

MASS TRANSFER

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TRANSFER**

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CONTENTS

1	Introduction	1
2	Molecular Diffusion	8
2.0	Scope	8
2.1	Principal Symbols	8
2.2	Molecular Diffusion	10
2.3	Simple Molecular Model of Diffusion in a Gas Mixture	11
2.4	Phenomenological Theory of Molecular Diffusion	16
2.5	Estimation of Diffusion Coefficients in Binary Gas Mixtures	17
2.6	Diffusion in Liquids	25
2.7	Diffusion in Electrolyte Solutions	35
2.8	Diffusion in Porous Materials	39
2.9	Diffusion in Polymers	43
	References	49
	Problems	51

19177

3	Rate Equations for Molecular Diffusion	54
3.0	Scope	54
3.1	Principal Symbols	54
3.2	Introduction	56
√ 3.3	Steady-State Molecular Diffusion	57
3.4	Diffusion in Multicomponent Mixtures	61
3.5	Transient Diffusion—Introduction	67
3.6	Transient Diffusion in Stagnant Media	70
√ 3.7	Mass Transfer in Laminar Flow	77
3.8	Quasi-Steady-State Diffusion	90
	Appendix	92
	References	94
	Problems	95
4	Turbulent Diffusion	101
4.0	Scope	101
4.1	Principal Symbols	101
4.2	Turbulence	103
4.3	The Eddy Viscosity	106
4.4	The Universal Velocity Distribution in Smooth Tubes	109
4.5	The Eddy-Diffusion Coefficient	112
4.6	Turbulent Diffusion	114
4.7	Experimental Studies of Turbulent Diffusion	119
4.8	Interaction of Molecular and Turbulent Diffusion	126
4.9	Turbulent Schmidt and Prandtl Numbers	127
4.10	Mixing and Dispersion in Packed Beds	129
4.11	Axial Dispersion in Pipe Lines	137
	References	141
	Problems	145
5	Mass Transfer at a Phase Boundary	148
5.0	Scope	148
5.1	Principal Symbols	149
√ 5.2	Models	150
5.3	Analogies between Mass, Heat, and Momentum Transfer	159
5.4	Mass Transfer at Large Fluxes and at High Concentration Levels	172
5.5	The Two-Film Theory	178
5.6	Mass Transfer at the Interface between Phases	181
	References	192
	Problems	196

6	Rates of Mass Transfer at Surfaces with Simple Geometry	199
6.0	Scope	199
6.1	Principal Symbols	200
6.2	Flat Surfaces	201
6.3	Falling Liquid Films	203
✓6.4	Mass Transfer between a Fluid and a Solid Sphere	214
6.5	Solid Particles Suspended in Agitated Vessels	220
6.6	Drops	224
6.7	Bubbles	231
6.8	Cylinders and Disks	236
6.9	Single-Phase Flow in Packed Beds	241
	References	247
	Problems	252
7	Simultaneous Heat and Mass Transfer	255
7.0	Scope	255
7.1	Principal Symbols	255
7.2	The Effect of Mass Transfer on the Rate of Heat Transfer at the Same Surface	257
7.3	The Theory of the Wet-Bulb Thermometer	261
7.4	The Design of Partial Condensers	263
7.5	Condensation from a Superheated Gas	265
7.6	The Formation of Fog in Partial Condensers	267
7.7	Effect of Variations in Interface Temperature	269
7.8	The Condensation of Mixed Vapors	273
7.9	The Mechanism of Vapor-Phase Nucleation in Partial Condensers	276
7.10	Water Cooling Towers	280
7.11	Values of the Mass-Transfer Coefficient for Water Cooling Towers	286
7.12	The Crossflow Cooling Tower	291
	References	296
	Problems	297
8	Mass Transfer and Simultaneous Chemical Reaction	301
8.0	Scope	301
8.1	Principal Symbols	302
8.2	Introduction	303
8.3	Effect of a Chemical Reaction in Gas Absorption	306
8.4	The Theory of Simultaneous Diffusion and Chemical Reaction near an Interface	310

8.5	The Film Theory for a First-Order Irreversible Reaction	312
8.6	The Theory of First-Order Reactions according to the Surface-Replacement Model	313
8.7	First-Order Reactions during Unsteady-State Diffusion into a Semiinfinite Medium: The Penetration Theory	314
8.8	Comparison of the Film, Surface-Replacement, and Penetration Theories for First-Order Reactions	321
8.9	Bimolecular Reactions	322
8.10	Bimolecular Reaction in a Turbulent Fluid near a Solid Interface	334
8.11	The Effect of Reversibility of the Chemical Reaction on the Mass-Transfer Rate	336
8.12	Computations of the Reaction Effect for a Few, More General Chemical Situations	343
8.13	The Reactions of NO_x with Water and Aqueous Solutions	346
8.14	The Reactions of CO_2 with Alkaline Aqueous Solutions	361
8.15	The Oxidation of Sulfite Ion by Dissolved Oxygen	371
8.16	Carrier-facilitated Mass Transfer through Membranes	376
8.17	Diffusion and Reaction in Porous Catalysts	379
	References	382
	Problems	385
9	Design Principles for Mass-Transfer Equipment	392
9.0	Scope	392
9.1	Principal Symbols	393
9.2	Introduction	395
9.3	Phase Equilibria	396
9.4	Absorption in a Single Equilibrium Stage	398
9.5	Multistage Countercurrent Absorption	399
9.6	Continuous Differential-Contact Packed-Column Design	427
9.7	Relation between Actual and Theoretical Plates; Plate Efficiency	507
9.8	Distillation	518
9.9	Solvent Extraction	524
	Appendix: A Digital Computer Program for a Packed-Column Absorption and Stripping	525
	References	534
	Problems	536
10	Design of Fixed-Bed Sorption and Ion Exchange Devices	548
10.0	Introduction and Scope	548
10.1	Principal Symbols	549
10.2	Fluid-Solid Equilibria	550

10.3	The Equations of Transport	554
10.4	The Local-Equilibrium Theory of Fixed-Bed Devices	555
10.5	The Effects of Mass-Transfer Resistance between Fluid and Solid Phases	561
10.6	The Thomas Solution for Sorption Breakthrough Curves	565
10.7	Breakthrough Curves for Linear Phase Equilibria and Chromatography	571
10.8	The Resistance to Mass Transfer between Phases for Ion Exchange and Sorption	579
10.9	The Design of Fixed-Bed Adsorbers for Repeated, Cyclic Use	586
	References	589
	Problems	591
11	The Performance of Mass-Transfer Equipment	593
11.0	Scope	593
11.1	Principal Symbols	594
11.2	Mass-Transfer Equipment	595
11.3	The Nature of the Available Design Data	598
11.4	Packed Columns	599
11.5	Tray or "Plate" Columns	624
11.6	Agitated Vessels and Bubble Columns	647
	References	656
	Problems	660
	Index	667

INTRODUCTION

Mass-transfer phenomena are to be found everywhere in nature, and are important in all branches of science and engineering. The phrase "mass transfer," which has come into common use only in recent years, refers to the motion of molecules or fluid elements caused by some form of potential or "driving force." It includes not only molecular diffusion but also transport by convection and sometimes simple mixing—not the conveyance of a material, as in the flow of a fluid in a pipe.

Mass transfer is involved wherever a chemical reaction takes place, whether in an industrial reactor, a biological system, or a research laboratory. As pointed out by Weisz [1], the reacting substances must come together if the reaction is to proceed; and in many cases, the reaction slows or stops if the reaction products are not removed. The reactants have little difficulty in coming together in the case of homogeneous reactions in a single well-mixed liquid or gas phase, but the rate of mass transfer may completely determine the chemical conversion when reactants must move from one phase to another in order that reaction may occur. This is the case, for example, when reaction occurs at the surface of a very active catalyst in contact with a fluid which carries the reactants and removes the reaction products. In the case of a reversible reaction, the conversion is improved

if the desired product is continuously removed by mass transfer to a second phase in which no reaction takes place. Furthermore, the relative rates of mass transfer of the several reacting and product species can greatly affect the selectivity when competing reactions are involved.

The general subject of mass transfer may be divided into four broad areas of particular interest and importance: molecular diffusion in stagnant media, molecular diffusion in fluids in laminar flow, eddy diffusion or mixing in a free turbulent stream, and mass transfer between two phases.

The first has been the subject of much study by scientists for more than a century, and the theory is in good shape for diffusion in gases, though not for diffusion in dense fluids. The second is an application of the first, and is treated by a mathematical manipulation, often difficult, of what is known about molecular diffusion in situations where the flow field can be described or calculated.

Eddy diffusion in a free stream, away from a phase boundary, is the process by which gases leaving a stack are dispersed into the atmosphere, and by which mixing occurs in many situations, as in turbulent jets. Transfer between two phases, across an interface, is of particular importance in engineering, largely because it is involved in most separation processes, as in the recovery of a pure product from a mixture. Evaporation from a reservoir, oxygenation of blood, removal of pollutants from the atmosphere by rain, chemical reaction at the surface of a solid catalyst or within its porous structure, deposition by electrolysis or electrophoresis, drying of wood, and removal of carbon from steel by blowing with air or oxygen are all examples of mass transfer between phases.

The chemical engineer's interest in mass transfer stems primarily from his traditional role as a specialist in the design of separation processes. The materials fed to a chemical process are purified by separation or concentration of the reactants, and the valuable products must be separated from the stream leaving the reactor. Though the separation equipment is ancillary to the reactor, its cost is often the major part of the investment in the plant. This point is illustrated by Fig. 1.1, which is a flow diagram of an industrial process for the production of formaldehyde by the oxidation of methanol. The small reactor contains several layers of a silver gauze catalyst. The rest of the plant involves typical mass-transfer equipment for purification of feed, recovery and purification of the product, and separation and recycling of unreacted methanol. Mass transfer is of concern in the reactor itself, since the production of formaldehyde cannot proceed faster than the rate of transport of methanol and oxygen from the gas stream to the surface of the silver.

Separation of a product from a very dilute stream is usually expensive. This largely explains the high prices of antibiotics, for example, which are produced in very dilute fermentation broths. The difficulty is partly explained by thermodynamics, since the isothermal reversible work required for recovery of a pure material from a mixture is roughly proportional to the logarithm of the reciprocal of the concentration in the mixture in which the substance is found or produced. Figure 1.2 indicates the general relation between the selling price of a pure product and the concentration of the mixture from which it is obtained.

The work or free energy needed for separation is not the only production

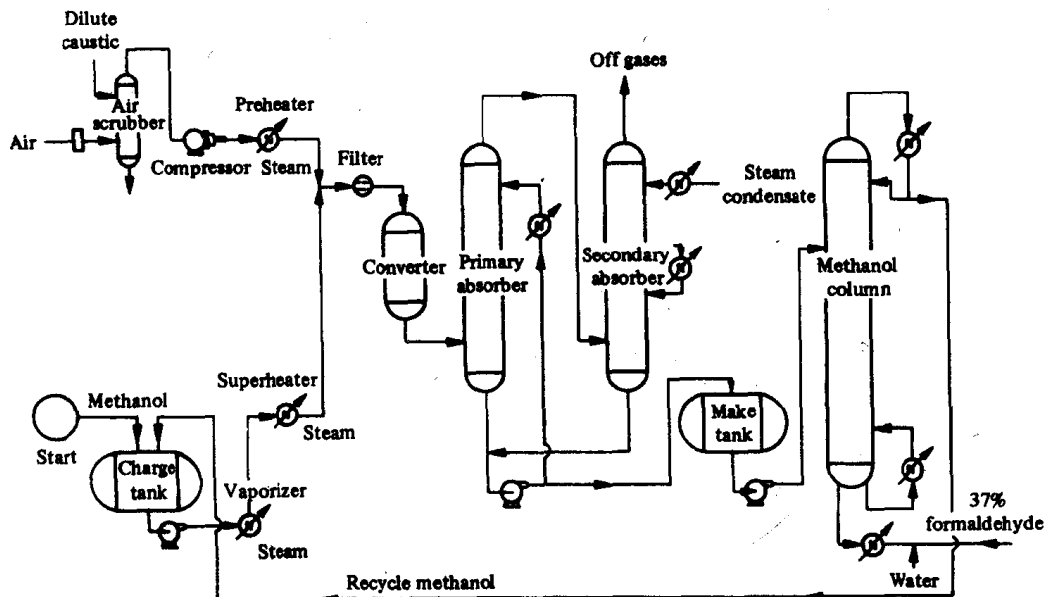


FIGURE 1.1

Process flow diagram for the manufacture of formaldehyde from methanol (from R. N. Shreve, "Chemical Process Industries," 3d ed., 1967. McGraw-Hill Book Co., N.Y.).

cost; Fig. 1.2 should thus not be taken too seriously. The free energy of separation of copper from the chemical compound in the natural ore, for example, is arbitrarily excluded in the energy represented by the abscissa. The point for sulfur from stack gases represents the *cost* of separation, not the selling price of sulfur. Mined sulfur, selling at roughly a cent per pound, requires very little purification. The point for gold from sea water, at the far right, illustrates that gold from this source cannot compete with gold from mined ores; the free energy required for the separation is enormously greater than that for separation from available ores. Though the selling prices are influenced by many things, the rough correlation suggested by Fig. 1.2 indicates that separation cost is usually a dominant factor.

Most practical separation schemes are based on the fact that concentrations of two phases in equilibrium with each other are usually quite different. For example, an equimolar mixture of benzene and toluene is in equilibrium with a vapor containing 70 mole percent benzene. Phases in contact tend to equilibrate by mass transfer from one to the other. Subsequent separation of the phases by mechanical means is usually simple and inexpensive. Any method of contacting two phases which results in the selective interphase transport of one of the constituents can form the basis of a separation process. The selectivity is ordinarily the result of different equilibrium relations for the different species; in a very few cases, it may be due to different rates of transport of the several constituents.

Considerations of phase equilibria are essential to an understanding or analysis

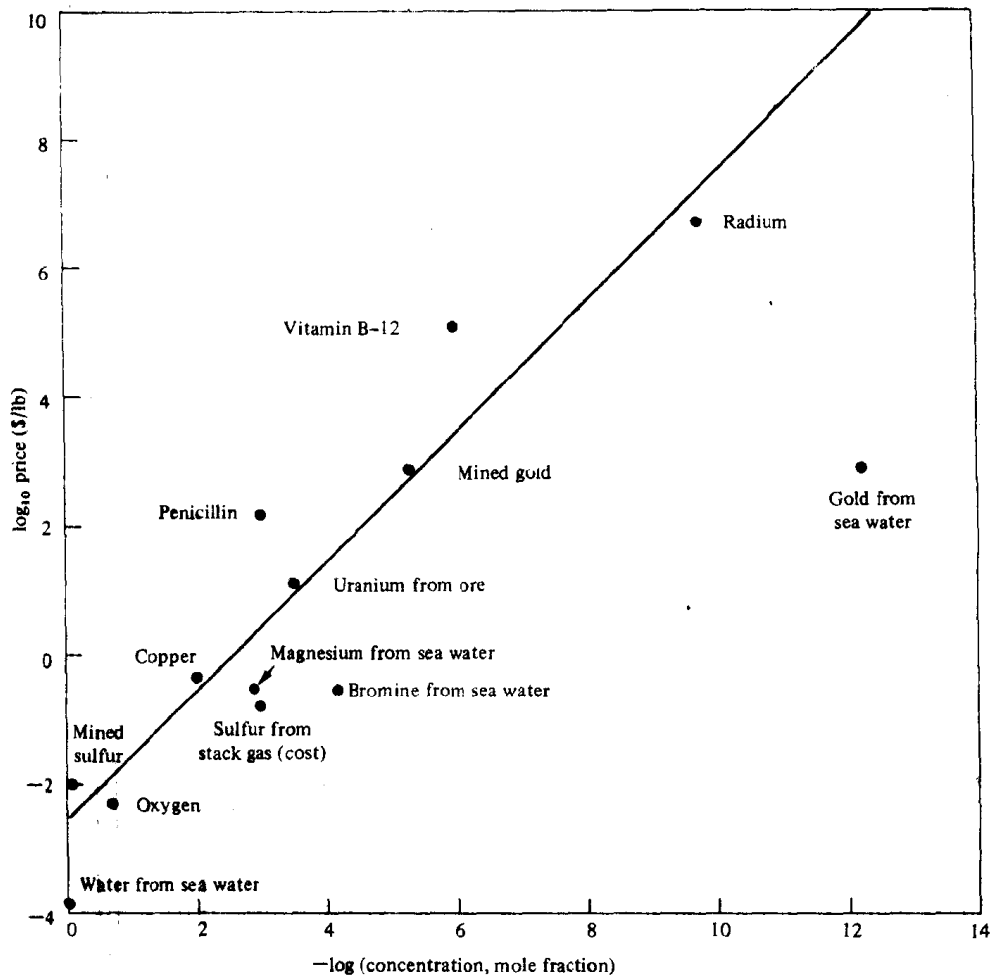


FIGURE 1.2

Relation between the values of pure products and the concentrations in the mixtures in which they are found or produced.

of any mass-transfer process. Here it is that thermodynamics has much to offer, since the second law states the conditions of equilibrium. The thermodynamic theory is well developed, though in many practical cases it does not provide the necessary connection between activities and concentrations. In a few situations, this relation is well known. In others, the empirical Lewis and Randall rule may prove adequate, although in some cases more sophisticated analyses based on complicated equations of state or on molecular theory may be required. In any event, the student or engineer dealing with problems of mass transfer must be familiar with both the theory and the empirical facts of the thermodynamics of phase equilibria. Furthermore, the first law of thermodynamics provides the basis for the calculation of the necessary enthalpy balances, including the heat effects often associated

with the mass-transfer phenomena. The important role of thermodynamics in connection with equilibria and enthalpy changes is presented in numerous texts; it is only touched on in the later chapters.

Since the subjects of molecular diffusion and thermodynamics are in relatively good shape, it is the factors determining the *rate* of interphase transfer that have been the particular concern of many chemical engineers. The size and cost of mass-transfer equipment of a given type is nearly inversely proportional to the mass flux, which plays a major role in process design. Despite its crucial importance, information on rates of transfer for various important applications is often unavailable and must be estimated from fragmentary data on the basis of the principles discussed in the chapters which follow.

Most industrial processes depending on mass transfer involve one or more fluids in turbulent flow, and the existing theory of turbulence is quite inadequate as a basis for the development of a practically useful theory of mass transfer at a phase boundary. This lack of understanding of turbulence presents a major stumbling block to the development of a theoretical basis for mass transfer between phases. G. K. Batchelor, a well-known authority on fluid mechanics, writes that "modern technology needs help in describing and analysing turbulent flow, and cannot wait for scientists to understand its mysteries" [2]. Written in 1957, this is evidently still true. Of necessity, therefore, the existing correlations of data on transport rates are largely empirical. These have proved extremely useful in the design of process equipment, although the needed data and correlations are often missing or provide only approximate estimates of the size of the mass-transfer devices and of their performance. Nevertheless, the design engineer must use the tools available, within the constraints of both equilibrium limitations and economics.

Thermodynamic potential gradients of several kinds may serve to implement mass transfer. In electrophoresis and in electrochemical processes, an electrical potential provides the motive force; in the Clusius and Dickel column for the separation of gaseous isotopes, it is a thermal gradient. In a majority of applications in the process industries, however, activity or concentration gradient is employed to effect mass transfer between two phases. Several inconclusive studies have been made to determine if transport rates in such cases are not more nearly proportional to the activity than to concentration gradients. Regardless of the outcome of such studies, however, the use of concentration has enormous practical appeal, since it makes it so much simpler to tie the rate process to the stoichiometry of the process streams. This has proved generally successful; it has a good theoretical basis in some situations, though in others it is a forced simplification employed with little reference to the mechanism by which mass transfer takes place.

In living tissue, diffusion may take place in the direction of a negative concentration gradient. This phenomenon of "active transport" is presumed to be due to an input of free energy or work needed for concentration by diffusion, causing a solute to diffuse "uphill." If this process were understood it might find application in industry.

The exposition which follows is intended to provide the chemical engineer with

an understanding of the phenomena of mass transfer and of the existing theory, where the latter may be available and helpful. Though intended primarily for the student, it will hopefully be found interesting and useful by the practicing engineer. Satisfying the needs of both may not be practicable because the former is usually more interested in the theory and the latter in design information. The literature on the subject is extremely voluminous, so that it is no longer possible to collect and correlate experimental data with the completeness that was attempted in the earlier versions of the book ("Absorption and Extraction," 1937 and 1952).

The authors have attempted to emphasize the *engineering* aspects of mass transfer to a greater extent than is done in many of the existing excellent texts on the subject. It has been said that "scientists tackle those problems which can be solved; engineers are faced with problems which *must* be solved." The design engineer must come up with a design. Of necessity he must rely largely on empirical correlations and incomplete theories. He develops a skill in the use of the *form* of a theory for extrapolation purposes, where the theory does not provide the absolute numbers needed for prediction. "Engineering estimates," often crude, are of great value as guides in the selection of feasible designs. It is important to be able to judge critically the validity of experimental data and the conditions under which existing correlations and theories may be employed with confidence. On such judgment hinges the decision about whether or not new laboratory or expensive pilot-plant data must be obtained before the design project should be pursued further. Clear understanding of elementary theory is often essential for making such decisions.

Only the last three chapters of the book deal specifically with design, and here the reader is referred to Perry's "Chemical Engineers' Handbook" and other sources for most of the needed design data. Chapters 2 through 8 attempt to lay a foundation for understanding the phenomena, theories, basic principles, and nature of existing data on mass transfer. Without this understanding, the use of handbook data can lead to serious design mistakes and costly failures of process equipment.

Although the text may appear to emphasize mass transfer in gas absorption, the phenomena, theory, and design principles are equally relevant to distillation, solvent extraction, crystallization, leaching, and other mass-transfer operations of industrial importance. These are treated in various other books, notably King's "Separation Processes" [3], which deals primarily with distillation, and the books on solvent extraction by Treybal [4] and Hanson [5].

An essential aspect of engineering design is optimization based on economic considerations. Alternative conceptual designs are proposed and the most promising selected for detailed analysis. This involves an economic balance of operating and investment charges and estimates of return. The techniques and cost information employed in these steps constitute a large additional body of knowledge, often more readily available to those in industry, which is beyond the scope of this book.

It seems inevitable that the United States will adopt the metric system of units, termed SI, for *Système International d'Unités*. The change has been promoted off

and on since John Quincy Adams's 1821 report, and the U.S. Congress is currently debating various bills proposing studies of how it might be implemented. All other major countries have either gone metric or are committed to metrication. However, it would appear to be a reasonable guess that the United States will change but gradually to SI during the useful life of this book.

Chemical engineers deal with plant and equipment—areas of engineering where the English system is almost universally employed. But the fundamental science is chemistry, and the literature of chemistry is based wholly on the metric system. Of necessity, the chemical engineer must become facile in the use of both systems. The use of both in this book (sometimes in a single calculation) is a deliberate attempt to encourage students to develop this useful skill.

A number of worked examples are included in the text. Whether a university student or a practicing engineer, the reader should consider these to be as important as the text material. Understanding the units to be employed and skill in simple calculation with a slide rule or desk computer are essential to the engineer. The use of numbers helps one to understand equations. In general, we have attempted to minimize the use of advanced mathematics and of machine computation. The problems appearing at the ends of the chapters, for which solutions are not given, are taken mostly from notes on courses taught at the University of California at Berkeley, the University of Delaware, and the Massachusetts Institute of Technology. Their shortcomings should stimulate instructors to develop new and better problems for their own use in class.

We acknowledge with thanks the advice and assistance of numerous colleagues and friends. We are grateful to Dr. Urs von Stockar for help in preparing the illustrative problems of Chap. 9. We owe a special debt to Professors K. A. Smith of Massachusetts Institute of Technology and T. Vermeulen of Berkeley, to our secretary, Miss Myra Baker, and to a number of teaching and research assistants with whom we have worked.

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2

MOLECULAR DIFFUSION

2.0 SCOPE

The chapter begins with definitions of diffusion coefficients. The manner in which mutual diffusion coefficients may be expected to vary with the properties of a binary gas system is illustrated by reference to classical kinetic theory. Methods of estimating binary diffusion coefficients in gases and liquids are described. A short treatment of diffusion in porous solids is included. Basic rate equations for diffusion in stagnant and moving systems are developed in Chap. 3.

2.1 PRINCIPAL SYMBOLS

a	Activity of component of mixture
c	Concentration, g moles/cm ³
c_+, c_-	Concentrations of cation, anion, g equiv/cm ³
D	Diffusion coefficient, cm ² /s
D^*	Tracer diffusion coefficient, cm ² /s
D_{AB}	Mutual diffusion coefficient species A in binary of A and B , cm ² /s
D_{AB}^0	Mutual diffusion coefficient of A in binary at infinite dilution of A in B , cm ² /s