Diffusion and Heat Flow in Liquids

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PREFACE

DIFFUSION and thermal conduction are of great interest in the technically important fields of material and heat transfer in liquids, and this has provided one major reason for the attention which has been devoted, over a very long period of time, to these two phenomena. More fundamental studies on the size and shape of large molecules have relied heavily on the measurement of diffusion coefficients, and the necessity for improving the accuracy of such measurements has led to advances in instrumentation, which have been of great value in investigating diffusion in other liquid systems. Thermal diffusion, or the separation (usually partial) of the components of a liquid mixture which may occur under the influence of a thermal gradient, has, by comparison, received little attention, though similar separations in gaseous systems are now of considerable technical importance. All three phenomena can be fitted into the same descriptive framework, and all three have something in common in so far as their experimental study is concerned. These factors have determined the form of the book, though, because of the current lack of a satisfactory general kinetic or statistical theory of the liquid state, theories which can be applied to the general body of experimental data lack general applicability, and a unified discussion of all three subjects from such a standpoint has not been attempted.

The close formal connection between diffusion and heat conduction was first recognized by Adolf Fick, an anatomist who might justly be regarded as a pioneer in biophysics. He took Fourier's law of heat conduction as a model for his law of diffusion, and defined a coefficient of diffusion for a binary system which bore a close resemblance to the coefficient of thermal conduction defined by Fourier. Both laws assume a *linear* relationship between a flow of heat or of matter, and the force causing the flow, assumed to be a gradient of temperature, and a gradient of concentration respectively. This idea has been extended in the thermodynamic treatment of transport processes which has been developed from some suggestions made, nearly thirty years ago, by Onsager. This provides a unified description, not only of diffusion and of thermal conduction, but of the migration of matter under a temperature gradient (Soret effect), and of the temperature gradient which, in principle, should be associated with any concentration gradient in a system of more than one component (Dufour effect). The discussion of the fundamentals of the theory, and of its application to these phenomena, which occupies the first four chapters, provides the foundation for the book as a whole. The account of the fundamentals owes much to Haase's excellent article in *Ergebnisse der Exacten Naturwissenschaften* which appeared in 1952, and it is intended to be complete enough for the applications of the theory to the subjects of the book to be understood by those who are not initially well acquainted with this form of thermodynamics. The second section, formed by Chapters 5 to 7, is devoted to diffusion, the main emphases being laid upon experimental methods, partly because of their interest in connection with studies on thermal diffusion, and on the interpretation of diffusion coefficients in terms of different theoretical pictures of the diffusion process. The problem of the integration of the diffusion equation with respect to particular sets of boundary conditions has not been discussed in detail because, in the case of liquid systems, only a small number of integral solutions are of practical importance, and these are well known already. The solution of the diffusion equation when both temperature and concentration gradients exist in the system is more difficult, and a rather full discussion of the problem, both for experimental arrangements where convection is eliminated, and for the Clusius–Dickel type of thermogravitational cell which has been widely used in the study of separation techniques using thermal diffusion, has been attempted in the course of the discussion of diffusion and related phenomena in non-isothermal liquid mixtures (Chapters 8 to 10). The final chapter covers those aspects of thermal conduction which seem relevant to the rest of the book; if the space devoted to it is relatively small in comparison with its practical importance, this is precisely because engineering rather than pure science has hitherto tended to dominate this field. It has not been my intention to attempt to write a book on heat transfer.

That performance falls short of intention is a common experience, and this book is no exception. I would like to acknowledge the help and advice of Professor D. H. Everett, who read and criticized a draft of the earlier chapters, and that of my colleague Dr. A. S. C. Lawrence who performed a similar service for the final typescript of the whole book. I am indebted to Dr. J. N. Agar for information on the conductimetric method of measuring Soret coefficients before a full description was published, to Drs. R. Haase and Toshio Ikeda for providing unpublished experimental data and calculations on non-isothermal liquid systems, and to Dr. L. P. Filippov of Moscow University who supplied reprints of a number of his papers on thermal conduction which would otherwise have been difficult to obtain. In covering such a wide field it is impossible to expect that errors of fact and emphasis have been entirely avoided, but one hopes that they are not too numerous or important.

As always, I have been greatly helped by my wife, both in general matters and in the particular tasks of checking the manuscript, preparing diagrams, compiling the index, and in proof-reading. Miss Elisabeth Gillett typed the difficult manuscript with great skill and patience.

Sheffield and Stockholm
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LIST OF PRINCIPAL SYMBOLS

Thermodynamic capacity factors have been represented by capital letters, and the corresponding intensity factors by lower case letters, without underline for partial molal or molal quantities, and with underline for specific quantities. Vector quantities have been distinguished by the use of bold type; when equations involving these are reduced to the one-dimensional case the vector notation is dropped, except in the case of velocities which are throughout indicated by $\mathbf{v}$ to avoid confusion with the italic symbol used principally to represent volume. Bold type has been used for quantities which are not vectors, as in the symbols for the Faraday and for Planck's constant, but this should not cause confusion. The symbol D is generally used to denote an experimental differential diffusion coefficient, as in Chapter 5. For binary systems of the kind considered, it can be closely identified with the single mutual diffusion coefficient required to define the diffusion process in such a system, and this identification has been assumed to be correct in the discussion of the experimental data. The distinction between a self-diffusion coefficient and a tracer diffusion coefficient has been explained on p. 38. There is an element of pedantry in distinguishing between them in any discussion of experimental values (see, for example, page 152), but, following much recent practice, the term 'tracer diffusion coefficient' has been used in connection with experimental data on the diffusion of ions. Otherwise, in such discussions, the name 'self-diffusion coefficient' has been used. Both have been symbolized by D^*.

A	Area (esp. Chaps. 1 and 5). Atomic weight. A_r, affinity of reaction r
B	$B_{ij} \equiv [1 + (\partial \ln f_i/\partial \ln N_i)_{T,P,N_j}]$ in multicomponent system
	$\mathbf{B}_1 \equiv [1 + (\partial \ln f_1/\partial \ln N_1)_{T,P}]$ for component 1 in a two-component system
	B_1^c, B_1^m, are defined similarly on the molar and molal scales respectively
C	Heat capacity
D	Experimental diffusion coefficient
	D_{12}, mutual diffusion coefficient
	$\bar{D}$, integral diffusion coefficient, D^i intrinsic diffusion coefficient
	D^*, self-diffusion, tracer diffusion coefficient
	$\mathscr{D}_{ij}$, diffusion coefficient in multi-component system
	D', coefficient of thermal diffusion
E	Total energy of system
	$E_M^{\neq}$, $E_D^{\neq}$, Arrhenius energies of activation for viscous flow and for diffusion respectively
	E^0, standard e.m.f. of isothermal reversible cell
F	Faraday ($\mathbf{F}$)
	F, $F^{\neq}$ partition functions per unit volume in initial and transition states
G	Gibbs free energy
	$\Delta G_M^{\neq}$, $\Delta G_D^{\neq}$ Gibbs free energy of activation per mole for viscous flow and for diffusion respectively
	Gradient of magnetic field in 'spin-echo' method of determining self-diffusion coefficients
H	Enthalpy
	$\Delta H_M^{\neq}$, $\Delta H_D^{\neq}$, enthalpy of activation for viscous flow and for diffusion repectively
	Function used in theory of thermogravitational column

LIST OF PRINCIPAL SYMBOLS

I	Ionic strength
	I, electric current
J	J (with appropriate subscript), flow per unit area per unit time. (J in one-dimensional system)
	Total fringe shift in integral fringe pattern
K	Thermometric conductivity
	$K(T)$, temperature-dependent equilibrium constant
	$K,K,^*$ functions used in theory of thermogravitational columns
L	L_{ij} etc., phenomenological coefficients
	$\mathscr{L}_{ij}$ etc., phenomenological coefficients defined with respect to solvent-fixed frame of reference
	L_{vap}, Latent heat of vaporization
	$\mathscr{L}_i$, negative of latent heat of vaporization of component i from the solution to the gaseous state
	$\overline{L}_i$, relative partial molar heat content of component i
M	M_i, molecular weight of substance i
	$\mathscr{M}_r$, rth semi-moment about refractive index gradient curve
N	N_i, mole fraction of component i
	N Avogadro number
	N_{Gr}, N_{Pr}, Grashof and Prandtl numbers
P	Pressure
	Optical path length
	P_ϵ, thermoelectric power of thermocell corrected for concentration and activity coefficient changes
Q	$\overline{\overline{Q}}_i$, total molar transported heat of component i
	Q_i^*, molar Eastman heat of transfer of component i
R	Gas constant
	Refractive index increment $\equiv (dn/dc)_{c=\bar{c}}$
	'Enrichment factor'
	R_{ij}, frictional coefficient
S	Entropy
	$\Delta S_M^{\neq}$, $\Delta S_D^{\neq}$, entropy of activation for viscous flow and for diffusion respectively
	$\overline{\overline{S}}$, total molar transported entropy
	S^*, molar Eastman entropy of transfer
T	Absolute temperature
U	Internal energy
V	Volume
	V_{max}, maximum induced voltage in 'spin-echo' method for self-diffusion
W	Work done by system
	Function defined by equation (8–81)
X	$\mathbf{X}$ (with appropriate suffix), general symbol for a force
Y	General symbol for a capacity factor. Y^+, per unit volume
Z	Reduced height in theory of optical diffusion methods

a	a_{pr}, phenomenological coefficient (Chapter 2)
	Activity
	Distance of closest approach in Debye-Hückel theory
	Plate separation ('slit width') in thermogravitational column
b	Optical distance
	Width of plates in thermogravitational column
c	Molar density
	c_i, molar concentration of component i
	Specific heat

d	d_c, collisional diameter (eqn. 6–11)
e	$\bar{e}$, unit electrical charge in e.s.u.
	e_k, electrical charge per unit mass of component k
	e_j^+, charge density around ion j
f	Activity coefficient on mole fraction scale
	$\mathbf{f}$, shearing force per unit area
g	Optical distance (eqn. 5–10)
	Gravitational acceleration
h	Molar enthalpy of system
	h_i, partial molar enthalpy of component i
	h_i^0, molar enthalpy of pure component i
	height of diffusion cell
	$\boldsymbol{h}$, Planck's constant
j	Frequency of molecular transition (Chap. 9)
k	Thermal conductivity coefficient
	k_{ab}, k^v, velocity constants
	$\boldsymbol{k}$, Boltzmann's constant
l	Length
m	Molality
	Mass
	m_r, rth moment about refractive index gradient curve
	m^*, m_d, m_c, matter fluxes in thermogravitational column
n	Refractive index
	n_i, number of molecules of component i
	n_H, hydration number
p	p_g, partial pressure of gas over electrode
q	Heat
	q_h, q_R, q_L, energy quantities used in Wirtz theory of transport processes
r	Radius of molecule
	r_{ij} Frictional coefficient (Klemm)
s	$\underline{s}$, entropy per unit mass
	s_i, partial molar entropy of component i
t	Time
	t_i, Hittorf transference number of ith ion
u	Molar internal energy of system
	$\underline{u}$, specific internal energy of system
	u_i, mobility of ith ion
v	Molar volume
	v_i, partial molar volume of component i, etc.
	v_f, free volume per molecule
	v_r, velocity of rth reaction
	v_r^+, velocity of reaction r in local volume element
	$\mathbf{v}$, velocity
w	w_k, mass fraction of component k
x	Abscissa in experimental refractive index gradient curve
y	Ordinate in experimental refractive index gradient curve
	y_i, activity coefficient of component i on molar scale
z	Valency
	Vertical coordinate in diffusion cell
α	Optical constant, fractional part of fringe displacement (Chap. 5)
	Thermal diffusion factor
α_k	'Solute fraction' (eq. 5–105)

LIST OF PRINCIPAL SYMBOLS

β	Optical magnification factor, cell constant for diaphragm diffusion cell (Chap. 5)
	Coefficient of sliding friction in Stokes' hydrodynamic theory of diffusion (Chap. 6)
	Coefficient of thermal expansion
γ	Ratio of specific heats
	Parameter used in theory of thermogravitational column
	Gyromagnetic ratio (Chap. 5)
γ_i	Activity coefficient on molal scale of component i
Δ^2	Mean square displacement of diffusing molecule
δ_{25}	Solubility parameter at 25°C
$\delta_+(\delta_-)$	Increments of velocity of positive (negative) ion due to electrophoretic effect
ε	Thermoelectric power
ε_{ij}	Interaction energy of molecular pair i, j
ζ	Normalized coordinate in Gaussian curve
	Viscous resistance per mole
η	Viscosity (η_{12} of binary solution, η_1, η_2, of pure components)
Θ	Coordinate of normalized Gaussian curve
θ	Entropy source (Chap. 2)
	Characteristic time ($\equiv \pi^2 D/h^2$)
κ	Coefficient of electrical conductivity
	Transmission coefficient (Chap. 6)
	Characteristic length (Chap. 6) in Debye-Hückel theory of electrolytes
λ	Wavelength of light
λ_i	Equivalent conductance of ion species i
μ_i	Molar chemical potential of component i
$\tilde{\mu}_i$	Molar electrochemical potential of ion species i
ν	Stoichiometric coefficient
	Number of ions produced per mole of salt ($\equiv \nu_+ + \nu_-$)
ξ	Degree of advancement
	Reduced height in diffusion cell
Π	Peltier coefficient
ρ	Density
ρ_i	Local density of component of component i (mass per unit volume)
σ	Soret coefficient
σ^T	Thomson coefficient
τ	Time interval (Chaps. 2 and 5)
	Temperature interval (Chaps. 8, 9, and 10)
Φ	Dissipation function (Chap. 2)
ϕ	Volume fraction (Chap. 7)
ϕ_i	'Apparent molar thermal conductivity coefficient' of component i
χ	Packing factor (Chap. 6)
ψ	Electrical potential
Ω	Relative fringe displacement of Gouy fringe pattern of polydisperse system (Chap. 5)
ω_1, ω_2,	Molecular velocities derived from 'platzwechsel' theory (Chap. 9)
$\backepsilon$,	dielectric constant

ERRATA

p. 9, eqn. (2.8). For μ_{i} , read μ_i

p. 26, line 5. For $P'\mathrm{d}'\overline{V}$, read $P'\mathrm{d}'V$

p. 34, ref. 30. Journal is *Z. phys. Chem.*

p. 62, eqn. (4.85) should read:

$$(\psi_B'''' - \psi_B''') + (\psi_B'' - \psi_B') \simeq -\frac{S^*_{\mathrm{el.}}}{F}.\Delta T$$

p. 67, line 1. For ' . . , $\bar{\bar{s}}^*_{\mathrm{el.}B}$) see . . ', read ' . . , $\bar{\bar{S}}_{\mathrm{el.}B}$, (see . . '
line 2. For ' ($s^0_{\mathrm{el.}B} + S_{\mathrm{el.}B}$. (The . . ' , read
' ($s^0_{\mathrm{el.}B} + S^*_{\mathrm{el.}B}$). The . . '
eqn. (4.104). For $\left(\frac{\Delta S^0_R}{z^-}\right)$ read $\left(\frac{\Delta S^0_R}{z_-}\right)'$ in the second term, and close brackets at end of last term

p. 68, line above eqn. (4.107). For $\bar{\bar{s}}_+$, read $\bar{\bar{S}}_+$. For $\bar{\bar{s}}_-$, read $\bar{\bar{S}}_-$

p. 114, line 22. For D_0,h , read $D_{0,h}$

p. 127, eqn. (6.3). For $\mathbf{V}_2$, read $\mathbf{v}_2$

p. 133, line 17. For $J^i_1 = D^i_1\,\mathrm{d}c_1/\mathrm{d}x$, read $J^i_1 = -D^i_1\,\mathrm{d}c_1/\mathrm{d}x$

p. 134, para. 2. For v_1 , read v^0_1 throughout

p. 135, eqn. (6.31). For $\frac{kT}{h}$, read $\frac{\boldsymbol{k}T}{\boldsymbol{h}}$

p. 137, line above eqn. (6.38). For $D^{\mathrm{id.}}_N$, read D^{id}

p. 138, eqn. (6.41). For $D^{\mathrm{id}.N}$, read D^{id}

p. 140, line 7. For $D^{\mathrm{id}.N}$, read D^{id}

p. 141, para. 2, line 11. For ' assumption ' read ' assumptions '

p. 152, line 10. For ' product $D^{12}B^c$ ', read ' quotient D^{12}/B^c '

p. 159, line 7. For D^*_1, η_1, v^0_1 , read D^*, η, v^0

p. 171, Table heading. For ' $D^{\mathrm{id}}_{12}, D^*_{12}$', read ' $D_{12}, D^{\mathrm{id}}_{12}$ '

p. 201, line 29. For ' shall ', read ' small '

p. 235. Table heading. For ' 1N ' , read ' 1M '

p. 241, eqn. (9.6). For $(\mathscr{P}_1 v_1 + \mathscr{P}^0_1 v^0_1)$, read $(\mathscr{P}_1 v_1 - \mathscr{P}^0_1 v^0_1)$

p. 266, 3 lines below eqn. (10.10). For s^*_+ , read S^*_+

p. 278, Figure 10.8. For 0·1M , read 0·01M

p. 280, line 8. For Di'/Di , read D'_i/D_i

p. 308, para. 2, line 10. For $\eta = l\bar{\mathbf{v}}_m/3$, read $\eta = \rho l\bar{\mathbf{v}}_m/3$

p. 309, line 14. For $\mathbf{v}_p$, read $\bar{\mathbf{v}}_p$

p. 313, eqn. (11.27). For $\left(\frac{8}{\pi\gamma}\right)^{1/2}\bar{\mathbf{v}}_m$, read $\left(\frac{8}{\pi\gamma}\right)^{-1/2}\bar{\mathbf{v}}_m$

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1

INTRODUCTORY SURVEY

THE diffusion of one liquid into another or that of a solid into a liquid, the transfer of heat or electricity from one point in space to another, are all examples of 'flows' taking place under the influence of 'forces'; in these examples the forces are the gradients of concentration, temperature, and electrical potential respectively. The analogy between heat flow and diffusion appears to have been pointed out for the first time by Berthollet[1], in his discussion of the mechanism of the dissolution of a salt crystal in water. The crystal dissolves, and removal of the dissolved solute from the surface may involve pure diffusion, occurring without visible movement of the solution as a whole, and, in addition, a macroscopic flow of the denser parts of the solution relative to the lighter parts. Similarly, heat flow by conduction may be accompanied by convection. There is no analogue in material transport processes to the process of radiation in heat transfer. Again, the flow of electricity in an electrical conductor is analogous to heat flow and to the process of pure diffusion. The first quantitative studies of these transport processes were directed towards the discovery of the relationships between the 'flows' and the 'forces' causing the 'flow'. In the case of heat conduction, the flow of heat was found by Fourier[2] to be a linear function of the temperature gradient causing the flow. Five years later Ohm showed that the electric current flowing in a conductor was a linear function of the potential difference between the ends of the conductor. Thus the relationship between the flow and the force causing the flow was found to have a simple linear form for the transport of both heat and electricity. Berthollet's analogy between heat conduction and diffusion was rediscovered by Fick[3] who assumed that the force responsible for diffusion flow in a binary mixture was the gradient of concentration, and formulated the relationships now known as Fick's first and second laws of diffusion in a manner exactly analogous to that used by Fourier in the heat conduction problem, replacing the temperature gradient in Fourier's equation by the concentration gradient.

The general form of these linear relationships for a one-dimensional system is,

$$J = -(\text{constant})\mathrm{d}f/\mathrm{d}x$$

where J represents a flow of heat matter or electricity across a suitably chosen reference plane per unit time in a one-dimensional system, and f is the corresponding potential, namely temperature (T), concentration in gram molecules of component i per unit volume (c_i), or electrical potential (ψ). The so-called phenomenological relationships for heat flow, matter flow, and electricity flow, are then written as,

$$J_q = -k\,\mathrm{d}T/\mathrm{d}x \qquad \text{(Fourier's Law)} \qquad (1.1)$$

$$J_i = -D\,\mathrm{d}c_i/\mathrm{d}x \qquad \text{(Fick's Law)} \qquad (1.2)$$

$$\mathrm{I} = -\kappa\mathrm{A}\,.\,\mathrm{d}\psi/\mathrm{d}x \qquad \text{(Ohm's Law)} \qquad (1.3)$$

J_q and I are respectively the heat flow per unit area per unit time, and the electricity flow across a defined reference plane perpendicular to the direction of flow, and k, κ are the coefficients of thermal and of electrical conductivity. J_i is the flow of component i in mass units per unit area per unit time across a reference plane perpendicular to the direction of flow and D is the diffusion coefficient. While the choice of a reference plane is usually simple for heat and electricity flow, and for matter flow in a solid mixture, this is not the case for diffusion in liquid mixtures, as Fick was himself aware. This problem is discussed in Chapter 3.

Usually Ohm's law is used for a uniform conductor across which a constant potential $(-\Delta\psi)$ is applied. Then, if the conductor is a uniform bar of length l:

$$\mathrm{I} = \kappa\mathrm{A}/l\,.\,\Delta\psi = \Delta\psi/R \qquad (1.4)$$

where R is called the electrical resistance of the bar, obtained by measuring the time-invariant or steady state value of the current I produced by a given $\Delta\psi$. This steady state is established almost instantaneously, and the *rate* at which it is established is not therefore of interest for most purposes. However, the time invariant state is established much less rapidly in the case of heat or matter flow, and the rate of establishment is of considerable interest. When systems not in a steady state are being studied it is convenient to eliminate the dependent variable J from equations (1.1) and (1.2). If, at a plane x the flows of heat and matter are given by J_q and J_i respectively, the fluxes at plane $x + \delta x$ will be given by $J_q + (\partial J_q/\partial x)\,.\,\delta x$ for heat flow, and by $J_i + (\partial J_i/\partial x)\,.\,\delta x$ for the flow of component i. For heat flow,

$$\partial/\partial t(J_q) = -\,\partial/\partial x(J_q)\,.\,\delta x$$

or

$$\rho\,.\,C\,.\,\delta x\;\partial T/\partial t = \partial/\partial x(k\,.\,\partial T/\partial x)\,.\,\delta x$$

and hence

$$\partial T/\partial t = 1/\rho C\,.\,\partial/\partial x(k\,.\,\partial T/\partial x)$$

$$= k/\rho C\,.\,\partial^2 T/\partial x^2 \qquad (1.5)$$

if k is independent of x. Here ρ is the density, t the time, and C the heat capacity of the conducting material. The quantity $k/\rho C$ is known as the diffusivity (Kelvin), or thermometric conductivity (Maxwell) and written K. For diffusion, a similar argument leads to the equation,

$$\partial c_i/\partial t = \partial/\partial x(D\,.\,\partial c_i/\partial x) = D\,.\,\partial^2 c_i/\partial x^2 \qquad (1.6)$$

if D is independent of x. This is now termed Fick's second law of diffusion, though Fick himself considered this to be the diffusion law, and equation (1.2) to be simply a necessary mathematical step in the derivation of (1.6). Equations (1.5) and (1.6) are of considerable importance in the interpretation of experimental work on systems not in a steady state. In order to obtain values of D or K from such measurements it is necessary to solve (1.5) or (1.6) subject to boundary conditions appropriate to the particular experimental arrangement used. An equation relating measurable quantities and the constants D or K is then obtained. For example, if a semi-infinite solid, initial temperature zero, is placed in contact with a source of heat maintained at a temperature T_0, in such a way that the boundary is at $x = 0$, then the temperature T at time t after contact is made, at a point in the solid distance x from the boundary, is given by,

$$T = T_0\left(1 - \operatorname{erf}\frac{x}{2\sqrt{(Kt)}}\right)$$

provided that K is constant throughout the system. The function erf $\{x/2\sqrt{(Kt)}\}$ is defined as

$$\int_0^x \exp[-x/2\sqrt{(Kt)}]\,.\,dx$$

Hence K can be calculated from measurements of T, T_0, x and t. Much attention has been paid to the solution of equations (1.5) and (1.6) for a variety of boundary conditions[4-6], and the nature of the particular experimental method used for the determination of K or D determines the particular solution which must be used in order to obtain the constants from experimental measurements. In many cases, the coefficients K and D cannot be considered as constant over a wide range of experimental conditions, and, unless these are carefully chosen, the integral forms of (1.5) and (1.6) obtained assuming K or D to be constant will no longer be appropriate. In some instances it is possible to obtain solutions for cases in which D or K are variable; these are limited in application, and more difficult to handle than the simpler ones. It is usually easier to choose experimental conditions such that the variation of the coefficients is sufficiently small to be ignored; the standard solutions of the differential equations (1.5) and (1.6) can then be used without noticeable error. Alternatively, steady state methods may be devised for which equations (1.1) and (1.2) can be used directly.

The above discussion has been concerned with the magnitude of the flow produced by a force which is obviously directly related to it, for example, the flow of heat under a temperature gradient. There are, however, a number of phenomena in which a force of one kind produces a flow of another. The classic example of this is the flow of electric current induced by a temperature gradient across a junction between two dissimilar metals (Seebeck effect), and the inverse effect, the liberation of heat at the junction when a current of electricity passes across it (Peltier effect). The presence of a concentration gradient in the solution of an electrolyte is associated with a gradient of electrical potential, the diffusion potential. If a temperature gradient is applied to a liquid system of more than one component, concentration gradients will be slowly built up in the solution until a steady state is reached in which a time invariant concentration gradient remains unchanged as long as the temperature gradient exists. When this is removed, the concentration gradient will gradually disappear.

This was first observed by Ludwig[7]. He enclosed a concentrated solution of sodium sulphate in an inverted U-tube, cooled one limb in ice, and heated the other. The solute migrated into the cooled limb under the influence of the temperature gradient, and, after a short time, crystals of the salt appeared in the cold limb. Solutions of electrolytes were first studied in detail by Soret[8] who found that small but definite increases in concentration occurred in the cooler portion of the solution after a long period of time had elapsed. A general explanation of the effect was proposed by Van't Hoff[9] who suggested that the solute distributed itself over the unequally heated column in such a way that the osmotic pressure of the solution was constant at all points along the column. This theory requires that for salts of similar valence type in dilute solution, the observed change in concentration should be the same under the same experimental conditions. Both Arrhenius[10] and Scarpa[11] obtained results which suggest that this was probably not the case. The phenomenon attracted no more than occasional interest for many years. It was suggested as an explanation for the observed separation of the components of rock magmas, and is probably valid in certain cases of such separations[12].

In the field of metallurgy, it was at one time used to account for *inverse segregation* in solidifying metal ingots[13]. In certain alloys the component with the lower melting point concentrates at points where the higher melting component would be expected in excess, and some notable experimental work was done on the magnitude of the effect in molten metal mixtures[14]. In fact the effect seems too small to account for the experimental observations on 'inverse segregation'. From time to time experimental studies which were principally, though not entirely, concerned with electrolyte solutions, were reported[15]. In most of these the liquid column was enclosed between two horizontal metal plates one or two centimetres apart and separated by insulating walls. The upper plate was heated with respect to the lower one to minimize the disturbing effect of convection currents. The temperature equilibrium is established within a few minutes in such cells but the thermal migration process or 'pure Soret effect' takes place over a period of many hours. Finally a steady state is attained in which a stable and characteristic concentration gradient is present in the liquid column. The measurement of this has been the object of the majority of researches with this form of apparatus, though it is possible to obtain an estimate of the ordinary diffusion coefficient of the system by measuring the rate at which the equilibrium is attained.

The separations found in such experiments are small, but the phenomenon can be used to obtain rapid, and in some cases complete, separation of the components of a mixture. The method was first suggested and used for the separation of isotopes in the gas phase[16], but was rapidly extended to the separation of liquid mixtures[17,18]. The temperature gradient is established between two vertical surfaces less than 1 mm apart. A steady state equilibrium is rapidly set up over this short distance in the horizontal plane, the solute being enriched at either the hot or the cold wall. In addition to this horizontal separation, there is a convective flow of the liquid upwards in the region of the hot wall and downwards in that of the cold wall. If the solute migrates to the hot wall under the influence of the temperature gradient, it is carried upward and becomes enriched at the top of the column. If it migrates initially to the cold wall, it concentrates at the bottom. There are some analogies with the process of separation in a distillation column and very considerable separations can be achieved rapidly in favourable cases. These columns have also been used in fundamental studies of the separation process and it will be shown that, in principle, the same information can be obtained from experiments with them as can be obtained from the pure Soret effect cells. The inverse effect, the heat flow associated with a concentration gradient, is known as the Dufour effect. It has not been observed for liquids, probably because of their high thermal conductivities, but it has been found in gaseous mixtures and studied, under the name 'diffusion thermo-effect', principally by Waldman[19].

A phenomenological description of the Soret effect can be given in terms of an extension of Fick's law and Fourier's law; other, similar, phenomena could be treated in the same general way. As in the simpler cases, these extended equations, and suitable integral solutions of them, are essential to the interpretation of the experimental measurements but contribute nothing to an understanding of the fundamental nature of the phenomena being studied. A classical thermodynamic treatment of these transport processes is not strictly possible because the systems are not in thermodynamic equilibrium. Certain *ad hoc* applications of these methods to transport phenomena have given the correct results, the earliest and best known example being Thomson's treatment[20] of the problem of metallic thermocouples. He divided the phenomena occurring in a thermocouple into two classes, *reversible* and *irreversible*, calculated the entropy changes in the reversible class, and equated the sum of these to zero. Entropy changes in the irreversible processes were neglected. The equations obtained by this method were found to be applicable to the experimental data, and this provided a necessary confirmation of the classification into reversible and irreversible phenomena. A quasi-thermostatic theory of this kind lacks generality since it depends for its truth upon a correct assignment of the observed effects in the system into reversible and irreversible. Neither can it give a complete description of all the possible effects which can appear in systems in which more than one kind of force is in operation, and of the relationships which must exist between them.

A general thermodynamic theory of systems which are not in equilibrium has been developed in recent years which is free from these objections (Chapter 2). It is possible to give a coherent account of diffusion, thermal diffusion, thermal conductivity, as well as of other transport processes, without introducing any special hypotheses. The general statements derived in this way are valid as long as the system does not depart too far from a state of true thermodynamic equilibrium. The theory is of particular use when applied to those states of pseudo-equilibrium which are characteristic of systems in which more than one irreversible process is occurring. In these, the properties of the system become independent of time, though it is certainly not in thermodynamic equilibrium. An example is a thermocouple from which no current is being drawn. As long as the temperature gradient is maintained constant, the thermal e.m.f. remains so, and the system is said to be in a *steady state*. In this instance the steady state is reached almost instantaneously, but in other cases it may take many hours or days to establish, e.g. the Soret equilibrium in liquid mixtures. It is for systems in such states that the thermodynamic theory is most effective.

However, with all its power to provide general relationships between different observables, at least within a range of experimental conditions, the thermodynamic theory cannot give any information about the magnitude of coefficients such as k, D or κ in equations (1.1), (1.2) and (1.3). To do this, kinetic theories must be formulated for each phenomenon. This is a difficult task for liquid mixtures. For dilute electrolyte solutions it is possible to predict the variation of electrical conductivity and of the diffusion coefficient with concentration, and to relate the limiting value of the latter to the limiting ionic conductivities. If there is a great disparity in the size of the two species of molecules forming a binary mixture, the velocity under an applied force of the larger one, if spherical, can be calculated from Stokes law since the medium in which the motion takes place can be regarded as continuous in these circumstances. Since 1946 considerable advances have been made in the statistical–mechanical treatment of transport processes in liquids, a treatment which in principle is applicable to any class of liquid or liquid mixture. In fact, because of mathematical difficulties the discussion is usually confined to the special case where the force between two molecules is derivable from a potential which is a function of intermolecular distance alone, i.e. to monatomic liquids. The most successful development of these theories is perhaps that due to Kirkwood[21], who assumed that the force on any sub-set of p particles due to the remaining $(N - p)$ is analogous to the average frictional force exerted on a particle of colloid dimensions undergoing Brownian motion. Other starting points are possible, but have so far proved rather less useful[22–24]. The first step in Kirkwood's theory (and in others) is the calculation of the time-average distribution, when the system is perturbed by the steady state transport process, of single and pair molecular densities in a hyperspace in which the $3N$ positional and $3N$ momentum coordinates of the system can be represented, and to express the transport coefficients in terms of these densities. This last problem has been solved[25,26] and the calculation of the time-average distribution of densities has been carried out for viscous flow[27–30] and thermal conductivity[25,31]. Fair success has been obtained in calculating the shear viscosity and thermal conductivity of liquid argon but the major unsolved problem in this field is the calculation of a frictional coefficient ζ which appears in all the final equations. This is introduced because of the analogy drawn between the force on the sub-set to the force $\mathbf{F}(t)$ on a colloid particle, mass m, undergoing Brownian motion, for which,

$$\mathbf{F}(t)/m = \mathbf{A}(t) - \zeta(\mathbf{v} - \mathbf{v}_0)$$

where $\mathbf{v}$ is the instantaneous velocity of the particle, $\mathbf{v}_0$ the local mass velocity of the liquid, and,

$$\mathbf{A}(t) = \dot{\mathbf{v}} + \zeta(\mathbf{v} - \mathbf{v}_0)$$

Some of the difficulties can be avoided by assuming that the fluid acts as a collection of rigid spheres[32,33], but calculations of the viscosity and of the temperature coefficient of the viscosity of a number of liquids agreed only moderately well with experimental data. An excellent review of these statistical theories has recently been published[34].