83 D_A \left(\frac{C_A^w - C_A^0}{r_0} \right) \quad (4.262)$$

It may also be mentioned here that the above treatment is applicable to systems having low solubilities of component A in the fluid.

Mass transfer by gas bubbles rising in a liquid bath

A large number of metallurgical processes related to extraction and refining of metals involve mass transfer between a liquid and a gas phase. This gas phase is brought in contact with the liquid by purging in the form of bubbles with the help of a nozzle provided at the bottom of the fluid mass. Some common examples of gas purging in metallurgical processes include:

- (i) Purging of argon in molten steel bath for removal of dissolved gases such as hydrogen and nitrogen
- (ii) Purging of molten aluminium with chlorine to remove hydrogen
- (iii) Precipitation of Cu, Ni and Co from their aqueous ammonical solutions by purging with hydrogen
- (iv) Purging of H₂S through copper and cobalt aqueous solutions to precipitate CuS and CoS respectively.

Thus, estimation of the rate at which gas bubbles affect mass transfer while rising through a liquid bath becomes important for the kinetic analysis of a number of metallurgical processes.

The role played by gas bubbles in such purging processes can be divided into two categories. Bubbles of the first category provide only a gaseous atmosphere for either absorption or desorption of another gaseous species present in the liquid. This is exemplified by the purging of argon in a molten steel bath for degassing of H₂ or N₂. In the second category are considered gas bubbles which react chemically with the liquid to form a third component, as exemplified under items (iii) and (iv) above. In the following paragraphs, we will analyse the mass transport problem with the first category of bubbles as an illustrative example.

For estimation of the rate of gas absorption or desorption, we consider a quiescent liquid bath through which gas bubbles of radius r_b are rising at a terminal velocity v_t . As a bubble rises through the liquid mass, it encounters fresh liquid at its top which in turn leaves it at the bottom during its further rise. The liquid near the surface can be assumed to develop a downward laminar flow because of the upward motion of the bubbles. Thus, under steady state conditions, the differential mass balance equation, i.e. Eq. (4.248) will assume the form

$$v_t \frac{\partial C_A}{\partial z} = D_A \frac{\partial^2 C_A}{\partial x^2} \quad (4.263)$$

where A refers to the gaseous component present in the liquid mass being absorbed or desorbed, z denotes the direction of movement of the bubble which is generally vertical, and, x is the direction normal to that of the bubble movement. It is important to note that instead of making use of conventionally used cylindrical coordinates, we have written this equation in the rectangular coordinate system. This system has been preferred because it considerably simplifies the mathematical treatment without appreciably affecting the accuracy of the results obtained.

The boundary conditions for the system under analysis will be:

$$(i) \quad C_A = C_{A,0} \text{ at } z = 0 \quad (4.264)$$

$$(ii) \quad C_A = C_{A,e} \text{ at } x = 0 \quad (4.265)$$

$$(iii) \quad C_A = C_{A,0} \text{ at } x = \infty \quad (4.266)$$

where the position $x = 0$ is assumed to be at the gas-liquid interface and the position $x = \infty$ at a far away point from the bubble-liquid interface inside the liquid.

In order to solve Eq. (4.263), we first introduce two new variables ΔC_A and $\Delta C_{A,e}$ such that

$$\Delta C_A = C_A - C_{A,0} \quad (4.267a)$$

and

$$\Delta C_{A,e} = C_{A,e} - C_{A,0} \quad (4.267b)$$

Thus, Eqs. (4.263) to (4.266) assume, respectively, the forms

$$\frac{\partial(\Delta C_A)}{\partial z} = \frac{D_A}{v_t} \frac{\partial^2(\Delta C_A)}{\partial x^2} \quad (4.268)$$

With transformed boundary conditions

$$(i) \Delta C_A = 0 \quad \text{at } z = 0 \quad (4.269)$$

$$(ii) \Delta C_A = C_{A,e} \quad \text{at } x = 0 \quad (4.270)$$

$$(iii) \Delta C_A = 0 \quad \text{at } x = \infty \quad (4.271)$$

To obtain an analytical solution of Eq. (4.268), we can make use of Laplace transforms. Thus, we can define a new variable ΔC_A^* such that

$$\Delta C_A^* = \int_0^\infty (\Delta C_A) \exp(-pz) dz \quad (4.272)$$

and

$$\begin{aligned} \left(\frac{\partial \Delta C_A^*}{\partial z} \right) &= \int_0^\infty \left[\frac{(\partial \Delta C_A)}{\partial z} \right] \exp(-pz) dz \\ &= [(\Delta C_A) \exp(-pz)]_0^\infty + p \int_0^\infty (\Delta C_A) \exp(-pz) dz = p(\Delta C_A^*) \end{aligned} \quad (4.273)$$

Thus, Eq. (4.268) can be written in a total differential form as

$$p(\Delta C_A^*) = \frac{D_A}{v_t} \frac{\partial^2(\Delta C_A^*)}{\partial x^2} \quad (4.274)$$

A general solution of the above equation can be written as

$$\Delta C_A^* = B_1 \exp \left[\left(\frac{D_A}{pv_t} \right)^{1/2} x \right] + B_2 \exp \left[- \left(\frac{D_A}{pv_t} \right)^{1/2} x \right] \quad (4.275)$$

The values of B_1 and B_2 can be obtained from the boundary conditions as follows. According to Eq. (4.270), at $x = 0$, we have

$$\begin{aligned} \Delta C_A^* &= \int_0^\infty \Delta C_{A,e} \exp(-pz) dz \\ &= \Delta C_{A,e} \int_0^\infty \exp(-pz) dz = \frac{\Delta C_{A,e}}{p} \end{aligned} \quad (4.276)$$

According to Eq. (4.271), we have

$$\text{at } x = \infty, \Delta C_A^* = 0 \quad (4.277)$$

Using Eqs. (4.276), (4.277) and also (4.275), we can arrive at the following results:

$$B_1 = 0 \quad (4.278)$$

and

$$B_2 = \frac{\Delta C_{A,e}}{p} \quad (4.279)$$

Substituting these values in Eq. (4.275), we get

$$\Delta C_A^* = \frac{\Delta C_{A,e}}{p} \exp \left[-x \left(\frac{D_A}{pv_t} \right)^{1/2} \right] \quad (4.280)$$

Making use of the inverse transform from Table 4.3, we can write

$$\Delta C_A = \Delta C_{A,e} \operatorname{erfc} \left[x \left(\frac{v_t}{4D_A z} \right)^{1/2} \right] \quad (4.281)$$

where

$$\operatorname{erfc} \left[x \left(\frac{v_t}{4D_A z} \right)^{1/2} \right] = 1 - \operatorname{erf} \left[x \left(\frac{v_t}{4D_A z} \right)^{1/2} \right] \quad (4.282)$$

Further, Eq. (4.281) can be rewritten as

$$\frac{C_A - C_{A,0}}{C_{A,e} - C_{A,0}} = \operatorname{erfc} \left[x \left(\frac{v_t}{4D_A z} \right)^{1/2} \right] \quad (4.283)$$

With the help of the above equation, we can calculate the concentration profile for component A in the liquid phase.

The rate of mass transfer J_A of component A from the surface of the bubble can be calculated with the help of Eq. (4.283) as

$$\begin{aligned} J_A &= -D_A \left(\frac{\partial C_A}{\partial x} \right)_{x=0} \\ &= -D_A \left[\frac{\partial}{\partial x} \int C_{A,0} + (C_{A,e} - C_{A,0}) \operatorname{erfc} \left\{ x \left(\frac{v_t}{4D_A z} \right)^{1/2} \right\} \right] \\ &= (C_{A,e} - C_{A,0}) \left(\frac{D_A v_t}{\pi z} \right)^{1/2} \end{aligned} \quad (4.284)$$

In order to calculate the average mass transfer rate from the above equation, we require to assume the shape of the bubble. If D be the diameter of a spherical bubble, we can write an equation for the average mass transfer rate $J_{A,av}$, as below:

$$J_{A,av} = \frac{1}{a} \iint_a (C_{A,e} - C_{A,0}) \left(\frac{D_A v_t}{\pi z} \right)^{1/2} da \quad (4.285)$$

where the symbol a represents the surface area of the bubble. Thus

$$J_{A,av} = (C_{A,e} - C_{A,0}) \left(\frac{4D_A v_t}{\pi D} \right)^{1/2} - \left(\frac{4D_A}{\pi t_e} \right)^{1/2} (C_{A,e} - C_{A,0}) \quad (4.286)$$

where $t_e = D/v_t$. This equation is found to be applicable to bubbles of small volumes and of spherical shapes.

Reduction kinetics of porous hematite pellets

We have earlier considered diffusion-controlled topochemical reduction of dense hematite pellets. In case the pellet under consideration is porous, this treatment cannot be applied, as diffusion and chemical reaction will occur simultaneously inside such a pellet. We can arrive at the reduction-rate equation for this case making use of Eq. (4.247) by assuming that (i) a steady state exists inside the system, and (ii) there is no convection inside the pellet. Thus Eq. (4.247) reduces to

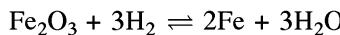
$$-\left(\frac{D}{r^2}\right)\left\{\frac{\partial}{\partial r}\left(r^2 \frac{\partial C}{\partial r}\right)\right\} = \gamma_{H_2} \frac{\partial \xi}{\partial t} \quad (4.287)$$

where the symbols used have already been defined.

It can be shown that for a first-order reversible reaction (see Chapter 7), as, for example, reduction of hematite by hydrogen, the reaction kinetics can be expressed by the relation

$$\gamma_{H_2} \frac{\partial \xi}{\partial t} = -K_b(1 + K_{eq})(C - C_e) \quad (4.288)$$

where C and C_e are respectively the concentration at time t and the equilibrium concentration, and the symbols K_b and K_{eq} respectively represent the backward reaction rate constant and the equilibrium constant for the reduction reaction



Combining Eqs. (4.287) and (4.288), we get

$$\frac{D}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial C}{\partial r} \right) = K_b a (1 + K_{eq})(C - C_e) \quad (4.289)$$

where a is the surface area per unit volume of the pellet. For a particular solution of this equation, the following boundary conditions should hold good:

$$(i) \quad C = C_0 \text{ at } r = R_0 \quad (4.290)$$

where R_0 is the radius of the pellet and C_0 the initial concentration.

$$(ii) \quad C \text{ is finite at } r = 0 \quad (4.291)$$

To obtain a general solution of Eq. (4.289) in a dimensionless form, we introduce the following variables:

$$C^* = \frac{C - C_e}{C_0 - C_e} \quad (4.292a)$$

and

$$r^* = \frac{r}{R_0} \quad (4.292b)$$

With the above variables, Eq. (4.289) assumes the form

$$\left(\frac{1}{r^*}\right)^2 \frac{\partial}{\partial r^*} \left\{ (r^*)^2 \left(\frac{\partial C^*}{\partial r^*} \right) \right\} = \alpha C^* \quad (4.293)$$

where $\alpha = \frac{aK_b(1 + K_{eq})R_0^2}{D}$ (4.294)

and the boundary conditions, expressed by Eqs. (4.290) and (4.291) become

$$(i) \quad C^* = 1 \text{ at } r^* = 1 \quad (4.295)$$

$$(ii) \quad C^* \text{ is finite at } r^* = 0 \quad (4.296)$$

Transformation of Eq. (4.293) by substituting

$$C^* = \frac{g[f(r^*)]}{r^*} \quad (4.297)$$

leads to the equation

$$\frac{\partial^2 g}{\partial r^{*2}} = \alpha g \quad (4.298)$$

A general solution of the above equation can be written as

$$g = C_1 \cosh(\alpha^{1/2}r^*) + C_2 \sinh(\alpha^{1/2}r^*) \quad (4.299a)$$

or

$$C^* = \frac{C_1}{r^*} \cosh(\alpha^{1/2}r^*) + \frac{C_2}{r^*} \sinh(\alpha^{1/2}r^*) \quad (4.299b)$$

Substitution of the boundary conditions represented by Eqs. (4.295) and (4.296) in the above equation yields

$$C_1 = 0 \quad (4.300a)$$

and

$$C_2 = [\sinh(\alpha^{1/2})]^{-1} \quad (4.300b)$$

Thus, the concentration profile inside the pellet will follow the relation

$$\frac{C - C_e}{C_0 - C_e} = \frac{R_0}{r} \frac{\sinh(\alpha^{1/2}r/R)}{\sinh(\alpha^{1/2})} \quad (4.301)$$

As we are interested in deriving an equation for the rate of reduction of the pellet, we need to determine the rate at which the reductant gas H₂ is entering the system from the surface of the pellet. Thus

$$\begin{aligned} \frac{dn_{H_2}}{dt} &= \pi R_0^2 (J_{H_2})_{r=R_0} \\ &= \pi R_0^2 \left[-D \left(\frac{\partial C}{\partial r} \right)_{r=R_0} \right] \\ &= 4\pi R_0 D C_0 [1 - (\alpha^{1/2}) \coth(\alpha^{1/2})] \end{aligned} \quad (4.302)$$

where (J_{H₂})_{r=R₀} is the hydrogen flux on the surface of the pellet.

For calculation of the fractional reduction, we can proceed further in a manner similar to that adopted in Section 4.1.4 and express the left-hand side

of the above equation in terms of fractional reduction f and derive a relation for f as a function of time t .

This mathematical treatment is applicable only if no other change takes place in the reactive system apart from diffusion and chemical reaction involving the reduction of porous pellet at the reaction interface. This is because otherwise, such changes may affect the porosity of the pellet and hence alter the effective value of the diffusion coefficient D . It is also obvious that this mathematical treatment is valid only till the surface of the porous pellet is not completely reduced.

4.3 OVERALL MASS BALANCES

In the previous sections, we have shown that application of differential mass balance equations present considerable mathematical complexity and many a time require drastic simplifying assumptions for application to industrial systems of complex geometries. These assumptions may sometimes affect considerably the accuracy of the final results obtainable by such analysis. In other words, we can state that the differential balances can be applied mainly to diffusion problems and to those involving laminar flow over objects of simple geometries. The advantage of this method is that it provides detailed information about the concentration profiles in the system. The ultimate objective in most of the metallurgical problems, however, is to arrive at the rate at which a particular reaction proceeds and also to know the extent to which it might proceed in a given time. These problems can also be solved by adopting a similar technique that involves an overall mass balance of the various components present in the system. This technique, in general, results in the development of only an algebraic equation under steady state conditions and a first order differential equation for an unsteady state system. These equations can then be solved in a straightforward manner to arrive at the final solution of the problem under study.

For derivation of the general overall mass balance equation, we consider a reactor as shown in Fig. 4.15. The mass balance for an arbitrary component i can be written as follows:

The amount of component i retained in the reactor per unit time =
(Amount of component i entering per unit time) – (Amount of component i leaving the reactor per unit time) + (Amount of component i supplied by the bounding surfaces per unit time) + (Amount of component i produced by various reactions per unit time) (4.303)

In mathematical form, this equation may be written as

$$\frac{\partial m_i}{\partial t} = (\rho_i v_i A)_{\text{entrance}} - (\rho_i v_i A)_{\text{exit}} + (A_s J_i) + r_i \quad (4.304)$$

where the symbol m_i represents the mass of component i present inside the reactor at time t , A_s is the area of bounding surfaces of the reactor, J_i is the rate

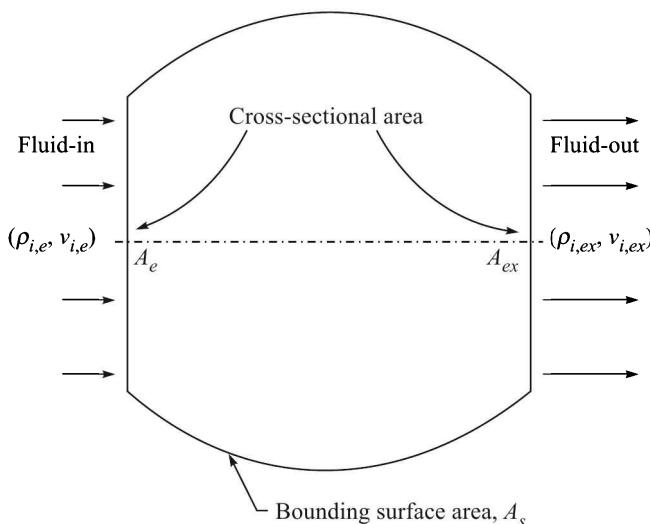


Fig. 4.15 Reactor for analysis of overall mass balance.

at which these surfaces supply component i , and r_i is the rate of production of component i through chemical reaction inside the reactor. The symbols ρ_i , v_i and A represent respectively the density of component i , its linear flow rate or velocity and area of the reactor perpendicular to the direction of flow. We can write similar equations for other components as well, in order to form a set of equations which can be simultaneously solved to obtain the desired result. In a number of cases, the various parameters in Eq. (4.304) can be expressed in terms of some other convenient functions to facilitate mathematical treatment. We now consider application of the above treatment to an important metallurgical reaction such as the reduction of dense hematite pellets in an isothermal packed bed.

4.3.1 Reduction Kinetics of Dense Hematite Pellets in an Isothermal Packed Bed

Packed bed columns are extensively used in several extractive metallurgical processes. For example, these are used in recovery of metal values by leaching and ion-exchange processes in hydrometallurgy. Blast furnaces and vertical shaft furnaces used for reduction smelting of iron, zinc and lead ores, and for calcinating, halogenizing and roasting are also excellent examples of packed bed reactors in metallurgical processes. Packed beds also form good examples for illustration of the application of overall mass balance as the basic principles used in mathematical analyses of all such reactors are the same. We will, for instance, consider a vertical cylindrical packed bed reactor filled with dense hematite pellets, as shown in Fig. 4.16, through which hydrogen gas is passed for reduction. In order to restrict the analysis to the problem of mass transfer only,

we assume that the bed is maintained at a constant temperature and the reduction is controlled by diffusion of gases through the porous reduced iron shells formed on each on the pellets. Let A be the cross-sectional area of the reactor and h its height. Consider now a strip of thickness δz across the cross-section of the reactor as shown in Fig. 4.16. If V be the volumetric rate of flow of gas in this reactor, v the velocity of flow and N_H the mole fraction of hydrogen in the gas flowing in it, we can then write the following relation in respect of the molar balance for hydrogen in this reactor in time δt .

(Moles of hydrogen entering the volume element of the reactor-bed at the position $z = z$) – (Moles of hydrogen leaving the volume element of the reactor-bed at the position $z = z + \delta z$) = (Moles of hydrogen reacted in the volume element) + (Moles of hydrogen retained inside the volume element)

(4.305)

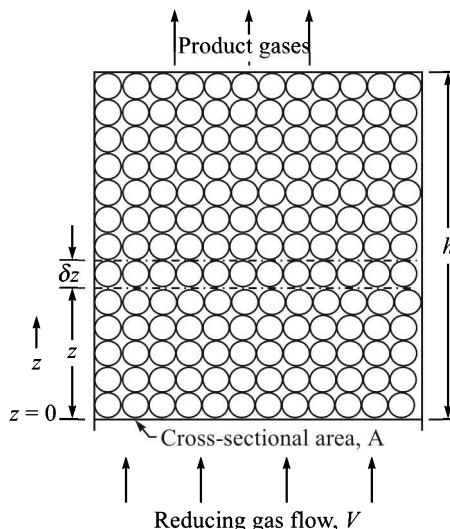


Fig. 4.16 Reactor for analysis of reduction kinetics of dense hematite pellets in isothermal packed bed.

Mathematically, this relation can be written as

$$\begin{aligned} & \left[N_H \frac{vA}{RT} \right]_{z=z} \delta t - \left[N_H \frac{vA}{RT} \right]_{z=z+\delta z} \delta t \\ &= R_H A \delta z \delta t + \frac{\partial C_H}{\partial t} A \delta z \delta t \end{aligned} \quad (4.306)$$

where R_H is the number of moles of hydrogen consumed per unit volume per unit time and C_H is the molar concentration of hydrogen retained per unit time. It has been assumed that the reactor is maintained under a constant pressure of 1 atm and has a negligible pressure gradient. Equation (4.306) can be rewritten in the following simplified form:

$$-\left(\frac{V}{RT}\right)\frac{\partial N}{\partial z} = R_H + \frac{\partial C_H}{\partial t}$$

or

$$\frac{\partial C_H}{\partial t} = -\left(\frac{V}{RT}\right)\left(\frac{\partial N_H}{\partial t}\right) - R_H \quad (4.307)$$

It may be mentioned that the volumetric gas flow rate inside the reactor does not change as a result of the reduction reaction occurring in the reactor, because one mole of hydrogen consumed leads to the formation of one mole of water vapour. Using the ideal gas law, we can also write the equation for concentration of hydrogen as follows:

$$C_H = \frac{N_H}{RT} \quad (4.308)$$

Hence, Eq. (4.307) can be written in either of the following forms:

$$\frac{\partial N_H}{\partial t} + V \frac{\partial N_H}{\partial z} = -RT R_H \quad (4.309)$$

or

$$\frac{\partial C_H}{\partial t} + V \frac{\partial C_H}{\partial z} = -R_H \quad (4.310)$$

Although either of the above equations can be used for further treatment, we will proceed with the use of Eq. (4.310). As the next step in the analysis of this problem, we arrive at an equation for the parameter R_H defined earlier as the number of moles of hydrogen consumed as a result of the reduction reaction inside the reactor per unit time per unit volume.

If R_0 be the radius of a pellet, r_H the rate of consumption of hydrogen per pellet and ε the void-fraction of the bed, then we can write the following equation for the function R_H , defined above:

$$R_H = \left(\frac{1-\varepsilon}{\frac{4}{3}\pi R_0^3}\right)r_H \quad (4.311)$$

Further, if the reaction is considered to be controlled only by diffusion through the pellet, then according to the analytical treatment used in Section 4.1.4, we can write for r_H the following equation:

$$r_H = +4\pi D_H \frac{(C_H - C_e)R_0 R_i}{R_0 - R_i} \quad (4.312)$$

where C_e is the equilibrium hydrogen concentration in the gas phase, D_H the diffusion coefficient of hydrogen, and R_i the radius of pellet at the reaction interface. Equation (4.311) can now be rewritten as

$$\begin{aligned} R_H &= \frac{4\pi D_H (1-\varepsilon)}{4\pi R_0^3/3} \frac{(C_H - C_e) R_0 R_i}{R_0 - R_i} \\ &= \frac{3(1-\varepsilon)(C_H - C_e) R_i D_H}{R_0^2 (R_0 - R_i)} \end{aligned} \quad (4.313)$$

Equation (4.313) can be written in an alternative form by substituting the value of R_i in terms of fractional reduction f of the pellet as done earlier in Section 4.1.4 as well. Thus, we get

$$R_H = \frac{3(1-\varepsilon)(C_H - C_e)D_H}{R_0^2 \{(1-f)^{-1/3} - 1\}} \quad (4.314)$$

In the above equation, the term R_H has been expressed as a function of bulk concentration of hydrogen. It can also be expressed alternatively in terms of the rate of fractional reduction as follows:

$$R_H = \left(\frac{1}{16}\right) \left\{ \frac{1-\varepsilon}{(4/3)\pi R_0^3} \right\} \left[\rho \left(\frac{3}{10}\right) \frac{4}{3} \pi R_0^3 \right] \left(\frac{\partial f}{\partial t} \right) \quad (4.315)$$

It should be noted that in this equation:

- (i) the factor 1/16 denotes that one kg-mole of hydrogen reacts with 16 kg of oxygen,
 - (ii) the factor $\left\{ \frac{1-\varepsilon}{(4/3)\pi R_0^3} \right\}$ represents the number of pellets per unit volume of the bed,
 - (iii) the term within the square brackets represents the mass of oxygen in the pellet, and $(\partial f / \partial t)$ the fractional rate of removal of oxygen.
- Equation (4.315) on simplification yields

$$R_H = \frac{3\rho(1-\varepsilon)}{160} \left(\frac{\partial f}{\partial t} \right) \quad (4.316)$$

Thus, Eqs. (4.310), (4.314) and (4.316) describe the variation in the state or the progress of reduction of hematite bed with time and position. To arrive at the final relations, these equations need to be solved under the boundary conditions:

$$(i) \text{ At } t = 0, C_H = C_e \text{ for } z > 0 \quad (4.317)$$

$$(ii) \text{ At } t > 0, C_H = C_0 \text{ at } z = 0 \quad (4.318)$$

$$(iii) \text{ In case the lowest layer is completely reduced, the alternative condition is, at } t > 0, f = 1 \text{ at } z = 0 \quad (4.319)$$

To obtain a general solution, we first introduce the following dimensionless variables:

$$\phi = \frac{C_H - C_e}{C_0 - C_e}; \eta = \frac{z}{h} \quad (4.320)$$

and

$$\tau = \frac{vt}{h}$$

With these variables, with the help of Eq. (4.313), Eq. (4.310) can be written as

$$\left(\frac{\partial \phi}{\partial \eta} \right)_\tau + \left(\frac{\partial \phi}{\partial \tau} \right)_\eta = -R^*(f)\phi \quad (4.321)$$

where

$$R^*(f) = \frac{3(1-\varepsilon)hD_H}{vR_0^2\{(1-f)^{-1/3}-1\}} \quad (4.322)$$

Similarly, using Eq. (4.313) the equation for fractional reduction, i.e. Eq. (4.316), can be rewritten as

$$\frac{\partial f}{\partial \tau} = \frac{160}{3\rho(1-\varepsilon)} R_H \quad (4.323)$$

$$= \frac{160(C_H - C_e) D_H h}{\rho R_0^2 \{(1-f)^{-1/3}-1\} v} \quad (4.323)$$

$$= \lambda R^*(f) \phi, \text{ say} \quad (4.324)$$

where

$$\lambda = \frac{160(C_0 - C_e)}{3\rho(1-\varepsilon)} \quad (4.325)$$

In order to arrive at an analytical solution of Eqs. (4.321) and (4.324), we introduce a new variable σ , such that

$$\sigma \equiv (\tau - \eta) \quad (4.326)$$

Thus

$$\left(\frac{\partial \sigma}{\partial \eta}\right)_\tau = -1 \text{ and } \left(\frac{\partial \sigma}{\partial \tau}\right)_\eta = 1 \quad (4.327)$$

Hence, Eq. (4.324) can be written as

$$\left(\frac{\partial f}{\partial \sigma}\right)_\eta = \lambda R^*(f) \phi \quad (4.328)$$

and Eq. (4.321) as

$$\left(\frac{\partial \phi}{\partial \eta}\right)_\sigma = -R^*(f) \phi \quad (4.329)$$

Application of the properties of exact differentials to Eqs. (4.328) and (4.329) shows that there exists a function $g(\sigma, \eta)$ such that

$$\left(\frac{\partial g}{\partial \sigma}\right)_\eta = \phi \quad (4.330a)$$

and

$$\left(\frac{\partial g}{\partial \eta}\right)_\sigma = -\frac{f}{\lambda} \quad (4.330b)$$

Substituting for ϕ from Eq. (4.328) in Eq. (4.330a), we get

$$\left(\frac{\partial g}{\partial \sigma}\right)_\eta = \frac{1}{\lambda R^*(f)} \left(\frac{\partial f}{\partial \sigma}\right)_\eta \quad (4.331)$$

or

$$g = \frac{1}{\lambda} \int \frac{df}{R^*(f)} + \theta(\eta) \quad (4.332)$$

where the constant of integration $\theta(\eta)$ can be a function of η .

Differentiation of Eq. (4.332) with respect to η yields

$$\frac{\partial g}{\partial \eta} = \frac{1}{\lambda} \frac{1}{R^*(f)} \left(\frac{\partial f}{\partial \eta} \right) + \frac{\partial \theta(\eta)}{\partial \eta} \quad (4.333)$$

With the help of Eqs. (4.330b) and (4.333), we can write

$$f = - \left[\frac{1}{R^*(f)} \frac{\partial f}{\partial \eta} + \lambda \frac{\partial \theta(\eta)}{\partial \eta} \right]_{\sigma} \quad (4.334)$$

At the beginning of the reduction process, i.e. at $t = 0$ and $z = 0$, $f = f_0$ (say), and therefore, $\sigma = 0$ and also

$$\frac{\partial f}{\partial \eta} = 0$$

Thus, from Eq. (4.334), it follows that

$$\frac{\partial \theta}{\partial \eta} = -f_0/\lambda \quad (4.335)$$

Hence, Eq. (4.334) yields the expression

$$\left[\frac{\partial f}{\partial \eta} = R^*(f)(f_0 - f) \right]_{\sigma} \quad (4.336)$$

On integration this equation yields

$$\left[\eta^* - \eta = \int_{f^*}^f \frac{df}{R^*(f)(f - f_0)} \right]_{\sigma} \quad (4.337)$$

where f^* is the value corresponding to η^* , a given dimensionless position.

We now interpret the above equation. It is seen that this equation is applicable under conditions of constant σ —a function considered equivalent to $(\tau - \eta)$, where these two functions, in turn, are defined by Eq. (4.320). Since the velocity of gas v in the reactor will, in general, be high, we can safely conclude that, except for a very small interval of time, $\tau \gg \eta$ and therefore $\sigma \approx \tau$. Thus, Eq. (4.337) becomes applicable in respect of constant τ or for a fixed time. In other words, Eq. (4.337) describes the profile of fractional reduction as a function of height h (or η) for a given time t (or τ). It can be used to calculate this profile provided the value of fractional reduction f^* , at some position η^* , in the bed is known at the time under consideration.

4.4 CONCEPT OF MASS TRANSFER COEFFICIENT

Till now we have restricted our discussion to formulation of mass transfer problems with a view to obtaining concentration profiles in stationary and

flowing systems. This approach requires a simultaneous solution of continuity, motion and diffusion equations. Although this type of mathematical analysis is possible in the case of laminar flow, in general, it is not possible in the case of turbulent flow systems.

Our main aim in solving these equations is to calculate the mass flux from one phase to the other, of which either both may be fluids, or one may be a fluid and the other a solid. Though such a solution is possible for evaluation from concentration profiles, this procedure is cumbersome and in a number of cases impossible. Therefore, we take the help of empirical relationships or resort to experimental studies to arrive at the mass fluxes. In these empirical relationships, we define a new variable called the *mass transfer coefficient*, represented by the symbol k_m which for any general component A is related to the mass flux J by the following equation:

$$J_A = k_{m,A} (C_{A,i} - C_{A,b}) \quad (4.338)$$

where $C_{A,i}$ and $C_{A,b}$ are respectively the interfacial and bulk concentrations of component A. As far as qualitative arguments are concerned, the statement made in Eq. (4.338) is fully justified since the flux is directly proportional to the concentration difference. However, it is not always possible to calculate the value of $k_{m,A}$ from the theoretical considerations. We, therefore, attempt to evaluate it on the basis of experimental data or from the analogies between mass transfer, heat transfer or momentum transfer. These analogues will be discussed in detail in Chapter 8.

The concept of mass transfer coefficient can also be extended to systems which involve two or more phases and in which the interfacial chemical reaction for the transfer of a component from one phase to the other is assumed to be very fast. For a system consisting of two phases in which a component, say A, gets transferred from phase I to phase II, we can write the following equation, analogous to Eq. (4.338):

$$J_A = k_{m,A}^I (C_{A,b}^I - C_{A,i}^I) = k_{m,A}^{II} (C_{A,i}^{II} - C_{A,b}^{II}) \quad (4.339)$$

where the subscripts b and i refer to the bulk and interface, and the superscripts I and II to the first and the second phase respectively. As the interfacial reaction is assumed to be very fast, we can, therefore, also assume that the system at the interface would attain equilibrium instantaneously. Hence, we can write

$$\frac{C_{A,i}^I}{C_{A,i}^{II}} = B_{eq} \quad (4.340)$$

where B_{eq} is the *equilibrium distribution coefficient*. Thus, Eq. (4.339) takes the form

$$J_A = \frac{\frac{C_{A,b}^I - C_{A,i}^I}{1}}{\frac{k_{m,A}^I}{k_{m,A}^I}} = \frac{\frac{C_{A,i}^I - B_{eq} C_{A,b}^{II}}{B_{eq}}}{\frac{k_{m,A}^{II}}{k_{m,A}^{II}}} = \frac{\frac{C_{A,b}^I - B_{eq} C_{A,b}^{II}}{1}}{\frac{1}{k_{m,A}^I} + \frac{B_{eq}}{k_{m,A}^{II}}}$$

$$= \frac{C_{A,b}^I - B_{eq} C_{A,b}^{II}}{\frac{1}{k_{m,ov}}} \quad (4.341)$$

where $k_{m,ov}$ is called the *overall mass transfer coefficient* of component A and is related to the mass transfer coefficients in both phases by the relation

$$\frac{1}{k_{m,ov}} = \frac{1}{k_{m,A}^I} + \frac{B_{eq}}{k_{m,A}^{II}} \quad (4.342)$$

It should also be noted from Eq. (4.341) that the net or overall concentration difference ΔC_A of component A is represented by the expression

$$\Delta C_A = C_{A,b}^I - B_{eq} C_{A,b}^{II} \quad (4.343)$$

Evaluation of the term $k_{m,ov}$ requires experimental determination of instant values of $C_{A,b}^I$ and $C_{A,b}^{II}$. This may involve considerable experimental work in some cases. By resorting to mass-balance analysis, however, we can eliminate one of these concentration variables and thus determine experimentally the value of mass transfer coefficient from chemical analysis data on concentration of only one component. To illustrate the procedure of elimination of one concentration variable, we assume that the concentration $C_{A,b}^I$ is easily determinable experimentally. Thus, we would like to express the value of the parameter $(C_{A,b}^I - B_{eq} C_{A,b}^{II})$ in terms of the concentration $C_{A,b}^I$ in phase I alone. For this, we assume that component A is only exchanged between the phases I and II and is not lost to the surroundings during the experiment. Thus, the total amount m_A of A at any instant will be

$$m_A = V_I C_{A,b}^I + V_{II} C_{A,b}^{II} \quad (4.344)$$

where the suffix b refers to concentration in bulk of the phases, and V_I and V_{II} are respectively the volumes of phases I and II. When the system has attained the state of equilibrium at the end of the experiment, we can write

$$m_A = V_I C_{A,e}^I + V_{II} C_{A,e}^{II} \quad (4.345)$$

where the suffix e refers to the equilibrium value in the bulk. In writing Eqs. (4.344) and (4.345), it has been assumed that there is no change in the volume of phases during the experiment or the volume change occurring in the two phases, if at all, is negligibly small.

With the help of Eq. (4.340), we can write Eq. (4.345) as

$$\begin{aligned} m_A &= V_I C_{A,e}^I + \frac{V_{II} C_{A,e}^I}{B_{eq}} \\ &= C_{A,e}^I \left(V_I + \frac{V_{II}}{B_{eq}} \right) \end{aligned} \quad (4.346)$$

From this equation and Eq. (4.344), we get

$$V_{II} C_{A,b}^{II} = V_{II} \frac{C_{A,e}^I}{B_{eq}} - V_I (C_{A,b}^I + C_{A,e}^I) \quad (4.347)$$

Hence

$$(C_{A,b}^I + B_{eq} C_{A,b}^{II}) = (C_{A,b}^I + C_{A,e}^I) \left(1 + \frac{B_{eq} V_I}{V_{II}} \right) \quad (4.348)$$

It is, therefore, clear that experimental determination of bulk concentration of A only in one phase is sufficient to evaluate $(C_{A,b}^I - B_{eq} C_{A,b}^{II})$. With the help of Eq. (4.348), we can rewrite Eq. (4.341) as follows:

$$J_A = k_{m,ov} (C_{A,b}^I + C_{A,e}^I) \left(1 + B_{eq} \frac{V_I}{V_{II}} \right) \quad (4.349)$$

We can also express J_A in terms of the rate of change of the amount of component A in the bulk of phase I. Thus

$$J_A = - \frac{V_I}{A} \frac{dC_{A,b}^I}{dt} \quad (4.350)$$

where A is the interfacial area.

With this, Eq. (4.349) can be rewritten as

$$\frac{dC_{A,b}^I}{dt} = -k_{ex} (C_{A,b}^I - C_{A,e}^I) \quad (4.351)$$

where

$$k_{ex} = A \left(\frac{1}{V_I} + \frac{B_{eq}}{V_{II}} \right) k_{m,ov} \quad (4.352)$$

On integration, we get from Eq. (4.351), the relation

$$\ln \left(\frac{C_{A,b}^I - C_{A,e}^I}{C_{A,0}^I - C_{A,e}^I} \right) = -k_{ex} t \quad (4.353)$$

where $C_{A,0}^I$ is the initial concentration of component A in the bulk of phase I. Equation (4.353) also shows that from the linear plot between the function on the left-hand side of the equation and time t , we can calculate the experimental value of k_{ex} and, therefore, on making use of Eq. (4.352), also the value of $k_{m,ov}$ which according to Eq. (4.342) is defined by the relation

$$\frac{1}{k_{m,ov}} = \frac{1}{k_{m,A}^I} + \frac{B_{eq}}{k_{m,A}^{II}} \quad (4.354)$$

With the help of the above equation, we can also identify the phase in which the rate controlling step lies. It can be easily seen that the second term on the right-hand side of this equation is a function of B_{eq} as well. So, if a change in the composition of phase II does not affect the value of $k_{m,ov}$, then the rate controlling step lies in phase I, but if it does, it lies in phase II. Further, from

the value of B_{eq} , we can also make such an inference. If $k_{m,A}^I$ and $k_{m,A}^{II}$ are of the same order, then for large values of B_{eq} , the first term can be neglected and the rate controlling step lies only in phase II and, vice-versa. In the case of slag-metal systems, in general, the value of B_{eq} is very small, and therefore, in such cases the rate controlling step lies in the metal phase.

Application of the above relations is demonstrated by an example given below.

EXAMPLE 4.17 100 g of pure liquid iron, at 1750°C and 1 atm nitrogen pressure, dissolve 35 cm³ (STP) of nitrogen. To remove this nitrogen, argon gas at 1 atm is brought in contact with the liquid iron. Calculate the overall mass transfer coefficient, if 2×10^{-5} cm³ of nitrogen is removed per unit area per second and also calculate the mass transfer coefficients in each phase, if they are assumed to be equal.

Solution Solubility of nitrogen in liquid iron = 35 cm³/100 g at 1750°C. Therefore, equilibrium concentration of nitrogen in liquid iron on per 100 g basis is 35/22400 g-mole.

Therefore, the mole fraction N_N of nitrogen under equilibrium in Fe-N system under study will be

$$N_N = \frac{35/22400}{35/22400 + 100/56} \approx 8.6 \times 10^{-4}$$

Using Sievert's law, we have

$$N_N = k_N \sqrt{P_{N_2}}$$

or

$$8.6 \times 10^{-4} = k_N \sqrt{I}$$

or

$$k_N = 8.6 \times 10^{-4}$$

This value will also be the equilibrium distribution coefficient under the given condition. Thus

$$B_{\text{eq}} = 8.6 \times 10^{-4}$$

Now, from Eq. (4.341)

$$J_N = \frac{\frac{C_{N,b}^I - C_{N,b}^{II} \times B_{\text{eq}}}{1}}{\frac{k_{m,ov}}{k_{m,ov}}} = k_{m,ov} (C_{N,b}^I - C_{N,b}^{II} \times B_{\text{eq}})$$

or the overall mass transfer coefficient

$$k_{m,ov} = \frac{J_N}{C_{N,b}^I - C_{N,b}^{II} \times B_{\text{eq}}}$$

From the given data, flux of nitrogen

$$J_N = 2 \times 10^{-5} \text{ cm}^3 \text{ cm}^{-2} \text{ s}^{-1}$$

Bulk concentration of nitrogen in phase I (on mole-fraction basis)

$$C_{N,b}^I = 8.6 \times 10^{-4}$$

and assuming total degassing of metal, in phase II

$$C_{N,b}^{II} = 0$$

Therefore

$$k_{m,ov} = \frac{2 \times 10^{-5} \times 10^{-2}}{8.6 \times 10^{-4}} = 2.33 \times 10^{-4} \text{ m s}^{-1} \quad \text{Ans.}$$

Again from Eq. (4.354), we have

$$\frac{1}{k_{m,ov}} = \frac{1}{k_{m,N}^I} + \frac{B_{eq}}{k_{m,N}^{II}}$$

and from the given data, we have

$$k_{m,N}^I = k_{m,N}^{II}$$

Hence

$$\frac{1}{k_{m,ov}} = \frac{1}{k_{m,N}^I} (1 + B_{eq})$$

or

$$\begin{aligned} k_{m,N}^I &= (1 + B_{eq}) \times k_{m,ov} \\ &= (1 + 8.6 \times 10^{-4}) \times 2.33 \times 10^{-4} \end{aligned}$$

Therefore

$$k_{m,N}^I = k_{m,N}^{II} = 2.332 \times 10^{-4} \text{ m s}^{-1} \quad \text{Ans.}$$

4.4.1 Mass Transfer Coefficient for Flow through Packed Beds

Mass transfer data for flow through packed beds of granular solids were correlated for air circulation in terms of functions j_D and $N_{Re,p}$ by Wilke and Hougen¹ as shown in Fig. 4.17. These functions were found to be interrelated by equations

$$j_D = 1.82(N_{Re,p})^{-0.51} \text{ for } N_{Re,p} < 350 \quad (4.355)$$

and

$$j_D = 0.989(N_{Re,p})^{-0.41} \text{ for } N_{Re,p} > 350 \quad (4.356)$$

The function $N_{Re,p}$ is known as *modified Reynolds number*, and equals the ratio $(\rho v d_p / \mu)$ where d_p represents the equivalent diameter of the particles assumed to be of spherical form. Function j_D will be defined appropriately in Chapter 8. It represents the j -factor in Chilton-Colburn analogy.

¹ C.R. Wilke and O.A. Hougen, *Trans. A.I.Ch. E.* **41**: 445 (1945).

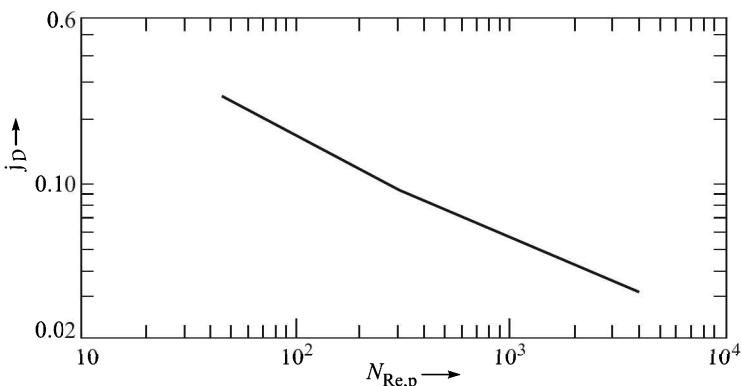


Fig. 4.17 Relationship between the function j_D and $N_{Re,p}$ for flow of air through packed beds.

4.4.2 Mass Transfer Coefficients for Spherical Objects

Froessling¹ arrived at the following semi-empirical equation for mass transfer to or from a single sphere:

$$N_{Sh} = 2 + 0.552 (N_{Re})^{1/2} (N_{Sc})^{1/3} \quad (4.357)$$

where the symbols N_{Sh} , N_{Re} and N_{Sc} refer to the Sherwood, Reynolds and Schmidt numbers respectively. It can be seen that for a stagnant fluid for which N_{Re} is zero, the value of the Sherwood number will be 2. Significance of Sherwood and Schmidt numbers will be discussed in detail in the next chapter.

4.5 INTERFACIAL MASS TRANSFER

In the above subsections, the study of mass transfer was restricted mainly to a single phase. However, most applications of mass transfer in metallurgical processes are concerned with transfer across a phase boundary which may be called the *interfacial mass transfer*. Thus, in iron- and steel-making, a molten slag phase is in contact with a molten metal phase and the transfer of components such as sulphur, phosphorus, silicon, manganese, etc. takes place between them. Mass transfer rates between these two fluid phases will, therefore, depend upon the physical properties of the two phases, the concentration difference, interfacial area and the degree of stirring. A number of mechanisms have been suggested to quantitatively express the conditions in the region of phase boundary and to calculate the mass transfer rate. The earliest of these was the two-film theory proposed by Lewis and Whitman. Thereafter Higbie proposed the penetration theory which was further modified by Danckwartz. Recently Toor and Marchello have proposed a more general theory

¹ N. Froessling, *Gerlands Beitrag. Geophy.*, **32**: 170 (1938).

called *the film-penetration theory*. All these theories will be discussed briefly in this section.

4.5.1 Two-film Theory

This theory, proposed by Lewis and Whitman¹ was the first attempt to explain quantitatively the rate of transfer of a component across an interface. In this theory, it is assumed that turbulence dies out at the interface and that a laminar layer around the interface exists in each of the two fluids. Outside these laminar layers, the composition of the phases is assumed to be uniform owing to the random movement of the fluid caused by turbulence. This approach thus, simplifies the actual distribution of the components as shown in Fig. 4.18.

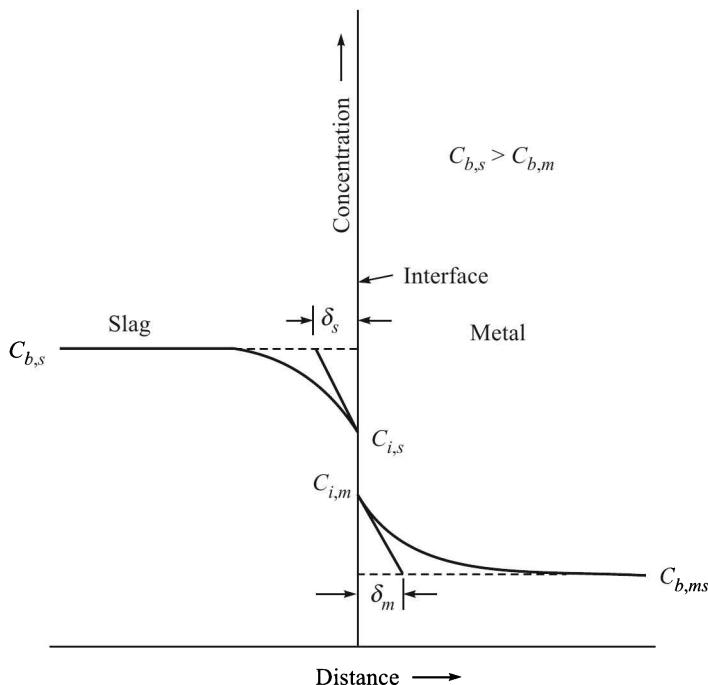


Fig. 4.18 Two-film theory for transfer of a component from slag-phase to metalphase.

Thus, the whole system can be replaced by two constant composition zones and two hypothetical layers around the interface having a linear variation in concentration of the component diffusing from one phase to the other. In Fig. 4.18, the diffusing component is transferred from slag to the metal phase. Further, the linear variation in composition implies that the transfer of mass is taking place under the steady state condition. The rate of transfer J_A of the

¹ W.K. Lewis and W. Whitman, *Ind. Engg. Chem.*, **16**: 1215 (1924).

component A per unit area per unit time can, therefore, is expressed as

$$J_A = \frac{D_s}{\delta_s} (C_{b,s} - C_{i,s}) = -\frac{D_m}{\delta_m} (C_{i,m} - C_{b,m}) \quad (4.358)$$

where D_s and D_m are the diffusion coefficients of component A in the slag and metal phases respectively and δ_s and δ_m are the boundary layer thicknesses in slag and metal phases respectively. Further, the symbols $C_{b,s}$ and $C_{i,s}$ refer to concentrations in bulk and at the interface in the slag phase and $C_{b,m}$ and $C_{i,m}$ refer to the corresponding bulk and interfacial concentrations in the metal phase. The flow conditions in the two phases are too complex to evaluate δ_s and δ_m , theoretically. Further, this theory predicts a linear dependence of flux on diffusion coefficient, which is not realized in practice. Thus, the theory gives a qualitative explanation only of the mass transfer rates.

4.5.2 Penetration Theory

Penetration theory was proposed by Higbie¹ for interpretation of the rates of absorption of a gas in liquids. In this theory, it is assumed that the eddies in the bulk liquid phase bring a chunk of the fluid to the interface. Here, it is exposed to the second phase for a definite interval of time after which this element gets mixed up with the bulk again. It is further assumed that as soon as the new fluid comes to the interface, it attains chemical equilibrium with the components on the other side of the interface and that a process of unsteady state molecular diffusion occurs for the time the element or chunk remains at the surface. The depth of the liquid element, i.e. the z -direction, is assumed to be infinite which is true only when the time of exposure of the element to the interface is short so that penetration is confined only to a small surface layer. Existence of any velocity gradient at the interface and the layers below up to which penetration takes place is ignored.

We consider for mathematical formulation, a system in which a component A from the interface diffuses towards the bulk of the phase. The equation for unsteady state diffusion, as per Fick's second law can be written as

$$\frac{\partial C_A}{\partial t} = D_A \frac{\partial^2 C_A}{\partial x^2} \quad (4.359)$$

for equimolecular diffusion, or for a process in which the concentration of the diffusing material is low. The above equation can be solved under the following boundary conditions:

$$C_A = C_{Ae} \text{ at } x = 0 \text{ for } t > 0 \quad (4.360)$$

$$C_A = C_{Ab} \text{ at } 0 < x < \infty \text{ for } t = 0 \quad (4.361)$$

$$C_A = C_{Ab} \text{ at } x = \infty \text{ for } t > 0 \quad (4.362)$$

¹ R. Higbie, *Trans A.I. Ch E.*, **31**: 365 (1935).

where C_A , C_{Ae} and C_{Ab} , respectively, refer to the concentrations of A at any instant t , equilibrium concentration of A and bulk concentration of A. For the sake of convenience, we define C_A^* by the relation

$$C_A^* = C_A - C_{Ab} \quad (4.363)$$

Thus, Eq. (4.359) takes the form

$$\frac{\partial C_A^*}{\partial t} = D_A \frac{\partial^2 C_A^*}{\partial x^2} \quad (4.364)$$

The above equation can be solved by using Laplace transforms. In this method, we introduce a function $\overline{C_A^*}$ such that

$$\overline{C_A^*} = \int_0^\infty C_A^* \exp(-pt) dt \quad (4.365)$$

Similarly

$$\begin{aligned} \frac{\partial C_A^*}{\partial t} &= \int_0^\infty \frac{\partial \overline{C_A^*}}{\partial t} \exp(-pt) dt \\ &= [C_A^* \exp(-pt)]_0^\infty + p \int_0^\infty C_A^* \exp(-pt) dt = p \overline{C_A^*} \end{aligned} \quad (4.366)$$

and

$$\begin{aligned} \frac{\partial^2 \overline{C_A^*}}{\partial x^2} &= \int_0^\infty \frac{\partial^2 C_A^*}{\partial x^2} \exp(-pt) dt \\ &= \frac{\partial^2}{\partial x^2} \int_0^\infty C_A^* \exp(-pt) dt = \frac{\partial^2 \overline{C_A^*}}{\partial x^2} \end{aligned} \quad (4.367)$$

With the help of Laplace transform of each term of Eq. (4.364), we can write

$$p \overline{C_A^*} = D_A \frac{\partial^2 \overline{C_A^*}}{\partial x^2} \quad (4.368)$$

Equation (4.368) is a linear homogeneous ordinary differential equation of the second order with constant coefficients. Hence, we can write its solution as

$$\overline{C_A^*} = \lambda_1 \exp\left(x \sqrt{\frac{p}{D_A}}\right) + \lambda_2 \exp\left(-x \sqrt{\frac{p}{D_A}}\right) \quad (4.369)$$

where λ_1 and λ_2 are constants of integration.

Using the boundary condition at $x = 0$, $C_A^* = (C_{A0} - C_0) = C_{Ae}$ for $t > 0$, we have

$$\overline{C_A^*} = \int_0^\infty C_A^* \exp(-pt) dt = \frac{C_{Ae}}{p} \quad (4.371)$$

Similarly using the boundary condition

$$\text{At } x = \infty, C_A^* = 0 \text{ for } t > 0$$

we get

$$\overline{C_A^*} = 0 \quad (4.372)$$

Substituting these values, we obtain

$$\lambda_1 = 0 \quad (4.373)$$

and

$$\lambda_2 = \frac{C_{Ae}^*}{p} \quad (4.374)$$

Hence, Eq. (4.369) can be rewritten on substitution of relevant values as

$$\overline{C_A^*} = \left(\frac{C_{Ae}^*}{p} \right) \exp \left(-x \sqrt{\frac{p}{D_A}} \right) \quad (4.375)$$

Taking inverse transforms from Table 4.5, we get

$$\overline{C_A^*} = C_{Ae}^* \operatorname{erfc} \left(\frac{x}{2\sqrt{D_A t}} \right) \quad (4.376)$$

where

$$\operatorname{erfc} \left(\frac{x}{2\sqrt{D_A t}} \right) = 1 - \frac{2}{\sqrt{\pi}} \int_0^{x/2\sqrt{D_A t}} \left(\frac{x}{2\sqrt{D_A t}} \right) \exp(-y^2) dy \quad (4.377)$$

Thus

$$\frac{C_A - C_{Ab}}{C_{Ae} - C_{Ab}} = \operatorname{erfc} \left(\frac{x}{2\sqrt{D_A t}} \right) \quad (4.378)$$

The concentration gradient of the diffusing species A is thus, given by

$$\begin{aligned} \frac{dC_A}{dx} &= (C_{Ae} - C_{Ab}) \left(\frac{2}{\sqrt{\pi}} \right) \left(\frac{1}{2\sqrt{D_A t}} \right) \left(-\exp \frac{-x^2}{4D_A t} \right) \\ &= - \left(\frac{C_{Ae} - C_{Ab}}{\sqrt{\pi D_A t}} \right) \exp \left(-\frac{x^2}{4D_A t} \right) \end{aligned} \quad (4.379)$$

Hence, the rate of transfer per unit area across the phase boundary is given by

$$\begin{aligned} J_A &= -D_A \left(\frac{\partial C_A}{\partial x} \right)_{x=0} \\ &= -(C_{Ae} - C_{Ab}) \left(\frac{D_A}{\pi t} \right)^{1/2} \end{aligned} \quad (4.380)$$

TABLE 4.5 Laplace transforms

$$\bar{T}(y) = \int_0^{\infty} e^{-pt} T(y)(t) dt, q' = \sqrt{\frac{p}{\alpha}}$$

$\bar{T}(y)$	$\bar{T}(y, t)$
$\frac{1}{p}$	1
$\frac{1}{p + \alpha}$	$e^{-\alpha t}$
$\frac{\omega}{p^2 + \omega^2}$	$\sin \omega t$
$\frac{p}{p^2 + \omega^2}$	$\cos \omega t$
$e^{-q't}$	$\frac{y}{2\sqrt{\pi\alpha t^3}} e^{-y/4\alpha t}$
$\frac{e^{-q'y}}{q'}$	$\left(\frac{\alpha}{\pi t}\right)^{1/2} e^{-y^2/4\alpha t}$
$\frac{e^{-q'y}}{p}$	$\operatorname{erfc} \frac{y}{2\sqrt{\alpha t}}$
$\frac{e^{-q'y}}{p(q' + h)}$	$\frac{1}{h} \operatorname{erfc} \left[\frac{y}{2\sqrt{\alpha t}} \right] - \frac{1}{h} e^{hy + h^2\alpha t} \operatorname{erfc} \left[\frac{y}{2\sqrt{\alpha t}} + h\sqrt{\alpha t} \right]$
$\frac{e^{-q'y}}{q'(q' + h)}$	$\alpha e^{hy + h^2\alpha t} \operatorname{erfc} \left[\frac{y}{2\sqrt{\alpha t}} + h\sqrt{\alpha t} \right] t$

The above equation gives the instantaneous rate of mass transfer when the surface element under consideration has an age t , if the element is exposed for a time t_e , the average rate $J_{A,av}$ of transfer is given by

$$\begin{aligned}
 J_{A,av} &= (C_{Ae} - C_{Ab}) \sqrt{\left(\frac{D_A}{\pi}\right)} \left(\frac{1}{t_e}\right) \left\{ \int_0^{t_e} \left(\frac{dt}{\sqrt{t}}\right) \right\} \\
 &= 2(C_{Ae} - C_{Ab}) \sqrt{\frac{D_A}{\pi t_e}}
 \end{aligned} \tag{4.381}$$

Thus, the shorter the time of exposure, the greater will be the rate of mass transfer. No precise value can be assigned to t_e in most of the practical cases, but qualitatively its value will become less as the degree of agitation of the fluid increases and thus the rate of mass transfer increases. It is seen that the rate of mass transfer is proportional to the square root of diffusivity in this case, whereas it is proportional to diffusivity in the case of the two-film theory.

Application of these equations is illustrated by an example given below.

EXAMPLE 4.18 Hydrogen gas at 1 atm pressure is flowing over liquid aluminium at 700°C. Calculate the rate of mass transfer of hydrogen into aluminium, based on penetration theory. The solubility of hydrogen is 1 cm³ per 100 g of aluminium and the diffusion coefficient of hydrogen in aluminium is 1×10^{-5} cm² s⁻¹. Assume the time of exposure to be 1 s.

Solution Mole fraction of hydrogen in bulk phase, $C_{H,b} = 1$.

Also, mole fraction of hydrogen in equilibrium $C_{H,e}$ is

$$C_{H,e} = \frac{1/22400}{1/22400 + 100/27} = 0.000012$$

Diffusion coefficient, $D_H = 1 \times 10^{-5}$ cm² s⁻¹ = 10^{-9} m² s⁻¹

Time of exposure, $t_e = 1$ s

Thus, using Eq. (4.381), we have

$$\begin{aligned} J_H &= 2(C_{H,b} - C_{H,e}) \sqrt{\frac{D_H}{\pi t_e}} \\ &= 2(1 - 0.000012) \sqrt{\frac{10^{-9}}{\pi \times 1}} \\ &= 2 \times 0.999988 \sqrt{\frac{10^{-9}}{\pi}} \\ &= 3.57 \times 10^{-5} \text{ m s}^{-1} \quad \text{Ans.} \end{aligned}$$

4.5.3 Surface Renewal Model

Dankwerts¹ proposed a modification of the penetration theory, by pointing out that each element travelling from the bulk to the interface shall not be exposed for the same time, but a random distribution of their life-times or ages will exist. He assumed that the probability of an element of surface getting mixed with the bulk of the fluid was independent of its age, i.e. the time of stay of the chunk of fluid at the surface. On the basis of this assumption, he derived the age distribution of the surface elements as follows.

Let S be the rate of production of fresh area per unit interfacial area of the system. The interfacial area per unit total area, having an age between t and $(t + \delta t)$ will be a function of time t only and will be equal to $f(t) \delta t$, where $f(t)$ is a function of time. This will be equal to the area in the age group $(t - \delta t)$ to t , minus that replaced by the fresh surface in the following time interval δt .

Thus

$$f(t)\delta t = [f(t - \delta t) \delta t - \{f(t - \delta t) \delta t\} \delta \delta t]$$

¹ P.U. Dankwerts, *Ind. Engg. Chem.*, **43**: 1460 (1951).

or

$$\frac{f(t) - f(t - \delta t)}{\delta t} = -Sf(t - \delta t) \quad (4.382)$$

For infinitesimal value of δt , we can write

$$\frac{d\{f(t)\}}{dt} = -S\{f(t)\} \quad (4.383)$$

which on integration will yield

$$f(t) = A \exp(-St) \quad (4.384)$$

where A is the constant of integration and can be evaluated as follows.

As the function $f(t)$ refers to unit total area, hence we can write

$$\int_0^{\infty} f(t) dt = 1 \quad (4.385)$$

Substitution of Eq. (4.384) in the above equation and subsequent integration leads to

$$A \frac{1}{S} = 1$$

or

$$A = S \quad (4.386)$$

Hence

$$f(t) = S \exp(-St) \quad (4.387)$$

According to Eq. (4.381), the mass transfer rate at unit area of surface of age t is expressed as

$$J_A = (C_{Ae} - C_{Ab}) \frac{D_A}{\sqrt{\pi t}} \quad (4.388)$$

Hence, the overall rate of mass transfer per unit area will be

$$J_A = (C_{Ae} - C_{Ab}) \left[\int_0^{\infty} \frac{D_A}{\sqrt{\pi t}} S \exp(-St) dt \right] \quad (4.389)$$

By making a substitution

$$St = \beta^2 \text{ we get for the above equation} \quad (4.390)$$

$$J_A = (C_{Ae} - C_{Ab}) \sqrt{D_A S} \left[\frac{2}{\sqrt{\pi}} \int_0^{\infty} (-\beta^2) d\beta \right] \quad (4.391)$$

The integral is the error function and has a value of unity for integration from 0 to ∞ (cf. Table 4.4). Thus, we get for J_A the relation

$$J_A = (C_{Ae} - C_{Ab}) (\sqrt{D_A S}) \quad (4.392)$$

or the mass transfer coefficient

$$k_m = \sqrt{D_A S} \quad (4.393)$$

The above equation may yield lower results as the upper limit for the age of any element cannot be infinite. However, the portion of surface in the older ages will be very small and thus the error will not be much. In this case too, a numerical value of function S can hardly be assessed but can be determined from the mass transfer data. Qualitatively, it also leads to the conclusion that in the case of stirred systems, the value of the function S will be high and thus the mass transfer coefficient will be high too.

4.5.4 Film-Penetration Theory

This theory was proposed by Toor and Marchello¹ and incorporates the basic concepts of both the two-film theory and the penetration theory. In this case, the whole of the resistance to mass transfer is assumed to be lying within a laminar film formed at the interface as in the case of the two-film theory. Further, it is assumed that the surface renewal takes place at a distance equal to the thickness of the film from the interface by the transfer of the fluid from the bulk to the interface by the action of eddy currents. Mass transfer then takes place as in the penetration theory with the concept that the concentration gradient exists only in the film and the material 'which traverses the film is completely mixed with the bulk of the fluid in accordance with the penetration theory. Thus, the mass transfer process is governed by unsteady state diffusion and will follow the boundary conditions.

$$(i) \text{ At } t = 0, C_A = C_{Ab} \text{ for } 0 < x < \infty \quad (4.394a)$$

$$(ii) \text{ At } t > 0, C_A = C_{Ae} \text{ for } x = 0 \quad (4.394b)$$

$$(iii) \text{ At } t > 0, C_A = C_{Ab} \text{ for } x = \delta \quad (4.394c)$$

where δ is the thickness of the laminar film.

We can further calculate from the instantaneous values of J_A , their average values by making use of the relevant mass transfer equation and by assuming either the same exposure time for each surface element or a surface distribution function as in the case of Dankwerts model.

We employ, in general, two limiting cases of this theory. For short surface life periods, the theory is similar to the penetration theory whereas for longer periods of time, it becomes identical with the two-film theory. It should be noted that the third boundary condition in this theory differentiates it from the penetration theory. The solution of Eq. (4.359) under the above boundary conditions yields

(i) for small values of t

$$J_A = \left(\frac{D_A}{\pi t} \right)^{1/2} \left[1 + 2 \left\{ \sum_{n=1}^{\infty} \exp \left(-\frac{n^2 \delta^2}{D_A t} \right) \right\} \right] (C_{Ae} - C_{Ab}) \quad (4.395)$$

¹ H.L. Toor and J.M. Marchello, *A.I.Ch E.J.*, **54**: 97 (1958).

(ii) for large values of t

$$J_A = \left(\frac{D_A}{\delta} \right)^{1/2} \left[1 + 2 \left\{ \sum_{n=1}^{\infty} \exp \left(-\frac{n^2 \pi^2 D_A t}{\delta^2} \right) \right\} \right] (C_{Ae} - C_{Ab}) \quad (4.396)$$

This theory suffers from the drawback that it involves determination of two system-dependent constants t_e and δ , from the experimental data for its application to industrial problems.

4.6 INTERFACIAL TURBULENCE

This is another phenomenon which requires consideration while analysing mass transfer problems. Mass transfer of a solute between stagnant, immiscible liquids might cause spontaneous interfacial turbulence. The effect of this turbulence is to cause much higher mass transfer rates than those expected or obtained solely by molecular diffusion. This turbulence may result because of unstable interfacial tension gradients caused by the transport of a component. This will also cause a concentration difference of the component along the interface, which will result in changes in density and induce a convective motion at the interface. It is understood that the phase with lower diffusion coefficients will have a higher concentration difference and a stronger convective stream effect. If this phase simultaneously has a higher kinematic viscosity, the currents will be stronger in this phase than in the other, leading to a *staupunkt* or stagnant point, having a higher concentration of the material and a lowering of concentration at the other points on the interface. The interfacial stability, thus developed causes ripples to form at the interface. It also leads to the formation of regularly shaped transport channels between the interface and the bulk fluid and thus markedly affects the rate of mass transfer. This is commonly known as Marangoni effect. This effect has not so far been well understood and the theory is not yet developed to quantitatively account for its roles in mass transfer processes.

REVIEW QUESTIONS

1. Discuss with the help of suitable examples the importance of mass transfer in metallurgical processes.
2. Discuss the various modes of mass transfer along with their fields of application.
3. State Fick's first law of diffusion. Based on this law, derive the dimensions of the diffusion coefficient.
4. Describe the different ways of expressing the concentration of components in a system. Derive the relation between weight percentage and mole fraction of a component present in a system.

5. Prove that molar flux M_i with respect to stationary coordinates is

$$M_i = -C_i D_i \frac{\partial N_i}{\partial x} + N_i (C_i v_i)$$

where the symbols have their usual meanings.

6. Discuss the applications of the kinetic theory of ideal gases for evaluation of diffusion coefficients in gases.
7. Discuss the different theories proposed for the calculation of diffusion coefficients in liquids.
8. Derive an equation for the diffusion coefficient of an interstitial solute.
9. Explain the following terms: inter-diffusion coefficient, intrinsic diffusion coefficient and self-diffusion coefficient. How are they interrelated?
10. Derive an equation for the rate of movement of the weld interface in a binary system.
11. Derive the equation between intrinsic and self-diffusion coefficients.
12. Describe Marano's method for experimental determination of inter-diffusion coefficients in binary systems.
13. Describe Grube's method for the determination of diffusion coefficients. Discuss the limitations of this method.
14. Derive the relationship between atomic mobilities and self-diffusion coefficients.
15. Derive the relationship between ionic conductivity and diffusion coefficient in ionic compounds.
16. Discuss the various modes by which diffusion in porous solids takes place.
17. Derive an equation for the permeability of gases through metallic membranes.
18. Derive an approximate expression for the position of an interface of desired composition as a function of time during diffusion of a component in a solid.
19. Discuss how Fick's second law of diffusion is applied to carburization of γ -iron.
20. How is Fick's second law applied to a case of diffusional mass transfer coupled with moving phase boundaries? Discuss with suitable examples.
21. Derive an equation for the oxidation of metals, affected by the migration of ions and electrons through the oxide film. Discuss some special cases of importance to metallurgical systems.
22. Derive an equation for the diffusion-controlled reduction kinetics of dense pellets.
23. Derive the general equation for convective mass transfer.
24. Explain the term reaction progress variable with suitable examples.

25. Derive an equation for mass transfer by forced convective flow in a pipe.
26. Derive an equation for the rate of hydrogen removal from a steel bath, by purging with argon.
27. Derive an equation for the reduction kinetics of a packed bed through which a fluid flows and involves a first order irreversible reaction.
28. Derive an equation for the reduction kinetics of porous hematite pellets. Compare the results obtained with those obtained in respect of dense pellet reduction kinetics.
29. Discuss the concept of mass transfer coefficient with suitable examples. How is the overall mass transfer coefficient related to mass transfer coefficients in individual phases?
30. Discuss the two-film theory of mass transfer in slag-matal reactions. Point out the limitations of this theory.
31. Discuss the penetration theory and its application to gas-metal reactions.
32. How does Dankwerts' surface renewal model differ from penetration theory? Discuss the salient features of this model.
33. Write notes on:
 - (i) Film penetration theory
 - (ii) Interfacial turbulence

PROBLEMS

1. Calculate C_i , ρ_i , X_i and N_i of various components at 250°C of a gas mixture containing 58% N₂, 28% CO and 14% CO₂ by volume. Assume the gas to behave ideally and the pressure to be one atom (atomic weights: C = 12, N = 14, O = 16).
2. Calculate the diffusion coefficient of helium in oxygen at 298 K and 0.1 atm pressure with the help of the kinetic theory of gases and also by making use of the Chapman-Enskog equation. The required data may be taken from Tables 4.1 and 4.2. Assume that the gas mixture behaves ideally. Atomic diameters of helium and oxygen are 2.44 Å and 1.82 Å respectively.
3. Calculate the diffusion coefficient of H₂ in oxygen at NTP with the help of critical data.
4. Calculate the diffusion coefficient of nitrogen in a mixture of 20% H₂ and 80% CO at 50°C and 75 atm pressure.
5. Using the Wilke and Chang's equation, calculate the diffusion coefficient of a liquid A of density 1200 kg m⁻³ and molecular weight 153 at 25°C in a solvent of $\psi = 1$ and $M_B = 83$. The viscosity of solution may be taken as 1.12 centipoise.

6. Calculate the diffusion coefficient of an interstitial solute from the given data. Lattice constant of the solvent = 3.12 Å, anelastic strain relaxation time = 5.3×10^{-11} s.
7. A plate of a binary alloy having 0.8 as mole fraction of component A was welded to another plate having 0.6 as mole fraction of this component. This diffusion couple was heated to 950°C for six days. The analysis of a sample 0.15 mm from the weld surface in the direction of the second plate showed $N_A = 0.62$. Calculate the diffusion coefficient of component A by Grube's method.
8. A copper-nickel plate containing 15 weight % Cu was welded to another containing 65 weight % Cu and heated for 30 days at 800°C. The analysis of copper on either side in the direction normal to the weld-plane was found to be as follows:

Distance (x), in cm	Weight% Cu
- 0.20	15.2
- 0.15	16.1
- 0.09	18.2
- 0.07	27.5
- 0.03	40.2
+ 0.03	52.6
+ 0.07	60.7
+ 0.13	62.0
+ 0.18	63.8
+ 0.25	64.9

Calculate the inter-diffusion coefficient at 35 weight% Cu by Matano's method.

9. A rod of pure copper was joined to another rod of 70.6 At % Cu-brass to form a diffusion couple. After annealing for 1.5 days at 800°C, At % Zn vs. distance was plotted to give the following data:

Distance x (10^{-2} cm)	At % Zn	Distance x (10^{-2} cm)	At % Zn
0.95	0.3	14.45	23.5
2.85	1.5	16.95	25.0
4.55	4.4	20.25	26.5
6.05	8.8	25.85	27.9
7.85	14.7	32.05	28.8
11.35	20.6	36.05	29.1

Calculate the inter-diffusion coefficient at 10 At % Zn.

10. An oxide M_xO is predominantly a cationic conductor. The value of interdiffusion coefficient for the oxide is found to be $3.1 \times 10^{-11} \text{ m}^2 \text{ s}^{-1}$. The value of x is known to vary with P_{O_2} as follows:

$$\ln x = -0.693 + 1.47 \times 10^{-2} \ln P_{O_2}$$

Calculate the self-diffusion coefficient of the cations.

11. Calculate the diffusion coefficient of sodium ions at 500°C in sodium chloride crystals in which the number of sodium ions per m³ is 4.9×10^{31} . The electrical conductivity of sodium chloride is 1.02×10^{-1} ohm⁻¹ m⁻¹, the transport number of sodium ion is 0.98, the unit electronic charge is 1.6×10^{-19} coulomb and the Boltzmann's constant is 1.38×10^{-23} J mol⁻¹ K⁻¹.
12. Calculate the diffusion coefficient of hydrogen at 500°C in an H₂ – H₂O mixture diffusing through a porous solid having a void fraction of 0.53, pore diameter of 130 Å and tortuosity factor of 1.78.
13. Calculate the case-thickness up to which carbon has a value of 0.5% when a mild steel plate having an initial carbon content of 0.17% is exposed for 2 h to an atmosphere which brings its surface concentration instantaneously to 0.95%. Diffusion coefficient of carbon in steel = 1.89×10^{-10} m² s⁻¹.
14. Calculate the carbon concentration profile of the sample in Example 4.13, if it is suspended in the carburizing bath for 18 hours.
15. Solubility of component A in a solvent B at 1000 K in two stable phases α and β at this temperature is 0.2% and 0.8% respectively. An alloy containing 0.05% of A is exposed to a phase which brought its surface concentration to a constant value of 1.4%. If the diffusion coefficient of component A is 2.5×10^{-13} m² s⁻¹, calculate the composition profile of A in the transformed layer after 3 days of treatment.
16. Liquid copper at 1200°C dissolves hydrogen at the rate of 7.5 cm³ (STP) per 100 g of copper under 1 atm pressure of hydrogen. Calculate the rate of transfer of hydrogen to a stream of flowing argon containing 40 ppm hydrogen if the overall mass transfer coefficient is 5.0×10^{-5} m s⁻¹.
17. Calculate the diffusion coefficient of oxygen in liquid silver at 1075°C using the penetration theory. The solubility of oxygen is 194 cm³ per 100 g of liquid silver at 1075°C and at 1 atm pressure of oxygen. Assume that the rate of mass transfer of pure oxygen is 4.5×10^{-4} m s⁻¹ and its time of exposure over liquid silver is 1 s.
18. Calculate the thickness of the scale formed in Example 4.15, after the metal is exposed to oxidizing atmosphere for 3 weeks.
19. Determine the relationship between f and t for the pellet considered for reduction in Example 4.16.
20. A gas is flowing around a sphere of radius 0.03 m at a velocity of 0.05 m s⁻¹. Calculate the mass transfer coefficient assuming the diffusion coefficient of the gas to be 1.6×10^{-6} m² s⁻¹ and its viscosity and density as 3.5×10^{-5} kg m⁻¹ s⁻¹ and 1.97 kg m⁻³ respectively.

CHAPTER **5**

Dimensional Analysis and Similitude

In Chapter 1, we discussed the concept of dimensions of different physical quantities and also emphasized the significance of the concept of dimensional homogeneity of equations. This concept is of immense importance and finds extensive applications in the analysis of problems related to transport phenomena and interpretation of related experimental results. Therefore in the present chapter, we will extend this concept of dimensional homogeneity and briefly explain the basic principles of dimensional analysis and similitude.

5.1 DIMENSIONLESS NUMBERS AND FUNCTIONAL RELATIONSHIPS

Consider an example of fluid flow in capillary pipes. From Eq. (2.94), the mass flow rate for laminar flow of an incompressible fluid through a pipe can be obtained from the following analytical relation:

$$G_m = \frac{\Delta P \rho \pi R^4}{8\mu L} \quad (5.1)$$

where G_m is the mass flow rate, i.e. mass flowing per unit time and has the dimensions¹ Mt^{-1} ; ΔP is the pressure difference across the length L of the capillary or pipe and has the dimensions $ML^{-1}t^{-2}$, ρ is the density of fluid with dimensions ML^{-3} , R and L are respectively the radius and length of the tube, each having the dimension L and μ is the viscosity of the fluid having $ML^{-1}t^{-1}$ as its dimensions. If the dimensions of the different physical quantities are

¹ Several authors have used the symbol T for the dimension of time, while analysing properties of mechanical systems only. However, in the present work, dealing with both mechanical and thermal systems, the symbol t will be used for dimension of time and the symbol T for dimension of temperature.

substituted in Eq. (5.1), we would observe that both the left- and right-hand sides of this equation will have the same dimensions, i.e. Mt^{-1} . This analysis illustrates that this equation is dimensionally homogeneous. The equation shows that different physical parameters involved in describing the phenomena of mass transport of a fluid through a capillary pipe are related by the functional form

$$G_m = G_m(\Delta P, \mu, L, R, \rho) \quad (5.2)$$

To determine experimentally the effect of the different variables in Eq. (5.2), within the parentheses on the right-hand side, we need to conduct a large number of experiments on flow of fluids of different viscosities (μ) and densities (ρ) through pipes of different lengths (L) and radii (R) under different pressure differentials (ΔP) across the tube to arrive at Eq. (5.1). A basic question then arises! ‘Is it possible to reduce this large number of experiments for arriving at the analytical relationship between the dependent and independent variables of the type, represented by Eq. (5.1)?’ The answer is, ‘Of course, yes’. For showing how it can be done, we rewrite this equation, in the following alternative form

$$\left[\frac{G_m^2}{\Delta P \rho (\pi R^2)^2} \right] = \left[\left(\frac{1}{64\pi} \right) \left(\frac{\Delta P \pi R^2 \rho}{\mu^2} \right) \left(\frac{R}{L} \right)^2 \right] \quad (5.3)$$

The above equation is written in such a way that each of the terms in different parentheses has zero dimensions; i.e. is dimensionless. In the form of a functional relationship, this equation can be rewritten as

$$\Pi_1 = \Pi_1(\Pi_2, \Pi_3) \quad (5.4)$$

where

$$\Pi_1 \equiv \left\{ \frac{G_m^2}{\Delta P \rho (\pi R^2)^2} \right\} \quad (5.5)$$

$$\Pi_2 \equiv \left\{ \frac{\Delta P \pi R^2 \rho}{\mu^2} \right\} \quad (5.6)$$

and

$$\Pi_3 \equiv \left(\frac{R}{L} \right)^2 \quad (5.7)$$

This functional relationship shows that we need only study the effect of functions Π_2 and Π_3 on function Π_1 to arrive at the relationship expressed by Eq. (5.1) instead of all the physical parameters expressed in functional relationship of Eq. (5.2). The functional relationship of Eq. (5.4) offers the following advantages, apart from the ones already stated above:

- (i) For experimental studies as well as interpretation of their results, it offers a new set of dimensionless parameters which can be conveniently varied by judiciously choosing the interdependent physical parameters instead of conducting extensive experimental studies to

determine the effect of each of the physical parameters involved. This is important because experimental studies to determine the effects of a large number of parameters are not only time consuming, costly and tedious but also cause several practical difficulties in the way of determination of reliable data.

- (ii) The functional relationship expressed by Eq. (5.4) is of a general nature for all types of flows in pipes. The analytical expressions may, however, be different for different types of flows and thus may assume different analytical forms for different values of some dimensionless numbers, namely the Reynolds number in the present case. These relationships can be easily determined by varying Π_2 and Π_3 and then determining Π_1 experimentally.

In the above analysis we have taken a simple example of the flow of a fluid through pipes for the sake of illustration and to stress the importance of dimensionless functional relationships. In this example, we considered a system in which the analytical relationship for fluid flow was known. However, by doing so we actually put the cart before the horse, i.e. followed the reverse procedure. In fact, in actual practice, we start with a general functional relationship such as Eq. (5.2) and transform it to the dimensionless functional relationship such as Eq. (5.4), and then determine their dimensionless analytical forms from experimental results. The technique of arriving at dimensionless functional relationships is called *dimensional analysis*. Various methods of dimensional analysis are discussed in the following section.

5.2 METHODS OF DIMENSIONAL ANALYSIS

The different methods used for dimensional analysis can be classified into three categories:

- (i) those based on our knowledge of the physical parameters affecting the dependent variables of the system under study. In this category, we have (a) Rayleigh's method, and (b) Buckingham's method,
- (ii) those based on our knowledge of differential equations governing the system under study, and
- (iii) those based on similarity criteria among similar systems of different sizes.

We will now discuss the basic concepts of the different methods with suitable examples.

5.2.1 Rayleigh's Method¹

In this method, the first step is to write the functional relationship between the independent physical quantities and the dependent variables in the form of a

¹ Lord Rayleigh, *Proc. Roy. Soc. (London)*, **66**: 68 (1899–1900).

product. For example, the functional relationship of Eq. (5.2) may be rewritten as

$$G_m = \alpha(\Delta P)^a(\rho)^b(R)^c(L)^d(\mu)^e \quad (5.8)$$

where α is a dimensionless constant.

In fact, such an equation may also be written in the form involving summation or difference between similar terms. However, because of the requirement of dimensional homogeneity of such equations, we need to analyse only one of these terms for arriving at the dimensionless functional relationship and the summation is taken care of in the actual analytical form obtained from the use of relevant experimental results.

As the next step, we substitute the dimensions of each of the variables in the functional relationship. Thus in the above example, substitution of relevant dimensions of different terms in Eq. (5.8) yields

$$(Mt^{-1}) = (ML^{-1}t^{-2})^a(ML^{-3})^b(L)^c(L)^d(ML^{-1}t^{-1})^e \quad (5.9)$$

Employing the concept of dimensional homogeneity, we write equations for the dimensions of each of the basic quantities, viz. mass, length, time, temperature on both sides of this equation. Thus, for the above example under study on the fluid flow, the LHS of Eq. (5.9) has powers 1, 0 and -1 respectively of mass M, length L and time t. Therefore, equating the powers of similar basic units in Eq. (5.9), we get

(i) For mass M

$$1 = a + b + e \quad (5.10)$$

(ii) For length L

$$0 = -a - 3b + c + d - e \quad (5.11)$$

(iii) For time t

$$-1 = -2a - e \quad (5.12)$$

In Eqs. (5.10) – (5.12), there are five unknown variables, namely a , b , c , d and e , and only three equations interrelating them. We can, therefore, express any three of them in terms of the rest two with the help of the above three equations. The selection of these two variables is generally arbitrary. In the present case, we choose d and e as these two variables. Thus from Eqs. (5.10) – (5.12) we can write the following equations

$$a = \frac{1-e}{2} \quad (5.13)$$

$$2b = \frac{1-e}{2} \quad (5.14)$$

$$c = (2 - e) - d \quad (5.15)$$

Substituting these values of a , b and c in Eq. (5.8), we get

$$G_m = \alpha(\Delta P)^{(1-e)/2} (\rho)^{(1-e)/2} (R)^{(2-e-d)} (L)^d (\mu)^e \quad (5.16)$$

or

$$G_m^2 = \alpha^2(\Delta P)^{(1-e)}(\rho)^{(1-e)} (R)^{(4-2e-2d)} (L)^{2d} (\mu)^{2e} \quad (5.17)$$

Rearrangement of terms, by putting terms with arithmetic powers on the RHS of the above equation and by coupling terms of similar powers together, leads to

$$\left(\frac{G_m^2}{\Delta P \rho R^4} \right) = \alpha^2 \left(\frac{\Delta P \rho R^2}{\mu^2} \right)^{-e} \left\{ \left(\frac{R}{L} \right)^2 \right\}^{-d} \quad (5.18)$$

Instead of writing R^4 or R^2 , we may as well write the above equation in terms of cross-sectional area (πR^2) of the pipe. Thus

$$\left\{ \frac{G_m^2}{\Delta P \rho (\pi R^2)^2} \right\} = \left(\frac{\alpha^2}{\pi^3} \right) \left(\frac{\Delta P \rho \pi R^2}{\mu^2} \right)^{-e} \left\{ \left(\frac{R}{L} \right)^2 \right\}^{-d} \quad (5.19)$$

Defining three functions Π_1 , Π_2 and Π_3 by the following expressions, we have

$$\Pi_1 \equiv \frac{G_m^2}{\Delta P \rho (\pi R^2)^2}$$

$$\Pi_2 \equiv \frac{\Delta P \rho \pi R^2}{\mu^2}$$

$$\Pi_3 \equiv \left(\frac{R}{L} \right)^2$$

which are identical to Eqs. (5.5)–(5.7). We can now write Eq. (5.19) in the following alternative form

$$\Pi_1 = \left(\frac{\alpha^2}{\pi^3} \right) (\Pi_2)^{-e} (\Pi_3)^{-2d} \quad (5.20)$$

or

$$\Pi_1 = \Pi_1(\Pi_2, \Pi_3) \quad (5.21)$$

which is the functional relationship identical to Eq. (5.4), but obtained without the use of analytical Eq. (5.3). The form in which the dimensionless groups appear in the functional relationship depends upon the choice of the variables in terms of which the dependent variables are expressed. In the above example, we selected d and e as the variables in terms of which a , b and c were expressed. If we choose a and c as the two variables for expressing the rest by following the already outlined procedure, we get

$$e = 1 - 2a$$

$$b = a$$

and

$$d = 2a - c + 1$$

Hence Eq. (5.8) takes the form

$$G_m = \alpha(\Delta P)^a \rho^b R^c L^{2a-c+1} \mu^{1-2a}$$

or

$$\frac{G_m}{\mu L} = \alpha \left(\frac{\rho \Delta P L^2}{\mu^2} \right)^a \left(\frac{R}{L} \right)^c \quad (5.21a)$$

Thus in this case, we have

$$\Pi_1 = \frac{G_m}{\mu L}$$

$$\Pi_2 = \frac{\rho \Delta P L^2}{\mu^2}$$

and

$$\Pi_3 = \frac{R}{L}$$

Although Eq. (5.21a) is of a different form from that of Eq. (5.19), it can easily be transformed to the latter by taking the square of the former and multiplying the resulting equation by the dimensionless quantity $\{\mu^2 L^2 / \rho \Delta P R^4\}$. Thus various dimensionless forms obtained by selecting different independent indices are interconvertible. Hence we can express them in a form which contains only the commonly occurring dimensionless numbers. Equations (5.10)–(5.12) implicitly sometimes put certain restrictions on the selection of independent indices. For example, a and c cannot be selected as independent indices.

We have explained the application of Rayleigh's method by the above example on a problem related to fluid flow. We now demonstrate the use of this method to obtain functional relationships for some other important transport functions.

Dimensional analysis of friction factor

To obtain a functional relationship using Rayleigh's method, we proceed as follows:

In Chapter 2, the frictional force F acting at the interface between the fluid and the solid surfaces was shown to be expressed by Eq. (2.125). Rearrangement of terms in this equation leads to

$$f_{fr} \equiv \frac{F_x}{A \left(\frac{1}{2} \bar{\rho} \bar{v}^2 \right)} \quad (5.22)$$

where f_{fr} , is the friction factor, F , the frictional force, A the area of contact and $1/2 \bar{\rho} \bar{v}^2$ the average kinetic energy per unit volume of the fluid.

On substituting the dimensions of different terms on the RHS of this equation, we get the dimensions of f_{fr} as

$$f_{fr} = \frac{MLt^{-2}}{L^2(ML^{-3})L^2t^{-2}} = M^0L^0t^0 \quad (5.23)$$

i.e. f_{fr} is a dimensionless parameter.

On the basis of physical analysis of fluid flow through a pipe we can conclude that the frictional force between the solid surface and fluid and hence the friction factor f_{fr} must be a function of the velocity v , density ρ and viscosity μ of the fluid and diameter D and length L of the pipe. This dependence of f_{fr} can thus be expressed by the following functional relationship:

$$f_{fr} = f_{fr}(v, \rho, \mu, D, L) \quad (5.24a)$$

Following Rayleigh's method, therefore, we can write this functional relationship as

$$f_{fr} = C(v)^a(\rho)^b(\mu)^e(D)^d(L)^f \quad (5.24b)$$

where C is a dimensionless constant and a, b, e, d and I are indices of powers to which the parameters v, p, m, D and L must be respectively raised, to arrive at the equality.

Substituting the dimensions of different quantities in the equation, we get the following equality

$$M^0L^0t^0 = \text{const} \times (Lt^{-1})^a (ML^{-1}t^{-1})^e (ML^{-3})^b (L)^d (L)^f \quad (5.25)$$

Therefore equating the powers of fundamental quantities, i.e. mass, time and length respectively on both sides of the above equation, we get,

$$e + b = 0 \quad (5.26a)$$

$$a + e = 0 \quad (5.26b)$$

$$a - e - 3b + d + f = 0 \quad (5.26c)$$

From these equations, we can obtain a, b and d in terms of f and e as follows:

$$a = b = -e \quad (5.26d)$$

and

$$d = -f - e \quad (5.26e)$$

Thus we can write Eq. (5.24b) in the following alternative form

$$\begin{aligned} f_{fr} &= C(v)^{-e}(\rho)^{-e}(\mu)^e(D)^{-f}(L)^f \\ &= C \left(\frac{vpD}{\mu} \right)^{-e} \left(\frac{L}{D} \right)^f \end{aligned} \quad (5.27)$$

or in a functional form, replacing (vpD/μ) by Reynolds number N_{Re} , we get

$$f_{fr} = f \left(N_{Re}, \frac{L}{D} \right) \quad (5.28)$$

However, it has been found experimentally that for smooth pipes the friction factor f_{fr} is independent of L/D ratio. We can thus write

$$f_{fr} = f(N_{Re}) \quad (5.29)$$

which is the required relationship obtainable from dimensional analysis. This also explains why friction factor has been expressed as a function of Reynolds number (Section 2.4).

Dimensional analysis of heat transfer coefficient

From the consideration of a fluid flowing through a pipe we can infer that the heat transfer coefficient h should be a function of velocity v , density ρ , viscosity μ , thermal conductivity k , specific heat C_p , and the diameter D of the tube. Thus, following similar arguments for heat flow, as put forward above for fluid flow, we can write the following equation analogous to Eq. (5.24b), for the heat transfer coefficient.

$$h = \alpha(v)^a(D)^b(\mu)^c(k)^d(\rho)^e(C_p)^f \quad (5.30)$$

where α is a dimensionless constant. By definition, dimensions of heat transfer coefficient h will be $Qt^{-1}L^{-2}T^{-1}$, where Q and T represent respectively the dimensions of quantities *heat* and *temperature*, which are considered fundamental quantities along with mass, length and time. Substitution of dimensions on both sides of Eq. (5.30) leads to

$$Qt^{-1}L^{-2}T^{-1} = (Lt^{-1})^a(L)^b(ML^{-1}t^{-1})^c(Qt^{-1}L^{-1}T^{-1})^d(ML^{-3})^e(QM^{-1}T^{-1})^f \quad (5.31)$$

Equating powers of each of the fundamental quantities in the above equation, we get the following set of equations:

$$\text{for } Q, \quad d + f = 1 \quad (5.32a)$$

$$\text{for } L, \quad a + b - c - d - 3e = -2 \quad (5.32b)$$

$$\text{for } t, \quad -a - c - d = -1 \quad (5.32c)$$

$$\text{for } T, \quad -d - f = -1 \quad (5.32d)$$

$$\text{for } M, \quad c + e - f = 0 \quad (5.32e)$$

Thus, we get the following values of indices a, b, c and d in terms of e and f .

$$d = 1 - f, \quad c = f - e, \quad a = e, \quad \text{and} \quad b = e - 1$$

Hence

$$h = \alpha(v)^e(D)^{(e-1)}(\mu)^{(f-e)}(k)^{(1-f)}(\rho)^e(C_p)^f \quad (5.33)$$

or

$$\frac{Dh}{k} = \alpha \left(\frac{vD\rho}{\mu} \right)^e \left(\frac{\mu C_p}{k} \right)^f \quad (5.34)$$

which yields the required relationship among the three dimensionless numbers as follows:

$$N_{Nu} = \alpha(N_{Re})^e(N_{Pr})^f \quad (5.35)$$

where

$$N_{\text{Nu}} = \frac{hD}{k} \text{ is called the Nusselt number,}$$

$$N_{\text{Re}} = \frac{vD\rho}{\mu} \text{ is called the Reynolds number,}$$

and

$$N_{\text{Pr}} = \frac{\mu C_p}{k} \text{ is called the Prandtl number.}$$

Numerical values of the constant α and indices e and f are determined experimentally from studies on heat flow in the system. Equation (5.35) agrees very well with the relationship given earlier for these numbers in Table 3.3.

Heat transfer in free convection

In free convection, the motion of fluid is caused by a buoyancy force. The buoyancy force is developed because of the difference in temperature at different positions in the fluid. This temperature difference causes a change in density and hence the gravitational force at different positions which consequently gives rise to fluid motion. Hence the velocity of the fluid is no longer an independent variable. Thus we may expect that a number of physical parameters would affect the heat transfer coefficient in such systems. These parameters will comprise (i) the density ρ of the fluid, (ii) viscosity μ of the fluid, (iii) specific heat C_p of the fluid, (iv) thermal conductivity k of the fluid, (v) characteristic length L of the interface, (vi) difference ΔT between the temperature of the undisturbed fluid and the hot surface, and (vii) parameter

$(g\beta)^1$, where g is the acceleration due to gravity and $\beta = \left(\frac{1}{\rho} \frac{\partial \rho}{\partial T}\right)$ is the thermal

coefficient of isobaric volume expansion. Thus, we can write the following equation for h in a manner analogous to Eq. (5.8) written for the analysis of fluid flow:

$$h = A(\rho)^a(\mu)^b(k)^c(C_p)^d(L)^e(g\beta)^f(\Delta T)^i \quad (5.36)$$

where A is a dimensionless constant. Substitution of dimensions of these quantities leads to the equation

$$Qt^{-1}T^{-1}L^{-2} = A(ML^{-3})^a(ML^{-1}t^{-1})^b(Qt^{-1}T^{-1}L^{-1})^c(QM^{-1}T^{-1})^d(L)^e(Lt^{-2}T^{-1})^f(T)^i \quad (5.37)$$

Equating the powers of similar basic parameters Q , M , L , T and t on both the sides of Eq. (5.37) leads to the following set of equations

$$\text{for } M, \quad a + b - d = 0 \quad (5.38a)$$

¹ The factor $g\beta$ will act together since g is the acceleration due to gravity and β a measure of change in density. Hence $g\beta$ is a measure of the difference in force acting at different positions in fluids.

$$\text{for } Q, \quad c + d = 1 \quad (5.38b)$$

$$\text{for } L, \quad -3a - b - c + f + e = -2 \quad (5.38c)$$

$$\text{for } T, \quad -c - d - f + i = -1 \quad (5.38d)$$

$$\text{for } t, \quad -b - c - 2f = -1 \quad (5.38e)$$

Expression of all other indices in terms of c and i , leads to the following relations:

$$d = 1 - c \quad (5.39a)$$

$$f = i \quad (5.39b)$$

$$b = 1 - 2i - c \quad (5.39c)$$

$$a = 1 - c + c + 2i - 1 = 2i \quad (5.39d)$$

$$e = -2 + 6i + 1 - 2i - c + c + i = 3i - 1 \quad (5.39e)$$

Thus, Eq. (5.36) for h can be rewritten in the following alternative form:

$$\begin{aligned} h &= A(\rho)^{2i} (\mu)^{(1-2i-c)} (k)^c (C_p)^{(1-c)} (L)^{(-1+3i)} (g\beta)^i (\Delta T)^i \\ &= A \left(\frac{\mu C_p}{L} \right) \left(\frac{\rho^2 L^3 g \beta \Delta T}{\mu^2} \right)^i \left(\frac{k}{C_p \mu} \right)^c \\ &= A \left(\frac{k}{L} \right) \left(\frac{\rho^2 L^3 g \beta \Delta T}{\mu^2} \right)^i \left(\frac{k}{C_p \mu} \right)^{c-1} \end{aligned} \quad (5.40)$$

Hence

$$\frac{hL}{k} = A \left(\frac{\rho^2 L^3 g \beta \Delta T}{\mu^2} \right)^i \left(\frac{C_p \mu}{k} \right)^{1-c} \quad (5.41)$$

or in a functional form involving the Nusselt, Greshof and Prandtl numbers, we can write

$$N_{\text{Nu}} = f(N_{\text{Gr}}, N_{\text{Pr}}) \quad (5.42)$$

where

$$\text{Nusselt number } N_{\text{Nu}} = \frac{hL}{k}$$

$$\text{Greshof number } N_{\text{Gr}} = \frac{\rho^2 L^3 g \beta \Delta T}{\mu^2}$$

$$\text{Prandtl number } N_{\text{Pr}} = \frac{C_p \mu}{k}$$

Equation (5.42) also agrees with similar relations as shown in Table 3.3.

Dimensional analysis of mass transfer coefficient

The mass transfer coefficient k_m of a component from the interior of a phase to the reaction interface or that of a product of a reaction from the reaction interface to the interior of a phase under forced convective flow can depend upon the following characteristics of the system:

- (i) Velocity v of the fluid
- (ii) Density ρ and viscosity μ of the fluid
- (iii) Diffusion coefficient D of the component in fluid
- (iv) Characteristic distance d such as diameter of the pipe, if fluid is flowing through it.

Thus, k_m can be expressed by the following functional relationship:

$$k_m = k_m(v, \rho, \mu, D, d) \quad (5.43)$$

For mass transfer coefficient, we can write the functional relationship

$$k_m = A(v)^a(\rho)^b(\mu)^c(D)^d(d)^e \quad (5.44)$$

where A is a dimensionless constant of proportionality, and a, b, c, d and e are the indices to which the velocity, density, viscosity, diffusion coefficient and characteristic distance respectively are to be raised for dimensional homogeneity in the above relation.

Taking mass (M) length (L) and time (t) as the fundamental dimensions, we can write the following equations for the dimensions of the different variables occurring in Eq. (5.44) in terms of fundamental dimensions M, L and t

$$k_m = Lt^{-1} \quad (5.45a)$$

$$v = Lt^{-1} \quad (5.45b)$$

$$\rho = ML^{-3} \quad (5.45c)$$

$$\mu = ML^{-1}t^{-1} \quad (5.45d)$$

$$D = L^2t^{-1} \quad (5.45e)$$

$$d = L \quad (5.45f)$$

Substitution of the above values of the dimensions of different variables in Eq. (5.44) leads to

$$Lt^{-1} = A(Lt^{-1})^n(ML^{-3})^b(ML^{-1}t^{-1})^c(L^2t^{-1})^d(L)^e \quad (5.46)$$

Equating powers of the same fundamental dimensions on both sides of this equation, we get

$$\text{for } M, \quad b + c = 0 \quad (5.47a)$$

$$\text{for } L, \quad a - 3b - c + 2d + e = 1 \quad (5.47b)$$

$$\text{for } t, \quad -a - c - d = -1 \quad (5.47c)$$

With the help of the above equations, we can express all of these five variables a, b, c, d and e in terms of any two, which let us arbitrarily select c and a .

We therefore get from Eqs. (5.47a) to (5.47c), the following relations for other variables:

$$b = -c \quad (5.48a)$$

$$d = 1 - a - c \quad (5.48b)$$

$$e = a - 1 \quad (5.48c)$$

Substituting values of these in Eq. (5.44) leads us to

$$\begin{aligned} k_m &= A(v)^a(\rho)^{-c}(\mu)^c(D)^{(1-a-c)}(d)^{(a-1)} \\ &= A \left(\frac{vd}{D} \right)^a \left(\frac{\mu}{\rho D} \right)^c \left(\frac{D}{d} \right) \end{aligned} \quad (5.49)$$

and rearrangement of the terms in the above equation gives us

$$\frac{k_m d}{D} = A \left(\frac{\rho v d}{\mu} \right)^a \left(\frac{\rho D}{\mu} \right)^{-(a+c)} \quad (5.50)$$

The dimensionless group ($k_m d/D$) in this equation is called the *Sherwood number* and is generally denoted by the symbol N_{Sh} . Similarly, the dimensionless group ($\rho D/\mu$) is known as the *Schmidt's number* and is generally denoted by the symbol N_{Sc} . Equation (5.50) can thus be expressed in the following functional form

$$N_{Sh} = \psi(N_{Re}, N_{Sc}) \quad (5.51)$$

This equation also agrees with that shown earlier in Section 4.4.2.

The above form of relationship is very useful for representation of experimental data as well as for making experimental study of the effect of different variables on mass transfer. It can also be shown by the same technique as used in the case of analysis of heat transfer coefficients that Sherwood number in case of natural convection is represented by the functional relationship

$$N_{Sh} = \psi(N_{Ge}, N_{Sc}) \quad (5.52)$$

where N_{Gr} is the Greshof number and N_{Sc} the Schmidt number.

EXAMPLE 5.1 Derive the relationship between the friction factor and Reynolds number for the flow of an incompressible fluid through a smooth horizontal pipe from the following readings:

Length of the pipe : 5.0 m

Diameter of the pipe : 10.0 cm

Density of the fluid : 1.0 g cm⁻³

Viscosity of the fluid : 1.0 centipoise

Pressure difference ΔP

across the pipe	290	1000	3360	16750	56000
(dynes/cm ²)					

Flow rate G (litre/h)	1400	2800	5600	14000	28000
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Solution As the first step, we calculate the Reynolds number N_{Re} for various flow rates.

$$N_{Re} = \frac{\rho dv}{\mu} = \frac{1 \times 10 \times v}{0.01} = 1000v$$

where

$$v = \frac{G \times 1000}{3600 \times \pi \times (5)^2} = (3.535 \times 10^{-3})G, \text{ where } G \text{ is the flow rate.}$$

Thus

$$N_{\text{Re}} = 3.535G$$

The values of N_{Re} for various values of G given in this problem are tabulated below.

G	N_{Re}	f_{fr}
1400	4949	0.118
2800	9898	0.102
5600	19796	0.086
14000	49490	0.068
28000	98980	0.057

According to the definition of friction factor as per (Eq. 2.125)

$$\begin{aligned} F\alpha &= f_{\text{fr}} \left(\frac{1}{2} \bar{\rho} \bar{v}^2 \right) A \\ &= f_{\text{fr}} \left(\frac{1}{2} \bar{\rho} \bar{v}^2 \right) (2\pi RL) \end{aligned}$$

where $F\alpha = \Delta P \pi R^2$. Hence

$$\Delta P \pi R^2 = f_{\text{fr}} \bar{\rho} \bar{v}^2 \pi RL$$

or

$$\begin{aligned} f_{\text{fr}} &= \frac{\Delta PR}{\bar{\rho} L \bar{v}^2} = \frac{\Delta P \times 5}{1 \times 500 \times \bar{v}^2} \\ &= \frac{0.01 \Delta P}{\bar{v}^2} = \frac{0.01 \Delta P}{(3.535 \times 10^{-3} G)^2} \end{aligned}$$

Substitution of values of ΔP and G in the above equation for various flow rates, leads us to the calculation of friction factor. The values of friction factor thus obtained are also tabulated above. In Fig. 5.1, $\ln f_{\text{fr}}$ is plotted against $\ln N_{\text{Re}}$. This plot is found to be a straight line. The equation of this straight line is

$$\ln f_{\text{fr}} = 4 \times 10^{-4} - 0.527 \times \ln N_{\text{Re}}$$

Thus

$$f_{\text{fr}} = 1.0004(N_{\text{Re}})^{-0.527} \quad \text{Ans.}$$

5.2.2 BUCKINGHAM METHOD¹

This method is a modified version of the Rayleigh's method and is based on what is known as Buckingham (Greek letter 'pi') Π -theorem. This theorem

¹ E. Buckingham, *Phys. Rev.*, **4**: 345; *Nature*, **96**: 396 (1915).

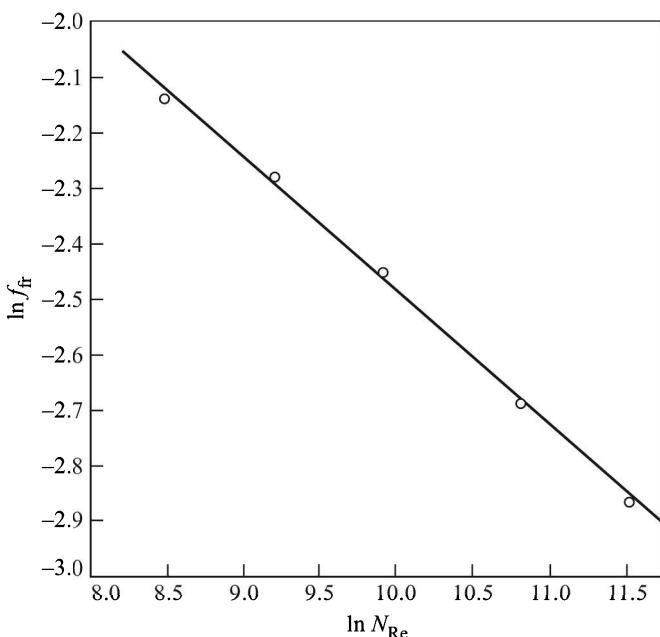


Fig. 5.1 Relationship between friction factor and Reynolds number for flow through a pipe.

states that if there are n physical quantities involved in a process and of which if a maximum number m called the primary variables, cannot form together a dimensionless group by any possible combination, then the number of dimensionless groups r which can completely describe the process is given by the equation

$$r = n - m \quad (5.53a)$$

These r groups are generally designated by the symbols $\Pi_1, \Pi_2, \dots, \Pi_r$. Thus according to the Buckingham P-theorem there exists a functional relationship of the type

$$F(\Pi_1, \Pi_2, \dots, \Pi_r) = 0 \quad (5.53b)$$

Now the question arises: 'how to arrive at the r dimensionless groups?' The procedure followed for this is quite simple. Each one of the $(n - m)$ physical quantities is combined with one or more of the m basic variables in such a way that the result is a dimensionless group. For doing this, the dimensions of different variables involved are made use of as illustrated by the following example.

EXAMPLE 5.2 The mass transfer coefficient k_m of a component is known to depend upon density ρ , viscosity μ and velocity v of the fluid, the diffusion coefficient D of the component under study in the fluid and a characteristic

distance d . Using the Buckingham method, derive the functional relationship among these parameters.

Solution The total number of physical quantities or parameters is

$$n = 6, \text{ namely } k_m, v, \rho, \mu, D \text{ and } d$$

Number of primary variables, $m = 3$, say, μ, D and d , as these three parameters cannot be grouped to form a dimensionless group.

Therefore $r = n - m = 6 - 3 = 3$, i.e. there will be three dimensionless groups for the system. These groups can be determined by combining in turn the remaining three parameters with primary ones. We first consider k_m . Its dimension is given by Lt^{-1} . We can obtain this dimension from n combinations of D and d . Therefore, in terms of dimensions, we have

$$k_m = Lt^{-1} = \frac{L^2 t^{-1}}{L} = \frac{D}{d} \quad (\text{Ex. 5.2.1})$$

or $k_m \times d/D$ is a dimensionless number or group, called the Sherwood number represented by N_{Sh} .

Similarly, a combination of ρ, μ and D , with dimensions $ML^{-3}, ML^{-1}t^{-1}$ and L^2t^{-1} respectively, yields

$$\rho = ML^{-3} = \frac{ML^{-1}t^{-1}}{L^2t^{-1}} = \frac{\mu}{D} \quad (\text{Ex. 5.2.2})$$

or $D\rho/\mu$ is also a dimensionless group called the Schmidt number and is represented by N_{Sc} . Also, dimensions of v, D and L are Lt^{-1}, L^2t^{-1} and L respectively, and thus we can write

$$v = Lt^{-1} = \frac{L^2 t^{-1}}{L} = \frac{D}{L} \quad (\text{Ex. 5.2.3})$$

or vL/D is another dimensionless group.

Therefore, the above three dimensionless groups can be considered to follow the functional relationship

$$\left(\frac{k_m d}{D} \right) = \psi \left\{ \left(\frac{D\rho}{\mu} \right) \left(\frac{vL}{D} \right) \right\} \quad (\text{Ex. 5.2.4})$$

A comparison of Buckingham's and Rayleigh's methods leads us to the conclusion that the Buckingham's method has the advantage as it enables us to formulate the fundamental relationships in terms of certain commonly occurring dimensionless numbers, thereby facilitating comparison of the same phenomenon in two different systems. For example, for mass transfer across a sphere and through a packed bed, the following dimensionless relationships are found to exist:

For mass transfer to spheres, the following equation is found to be applicable (ref. Eq. 4.357):

$$N_{Sh} = 2 + 0.552(N_{Re,p})^{0.50}(N_{Sc})^{0.33} \quad (5.54a)$$

Ranz and Marshall¹ tested the use of this equation on their studies of evaporation of water and benzene drops in air. This equation can also be used for the rate of mass transfer between fluids and packed beds for particle Reynolds numbers below 80.

Rowe and Claxton's² correlation, applicable to heat transfer between a gas stream and packed bed of solid can also be used for mass transfer in the form of the following equation:

$$\frac{k_m d_p}{D} = \frac{2}{1 - (1 - \varepsilon)^{1/3}} + \frac{2}{3\varepsilon} \left(\frac{d_p \mu_0 \rho_g}{\mu} \right)^n \left(\frac{\mu}{\rho_g D} \right)^{1/3}$$

i.e.

$$N_{Sh} = \left\{ \frac{2}{1 - (1 - \varepsilon)^{1/3}} \right\} + \frac{2}{3\varepsilon} N_{Re,p}^n (N_{Sc})^{1/3} \quad (5.54b)$$

where the exponent n is defined by

$$\frac{2-n}{2n-1} = 4.65 \left(\frac{d_p \mu_0 \rho_g}{\mu} \right)^{-0.28} = 4.65 N_{Re}^{-0.28} \quad (5.54c)$$

where k_d is the mass transfer coefficient, D the diffusion coefficient and other symbols have their usual meanings as in the analysis of mass transfer through packed beds described in Chapter 4.

For mass transfer in fluidized beds, the following correlation has been used by Richardson and Szekely³ for shallow beds operated at velocities near the minimum fluidization velocity, i.e. in the absence of bubbling

$$N_{Sh} = 0.374 (N_{Re,p})^{1/2} (N_{Sc})^{1/3} \quad \text{for } 0.1 < N_{Re,p} < 15 \quad (5.54d)$$

and

$$N_{Sh} = 2.01 (N_{Re,p})^{1/2} (N_{Sc})^{1/3} \quad \text{for } 15 < N_{Re,p} < 250 \quad (5.54e)$$

where N_{Sh} , $N_{Re,p}$ and N_{Sc} are respectively the Sherwood number, particle Reynolds' number and Schmidt number.

Had we expressed the above two relations in some different dimensionless numbers, such a comparison could not have been evident.

Limitations of both Rayleigh's and Buckingham's methods, however, lie in the fact that in the functional relationship, all the independent parameters must occur, otherwise one may miss some important dimensionless groups affecting the process or system under study.

In dimensional analysis, we deal with a number of dimensionless groups. Some of these groups are used very frequently in the study of transport phenomena and are named after the scientists who introduced them. The commonly used dimensionless groups, also called the *dimensionless numbers*, are presented in Table 5.1 along with their formulae and applications.

¹ W.E. Ranz and W.R. Marshall, *Chem. Engg. Progr.* **48**: 141, 173 (1952).

² P.N. Rowe and K.T. Claxton, *Trans. Inst. Chem. Engrs.*, **43**: 107-321 (1965).

³ J.F. Richardson and J. Szekely. *Trans. Inst. Chon. Engrs.*, **39**: 312 (1961).

TABLE 5.1 Important dimensionless groups (written alphabetically)

Group	Quantities represented	Formula	Nomenclature	Applications
Arrhenius group	$\frac{\text{activation energy}}{\text{potential energy of fluid}}$	E/RT	E —activation energy R —universal gas constant T —absolute temperature	Reaction kinetics
Biot number, N_{Bi}	$\frac{\text{internal thermal resistance}}{\text{surface film resistance}}$	$N_{Bi} = \frac{h r_m}{k}$	h —heat transfer coefficient K —thermal conductivity r_m —distance from mid-point to surface	Unsteady state heat conduction
Drag coefficient, C_d (or frictional factor, ffr)	$\frac{\text{gravitational force}}{\text{inertial force}}$	$C_d = \frac{g(\rho - \rho_f)L}{\rho u^2}$	L —characteristic length dimension of the object ρ —density of the object u —relative velocity ρ_f —density of fluid g —acceleration due to gravity	Free settling
Fourier number, N_{Fo}	$\frac{\text{time elapsed}}{\text{time required to heat solid to steady state condition}}$	$N_{Fo} = \frac{kt}{\rho C_p r_m^2}$	k —thermal conductivity t —time of heating C_p —sp. heat of material ρ —density of material	Unsteady state heat conduction
Froude number, N_{Fr}	$\frac{\text{inertial force}}{\text{gravitational force}}$	$N_{Fr} = \frac{v^2}{gL}$	L —characteristic length dimension of the system v —relative velocity g —gravitational acceleration	Wave and surface behaviour

(Contd.)

TABLE 5.1 Important dimensionless groups (written alphabetically) (Contd.)

Group	Quantities represented	Formula	Nomenclature	Applications
Froude number modified, N_{Fr}	inertial force gravitational force	$N_{Fr} = \frac{\rho_g u^2}{(\rho_l - \rho_g)gL}$	ρ_g —gas density ρ_l —liquid density L —characteristic length dimension of the system u —relative velocity g —gravitation acceleration	Fluid behaviour of gas-liquid system
Galileo number, N_{Ga}	inertial force \times gravitational force (viscous force) ²	$N_{Ga} = \frac{g\rho^2 L^3}{\mu^2}$ [= $(N_{Re})^2/N_{Fr}$]	g —viscosity, and other symbols as above	Flow in baths of viscous liquids
Grashof number, N_{Gr} (= $N_{Ga}\beta\Delta T$)	$N_{Re} \left(\frac{\text{buoyancy force}}{\text{viscous force}} \right)$	$N_{Gr} = \frac{g\rho^2 L^3 \beta \Delta T}{\mu^2}$	L —characteristic length dimension ρ —density of fluid β —coefficient of thermal volume expansion	Free convection
Mach number, N_{Ma}	—	$N'_{Gr} = \frac{g\rho^2 L^3 \beta \Delta x}{\mu^2}$	ΔT —temperature difference.	Free convection in mass transfer
		$N_{Ma} = \frac{u}{u_s}$	$= -\frac{1}{\rho} \left(\frac{\partial \rho}{\partial x} \right)_T$	Compressible flow

(Contd.)

TABLE 5.1 Important dimensionless groups (written alphabetically) (Contd.)

Group	Quantities represented	Formula	Nomenclature	Applications
Nusselt number, N_{Nu}	$\frac{\text{total heat transfer}}{\text{conductive heat transfer}}$ [$N_{Nu} = \text{const. } (N_{Re})^f (N_{Pr})^e$] — const, f and e are characteristic for the system under study and found experimentally]	$N_{Nu} = \frac{hL}{k}$	u_s —velocity of sound in fluid h —heat transfer coefficient L —characteristic length dimension k —thermal conductivity of fluid	Forced convection
Peclet number, N_{Pe}	$\frac{\text{heat transfer by bulk motion}}{\text{conductive heat transfer}}$	$N_{Pe} = \frac{Lu\rho C_p}{k}$ $= \frac{Lu}{\alpha}$	L —characteristic length m —fluid velocity	Forced convection
Peclet number, for mass transfer N'_{Pe}	$\frac{\text{bulk mass transfer}}{\text{mass transfer by diffusion}}$	$N'_{Pe} = \frac{Lu}{D'_v}$	C_p —sp. heat k —thermal conductivity α —thermal diffusivity L —characteristic length D'_v —characteristic diffusion coefficient	Mass transfer in reactors
Prandtl number, N_{Pr}	$\frac{\text{momentum diffusivity}}{\text{thermal diffusivity}}$	$N_{Pr} = \frac{C_p \mu}{k}$	C_p —sp. heat of fluid μ —viscosity k —thermal conductivity	Forced and free convection (Contd.)

TABLE 5.1 Important dimensionless groups (written alphabetically) (Contd.)

Group	Quantities represented	Formula	Nomenclature	Applications
Rayleigh number, N'_R	$\frac{\text{heat transfer by convection}}{\text{heat transfer by conduction}}$	$N'_R = \frac{g_c \rho^2 L^3 C_p \beta \Delta T}{k}$	g_c —conversion constant from lb-force to pounds β —coefficient of thermal volume expansion ΔT —temperature difference across the film L —characteristic length dimension ρ , C_p and k —density, sp. heat and thermal conductivity of fluid, respectively	Free convection
Reynolds number, N_{Re}	$\frac{\text{interstitial force}}{\text{viscous force}}$	$N_{Re} = \frac{L \rho \mu}{\mu}$	L —characteristic length μ —viscosity ρ —density	Fluid flow
Schmidt number, N_{Sc}	$\frac{\text{momentum diffusivity}}{\text{molecular diffusivity}}$	$N_{Sc} = \frac{\mu}{\rho D_{A-B}}$	μ —fluid viscosity ρ —density D —molecular diffusivity	Mass transfer by forced and free convection
Sherwood number, N_{Sh}	—	$N_{Sh} = \frac{k_d L}{D_{A-B}}$	k_d —mass transfer coefficient L —characteristic dimension D_{A-B} —molecular diffusivity	Mass transfer by forced and free convection

(Contd.)

TABLE 5.1 Important dimensionless groups (written alphabetically) (*Contd.*)

<i>Group</i>	<i>Quantities represented</i>	<i>Formula</i>	<i>Nomenclature</i>	<i>Applications</i>
Stanton number, N_{st}	$\frac{\text{total heat transfer}}{\text{thermal capacity of fluid}}$	$N_{st} = \frac{h}{\rho C_p u}$	h —heat transfer coefficient u —velocity ρ and C_p —density and sp. heat of fluid respectively	Heat transfer by forced convection
Weber number, N_{we}	$\frac{\text{inertial force}}{\text{surface temperature force}}$	$N_{we} = \frac{\rho L u^2}{\varepsilon_c \sigma}$	σ —surface tension, other symbols as above	Bubble formation, atomization of liquid jets

Abstracted from J. Szekely and N.J. Themelis, Rate Phenomena in Process Metallurgy, Wiley-Interscience, New York, pp. 590–595 (1971).

5.2.3 Use of Differential Equations

Though it may not be possible to integrate the differential equations describing the behaviour of a system, we can use them to arrive at the way in which the different variables must be grouped to form dimensionless groups in order to represent a functional form of the solution of the problem. As an example, we consider the equation of motion for the flow of a fluid in the x -direction and from it derive the various dimensionless groups. This equation can be rewritten from Eq. (2.71) in the following algebraic form for an incompressible fluid:

$$\frac{dv_z}{dt} + v_x \frac{dv_z}{dx} + v_y \frac{\partial v_z}{\partial y} + v_z = - \frac{1}{\rho} \frac{\partial P}{\partial x} + g_x + \frac{\mu}{\rho} \left(\frac{\partial^2 v_x}{\partial x^2} + \frac{\partial^2 v_x}{\partial y^2} + \frac{\partial^2 v_x}{\partial z^2} \right) \quad (5.55)$$

It will be noted that this equation is dimensionally homogeneous with each term having the dimensions [Lt^{-2}]. Since we are interested only in formulation of the dimensionless groups, we can write each term of this equation in terms of its units, e.g. $\partial v_x / \partial t$ has the unit v/t and so on. Thus we can write from Eq. (5.55) the relation

$$\frac{v}{t} + \frac{v^2}{L} = - \frac{P}{\rho L} + g_x + \frac{\mu v}{\rho L^2} \quad (5.56)$$

This equation is only a functional relationship for the formulation of dimensionless groups. These groups can be obtained by taking any two of the five terms in this equation and dividing one by the other. Thus, we can arrive at the following ten dimensionless groups.

- (i) $\frac{\text{inertial force } (= v^2/L)}{\text{gravitational force } (= g)} = \frac{v^2}{gL}$
- (ii) $\frac{\text{inertial force } (= v^2/L)}{\text{viscous force } (= \mu v / \rho L^2)} = \frac{v L \rho}{\mu}$
- (iii) $\frac{\text{inertial force } (= v^2/L)}{\text{pressure force } (= P / \rho L)} = \frac{v^2 \rho}{P}$
- (iv) $\frac{\text{inertial force } (= v^2/L)}{\text{momentum force } (= v/t)} = \frac{vt}{L}$
- (v) $\frac{\text{momentum force } (= v/t)}{\text{pressure force } (= P / \rho L)} = \frac{v \rho L}{t P}$
- (vi) $\frac{\text{momentum force } (= v/t)}{\text{gravitational force } (= g)} = \frac{v}{tg}$
- (vii) $\frac{\text{momentum force } (= v/t)}{\text{viscous force } (= \mu v / \rho L^2)} = \frac{\rho L^2}{\mu t}$
- (viii) $\frac{\text{pressure force } (= P / \rho L)}{\text{gravitational force } (= g)} = \frac{P}{\rho L g}$

$$(ix) \frac{\text{pressure force} (= P/\rho L)}{\text{viscous force} (= \mu v/\rho L^2)} = \frac{PL}{\mu v}$$

$$(x) \frac{\text{gravitational force} (= g)}{\text{viscous force} (= \mu v/\rho L^2)} = \frac{g\rho L^2}{\mu v}$$

As per the Buckingham's Π -theorem, there are seven variables (v, t, L, P, μ, g and ρ) of the system under study and there are three primary variables (say, v, L and ρ), hence we have only four of the above four ($r = n - m = 7 - 3 = 4$) dimensionless groups by which the functional relation for the solution of the above equation can be expressed. The application of this method is illustrated by the following example.

EXAMPLE 5.3 Express the solution of the equation of flow of a fluid in the x -direction in terms of dimensionless groups using the differential equation of flow.

Solution In the previous section, it has already been shown that the solution of the equation of flow of a fluid can be expressed in terms of four dimensionless groups, out of the ten groups indicated.

Of the seven variables (v, t, L, P, μ, g and ρ), we may identify three (t, P and g) which cannot be combined in any way to form any dimensionless group. Thus we may exclude those dimensionless groups which contain more than one of these three variables. This way we may consider only the following dimensionless groups, i.e. v^2/gL , $vL\rho/\mu$, vt/L and $\rho L^2/\mu t$ and write the relation

$$\frac{v^2}{gL} = f \left\{ \left(\frac{vL\rho}{\mu} \right), \left(\frac{vt\rho}{L} \right), \left(\frac{\rho L^2}{\mu t} \right) \right\} \quad (\text{Ex. 5.3.1})$$

as one of the solutions. It may be noted that a few other relations in terms of some other dimensionless groups can also be given as solution.

5.2.4 Analysis Based on Similarity Criteria

Relationships in terms of dimensionless numbers have the advantage of being applicable to systems of various sizes. This offers the advantage of designing similar systems on different scales, i.e., industrial, pilot plant and laboratory scales. For a given system to have similarity on different scales, certain dimensionless numbers should have the same value. These numbers are decided by the similarity criteria. Thus we can also derive relationships in terms of dimensionless numbers from similarity considerations of the systems. This will be discussed now.

The concept of similarity originated from the geometric similarity of forms such as similar circles, triangles, etc. Newton extended this concept to fluid dynamic systems by defining dynamically similar systems as those which have the same length, time and mass ratios. The necessary conditions for one system to be similar to another are expressed by a set of parameters called *similarity*

criteria. On the basis of comparison of different types of systems, we can have the following different types of similarities among such systems:

- (i) Geometric similarity
- (ii) Static similarity
- (iii) Kinematic similarity
- (iv) Dynamic similarity
- (v) Thermal similarity
- (vi) Mass transport similarity
- (vii) Chemical similarity.

Geometric similarity implies that the two systems or reactors under consideration have similar shapes and the parameters expressing their dimensions have the same ratios, e.g. two pipes will be considered geometrically similar if their length to diameter ratios are the same.

Static similarity of two bodies implies that under identical and constant stress conditions, their relative deformation will be in the same proportion to their characteristic geometric dimensions.

Kinematic similarity implies that the ratio of velocities of the fluids at corresponding locations in two geometrically similar systems is the same.

Dynamic similarity requires that the forces acting at corresponding times and on corresponding locations in two similar systems or reactors bear a fixed ratio.

For *thermal similarity*, it is necessary that the temperature gradients in the two similar systems or reactors correspond to each other. Further, it is necessary that the heat transfer rates by the various processes at a certain location of one reactor bear a fixed ratio to the corresponding rates in the other reactor.

Mass transport similarity, in analogy to the thermal similarity, also requires that the concentration gradients in the two similar systems or reactors must correspond to each other. Further, the mass transport rates at a certain location of one system must bear a fixed ratio to the corresponding rates in the other system.

Chemical similarity is concerned with the establishment of the necessary conditions in the different similar systems, so that the rate of chemical reaction at any time and location in one system will be proportional to the rate of the same reaction at the corresponding time and location in the prototype or similar system.

A combination of kinematic, thermal and mass transport similarities may be termed the *overall* or *complete transport* similarity. We can make use of the different similarity criteria to arrive at the dimensionless numbers or variables which can completely describe a system. For this purpose we require a knowledge of the relevant mathematical formulation governing the system. We now consider, as an example, the transient heat conduction in axial directions

in two similar rods, designated by subscripts 1 and 2. These two rods will follow the equations

$$\frac{\partial T_1}{\partial t_1} = \alpha_1 \frac{\partial^2 T_1}{\partial X_1^2} \quad (5.57)$$

$$\frac{\partial T_2}{\partial t_2} = \alpha_2 \frac{\partial^2 T_2}{\partial X_2^2} \quad (5.58)$$

where α_1 and α_2 are thermal diffusivities for these two rods. Further they must also be geometrically similar. Thus if L_1 and L_2 be the lengths of these two rods, we can write the following equation for the corresponding points X_1 and X_2 on the two rods

$$\frac{X_1}{X_2} = \frac{L_1}{L_2} = C_L \quad (5.59)$$

where C_L is a constant.

Further, the thermal similarity requires that these two rods must have corresponding temperatures at corresponding times at these corresponding locations, for which we can write the following equations.

(i) For time correspondence

$$\frac{t_1}{t_2} = C_t \quad (5.60)$$

(ii) For temperature correspondence

$$\frac{T_1}{T_2} = C_T \quad (5.61)$$

(iii) For thermal diffusivity correspondence

$$\frac{\alpha_1}{\alpha_2} = C_\alpha \quad (5.62)$$

where C_t , C_T and C_α are constants representing these similarities.

Substitution of the values of X_1 , t_1 , T_1 and α_1 in Eq. (5.57) from Eqs. (5.59)–(5.62) yields

$$\frac{C_T}{C_t} \frac{\partial T_2}{\partial t_2} = \frac{C_\alpha C_T}{C_L^2} \alpha_2 \frac{\partial^2 T_2}{\partial X_2^2} \quad (5.63)$$

Now according to similarity criteria, on substitution of corresponding values of variables in the equations governing the process under study in one system, we should get the equations governing the similar process in the other system. Comparison of Eq. (5.58) with Eq. (5.63) shows that this is possible only if

$$\frac{C_T}{C_t} = \frac{C_\alpha C_T}{C_L^2}$$

or

$$\frac{C_\alpha C_t}{C_L^2} = 1 \quad (5.64)$$

which on substitution of relevant parameters means that

$$\frac{\alpha_1 t_1}{L_1^2} = \frac{\alpha_2 t_2}{L_2^2} \quad (5.65)$$

i.e. the two systems will be similar if the dimensionless number $\alpha t/L^2$ is the same for both the systems.

Such a treatment on the one hand leads to the determination of dimensionless groups affecting the process under study and on the other, it also shows their significance for the particular system under study.

EXAMPLE 5.4 Determine the dimensionless group which affects the flow of fluid based on the Navier-Stokes equations in the different systems.

Solution If the effects of pressure and gravity are neglected, from Eq. (2.75), we have for the two systems in the x -direction

$$\rho_1 \frac{\partial v_1}{\partial t_1} = \mu_1 \frac{\partial^2 v_1}{\partial X_1^2} \quad (\text{Ex. 5.4.1})$$

and

$$\rho_2 \frac{\partial v_2}{\partial t_2} = \mu_2 \frac{\partial^2 v_2}{\partial X_2^2} \quad (\text{Ex. 5.4.2})$$

where the symbols have their usual meanings. Now, if different constant ratios are introduced for different correspondences, for maintaining similarity, we have

$$\frac{\rho_1}{\rho_2} = C_\rho \quad (\text{Ex. 5.4.3})$$

$$\frac{v_1}{v_2} = C_v \quad (\text{Ex. 5.4.4})$$

$$\frac{t_1}{t_2} = C_t \quad (\text{Ex. 5.4.5})$$

$$\frac{\mu_1}{\mu_2} = C_\mu \quad (\text{Ex. 5.4.6})$$

and

$$\frac{X_1}{X_2} = \frac{L_1}{L_2} = C_L \quad (\text{Ex. 5.4.7})$$

Substituting Eq. (Ex. 5.4.3 to 5.4.7) in Eq. (Ex. 5.4.1), we have

$$\frac{C_\rho C_v}{C_t} \rho_2 \frac{\partial v_1}{\partial t_2} = \frac{C_\mu C_v}{C_L^2} \mu_2 \frac{\partial^2 v_2}{\partial X_2^2} \quad (\text{Ex. 5.4.8})$$

Comparing Eqs. (Ex. 5.4.2) and (Ex. 5.4.8), we have

$$\frac{C_\rho C_v}{C_t} = \frac{C_\mu C_v}{C_L^2}$$

or

$$\frac{C_p C_L^2}{C_t \cdot C_\mu} = 1 \quad (\text{Ex. 5.4.9})$$

Now we may take $C_L/C_t = C_v$.

So Eq. (Ex. 5.4.9) becomes

$$\frac{C_p C_L C_v}{C_\mu} = 1 \quad (\text{Ex. 5.4.10})$$

Substituting the values from Eqs. (Ex. 5.4.3) (Ex. 5.4.6), we have

$$\frac{\rho_1 L_1 v_1}{\mu_1} = \frac{\rho_2 L_2 v_2}{\mu_2} \quad (\text{Ex. 5.4.11})$$

In other words, the two systems will be similar if the dimensionless group $\rho Lv/\mu$ is the same for both the systems. Therefore, $\rho Lv/\mu_s$, which is known as the Reynolds number, is the dimensionless group which affects the similarity in the case of the flow of a fluid as given in the present problem.

5.3 NORMALIZATION

The concept of normalization has already been introduced indirectly at the beginning of this chapter. Normalization is a special form of expressing a quantity of a parameter into a dimensionless form by considering its value at some specified point or taking its value to be unity. For example, consider a rod of length L . Now consider a point on this rod at a distance X from one end of the rod. This point can as well be expressed as being situated at a fractional length X/L of the rod. This fraction (X/L) is the normalized distance from the end under consideration, expressed in such a way that the total length L is taken to be equal to unity. We may also illustrate the advantage of the use of normalized quantities with the help of another example. For laminar axial flow of an incompressible fluid through a pipe, the velocity v_z of the fluid is related to the radius of the pipe by the following equation, obtained by rewriting Eq. (2.93):

$$v_z = \frac{1}{4\mu} \frac{\Delta P}{\Delta z} (R^2 - r^2) \quad (5.66)$$

If we wish to plot the function v_z at different radii r of the pipe, we can fix the values of the parameters μ , $\Delta P/\Delta z$, and R and then make innumerable number of plots by varying one by one the values of these parameters. Such a method is very cumbersome. An excellent simplification of the problem can be achieved by rewriting the above equation in the following alternative form:

$$v_z = \frac{1}{4\mu} \frac{\Delta P R^2}{\Delta z} \left[1 - \left(\frac{r}{R} \right)^2 \right] \quad (5.67)$$

Since the term within the square bracket on the right-hand side of this equation is dimensionless, the term outside this bracket should have the dimensions of

velocity v_z . On transposing this term to the left-hand side of the equation, we can write it in the form

$$\frac{\frac{v_z}{1 \frac{\Delta P}{\Delta z} R^2}}{4\mu} = 1 - \left(\frac{r}{R}\right)^2 \quad (5.68)$$

where the left-hand side term may be called the *reduced, dimensionless* or *normalized* velocity, represented by the symbol \bar{v}_z and expressed by the following equation:

$$\bar{v}_z = 1 - (\bar{r})^2 \quad (5.69)$$

The symbol \bar{r} here is called the *reduced radius* and is equal to the ratio (r/R) .

Notice that v_z is maximum at $r = 0$ and this maximum value $v_{z, \text{max}}$ is expressed as

$$v_{z, \text{max}} = - \frac{1}{4\mu} \frac{\Delta P}{\Delta z} R^2 \quad (5.70)$$

and therefore,

$$\bar{v}_z = \frac{v_z}{v_{z, \text{max}}} \quad (5.71)$$

The reader will note that, whereas the velocity v_z was a function of four parameters, namely μ , $\Delta P/\Delta z$, R and r , the reduced or normalized velocity is only a function of reduced or normalized radius. Thus, in this form a general graphical representation of this problem of fluid flow can be made by only one curve, i.e. plot of the parameter \bar{v}_z vs. \bar{r} .

In respect of the engineering problems, normalization of differential equations along with the initial and boundary conditions is of immense use before proceeding to solve them by either analytical or computational means. This step will lead to a general solution involving only dimensionless numbers instead of absolute parameters that govern the system. To illustrate the procedure of normalizing differential equations, we take the example of an unsteady state diffusion through an infinitely long cylindrical rod of length L , in the axial direction. Such a process takes place under the conditions enunciated by the following differential equation based on Fick's second law of diffusion where the symbols have the meanings mentioned in Chapter 4. That is

$$\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial z^2} \quad (5.72)$$

with the (a) initial condition-inside the rod,

$$C = C_i \text{ at } t = 0 \quad \text{for } 0 << z << L$$

i.e. to start with, the rod has a constant uniform concentration C_i , of the component i , whose diffusion behaviour is to be studied.

(b) Boundary condition,

$$C = C_0 \quad \text{for } t > 0 \text{ at } z = 0$$

i.e. when the supplier of the component is brought in contact with the rod at one end, defined by $z = 0$, there is an instantaneous attainment of the state of equilibrium which raises the concentration of the concerned component to a constant value of C_0 at this end.

Now, with diffusion of this component taking place in the rod with time, the concentration at any instant and position $C(z, t)$ will have some value between C_0 and C_i , i.e. $C_i < C < C_0$. We can, therefore, define a normalized concentration η by the equation

$$\eta \equiv \frac{C - C_i}{C_0 - C_i} \quad (5.73)$$

Further, we can also define the normalized time \bar{t} , and the normalized position \bar{z} along the axis of the rod by the respective equations

$$\bar{t} = \frac{t}{t_0} \quad (5.74)$$

and

$$\bar{z} = \frac{z}{L} \quad (5.75)$$

where t_0 is some reference time. Substitution of t , z and C in terms of these normalized functions in Eq. (5.72) leads to the equation

$$\frac{\partial \eta}{\partial \bar{t}} = \frac{Dt_0}{L^2} \frac{\partial^2 \eta}{\partial \bar{z}^2} \quad (5.76)$$

By substitution of relevant dimensions of terms D , t_0 and L , we may verify that function (Dt_0/L^2) is a dimensionless number. We can also select the reference time t_0 in such a way that

$$\frac{Dt_0}{L^2} = 1$$

or

$$t_0 = \frac{L^2}{D} \quad (5.77)$$

so that the normalized differential equation takes the following simplified form

$$\frac{\partial \eta}{\partial \bar{t}} = \frac{\partial^2 \eta}{\partial \bar{z}^2} \quad (5.78)$$

and the initial and boundary conditions take the following forms respectively:

$$\eta = 0 \text{ at } \bar{t} = 0 \quad \text{for } 0 < \bar{z} < 1$$

and

$$\eta = 1 \text{ at } \bar{t} > 0 \quad \text{for } \bar{z} = 0$$

The use of these equations will be explained by some examples below.

EXAMPLE 5.5 A fluid of viscosity 3.05 Pa s is flowing in a pipe of inside diameter 75 mm where the pressure drop over a length of 300 m of pipe is 1.41×10^5 Pa. Show the relationship between the local velocity and the radius of the pipe in terms of normalized parameters.

Solution The relationship between the normalized velocity (\bar{v}) and the normalized radius (\bar{r}) is given by Eq. (5.69) as

$$\bar{v}_z = 1 - (\bar{r})^2$$

Thus by considering different values of \bar{r} , the values of \bar{v}_z can be calculated from the above equation without taking into account the values of viscosity and pressure gradient. The following table gives the different values of \bar{v}_z for various values of r and \bar{r} .

r (cm)	\bar{r}	\bar{v}_z
0	0	1.00
7.5	0.2	0.96
15.0	0.4	0.84
22.5	0.6	0.64
30.5	0.8	0.36
37.5	1.0	0.00

This shows that \bar{v}_z changes from a maximum value of 1.00 to a minimum value of 0.00 parabolically as \bar{r} increases from 0 to 1.0. Such a parabolic relationship is characteristic of laminar fluid flow in pipes.

EXAMPLE 5.6 For unsteady state diffusion through an infinitely long cylindrical rod, establish a relationship among the normalized concentration of a species i , the normalized time and the normalized position.

Solution The solution is based on integration of the differential equation given in Eq. (5.78), where we have

$$\frac{\partial \eta}{\partial \bar{t}} = \frac{\partial^2 \eta}{\partial \bar{z}^2} \quad (\text{Ex. 5.6.1})$$

with the symbols representing the parameters mentioned in the text. The integration can be done by trial and error. First, assuming $\eta = f(\bar{z}/\sqrt{\bar{t}})$ and $y = \bar{z}/\sqrt{\bar{t}}$ and $\frac{d\eta}{dy} = p$, it is seen that

$$\left(\frac{\partial \eta}{\partial \bar{t}} \right)_{\bar{z}} = \frac{-y}{2\bar{t}} \left(\frac{\partial \eta}{\partial y} \right)_{\bar{z}} \quad \text{and} \quad \left(\frac{\partial^2 \eta}{\partial \bar{z}^2} \right)_{\bar{t}} = \frac{1}{\bar{t}} \left(\frac{\partial^2 \eta}{\partial y^2} \right)_{\bar{t}}$$

This gives

$$\frac{-py}{2} = \frac{dp}{dy} \quad (\text{Ex. 5.6.2})$$

Thus the trial solution is correct, since \bar{z} and \bar{r} have disappeared. On integration, this equation gives

$$\frac{-y^2}{4} = \log_e p + I \quad (\text{Ex. 5.6.3})$$

and setting

$$I = \log_e A$$

we get

$$P = \frac{d\eta}{dy} = Ae^{-y^2/4} \quad (\text{Ex. 5.6.4})$$

or

$$d\eta = Ae^{-y^2/4} dy \quad (\text{Ex. 5.6.5})$$

or

$$\eta = A \int e^{-y^2/4} dy \quad (\text{Ex. 5.6.6})$$

$$\text{where } y = \frac{\bar{z}}{\sqrt{t}}.$$

This equation is not analytically integrable but can be graphically solved by taking the right-hand side of Eq. (Ex. 5.6.6) as the normalized probability integral ϕ .

The parameter η is then plotted as a function of (\bar{z}/\sqrt{t}) by taking the values of f from standard tables to yield the *dimensionless concentration profile* also known as the *penetration curve* as shown in the Fig. 5.2. This curve has the same form at all times irrespective of the individual position as it involves only dimensionless or normalized parameters.

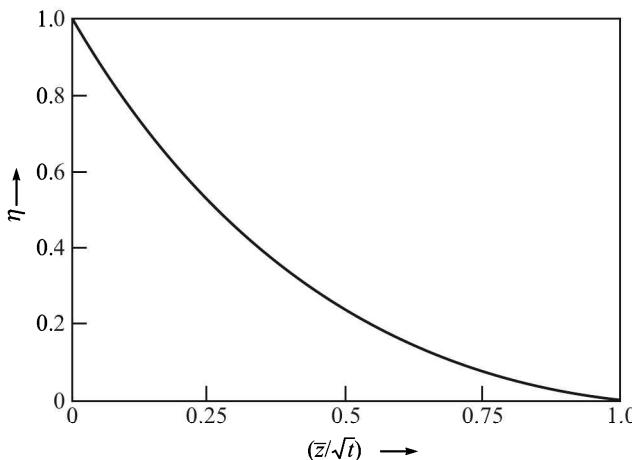


Fig. 5.2 Penetration curve for unsteady state diffusion through an infinitely long cylindrical rod.

Normalization of differential equations is of great help in experimental simulation of industrial process systems to a lower scale such as laboratory scale or pilot plant scale from commercial scale operating data, and is also helpful in representation of experimental data in a very compact manner.

REVIEW QUESTIONS

1. Discuss the importance of dimensionless numbers.
2. Describe with the help of suitable examples, Rayleigh's method of dimensional analysis.
3. Enunciate the Buckingham Π -theorem and discuss its application to dimensional analysis with the help of suitable examples.
4. Describe how the dimensional analysis of heat transfer coefficient, mass transfer coefficient and friction factor is done making use of the Buckingham method.
5. Describe how differential equations can be used for dimensional analysis.
6. Discuss the various types of similarities that can exist among systems.
7. With the help of an example describe how transport similarity between two systems leads to dimensionless numbers.
8. What do you understand by the term 'normalization'? Explain your answer with the help of suitable examples.
9. State, with the help of an example, how differential equations are normalized.
10. Explain the significance of the following dimensionless numbers: Reynolds number, Nusselt number, Weber number, Sherwood number, Schmidt number, Prandtl number and Grashof number.

PROBLEMS

1. A dynamic variable x having the dimensions sec^{-1} is considered to be a function of ρ, v, d, μ, C_p, k . By the application of Rayleigh's method, arrive at the functional relationship among various dimensionless groups involved in this system.
2. Apply Rayleigh's method to Eq. (5.30) by taking a and d as independent indices. Also, calculate the value of the conversion factor for the relationship thus obtained, in order to arrive at Eq. (5.35).
3. Apply Buckingham method to the dimensional analysis of mass and heat transfer coefficients.
4. Prove that, in case of natural convection, the Sherwood number is a function of Grashof and Schmidt numbers.

5. Calculate the pressure difference across a smooth horizontal pipe of diameter 15 cm and length 12 m for a steady state flow rate of 30,000 litres per hour of a fluid of density 1.2 g cm^{-3} and viscosity 1.5 centipoise. The friction factor for the pipe is related to Reynolds number by the equation

$$f_f = 0.079 (N_{Re})^{-1/4}$$

6. Calculate the terminal velocity of an iron sphere of diameter 2 mm and density 7.8 g cm^{-3} settling through a water column of density 1.0 g cm^{-3} and viscosity 1.0 centipoise. Assume the drag coefficient for the sphere to be 0.44.
7. The following equation is known to hold good for unsteady state laminar flow in a circular tube

$$\frac{\partial v_z}{\partial t} = \frac{\Delta P}{\rho L} + \frac{\mu}{\rho r} \frac{\partial}{\partial r} \left(r \frac{\partial v_z}{\partial r} \right)$$

- (i) Making use of dimensions of various terms in the above equation, derive various dimensionless numbers affecting the flow.
- (ii) With the help of similarity criteria, arrive at the dimensionless groups affecting the flow.
8. Deduce the conditions for similarity between two systems following the equation.

$$\rho C_p v_z \frac{\partial T}{\partial z} = k \left[\frac{1}{r} \frac{\partial}{\partial r} \left(r \frac{\partial T}{\partial r} \right) + \frac{\partial^2 T}{\partial z^2} \right]$$

9. Establish the conditions for mass transport similarity between two systems in which unsteady state uni-directional diffusion is taking place.
10. Normalize the one-dimensional unsteady state diffusion equation in rectangular coordinates.

Boundary Layer Theory

Complex forms of differential equations arrived at in the analysis of momentum-energy- and mass-balances have made it very difficult to obtain the exact solutions of these equations for different practical problems. The early theoretical approaches were, therefore, mainly based on the solution of momentum-balance equations which neglected the effect of various other forces, thereby implicitly assuming the fluid under consideration to be ideal. However, theoretical results thus obtained were found to have wide variations from the experimental data. Through analysis of fluid flow around spheres, Prandtl showed that a much more accurate theoretical treatment could be provided by considering the fluid to consist of two regions. The first region, resulting from the formation of a thin layer immediately around the sphere, is called the *boundary layer*, in which the viscous or drag forces play a predominant role. The second region is located away from the sphere and in this region the effect of viscous forces can be neglected. This concept was later extended to objects of other shapes for theoretical analysis of flow of fluids either through, around or on them. The theoretical analytical treatment of this layer of fluid in the neighbourhood of solid surfaces is generally referred to as *boundary layer theory*.

Though boundary layer theory finds extensive applications in the field of aerodynamics, it has recently been applied to analysis of some problems related to the flow of fluids in metallurgical systems and found to be extremely satisfactory. This will be illustrated in the course of analytical treatment in the present chapter. We will consider application of this theory to all the three modes of transport phenomena, namely the momentum-, heat- and mass-transports. The boundary layer for these cases is referred to as the velocity- or mechanical-boundary layer, the thermal-boundary layer and the concentration- or chemical-boundary layer respectively. A brief account of these three cases with some common applications will be considered in the following sections.

6.1 VELOCITY BOUNDARY LAYER

To elaborate the boundary layer concept, we consider flow of a fluid on a flat plate as shown in Fig. 6.1. At some distance from the leading edge of the flat plate, where the fluid touches the plate for the first time, the flow of fluid in the boundary layer will be laminar, even though the fluid in the main stream may have turbulent motion. As the laminar boundary layer increases in thickness, it becomes unstable and the flow becomes turbulent. Figure 6.1 also represents schematically the change from a laminar boundary layer to a turbulent boundary layer through a transition zone. Thus, for a certain distance along the plate, a laminar zone exists in the flowing fluid, immediately following which will be a short transition zone followed, in turn, by a turbulent zone. A laminar sub-layer exists adjacent to the wall of the turbulent boundary layer.

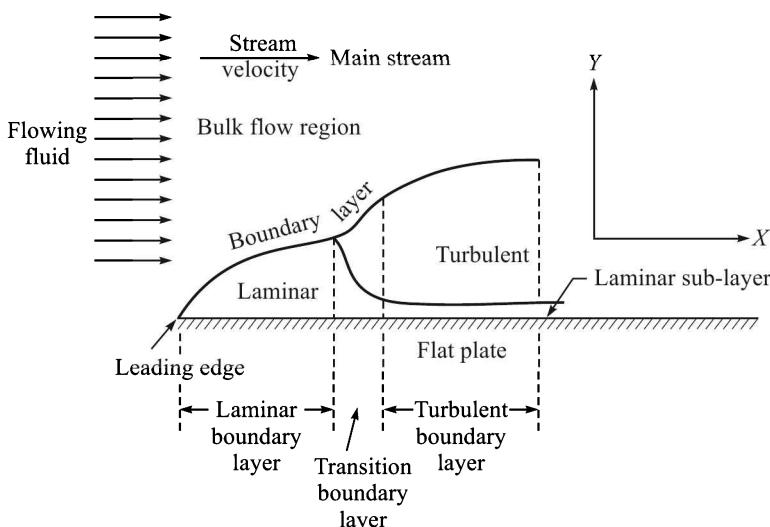


Fig. 6.1 Fluid-flow past a flat plate showing different boundary layers.

For analysis of the flow of fluids in this layer, it is generally assumed that there is no slip between the solid surface, surrounding or submerged in the fluid, and the layer of fluid adjacent to it. In other words, the fluid immediately in the neighbourhood of the solid, moves with the same velocity as the solid surface. This assumption of 'no-slip' is generally valid, the only exception being the fluids that do not wet the solid. As one moves away from the solid surface, the velocity of the flowing fluid increases and at some distance from the solid, it attains the value equivalent to that of the main stream or the stream-velocity. The boundary layer, therefore, extends from the solid surface to a point in the fluid at which the velocity gradient becomes zero, i.e. the point at which the fluid attains the velocity of the main stream. However, the boundary layer thickness is usually taken to be equal to the distance from the solid surface at which the velocity reaches some fraction of the velocity in the undisturbed stream.

The velocity profiles in the boundary layer can be determined by the application of differential mass and momentum balance equations derived in Chapter 2. The solutions thus obtained are the exact solutions, but such analyses are very complicated. Therefore, approximate methods are applied in a number of cases. These methods yield results which are sufficiently accurate for practical applications.

For mathematical analysis, the boundary layer is divided into two regions, namely (i) a laminar region, and (ii) a turbulent region. In the following subsections, we will obtain an exact solution for laminar boundary layer for flow on a flat plate and then show the application of an approximate method to the turbulent boundary layer.

6.1.1 Laminar Boundary Layer for Flow on a Flat Plate

We assume an incompressible Newtonian fluid flowing on a flat plate as shown in Fig. 6.1. Further, let the plane of the plate lie in a horizontal direction. For this case, we can arrive at the following continuity- and momentum-balance relations from Eqs. (2.43), (2.71) and (2.72), assuming that there is no velocity-gradient in the z -direction,

(a) Continuity equation:

$$\frac{\partial v_x}{\partial x} + \frac{\partial v_y}{\partial y} = 0 \quad (6.1)$$

(b) Momentum balance equations:

(i) For flow in the x -direction,

$$\frac{\partial v_x}{\partial t} + v_x \frac{\partial v_x}{\partial x} + v_y \frac{\partial v_x}{\partial y} = -\frac{1}{\rho} \frac{\partial P}{\partial x} + \frac{\mu}{\rho} \left(\frac{\partial^2 v_x}{\partial x^2} + \frac{\partial^2 v_x}{\partial y^2} \right) \quad (6.2)$$

(ii) For flow in the y -direction,

$$\frac{\partial v_y}{\partial t} + v_x \frac{\partial v_y}{\partial x} + v_y \frac{\partial v_y}{\partial y} = -\frac{1}{\rho} \frac{\partial P}{\partial y} + g_y + \frac{\mu}{\rho} \left(\frac{\partial^2 v_y}{\partial x^2} + \frac{\partial^2 v_y}{\partial y^2} \right) \quad (6.3)$$

Assuming steady state conditions to prevail, Prandtl suggested a simplification of the equations, by reducing them to dimensionless forms and then comparing the numerical values of the order of magnitude of various terms. This is done by introducing different dimensionless variables such as

$$v_x^* = \frac{v_x}{v_\infty}, \quad x^* = \frac{x}{L}, \quad \delta^* = \frac{\delta}{L}$$

$$v_y^* = \frac{v_y}{v_\infty}, \quad y^* = \frac{y}{L}, \quad N_{Re, L} = \frac{v_\infty L \rho}{\mu}$$

where L is the length of the plate, δ the thickness of the boundary layer and v_∞ the free stream velocity. With the help of the above variables, we can rewrite, respectively, Eqs. (6.1)–(6.3) as follows:

$$\frac{\partial v_x^*}{\partial x^*} + \frac{\partial v_y^*}{\partial y^*} = 0 \quad (6.4)$$

$$v_x^* \frac{\partial v_x^*}{\partial x^*} + v_y^* \frac{\partial v_x^*}{\partial y^*} = \frac{1}{N_{Re,L}} \left[\frac{\partial^2 v_x^*}{\partial(x^*)^2} + \frac{\partial^2 v_x^*}{\partial(y^*)^2} \right] - \left(\frac{1}{\rho v_\infty^2} \frac{\partial P}{\partial x^*} \right) \quad (6.5)$$

$$v_x^* \frac{\partial v_y^*}{\partial x^*} + v_y^* \frac{\partial v_y^*}{\partial y^*} = \frac{1}{N_{Re,L}} \left[\frac{\partial^2 v_y^*}{\partial(x^*)^2} + \frac{\partial^2 v_y^*}{\partial(y^*)^2} \right] - \left(\frac{1}{\rho v_\infty^2} \frac{\partial P}{\partial y^*} \right) + \left(\frac{g L}{v_\infty^2} \right) \quad (6.6)$$

We now compare the order of magnitude of various functions occurring in the above equations, keeping in mind that we are concerned with a small region of thickness δ above the plate which has a length L such that $\delta \ll L$,

$$\begin{aligned} \Delta x^* &\sim 1; & \Delta y^* &\sim \delta^*; & \Delta v_x^* &\sim 1 \\ \frac{\partial v_x^*}{\partial x^*} &\sim 1; & \frac{\partial v_y^*}{\partial y^*} &\sim 1; & \frac{\partial v_x^*}{\partial y^*} &\sim \frac{1}{\delta^*} \\ \frac{\partial v_y^*}{\partial x^*} &\sim \delta; & \frac{\partial^2 v_x^*}{\partial(x^*)^2} &\sim 1; & \frac{\partial^2 v_x^*}{\partial(y^*)^2} &\sim \frac{1}{(\delta^*)^2} \\ \frac{\partial^2 v_y^*}{\partial(x^*)^2} &= \frac{\partial}{\partial x^*} \left(\frac{\partial v_y^*}{\partial x^*} \right) \sim \delta; & \frac{\partial v_y^*}{\partial(y^*)^2} &\sim \frac{1}{\delta} \end{aligned}$$

where the symbol \sim represents parameters of the same order of magnitude. Substitution of the above values in Eq. (6.5), leads to the following inequality

$$\frac{\partial^2 v_x^*}{\partial(x^*)^2} \ll \frac{\partial^2 v_x^*}{\partial(y^*)^2}$$

we can, therefore, neglect $\partial^2 v_x^*/\partial(x^*)^2$ in Eq. (6.5). Further, it can be inferred that the inertial forces on the left-hand side of this equation will be of the same order of magnitude as the viscous force on the right-hand side if the Reynolds number $N_{Re,L}$ is of the same order of magnitude as $1/(\delta^*)^2$. If it is so, all the terms of Eq. (6.6) are of similar order as that of δ^* , i.e. these are all very small. Further, the continuity equation, i.e. eq. (6.4) remains unaltered. With these inferences, we can describe the velocity profile in boundary layer by Eq. (6.1) and the following simplified form of Eq. (6.2).

$$v_x \frac{\partial v_x}{\partial x} + v_y \frac{\partial v_x}{\partial x} = - \frac{1}{\rho} \left(\frac{\partial P}{\partial x} \right) + \left(\frac{\mu}{\rho} \right) \frac{\partial^2 v_x}{\partial y^2} \quad (6.7)$$

The set of Eqs. (6.1) and (6.7) is known as *Prandtl's boundary layer equations* which are to be solved with the following boundary conditions.

$$(i) \text{ At } y = 0, v_x = 0 \text{ and } v_y = 0 \quad (6.8)$$

$$(ii) \text{ At } y = \infty, v_x = v_\infty \quad (6.9)$$

It may be mentioned that condition (i) follows from the assumption of no slip between the fluid and the plate.

Since the free stream velocity is constant, it follows that $\partial P/\partial x$ is equal to zero. Thus, the two equations for flow in boundary layer assume the following forms:

$$\frac{\partial v_x}{\partial x} + \frac{\partial v_y}{\partial y} = 0 \quad (6.10)$$

and

$$v_x \frac{\partial v_x}{\partial x} + v_y \frac{\partial v_x}{\partial y} = \frac{\mu}{\rho} \frac{\partial^2 v_x}{\partial y^2} \quad (6.11)$$

In order to solve the above set of equations, we introduce a stream function ψ , such that

$$\frac{\partial \psi}{\partial y} \equiv v_x \quad \text{and} \quad \frac{\partial \psi}{\partial x} \equiv -v_y \quad (6.12)$$

It is seen that this stream function automatically satisfies Eq. (6.1) and thus we are required to solve Eq. (6.11), only in terms of stream function. Substitution of Eq. (6.12) in Eq. (6.11) yields

$$\frac{\partial \psi}{\partial y} \frac{\partial^2 \psi}{\partial x \partial y} - \frac{\partial \psi}{\partial x} \frac{\partial^2 \psi}{\partial y^2} = \frac{\mu}{\rho} \frac{\partial^3 \psi}{\partial y^3} \quad (6.13)$$

The above partial differential equation is reduced to an ordinary differential equation with the help of similarity argument as follows. It is reasonable to assume that velocity profiles in boundary layer at various distances from the leading edge are similar to each other. In other words, the velocity curve $v_x(y)$ at any distance from the leading edge can be made identical to that at any other distance by selecting suitable multiplication factors for v_x and y . These scale factors, by simple considerations shall be $1/v_\infty$ and $1/\delta_x$. Hence according to similarity principle, we can write

$$\frac{v_x}{v_\infty} = f\left(\frac{y}{\delta}\right) \quad (6.14)$$

It has been found that the boundary layer thickness for a suddenly accelerated plate is proportional to $(\mu t/\rho)^{1/2}$ where t in the case of a stationary plate can be replaced by x/v_∞ . Thus Eq. (6.14) assumes the form

$$v_x = v_\infty f\left[y\left(\frac{v_\infty \rho}{x \mu}\right)^{1/2}\right] \quad (6.15)$$

Hence we can introduce a new function η such that

$$\eta = y\left(\frac{\rho v_\infty}{\mu x}\right)^{1/2} \quad (6.16)$$

Further as

$$v_x = \frac{\partial \psi}{\partial y}$$

we have

$$\frac{\partial \psi}{\partial y} = v_\infty f(\eta) \quad (6.17)$$

Hence

$$\psi = (v_x v_\infty)^{1/2} f(\eta) \quad (6.18)$$

where $v = (\mu/\rho)$ is the *kinematic viscosity* and $f(\eta)$ is known as the *dimensionless stream function*. Substitution of the above equation for ψ in Eq. (6.13) yields

$$-\frac{v_\infty^2}{2x} \eta f' f'' + \frac{v_\infty^2}{2x} (\eta f' - f) f'' = v \frac{v_\infty^2}{2x} f'''$$

or

$$ff'' + vf''' = 0 \quad (6.19)$$

where the single, double and triple primes denote respectively the first, second and the third order differentials of function f with respect to η . Equation (6.19) is to be solved under the following boundary conditions obtained after necessary transformations of Eqs. (6.8) and (6.9).

$$(i) \text{ At } \eta = 0, \quad f = 0 \text{ and } f' = 0 \quad (6.20)$$

$$(ii) \text{ At } \eta = \infty, \quad f' = 1 \quad (6.21)$$

It should, however, be noted that Eq. (6.19) cannot be solved in a closed form, i.e. an exact analytical solution for the equation is not available but an expression for f can be obtained in the form of a polynomial. Thus we can express the variable f as

$$f = C_0 + C_1 \eta + C_2 \frac{\eta^2}{2!} + C_3 \frac{\eta^3}{3!} + \dots \quad (6.22)$$

where C_0, C_1, C_2, \dots are constants to be evaluated by using the differential equation and the boundary conditions. From Eq. (6.22) we get on differentiation

$$\frac{df}{d\eta} = C_1 + 2C_2 \frac{\eta}{2!} + 3C_3 \frac{\eta^2}{3!} + \dots \quad (6.23)$$

Since both the functions f and f' are zero at $\eta = 0$, the constants C_0 and C_1 must each be equal to zero. Substitution of derivatives of f in Eq. (6.19) and cancellation of coefficients of the terms of like powers of η , lead to the values of constants C_3 and C_4 both becoming zero.

We can therefore write the following expression:

$$f = \frac{C_2 \eta^2}{2!} - \frac{C_2^2 \eta^5}{5!} + \frac{11C_2^3 \eta^8}{8!} - \frac{375C_2^4 \eta^{11}}{11!} + \dots \quad (6.24)$$

The numerical value of the constant C_2 is evaluated by using the boundary layer, expressed by Eq. (6.21). Goldstein¹ obtained a value of 0.332 for the coefficient C_2 .

¹ S. Goldstein, *Modern Development in Fluid Dynamics*. Oxford University Press, London (1938).

Thus the flow pattern in the system is completely known. We can now proceed to determine the laminar boundary layer thickness, denoted by the symbol δ , which is generally defined as the distance from the plate in the perpendicular direction for which,

$$\frac{v_x}{v_\infty} = 0.99 \quad (6.25)$$

For this, the function η has a calculated value of 2.5. Thus,

$$\frac{\delta}{x} \left(\frac{v_\infty \rho}{\mu x} \right)^{1/2} = 2.48 \simeq 2.5 \quad (6.26)$$

which yields the value of δ in terms of the local Reynolds number $N_{Re,x}$ as

$$\frac{\delta}{x} \simeq 5.0 \times (N_{Re,x})^{-1/2} \quad (6.27)$$

where the local Reynolds number $N_{Re,x}$ is expressed as

$$N_{Re,x} = \frac{v_\infty x \rho}{\mu} \quad (6.28)$$

It should, however, be noted that the above equations in respect of flat plates are applicable under the condition

$$N_{Re,x} < 10^5 \quad (6.29)$$

for which the flow is laminar.

Application of these equations will now be illustrated by an example.

EXAMPLE 6.1 A fluid of density 900 kg m^{-3} and viscosity $8.5 \times 10^{-4} \text{ kg m}^{-1} \text{ s}^{-1}$ is flowing at an average velocity of 5 m s^{-1} over a flat plate. Calculate the thickness of the laminar boundary layer at a distance of 50 cm from the leading edge of the plate.

Solution Density of the fluid, $\rho = 900 \text{ kg m}^{-3}$

Viscosity of the fluid, $\mu = 8.5 \times 10^{-4} \text{ kg m}^{-1} \text{ s}^{-1}$

Average velocity of the fluid, $v_x^0 = 5 \text{ m s}^{-1}$

Distance, $x = 50 \text{ cm} = 0.5 \text{ m}$

$$\begin{aligned} \text{The local Reynolds number, } N_{Re,x} &= \frac{v_x x \rho}{\mu} \\ &= \frac{5 \times 0.5 \times 900}{8.5 \times 10^{-4}} = 264.4 \end{aligned}$$

Using Eq. (6.27), the thickness of the laminar boundary layer δ is

$$\begin{aligned} \delta &= \frac{5x}{\sqrt{N_{Re,x}}} \\ &= \frac{5 \times 0.5}{\sqrt{264.4}} = 0.152 \quad \text{Ans.} \end{aligned}$$

Displacement thickness

It is clear from a physical picture of the fluid that it is impossible to indicate precisely the boundary layer thickness because v_x in the boundary layer asymptotically tends to be v_∞ . A physically meaningful term used in connection with the boundary layer theory is the *displacement thickness*. It is defined as the effective thickness or distance from the solid surface which is assumed to have the same velocity as the solid surface and the rest of the fluid has velocity equal to the free stream-velocity. Mathematically it is defined as

$$\delta_v^* = \int_0^\delta \left(1 - \frac{v_x}{v_\infty}\right) dy \quad (6.30)$$

where the symbol δ_v^* represents the velocity displacement thickness. The above integral can be evaluated as follows:

From Eq. (6.16), we have

$$\frac{d\eta}{dy} = \left(\frac{\rho v_\infty}{\mu x}\right)^{1/2} \quad (6.31)$$

and from Eqs. (6.17) and (6.18), we get

$$\begin{aligned} v_x &= \frac{\partial \psi}{\partial y} = \frac{\partial \psi}{\partial f} \frac{\partial f}{\partial \eta} \frac{\partial \eta}{\partial y} \\ &= (v_x v_\infty)^{1/2} f' \left(\frac{\rho v_\infty}{\mu x}\right)^{1/2} = v_\infty f' \end{aligned} \quad (6.32)$$

Substituting for dy and v_x from the above equations in Eq. (6.30), we get

$$\delta_v^* = \int_0^\infty (1 - f') \left(\frac{v_x}{v_\infty}\right)^{1/2} d\eta \quad (6.33)$$

Further since at $y = \delta$, $\eta = \infty$, therefore

$$\delta_v^* = \left(\frac{v_x}{v_\infty}\right)^{1/2} [\eta_\delta - f(\eta_\delta)] \quad (6.34)$$

where η_δ and $f(\eta_\delta)$ represent the values of these functions at $y = \delta$. Data presented in standard tables for the values of η and $f(\eta)$ for flow over a plate show that

$$\eta_\delta = f(\eta_\delta) = 1.7208 \quad (6.35)$$

Hence the displacement thickness is given as

$$\begin{aligned} \delta_v^* &= 1.7208 \left(\frac{v_x}{v_\infty}\right)^{1/2} \simeq 1.721 \left(\frac{v_x}{v_\infty}\right)^{1/2} \\ &= 1.721 \left(\frac{v}{v_\infty x}\right)^{1/2} x = \frac{1.721 x}{\sqrt{N_{Re,x}}} \end{aligned} \quad (6.36)$$

The use of these equations is demonstrated by the following example.

EXAMPLE 6.2 Water is flowing down through an opening at the bottom of a vessel at a velocity of 20 m s^{-1} . If the radius of the stream is 25 cm, calculate the mass rate of air entrained at a distance of 10 cm from the vessel bottom. The kinematic viscosity of water is $10^{-4} \text{ m}^2 \text{ s}^{-1}$ and the density of air is 1.2 kg m^{-3} .

Solution Stream velocity, $v_\infty = 20 \text{ m s}^{-1}$

$$\text{Kinematic viscosity, } v = 10^{-4} \text{ m}^2 \text{ s}^{-1}$$

$$\text{Distance from the vessel bottom, } x = 10 \text{ cm} = 0.1 \text{ m}$$

$$\begin{aligned}\text{The local Reynolds number, } N_{\text{Re},x} &= \frac{v_\infty x}{v} \\ &= \frac{20 \times 0.1}{10^{-4}} = 2 \times 10^4\end{aligned}$$

From Eq. (6.36), the displacement thickness δ_v^* is

$$\delta_v^* = \frac{1.721x}{\sqrt{N_{\text{Re},x}}} = \frac{1.721 \times 0.1}{\sqrt{2 \times 10^4}} = 1.22 \times 10^{-2} \text{ m}$$

The radius of the moving cylindrical stream, $r_c = 25 \text{ cm} = 0.25 \text{ m}$. Thus

$$r_c \gg \delta_v^*$$

The volumetric rate of entrainment by a cylindrical body moving in a stationary fluid is given by

$$\begin{aligned}Q &= v_\infty \pi [(r_c + \delta_v^*)^2 - r_c^2] \\ &= 20\pi[(0.25 + 0.0122)^2 - (0.25)^2] \\ &= 0.3924 \text{ m}^3 \text{ s}^{-1}\end{aligned}$$

But since the density of air, $\rho_a = 1.2 \text{ kg m}^{-3}$, the mass rate of air entrained $= Q \times \rho_a = 0.3924 \times 1.2 = 0.471 \text{ kg s}^{-1}$. **Ans.**

In the boundary layer, there will be a loss in momentum, along with decrease in velocity. This loss is expressed in terms of momentum displacement thickness δ_m^* which can be expressed as follows:

$$\delta_m^* = \int_{y=0}^{\infty} \frac{\rho v_x}{\rho v_\infty} \left(1 - \frac{v_x}{v_\infty}\right) dy \quad (6.37)$$

On substitution from Eqs. (6.31) and (6.32) for dy and v_x , we get

$$\delta_m^* = \left(\frac{vx}{v_\infty}\right)^{1/2} \int_0^\infty f'(1-f') d\eta \quad (6.38)$$

which on further simplification and substitution of values, leads to the equation

$$\delta_m^* = 0.664 \left(\frac{vx}{v_\infty}\right)^{1/2} \quad (6.39)$$

The use of this equation is demonstrated by the following example:

EXAMPLE 6.3 Calculate the momentum displacement thickness for flow described in Example 6.2.

Solution Substitution of the relevant data from Example 6.2 in Eq. (6.39) yields

$$\delta_m^* = 0.664 \left(\frac{10^{-4} \times 0.1}{20} \right)^{1/2}$$

$$= 4.7 \times 10^{-4} \text{ m} \quad \text{Ans.}$$

We have discussed above the exact solution of the equations of motion, for the simplest case of flow over a flat plate. Application of this method to flow of fluids along, around or on objects of other geometries presents considerable mathematical difficulties. It was, therefore, felt necessary to devise approximate methods which would lead to solutions considered accurate enough for application to general practical problems. In the following sub-section, we will illustrate the application of the commonly employed integral method to the turbulent flow over a flat plate.

6.1.2 Integral Method

This method differs from the exact method in the sense that it is based on striking overall mass and momentum balances instead of differential mass and momentum balance equations. These overall balances are struck on the fluid between two planes AB and CD placed perpendicular to the surface of the plate at a distance Δx from each other, as shown in Fig. 6.2. Let h (with $h > \delta$) and b (not shown in the figure), be the heights and breadths respectively of the planes. For striking the balances, we ignore the laminar sub-layer.

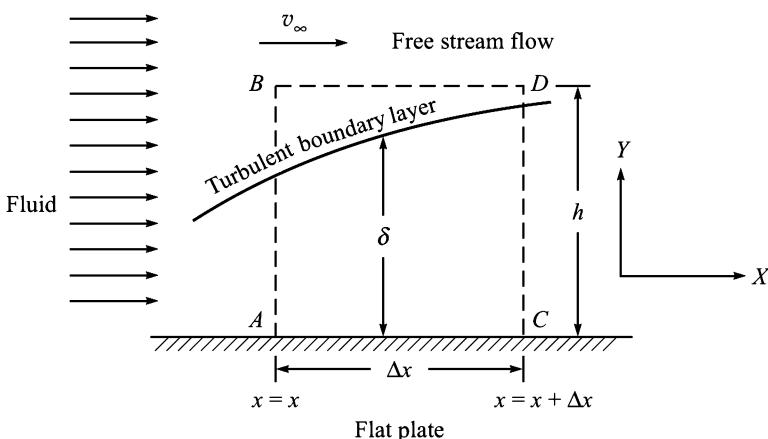


Fig. 6.2 Analysis of turbulent flow over a flat plate by the integral method.

For mass balance, we can write the relation (Mass entering through the plane AB) = (Mass leaving from the plane CD) + (Mass leaving from the surface BD). Thus

$$\rho \left[\int_0^h v_x b dy \right]_{x=x} = \rho \left[\int_0^h v_x b dy \right]_{x=x+\Delta x} + \delta M$$

or

$$\delta M = -\rho b \left[\frac{\partial}{\partial x} \int_0^h v_x dy \right] \Delta x \quad (6.40)$$

where δM is the mass leaving from the surface BD.

Similarly, for momentum balance, we can write

$$\left[\int_0^h (\rho v_x) v_x b dy \right]_{x=x} = \left[\int_0^h (\rho v_x) v_x b dy \right]_{x=x+\Delta x} + \delta_m + F_s$$

or

$$\delta_m = -(\rho b) \frac{\partial}{\partial x} \left[\int_0^h v_x^2 dy \right] \Delta x + F_s \quad (6.41)$$

where F_s is the shear force acting on the fluid flowing over the plate and δ_m is the momentum transferred through this surface. Since the surface BD lies in the free stream of the fluid, we can write for δ_m , the equation (using Eq. 6.40)

$$\delta_m = v_\infty \delta M = -v_\infty \rho b \left[\frac{\partial}{\partial x} \int_0^h v_x dy \right] \Delta x \quad (6.42)$$

Further, the shear force, F_s may be expressed as

$$F_s = +\tau_s b \Delta x \quad (6.43)$$

where τ_s is the shear stress.

Substitution of Eqs. (6.42) and (6.43) in Eq. (6.41) leads to

$$\frac{\partial}{\partial x} \int_0^h \rho (v_\infty - v_x) v_x dy = +\tau_s \quad (6.44)$$

This is the integral form of the momentum balance equation.

Blasius has proposed the following relationships for the shear stress τ_s at the surface of the plate for turbulent flow having Reynolds numbers less than 10^7 .

$$\tau_s = 0.0228 (\rho v_\infty^2) \left(\frac{v}{v_\infty \delta} \right)^{1/4} \quad (6.45)$$

We can assume, as a first approximation, that the velocity at any value of y inside the boundary layer is related to the free stream velocity by the following equation:

$$\frac{v_x}{v_\infty} = \left(\frac{y}{\delta} \right)^f \quad \text{where } f \text{ is a constant} \quad (6.46)$$

Substituting for v_∞ from this equation in Eq. (6.45), we get

$$\tau_s = 0.0228(\rho)^{3/4}(v)^{1/4}(v_x)^{7/4}(\delta)^{(7f/4)-(1/4)}(y)^{-7f/4} \quad (6.47)$$

Since τ_s is basically a function of v_x and y and not δ , therefore, we can write

$$\frac{7f}{4} - \frac{1}{4} = 0$$

or

$$f = \frac{1}{7} \quad (6.48)$$

Hence, from Eq. (6.46), we get

$$\frac{v_x}{v_\infty} = \left(\frac{y}{\delta} \right)^{1/7} \quad (6.49)$$

This equation is generally referred to as *Prandtl's one-seventh power law*. Substitution of Eqs. (6.45) and (6.49) in Eq. (6.44) yields

$$\frac{\partial}{\partial x} \left[\int_0^\delta \rho \left\{ v_\infty - \left(\frac{y}{\delta} \right)^{1/7} v_\infty \right\} v_\infty \left(\frac{y}{\delta} \right)^{1/7} dy \right] = 0.0228(\rho v_\infty)^2 \left(\frac{v}{v_\infty \delta} \right)^{1/4} \quad (6.50)$$

or

$$\frac{\partial}{\partial x} \left(\frac{7}{72} \rho v_\infty^2 \delta \right) = 0.0228 (\rho v_\infty^2)^2 \left(\frac{v}{v_\infty \delta} \right)^{1/4} \quad (6.51)$$

or

$$\frac{7}{72} (\delta)^{1/4} \partial \delta = 0.0228 \left(\frac{v}{v_\infty} \right)^{1/4} \partial x \quad (6.52)$$

Hence

$$\delta = 0.376x \left(\frac{v}{v_\infty} \right)^{0.2} \quad (6.53)$$

In Eq. (6.50), the limit of integration has been changed from h to δ , since $(v_\infty - v_x) = 0$ for $h > y > \delta$. In Eq. (6.53), the constant of integration does not appear since at $x = 0$, $\delta = 0$. Equation (6.53) can be rewritten in the following commonly used form:

$$\frac{\delta}{x} = 0.376(N_{Re, x})^{-0.2} \quad (6.54a)$$

In the case of laminar flow, we can also arrive at the following equation using this method:

$$\frac{v_x}{v_\infty} = \frac{3}{2} \left(\frac{y}{\delta} \right) - \frac{1}{2} \left(\frac{y}{\delta} \right)^3 \quad (6.54b)$$

The displacement thickness can now be calculated as follows:

$$\begin{aligned}\delta_v &= \int_0^{\infty} \left(1 - \frac{v_x}{v_{\infty}}\right) dy \simeq \int_0^{\delta} \left[1 - \left(\frac{y}{\delta}\right)^{1/7}\right] dy \\ &= \frac{\delta}{8} = 0.047x(N_{Re, x})^{-0.2} \\ &= \frac{0.047x}{(N_{Re, x})^{0.2}}\end{aligned}\quad (6.55)$$

Comparison of this equation with Eq. (6.36) shows that the two equations are similar in form but will yield different values of displacement thickness depending on the values of the local Reynolds number $N_{Re, x}$.

6.2 THERMAL BOUNDARY LAYER

When a fluid flows past an immersed body, such as a plate, a cylinder or a sphere, having a temperature different from that of the fluid, there is an exchange of heat between the fluid and the body. This exchange of heat takes place through the hydrodynamic or the velocity boundary layer which forms on the immersed object. Thus, apart from the hydrodynamic or velocity boundary layer, a thermal boundary layer is also formed. In the thermal boundary layer, it is assumed that the temperature of the layer of fluid in contact with the solid is equal to that of the solid. On moving away from the surface, the temperature of the fluid changes and becomes practically equal to the temperature of the undisturbed stream at the edge of the thermal boundary layer. It must, however, be noted that the thickness of the thermal boundary layer may be different from that of the velocity boundary layer as, in general, the velocity gradient will not be equal to the temperature gradient in such systems. Section 2.1 shows a specific application of the concept of thermal boundary layer.

6.2.1 Forced Convective Laminar Flow

The flow of fluid in such systems can be classified into two types, namely *natural* and *forced* flow. In case of natural flow, the fluid moves because of the density differences between various parts of the system resulting from the variation in temperature. Such a flow is termed natural or free convection. An exact analytical solution of the problem of natural convection has been presented in Section 3.2.2. In forced flow, the fluid moves under an external pressure gradient. Such a flow is generally termed forced convection. In this section, we will deal with the treatment of the boundary layer in such systems, taking a simple example of the flow over a flat plate as done in the preceding section.

We now proceed to calculate the thickness of the thermal boundary layer in respect of forced convection for the two dimensional laminar flow of an incompressible fluid over a flat plate. These restrictions, namely (i) the two-

dimensional flow and (ii) flow of incompressible fluid, have been applied only for the sake of simplification of the mathematical treatment which consists of simultaneous solution of continuity, motion and the total energy balance equations. These equations can be written as follows:

- (i) *Continuity equation of a two-dimensional incompressible fluid:*

$$\frac{\partial v_x}{\partial x} + \frac{\partial v_y}{\partial y} = 0 \quad (6.56)$$

- (ii) *Steady state equation of motion for a two-dimensional fluid:*

$$v_x \frac{\partial v_x}{\partial x} + v_y \frac{\partial v_x}{\partial y} = -\frac{1}{\rho} \frac{\partial P}{\partial x} + \frac{\mu}{\rho} \frac{\partial^2 v_x}{\partial y^2} \quad (6.57)$$

which may be stated as

$$v_x \frac{\partial v_x}{\partial x} + v_y \frac{\partial v_x}{\partial y} = \frac{\mu}{\rho} \frac{\partial^2 v_x}{\partial y^2} \quad (6.58)$$

for the boundary layer region because of the reason outlined in Section 6.1.1.

- (iii) *Steady state total energy balance equation for a two-dimensional fluid:*
Neglecting the friction effects, i.e. only for low Mach numbers, we have

$$C_p \rho \left(v_x \frac{\partial T}{\partial x} + v_y \frac{\partial T}{\partial y} \right) = k \left(\frac{\partial^2 T}{\partial x^2} + \frac{\partial^2 T}{\partial y^2} \right) \quad (6.59)$$

The different boundary conditions followed by the above equation are

- (i) $v_x = v_y = 0$ at $y = 0$
- (ii) $v_x = v_\infty$ at $y = \infty$
- (iii) $T = T_s$ at $y = 0$
- (iv) $T = T_\infty$ at $y = \infty$

It may also be mentioned here that the momentum balance equation in the y -direction has not been considered because of the reasons outlined in Section 6.1.1. On the basis of similar arguments, we can write

$$\frac{\partial^2 T}{\partial x^2} \ll \frac{\partial^2 T}{\partial y^2} \quad (6.60)$$

Thus the total energy balance equation, Eq. (6.59), simplifies to

$$v_x \frac{\partial T}{\partial x} + v_y \frac{\partial T}{\partial y} = \alpha \frac{\partial^2 T}{\partial y^2} \quad (6.61)$$

where α is the thermal diffusivity and defined as before by the relation

$$\alpha = \frac{k}{\rho C_p} \quad (6.62)$$

The above equation is very similar to the velocity boundary layer equation. It is seen that if $\alpha \equiv \mu/\rho$, these equations become identical and hence the thermal boundary layer will become equal in thickness to the velocity or the hydrodynamic boundary layer. In other cases, i.e. when these thicknesses are not equal, a treatment similar to that for the velocity boundary layer is followed to obtain a mathematical solution. For this, the equations are transformed by the introduction of new variables. But before doing so, they are changed into a dimensionless form with the introduction of the following dimensionless variables:

$$\theta = \frac{T - T_s}{T_\infty - T_s} \quad (6.63)$$

$$v_x^* = \frac{v_x}{v_\infty} \quad (6.64)$$

and

$$v_y^* = \frac{v_y}{v_\infty} \quad (6.65)$$

where T_s and T_∞ are the temperatures of the solid surface and the free stream fluid respectively. Similarly v_x and v_y are velocities of fluid at the point under study in the x - and y -directions respectively and v_∞ is the velocity of free stream fluid. Thus, Eqs. (6.58) and (6.61) take the forms

$$v_x^* \frac{\partial v_x}{\partial x} + v_y^* \frac{\partial v_y^*}{\partial y} = \frac{\mu}{\rho v_\infty} \frac{\partial^2 v_x^*}{\partial y^2} \quad (6.66)$$

and

$$v_x^* \frac{\partial \theta}{\partial x} + v_y^* \frac{\partial \theta}{\partial y} = \frac{\alpha}{v_\infty} \frac{\partial^2 \theta}{\partial y^2} + \frac{\mu}{\rho C_p} \left(\frac{\partial v_x}{\partial y} \right)^2 \quad (6.67)$$

The last term in the above equation represents the frictional heat produced during the flow. Equations (6.66) and (6.67) are solved under the following transformed boundary conditions:

$$v_x^* = 0 \text{ at } y = 0 \quad (6.68)$$

$$v_x^* = 1 \text{ at } y = \infty \quad (6.69)$$

$$\theta = 0 \text{ at } y = 0 \quad (6.70)$$

and

$$\theta = 1 \text{ at } y = \infty \quad (6.71)$$

As in the case of forced convection, the velocity field is independent of the temperature field. So, the two flow equations, i.e. the continuity- and the motion-equations can be solved first and the results can be employed to solve the total energy balance equation by use of the numerical method. It is seen that Eqs. (6.66) and (6.67) are similar and will yield the same result if

$$\alpha = \frac{\mu}{\rho} \quad \text{or} \quad \frac{\mu}{\alpha \rho} = 1 \quad (6.72)$$

However, by definition

$$\frac{\mu}{\alpha\rho} = \text{Prandtl number } (N_{\text{Pr}})$$

Therefore, for $N_{\text{Pr}} = 1$, both Eqs. (6.66) and (6.67) will yield the same result, i.e. the temperature and velocity boundary layers will have the same thickness and profiles. Mathematically, this statement is expressed by the relation

$$\frac{T - T_s}{T_\infty - T_s} = \frac{v_x}{v_\infty} \quad (6.73)$$

This result is of immense practical importance in the case of flow of gases which have Prandtl numbers approximately equal to unity. Thus with the help of the treatment given in Section 6.1.1, we can calculate the temperature distribution and allied functions such as the heat transfer coefficient. We can write Eq. (6.66) in the following alternative form with the help of functions introduced in Eqs. (6.16) and (6.18). Thus

$$f \frac{\partial^2 f}{\partial \eta^2} + \frac{\partial^3 f}{\partial \eta^3} = 0 \quad (6.74)$$

Similarly, Eq. (6.67) will take the following alternative form:

$$\frac{d^2 T}{d\eta^2} + \left(\frac{N_{\text{Pr}}}{2} \right) f \frac{dT}{d\eta} = -(N_{\text{Pr}}) \frac{v_\infty^2}{2C_p} \left(\frac{df}{d\eta} \right)^2 \quad (6.75)$$

The above equation is a non-homogeneous differential equation. So it is convenient to write its solution in the form

$$T(\eta) - T_\infty = A \left[\lambda_1(\eta) + \frac{v_\infty^2}{2C_p} \lambda_2(\eta) \right] \quad (6.76)$$

where A is a constant and $\lambda_1(\eta)$ and $\lambda_2(\eta)$ denote respectively the general solutions of the homogeneous equation and a particular solution of the non-homogeneous equation. Thus $\lambda_1(\eta)$ and $\lambda_2(\eta)$ should satisfy the equations

$$\frac{d^2 \lambda_1(\eta)}{d\eta^2} + \frac{N_{\text{Pr}}}{2} f \frac{d\lambda_1(\eta)}{d\eta} = 0 \quad (6.77)$$

with the boundary conditions

$$\begin{aligned} \lambda_1(\eta) &= 1 \text{ at } \eta = 0 \\ \lambda_1(\eta) &= 0 \text{ at } \eta = \infty \end{aligned}$$

and also

$$\frac{d^2 \lambda_2(\eta)}{d\eta^2} + \left(\frac{N_{\text{Pr}}}{2} \right) f \left(\frac{d\lambda_2(\eta)}{d\eta} \right) = -2N_{\text{Pr}} \left(\frac{df}{d\eta} \right)^2 \quad (6.78)$$

with the boundary conditions

$$\begin{aligned} \frac{d\lambda_2(\eta)}{d\eta} &= 0 \text{ at } \eta = 0 \\ \lambda_2(\eta) &= 0 \text{ at } \eta = \infty \end{aligned}$$

The constant A can be evaluated from Eq. (6.76) by substitution of the boundary condition $T = T_s$ for $\eta = 0$. Thus

$$A = (T_s - T_\infty) \left/ \left(\frac{v_\infty^2}{2C_p} \right) \lambda_2(0) \right. \quad (6.79)$$

Equations (6.76)–(6.78) are solved numerically for obtaining the temperature profiles. These profiles for cooling of a heated flat plate are shown in Fig. 6.3 for different values of Prandtl numbers.

It is seen from Fig. 6.3, which is plotted for cases in which the generation of frictional heat is negligible, as well as from Eqs. (6.77) and (6.78), that in respect of fluids with large values of Prandtl number, the thermal boundary layer thickness will be much smaller than the velocity boundary layer thickness. This is because of the fact that the ability of fluids to transport momentum is greater than that to transport thermal energy. Such a condition holds good in the case of slags. In the case of metals, however, the value of the Prandtl number is much smaller than unity and thus the thickness of the velocity boundary layer is much smaller than that of the thermal boundary layer. As a result, we may safely neglect any velocity gradient in the velocity boundary layer and assume, as a simplification, that the entire fluid moves at the free stream velocity. Thus in the case of metals for analysis of the thermal boundary layer, we are left with the solution of one differential equation only, leading us to an explicit solution.

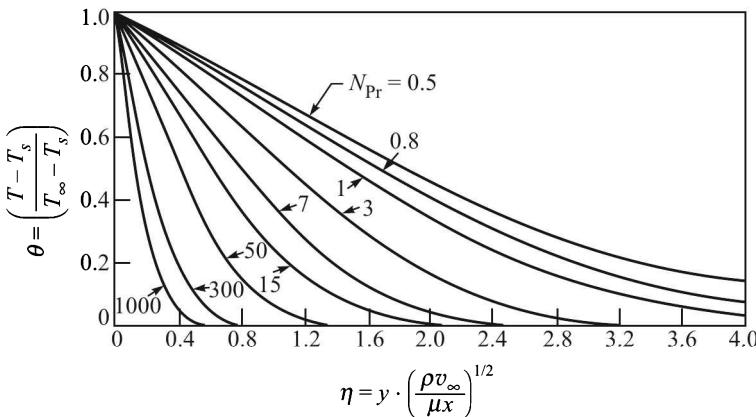


Fig. 6.3 Temperature profiles for cooling of a heated flat plate.

Pohlhausen, while analysing the temperature gradient at the surface of the flat plate under the conditions when it is cooled, obtained the following approximate values:

$$\left. \left(\frac{d\theta}{d\eta} \right) \right|_{\eta=0} = -0.332 (N_{Pr})^{1/3} \text{ for } 0.6 < N_{Pr} < 10 \quad (6.80a)$$

$$= -0.564 (N_{Pr})^{1/2} \text{ for } N_{Pr} \rightarrow 0 \quad (6.80b)$$

$$= -0.339 (N_{Pr})^{1/3} \text{ for } N_{Pr} \rightarrow \infty \quad (6.80c)$$

For the rate of heat transfer from the surface of the plate, we can write

$$q(x) = -k \left(\frac{\partial T}{\partial y} \right)_{y=0} \quad (6.81)$$

With the help of Eq. (6.16), we can express this equation in the following alternative form as well:

$$q(x) = -k \left(\frac{v_\infty}{vx} \right)^{1/2} \left(\frac{\partial T}{\partial \eta} \right)_{\eta=0} \quad (6.82)$$

Neglecting frictional effects and making use of Eqs. (6.80 a, b, c) we can rewrite the above equation in the form

$$h \equiv \frac{q(x)}{T_s - T} = 0.332 k \left(\frac{v_\infty}{vx} \right)^{1/2} (N_{Pr})^{1/3} \text{ for } 0.6 < N_{Pr} < 10 \quad (6.83a)$$

$$= 0.564 k \left(\frac{v_\infty}{vx} \right)^{1/2} (N_{Pr})^{1/2} \text{ for } N_{Pr} \rightarrow 0 \quad (6.83b)$$

$$= 0.339 k \left(\frac{v_\infty}{vx} \right)^{1/2} (N_{Pr})^{1/3} \text{ for } N_{Pr} \rightarrow \infty \quad (6.83c)$$

Rearrangement of the above equations gives the relationships shown earlier in Table 3.2.

Application of these equations is demonstrated below by an example.

EXAMPLE 6.4 A fluid at a temperature of 30°C is allowed to flow at a rate of 10 m s⁻¹ over a heated plate at a surface temperature of 200°C. Calculate the temperature of the fluid at a point where the local velocity is 3 m s⁻¹. Assume Prandtl number of the fluid to be unity.

Solution The given data is:

Surface temperature of the plate, $T_s = 200 + 273 = 473$ K

Bulk temperature of the fluid, $T_\infty = 30 + 273 = 303$ K

Local velocity, $v_x = 3$ m s⁻¹

Average velocity, $v_\infty = 10$ m s⁻¹

Since the Prandtl number of the fluid is unity, we can calculate the desired temperature T using Eq. (6.73). Thus, we have

$$\frac{T - T_s}{T_\infty - T_s} = \frac{v_x}{v_\infty}$$

and which on substitution of values yields

$$\frac{T - 473}{303 - 473} = \frac{3}{10}$$

or

$$T - 473 = \frac{3}{10}(-170) = -51$$

or

$$T = 473 - 51 = 422 \text{ K} = 149^\circ\text{C}$$

Therefore, the temperature of the fluid at the required point is 149°C . Ans.

6.2.2 Integral Method

The above analytical treatment shows that it would be difficult to obtain an exact solution in respect of other geometries of solids. Therefore, a number of approximate approaches have been proposed to analyse thermal boundary layer in such cases. The simplest and the most commonly used approach is the integral method. As an illustration, this approach will now be applied to the flow over a flat plate for a case in which laminar boundary layer is formed.

The application of the integral method to the thermal boundary layer involves striking energy balance in a manner similar to one described in Section 6.1.2. For this purpose, we consider, the laminar portion of the velocity boundary layer as shown in Fig. 6.4. The heat balance equation for the space bound by planes AB and CD and surfaces AC and BD can be written as follows:

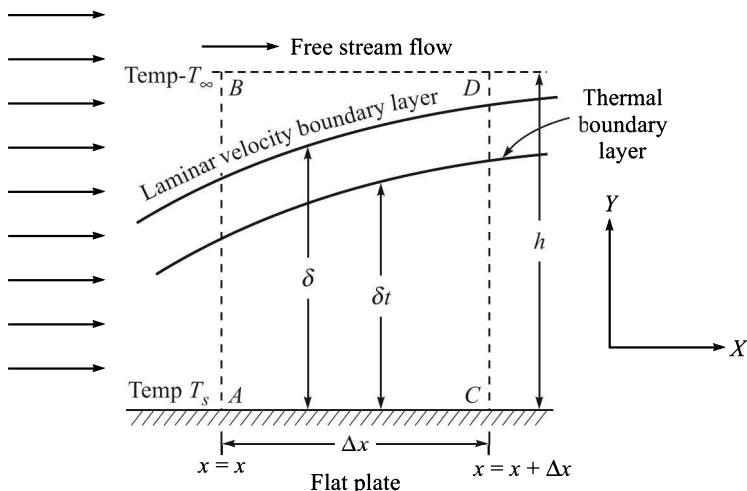


Fig. 6.4 Laminar portion of hydrodynamic boundary layer for analysis of thermal boundary layer by integral method.

Heat entering from the surface AB + heat entering from the surface AC = Heat leaving the surface CD + heat leaving the surface BD.

Mathematically, the above equation can be written as follows with the help of Eq. (6.40):

$$\left[\int_0^h \rho C_p v_x T dy \right]_{x=x} b + k \left(\frac{\partial T}{\partial y} \right)_{y=0} \Delta x b$$

$$= \left[\int_0^h \rho C_p v_x T dy \right]_{x=x+\Delta x} - C_p \rho T_\infty \frac{\partial}{\partial x} \left[\int_0^h v_x dy \right] \Delta x \quad (6.84)$$

where b is the breadth of the plate. The integral in the last term on right-hand side denotes the mass exchanged by the main stream with the volume under consideration. Simplification of Eq. (6.84) yields

$$C_p \rho \frac{\partial}{\partial x} \left[\int_0^h T v_x dy \right] = C_p \rho T_\infty \frac{\partial}{\partial x} \left[\int_0^h v_x dy \right] - k \left(\frac{\partial T}{\partial y} \right)_{y=0} \quad (6.85)$$

and therefore

$$\frac{\partial}{\partial x} \left[\int_0^h v_x (T_\infty - T) dy \right] = \frac{k}{\rho C_p} \left(\frac{\partial T}{\partial y} \right)_{y=0} = \alpha \left(\frac{\partial T}{\partial y} \right)_{y=0} \quad (6.86)$$

where $\alpha = k/\rho C_p$ is the thermal diffusivity of the fluid.

In order to integrate the left-hand side of the above equation, we must know the relationship between T and y . We assume that this relationship is of the polynomial form

$$T = a_0 + a_1 y + a_2 y^2 + a_3 y^3 \quad (6.87)$$

where a_0, a_1, a_2, a_3 are the system-dependent constants and can be determined as follows:

- (i) At $y = 0$, $T = T_s$ which gives $a_0 = T_s$ (6.88)
- (ii) At the surface of the plate, heat is transferred to the fluid by conduction. Therefore, at

$$y = 0, q = -k \left(\frac{\partial T}{\partial y} \right)_{y=0} = \text{constant}$$

Hence

$$\frac{\partial^2 T}{\partial y^2} = 0 \quad (6.89)$$

- (iii) At the edge of the thermal boundary layer, the temperature gradient will be zero and temperature constant, equal to the free stream temperature. Thus, using Eq. (6.87) as well, we can write

$$\left(\frac{\partial T}{\partial y} \right)_{y=\delta_T} = 0 = a_1 + 2a_2 \delta_T + 2a_3 \delta_T^2 \quad (6.90)$$

and

$$T = T_\infty = T_s + a_1 \delta_T + a_2 \delta_T^2 + a_3 \delta_T^3 \quad (6.91)$$

With the help of Eqs. (6.88)–(6.91), we can write Eq. (6.87) in the form

$$T - T_s = (T_\infty - T_s) \left[\frac{3}{2} \left(\frac{y}{\delta_T} \right) - \frac{1}{2} \left(\frac{y}{\delta_T} \right)^3 \right] \quad (6.92)$$

Further, from this equation, we get

$$\left(\frac{\partial T}{\partial y} \right)_{y=0} = \frac{3}{2} \left(\frac{T_\infty - T_s}{\delta_T} \right) \quad (6.93)$$

On substitution of equations for T and $(\partial T / \partial y)_{y=0}$ from Eqs. (6.92) and (6.93), in Eq. (6.86), we, therefore, get the following equation:

$$\begin{aligned} \left(\frac{3\alpha}{2} \right) \left(\frac{T_\infty - T_s}{\delta_T} \right) &= (T_\infty - T_s) v_\infty \frac{\partial}{\partial x} \\ &\quad \left[\int_0^\delta \left\{ 1 - \frac{y}{\delta_T} + 3 \left(\frac{y}{\delta_T} \right)^3 \right\} \times \left\{ \frac{3y}{2\delta} - \frac{1}{2} \left(\frac{y}{\delta} \right)^3 \right\} dy \right] \\ &= \frac{3}{20} (T_\infty - T_s) v_\infty \frac{\partial}{\partial x} \left[\partial \left\{ \left(\frac{\delta_T}{\delta} \right)^2 - \frac{1}{14} \left(\frac{\delta_T}{\delta} \right)^4 \right\} \right] \end{aligned} \quad (6.94)$$

It is to be noted that in the above equation

$$v_x = v_\infty \left\{ \frac{3}{2} \left(\frac{y}{\delta} \right) - \frac{1}{2} \left(\frac{y}{\delta} \right)^3 \right\}$$

This can be proved by the application of the integral method to laminar boundary layer. Further, in the above derivation, it has also been assumed that $\delta_T < \delta$. With this assumption, we can neglect the term containing $(\delta_T/\delta)^4$. Thus, Eq. (6.94) simplifies to

$$\frac{\alpha}{\delta_T} = \frac{1}{10} v_x \frac{\partial}{\partial x} \left[\left(\frac{\delta_T}{\delta} \right)^2 \right] \quad (6.95)$$

from which one can arrive at the equation

$$\frac{10\alpha}{v_\infty} = \delta \sigma^3 \frac{\partial \delta}{\partial x} + 2(\delta \sigma) \frac{\partial \sigma}{\partial x} \quad (6.96)$$

where

$$\sigma \equiv \frac{\delta_T}{\delta}$$

Further, according to Eq. (6.26), we have

$$\delta^2 = 25 \left(\frac{vx}{v_\infty} \right) \quad (6.97)$$

Hence

$$2\delta \frac{d\delta}{dx} = \frac{25v}{v_\infty} \quad (6.98)$$

Substitution of Eq. (6.98) in Eq. (6.96) and simplification of the resulting equation yields

$$\frac{3\alpha}{5v} = \frac{3}{4} \sigma^3 + x \frac{\partial(\sigma^3)}{\partial x} \quad (6.99)$$

Integration of the above equation yields

$$\frac{4}{3}(N_{Pr})^{-1} (x^{3/4} - x_0^{3/4}) = \sigma^3(x)^{3/4} \quad (6.100)$$

where $N_{Pr} = v/\alpha$, and x_0 is the distance from the leading edge of the plate, i.e. from where the thermal boundary layer starts developing. At $x_0 = 0$, Eq. (6.100) simplifies to

$$\sigma = 0.93(N_{Pr})^{-1/3} \simeq (N_{Pr})^{-1/3} \quad (6.101)$$

Application of these equations is demonstrated below by an example.

EXAMPLE 6.5 Energy-displacement thickness, represented by the symbol δ_E for flow of a fluid is defined by the equation

$$\delta_E = \int_0^\infty \left[\frac{v_x}{v_\infty} \left\{ 1 - \left(\frac{T_s - T}{T_s - T_\infty} \right) \right\} \right] dy$$

Calculate the value of δ_E for a laminar thermal boundary layer for a fluid of $N_{Pr} = 1$, flowing over a flat plate.

Solution According to Eqs. (6.73) and (6.54b), for a laminar boundary layer on a flat plate, we have

$$\frac{T - T_s}{T_\infty - T_s} = \frac{v_x}{v_\infty} = \frac{3}{2} \left(\frac{y}{\delta} \right) - \frac{1}{2} \left(\frac{y}{\delta} \right)^3$$

Substitution of these equations in the above equation for δ_E yields

$$\begin{aligned} \delta_E &= \int_0^\infty \left[\left(\frac{v_x}{v_\infty} \right) - \left(\frac{v_x}{v_\infty} \right)^2 \right] dy \\ &= \int_0^\infty \left[\frac{3}{2} \left(\frac{y}{\delta} \right) - \frac{9}{4} \left(\frac{y}{\delta} \right)^2 - \frac{1}{2} \left(\frac{y}{\delta} \right)^3 - \frac{3}{2} \left(\frac{y}{\delta} \right)^4 - \frac{1}{4} \left(\frac{y}{\delta} \right)^6 \right] dy \\ &= 0.14 \delta \end{aligned}$$

Ans.

which on using Eq. (6.27) can be written as

$$\begin{aligned} \delta_E &= 0.14 \delta = 0.14 \times 5x(N_{Re})^{-0.5} \\ &= 0.7x(N_{Re})^{-0.5} \end{aligned}$$

It is important to note that Eq. (6.101) holds good for most fluids except liquid metals as these have $N_{Pr} < 1$. But in liquid metals too, this relationship holds approximately true and can be used for rough calculations. We now calculate the heat transfer coefficient h . According to the definition of heat transfer coefficient, we have

$$h = \frac{q(x)}{T_s - T_\infty} = + \frac{1}{T_s - T_\infty} k \left(\frac{\partial T}{\partial y} \right)_{y=0} \quad (6.102)$$

Substituting for $(\partial T / \partial y)_{y=0}$ from Eq. (6.93) yields

$$h = \frac{3k}{2\delta_T} = \frac{3k}{2\delta\sigma} = 0.3k \left(\frac{v_\infty}{Vx} \right)^{1/2} (N_{Pr})^{1/3} \quad (6.103)$$

A comparison of this equation with Eq. (6.83a) shows that this approximate approach leads to nearly the same result as the exact solution.

In the development of the above mathematical treatment, we have assumed a relationship between T and y . The form of such a relationship is, however, not known in the case of turbulent flow. This approach, therefore, cannot be applied to this type of flow. In order to calculate heat transfer coefficients in such a case, we take advantage of the similarity between momentum- and heat-transfers. This will be discussed later in Chapter, 8.

6.3 CONCENTRATION BOUNDARY LAYER

Whenever a multicomponent fluid is made to flow over a reacting surface, a concentration gradient develops between the fluid at the surface of the solid and the free stream fluid. This leads to the setting up of a concentration boundary layer from the point where the fluid first touches the surface of reacting solid. Such a change in concentration of components in the fluid may lead to a change in its density. Therefore, a flow of the fluid is generated from a region of high density to that of low density. Such a flow is termed *natural convection*. It must, however, be noted that the concentration boundary layer can also form forced convective flows. We shall consider both these types of flows for their exact solutions in this section. Further, an outline of the integral method for forced convective flow will also be discussed.

6.3.1 Mass Transfer by Natural Convection

Natural convection occurs under the influence of buoyancy forces which may be due to differences either in concentration or in temperature or in both. In the present case, we will consider natural convection to be due only to the concentration gradient. For low concentration gradients of the diffusing species and in the absence of a chemical reaction in the fluid, the equations for mass transfer will be analogous to the corresponding equations for heat transfer. This enables occasional use of similarity principles for solution of mass transfer problems, using the corresponding examples of heat transfer.

We now consider the mass transfer of a component A from a vertical plate placed in contact with an infinitely long liquid bath as shown in Fig. 6.5. Let C_{AS} and $C_{A\infty}$ be the concentrations of the liquid in contact with the plate and at a very large distance from the plate—or, in other words, the bulk concentration—respectively. Such a situation occurs during solidification of alloys in which case a concentration differential exists between the bulk of the melt and the melt at the solidification front or the plane of solidification.

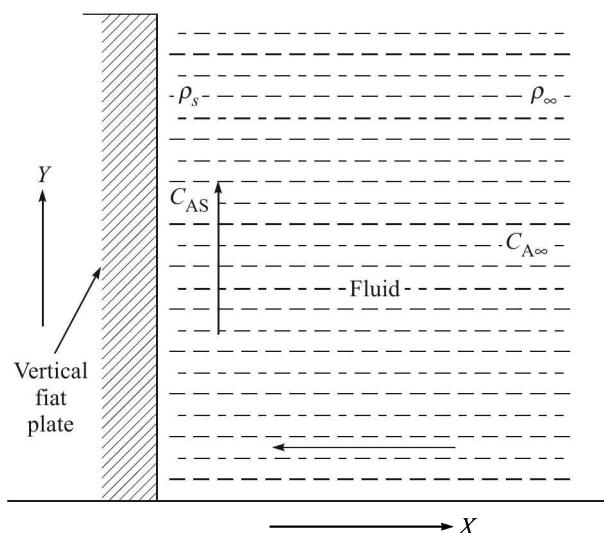


Fig. 6.5 Mass transfer of component A by natural convection from a vertical plate for $\rho_s > \rho_\infty$.

The continuity equation for such a system can be written as

$$\frac{\partial v_x}{\partial x} + \frac{\partial v_y}{\partial y} = 0 \quad (6.104)$$

The equation of motion taking into account the simplification made in Section 6.1.1, can be written for the y -direction as

$$v_x \frac{\partial v_y}{\partial x} + v_y \frac{\partial v_y}{\partial x} = v \frac{\partial^2 v_y}{\partial x^2} - \left(\frac{1}{\rho} \frac{\partial P}{\partial y} + g \right) \quad (6.105)$$

where v is the kinematic viscosity and the function in parentheses on the right-hand side of the equation will depend upon the variation in density affected by the change in concentration of component A and will thus cause natural convection. At any position faraway from the plate and in a direction normal to the vertical plate, the fluid will be in a quiescent state. Therefore Eq. (6.105) reduces at this distance to the form

$$\left[\frac{1}{\rho} \left(\frac{\partial P}{\partial y} \right) \right]_{x \rightarrow \infty} + g = 0 \quad (6.106)$$

Thus

$$\left(\frac{\partial P}{\partial y} \right) \simeq \left(\frac{\partial P}{\partial y} \right)_{x \rightarrow \infty} = -\rho_\infty g \quad (6.107)$$

where ρ_∞ is the density of the fluid at $x = \infty$.

As the composition of a vertical layer of fluid at any distance from the plate can be assumed to be constant, we can write

$$\frac{\partial P}{\partial y} + \rho g = (\rho - \rho_\infty)g$$

or

$$\frac{1}{\rho} \frac{\partial P}{\partial y} + g = \left(\frac{\rho - \rho_{\infty}}{\rho} \right) g \quad (6.108)$$

Thus, Eq. (6.105) can be rewritten as

$$v_x \frac{\partial v_y}{\partial x} + v_y \frac{\partial v_y}{\partial y} = \nu \frac{\partial^2 v_y}{\partial x^2} + g \left(\frac{C_A - C_{A\infty}}{C_A} \right) \quad (6.109)$$

where C_A and $C_{A\infty}$ are the concentrations in terms of moles per unit volume. Next the mass balance equation for component A can be written as

$$v_x \frac{\partial C_A}{\partial x} + v_y \frac{\partial C_A}{\partial y} = D_A \frac{\partial^2 C_A}{\partial y^2} \quad (6.110)$$

For the calculation of rate of mass transfer and concentration boundary layer thickness, we need to solve simultaneously Eqs. (6.104), (6.109) and (6.110) under the boundary conditions

$$(i) \text{ At } x = 0, v_x = v_y = 0 \quad (6.111)$$

$$(ii) \text{ At } x = \infty, v_y = 0 \quad (6.112)$$

$$(iii) \text{ At } x = 0, C_A = C_{AS} \quad (6.113)$$

As a first step in the solution of this equation, we reduce the concentration term into a dimensionless form by introduction of the variable

$$C_A^* = \frac{C_A - C_{A\infty}}{C_{AS} - C_{A\infty}} \quad (6.114)$$

Further, we introduce the stream function ψ , such that

$$\frac{\partial \psi}{\partial y} = v_x \quad (6.115a)$$

and

$$\frac{\partial \psi}{\partial x} = -v_y \quad (6.115b)$$

Thus, Eq. (6.104) is automatically satisfied and Eq. (6.109) assumes the form

$$\frac{\partial \psi}{\partial y} \left[\frac{\partial}{\partial x} \left(\frac{\partial \psi}{\partial y} \right) \right] + \frac{\partial \psi}{\partial x} \left[\frac{\partial}{\partial y} \left(\frac{\partial \psi}{\partial x} \right) \right] = \nu \frac{\partial^2}{\partial x^2} \left(\frac{\partial \psi}{\partial y} \right) + \frac{g(C_{AS} - C_{A\infty}) C_A^*}{(C_{AS} - C_{A\infty}) C_A^* + C_{A\infty}} \quad (6.116)$$

We now assume the stream function to have the form

$$\psi = 4\nu C(y)^{3/4} \zeta(\eta) \quad (6.117)$$

where

$$C = \left[\frac{g(C_{AS} - C_{A\infty})}{4\nu^2} \right]^{1/4} \quad (6.118)$$

$$\eta = \frac{Cx}{y^{1/4}} \quad (6.119)$$

Thus, Eqs. (6.116) and (6.110) can be rewritten, respectively, as

$$\frac{d^3\xi}{d\eta^3} + 3\xi \frac{d^2\xi}{d\eta^2} - 2\left(\frac{d\xi}{d\eta}\right)^2 + C_A^* = 0 \quad (6.120)$$

and

$$\frac{d^2C_A^*}{d\eta^2} + 3N_{Sc}\xi + \frac{dC_A^*}{d\eta} = 0 \quad (6.121)$$

where $N_{Sc} = \frac{V}{D_A}$, the Schmidt number. With the boundary conditions assuming the forms

$$(i) \text{ At } \eta = 0, C_A^* = 1 \text{ and } \frac{d\xi}{d\eta} = \frac{d^2\xi}{d\eta^2} = 0 \quad (6.122)$$

$$(ii) \text{ At } \eta = \infty, C_A^* = 0 \text{ and } \frac{d\xi}{d\eta} = 0 \quad (6.123)$$

Eqs. (6.120) and (6.121) can be solved simultaneously by numerical techniques. The velocity and concentration profiles and the velocity and the concentration boundary layer thicknesses are shown in Figs. 6.6–6.8. The Grashof number N_{Gr} plotted in Figs. 6.6 and 6.8 is defined as

$$N_{Gr} = \frac{gy^3\beta(N_{AS} - N_{A\infty})}{V^2} \quad (6.124)$$

where N_{AS} and $N_{A\infty}$ are the mole fractions of component A in the fluid in contact with the plate and in the bulk of the fluid respectively, and

$$\beta = -\frac{1}{\rho} \left(\frac{\partial \rho}{\partial N_A} \right) \quad (6.125)$$

and is the coefficient of density change with concentration.

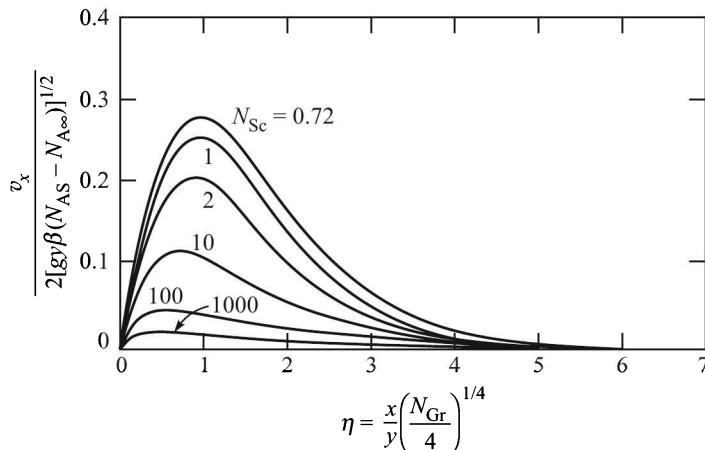


Fig. 6.6 Velocity profile in natural convection along a vertical flat plate.

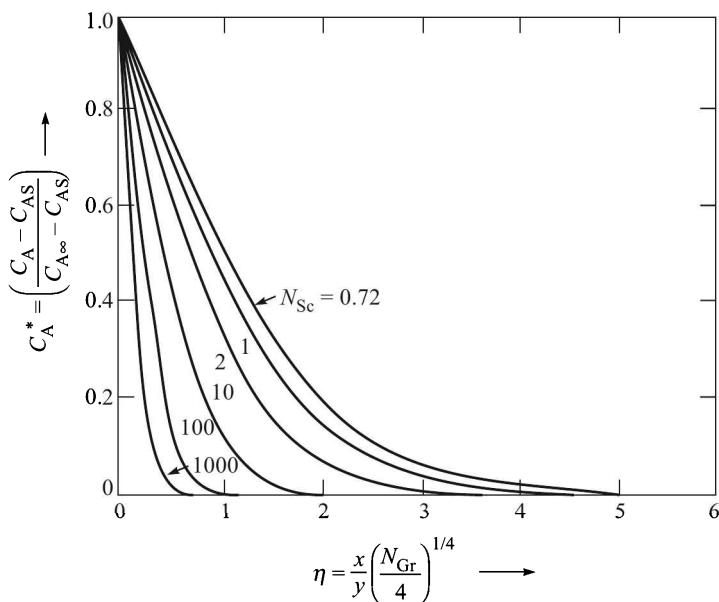


Fig. 6.7 Concentration profile in natural convection along a vertical flat plate.

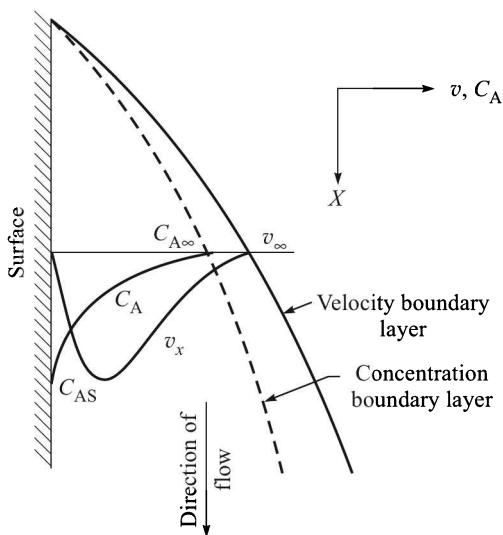


Fig. 6.8 Velocity and concentration boundary layer thicknesses in natural convection for flow along a vertical flat plate.

Figure 6.7 shows that with the increase in Schmidt number, the concentration profile at the surface of the plate becomes steeper. The maxima in velocity curves in Fig. 6.6 are self-explanatory. It can further be proved that with increase in Schmidt number or in the thickness of the velocity boundary layer, the thickness of the concentration boundary layer decreases.

6.3.2 Mass Transfer During Forced Convection

We consider here the case of concentration boundary layer for laminar region of flow over a horizontal flat plate, since it makes possible comparison with our analysis of fluid flow and heat transfer. We consider a flat plate over which a fluid is flowing at a free stream velocity of v_∞ . If the concentration of the diffusing component from or to the plate is small, we can write the following equations for the concentration boundary layer region, in a manner similar to that discussed in Section 4.1.1.

(i) Continuity equation

$$\frac{\partial v_x}{\partial x} + \frac{\partial v_y}{\partial y} = 0 \quad (6.126)$$

(ii) Equation of motion (excluding the pressure gradient)

$$v_x \frac{\partial v_x}{\partial x} + v_y \frac{\partial v_x}{\partial y} = \nu \frac{\partial^2 v_x}{\partial y^2} \quad (6.127)$$

(iii) The mass balance equation for component A (assuming that diffusion in the x -direction is negligibly small in comparison with mass flow

$$v_x \frac{\partial C_A}{\partial x} + v_y \frac{\partial C_A}{\partial y} = D_A \frac{\partial^2 C_A}{\partial y^2} \quad (6.128)$$

The boundary conditions imposed by the system under consideration for solution of these equations are

(i) At $y = 0$, $v_x = v_y = 0$, and $C_A = C_{AS}$ (6.129)

(ii) At $y = \infty$, $v_x = v_\infty$, and $C_A = C_{A\infty}$ (6.130)

(iii) At $x = 0$, $C_A = C_{A\infty}$ (6.131)

To obtain a general solution of the above equations, we introduce the following dimensionless variables:

$$C_A^* = \frac{C_A - C_{AS}}{C_{A\infty} - C_{AS}}; \quad v_x^* = \frac{v_x}{v_\infty} \text{ and } v_y^* = \frac{v_y}{v_\infty} \quad (6.132)$$

Thus, Eqs. (6.126)–(6.128) can respectively be rewritten as follows:

$$\frac{\partial v_x^*}{\partial x} + \frac{\partial v_y^*}{\partial y} = 0 \quad (6.133)$$

$$v_x^* \left(\frac{\partial v_x^*}{\partial x} \right) + v_y^* \left(\frac{\partial v_x^*}{\partial y} \right) = \frac{\nu}{v_\infty} \left(\frac{\partial^2 v_x^*}{\partial y^2} \right) \quad (6.134)$$

and

$$v_x^* \left(\frac{\partial C_A^*}{\partial x} \right) + v_y^* \left(\frac{\partial C_A^*}{\partial y} \right) = \frac{D_A}{v_\infty} \left(\frac{\partial^2 C_A^*}{\partial y^2} \right) \quad (6.135)$$

The new boundary conditions assume the following forms:

$$(i) \text{ At } y = 0; v_x^* = v_y^* = 0 \text{ and } C_A^* = 0 \quad (6.136)$$

$$(ii) \text{ At } y = \infty, v_x^* = 1 \text{ and } C_A^* = 1 \quad (6.137)$$

$$(iii) \text{ At } x = 0, C_A^* = 1 \quad (6.138)$$

It will be noted that Eqs. (6.66) and (6.135) are similar and will yield the same result if

$$D_A = \frac{\mu}{\rho} \text{ or } \frac{\mu}{D_A \rho} = 1 \quad (6.139)$$

The term $\left(\frac{\mu}{D_A \rho}\right)$ is the Schmidt's number and is denoted by the symbol N_{Sc} .

Thus in case $N_{Sc} = 1$, we can write

$$C_A^* = \frac{C_A - C_{AS}}{C_{A\infty} - C_{AS}} = \frac{v_x}{v_\infty} = v_x^* \quad (6.140)$$

or, in other words, the dimensionless velocity and concentration profiles will overlap. In order to transform the partial differential equation, i.e. Eq. (6.135) into a total differential equation, we introduce the following functions:

$$\eta = y \left(\frac{v_\infty}{vx} \right)^{1/4} \quad (6.141)$$

and

$$\psi = (v_\infty vx)^{1/2} f(\eta) \quad (6.142)$$

It is seen that the stream function ψ automatically satisfies Eq. (6.126) and has the properties

$$\frac{\partial \psi}{\partial y} = v_x^* v_\infty \quad \text{and} \quad \frac{\partial \psi}{\partial x} = -v_y^* v_\infty \quad (6.143)$$

With the help of Eqs. (6.140)–(6.142), we can write Eq. (6.128) in the form

$$\frac{d^2 C_A^*}{d\eta^2} + \frac{1}{2} N_{Sc} f(\eta) \frac{dC_A^*}{d\eta} = 0 \quad (6.144)$$

where by definition $N_{Sc} = \frac{\mu}{\rho D_A}$.

The boundary conditions now assume the following forms:

$$(i) \text{ At } \eta = 0, C_A^* = 0 \quad (6.145)$$

$$(ii) \text{ At } \eta = \infty, C_A^* = 1 \quad (6.146)$$

Equation (6.144) can be solved by numerical methods. In Fig. 6.9, C_A^* is plotted against η . It is seen that as the Schmidt number N_{Sc} increases, the concentration profile becomes steeper and the thickness of the concentration boundary layer therefore decreases. This thickness is less than that for the velocity boundary

layer for $N_{Sc} > 1$ and more for $N_{Sc} < 1$. For $N_{Sc} = 1$, both boundary layers have the same thickness.

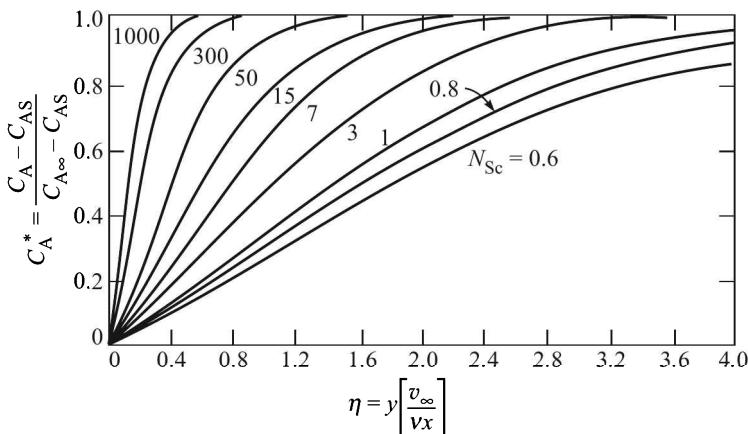


Fig. 6.9 Concentration profile for forced convective flow past a horizontal flat plate.

In some limiting cases, the concentration gradient at the plate surface can be expressed by the following equations:

$$\left(\frac{\partial C_A^*}{\partial \eta} \right)_{\eta=0} = -0.332 (N_{Sc})^{1/3} \text{ for } 0.6 < N_{Sc} < 10 \quad (6.147)$$

$$= -0.564 (N_{Sc})^{1/2} \text{ for } N_{Sc} \rightarrow 0 \quad (6.148)$$

$$= -0.339 (N_{Sc})^{1/3} \text{ for } N_{Sc} \rightarrow \infty \quad (6.149)$$

With the help of these equations, we can calculate the mass transfer coefficients in the boundary layer region.

EXAMPLE 6.6 Liquid iron at 1550°C is flowing over a graphite surface at a velocity of 10 m s^{-1} . Calculate the concentration of carbon at a distance of 25 cm from the leading edge and 1 cm from the solid surface. Given that the kinematic viscosity of liquid iron at 1550°C is $8 \times 10^{-7} \text{ m}^2 \text{ s}^{-1}$ and the diffusivity of carbon in liquid iron at 1550°C is $1.62 \times 10^{-8} \text{ m}^2 \text{ s}^{-1}$.

Solution The given data is:

Velocity of bulk liquid, $v_\infty = 10 \text{ m s}^{-1}$

Distance, $x = 25 \text{ cm} = 0.25 \text{ m}$

Distance, $y = 1 \text{ cm} = 0.01 \text{ m}$

Kinematic viscosity, $v = 8 \times 10^{-7} \text{ m}^2 \text{ s}^{-1}$

Diffusivity, $D = 1.62 \times 10^{-8} \text{ m}^2 \text{ s}^{-1}$

Thus, η from Eq. (6.141) is

$$\begin{aligned}\eta &= y \left(\frac{v_\infty}{vx} \right)^{1/4} \\ &= 0.01 \left(\frac{10}{8 \times 10^{-7} \times 0.25} \right)^{1/4} = 0.84\end{aligned}$$

Also Schmidt number, $N_{Sc} = \frac{v}{D} = \frac{8 \times 10^{-7}}{1.61 \times 10^{-8}} = 50$

Thus from Fig. (6.9), the dimensionless concentration, C_C^* is obtained equal to 0.9.

Now from Eq. (6.140), we have

$$C_C^* = \frac{C_C - C_{Cs}}{C_{C\infty} - C_{Cs}}$$

where C_C is the concentration of carbon at any point,

$$C_C = C_{Cs} \text{ at } y = 0$$

and

$$C_C = C_{C\infty} \text{ at } y = \infty \text{ and } x = 0$$

Taking the concentration in terms of mole-fraction of carbon in iron, we have

$$\begin{aligned}C_{Cs} &= 1 \\ C_{C\infty} &= 0\end{aligned}$$

Therefore,

$$0.9 = \frac{C_C - 1}{0 - 1}$$

or

$$C_C - 1 = -0.9$$

Therefore,

$$C_C = 0.1$$

Therefore, the mole fraction of carbon in iron at the specified place is 0.1.

Ans.

Integral method

As has been done in the case of velocity- and thermal-boundary layers, we can apply the integral method in this case as well to determine the thickness of the concentration boundary layer in the laminar flow region. The method is similar to one already outlined in Sections 6.1.2 and 6.2.2 and will therefore be described here briefly. We again consider a horizontal flat plate over which a fluid flows with a free stream velocity v_∞ . Let one of the components of the

fluid, say A, react with the plate. This will result in changes in the concentration of the fluid in contact with the plate. These changes will generate a concentration gradient inside the fluid in a direction normal to the plate and thus form a concentration boundary layer from the leading edge of the plate as shown in Fig. 6.10. Let the thickness of the concentration boundary layer δ_c be less than that of the laminar hydrodynamic or velocity boundary layer δ .

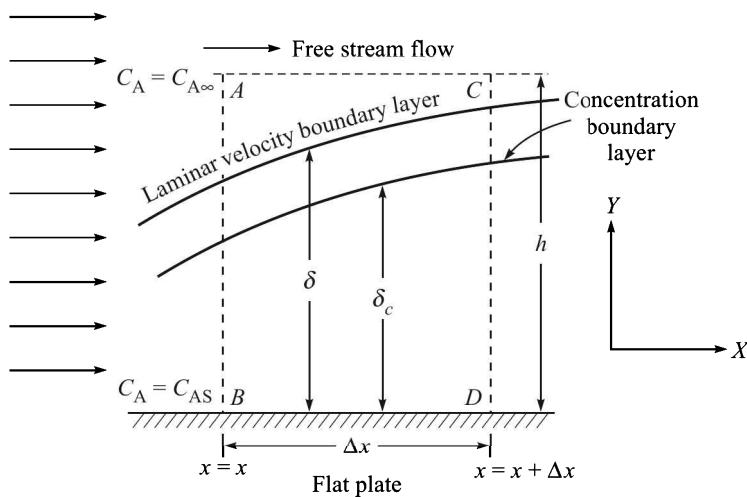


Fig. 6.10 Laminar portion of hydrodynamic boundary layer for analysis of concentration boundary layer by integral method.

The mass- and momentum-balance equations for the volume bound by the planes AB, CD, AC and BD, each having breadth b will be the same as given in Eqs. (6.40) and (6.41). The mass-balance equation for component A in this volume element may be written as

$$\begin{aligned} & b \left[\int_0^h (v_x C_A dy) \right]_{x=x} - D_A \left(\frac{\partial C_A}{\partial y} \right)_{y=0} b \Delta x \\ &= b \left[\int_0^h (v_x C_A dy) \right]_{x=x+\Delta x} - b \Delta x \frac{\partial}{\partial x} \left[\int_0^h (C_{A\infty} v_x dy) \right] \quad (6.150) \end{aligned}$$

which on simplification yields

$$\frac{\partial}{\partial x} \left[\int_0^h (C_{A\infty} - C_A) v_x dy \right] = -D_A \left(\frac{\partial C_A}{\partial y} \right)_{y=0} \quad (6.151)$$

In order to evaluate the above integral, we assume that the concentration profile in the direction normal to the plate follows a polynomial relationship of the type

$$C_A = a_0 + a_1 y + a_2 y^2 + a_3 y^3 \quad (6.152)$$

For determination of the values of coefficients a_0, a_1, a_2, a_3 , we apply the following boundary conditions:

$$(i) \text{ At } y = 0; C_A = C_{AS} \text{ and } \frac{\partial^2 C_A}{\partial y^2} = 0 \quad (6.153)$$

$$(ii) \text{ At } y = \delta_C, C_A = C_{A\infty} \text{ and } \frac{\partial C_A}{\partial y} = 0 \quad (6.154)$$

Thus, we get

$$\begin{aligned} a_0 &= C_{AS}, a_1 = \frac{3}{2} \frac{C_{AS} - C_{A\infty}}{\delta_C} \\ a_2 &= 0, a_3 = -\frac{C_{AS} - C_{A\infty}}{2\delta_C} \end{aligned} \quad (6.155)$$

Substitution of the above values in Eq. (6.152) leads to

$$\frac{C_A - C_{AS}}{C_{A\infty} - C_{AS}} = \frac{3}{2} \left(\frac{y}{\delta_C} \right) - \frac{1}{2} \left(\frac{y}{\delta_C} \right)^2 \quad (6.156)$$

and therefore

$$\left(\frac{\partial C_A}{\partial y} \right)_{y=0} = \frac{3}{2\delta_C} = \frac{3}{2\sigma_C \delta} \quad (6.157)$$

where

$$\sigma_C = \frac{\delta_C}{\delta} \quad (6.158)$$

Substitution of Eq. (6.156) and the following equation for v_x obtained from Eq. (6.54b).

$$v_x = v_\infty \left[\frac{3}{2} \left(\frac{y}{\delta} \right) - \frac{1}{2} \left(\frac{y}{\delta} \right)^3 \right] \quad (6.159)$$

in Eq. (6.151) and the resulting integration yields

$$\sigma_C = 0.93(N_{Sc})^{-1/3} \simeq (N_{Sc})^{-1/3} \quad (6.160)$$

where

$$N_{Sc} = \frac{\mu}{\rho D_A} \quad (6.161)$$

With the help of the above equation and considering the mass flux balance we can arrive at the following relationship for mass transfer coefficient k_m for this system, which is expressed in terms of the Sherwood number, N_{Sh} as

$$N_{Sh,x} = 0.33 (N_{Sc})^{1/3} (N_{Re,x})^{1/3} \quad (6.162)$$

where

$$N_{Sh,x} \equiv \frac{k_m x}{D_A} \quad (6.163)$$

The local Sherwood number $N_{Re,x}$ here is the local Reynolds number as well.

In analogy to velocity and thermal displacement thicknesses, we can define concentration displacement thickness represented by the symbol δ_C^* as follows:

$$\delta_C^* = \int_0^\infty [v^*(1 - C_A^*)] dy \quad (6.164)$$

6.4 BOUNDARY LAYER THEORY FOR SIMULTANEOUS HEAT, MASS AND MOMENTUM TRANSFER

So far we have considered the three boundary layers in isolation. But in a number of industrial applications, these may interact with one another. For example, there are, in general, heat effects and density variations associated with changes in concentration of a component present in a flowing fluid. In such cases, we will be interested in simultaneous solution of heat, mass and momentum transfer equations for the flowing fluid. For the sake of simplicity, we again consider flow past a horizontal flat plate. The basic relevant equations for such a system will be as follows:

(i) Continuity equation

$$\frac{\partial v_x}{\partial x} + \frac{\partial v_y}{\partial y} = 0 \quad (6.165)$$

(ii) Equation of motion

$$v_x \frac{\partial v_x}{\partial x} + v_y \frac{\partial v_x}{\partial y} = \nu \frac{\partial^2 v_x}{\partial y^2} \quad (6.166)$$

(iii) Energy balance equation

$$v_x \frac{\partial T}{\partial x} + v_y \frac{\partial T}{\partial y} = \alpha \frac{\partial^2 T}{\partial y^2} \quad (6.167)$$

(iv) Mass balance equation for component A

$$v_x \frac{\partial C_A}{\partial x} + v_y \frac{\partial C_A}{\partial y} = D_A \frac{\partial^2 C_A}{\partial y^2} \quad (6.168)$$

The boundary conditions applicable to this system will be:

(i) At $y = 0$, $v_x = 0$, $T = T_s$ and $C_A = C_{AS}$ (6.169)

(ii) At $y = \infty$, $v_x = v_\infty$, $T = T_\infty$ and $C_A = C_{A\infty}$ (6.170)

Equation (6.165) can also be written in the following integral form

$$v_y = v_{ys} - \int_0^y \left(\frac{\partial v_x}{\partial x} \right) dy \quad (6.171)$$

where v_{ys} is the velocity of the fluid in the y -direction at the surface of the plate. This can be expressed in terms of mass flux of component A as follows:

$$v_{ys} = \frac{M_A J_{AS}}{\rho} = \frac{M_A}{\rho} (J_A)_{y=0} = \frac{M_A}{\rho} \left[-D_A \left(\frac{\partial C_A}{\partial y} \right)_{y=0} + (J_{AS} + J_{BS}) N_{AS} \right] \quad (6.172)$$

where M_A is the molecular weight of A and J_{AS} and J_{BS} are the mass fluxes of A and B on the surface respectively.

If the concentration of component B, which forms the solvent, does not change appreciably across the boundary layer, we may take $J_{BS} \approx 0$ and hence write

$$J_{AS} = -D_A C_A \left(\frac{\partial N_A}{\partial y} \right)_{y=0} + N_{AS} J_{AS}$$

This gives

$$J_{AS} = -D_A C_A \left(\frac{\partial N_A}{\partial y} \right)_{y=0} / (1 - N_{AS}) \quad (6.173)$$

where C_A is the mass density of the fluid in terms of moles per unit volume and N_{AS} the mole fraction of component A in the fluid in contact with the surface. Substitution of the value of J_{AS} from the above equation in Eq. (6.172) yields

$$v_{ys} = - \frac{M_A C_A D_A}{\rho (1 - N_{AS})} \left(\frac{\partial N_A}{\partial y} \right)_{y=0} \quad (6.174)$$

In case the molecular weights of components A and B are nearly equal, i.e. $M_A \approx M_B$, we can write $M_A C_A \approx \rho$. Hence Eq. (6.174) simplifies further to the form

$$v_{ys} = - \frac{D_A}{1 - N_{AS}} \left(\frac{\partial N_A}{\partial y} \right)_{y=0} \quad (6.175)$$

It may be mentioned that if the reaction between the fluid and the surface of the plate is fast, we can calculate N_{AS} making use of the equilibrium constant of the involved reaction. Substitution of the equation for v_{ys} from Eq. (6.175) in Eq. (6.171) yields

$$v_y = - \left(\frac{D_A}{1 - N_{AS}} \right) \left(\frac{\partial N_A}{\partial y} \right)_{y=0} - \int_0^y \left(\frac{\partial v_x}{\partial x} \right) dy \quad (6.176)$$

We now define the following dimensionless variables to reduce Eqs. (6.166)–(6.168) to a dimensionless form.

$$\Omega_v \equiv \frac{v_x}{v_\infty}, \quad \Omega_T \equiv \frac{T - T_s}{T_\infty - T_s} \quad \text{and} \quad \Omega_C \equiv \frac{N_A - N_{AS}}{N_{A\infty} - N_{AS}} \quad (6.177)$$

With these expressions Eqs. (6.166)–(6.168) assume the following common form

$$\Omega_v v_\infty \left(\frac{\partial \Omega_j}{\partial x} \right) - \left[\left(\frac{D_A}{1 - N_{AS}} \right) \left(\frac{\partial N_A}{\partial y} \right)_{y=0} + v_\infty \int_0^y \left(\frac{\partial \Omega_v}{\partial x} \right) dy \right] \frac{\partial \Omega_j}{\partial y} = \frac{v}{N_r} \frac{\partial^2 \Omega_j}{\partial y^2} \quad (6.178)$$

where the suffix j represents v , T or C for velocity, temperature, or concentration profiles respectively and the values of N_r (a dimensionless number which equals unity), N_{Pr} and N_{Sc} in the case of these three profiles respectively. On the basis of arguments advanced in Section 6.1, we introduce the function

$$\eta = y \left(\frac{v_\infty}{vx} \right)^{1/2} \quad (6.179)$$

Thus Eq. (6.178) assumes the form

$$\left[\frac{1}{N_{Sc}} \left(\frac{N_{AS} - N_{A\infty}}{1 - N_{AS}} \right) \left(\frac{d\Omega_C}{d\eta} \right)_{\eta=0} - \int_0^\eta 2\Omega_v d\eta \right] \left(\frac{d\Omega}{d\eta} \right) = \frac{1}{N_r} \frac{d^2 \Omega}{d\eta^2} \quad (6.180)$$

or

$$N_r \lambda \frac{d\Omega}{d\eta} = \frac{d^2 \Omega}{d\eta^2} \quad (6.181)$$

where

$$\lambda \equiv \left[\frac{1}{N_{Sc}} \left(\frac{N_{AS} - N_{A\infty}}{1 - N_{AS}} \right) \left(\frac{\partial \Omega_C}{\partial \eta} \right) \right]_{\eta=0} - \left[\int_0^\eta 2\Omega_v d\eta \right] \quad (6.182)$$

The first term on the right-hand side of the above equation represents the rate of mass transfer from the surface of the plate. In case of the laminar boundary layer, it is a constant.

Equation (6.182) shows that λ , which is a function of the rate of mass transfer from the surface of the fluid, affects all Ω terms. i.e. the velocity, temperature and concentration profiles. The boundary conditions for the system now assume the general form

$$(i) \text{ At } \eta = 0, \Omega = 0 \quad (6.183)$$

$$(ii) \text{ At } \eta = 1, \Omega = 1 \quad (6.184)$$

Thus Eq. (6.181) becomes a total differential equation with η as an independent variable. This equation can be solved by numerical methods to compute various profiles. The procedure adopted is to calculate the velocity profile for a known or calculated value of mass flux and then the other two profiles are calculated.

In some limiting cases, we can arrive at approximate analytical solutions from the above equation. For example, for very low mass flux at the surface

of the plate and very high Prandtl and Schmidt numbers, the thermal and concentration boundary layers will be much thinner and hence the velocity gradient at the wall will be sufficient to obtain temperature and concentration profiles. Velocity profile near the wall, however, for this case is given by the equation

$$\Omega_v = 0.664\eta \quad (6.185)$$

Hence we obtain from Eq. (6.181). the following relation

$$\Omega_C \text{ (or } \Omega_T) = \frac{\int_0^{\eta} \exp(-0.221N_r\eta^3)d\eta}{\int_0^{\infty} \exp(-0.221N_r\eta^3)d\eta}$$

In the above relation, the symbol N_r will represent N_{Sc} in respect of the relation for Ω_C , and N_{Pr} in respect of the relation Ω_T . Further, the concentration and thermal gradients at the wall will be calculated from the equations

$$\frac{\partial \Omega_C}{\partial \eta} = 0.664(N_{Sc})^{1/3} \quad (6.186)$$

and

$$\frac{\partial \Omega_T}{\partial \eta} = 0.664(N_{Pr})^{1/3} \quad (6.187)$$

Using values of these gradients, we can calculate the heat and mass transfer coefficients.

The above treatment shows that, in any system, heat, mass and momentum transfer coefficients are interrelated. In other words, they are coupled. These analogies among the three modes of transport phenomena will form the subject matter of a section in Chapter 8.

REVIEW QUESTIONS

1. Define the terms boundary layer thickness, displacement thickness, and momentum displacement thickness.
2. Discuss the exact solution of mass and momentum balance equations for laminar boundary layer for flow over a flat plate.
3. Derive equations for thickness of the boundary layer by the integral method for turbulent flow over a flat plate.
4. Discuss the formation of boundary layer and laminar sublayer for flow through pipes.
5. Derive equations for thermal boundary layer and heat transfer coefficient by solving simultaneously differential mass, momentum and energy balance equations.

6. Discuss the application of the integral method for evaluation of the thermal boundary layer and heat transfer coefficient.
7. Compare the integral method and the exact solution method for evaluation of the thermal boundary layer.
8. Derive the mathematical relationship governing natural convection for mass transfer in a laminar boundary layer.
9. Derive an equation for concentration boundary layer thickness by considering equations of continuity and motion.
10. Discuss the application of the integral method for evaluation of the concentration boundary layer in non-reacting systems.
11. Discuss the application of differential balances as applied to simultaneous solution of heat, mass and momentum transfer equations.

PROBLEMS

1. Prove that the velocity distribution for laminar boundary layer for flow over a flat plate is given by the equation

$$v_x = v_\infty \left[\frac{3}{2} \left(\frac{y}{\delta} \right) - \frac{1}{2} \left(\frac{y}{\delta} \right)^3 \right]$$

2. Compare the different methods of calculating the boundary layer thickness.
3. Draw the boundary layer profile for the flow of mercury ($\mu = 2$ centipoise, $\rho = 13600 \text{ kg m}^{-3}$) over a 3 long flat plate for a free stream flow rate of 1800 m h^{-1} . Also calculate (i) the velocity and momentum displacement thicknesses at 1, 2 and 3 m from the leading edge, (ii) the thickness of laminar sublayer at 2.5 m, and (iii) the distance from the leading edge at which transition from laminar to turbulent boundary layer takes place.
4. Liquid aluminium flows through a pipe of 0.1 m diameter at a mass flow rate of 4700 kg h^{-1} . Calculate (i) the distance from the entrance of the pipe at which the flow is fully developed, (ii) the thickness of laminar sublayer, and (iii) the velocity at the edge of laminar sublayer. Given: (i) viscosity of liquid aluminium = 2.3 centipoise (ii) density of liquid aluminium = 2600 kg m^{-3} .
5. Prove that the velocity boundary layer is equal to thermal boundary layer for $N_{Pr} = 1$.
6. Liquid sodium ($\mu = 0.75$ centipoise, $C_p = 31500 \text{ J kg}^{-1} \text{ K}^{-1}$, $\rho = 970 \text{ kg m}^{-3}$, $k = 84 \text{ J m}^{-1} \text{ s}^{-1} \text{ K}^{-1}$) at 373 K is made to flow over a flat plate of length 1.3 m and maintained at 425 K. The free stream velocity of the fluid is 11 m h^{-1} . Calculate (i) the local heat transfer coefficient at a distance of 0.5 m from the leading edge, (ii) the average heat transfer

coefficient, and (iii) the amount of heat transferred from the plate per minute assuming the breadth of the plate to be 0.20 m.

7. Calculate the thermal boundary layer thickness for the above problem. Verify if the thickness is less than that of the velocity boundary layer or not. Hence comment on the validity of the equations used.
8. Calculate the local thermal boundary layer thickness and the energy displacement thickness at a distance of 0.3 m from the leading edge for flow of a slag at a velocity of 5000 m h^{-1} over a flat plate of length 4 m. The properties of the slag are as follows:

$$\begin{aligned}\mu &= 5 \text{ poise}; C_p = 780 \text{ J kg}^{-1} \text{ K}^{-1}; \\ k &= 12 \text{ J m}^{-1} \text{ s}^{-1} \text{ K}^{-1}; \rho = 3400 \text{ kg m}^{-3}\end{aligned}$$

Also, calculate the ratio of hydrodynamic to thermal boundary layer thicknesses.

9. Calculate the local mass transfer coefficient for flow over a flat plate from the following data:

Density of the fluid	= 1049 kg m^{-3}
Viscosity of the fluid	= 0.1 centipoise
Diffusion coefficient of the component	= $1.5 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$
Distance from the leading edge	= 0.21 m
Free stream velocity of the fluid	= 80 m h^{-1}

10. Compare the natural and forced convective mass transfer coefficients.
11. Prove the relationship

$$\delta = \left(\frac{12 v x}{v_\infty} \right)^{1/2}$$

under the following conditions:

$$\frac{y}{\delta} = v_x^* \text{ for } y \leq \delta$$

and

$$v_x^* = 1 \text{ for } y \geq \delta.$$

Reaction Kinetics

The importance of reaction kinetics in the analysis of metallurgical processes cannot be overemphasized as most of them, especially the extractive metallurgical ones, involve one or more reactions such as chemical reactions or physical changes. Proper understanding of the kinetics of the concerned reactions, therefore, forms an integral part of the complete analysis of rate processes. Accordingly, we frequently encounter experimental studies on the kinetics of different chemical reactions and physical changes in metallurgical literature.

The present chapter, therefore, presents a brief survey of reaction kinetics. Though it is impossible to deal with all aspects of such kinetics, nevertheless, the subject matter presented here will assist the reader to become conversant with the basic concepts. The inquisitive reader, interested in a comprehensive understanding of the treatment of reaction kinetics may refer to some standard texts on this subject.¹

7.1 BASIC DEFINITIONS AND CONCEPTS

A reaction is said to occur, if one or more components called *reactants*, present in a system, change into other components called *products* with the passage of time. Reactions are classified in a number of ways as regards their kinetic studies. Depending upon the rate of conversion of reactants into products, these are classified as *instantaneous*, *moderate* or *intermediate* and *very slow* reactions. Reactions involving all components in one phase only are termed *homogeneous reactions*, whereas those involving more than one phase are called *heterogeneous reactions*. Simple reactions involve change only in one direction but complex reactions have more than one direction of reactions. Thus opposing

² K.J. Laidler, *Chemical Kinetics*, McGraw-Hill, New York (1973); S. Glasstone, K.J. Laidler and H. Eyring, *Theory of Rate Processes*, McGraw-Hill, New York (1941); K. Vetter, *Electrochemical Kinetics*, Academic Press, New York (1967).

or reversible reactions involve simultaneous conversion of reactants into products and vice versa; consecutive, chain or sequential reactions involve conversion of reactants into one set of products which in turn changes to others and so on; parallel or side reactions involve simultaneous conversion of one set of reactants to two or more sets of products. Surface reactions occur almost wholly on a surface—solid or liquid—and auto-catalytic reactions have one of the products of reaction acting as a catalyst.

The rate of a reaction may be expressed in terms of change in mass of a component per unit time. Mathematically we can write it as

$$r = \frac{dm_i}{dt} \quad (7.1)$$

where r is the rate of reaction, and m_i the mass of component i in the system. Equation (7.1) represents r in the form of an extensive variable. In general, the rate is expressed in an intensive form such as specific rate, represented by the symbol J and is defined as

$$J \equiv \frac{r}{V} = \frac{1}{V} \left(\frac{dm_i}{dt} \right) \quad (7.2)$$

In case the volume of the system does not change during the process, we can rewrite the above equation as

$$J = \frac{d(m_i/V)}{dt} = \frac{dC_i}{dt} \quad (7.3)$$

where C_i is the concentration of the component i in the system, expressed in terms of mass per unit volume.

In the case of heterogeneous reactions, these take place on a specific surface. Therefore, instead of using volume, the reaction interfacial area A is used to express the specific reaction rate. Mathematically, for such cases, we write

$$J = \frac{1}{A} \frac{dm_i}{dt} \quad (7.4)$$

In case the ratio of volume to surface area for the reacting system is a constant, we can obtain from Eq. (7.4) an equation similar to Eq. (7.2). For reactions involving gases, the change in partial pressure of any gaseous component of the reactive system per unit time can also be used as the expression of their reaction rates.

From the above equations, we may infer that the reaction rate will be a function of the component i , which may be selected from amongst the products or reactants. But such an inference will not be strictly correct as illustrated with the help of the following general reaction:



This equation shows that components A, B, C and D react in the ratio $a : b : c : d$ respectively on molar basis. From this, we can easily find the ratios on weight basis. Equation (7.5) shows that for this reaction

$$J = -\frac{dC_A}{dt} = -\frac{b}{a} \frac{dC_B}{dt} = +\frac{c}{a} \frac{dC_C}{dt} = +\frac{d}{a} \frac{dC_D}{dt} \quad (7.6)$$

where the negative and positive signs refer to reactants and products respectively and concentrations are expressed on moles per unit volume basis. This equation shows that the reaction rates based on different components differ only by constant multiplying factors. For example,

$$J_A = \frac{b}{a} J_B \quad (7.7)$$

and hence the rates are identical. To avoid this constant factor, a variable called the *reaction progress variable*, denoted by the symbol ξ , is introduced. It is defined by the following equations:

$$\begin{aligned} \xi &= \frac{m_A - m_A^0}{a} = \frac{m_B - m_B^0}{b} \\ &= \frac{m_C - m_C^0}{c} = \frac{m_D - m_D^0}{d} \end{aligned} \quad (7.8)$$

where m_A , m_B , m_C , and m_D are the moles of components A, B, C and D, respectively, present in the system at time t and the suffix '0' refers to the values at $t = 0$, i.e. at the start of the reaction.

With the help of Eq. (7.8), we can also express J in an alternative form as

$$\begin{aligned} J &= \frac{d\xi}{dt} = \frac{1}{aV} \frac{dm_A}{dt} \\ &= \frac{1}{bV} \frac{dm_B}{dt} = \frac{1}{cV} \frac{dm_C}{dt} = \frac{1}{dV} \frac{dm_D}{dt} \end{aligned} \quad (7.9)$$

or for a constant volume system we can write, on the concentration basis, the relations

$$\begin{aligned} J &= \frac{d\xi}{dt} = \frac{1}{a} \frac{dC_A}{dt} = \frac{1}{b} \frac{dC_B}{dt} \\ &= \frac{1}{c} \frac{dC_C}{dt} = \frac{1}{d} \frac{dC_D}{dt} \end{aligned} \quad (7.10)$$

7.1.1 General Observations on Reaction Rates

It has been found that kinetics of all reactions conform to a set of general observations. These observations are summarized as follows:

- (i) In all reactions, the reaction progress variable increases with the passage of time. The rate of increase of this variable depends upon temperature, pressure and composition of the systems.
- (ii) Under conditions of constant temperature and pressure, the rate of increase of the reaction progress variable, i.e. reaction rate, decreases with the passage of time.

- (iii) The dependence of the reaction rate, on concentration of various components for irreversible reactions, is expressed by the equation

$$\frac{d\xi}{dt} = \pm k C_A^a C_B^b C_C^c C_D^d \quad (7.11)$$

where the positive sign is used when the component i appears as a product and the negative sign when it forms a reactant. Further, the symbols C_A , C_B , C_C and C_D , etc. are concentrations of the components A, B, C, D respectively, either of the reactants or the products of the reactive system under study at time t . In the case of a gaseous component, however, these concentration terms are substituted by the respective partial pressures; the indices a , b , c , and d , are generally positive integers including zero, but may also be fractions for gaseous reactions occurring on solid surfaces and their values are determined experimentally by methods described in Section 7.2; k is a constant known as the specific reaction rate or *rate constant* for the reaction under study. Reactions which follow Eq. (7.11) are said to be of the order a in component A, order b in component B, and so on. The total or overall order n of the reaction is calculated by adding orders with respect to different reactants and is expressed by the relation

$$n = a + b + c + d + \dots \quad (7.12)$$

Molecularity of any chemical reaction, on the other hand, is defined as the sum of the number of moles of different reactants, taking part in the chemical reaction, as reflected by a stoichiometrically balanced chemical equation depicting the reaction under study. It is thus obvious that molecularity will always be a positive integer greater than zero and may be equal to or greater than the overall order of the reaction.

Equation (7.11) shows that the specific reaction rate and the order of a reaction form the two main parameters by which the reaction rate is described. Thus their experimental determination forms an integral part of the study of reaction kinetics. This is briefly discussed in the next section.

- (iv) The specific reaction rate or the rate constant k is found, in general, to vary with absolute temperature T , according to the Arrhenius relationship

$$k = A \exp\left(-\frac{E}{RT}\right) \quad (7.13)$$

where E is known as the activation energy of the reaction, A is called the frequency factor, R is the universal gas constant and T the absolute temperature.

- (v) The presence of some elements or components in the reacting system strongly affects the rate of reaction though these species neither appear in the stoichiometric reaction equation nor affect the equilibrium state of the reaction. These materials are called *catalysts* or *inhibitors*

- depending upon whether they increase or decrease the rates of reactions.
- (vi) For reversible reactions, the net rate J is equal to the difference between the rates of forward and backward directions, i.e.

$$J = \vec{J} - \vec{J} \quad (7.14)$$

7.2 DETERMINATION OF RATE CONSTANT AND ORDER OF REACTION

The order of a reaction and its specific reaction rate or the rate constant are calculated from the experimental data on variation of concentrations of different components of the reactive system with time. The following methods are used for the determination and calculation of these parameters for reactions proceeding at moderate rates.

7.2.1 Integration Method

In this method, the rate equations for reaction of various orders are integrated to yield concentration functions varying linearly with time. Such concentration-time relationships are generally referred to as rate laws for reactions of specific orders. For example, we can derive the rate law for a first order reaction. For such a case

$$\frac{dC}{dt} = -kC \quad (7.15)$$

or

$$\frac{dC}{C} = -kdt \quad (7.16)$$

which on integration yields

$$\ln C = -kt + I \quad (7.17)$$

where I is the constant of integration and can be evaluated by using the initial condition

$$\text{At } t = 0, \quad C = C_0$$

Thus

$$\ln (C/C_0) = -kt \quad (7.18)$$

Thus the rate law for a first order reaction can be stated as follows. The parameter $\ln (C/C_0)$ is a linear function of time t for a first order reaction and the plot $\ln C$ vs. t will be linear with a negative slope equal in magnitude to k .

Similarly, we can derive the rate laws for reactions of other orders. These laws are listed in Table 7.1. Application of the integration method, therefore,

TABLE 7.1 Rate laws of simple reactions

Order of reaction for reaction	Simplified equation	Rate law		Dimensions of the rate constant, k
		Differential form	Integral form	
Zero	$A \rightarrow \text{products}$	$\frac{dx}{dt} = k_c$	$k_0 = \frac{x}{t} = \frac{x_2 - x_1}{t_2 - t_1}$	$t_{1/2} \propto a$ conc ⁻¹ time ⁻¹
Fractional $\left(\frac{2n+1}{2}\right) A$		$\frac{dx}{dt} = k_f(a-x)^{(2n+1)/2}$	$k_f = \frac{2}{(2n-1)t}$ $\left[\frac{1}{(a-x)^{(2n-1)/2}} - \frac{1}{(a)^{(2n-1)/2}} \right]$	$t_{1/2} \propto a^{-(2n-1)/2}$ conc ^{-(2n-1)/2} time ⁻¹
$\left(\frac{2n-1}{2}\right) \rightarrow \text{product}$				
First	$A \rightarrow \text{products}$	$\frac{dx}{dt} = k_1(a-x)$	$k_1 = \frac{2.303}{t} \log_{10} \left(\frac{a}{a-x} \right)$	$t_{1/2}$ independent of a time ⁻¹
Second	$A + B \rightarrow \text{products}$	$\frac{dx}{dt} = k_2(a-x)(b-x)$	$k_2 = \frac{2.303}{t(a-b)} \log_{10} \left[\frac{b(a-x)}{a(b-x)} \right]$	$t_{1/2} \propto \frac{1}{a}$ conc ⁻¹ time ⁻¹
2A $\rightarrow \text{products}$		$\frac{dx}{dt} = k'_2(a-x)^2$	$k'_2 = \frac{1}{t} \frac{x}{a(a-x)}$	$t_{1/2} \propto \frac{1}{a}$ conc ⁻¹ time ⁻¹

(Contd.)

TABLE 7.1 Rate laws of simple reactions (*Contd.*)

Order of reaction for reaction	Simplified equation for reaction	Rate law		Dimensions of the rate constant, k
		Differential form	Integral form	
Third	$3A \rightarrow \text{products}$	$\frac{dx}{dt} = k_3(a-x)^3$	$k_3 = \frac{1}{2t} \left[\frac{1}{(a-x)^2} - \frac{1}{a^2} \right]$	$t_{1/2} \propto \frac{1}{a^2}$ conc ⁻² time ⁻¹
	$2A + B \rightarrow \text{products}$	$\frac{dx}{dt} = k'_3(a-2x)^2 (b-x)$	$k'_3 = \frac{1}{t} \frac{1}{(2b-a)^2} \times \left[\frac{2(2b-a)x}{a(a-2x)} + 2.303 \right]$	$t_{1/2} \propto \frac{1}{a^2}$ conc ⁻² time ⁻¹
			$\log_{10} \frac{b(a-2x)}{a(b-2x)}$	$t_{1/2} \propto \frac{1}{a^2}$ conc ⁻² time ⁻¹
n^{th}	$nA \rightarrow \text{products}$	$\frac{dx}{dt} = k_n(a-x)^n$	$k_n = \frac{1}{t(n-1)} \times \left[\frac{1}{(a-x)^{n-1}} - \frac{1}{a^{n-1}} \right]$	$t_{1/2} \propto \frac{1}{a^{n-1}}$ conc ⁻⁽ⁿ⁻¹⁾ time ⁻¹

Notes: A, B — are reactants.
 a, b — are initial concentrations and $(a-x), (b-x)$ are concentrations at any instant t , and k_n, k'_n are rate constants of n th order reaction.

involves determination of concentrations of reactants at different time intervals as the reaction proceeds, starting from initial concentrations, and calculation and plotting of the above referred parameters against time to arrive at values of both k and n for the reaction. The use of this is illustrated by the following example.

EXAMPLE 7.1 The following results have been obtained¹ for decarburization of iron-carbon melts in low carbon ranges using a 10% O₂–90% Ar mixture at 1600°C. Determine the order of reaction by the method of integration and the concerned rate constant.

Time, s	%C
0	0.164
600	0.118
1200	0.080
1800	0.055
2400	0.045

Solution In this problem, the reaction can only have an order of reaction with respect to carbon, as the other reactant, i.e. oxygen is supplied at a fixed rate. Two graphs are now plotted considering the integral form of rate law—one between $\log [\%C_0/\%C]$ vs. time, as shown in Fig. 7.1, assuming first order reaction, and the other between $\{[\%C_0] - [\%C]\}/\{[\%C_0] \times [\%C]\}$ vs. time, as shown in Fig. 7.2, assuming second order reaction. It can be seen from these two graphs that the reaction is of the first order. The rate constant k obtained from Fig. 7.1 is $5.76 \times 10^{-4} \text{ s}^{-1}$.

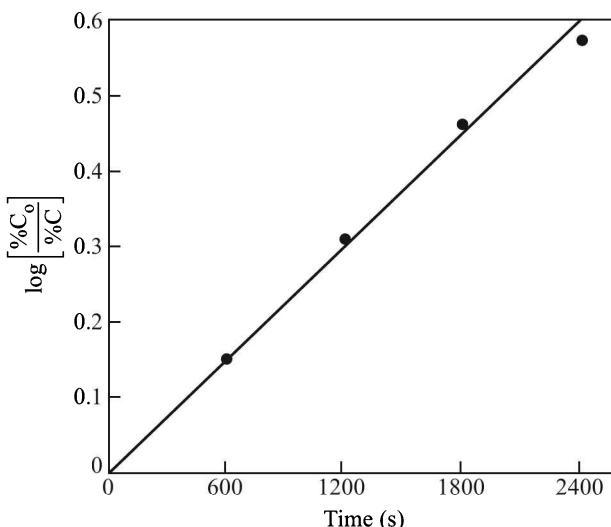


Fig. 7.1 Relationship between the function $\log [\%C_0/\%C]$ and time for decarburization of Fe—C melt.

¹ D.N. Ghosh and P.K. Sen, *Trans. I.I.M.*, **28**(3), 259 (1975).

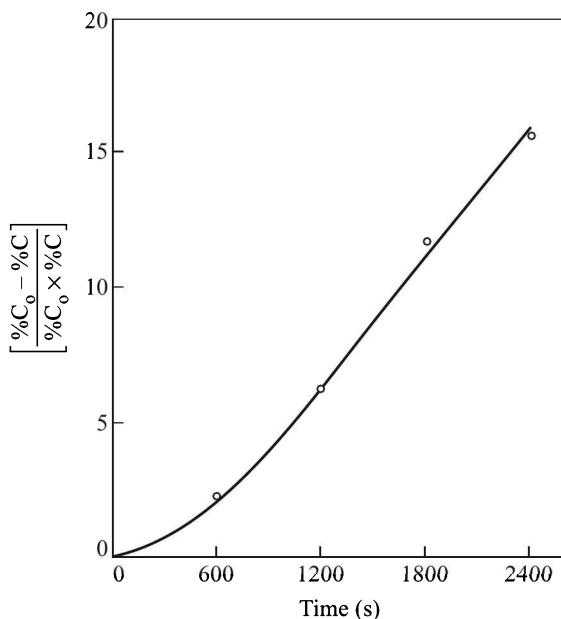


Fig. 7.2 Relationship between the function $[\%C_0 - \%C]/[\%C_0 \times \%C]$ and time for decarburization of Fe–C melts.

Equation (7.18) and those given in Table 7.1 are applicable to systems in which there is no change in volume during the reaction, but a number of reactions of industrial importance, involving gases in particular, are accompanied by change in specific volume of the system which is a function of the partial molar volumes of the components. This aspect considerably complicates the mathematical treatment of reactions of various orders and it is not possible to arrive at explicit closed form integrated expressions for reaction orders greater than one. In order to describe the procedure adopted in this case, we consider a first order reaction for which an analytical equation can be derived. According to Eq. (7.2), we can write for a first order reaction for a component A

$$J_A = \frac{1}{V} \frac{dm_A}{dt} = kC_A = k \frac{m_A}{V} \quad (7.19)$$

Integration of the above equation and application of the initial condition to the resulting equation yields

$$\ln \left(\frac{m_A}{m_A^0} \right) = kt \quad (7.20)$$

In terms of concentrations, the above equation can be written as

$$\ln \left(\frac{C_A V}{C_A^0 V_A^0} \right) = kt \quad (7.21)$$

where V and V_A^0 are respectively the specific volumes of the system at any time t and at the start of the reaction, i.e. at $t = 0$.

Equation (7.20) can also be expressed in terms of the reaction progress variable ξ , and we can thus write

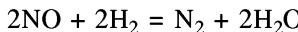
$$\xi = \frac{m_A^0}{|a|} [\exp (kt) - 1] \quad (7.22)$$

Equations (7.21) and (7.22) are commonly employed for mathematical characterization of the first order irreversible reactions of variable volumes.

7.2.2 Method of Equi-fractional Parts or Half-life Period

In this method, time $t_{1/n}$, in which the concentration of the reactant reduces by an amount $1/n$ of the initial value, e.g. the half-life period $t_{1/2}$ in which the concentration reduces to half of the initial values, is determined experimentally for various initial concentrations C_0 , and from the relationship between $t_{1/2}$ and C_0 also given in Table 7.1 for reactions of different orders, values of the specific reaction rate k and order n of the reaction under study are determined. The use of this method is demonstrated by the following example.

EXAMPLE 7.2 When equimolar amounts of nitric oxide and hydrogen were mixed and heated to 826°C, the following reaction took place.



If the half-life for the reaction varies with the total initial pressure as follows, what is the order of reaction?

Pressure, mm	$t_{1/2}$, s
354	81
243	176

Solution As shown in Table 7.1, for a reaction with order of reaction n , the half-life period $t_{1/2}$, is given by

$$t_{1/2} \propto \frac{1}{a^{n-1}}$$

where a is the initial concentration. Thus

$$t_{1/2} a^{n-1} = \text{constant}$$

In the present problem, a can be substituted by initial pressure, p .

$$\therefore \text{Therefore, } \frac{(t_{1/2})_1}{(t_{1/2})_2} = \left(\frac{p_2}{p_1} \right)^{n-1}$$

or

$$(n-1) \log \left(\frac{p_2}{p_1} \right) = \log \left\{ \frac{(t_{1/2})_1}{(t_{1/2})_2} \right\}$$

or

$$\begin{aligned} n &= 1 + \frac{\log [(t_{1/2})_1 / (t_{1/2})_2]}{\log (p_2 / p_1)} = 1 + \frac{\log (81/176)}{\log (243/354)} \\ &= 1 + 2.06 = 3.06 \end{aligned}$$

Hence the order of reaction is 3.

Ans.

7.2.3 Differential Method

In this method, which was first suggested by van't Hoff, instantaneous reaction rates are determined by drawing tangents at various points on the concentration vs. time plots obtained experimentally for the reaction under study. If the rate of a reaction dC/dt is also denoted by the symbol v , it can be related to concentration C of a reactant by the equation

$$v = k(C)^n \quad (7.23)$$

where k is the rate constant and n the order of reaction, then taking logarithms, we have

$$\log v = \log k + n \log C \quad (7.24)$$

If $\log v$ is now plotted against $\log C$, linear plots will be obtained. The slope of this plot will give the order of reaction n whereas the intercept will give the value of $\log k$. Application of this method is illustrated by the following example.

EXAMPLE 7.3 Using the results of Example 7.1, determine the order of reaction based on the differential method.

Solution A graph is first plotted between % carbon and time for decarburization of Fe-C melt as shown in Fig. 7.3. Tangents are then drawn to the curve thus obtained, at different concentrations of carbon and the slopes of these tangents give the rate of reaction v at these concentrations. The different values of concentration C , rate of reaction v , $\log C$ and $\log v$ values are given below:

C	v	$\log C$	$\log v$
0.164	8.04×10^{-5}	-0.7855	-4.0947
0.118	5.00×10^{-5}	-0.9281	-4.3010
0.08	2.83×10^{-5}	-1.0969	-4.5482
0.055	1.81×10^{-5}	-1.2596	-4.7423

The $\log v$ values are then plotted against $\log C$ values as shown in Fig. 7.4. A linear relationship is obtained between $\log v$ and $\log C$ and the slope of this line is found to be 1.2. The order of reaction may therefore be taken as unity.

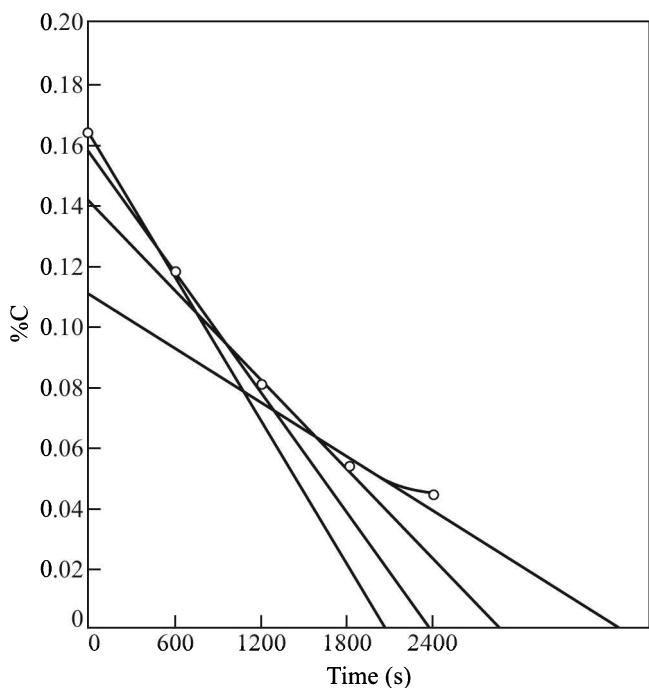


Fig. 7.3 Relationship between % carbon and time for decarburization of Fe–C melt.

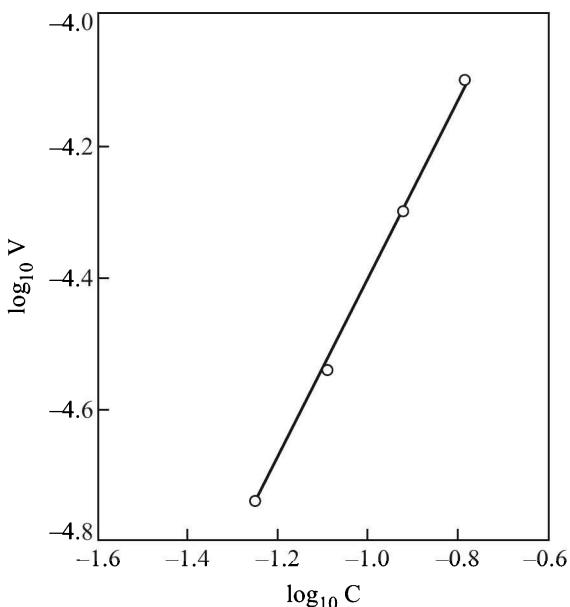


Fig. 7.4 Relationship between $\log v$ and $\log C$ for decarburization of Fe–C melt.

7.2.4 Isolation Method

If a reaction has a number of reactants, then the order of the reaction with respect to each of the reactants is determined by this method. The reaction in this method is studied under the conditions that the concentration of one of the reactants with respect to which the order is to be determined, is kept far less than the stoichiometric requirements and those of all others far in excess. The change in concentration of this reactant is then studied with time and finally the application of one of the already outlined techniques will yield the value of order and specific reaction rate of reaction with respect to the reactant under consideration. A similar procedure can be applied with respect to other reactants as well. We can thus arrive at the values of orders of the reaction with respect to each of the reactants as well as the overall order of reaction by addition of the individual orders.

All the above methods require an initial mixing of the reactants followed by recording of the changes in concentration with time. These methods can only be applied to slow and moderately fast reactions. In case of fast reactions, however, the relaxation method is applied, details of which can be found in the textbooks mentioned in the beginning of this chapter.

There are some complex reactions, such as *opposing*, *parallel* or *chain* reactions where determination of the order of reaction is slightly more complicated. However, since such reactions are not frequently encountered in the metallurgical field, they are not being discussed here. A detailed account of these reactions can also be found in the textbooks mentioned earlier.

Once the values of specific reaction rates and orders of reaction are determined, these data are used to arrive at the mechanism of the reaction and to suggest theoretical explanation for the reaction rate constant.

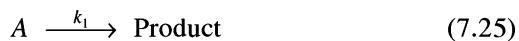
7.3 REACTION MECHANISM

The term *reaction mechanism* refers to the description of molecular events leading to the explanation of the order of reaction with respect to various reactants. Postulation of a reaction mechanism is a complex mental exercise and is done in terms of a sequence of thought of molecular events, consisting of several consecutive elementary reactions. Though there are no hard and fast rules for writing either such a sequence or the elementary reaction, there are some guidelines which should be adhered to for doing this.

For writing the elementary reaction, we should keep in mind the following two criteria:

(i) Each elementary reaction is written in the form it is supposed to occur.

For example, for a first order irreversible reaction, we write an elementary reaction in a unimolecular form such as



for which

$$J = k_1 C_A \quad (7.26)$$

Similar expressions can be written for the second and third order reactions in terms of bimolecular and trimolecular elementary reactions. It has been found that majority of the elementary reactions are bimolecular in nature. It is not always necessary that the elementary reactions contain those reactants or products which appear in the overall stoichiometric equation. These may contain only intermediate species formed in the presumed sequence of reactions. These intermediate species may be either stable molecules or highly reactive components. A complete analysis of reaction products can provide information about the stable intermediate species. The possibility of formation of strongly reactive species is explored on the basis of atomic and electronic structure of reactants and products.

- (ii) Elementary reactions should be such that these lead to the formation or breaking up of minimum number of bonds. Generally a reaction is written in such a way that only one bond is made or broken. Occasionally, a reaction involves two bonds, but rarely a reaction with more than two bonds is encountered. The formation or breaking up of bonds in an elementary reaction should be justifiable from the point of view of its energetics, atomic geometry and electronic movements.

For writing the sequence of elementary reactions, we should take the following points into account:

- (i) The net effect, arrived at by summing up all elementary reactions of the reaction sequence must be the overall reaction. It should lead to the consumption of all the intermediate products and explain the formation of all final products.
- (ii) It should not contain any elementary reaction in which stoichiometric coefficients of the reactant add up to four or more, as such a reaction is not probable on the basis of theoretical considerations.
- (iii) Strongly reactive intermediate species are not supposed to react with each other, because of their usually low concentrations during the reaction process.
- (iv) Once the sequence of these elementary reactions is written, we can assume one of these to be the slowest. It is this step which is considered to be the rate determining step for the overall reaction. The rate of product formation depends upon all the steps preceding this slowest step and not on those following it. In order to arrive at a mathematical formulation of the reaction kinetics from this sequence, we either assume that all reactions preceding the slowest step are in a state of equilibrium, i.e. a state of pseudo-equilibrium prevails in respect of these, or assume that the rate of production of all intermediate

products is equal to zero. This assumption is generally referred to as *steady state assumption*. Both these assumptions lead to similar results and their application will be illustrated with the help of examples, considered in the course of this section. This step leads to the rate expression for the proposed mechanism. This expression must be consistent with the observed order of the reaction for the mechanism to be accepted. In fact, as will be shown later, we can propose a number of mechanisms for any reaction which are able to explain experimentally the observed order of reaction. In the case of heterogeneous reactions involving more than one phase the reaction is also broken up into several elementary steps. The slowest of these steps is again the rate-controlling step for the overall reaction.

- (v) In case the overall order of a reaction is more than three, there will be one or more elementary reactions preceding the slowest step.
- (vi) Experimentally observed fractional orders are definite indicators of formation of intermediate products.
- (vii) If the order of a reaction increases with an increase in the concentration of a component, it can be inferred that the reaction proceeds by two or more parallel paths.
- (viii) In case there is a decrease in the order of a reaction with an increase in the concentration of a component, it reflects that the reaction dominating species undergoes a change with the change in concentration.
- (ix) Finally, a postulated mechanism must hold good for reverse overall reaction as well.

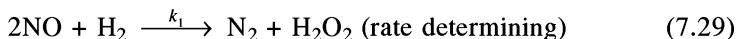
We now explain the above points with the help of a reaction whose mechanism is well established. This reaction occurs in the gas phase and its overall equation is



Its rate equation is given experimentally as

$$J = k(C_{\text{NO}})^2 C_{\text{H}_2} \quad (7.28)$$

Two mechanisms have been suggested for this reaction. According to the first mechanism, this reaction is supposed to take place in two steps, namely

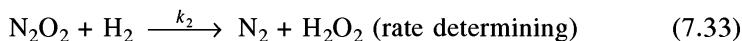


The rate of reaction J of the rate determining (slow) step [Eq. (7.29)] is given as

$$J = k(C_{\text{NO}})^2 C_{\text{H}_2} \quad (7.31)$$

This explains the experimentally determined order of the reaction.

According to the second mechanism, this reaction is assumed to take place in three steps, namely



According to Eq. (7.33), the rate of reaction will be

$$J = k_2 C_{\text{N}_2\text{O}_2} C_{\text{H}_2} \quad (7.35)$$

From Eq. (7.32)

$$\bar{k}_1 (C_{\text{NO}})^2 = \bar{k}_1 C_{\text{N}_2\text{O}_2}$$

or

$$C_{\text{N}_2\text{O}_2} = \frac{\bar{k}_1}{\bar{k}_1} (C_{\text{NO}})^2 \quad (7.36)$$

Substitution of $C_{\text{N}_2\text{O}_2}$ from Eq. (7.36) in Eq. (7.35) leads to

$$J = \frac{k_2 \bar{k}_1}{\bar{k}_1} (C_{\text{NO}})^2 C_{\text{H}_2} \quad (7.37)$$

Thus, we obtain the experimentally observed rate equation. So, as far as the explanation of the experimental data is concerned, both the mechanisms are equivalent. But reaction (7.29) in the first mechanism involves a trimolecular step whereas the second mechanism consists solely of uni- and bi-molecular steps and is, hence, considered to be more probable than the first.

In the derivation of the rate equation we have used the pseudoequilibrium approach. We can make use of steady-state approach as well to come to the same result as shown below. According to this approach

$$\frac{dC_{\text{N}_2\text{O}_2}}{dt} = \bar{k}_1 (C_{\text{NO}})^2 - \bar{k}_1 C_{\text{N}_2\text{O}_2} - k_2 C_{\text{N}_2\text{O}_2} = 0 \quad (7.38)$$

or

$$C_{\text{N}_2\text{O}_2} = \frac{\bar{k}_1 (C_{\text{NO}})^2}{\bar{k}_1 + k_2} \quad (7.39)$$

$$\simeq \frac{\bar{k}_1}{\bar{k}_1} (C_{\text{NO}})^2 \text{ as } k_2 \ll \bar{k}_1 \quad (7.40)$$

Substitution of Eq. (7.40) in Eq. (7.35) leads to the required result as given by Eq. (7.37).

Once we have arrived at the mechanism of a reaction, we can proceed to the interpretation of the specific reaction rate in terms of reaction rate theories which are briefly described in the following section.

7.4 REACTION RATE THEORIES

Modern development of reaction rate theories started with Arrhenius' analysis of equilibrium constants. According to him, the equilibrium constant, which is the ratio of the forward to backward specific reaction rates for the process under study, and the van't Hoff equation can be used to predict temperature dependence of reaction rates as explained below. According to van't Hoff equation

$$\frac{d \ln K}{d\left(\frac{1}{T}\right)} = -\frac{\Delta H^0}{R} \quad (7.41)$$

where K is the equilibrium constant, ΔH^0 the standard enthalpy change for the reaction and R and T are universal gas constant and absolute temperature respectively. We can split $\ln K$ and ΔH^0 in terms of backward and forward reaction characteristics as follows:

$$\ln K = \ln k_f - \ln k_b \quad (7.42)$$

and

$$\Delta H^0 = E_f - E_b \quad (7.43)$$

where k_f and E_f are respectively the specific reaction rate and energy of activation of the forward reaction and k_b and E_b , those of the backward reaction respectively. Substitution of Eqs. (7.42) and (7.43) in Eq. (7.41) and splitting of the resulting equation into two parts, one for the forward and the other for the backward reaction, leads us to the equations

$$\frac{d \ln k_f}{d\left(\frac{1}{T}\right)} = -\frac{F_f}{R} + C \quad (7.44)$$

and

$$\frac{d \ln k_b}{d\left(\frac{1}{T}\right)} = -\frac{F_b}{R} + C \quad (7.45)$$

where C is a constant and has been found experimentally to be equal to zero. With this, the integration of Eqs. (7.44) and (7.45) yields the following equations:

$$k_f = A_f \exp\left(-\frac{E_f}{RT}\right) \quad (7.46)$$

$$k_b = A_b \exp\left(-\frac{E_b}{RT}\right) \quad (7.47)$$

where it has been assumed that the values of activation energies E_f and E_b are independent of temperature. Equations of the type shown in Eqs. (7.46) and (7.47) are known as Arrhenius equations.

Because of the constant C being zero in Eqs. (7.44) and (7.45), we can arrive at the following conclusions from the Arrhenius equation:

- (i) The overall reaction can be divided into two paths, one involving the reactants and the other the products.
- (ii) The factors $\exp(-E_f/RT)$ and $\exp(-E_b/RT)$, which may be recognized as Boltzmann expressions for the fractions of reactants and products having energies in excess of E_f and E_b respectively, suggest that between initial and final states there is an intermediate high energy state over which the reaction proceeds. This high energy state has energies E_f and E_b in excess of those of average energies of reactants and products. This statement can be expressed in another way too, i.e. whenever a reaction occurs, first the reactants come together to form a high energy complex called the *activated complex*, which ultimately leads to the formation of the products. As there is a close analogy between the temperature dependence of the equilibrium constant in Eq. (7.41) and the rate constants in Eqs. (7.44) and (7.45), we can conclude that there exists an equilibrium between the reactants and the activated complex. In fact there may be many complexes in existence during the progress of the reaction under study, but only those having energies in excess of E_f are capable of forming products and are hence referred to as *activated complex*. The energy E_f , as already pointed out, is generally referred to as *activation energy*. We can similarly consider the backward reaction in a system for which the activation energy is E_b .
- (iii) The factors A_f and A_b in Eqs. (7.46) and (7.47), which are related to the constants of integration for Eqs. (7.44) and (7.45) respectively, when considered in the light of the arguments put forward above, denote the number of times the reactants come together which, in turn, may lead to the formation of the products. These factors A_f and A_b are thus termed either *collision frequency* or simply *frequency factor*.

Considerable work has been done to theoretically arrive at the values of frequency factor and activation energy. These efforts can be classified into two categories, namely (i) those based on the concepts of classical physics or mechanics, and (ii) those based on quantum statistical mechanics. Efforts made in the first category led to the development of collision theory whereas those in the second category to the absolute reaction rate theory. Both these theories will be briefly discussed, based on an elementary treatment, in the following subsections.

7.4.1 Collision Theory

This theory is concerned with the calculation of the frequency factor which is taken to be equal to the frequency of collisions of reacting particles with each

other. It was proposed by Lewis in 1918 and is based on the kinetic theory of gases, according to which the frequency of collision A between two molecules of species A and B is given by the equation

$$A = n_A n_B \sigma_{A,B}^2 \left[8\pi k_B T \left(\frac{1}{m_A} + \frac{1}{m_B} \right) \right]^{1/2} \quad (7.48)$$

where $\sigma_{A,B}$ is the mean collision diameter, being equal to the sum ($r_A + r_B$) of radii r_A and r_B respectively of the two reacting species A and B, n_A and n_B are the respective numbers of their molecules in a unit volume of the gas, k_B is the Boltzmann constant, and m_A and m_B are the masses of one molecule of reactants A and B respectively. With Eq. (7.48), the equation for rate J of reaction with an activation energy E , takes the forms

$$J = n_A n_B \sigma_{A,B}^2 \left[8\pi k_B T \frac{m_A + m_B}{m_A m_B} \right]^{1/2} \exp \left(-\frac{E}{kT} \right) \quad (7.49)$$

Hence the specific reaction rate or rate constant k_i will be given by the equation

$$\begin{aligned} k_i &= N \sigma_{A,B}^2 \left[8\pi k_B T \frac{m_A + m_B}{m_A m_B} \right]^{1/2} \exp \left(-\frac{E}{kT} \right) \\ &= A \exp \left(-\frac{E}{kT} \right) \end{aligned} \quad (7.50)$$

where N is the Avogadro's number and k_i is expressed in $\text{L mol}^{-1} \text{ s}^{-1}$ units.

From the experimental data on the study of the kinetics of reactions, we can calculate the values of the frequency factor and the activation energy. Equation (7.50) can also lead to the calculation of these two parameters and a comparison of the experimental and calculated values shows a good agreement for simple molecules behaving as hard spheres. But for complex molecules, the calculated values are found to be much higher than the experimental ones. In order to take into account this disparity in calculations, it was assumed that the orientation of the complex molecules at the time of collision should also be considered. Hence the equation for frequency factor was modified to the form

$$A = p \sigma_{A,B}^2 \left[8\pi k_B T \left(\frac{m_A + m_B}{m_A m_B} \right)^{1/2} \right] \quad (7.51)$$

where p is the probability of a collision occurring in a particular orientation of the colliding species. This formulation presents the difficulty of precisely calculating the value of p for which no exact method is available. Further this theory is unable to explain very high rates of reactions observed in some reacting systems. This theory also cannot explain the rates of opposing reactions which are affected by backward reactions.

To overcome these limitations of the collision theory, Eyring and coworkers proposed a new approach which is discussed below.

7.4.2 Absolute Reaction Rate Theory

This theory is based on statistical quantum mechanics and presents a quantitative approach to both parameters of the rate equation, i.e. the frequency factor and the activation energy. A detailed treatment of this theory is very complex and beyond the scope of the present work. Here we will consider the theory briefly and discuss its salient features only. The inquisitive reader is, however, referred to some standard texts on reaction kinetics.¹

We first consider the significance of activation energy in a chemical reaction. It is evident that for a chemical reaction to take place, the reactants must come together. This results in changes in electronic configuration leading to the formation of some complexes. As the atoms or molecules of reactants approach each other, the interatomic distances change and thus the potential energy of these reactants, which is a function of the interatomic distances, will change. A plot of the potential energy of the reactant vs. interatomic distance is called a *potential energy surface*. It is, therefore, obvious that in the simple case of a reaction between two types of atoms, such a plot will only be a curve whereas for reactions involving three types of atoms it will form a three-dimensional surface, as three different distances shall have to be considered. The dimensions of such a surface shall increase further with the increase in the number of reactants. Values of potential energy of atoms or molecules of the reacting species in these cases are calculated using quantum mechanical methods, i.e. by solving Schrödinger's equation applicable to the system under consideration. A solution of such a complex equation can only be achieved in a few simple cases, and hence we make a number of simplifying assumptions for calculation of potential energy surfaces for most of the common reactions. These potential energy surfaces can be represented in two dimensions by drawing constant energy contours. Such a representation is very similar to the geological mapping of a hilly terrain, which shows contours of constant height. A close examination of these contours reveals that it is characterized by low energy path or paths called a *valley*. During a chemical reaction, it is this path which is followed by the reactants. The interatomic distance axis along this path is referred to as the reaction coordinate. The energy along this path is neither constant nor a monotonic function, but consists of crests, called *cols*, and troughs. The variation of free energy along the reaction coordinate for a reaction having only one col is shown in Fig. 7.5. The configuration of the reactants at such a col is referred to as *activated complex*. Thus the number of cols along the reaction coordinate, while proceeding from reactants to products, represents the number of activated complexes. The difference between the energy of the activated complex and that of the reactants is referred to as *activation energy*.

¹ H. Eyring and M. Eyring, *Modern Chemical Kinetics*, Reinhold Publishing Corp. New York (1963); K.J. Laidler, *Chemical Kinetics*, McGraw-Hill, New York (1973); S. Glasstone, K.J. Laidler and H. Eyring, *Theory of Rate Processes*, McGraw-Hill, New York (1941).

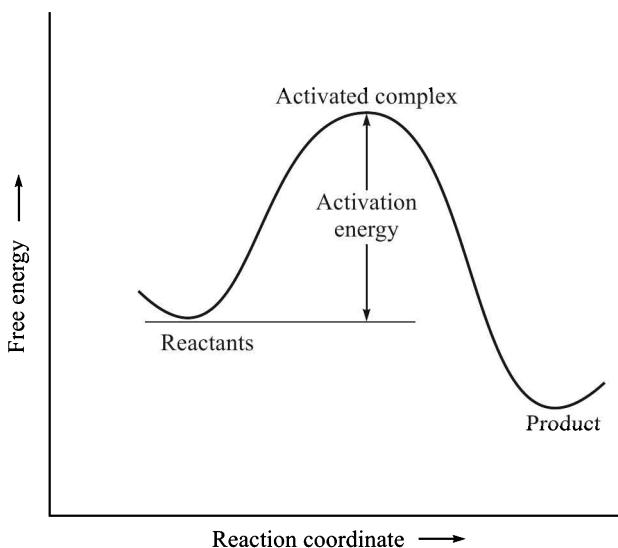
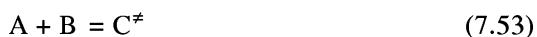


Fig. 7.5 Schematic representation of variation of free-energy along the reaction coordinate.

The activated complexes, because of being in troughs in all other directions except the reaction coordinate, behave like ordinary molecules having vibratory motion in all directions except the one mentioned above. As its movement in either direction along the reaction coordinate will lead to its fall in a trough, it cannot therefore vibrate along this coordinate. Hence its vibrational degree along this coordinate changes to translational. It is this fact which differentiates it from a stable molecule and forms one of the assumptions leading to the mathematical formulation of the reaction kinetics in this theory. Quantum mechanical considerations show that the period of life of an activated complex would be expressed by the term $h/k_B T$, where k_B is the Boltzmann constant and h the Planck's constant and T the absolute temperature of the reacting system. As an activated complex can break either into reaction products or back into reactants, so for the formation of products from the activated complex, we introduce a constant κ (kappa), known as *transmission coefficient*, in the equation for lifetime of the activated complex. Thus the rate of decomposition J^\ddagger of unit concentration of the activated complex into products is expressed by the equation

$$J^\ddagger = \kappa \frac{kT}{h} \quad (7.52)$$

The other assumption is that the formation of the activated complex from the reactants follows the laws of chemical equilibrium. Thus, if reactants A and B lead to the formation of activated complex designated by the symbol C^\ddagger according to the equation



then (assuming activity coefficient to be unity)

$$K^\ddagger \simeq \frac{N_{C^\ddagger}}{N_A N_B} \quad (7.54)$$

where K^\ddagger is the equilibrium constant for the reaction for the formation of activated complex, i.e. Eq. (7.53), and the different N terms refer to concentrations of the species indicated by the respective suffices. From Eq. (7.54), it also follows that the concentration N_{C^\ddagger} of the activated complex can be expressed by the equation

$$N_{C^\ddagger} = K^\ddagger N_A N_B \quad (7.55)$$

Further, the rate \dot{J}_C of the chemical reaction under study will be expressed by the relation

$$\dot{J}_C = J^\ddagger N_{C^\ddagger} \quad (7.56)$$

Substitution of expressions for J^\ddagger and N_{C^\ddagger} from Eqs. (7.52) and (7.55) respectively leads to

$$\dot{J}_C = \kappa \frac{kT}{h} K^\ddagger C_A C_B \quad (7.57)$$

Thus the specific reaction rate \dot{r} of the reaction will be expressed as

$$\dot{r} = \kappa \frac{kT}{h} K^\ddagger \quad (7.58)$$

Further, according to basic thermodynamics, the free energy, enthalpy and entropy of activation and the equilibrium constant for the reaction of formation of the activated complex are related by the equation

$$\begin{aligned} \Delta G^\ddagger &= \Delta H^\ddagger - T\Delta S^\ddagger \\ &= -RT \ln K^\ddagger \end{aligned} \quad (7.59)$$

Hence

$$K^\ddagger = \exp\left(-\frac{\Delta H^\ddagger}{RT}\right) \exp\left(\frac{\Delta S^\ddagger}{R}\right) \quad (7.60)$$

Thus the specific reaction rate \dot{r} is expressed as

$$\dot{r} = \kappa \frac{kT}{h} \exp\left(-\frac{\Delta H^\ddagger}{RT}\right) \exp\left(\frac{\Delta S^\ddagger}{R}\right) \quad (7.61)$$

This relation has been successfully applied to a number of chemical reactions. In the present context, its application to the two important metallurgical reactive systems will be considered in the following section, as illustrative examples. In both cases, it may be pointed out that as indicated in Section 4.3.4 chemical reaction at the interface is the slowest.

7.5 OXIDATION OF CARBON

Oxidation of carbon is an important reaction for chemists, fuel technologists, and chemical and metallurgical engineers. Reaction of carbon with oxygen leads to two gaseous products, namely carbon monoxide and carbon dioxide. The equilibrium ratio of these two gases varies with temperature and pressure and is shown as a function of temperature in Fig. 7.6 under different total pressures. It is seen that as the temperature increases, the fraction of carbon monoxide in the gaseous product mixture increases and at around 1000°C, the product of combustion is predominantly this gaseous species. Formation of carbon monoxide, which is more significant because of the higher temperature conditions in industrial practices, takes place through two chemical reactions, expressed by the following chemical equations



Experimental studies have shown that the reaction expressed by Eq. (7.62) is very fast and the rate of formation of carbon monoxide is controlled by the reaction expressed by Eq. (7.63). Therefore, most of the experimental studies are made on the kinetics of this reaction. These studies have revealed that both the order as well as the specific reaction rate of this reaction vary with pressure and temperature of the experiments. In order to explain these observations, the following theoretical treatment has been proposed for this reaction.

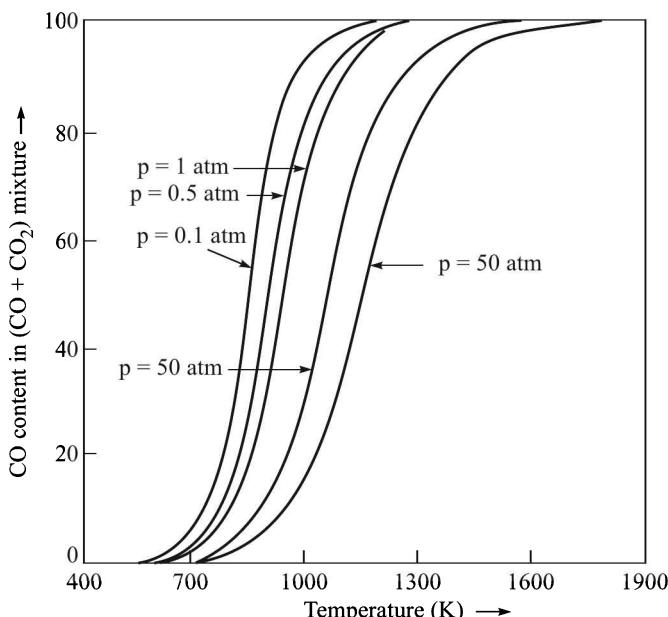
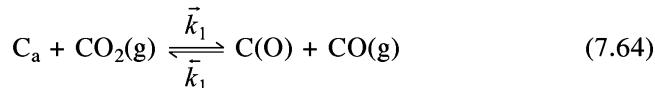
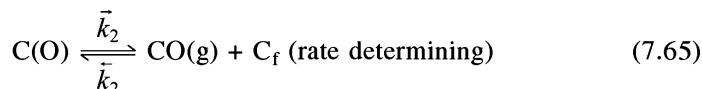


Fig. 7.6 Relationship between equilibrium CO content in (CO + CO₂) mixture and temperature under different total pressures.

Oxidation of carbon by carbon dioxide is a heterogeneous reaction and can be considered to occur in two steps. In the first step, carbon dioxide molecules interact with an active site (C_a) on the surface of carbon particles resulting in the formation of chemisorbed oxygen $C(O)$ at this site and a molecule of gaseous carbon monoxide as expressed by the reaction



In the second step, the chemisorbed oxygen leads to the formation of carbon monoxide and a site C_f from which carbon atom has been removed. This is expressed by the equation



The symbols, \bar{k}_1 , \bar{k}_2 , \bar{k}_1 and \bar{k}_2 in the above equations represent the specific reaction rates of forward and backward reactions as indicated on the reactions. For the mathematical analysis of order of this reaction, we make use of steady state approximation. If $J_{C(O)}$ and J_{CO} be the rates of formation of $C(O)$ and $CO(g)$ respectively, according to the kinetic theory, we can write the following equations for these reactions:

$$J_{C(O)} = \bar{k}_1 [C_a]p_{CO_2} - \bar{k}_1 [C(O)]p_{CO} - \bar{k}_2 [C(O)] + \bar{k}_2 p_{CO}[C_f] \quad (7.66)$$

$$J_{CO} = \bar{k}_1 [C_a]p_{CO_2} - \bar{k}_1 [C(O)]p_{CO} + \bar{k}_2 [C(O)] - \bar{k}_2 [C_f]p_{CO} \quad (7.67)$$

where the square brackets represent the concentrations of components indicated inside them. Further, the rate of consumption of carbon dioxide is given by the equation

$$J_{CO_2} = - \bar{k}_1 [C_a]p_{CO_2} + \bar{k}_1 [C(O)]p_{CO} \quad (7.68)$$

According to steady state approximation

$$J_{C(O)} = 0 \quad (7.69)$$

Thus, from Eq. (7.66) we get

$$[C(O)] = \frac{\bar{k}_1 [C_a]p_{CO_2} - \bar{k}_2 [C_f]p_{CO}}{\bar{k}_1 p_{CO} - \bar{k}_2} \quad (7.70)$$

Also since

$$[C_a] + [C(O)] \equiv n_C \text{ (a constant)} \quad (7.71)$$

and

$$[C_a] = [C_f] \quad (7.72)$$

With the help of Eqs. (7.70), (7.71) and (7.72), we can write the following equations:

$$[\text{C(O)}] = \frac{[\vec{k}_1 p_{\text{CO}_2} + \vec{k}_2 p_{\text{CO}}] n_{\text{C}}}{\vec{k}_2 + \vec{k}_1 p_{\text{CO}} + \vec{k}_1 p_{\text{CO}_2} + \vec{k}_2 p_{\text{CO}}} \quad (7.73)$$

$$[\text{C}_a] = \frac{[\vec{k}_2 + \vec{k}_1 p_{\text{CO}}] n_{\text{C}}}{\vec{k}_2 + \vec{k}_1 p_{\text{CO}_2} + (\vec{k}_1 + \vec{k}_2) p_{\text{CO}}} \quad (7.74)$$

The rate of reaction of carbon dioxide is equal to the rate of production of oxygen-adsorbed sites expressed by Eq. (7.64), which in turn is equal to the rate of consumption of C(O) sites expressed by Eq. (7.65) under steady state conditions. Hence from Eqs. (7.66) and (7.68), we get

$$\begin{aligned} J_{\text{CO}_2} &= \vec{k}_1 [\text{C}_f] p_{\text{CO}_2} + \vec{k}_1 [\text{C(O)}] p_{\text{CO}} \\ &= -\vec{k}_2 [\text{C(O)}] + \vec{k}_2 p_{\text{CO}} [\text{C}_f] \end{aligned} \quad (7.75)$$

Substituting for [C(O)] and [C_f] from Eqs. (7.72)–(7.74) leads to

$$J_{\text{CO}_2} = \frac{-\vec{k}_2 n_{\text{C}} (\vec{k}_1 p_{\text{CO}_2} + \vec{k}_2 p_{\text{CO}}) + \vec{k}_2 p_{\text{CO}} (\vec{k}_2 + \vec{k}_1 p_{\text{CO}}) n_{\text{C}}}{\vec{k}_2 + \vec{k}_1 p_{\text{CO}_2} + (\vec{k}_1 + \vec{k}_2) p_{\text{CO}}} \quad (7.76)$$

It has been shown that \vec{k}_2 is very small. Hence Eq. (7.76) simplifies to

$$J_{\text{CO}_2} = - \frac{\vec{k}_1 n_{\text{C}} p_{\text{CO}_2}}{1 + \frac{\vec{k}_1 p_{\text{CO}_2}}{\vec{k}_2} + \frac{\vec{k}_1 p_{\text{CO}}}{\vec{k}_2}} \quad (7.77)$$

As p_{CO_2} will be high at low temperatures and high pressures, we can therefore assume that

$$\frac{\vec{k}_1}{\vec{k}_2} p_{\text{CO}_2} \gg \left[1 + \frac{\vec{k}_1}{\vec{k}_2} p_{\text{CO}} \right] \quad (7.78)$$

Hence, Eq. (7.77) becomes

$$J_{\text{CO}_2} = - \vec{k}_2 n_{\text{C}} \quad (7.79)$$

i.e. the reaction will be of zero order. This has been found to be the actual case under the already mentioned conditions.

Further, under very low pressures and high temperatures, we have

$$\left(\frac{\vec{k}_1}{\vec{k}_2} p_{\text{CO}_2} + \frac{\vec{k}_1}{\vec{k}_2} p_{\text{CO}} \right) \ll 1 \quad (7.80)$$

Hence, Eq (7.77) would become

$$J_{\text{CO}_2} = - \vec{k}_1 \eta_{\text{C}} p_{\text{CO}_2} \quad (7.81)$$

i.e. the reaction will be of the first order as has also been found in experimental studies. For intermediate temperatures and pressures, the reaction is known to follow Eq (7.77) and will be of fractional order.

7.6 SLAG-METAL REACTION

In pyrometallurgical smelting and refining processes, a multicomponent metallic phase, also containing one or more unwanted or impurity components, is brought in contact with a slag phase which is a mixture of inorganic compounds, generally oxides but in some cases halides too, to remove unwanted components from the former phase. It is well-known that slags are ionic in nature whereas a metal phase is an electronic conductor. Thus during refining of metals, the transfer of any impurity component from metal to slag phase in ionic form will result in the metal phase either with excess or deficiency of electrons. This, in turn, will result in the development of an electrical potential across the slag-metal interface. Thus this interface behaves as an electrified membrane through which ions of different charges flow in such a way as to maintain electrical neutrality of each of the phases. The direction of flow of ions will obviously be such that the electrical potential difference across the interface is neutralized. Such a flow involves the transfer of ions through a number of activation energy barriers existing in the interface. For the sake of simplicity, we consider here that there exists only one activation energy barrier in the interface. Further treatment of the kinetics of interfacial slag-metal reactions can be illustrated with the help of the sulphur transfer reaction between a hot metal and a desulphurizing slag, the behaviour of which in the interfacial region is well-established. The overall desulphurization reaction in ionic form from thermodynamic point of view is expressed by the equation



In the above equation, the square brackets refer to a component present in the metal phase, the parentheses refer to that present in the slag phase, and, the curl brackets to that in the gas phase. The above equation, therefore, states that at the interface, sulphur in the metal phase exchanges its charge with an oxygen ion in the slag phase also present at the interface and the resultant oxygen atom reacts with carbon in the metal phase to form carbon monoxide which escapes in the gas phase. But from the kinetic point of view, this reaction proceeds through a number of electrochemical reaction steps which are not reflected by the overall thermodynamic equation. King and Ramachandran¹ studied the transfer of sulphur from carbon saturated iron to a slag containing lime, alumina and silica. The system was vigorously stirred to reduce the resistance due to mass transport steps as explained in Chapter 4 and to make the reaction predominantly

¹ T.B. King and S. Ramachandran, *Physical Chemistry of Steelmaking*, in J.E Elliot (Ed.), Tech. Press, Cambridge, Mass. and Wiley, New York, p. 125 (1958).

chemically controlled by the interactions across the interface. During the experiments, they took metal and slag samples at regular time intervals and analysed them chemically for the presence of various components therein. The change in the concentration of the different components and the amount of gas evolved are shown in Fig. 7.7 (Hemptinne et al.)¹. This figure shows that apart from transfer of oxygen ions at the interface, which ultimately leads to the formation of carbon monoxide, simultaneous transfer of iron and silicon also occurs first from the metal phase to the slag phase and then in the reverse direction. This fact was explained in terms of a number of electrochemical reactions taking place across the interface. The transfer of sulphur from metal to slag takes place according to the reaction

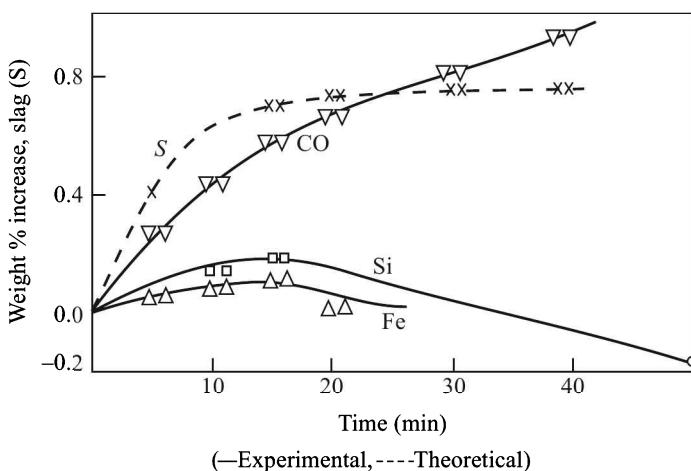
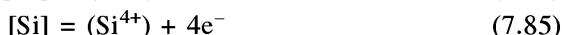


Fig. 7.7 Weight percentage change in sulphur and sulphur-equivalents of silicon and iron in the slag and in carbon monoxide evolved at 1778 K.

In order to neutralize the excess charge, which is due to the deficiency of two electrons in the metal phase, simultaneous transfer of iron and silicon to the slag phase or oxygen to the metal phase can take place according to the following reactions:



The flow of these charged particles affects the electrical potential difference, say E , across the slag-metal interface. This electrical potential results in corresponding changes in the free energy of activation for both

¹ X. De Hemptinne H. Eyring and T. Ree, *Physical Chemistry of Process Metallurgy*, in G.R. St. Pierre (Ed.), Part I, Vol. VII, Interscience, New York, p. 65 (1961).

forward and backward reactions related to the transfer of sulphur from the metal phase to the slag phase. It is assumed that the free energy because of this potential varies uniformly along the reaction coordinate. If \tilde{G}_S^\ddagger be the free energy of activation for the forward reaction, namely the transfer of sulphur from metal to slag under the conditions when no potential difference exists, then under the existence of the potential difference E , this energy, designated by the symbol \tilde{G}_{SE}^\ddagger , will be given by the equation

$$\tilde{G}_{SE}^\ddagger = (\tilde{G}_S^\ddagger - EF) \quad (7.87)$$

where F is the Faraday equivalent.

Thus the rate of transfer of sulphur \vec{J}_S in the forward direction can be expressed according to Eqs. (7.57)–(7.60) and (7.87) as

$$\begin{aligned} \vec{J}_S &= \kappa a_{S,m} \frac{k_B T}{h} \exp\left(-\frac{\tilde{G}_{SE}^\ddagger - EF}{RT}\right) \\ &= \vec{k}_S a_{S,m} \exp\left(\frac{EF}{RT}\right) \end{aligned} \quad (7.88)$$

where

$$\vec{k}_S = \kappa \frac{k_B T}{h} \exp\left(-\tilde{G}_S^\ddagger / RT\right) \quad (7.89)$$

Here $a_{S,m}$ is the activity of sulphur in the metal phase and, \vec{k}_S the specific reaction rate under zero potential conditions. Similarly, the backward reaction rate \vec{J}_S can be expressed as

$$\vec{J}_S = \vec{k}_S a_{S,s} \exp\left(-\frac{EF}{RT}\right) \quad (7.90)$$

where

$$\vec{k}_S = \kappa \frac{k_B T}{h} \exp\left(-\tilde{G}_S^\ddagger / RT\right) \quad (7.91)$$

and the symbols refer to properties in the slag phase and for transfer of sulphur from slag to metal phase. Hence the net rate of transfer J_S of sulphur from metal to slag is given by the equation

$$\begin{aligned} J_S &= \vec{J}_S - \vec{J}_S \\ &= \vec{k}_S a_{S,m} \exp\left(\frac{EF}{RT}\right) - \vec{k}_S a_{S,s} \exp\left(-\frac{EF}{RT}\right) \end{aligned} \quad (7.92)$$

Similarly, we can write the following equations for the net rates, J_{Fe} , J_{Si} and J_O in respect of transfer of iron, silicon and oxygen respectively,

$$J_{Fe} = \vec{J}_{Fe} - \vec{J}_{Fe}$$

$$= \bar{k}_{\text{Fe}} a_{\text{Fe, m}} \exp\left(-\frac{EF}{RT}\right) - \bar{k}_{\text{Fe}} a_{\text{Fe, s}} \exp\left(\frac{EF}{RT}\right) \quad (7.93)$$

$$\begin{aligned} J_{\text{Si}} &= \bar{J}_{\text{Si}} - \bar{J}_{\text{Si}} \\ &= \bar{k}_{\text{Si}} a_{\text{Si, m}} \exp\left(-\frac{2EF}{RT}\right) - \bar{k}_{\text{Si}} a_{\text{Si, s}} \exp\left(-\frac{2EF}{RT}\right) \end{aligned} \quad (7.94)$$

$$\begin{aligned} J_{\text{O}} &= \bar{J}_{\text{O}} - \bar{J}_{\text{O}} \\ &= 0 - \bar{k}_{\text{O}} a_{\text{O, s}} \exp\left(-\frac{EF}{RT}\right) \end{aligned} \quad (7.95)$$

In Eq. (7.95), the rate of transfer of oxygen ions from metal to slag is taken to be equal to zero as dissolved oxygen in carbon-saturated iron will be very small, maintaining a constant level. Oxygen ions transferred from slag to metal will react with carbon to form gaseous carbon monoxide. So, J_{O} will also be equal to the rate of evolution of carbon monoxide gas from the system.

As the value of E in the above equations is not measured, Hemptinne et al.¹ proceeded as follows to calculate the amounts of various species transferred across the interface.

- (i) It was assumed that during the experiment, the activity of oxygen ion in the slag remained practically constant, which is true for small amounts of transfer of sulphur as was the case in the experimental work of King and Ramachandran.² Thus from Eq. (7.95), we get

$$J_{\text{CO}} \equiv -\bar{J}_{\text{O}} = \bar{k}_{\text{O}} a_{\text{O, s}} \exp\left(-\frac{EF}{RT}\right) \quad (7.96)$$

or

$$\exp\left(\frac{EF}{RT}\right) = \frac{\bar{k}_{\text{O}} a_{\text{O, s}}}{J_{\text{CO}}} \quad (7.97)$$

- (ii) Further, we can conveniently assume the activity of iron in the metal-phase $a_{\text{Fe, m}}$ to be equal to unity and write the following equation by coupling Eqs. (7.93) and (7.97)

$$\begin{aligned} J_{\text{Fe}} &= \frac{\bar{k}_{\text{Fe}}}{k_{\text{O}} a_{\text{O}}} J_{\text{CO}} - \frac{\bar{k}_{\text{Fe}} a_{\text{Fe, s}}}{J_{\text{CO}}} \bar{k}_{\text{O}} a_{\text{O}} \\ &= A_1 J_{\text{CO}} - A_2 a_{\text{Fe, s}} (J_{\text{CO}})^{-1} \end{aligned} \quad (7.98)$$

where A_1 and A_2 are constants.

¹ X. De Hemptinne, H. Eyring and T. Ree, *Physical Chemistry of Process Metallurgy*, in St. Pierre (Ed.), Part I, Vol. VII, Interscience, New York, p. 65 (1961).

² T.B. King and S. Ramachandran, *op. cit.*

Similarly, we can write

$$J_{\text{Si}} = A_3 a_{\text{Si}, \text{m}} J_{\text{O}}^2 - A_4 a_{\text{Si}, \text{s}} J_{\text{O}}^{-2} \quad (7.99)$$

Finally, considering the requirement of electroneutrality

$$J_{\text{S}} = J_{\text{CO}} + J_{\text{Fe}} + J_{\text{Si}} \quad (7.100)$$

Hamptinne et al.¹ also integrated Eqs. (7.98) and (7.99) under the conditions prevailing in the experimental work of King and Ramachandran, namely that initially the slag contained no iron and sulphur and $a_{\text{Si}, \text{s}}$ remained practically constant throughout the experiments. They also found a good correspondance between experimental and theoretical plots as shown in Fig. 7.7. This figure also shows an interesting feature that in the initial stages of desulphurization, iron and silicon increase in the slag phase and after some time get reverted to metal phase.

REVIEW QUESTIONS

1. What is meant by the order of a chemical reaction? In what respects does the order of a reaction differ from the molecularity of the reaction?
2. Enumerate and briefly outline the different methods which can be used to determine the order of a reaction. Which method do you think is the most convenient and which the most accurate?
3. Explain how the following methods can be used to determine the order of a reaction:
 - (i) Integration method
 - (ii) Differential method
 - (iii) Half-life period method
4. What is Arrhenius equation? Explain the significance of the different terms in the Arrhenius equation in reaction kinetics.
5. Discuss the guidelines for arriving at the mechanism of a reaction.
6. Explain how the Arrhenius equation can be derived from the van't Hoff equation.
7. What is an activated complex? Discuss its different properties and explain its significance in the theory of absolute reaction rates.
8. Explain the basic principles of the collision theory of reaction rates pointing out its scope and limitations.
9. Discuss the significance of activation energy in a chemical reaction. How can the activation energy be obtained for any reaction?
10. What are the basic postulates of the theory of absolute reaction rate? Derive the rate equation based on this theory.
11. How does the theory of absolute reaction rate compare with the Arrhenius equation?

¹ X. De Hemptinne, H. Eyring and T. Ree, *op. cit.*

12. Explain in brief the application of the theory of absolute reaction rates to any particular reaction.
13. Discuss the slag-metal reactions in the light of absolute reaction rate theory.
14. Discuss the mechanism of oxidation of carbon by carbon dioxide. Derive the rate equation on the basis of steady state approximation.

PROBLEMS

1. The initial rate of a first order reaction is $7.6 \times 10^{-6} \text{ mol L}^{-1} \text{ s}^{-1}$ and the initial reactant concentration is 0.098 mol L^{-1} . Calculate the
 - (i) rate constant from the initial rate;
 - (ii) reaction half-life;
 - (iii) time required for the reaction to reach (a) 25% and (b) 75% completion.
2. The half-life period of a first order reaction is 30 minutes. What percentage of the reactant would remain after 2 hours?
3. Bismuth has a half-life of $1.6 \times 10^3 \text{ s}$. Assuming first order reaction, calculate its rate constant for disintegration. How much disintegration will occur from 1 mg of bismuth in 1 min?
4. A second order reaction with reactants initially present at 0.5 mol L^{-1} is found to be 25% complete in 60 minutes. Calculate the
 - (i) rate constant;
 - (ii) half-life period;
 - (iii) time taken for the reaction to be 75% complete.
5. It is observed that the decomposition of HI to H₂ and I₂ at 508°C has a half-life of 270 minutes when the initial pressure is 0.05 atm, and 27 minutes when the pressure is 0.5 atm. (a) Prove that the reaction is of the second order. (b) Find the values of the rate constant in $\text{atm}^{-1} \text{ s}^{-1}$. (c) Calculate the rate constant in $\text{L-mol}^{-1} \text{ s}^{-1}$.
6. The following data were obtained for a chemical reaction:

Time, min	0	16	36	43	52
Conc., mol L ⁻¹ × 10 ⁻³	20.40	10.30	5.18	4.16	3.13

 - (a) Determine the order of reaction by the method of integration.
 - (b) Calculate the rate constant.
7. Using the differential method, find the order of reaction and the rate constant of a reaction with the following data:

Time, min	0	9.82	59.60	93.18	142.90	294.8
Conc., %	100	96.5	80.3	71.0	59.1	32.8
8. The thermal decomposition of nitrous oxide in the gas phase was studied by recording the change in total pressure with time. The half-

life period at 757°C was found to vary with the initial pressure as follows:

Initial pressure, mm Hg	52.5	139	290	360
$t_{1/2}$, s	860	470	255	212

Find the reaction order.

9. The rate constant of a reaction at 40°C is three times that at 20°C. Calculate the experimental activation energy.
10. Two second order reactions have identical frequency factors, but their activation energies differ by 20.9 kJ. Calculate the ratio of their rate constants at 500°C.
11. The activation energy of a given reaction is suddenly changed from 125.4 kJ/mole to 250.8 kJ/mole at the same temperature. What is the corresponding change in the rate of reaction?
12. Calculate the activation energy for the decompositon of hydrogen iodide if the rate constant is $3.95 \times 10^{-6} \text{ L}\cdot\text{mol}^{-1} \text{ s}^{-1}$ at 321.4°C and $1.07 \times 10^{-6} \text{ L}\cdot\text{mol}^{-1} \text{ s}^{-1}$ at 300°C. Assume that the decomposition follows a second order behaviour.
13. The diffusion rate of carbon in alpha titanium was determined at the following temperatures:

Temp °C	Diffusion coefficient, D
736	2×10^{-9}
782	5×10^{-9}
835	1.3×10^{-8}

Determine whether the equation $D = Ae^{-E/RT}$ applies and evaluate the frequency factor A and activation energy E.

14. The viscosity of water changes about 2% per degree at room temperature. What is the activation energy for this process?
15. The rate constant and the experimental activation energy for a chemical reaction are $6.3 \times 10^5 \text{ s}^{-1}$ and 49.66 kJ respectively at 27°C. Calculate the entropy and the free energy of activation using the theory of absolute reaction rates. Given that:

Boltzmann constant, $k_B = 1.38 \times 10^{-16} \text{ erg deg}^{-1}$

Planck's constant, $h = 6.625 \times 10^{-27} \text{ erg s}$.

Coupled Phenomenon

In most of the metallurgical processes, simultaneous transfer of mass, momentum and heat takes place. As already pointed out in Chapter 1, the analysis of all the three aspects of the transport phenomena is based on similar principles, viz. the conservation of mass and energy and the linear relationship between fluxes and forces. Thus, it should be possible to correlate the rates of all the three modes of transport phenomena. This aspect will be discussed in Section 8.1 under transport coupling.

There is yet another aspect of the kinetics of processes related to irreversible thermodynamics, according to which all natural processes are associated with the production of entropy. The expressions for entropy-production coupled with conservation laws and phenomenological rate expressions, lead to another set of coupling, which may be referred to as *thermodynamic coupling*. These couplings can take place among different chemical reactions or among various transport processes. The former group is called the *scalar coupling* whereas the latter is called the *vectorial coupling*. However, discussion on these types of couplings is considered beyond the scope of the present work. We will therefore now consider transport coupling.

8.1 TRANSPORT COUPLING

As momentum, heat and mass transfer are analogous processes, the correlations among them are expressed in terms of proposed by different workers. Some of the important ones among them are discussed in the following subsections.

8.1.1 Reynolds' Analogy between Heat and Momentum Transfer¹

The transfer of heat between a surface and a fluid follows the same laws as in respect of exchange of momentum between them. It should, therefore, be

¹ O. Reynolds, Proc. Manchester Lit. Phil. Soc. 8 (1874), reprinted in *Scientific Papers of Osborne Reynolds*, Vol. II. Cambridge University Press, London (1901).

possible to predict the rate of heat transfer from the rate of momentum transfer and also to predict the temperature profiles from the velocity profiles. Reynolds was the first to express the analogy between heat and momentum transfer in a mathematical form. In this treatment, called *Reynolds analogy*, he assumed that thermal and kinematic equilibria are reached when an element of fluid comes in contact with the boundary of a solid surface. Further, during the movement of fluid from the bulk of the fluid to the solid surface, no mixing with the intermediate fluid takes place. This state of heat and momentum transfer is represented in Fig. 8.1. The relationship between the rates of heat and momentum transfer for this system can be derived as follows:

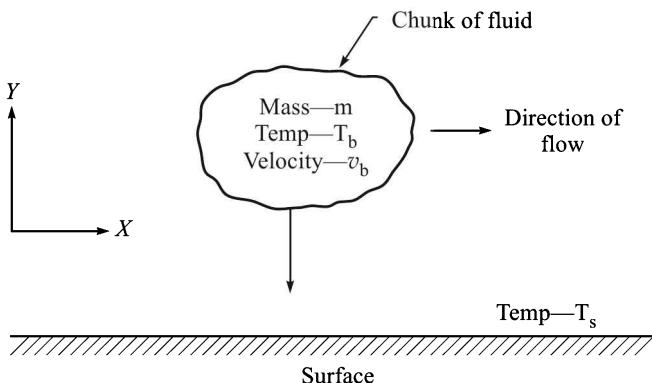


Fig. 8.1 Heat and momentum transferred by a chunk of fluid to a surface—Reynolds' analogy.

Consider a fluid flowing in the x -direction with a bulk velocity v_b and heat and momentum transfer taking place in the y -direction. Suppose a chunk of fluid of mass m travels in time t from the bulk of the fluid to the solid surface owing to turbulence and gives up its heat and momentum to it. Thus,

$$\text{Momentum transferred in time, } t = mv_b \quad (8.1)$$

Similarly

$$\text{Heat transferred in time, } t = mC_p(T_b - T_s) = -qA \quad (8.2)$$

where q is the heat transferred per unit time per unit area from the surface, C_p is the heat capacity of the fluid, T_b and T_s are the bulk fluid temperature and surface temperature in K respectively and A is the surface area. If the shear stress at the surface be τ_0 , then we can write the equation for the force F causing motion as follows

$$F = -\tau_0 A = \frac{mv_b}{t} \quad (8.3)$$

Eliminating m from Eqs. (8.2) and (8.3) and rearranging the terms, we get

$$\frac{C_p(T_b - T_s)}{v_b} = +\frac{q}{\tau_0} \quad (8.4)$$

Further, making use of the definition of heat transfer coefficient h and friction factor f_{fr} , we can write the equation

$$\frac{q}{T_b - T_s} \equiv h = \frac{\tau_0 C_p}{v_b} \quad (8.5)$$

or

$$\frac{h}{C_p \rho v_b} = \frac{\tau_0}{\rho v_b^2} = \frac{1}{2} f_{fr} \quad (8.6)$$

Further since the dimensionless number, i.e. Stanton number N_{St} is defined as

$$\frac{h}{C_p \rho v_b} = N_{St} \quad (8.7)$$

Hence, from Eq. (8.6), we get

$$N_{St} = \frac{1}{2} f_{fr} \quad (8.8)$$

Equation (8.8) represents the simple correlation between the heat transfer coefficient and the friction factor. The above treatment is very simple, but it suffers from the following drawbacks:

- (i) No allowance has been made for variation in physical properties of the fluid with temperature.
- (ii) Existence of laminar sublayer close to the surface has been ignored.
- (iii) No intermediate mixing has been assumed.
- (iv) Fluid is assumed to come to rest when it touches the surface.

Therefore, the use of Eq. (8.8) only yields an approximate correlation between heat and momentum transfer.

Application of the relationships derived above is illustrated by the following example.

EXAMPLE 8.1 Hot water at 80°C is flowing over a flat plate at the rate of 5 m s⁻¹. Calculate the rate of heat transfer to the plate which is at a temperature of 40°C. The heat capacity and the density of water may be taken as 4200 J kg⁻¹ K⁻¹ and 1000 kg m⁻³ respectively. The corresponding friction factor is given as 0.005.

Solution The given data is:

Average velocity, $v_b = 5 \text{ m s}^{-1}$

Heat capacity of water, $C_p = 4200 \text{ J kg}^{-1} \text{ K}^{-1}$

Density of water, $\rho = 1000 \text{ kg m}^{-3}$

Friction factor, $f_{fr} = 0.005$

Using Eq. (8.6), heat transfer coefficient h is given by

$$h = \frac{1}{2} f_{fr} C_p \rho v_b$$

$$\begin{aligned}
 &= \frac{1}{2} \times 0.005 \times 4200 \times 1000 \times 5 \\
 &= 52500 \text{ W m}^{-2} \text{ K}^{-1}
 \end{aligned}$$

Temperature of bulk water, $T_b = 80^\circ\text{C} = (80 + 273) \text{ K} = 353 \text{ K}$

Temperature of solid surface, $T_s = 40^\circ\text{C} = (40 + 273) \text{ K} = 313 \text{ K}$

Using Eq. (8.5), the heat transfer rate q is

$$\begin{aligned}
 q &= h(T_b - T_s) \\
 &= 52500(353 - 313) \\
 &= 2.1 \times 10^6 \text{ W m}^{-2} \quad \text{Ans.}
 \end{aligned}$$

To overcome some of the above-mentioned limitations of Reynolds' analogy, several modifications have been suggested. The most important among these is the modification suggested by Prandtl which we will deal with briefly at a later stage.

8.1.2 Reynolds' Analogy between Mass and Momentum Transfer¹

We now consider the flow of a multicomponent fluid. If there is a concentration gradient existing in the fluid, the transfer of a chunk of fluid from the bulk to any interface, which can be provided either by the bounding surface or by any submerged object, will result in the net transfer of mass of some components. Thus, the mass transfer in such cases will also be accompanied by the transfer of momentum. Hence these two may be related to each other. To arrive at the relationship between these two parameters, we consider a two-component system containing fluids A and B. We further assume that a chunk of volume V , having ρ_A^b and ρ_B^b as their respective densities in bulk, travels to the interface as shown in Fig. 8.2. Thus the amounts W_A and W_B of components A and B brought to the surface can be expressed respectively by the relation

$$W_A = V\rho_A^b \quad (8.9)$$

and

$$W_B = V\rho_B^b \quad (8.10)$$

The incoming fluid of volume V will replace an equivalent volume V of the fluid in contact with the surface. Thus the amounts W'_A and W'_B of components A and B moving away from the surface will be respectively

$$W'_A = V\rho_A^s \quad (8.11)$$

and

$$W'_B = V\rho_B^s \quad (8.12)$$

¹ O. Reynolds, *ibid.*

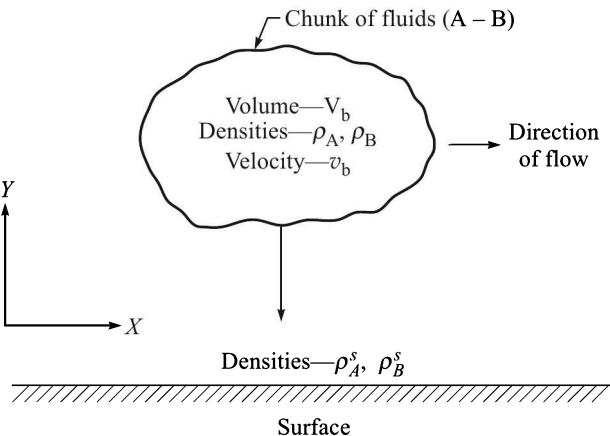


Fig. 8.2 Mass and momentum transferred by a chunk of multicomponent fluid to a surface—Reynolds' analogy.

where ρ_A^s and ρ_B^s are the densities of the components A and B respectively at the surface. Thus, the net amount ($W_A - W'_A$) of component A brought to the surface will be

$$W_A - W'_A = V(\rho_A^b - \rho_A^s) \quad (8.13)$$

Similarly, the net amount of component B brought to the surface will be

$$W_B - W'_B = V(\rho_B^b - \rho_B^s) \quad (8.14)$$

If A be the contact area of the volume element and t the time taken for the transfer of this amount, the rate J_A of transfer of A can be written as

$$J_A tA = V(\rho_A^b - \rho_A^s) \quad (8.15)$$

J_A in the above equation is the mass flux of component A. Similarly, the rate of transfer of momentum may be written as

$$\frac{\rho V v_b}{rA} = \tau_0 \quad (8.16)$$

where v_b is the bulk velocity of the fluid. Thus,

$$V = \frac{\tau_0 t A}{\rho v_b} \quad (8.17)$$

Substituting this value of V in Eq. (8.15), we get

$$J_A tA = \frac{\tau_0 t A (\rho_A^b - \rho_A^s)}{\rho v_b} \quad (8.18)$$

or

$$\frac{J_A}{\rho_A^b - \rho_A^s} = \frac{\tau_0}{\rho v_b} \quad (8.19)$$

Therefore, the mass transfer coefficient $k_{m,A}$ of component A which equals the LHS of Eq. (8.19) will be expressed as

$$k_{m,A} = \frac{\tau_0}{\rho v_b} \quad (8.20)$$

or we can write

$$\frac{k_{m,A}}{v_b} = \frac{1}{2} \left(\frac{\tau_0}{\rho v_b^2 / 2} \right) = \frac{1}{2} f_{fr} \quad (8.21)$$

The above equation gives the relationship between the mass transfer coefficient and the friction factor. Though this equation is simple, it can only yield approximate results owing to the following reasons:

- (i) It is assumed that during the travel of the fluid element from the bulk to the surface, no mixing with the intermediate fluid takes place.
- (ii) The effect of laminar sub layer has been neglected.

Application of the above equations is now illustrated below by an example.

EXAMPLE 8.2 Liquid steel saturated with oxygen at 0.16% by weight is moving towards the surface of a container at a speed of 2 m s^{-1} . The surface layer is having a composition of 0.04% oxygen. The densities of oxygen in the bulk and at the surface are 1.43 kg m^{-3} respectively. If the mass transfer coefficient of oxygen in steel is $1.66 \times 10^{-4} \text{ m s}^{-1}$, calculate the friction factor and the mass flux rate of oxygen in steel.

Solution Given

Velocity of liquid steel, $v_b = 2 \text{ m s}^{-1}$

Mass transfer coefficient, $k_m = 1.66 \times 10^{-4} \text{ m s}^{-1}$

Using Eq. (8.21), we get

$$\frac{k_m}{v_b} = \frac{1}{2} f_{fr}$$

or

$$\frac{1.66 \times 10^{-4}}{2} = \frac{1}{2} f_{fr}$$

Therefore

$$\text{Friction factor, } f_{fr} = 1.66 \times 10^{-4} \quad \text{Ans.}$$

Now the density of oxygen in bulk, $\rho_O^b = 1.43 \text{ kg m}^{-3}$
and density of oxygen at surface, $\rho_O^s = 1.41 \text{ kg m}^{-3}$

Using Eqs. (8.19) and (8.20), mass flux rate J is given by

$$\begin{aligned} J &= k_m (\rho_O^b - \rho_O^s) \\ &= 1.66 \times 10^{-4} (1.43 - 1.41) \end{aligned}$$

$$\begin{aligned}
 &= 1.66 \times 0.02 \times 10^{-4} \\
 &= 3.32 \times 10^{-6} \text{ kg m}^{-2} \text{ s}^{-1} \quad \text{Ans.}
 \end{aligned}$$

8.1.3 Prandtl's Analogy between Heat and Momentum Transfer¹

Prandtl, in the analysis of simultaneous heat and momentum transfer, assumed the existence of the laminar sublayer but ignored the existence of a buffer layer or the turbulent boundary layer. Thus he assumed that Reynolds' analogy was applicable only from the main stream to the edge of the laminar sublayer and the transfer through the laminar sublayer was assumed to be attributed solely to molecular motion. Thus, the application of Reynolds' analogy Eq. (8.4) to the region between the main stream and the boundary of laminar sublayer yields

$$\frac{q}{\tau_{LS}} = \frac{C_p(T_b - T_{LS})}{v_b - v_{LS}} \quad (8.22)$$

where T_{LS} is the temperature, τ_{LS} the stress and v_{LS} the velocity of flow at the edge of the laminar sublayer, and v_b and T_b are the bulk velocity in the x -direction and bulk temperature respectively.

The rate of heat transfer q through the laminar sublayer can be expressed as

$$q = -k \frac{T_{LS} - T_s}{\delta_{LS}} \quad (8.23)$$

where T_s is the temperature of the surface.

Also, for the laminar sublayer, the thickness, velocity and shear stress are related as

$$\tau_{LS} = -\frac{\mu v_{LS}}{\delta_{LS}} \quad (8.24)$$

From Eqs. (8.23) and (8.24), we get

$$\frac{q}{\tau_{LS}} = \frac{k}{\mu} \frac{(T_{LS} - T_s)}{v_{LS}} = \frac{k}{\mu} \frac{(T_{LS} - T_s)}{(T_b - T_s)} \left(\frac{v_b}{v_{LS}} \right) \left(\frac{T_b - T_s}{v_b} \right) \quad (8.25)$$

Making use of Eqs. (8.22) and (8.25), we get

$$\frac{k(T_{LS} - T_s)}{\mu v_{LS}} = \frac{C_p(T_b - T_{LS})}{(v_b - v_{LS})} \quad (8.26)$$

which can also be written as

$$\left(\frac{1 - \beta}{\beta} \right) (N_{Pr}) = \left(\frac{1 - \alpha}{\alpha} \right) \quad (8.27)$$

where N_{Pr} is the Prandtl number, i.e. $C_p \mu / k$,

$$\beta = \frac{T_{LS} - T_s}{T_b - T_s} \quad (8.28)$$

¹ L. Prandtl, Z. Physick, 11, 1073 (1910), 29, 487 (1928).

and

$$\alpha = \frac{v_{LS}}{v_b} \quad (8.29)$$

Rearrangement of Eq. (8.27) yields

$$\beta = \frac{\alpha N_{Pr}}{N_{Pr}\alpha + (1 - \alpha)} = \frac{\alpha N_{Pr}}{1 + \alpha(N_{Pr} - 1)} \quad (8.30)$$

Now Eq. (8.25) can be written as

$$\frac{q}{\tau_{LS}} = \frac{k}{\mu} \frac{\beta}{\alpha} \left(\frac{T_b - T_s}{v_b} \right)$$

Since

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

we have by using Eq. (8.30),

$$\frac{q}{\tau_{LS}} = \frac{C_p(T_b - T_s)}{v_b} \left[\frac{1}{1 + \alpha(N_{Pr} - 1)} \right] = + \frac{h(T_b - T_s)}{f_{fr} \left(\frac{1}{2} \rho v_b^2 \right)} \quad (8.31)$$

because

$$q = h(T_b - T_s) \quad \text{and} \quad f_{fr} = \frac{2\tau_{LS}}{\rho v_b^2}$$

Hence

$$N_{St} \equiv \frac{h}{C_p \rho v_b} = \frac{f_{fr}/2}{1 + \alpha(N_{Pr} - 1)} \quad (8.32)$$

Analysis of experimental data on fluid flow has yielded the following relations for α with N_{Re} .

(i) For flow over a smooth plane surface,

$$\alpha = 2.1 (N_{Re})^{-0.1} \quad (8.33)$$

(ii) For flow through a pipe,

$$\alpha = 2.0 (N_{Re})^{-1/8} \quad (8.34)$$

By comparison of Eq. (8.8) with (8.32), it is seen that Prandtl's analogy provides a correction factor $\{1/[1 + \alpha(N_{Pr} - 1)]\}$ over Reynolds' analogy. The value of this correction factor is found to be equal to unity in the following cases:

- (i) In respect of the flow of gases, for which $N_{Pr} = 1$.
- (ii) In respect of the highly turbulent flow, since in this case the laminar sublayer will be very small; hence its effect can be neglected. Therefore in these cases Reynolds' and Prandtl's analogies will yield the same results.

Application of the above equations is now illustrated below by an example.

EXAMPLE 8.3 With the data given in Example 8.1, calculate the heat transfer coefficient at a distance of 20 cm from the leading edge, using Prandtl's analogy, given that the Prandtl number for water at 80°C is 2 and the viscosity of water is $3.0 \times 10^{-4} \text{ kg m}^{-1} \text{ s}^{-1}$.

Solution The given data is:

Distance from the leading edge, $x = 20 \text{ cm} = 0.2 \text{ m}$

Density of water, $\rho = 1000 \text{ kg m}^{-3}$

Average velocity, $v_x = 5 \text{ m s}^{-1}$

Viscosity, $\mu = 3.0 \times 10^{-4} \text{ kg m}^{-1} \text{ s}^{-1}$

Reynolds number at distance x is

$$\begin{aligned} N_{\text{Re}, x} &= \frac{v_x \rho x}{\mu} \\ &= \frac{5 \times 1000 \times 0.2}{3.0 \times 10^{-4}} = 3.33 \times 10^6 \end{aligned}$$

Factor α from Eq. (8.33) is

$$\begin{aligned} \alpha &= 2.1 (N_{\text{Re}, x})^{-0.1} \\ &= 2.1 \times (3.33 \times 10^6)^{-0.1} \\ &= 0.49 \end{aligned}$$

Prandtl number, $N_{\text{Pr}} = 2$.

Using Eq. (8.32), we have

$$\begin{aligned} h &= \frac{1}{2} f_{\text{fr}} C_p \rho v_x \left[\frac{1}{1 + \alpha(N_{\text{Pr}} - 1)} \right] \\ &= \frac{1}{2} \times 0.005 \times 4200 \times 1000 \times 5 \times \left[\frac{1}{1 + 0.49(2-1)} \right] \\ &= 35240 \text{ W m}^{-2} \text{ K}^{-1} \quad \text{Ans.} \end{aligned}$$

8.1.4 Prandtl's Analogy between Mass and Momentum Transfer¹

Though various modifications of Reynolds' analogy have been suggested, the one suggested by Prandtl takes into account the effect of laminar sublayer and is the most popular and useful. Prandtl assumed that the transfer of the volume element V takes place by turbulent flow only up to the boundary of laminar sublayer and the transfer of components in the laminar sublayer takes place only by diffusion. Thus if ρ_A^{LS} and ρ_B^{LS} be the concentrations of components A and B, respectively, in the fluid at the outer edge of the laminar sublayer and ρ_A^b and ρ_B^b be their bulk concentrations, then according to Reynolds' analogy we can write Eq. (8.15) as

$$J_A At = V(\rho_A^b - \rho_A^{\text{LS}}) \quad (8.35)$$

¹ L. Prandtl, *ibid.*

Similarly for momentum transferred from bulk to the outer edge of the boundary layer, we get for the shearing stress at surface τ_0 the equation,

$$\tau_0 A t = V \rho (v_b - v_{LS}) \quad (8.36)$$

where ρ is the density of the bulk fluid.

Dividing Eq. (8.35) by Eq. (8.36), we get

$$\frac{J_A}{\tau_0} = \frac{\rho_A^b - \rho_A^{LS}}{\rho (v_b - v_{LS})} \quad (8.37)$$

For diffusion of component A from the outer edge of the boundary layer to the surface, we can write

$$J_A = -D \frac{\rho_A^{LS} - \rho_A^s}{\delta_{LS}} \quad (8.38)$$

where ρ_A^s is the concentration of component A at the surface and δ_{LS} is the thickness of laminar sublayer.

It should be noted that since δ_{LS} is small, the gradient is replaced by the concentration difference divided by δ_{LS} in Eq. (8.38). Similarly, for momentum transfer, we have

$$\tau_0 = -\mu \frac{v_{LS}}{\delta_{LS}} \quad (8.39)$$

Dividing Eq. (8.38) by Eq. (8.39) and using Eq. (8.37), we get

$$\frac{J_A}{\tau_0} = \frac{D(\rho_A^{LS} - \rho_A^s)}{\mu v_{LS}} = \frac{\rho_A^{LS} - \rho_A^s}{\rho N_{Sc} v_{LS}} = \frac{\rho_A^b - \rho_A^{LS}}{\rho (v_b - v_{LS})} \quad (8.40)$$

where N_{Sc} is the Schmidt number given by $\mu/\rho D$.

From the last two terms of this equation after rearrangement and introducing $\alpha = v_{LS}/v_b$, we get

$$\frac{\rho_A^{LS} - \rho_A^s}{\rho_A^b - \rho_A^{LS}} = \frac{\alpha N_{Sc}}{(1 - \alpha) + \alpha N_{Sc}}$$

or

$$\rho_A^{LS} - \rho_A^s = \frac{(\rho_A^b - \rho_A^s)\alpha N_{Sc}}{(1 - \alpha) + \alpha N_{Sc}} \quad (8.41)$$

From Eqs. (8.40) and (8.41), we get

$$\begin{aligned} \frac{J_A}{\tau_0} &= \frac{D(\rho_A^b - \rho_A^s)\alpha N_{Sc}}{\mu v_{LS}\{(1 - \alpha) + \alpha N_{Sc}\}} \\ &= \frac{D(\rho_A^b - \rho_A^s)v_{LS}\mu}{\mu v_{LS}\{(1 - \alpha) + \alpha N_{Sc}\}v_b\rho D} \\ &= \frac{\rho_A^b - \rho_A^s}{\rho v_b\{(1 - \alpha) + \alpha N_{Sc}\}} \end{aligned}$$

But from the definitions of J_A and τ_0 , we have

$$\frac{J_A}{\tau_0} = \frac{k_{m,A}(\rho_A^b - \rho_A^s)}{f_{fr}\rho v_b^2/2}$$

where $k_{m,A}$ is the mass transfer coefficient and f_{fr} the friction factor. Therefore,

$$\frac{(\rho_A^b - \rho_A^s)}{\rho v_b \{(1-\alpha) + \alpha N_{Sc}\}} = \frac{k_{m,A}(\rho_A^b - \rho_A^s)}{f_{fr}\rho v_b^2/2} \quad (8.42)$$

Thus

$$\frac{k_{m,A}}{v_b} = \frac{f_{fr}/2}{(1-\alpha) + \alpha N_{Sc}} \quad (8.43)$$

It will be observed that the factor $[(1 - \alpha) + \alpha N_{Sc}]^{-1}$ serves as a correction factor to Reynolds' analogy. As for gases and for highly turbulent fluids, this factor is approximately equal to unity, so Reynolds' analogy holds good in such cases.

8.1.5 Chilton-Colburn¹ Analogy among Heat, Mass and Momentum Transfer

Chilton-Colburn developed useful empirical data which correlated mass transfer and heat transfer coefficients to the friction factor. Dimensional analysis formed the basis of their analysis. For heat transfer, the functional relation for the Nusselt number N_{Nu} is expressed as

$$N_{Nu} = N_{Nu}(N_{Re}, N_{Pr}) \quad (8.44)$$

where N_{Re} and N_{Pr} are the Reynolds and Prandtl numbers respectively. Similarly, for mass transfer, the Sherwood number N_{Sh} is expressed by the functional relation

$$N_{Sh} = N_{Sh}(N_{Re}, N_{Sc}) \quad (8.45)$$

where N_{Sc} is the Schmidt number.

Also, dimensional analysis of the friction factor yields the functional relation

$$f_{fr} = f_{fr}(N_{Re}) \quad (8.46)$$

For example, for convective heat and mass transfer for the flow through a pipe, the above relations, using empirical data, take the following analytical forms:

$$N_{Nu} = 0.023 (N_{Re})^{0.8} (N_{Pr})^{0.33} \quad (8.47)$$

$$N_{Sh} = 0.023 (N_{Re})^{0.83} (N_{Sc})^{0.33} \quad (8.48)$$

$$f_{fr} = 0.046 (N_{Re})^{-0.2} \quad (8.49)$$

To arrive at the relationships among the above three variables, Chilton-Colburn defined two new functions known as j -factors which are designated for the

¹ T.H. Chilton and A.P. Colburn, *Ind. Engg. Chem.*, **26**, 1183 (1934).

mass transfer as j_M and for the heat transfer as j_H . These functions are defined by the equations

$$j_M = \frac{N_{Sh}}{(N_{Re})(N_{Sc})^{1/3}} \quad (8.50)$$

and

$$j_H = \frac{N_{Nu}}{(N_{Re})(N_{Pr})^{1/3}} \quad (8.51)$$

Thus for flow through pipes, these functional relations assume the following forms with the help of Eqs. (8.47)–(8.49).

$$j_M = 0.023 (N_{Re})^{-0.17} \simeq 0.023 (N_{Re})^{-0.2} \quad (8.52)$$

$$j_H = 0.023 (N_{Re})^{-0.2} \quad (8.53)$$

$$f_{fr} = 0.046 (N_{Re})^{-0.2} \quad (8.54)$$

If may be noted that both j_M and j_H are dimensionless quantities. Thus j_M , j_H and f_{fr} have the same algebraic relationship with the Reynolds number. It may also be noted that

$$j_M = j_H = \frac{1}{2} f_{fr} \quad (8.55)$$

Application of the above equations is now illustrated by an example.

EXAMPLE 8.4 Air flows at 5 m s^{-1} under 1 atm pressure and 35°C in a wetted-wall tube of 5 cm diameter. Calculate the mass transfer coefficient of water vapour in air. Assume the density and viscosity of air at 35°C to be 1.25 kg m^{-3} and $1.9 \times 10^{-5} \text{ kg m}^{-1} \text{ s}^{-1}$ respectively, and also that the Schmidt number and diffusion coefficient for water in air are 0.6 and $2.19 \times 10^{-5} \text{ m}^2 \text{ s}^{-1}$ respectively.

Solution The given data is:

Velocity of air in the tube, $v = 5 \text{ m s}^{-1}$

Diameter of the tube, $d = 5 \text{ cm} = 0.05 \text{ m}$

Density of air, $\rho = 1.25 \text{ kg m}^{-3}$

Viscosity of air, $\mu = 1.9 \times 10^{-5} \text{ kg m}^{-1} \text{ s}^{-1}$

$$\begin{aligned} \text{Reynolds number, } N_{Re} &= \frac{vd\rho}{\mu} \\ &= \frac{5 \times 0.05 \times 1.25}{1.9 \times 10^{-5}} = 1.64 \times 10^4 \end{aligned}$$

From Eq. (8.52), mass transfer j -factor is

$$\begin{aligned} j_M &= 0.023 \times (N_{Re})^{-0.2} \\ &= 0.023 \times (1.64 \times 10^4)^{-0.2} \\ &= 3.294 \times 10^{-3} \end{aligned}$$

Now using Eq. (8.50), we have

$$N_{Sh} = j_M(N_{Re})(N_{Sc})^{1/3}$$

or

$$\frac{k_m d}{D} = j_M(N_{Re})(N_{Sc})^{1/3}$$

or

$$\begin{aligned} k_m &= \frac{D j_M (N_{Re})(N_{Sc})^{1/3}}{d} \\ &= \frac{(2.19 \times 10^{-5})(3.294 \times 10^{-3})(1.64 \times 10^4)(0.6)^{1/3}}{0.05} \\ &= 2.0 \times 10^{-2} \text{ m s}^{-1} \end{aligned} \quad \text{Ans.}$$

Similarly, based on empirical data for flow over flat plates, we can arrive at the following relations:

(i) For laminar flow

$$j_M = j_H = \frac{1}{2} f_{fr} = 0.664 (N_{Re})^{1/2} \quad (8.56)$$

(ii) For turbulent flow

$$j_M = j_H = \frac{1}{2} f_{fr} = 0.037 (N_{Re})^{-0.2} \quad (8.57)$$

For flow around spheres, we need to define modified j factors which are corrected for transfer under stagnant conditions. Thus we can write the following relations for these j -factors:

$$j'_M = \frac{N_{Sh} - 2}{(N_{Re})(N_{Sc})^{1/3}} = 0.552 (N_{Re})^{-1/2} \quad \text{for } 2 < N_{Re} < 800 \quad (8.58)$$

$$j'_H = \frac{N_{Nu} - 2}{(N_{Re})(N_{Pr})^{1/3}} = 0.552 (N_{Re})^{-1/2} \quad (8.59)$$

In general, for a wide range of Reynolds numbers the algebraic form of these relations is

$$j'_M = j'_H = A (N_{Re})^B \quad (8.60)$$

where A and B are two constants, which depend upon the system under study. Equations for j -factors for packed-beds and fluidized-beds can also be similarly derived.

Application of the above equations is now demonstrated by the following examples.

EXAMPLE 8.5 Liquid lead at 370°C is flowing over a 1 m long refractory surface at the rate of 10 m s⁻¹. Calculate the heat transfer coefficient for lead, given that the kinematic viscosity, Prandtl number and thermal conductivity of

liquid lead at 370°C are $2.3 \times 10^{-7} \text{ m}^2 \text{ s}^{-1}$, 0.024 and $16.1 \text{ W m}^{-1} \text{ s}^{-1}$ respectively.

Solution Velocity of liquid lead, $v = 10 \text{ m s}^{-1}$

Kinematic viscosity, $\nu = 2.3 \times 10^{-7} \text{ m}^2 \text{ s}^{-1}$

Distance, $D = 1 \text{ m}$

$$\text{Local Reynolds number, } N_{\text{Re}, D} = \frac{vD}{\nu} = \frac{10 \times 1}{2.3 \times 10^{-7}} = 4.35 \times 10^7$$

Thus the flow is turbulent.

Using Eq. (8.57), the heat transfer j -factor J_H is

$$\begin{aligned} J_H &= 0.037 (N_{\text{Re}})^{-0.2} \\ &= 0.037 (4.35 \times 10^7)^{-0.2} \\ &= 1.097 \times 10^{-3} \end{aligned}$$

Now, using Eq. (8.51), we have

$$j_H = \frac{N_{\text{Nu}}}{(N_{\text{Re}})(N_{\text{Pr}})^{1/3}} = \frac{hD}{k(N_{\text{Re}})(N_{\text{Pr}})^{1/3}}$$

or

$$\text{Heat transfer coefficient, } h = \frac{j_H k (N_{\text{Re}}) (N_{\text{Pr}})^{1/3}}{D}$$

Given, thermal conductivity, $k = 16.1 \text{ W m}^{-1} \text{ K}^{-1}$, Prandtl number, $N_{\text{Pr}} = 0.024$. Therefore

$$\begin{aligned} h &= \frac{1.097 \times 10^{-3} \times 16.1 \times (4.35 \times 10^7) (0.024)^{1/3}}{1} \\ &= 2.22 \times 10^5 \text{ W m}^{-2} \text{ K}^{-1}. \quad \text{Ans.} \end{aligned}$$

EXAMPLE 8.6 Air at 800°C is flowing past a suspended sphere of diameter 2 cm at the rate of 8 m s^{-1} . Calculate the heat transfer coefficient with the following data. Neglect any chemical reaction between the air and the sphere. Kinematic viscosity; thermal conductivity and Prandtl number for air at 800°C are $1.34 \times 10^{-4} \text{ m}^2 \text{ s}^{-1}$, $0.071 \text{ W m}^{-1} \text{ K}^{-1}$ and 0.71 respectively.

Solution Velocity of air, $v = 8 \text{ m s}^{-1}$

Diameter of sphere, $d = 2 \text{ cm} = 0.02 \text{ m}$

Kinematic viscosity of air, $\nu = 1.34 \times 10^{-4} \text{ m}^2 \text{ s}^{-1}$

$$\text{Reynolds number } N_{\text{Re}} = \frac{vD}{\nu} = \frac{8 \times 0.02}{1.34 \times 10^{-4}} = 1.19 \times 10^3$$

Using Eq. (8.59), we have

$$\frac{N_{\text{Nu}} - 2}{(N_{\text{Re}})(N_{\text{Pr}})^{1/3}} = 0.532 (N_{\text{Re}})^{-1/2}$$

or

$$\begin{aligned} N_{\text{Nu}} - 2 &= 0.532 (N_{\text{Re}})^{1/2} (N_{\text{Pr}})^{1/3} \\ &= 0.532 (1.19 \times 10^3) (0.71)^{1/3} = 16.37 \end{aligned}$$

Therefore

$$N_{\text{Nu}} = \frac{hd}{k} = 16.37 + 2 = 18.37$$

Thermal conductivity, $k = 0.071 \text{ W m}^{-1} \text{ K}^{-1}$

$$\begin{aligned} \text{Heat transfer coefficient, } h &= \frac{N_{\text{Nu}} \times k}{d} = \frac{18.37 \times k}{d} \\ &= \frac{18.37 \times 0.071}{0.02} = 65.21 \text{ W m}^{-2} \text{ K}^{-1} \quad \text{Ans.} \end{aligned}$$

Apart from the above analogies, there are a number of others as well for which the reader may refer to any standard text on the subject.

REVIEW QUESTIONS

1. Discuss the similarities among momentum, heat and mass transfer.
2. Explain Reynolds' analogy between momentum and heat transfer.
3. Compare Reynolds' and Prandtl's analogies. Discuss the conditions under which they yield the same result.
4. Derive the equation between mass and momentum transfers by Prandtl's analogy.
5. Derive the equation between heat and mass transfer coefficients according the Reynolds' and Prandtl's analogies.
6. What are j factors for heat and mass transport and how are they related to the friction factor?
7. Discuss the Chilton-Colburn analogy among heat, mass and momentum transfer.

PROBLEMS

1. Calculate the change in temperature of water flowing at the rate of 10 m s^{-1} in a smooth 10 m long, 0.03 m dia pipe. Water may be assumed to enter at 60°C and the tube may be considered to be maintained at 20°C . Make use of the following analogies for this purpose and of the data in Examples 8.1 and 8.3.
 - (i) Reynolds' analogy
 - (ii) Prandtl's analogy

-
2. Compare the values of Nusselt number for flow of mercury in a smooth pipe of 0.005 m dia as predicted by Reynolds, Prandtl and Chilton-Colburn analogies at N_{Re} of 10,000, 50,000 and 100,000. The viscosity, thermal conductivity, density and the specific heat of mercury may be taken as 1.56 centipoise, $7.94 \text{ J m}^{-1} \text{ s}^{-1} \text{ K}^{-1}$, 13600 kg m^{-3} and $1.37 \times 10^2 \text{ J kg}^{-1} \text{ K}^{-1}$ respectively.
 3. Calculate the Sherwood and Nusselt numbers for the flow of a mixture of hydrogen and water vapour around a spherical pellet at 800°C at N_{Re} value of 10,000, assuming the gases to behave ideally. Viscosity, thermal conductivity, specific heat, density and diffusion coefficients are 0.009 centipoise, $0.24 \text{ J m}^{-1} \text{ s}^{-3} \text{ K}^{-1}$, $8200 \text{ J kg}^{-1} \text{ K}^{-1}$, 0.1133 kg m^{-3} and $4 \times 10^{-5} \text{ m}^2 \text{ s}^{-1}$ respectively.

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Answers to Problems

Chapter 1

1. (i) 1434.5 kg (ii) 745.9 kg, 93.7 kg (iii) 793.5 kg (iv) 2005 m³ at NTP
3. (i) 662.6 kg, 42.3 (ii) 413.7 kg (iii) Quartz—176.5 kg, limestone—401.6 kg
4. 40.74 m³ at NTP

Chapter 2

1. 33.33, laminar flow
9. 386 micropoise
10. 4.16×10^{-2} poise, 2.96×10^{-2} poise
12. 1.79 poise
13. 2.982 poise
15. (i) 5.8 atm (ii) 341.95 m s⁻¹ (iii) 289.6 K
16. 1440 m s⁻¹
17. 0.097 atm
18. (i) 0.0043 m s⁻¹ (ii) 0.397 m s⁻¹
19. 3.29×10^{-1} m s⁻¹

Chapter 3

2. (a) $49.2 \text{ W m}^{-1} \text{ K}^{-1}$, $5.49 \times 10^{-2} \text{ m}^2 \text{ s}^{-1}$
(b) $1.47 \times 10^{-3} \text{ W m}^{-1} \text{ K}^{-1}$, $1.63 \times 10^{-6} \text{ m}^2 \text{ s}^{-1}$
3. $7.22 \times 10^{-2} \text{ W m}^{-1} \text{ K}^{-1}$
4. $5.19 \times 10^{-2} \text{ W m}^{-1} \text{ K}^{-1}$
5. $2.71 \times 10^{-4} \text{ W m}^{-1} \text{ K}^{-1}$
6. 9 cm, 15.8 cm
7. 0.041 W.

8. 4116 W m^{-2}
 9. $T = 1328 \text{ K}$
 10. 0.054 m
 11. $1.22 \times 10^6 \text{ W}$
 12. $3.97 \times 10^5 \text{ W}$
 13. $2.17 \times 10^5 \text{ W}$

Chapter 4

1. (a) $C_{\text{N}_2} = 1.48 \times 10^{-2} \text{ kg mol m}^{-3}; C_{\text{CO}} = 7.1 \times 10^{-3} \text{ kg mol m}^{-3}; C_{\text{CO}_2} = 3.55 \times 10^{-3} \text{ kg mol m}^{-3}$
 (b) $\rho_{\text{N}_2} = 4.14 \times 10^{-1} \text{ kg m}^{-3}; \rho_{\text{CO}} = 1.99 \times 10^{-1} \text{ kg m}^{-3}$
 $\rho_{\text{CO}_2} = 1.56 \times 10^{-1} \text{ kg m}^{-3}$
 (c) $X_{\text{N}_2} = 0.538; X_{\text{CO}} = 0.258; X_{\text{CO}_2} = 0.204$
 (d) $N_{\text{N}_2} = 0.582; N_{\text{CO}} = 0.279; N_{\text{CO}_2} = 0.139$
2. (a) $6.1 \times 10^{-13} \text{ m}^2 \text{ s}^{-1}$ (b) $7.4 \times 10^{-6} \text{ m}^2 \text{ s}^{-1}$
3. $1.67 \times 10^{-2} \text{ m}^2 \text{ s}^{-1}$
4. $6.8 \times 10^{-5} \text{ m}^2 \text{ s}^{-1}$
5. $1.45 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$
6. $5.1 \times 10^{-11} \text{ m}^2 \text{ s}^{-1}$
7. $1.34 \times 10^{-14} \text{ m}^2 \text{ s}^{-1}$
8. $1.3 \times 10^{-11} \text{ m}^2 \text{ s}^{-1}$
9. $3.05 \times 10^{-12} \text{ m}^2 \text{ s}^{-1}$
10. $1.82 \times 10^{-13} \text{ m}^2 \text{ s}^{-1}$
11. $8.5 \times 10^{-15} \text{ m}^2 \text{ s}^{-1}$
12. $3.42 \times 10^{-6} \text{ m}^2 \text{ s}^{-1}$
13. $1.34 \times 10^{-3} \text{ m}$
14. $\%C = 0.95 - 111.44 x_f$
15. $C_{\text{centre}} = 0.32\%$
 $C_{\text{at } 0.7 \text{ cm from surface}} = 0.85\%$
 $C_{\text{at } 0.4 \text{ cm from surface}} = 1.45\%$
 $C_{\text{surface}} = 1.48\%$
16. $1.06 \times 10^{-8} \text{ m}^3/\text{m}^2 \text{ s}$
17. $1.62 \times 10^{-7} \text{ m}^2 \text{ s}^{-1}$
18. $1.57 \times 10^{-3} \text{ m}$
19. $2f - 3 + 3(1 - f)^{2/3} = 9.8 \times 10^{-4} t$
20. $4.03 \times 10^{-3} \text{ m s}^{-1}$

Chapter 5

1. $\left(\frac{Xd}{v}\right) = f \left[\left(\frac{\rho v d C_p}{k} \right) \left(\frac{\mu}{\rho v d} \right) \right]$

2. (a) $\left(\frac{hD}{\mu C_p}\right) = \alpha \left(\frac{vD\rho}{\mu}\right)^a \left(\frac{k}{C_p\mu}\right)^d$
 (b) Conversion factor $x = (N_{Pr})^{d-f-1} (N_{Re})^{e-a}$
5. 18.33 dyne cm⁻²
6. 14.8 m s⁻¹
7. (i) $\frac{v_z \rho L}{Pt}, \frac{\rho r^2}{\mu t}, \frac{PL}{\mu v_z}$ (ii) $\frac{\rho r^2}{\mu t}, \frac{Lv\rho}{Pt}, \frac{Pr^2}{L\mu v}$
8. $\frac{\rho C_p v_z r}{k}, \frac{\rho C_p v_z x^2}{rk}, \frac{r}{x}$
9. $\frac{x^2}{Dt}$ is similar
10. $\frac{\partial \bar{\eta}}{\partial \bar{t}} = \frac{Dt_0}{x_\infty} - \frac{\partial^2 \bar{\eta}}{\partial \bar{x}^2}$

Chapter 6

3. (i) (a) 0.0185 m, 0.0323 m, 0.0447 m
 (b) 0.0023 m, 0.0041 m, 0.0056 m
 (ii) 2.67×10^{-6} m (iii) 0.058 cm
4. (i) 20.8 m (ii) 2.6×10^{-3} m (iii) 0.042 m s⁻¹
6. (i) 1023 W m⁻² K⁻¹ (ii) 1007 W m⁻² K⁻¹ (iii) 8.2×10^5 J
7. (a) $\partial_T = 0.085$ m (b) $\partial_v = 0.056$ m
8. (a) $\partial_T = 0.0072$ m (b) $\partial_E = 0.0032$ m (c) $\sigma = 0.314$
9. $k_m = 3.42 \times 10^{-7}$ m s⁻¹

Chapter 7

1. (i) 7.55×10^{-5} s⁻¹ (ii) 9.18×10^3 s
 (iii) (a) 3.81×10^3 s (b) 1.84×10^4 s
2. 6.2%
3. (i) 4.33×10^{-4} s⁻¹ (ii) 0.026 mg
4. (i) 1.85×10^{-4} L-mol⁻¹ s⁻¹ (ii) 1.08×10^4 s (iii) 3.24×10^4 s
5. (b) 1.23×10^{-3} atm⁻¹ s⁻¹ (c) 2.76×10^{-2} L-mol⁻¹ s⁻¹
6. (a) First order (b) 6.67×10^{-4} s⁻¹
7. (i) First order (ii) 6.31×10^{-4} s⁻¹
8. Second order
9. 41.9 kJ

10. 26.0
11. $(\text{Rate})_2 = (\text{Rate})_1 \times e^{-15.15/T}$
12. 172.63 kJ
13. (i) Yes (ii) $A = 1.38 \times 10^{-8}$ (iii) $E = 176.22$ kJ
14. 14.95 kJ
15. (i) 5.34 eV (ii) 40.14 kJ

Chapter 8

1. (i) 9.95°C (ii) 15.75°C
2. (a) At $N_{\text{Re}} = 10,000$ (i) 1.06 (ii) 1.71 (iii) 11.06
(b) At $N_{\text{Re}} = 50,000$ (i) 3.57 (ii) 5.04 (iii) 40.12
(c) At $N_{\text{Re}} = 100,000$ (i) 5.92 (ii) 8.08 (iii) 69.85
3. (i) $N_{\text{Sh}} = 71.2$ (ii) $N_{\text{Nu}} = 39.4$

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A.K. MOHANTY (Ph.D.) is former Principal, National Institute of Technology, Rourkela. He has over 32 years of teaching experience in metallurgy. His areas of interest include physical chemistry of metal extraction and process metallurgy. Dr. Mohanty has also published several papers in reputed national and international journals.

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