DIFFUSION OF DISSOLVED GASES IN LIQUIDS

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CONTENTS

I. INTRODUCTION

Study of the molecular diffusion of dissolved gases in liquids has been of interest for two reasons. First, from a theoretical viewpoint, our understanding of the liquid state is still in a preliminary stage of development, and diffusivity data can provide important checks on any proposed theory or model of the liquid state. Dissolved gases form a special class of molecules of small size in the broad category of liquid diffusion. Second, diffusivities of gases in liquids are important to engineers in gas–liquid mass transfer calculations and correlations.

In this review, "dissolved gases" refers to those gases which are for practical purposes noncondensable at the temperature and pressure of interest, although not necessarily gases above their critical points. Such gases are characteristically only slightly soluble in water but they may be more soluble in organic solvents.

The purpose of this review is to describe and evaluate experimental results of diffusivities of dissolved gases in liquids, and to discuss the applicability of general diffusion theory to this specific topic. The literature through 1963 is covered.

A. NOTATION

A systematic notation has been adopted and used throughout this review. The symbols and their meanings are as follows (boldface letters are vectors).

a_i	activity of component i
A, A', A''	constants
A_1, A_2	abnormality factors for solute and solvent, respectively, in Arnold's correlation
A_{ij}	coefficient in the Stefan–Maxwell equations involving molecular weights and corrections for non-ideality
B, B', B''	constants
c	concentration expressed as moles per unit volume; with subscripts f and 0, meaning is final and initial concentrations
c_i	molar concentration of component i

c^*	equilibrium concentration
C, C'	constants
C_p	heat capacity
$\mathbf{d}_i$	phenomenological force $= (c_iM_i/p_i)X_i$
D_i	self-diffusion coefficient of component i
$D_i^{\bigcirc}$	self-diffusion coefficient of component i for a volume frame of reference using partial mass volumes as weights
$D_i^{\bullet}$	self-diffusion coefficient of component i for a volume frame of reference using partial molal volumes as weights
D_i^{∞}	self-diffusion coefficient of component i at infinite dilution
D_P	diffusivity calculated from the penetration theory
D_{12}	mutual diffusion coefficient of component 1 in solvent 2, reference frame unspecified
D_{ij}^*	diffusivity of the pair i–j in a multicomponent mixture
D_{im}	effective binary diffusion coefficient of component i in mixture m
$D_{12}^{\bigcirc}$; $D_{12}^{\bullet}$	binary diffusivity based on flux relation $\mathbf{J}_1^{\bigcirc} = -D_{12}^{\bigcirc}\nabla c_1$; or $\mathbf{J}_1^{\bullet} = -D_{12}^{\bullet}\nabla c_1$
D_{ij}'	diffusion coefficients defined by Eq. 41
D_{12}^{∞}	mutual diffusion coefficient of binary 1–2 at infinite dilution of species 1 (and equal to $D_1^{\bigcirc}$ at that concentration)
D_{12}^{w}	defined in Eq. 89
$\bar{D}_{12}$	integral mutual diffusion coefficient of component 1 in solvent 2, reference frame unspecified
$\mathfrak{D}_{ij}$	binary diffusion coefficient of pair i–j
$\hat{\mathfrak{D}}_{ij}$	binary diffusion coefficient defined by Eq. 32
E	constant
E_{D}, E_{V}	activation energy for diffusion and viscosity, respectively
f_i	activity coefficient defined by $a_i = c_if_i$
F	factor in Wilke correlation
F	Faraday number in Eq. 101
$\bar{F}_1^{(1)}$	force on species 1 in a multicomponent mixture
$\bar{F}_1^{(1,1)*}$	frictional force on component 1 for molecular mass transport
ΔF^*	change in total free energy of activity for a viscous (η) or diffusional (D) process
g_{ij}	statistical mechanical molecular distribution functions
$\bar{G}_i$	partial molal free energy of component i
h	Planck constant
H	jet length
i_d	limiting current
$\mathbf{j}_i$	mass diffuse flux of component i with respect to a mass average velocity $\mathbf{v}$ frame of reference
$\mathbf{j}_i^{\bigcirc}$	mass diffusive flux of component i with respect to a volume average velocity, $\mathbf{v}^{\bigcirc}$, frame of reference
$\mathbf{J}_i^{\bullet}$	mole diffuse flux of component i with respect to a volume average velocity, $\mathbf{v}^{\bullet}$, frame of reference, $\mathbf{J}_i^{\bullet} = c_i\bar{V}_i(\mathbf{v}_i - \mathbf{v}_i^{\bullet})$
$\mathbf{J}_i^*$	mole diffusive flux of component i with respect to a mole average velocity, $\mathbf{v}^*$, frame of reference
k	Boltzman constant
k''/k'	ratio of diffusion velocity in solution to that of self-diffusion, which is the same as the ratio of the jumping frequency in a pure liquid to that in solution
L	molar latent heat of vaporization at T
L_{ij}	phenomenological coefficients of the "linear law" of irreversible thermodynamics
m	weight of mercury flowing from the capillary per second in Eq. 101
M	molecular weight
$\mathfrak{M}$	defined in Eq. 33
n	number of electrons transferred in Eq. 101
n	number of moles
$\mathbf{n}_i$	mass of flux of component i with respect to a fixed coordinate frame of reference
N	total number of moles of gas absorbed per unit time
N	number of components in a multicomponent mixture
N_{A}	Avagadro's number
N_{T}	total moles of gas transferred
$\mathbf{N}_i$	mole flux of component i with respect to a fixed coordinate frame of reference
p	pressure
P^*	vapor pressure
q	volumetric flow rate of liquid
Q	dissolved gas $= \alpha(T/273)\,(p/760)$
r	molecular radius (with appropriate subscript)
$\mathbf{r}$	position vector
r_i	chemical reaction term in mass balance
R	gas constant
R^*	volume ratio of chambers for diaphragm cell, and equal to V''/V'
s	entropy
S	area of transfer surface
t	time
T	absolute temperature
u_s	sonic velocity of solvent
U	internal energy
v_s	surface velocity of a laminar jet
v_y	velocity in y-coordinate direction
$\mathbf{v}$	mass average velocity vector
$\mathbf{v}_i$	velocity vector of component i
$\mathbf{v}^{\bigcirc}$	volume average velocity vector
$\mathbf{v}^{G}$	generalized average velocity vector
V	volume, or molecular volume with numbered subscripts
V_f	free volume
V_0	molar volume, either experimental at the normal boiling point, or the Le Bas values
$\bar{V}_i$	partial molal volume
$\bar{V}_i^{\bigcirc}$	partial mass volume
$V_0^{\mathrm{m}}/V^{\mathrm{m}}$	ratio of the molecular and incompressible volumes, *i.e.*, occupied volume and total volume per molecule
x	coordinate perpendicular to surface of jet in Eq. 97
x	association factor in Wilke equation
x_i	mole fraction of component i
$\mathbf{X}_i$	phenomenological "forces" in the linear law
y	linear dimension in rectangular coordinates
z	axial direction in Eq. 97
z_i	weighting factor

Greek Letter Symbols

α	Bunsen coefficient at the T and p of the experiment in Eq. 103
α	distance between nearest neighbors
β	coefficient of sliding friction between molecules
γ_i	activity coefficient defined by $a_i = x_i\gamma_i$
δ	displacement of a molecule
ϵ	defined in Eq. 53
ϵ°	bond energy, calories/gram mole
ζ_{1j}	friction coefficient for diffusion
$\langle\zeta_{12}\rangle$	binary friction coefficient defined by Einstein's equation

η	viscosity of a binary solution
η_g	viscosity of gas
η_i	viscosity of pure species i
η_m	viscosity of a multicomponent mixture
η_w	defined in Eq. 89
λ	coordination number
$\lambda_1, \lambda_2, \lambda_3$	parameters representing molecular dimensions; λ_1 is the distance between equilibrium jump positions of the diffusing molecules $\cong (V_0/N_A)^{1/3}$
μ	chemical potential; partial mass free energy
ξ	average number of nearest neighbors with respect to which the solute species moves, or in effect the number of viscous shears each diffusing molecule makes with its neighbors
ρ	mass of fluid per unit volume
ρ_i	concentration expressed as mass of component i per unit volume
σ	number of closest neighbors in all directions
σ	rate of entropy production
σ_{12}	mean collision diameter of molecules of species 1 and 2
τ	number of closest neighbors in one layer
τ	characteristic time for displacement in random walk analysis
ϕ	flux of molecules in y-direction in random walk analysis
ϕ_{1j}	intermolecular potential between species 1 and species j
ω_i	mass fraction of component i

B. THE GENESIS OF THE DIFFUSION FLUX

The well-known equation for the mass balance of the ith species in vector notation[1] is

$$\frac{\partial \rho_i}{\partial t} + (\nabla \cdot \mathbf{n}_i) = r_i \qquad \text{(Eq. 1)}$$

Equation 1 describes the change with time of the mass of the ith component at a point in a fluid with respect to a fixed coordinate system. The equation is not useful in this form until both the flux $\mathbf{n}_i$ and the reaction term r_i are replaced by suitable expressions involving the dependent variable ρ_i. In this review the reaction term will not be considered, although for a gas such as Cl_2 in water the reaction term must be taken into account.

Ordinarily, the flux $\mathbf{n}_i$ is split into two parts: a term called the bulk flow of the fluid, $\rho_i\mathbf{v}$, and a term called the diffusive flux, $\mathbf{j}_i$.

$$\mathbf{n}_i = \rho_i \mathbf{v} + \mathbf{j}_i = \rho_i \mathbf{v}_i \qquad \text{(Eq. 2)}$$

The mass diffusive flux in a multicomponent system consists of the sum of four terms, the fluxes due to "ordinary" diffusion, pressure diffusion, "forced diffusion" (diffusion due to external force field), and thermal diffusion. Our concern will be solely with the first mechanism, but the interested reader can refer to DeGroot and Mazur (26) or Fitts (38) for further details as to the origin of the other mechanisms.

Equation 2 is still a formalism in that the term $\rho_i\mathbf{v}$ can in principle be measured, but the term $\mathbf{j}_i$ still needs to be related to the dependent variable ρ_i. Since our theories of liquids are imperfect, there is no single way to express the diffusion flux from a molecular view as there is for the case of dilute gases, and consequently those working on diffusion in liquids have imitated models used in the gas-like state or the solid-like state. Truesdell (134) lists four general approaches which have been used to express the desired relation:

(a) Kinematic, leading to Fick's equation (37) of diffusion

$$\mathbf{j}_1 = -\rho \mathfrak{D}_{12} \nabla \omega_1 \qquad \text{(Eq. 3)}$$

where $\mathfrak{D}_{12}$ is Fick's diffusion coefficient.

(b) Hydrodynamic, leading to the Stefan–Maxwell equations

$$\nabla \omega_i = \sum_{j=1}^{N} \frac{A_{ij}\rho_i\rho_j}{\rho^2 \mathfrak{D}_{ij}}(\mathbf{v}_j - \mathbf{v}_i) = \sum_{j=1}^{N} \frac{A_{ij}}{\rho^2 \mathfrak{D}_{ij}}(\rho_i \mathbf{n}_j - \rho_j \mathbf{n}_i) \qquad \text{(Eq. 4)}$$

(c) Kinetic, leading to the Chapman–Enskog formulation

$$\mathbf{j}_i = \frac{c^2}{\rho RT} \sum_{j=1}^{N} M_i M_j D_{ij}{}^* \left[x_j \sum_{\substack{k=1 \\ k \neq j}}^{N} \left(\frac{\partial \bar{G}_j}{\partial x_k} \right)_{\substack{T,\, P,\, xs \\ s \neq j,k}} \nabla x_k \right] \qquad \text{(Eq. 5)}$$

where $D_{ij}{}^*$ is the diffusivity of the pair i–j in a multicomponent mixture.

(d) Irreversible thermodynamic, leading to the Eckart–Meixner relations

$$\mathbf{j}_i = \sum_{k=1}^{N} L_{ik} \mathbf{X}_k \qquad \text{(Eq. 6)}$$

subject to

$$\sum_{i=1}^{N} \mathbf{j}_i = 0 \qquad \text{(Eq. 7)}$$

It can be seen that there are a wide variety of diffusion coefficients which can be defined for liquids and that one coefficient is not simply related to another. In any case, after introducing the appropriate flux expression in Eq. 1, picking a suitable coordinate system, and detailing the boundary and initial conditions, Eq. 1 is ready for solution. Crank (19) lists a considerable number of these.

This review first considers phenomenological diffusion theories for binary and multicomponent mixtures in order to categorize the modes of mathematical description which are used to describe the process of diffusion of gases in liquids. Since the phenomenological equations are microscopic equations, the molecular basis of diffusion is next examined in the hope of predicting the phenomenological diffusion coefficients from our knowledge of molecular phenomena. Finally, the empirical basis of diffusion is discussed along with the common ways diffusion coefficients of gases in liquids are determined and correlated.

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(1) Notation is defined in section IA.

C. ALTERNATE REFERENCE FRAMES FOR THE DIFFUSION FLUX

When molecular diffusion takes place in multicomponent systems each species moves at its unique velocity. The equations presented above have referred the total mass flux $\mathbf{n}_i = \rho_i \mathbf{v}_i$ to a fixed coordinate system. In defining the diffusion flux it is possible, besides using mass or mole units, to select many types of reference coordinates, such as the local mass average velocity ($\mathbf{v}$), the local mole average velocity ($\mathbf{v}^*$), or the local volume average velocity ($\mathbf{v}^{\bigcirc}$ or $\mathbf{v}^{\bullet}$). Such average velocities can be defined in general ($\mathbf{v}^G$) as

$$\mathbf{v}^G = \frac{\sum_{i=1}^{N} z_i \mathbf{v}_i}{\sum_{i=1}^{N} z_i} \qquad \text{(Eq. 8)}$$

where z_i is a weighting factor and is equal to ρ_i for $\mathbf{v}$, c_i for $\mathbf{v}^*$, $\rho_i \bar{V}_i^{\bigcirc}$, for $\mathbf{v}^{\bigcirc}$ and $c_i \bar{V}_i$ for $\mathbf{v}^{\bigcirc}$. With these identifications it becomes apparent that the definition of the diffusion flux is not complete until both the units and reference frame have been specified. Furthermore it is easy to show that the sum over all species of the diffusion flux times the weighting factor is zero as in the following cases.

Mass flux $\mathbf{j}_i$ referred to mass average velocity $\mathbf{v}$

$$\mathbf{j}_i = \rho_i(\mathbf{v}_i - \mathbf{v}) \qquad \Sigma \mathbf{j}_i = 0 \qquad \text{(Eq. 7a)}$$

Mole flux $\mathbf{J}_i^*$ referred to mole average velocity $\mathbf{v}^*$

$$J_i^* = c_i(\mathbf{v}_i - \mathbf{v}^*) \qquad \Sigma \mathbf{J}_i^* = 0 \qquad \text{(Eq. 7b)}$$

Mass flux $\mathbf{j}_i^{\bigcirc}$ referred to volume average velocity $\mathbf{v}^{\bigcirc}$

$$\mathbf{j}_i^{\bigcirc} = \rho_i \bar{V}_i^{\bigcirc}(\mathbf{v}_i - \mathbf{v}^{\bigcirc}) \qquad \Sigma \mathbf{j}_i \bar{V}_i^{\bigcirc} = 0 \qquad \text{(Eq. 7c)}$$

Mole flux $\mathbf{J}_i^{\bullet}$ referred to volume average velocity $\mathbf{v}^{\bullet}$

$$\mathbf{J}_i^{\bullet} = c_i \bar{V}(\mathbf{v}_i - \mathbf{v}^{\bullet}) \qquad \Sigma \mathbf{J}_i^{\bullet} \bar{V}_i = 0 \qquad \text{(Eq. 7d)}$$

Further details of the conversion relationships between the fluxes, velocities, and diffusion coefficients in any arbitrarily chosen coordinate system are given by ref. 72 and 133. In the experimental determination of diffusion coefficients of slightly soluble gases in liquids, the diffusivities often prove to be essentially the same for the common reference frames, but one must always carefully examine the details of how the diffusion coefficients are defined for each specific case.

II. DIFFUSION THEORY AND MOLECULAR DYNAMICS

In common with other transport phenomena, the process of diffusion can be examined from the molecular or from the microscopic viewpoints; both are considered below. Molecular descriptions of diffusion in principle should lead to the prediction of the microscopic parameter known as the diffusivity introduced in Eq. 2 as part of the diffusion flux. In practice, we find molecular descriptions are so intractable that diffusivities cannot be predicted from basic statistical mechanical principles without introducing unknown parameters which must be evaluated empirically on a microscopic basis in the same fashion as the diffusivity. Nevertheless, there is always hope for the future that as our mathematical tools become more versatile and as our mathematical models become better developed the present obstacles will disappear.

A. DIFFUSIONAL FLUX IDENTIFIED BY MEANS OF IRREVERSIBLE THERMODYNAMICS

The study of irreversible thermodynamics permits one to identify the fluxes and forces involved in ordinary and other types of diffusion. One of the main attributes of irreversible thermodynamics is that these quantities agree with those obtained from the only self-consistent nonequilibrium theory yet developed, namely the kinetic theory of gases.

Given two basic postulates

(a) entropy can be defined out of equilibrium by the Gibbs equation ($dU = Tds - pdV + \Sigma \mu_k dn_k$)

(b) the fluxes ($\mathbf{j}_i$) and forces are related by a linear law, Eq. 6

it can be shown (26) from postulate a that the entropy production, σ, is always given by an equation of the following form.

$$\sigma = \sum_{i=1}^{N} \mathbf{j}_i \cdot \mathbf{X}_i \qquad \text{(Eq. 9)}$$

The phenomenological coefficients in Eq. 6 may be functions of concentration, temperature, pressure, etc., but not of $\mathbf{X}_k$.

Equation 9 permits the identification of the appropriate fluxes and forces to use in the linear law of postulate b. For multicomponent ordinary diffusion, that is, in a uniformly acting external field, with constant temperature and pressure, the phenomenological force term for the *i*th component can be identified (26) as

$$\mathbf{X}_i = -\frac{1}{T}\nabla \mu_i \qquad \text{(Eq. 10)}$$

where μ_i is the partial mass (not molal) free energy.

Since one restriction on Eq. 9 is given by Eq. 7, we find also

$$\sigma = \sum_{i=1}^{N-1} \mathbf{j}_i \cdot (\mathbf{X}_i - \mathbf{X}_N) \qquad \text{(Eq. 11)}$$

and

$$\mathbf{j}_i = \sum_{k=1}^{N-1} L_{ik}(\mathbf{X}_k - \mathbf{X}_N) \qquad \text{(Eq. 12)}$$

For the case of a *binary*, the linear law states for component 1

$$\mathbf{j}_1 = L_{11}(\mathbf{X}_1 - \mathbf{X}_2) + L_{12}(\mathbf{X}_2 - \mathbf{X}_2) = -\mathbf{j}_2$$

or

$$\mathbf{j}_1 = \frac{L_{11}}{T}(-\nabla \mu_1 + \nabla \mu_2) \qquad \text{(Eq. 13)}$$

Equation 13 can be further simplified using the identity

$$\nabla\mu_i = \frac{\partial\mu_i}{\partial\omega_i}\nabla\omega_i$$

plus the fact that for a binary $\omega_1 + \omega_2 = 1$, so that $\nabla\omega_1 = -\nabla\omega_2$. Then the Gibbs–Duhem equation

$$\omega_1\frac{\partial\mu_1}{\partial\omega_1} + \omega_2\frac{\partial\mu_2}{\partial\omega_2} = 0$$

is introduced to give the following

$$\mathbf{j}_1 = -\rho\left(\frac{L_{11}}{\rho T}\frac{1}{\omega_2}\frac{\partial\mu_1}{\partial\omega_1}\right)\nabla\omega_1 \qquad \text{(Eq. 14)}$$

Now, with the above grouping, the phenomenological coefficient L_{11} and the diffusion coefficient $\mathfrak{D}_{12}$ from eq. 3 can be related.

$$\mathfrak{D}_{12} = \left(\frac{L_{11}}{\rho T}\frac{1}{\omega_2}\frac{\partial\mu_1}{\partial\omega_1}\right) \qquad \text{(Eq. 15)}$$

Although the true driving force for diffusion is the chemical potential, there is no inherent reason why L_{11} should be a more constant coefficient than $\mathfrak{D}_{12}$, and, in general, results from binary diffusion experiments are nearly always reported as diffusion coefficients rather than phenomenological coefficients. Note also that $\mathfrak{D}_{12} = \mathfrak{D}_{21}$, *i.e.*, one diffusion coefficient characterizes a binary system as well as one Onsager coefficient.

Consider next a *ternary* system. The linear law gives two independent equations.

$$\mathbf{j}_1 = L_{11}(\mathbf{X}_1 - \mathbf{X}_3) + L_{12}(\mathbf{X}_2 - \mathbf{X}_3) \qquad \text{(Eq. 16a)}$$

$$\mathbf{j}_2 = L_{21}(\mathbf{X}_1 - \mathbf{X}_3) + L_{22}(\mathbf{X}_2 - \mathbf{X}_3) \qquad \text{(Eq. 16b)}$$

[Note again $\mathbf{j}_3 = -(\mathbf{j}_1 + \mathbf{j}_2)$.] The well-known Onsager reciprocal relations state that $L_{ik} = L_{ki}$, and consequently, a ternary system will be characterized by three independent parameters, L_{11}, $L_{12} = L_{21}$, and L_{22}.

Quite a few possible definitions of diffusion coefficients for ternary systems have been suggested. With a few new definitions, it is possible to relate Eq. 5 to Eq. 16. Let

$$\mathbf{d}_i = \frac{c_iM_i}{p}\mathbf{X}_i$$

and

$$L_{13} = -(L_{11} + L_{12})$$

$$L_{23} = -(L_{21} + L_{22})$$

Then

$$\mathbf{j}_1 = L_{11}\frac{p}{c_1M_1}\mathbf{d}_1 + L_{12}\frac{p}{c_2M_2}\mathbf{d}_2 + L_{13}\frac{p}{c_3M_3}\mathbf{d}_3$$

or in general

$$\mathbf{j}_i = \sum_{k=1}^{N} L_{ik}\frac{p}{c_kM_k}\mathbf{d}_k \qquad \text{(Eq. 17)}$$

Define the generalized diffusion coefficients of a binary pair in a multicomponent mixture by the following equation

$$\mathbf{j}_i = \frac{c^2}{\rho}\sum_{n=1}^{N} M_iM_nD_{in}{}^*\mathbf{d}_n \qquad \text{(Eq. 18)}$$

subject to $D_{ii}{}^* = 0$. (For $N > 2$, in general $D_{in}{}^* \neq D_{ni}{}^*$.) Then the relation between the diffusion coefficients and the phenomenological coefficients proves to be

$$D_{12}{}^* = \frac{p}{c^2M_1M_2}\left[\frac{L_{12}}{c_2M_2} - \frac{L_{11}}{c_1M_1}\right] \qquad \text{(Eq. 19a)}$$

or in general

$$D_{in}{}^* = \frac{p}{c^2M_iM_n}\left[\frac{L_{in}}{c_nM_n} - \frac{L_{ii}}{c_iM_i}\right] \qquad \text{(Eq. 19b)}$$

For the special case of a ternary system with $D_{ii}{}^* = 0$, it appears as if six diffusion coefficients are needed to characterize a system, but by using the relation

$$\sum_{k=1}^{N} L_{ik} = 0$$

plus the Onsager relations $L_{ik} = L_{ki}$, it can be shown that the diffusion coefficients are not independent and that the following restriction holds.

$$\sum_{i=1}^{N}(M_iM_jD_{ij}{}^* - M_iM_kD_{ik}{}^*) = 0 \qquad \text{(Eq. 20)}$$

Consequently, only four diffusion coefficients are independent.

If we wished to see how the binary diffusion coefficients $\mathfrak{D}_{ij}$ in the Stephen–Maxwell equations (Eq. 4) are related to the Onsager coefficients or to the coefficients defined by Eq. 5, *i.e.*, 18, for ternary or more complicated systems, we encounter heavy going. For example, for a ternary (9)

$$D_{12}{}^* = \mathfrak{D}_{12}\left\{1 + \frac{x_3[(M_3/M_2)\mathfrak{D}_{13} - \mathfrak{D}_{12}]}{x_1\mathfrak{D}_{23} + x_2\mathfrak{D}_{13} + x_3\mathfrak{D}_{12}}\right\} \qquad \text{(Eq. 21)}$$

Although the set of Eq. 5 are linear and can be formally inverted to solve for ∇x_k or $D_{in}{}^*$ by matrix methods, the actual details of the inversion become extremely tedious for large N.

B. DIFFUSION FLUX AND DIFFUSIVITY IDENTIFIED FROM STATISTICAL MECHANICS

Although the statistical mechanical analysis of diffusion in liquids is more complicated than most other approaches, it does clarify the physical meaning of the parameters which arise, and it sheds light on simpler theories. For example, Bearman has developed a unified statistical mechanical theory of transport processes in solutions based on Kirkwood's work; the appropriate references will be found in ref. 8. Essentially this series of papers shows how to calculate diffusion coefficients (and other transport properties) for regular solutions in terms of equilibrium properties. ("Regular" solutions are those in which the molecules have similar size, shape, and interaction potentials.) For more complex systems, the prediction of transport properties is no better than the corresponding prediction of thermodynamic equilibrium properties. Furthermore, it should be pointed out that this approach does not permit direct calculation of diffusion coefficients from basic considerations; it is still necessary to evaluate certain parameters experimentally and from these obtain the diffusion coefficients.

A brief summary of the treatment is as follows. By assuming the mean nonequilibrium force, $\bar{F}_1^{(1)}$, on a species 1 in a N-component system is the sum of the average forces exerted by all the other molecules in the system, it is possible to break $c_1\bar{F}_1^{(1)}$ into a sum of two terms. The first yields the phenomenological equations for mass and energy fluxes; the second leads to the Newtonian stress tensor. A frictional force, $\bar{F}_1^{(1,1)*}$, is defined for the isothermal, isobaric case as

$$\bar{F}_1^{(1,1)*} = \bar{F}_1^{(1)*} - \bar{F}_1^{(1,0)*} \qquad \text{(Eq. 22)}$$

where $\bar{F}_1^{(1,0)*}$ is the nonvanishing component which exists even at equilibrium. $\bar{F}_1^{(1,1)*}$ is expressed in terms of the distribution functions, g_{1j} and g_{j2} as

$$\bar{F}_1^{(1,1)*} = \frac{1}{2}\sum_{j=2}^{N}\int c_j\left(\frac{\mathbf{r}}{r}\right)\frac{d\phi_{ij}(\mathbf{r})}{dr}[g_{1j}^{(2,1)} - g_{j1}^{(2,1)}]d^3\mathbf{r} \qquad \text{(Eq. 23)}$$

ϕ is a smoothed potential which averages out the effects of orientation and internal degrees of freedom; $g_{1j}^{(2,1)}$ is the difference between the pair correlation function $g_{1j}^{(2)}$ and the (equilibrium) radial distribution function $g_{1j}^{(2,0)}$ used in treating thermodynamic behavior.

If $g_{1j}^{(2,1)}$ is expanded in series of spherical harmonics, only the first harmonic contributes to the integral in Eq. 23 and the resultant expression yields

$$\bar{F}_1^{(1,1)*} = -\sum_{j=2}^{N}c_j\zeta_{1j}(\mathbf{v}_1 - \mathbf{v}_j) = \nabla\ \mu_1 \qquad \text{(Eq. 24)}$$

In this way the coefficients of friction ζ_{1j} become defined. Since $\phi_{j1} = \phi_{1j}$ and $g_{1j}^{(2,0)} = g_{j1}^{(2,0)}$, it can be concluded that $\zeta_{1j} = \zeta_{j1}$.

To illustrate the application of Eq. 24, consider a binary system in which the mutual diffusion coefficient is based on a volume average reference frame. In addition to Eq. 24 the following well-known definition is used.

$$\nabla\mu_i = RT\left(\frac{\partial \ln a_i}{\partial c_i}\right)\nabla c_i$$

After adding and subtracting $\mathbf{v}^\bullet = \sum_i c_i\bar{V}_i\mathbf{v}_i$ in

$$\nabla\mu_1 = -c_2\zeta_{12}(\mathbf{v}_1 - \mathbf{v}_2) \qquad \text{(Eq. 25a)}$$

$$\nabla\mu_2 = -c_1\zeta_{12}(\mathbf{v}_2 - \mathbf{v}_1) \qquad \text{(Eq. 25b)}$$

and employing

$$\bar{V}_1\mathbf{J}_1^\bullet + \bar{V}_2\mathbf{J}_2^\bullet = 0 \qquad \text{(Eq. 26)}$$

where $\mathbf{J}_1^\bullet = c_1(\mathbf{v}_1 - \mathbf{v}^\bullet) = -D_{12}^\bullet\nabla c_1$, one finds

$$D_{12}^\bullet = \frac{\bar{V}_1RT}{\zeta_{12}}\left[1 + \left(\frac{\partial \ln f_2}{\partial \ln c_1}\right)_{T,p}\right] = \frac{\bar{V}_2RT}{\zeta_{12}}\left[1 + \left(\frac{\partial \ln f_1}{\partial \ln c_1}\right)_{T,p}\right] \qquad \text{(Eq. 27)}$$

Both the friction coefficients and $D_{12}^\bullet$ will in general depend on composition and temperature.

When the ratios of the friction coefficients are constant, Bearman has shown (7) that

$$\frac{D_1^\bullet}{D_2^\bullet} = \frac{V_1}{V_2} \qquad \text{(Eq. 28)}$$

where $D_1^\bullet$ and $D_2^\bullet$ are the self-diffusion coefficients ($D_1^\bullet = RT/\zeta_1$), and V_1 and V_2 are the molar volumes of the pure components, and also

$$D_{12}^\bullet = D_1^\bullet\left[1 + \left(\frac{\partial \ln f_1}{\partial \ln c_1}\right)_{T,p}\right] \qquad \text{(Eq. 29)}$$

$$= [D_1^\bullet x_2 + D_2^\bullet x_1]\left(\frac{\partial \ln a_1}{\partial \ln x_1}\right)_{T,p} \qquad \text{(Eq. 30)}$$

Statistical mechanics also provides a method of determining the coefficient of shear viscosity, η, which can be introduced in Eq. 27 to eliminate the unknown friction coefficient. For regular solutions, $D_1^\bullet\eta$ is concentration independent, and it can be shown (8) that

$$D_{12}^\bullet\eta = D_{12}^\infty\eta_2\left[1 + \left(\frac{\partial \ln f_1}{\partial \ln c_1}\right)_{T,p}\right]$$

$$= D_{12}^\infty\eta_2\left[1 + \left(\frac{V_1}{V_2} - 1\right)x_1\right]\left(\frac{\partial \ln a_1}{\partial \ln x_1}\right)_{T,p} \qquad \text{(Eq. 31)}$$

If it is not desirable to introduce the viscosity into Eq. 27, the friction coefficient itself, in principle, can be expressed in terms of other measurable or known quantities. Consider the binary diffusion coefficient defined by Einstein (32) as

$$\hat{\mathfrak{D}}_{12} = \frac{kT}{\langle\zeta_{12}\rangle} \qquad \text{(Eq. 32)}$$

A number of investigators using various assumptions have carried out the complicated integrations required to express $\langle\zeta_{12}\rangle$ in terms of measurable and known quantities. Collins and Raffel (18) treated an idealized liquid of rigid spheres taking into account only the collisional transport of momentum to yield

$$\langle\zeta_{12}\rangle = \frac{3\left[\frac{\pi}{2}\left(\frac{M_1M_2}{M_1 + M_2}\right)kT\right]^{1/2}\mathfrak{M}}{\pi\sigma_{12}[1 - (V_0^{\mathrm{m}}/V^{\mathrm{m}})^{1/3}]} \qquad \text{(Eq. 33)}$$

$$\mathfrak{M} = 1 + \frac{M_1 + M_2}{M_1} - \frac{\left(\frac{M_1}{M_1 + M_2}\right)^{3/2}}{\left(\frac{M_2}{M_1 + M_2}\right)^{3/2}}\ln\frac{1 + \left(\frac{M_2}{M_1 + M_2}\right)^{1/2}}{\left(\frac{M_1}{M_1 + M_2}\right)^{1/2}}$$

The collision diameter σ_{12} must be estimated from an assumed molecular packing ratio, from the density, and from $[(V_0^{\mathrm{m}}/V^{\mathrm{m}})^{1/3}(V^{\mathrm{m}})^{1/3}]$, while $(V_0^{\mathrm{m}}/V^{\mathrm{m}})^{1/3}$ can be obtained from sonic velocity measurements, u_s.

$$u_s = \frac{1 - (2/3)(V_0^{\mathrm{m}}/V^{\mathrm{m}})^{1/3}}{1 - (V_0^{\mathrm{m}}/V^{\mathrm{m}})^{1/3}}\left[\frac{C_pRT/M_{\text{solvent}}}{C_p[1 - (2/3)(V_0^{\mathrm{m}}/V^{\mathrm{m}})^{1/3}] - R}\right]^{1/2} \qquad \text{(Eq. 34)}$$

Kamal and Canjar (68) using the equations developed for self-diffusion in liquids (115–117) arrived at the following relationship for liquid–liquid systems.

$$D_{12}^{\infty} = [(A)(B)]_{\text{solvent}}(H)_{\text{solute}} \qquad \text{(Eq. 35)}$$

where

$$A = \left\{1.6\left(\frac{V_0^{\text{m}}}{V^{\text{m}}}\right) + 2.56\left(\frac{V_0^{\text{m}}}{V^{\text{m}}}\right)^2\left[1 + 2.5\left(\frac{V_0^{\text{m}}}{V^{\text{m}}}\right) + 4.5864\left(\frac{V_0^{\text{m}}}{V^{\text{m}}}\right)^2\right]\right\}\left(\frac{V^{\text{m}}}{V_0^{\text{m}}}\right)^{2/3}$$

$$B = 6.19 \times 10^{-5}(T/M)^{1/2}(V_0)^{1/3}$$

$$H = RT/(24L - 39RT)$$

L being the heat of vaporization of the solute at T. If data on the velocity of sound are not available to obtain $(V_0^{\text{m}}/V^{\text{m}})$, the ratio can be calculated by trial and error from data on the diffusion coefficient of one solute in the solvent of interest or from self-diffusion coefficients of the solvent.

Kamal and Canjar tested Eq. 35 on 56 different liquid–liquid systems and found an average deviation of 13% compared to 11% for Wilke's equation (discussed in section IIIB). No attempt was made to test Eq. 35 on dissolved gases in liquids because the value of L is hypothetical, but future work may indicate proper empirical values to be employed.

C. EFFECTIVE (PSEUDO) BINARY DIFFUSION COEFFICIENTS

Specification of the diffusion flux in multicomponent systems is much more difficult than in binary systems as can be seen from the preceding sections. Historically, since most of the experimental work on diffusion has been for binary systems, one would like to have a simple method which permits the estimation of an effective binary diffusion coefficient from the binary diffusion coefficients of the solute in the individual solvents.

Bird, *et al.*, (9) have defined an effective (or pseudo) binary diffusion coefficient by

$$\mathbf{N}_i = -cD_{i\text{m}}\nabla x_i + x_i\sum_{j=1}^{N}\mathbf{N}_j \qquad \text{(Eq. 36)}$$

For the diffusion of a dilute component i through a stagnant solvent mixture, m, both the molar density c and the mass density ρ of the solution may be considered to be constant, and the molar average velocity is essentially the same as the mass average velocity. Equation 36 then becomes

$$\mathbf{j}_i = -D_{i\text{m}}\nabla c_i \qquad \text{(Eq. 37)}$$

Several empirical or semi-empirical methods have been given in the literature to predict $D_{i\text{m}}$ from the respective binary diffusion coefficients for the diffusion of a dilute liquid component in mixed solvents (54, 80). For a ternary, for example,

Wilke (142); Hsu and Bird (58)

$$D_{1\text{m}} = (1 - x_1)/\sum_{=2}^{3}(x_j/D_{1j}) \qquad \text{(Eq. 38)}$$

Holmes, Olander, and Wilke (54)

$$D_{1\text{m}}\eta_{\text{m}} = x_2D_{12}\eta_2 + x_3D_{13}\eta_3 \qquad \text{(Eq. 39)}$$

Lightfoot, Cussler, and Rettig (80)

$$\frac{1}{D_{1\text{m}}} = \left(\frac{x_2}{D_{12}'} + \frac{x_3}{D_{13}'}\right)\left(\frac{\partial \ln x_1}{\partial \ln a_1}\right) \qquad \text{(Eq. 40)}$$

Other obvious relations are

$$D_{1\text{m}} = x_2D_{12} + x_3D_{13} \qquad \text{(Eq. 41)}$$

$$\log (D_{1\text{m}}) = x_2 \log (D_{12}) + x_3 \log (D_{13}) \qquad \text{(Eq. 42)}$$

None of these equations satisfactorily predict $D_{i\text{m}}$ when the mixed solvent is highly nonideal, and some do not even work satisfactorily for ideal systems; Eq. 54 below is more reliable in general.

D. HYDRODYNAMIC ANALYSIS OF DIFFUSION

Einstein (31, 33) and Sutherland (127) proposed independently that the diffusivity of a solute in a solvent could be correlated by considering the frictional force experienced by a body falling through a viscous medium (as given by Stokes' law)

$$\frac{\hat{\mathfrak{D}}_{12}\eta_2}{kT} = \frac{1}{6\pi r_1}\frac{1 + 3\eta_2/\beta r_1}{1 + 2\eta_2/\beta r_1} \qquad \text{(Eq. 43)}$$

Equation 43 can be reduced at the extremes to

$$\frac{\hat{\mathfrak{D}}_{12}\eta_2}{kT} = \frac{1}{4\pi r_1}\ \text{(when } \beta = 0\text{)} \qquad \text{(Eq. 44)}$$

$$\frac{\hat{\mathfrak{D}}_{12}\eta_2}{kT} = \frac{1}{6\pi r_1}\ \text{(when } \beta = \infty\text{)} \qquad \text{(Eq. 45)}$$

Physically, when the solvent and solute molecules are of the same size, $\beta = 0$. One might also assume

$$2r_1 \cong \left(\frac{V_0}{N_{\text{A}}}\right)^{1/3} \qquad \text{(Eq. 46)}$$

For large molecules of solute such as colloidal particles or large polymers, Eq. 45 is found to reproduce experimental data fairly well. For molecules approximately the size of the solvent molecules, Eq. 44 seems to hold better. It is moderately successful in predicting diffusivities of dissolved gases in water as can be seen from Fig. 7–11. For diffusing molecules smaller than the solvent molecules, the factor 4 in Eq. 44 has to be replaced by a still smaller factor.

Li and Chang (79) proposed that

$$\frac{\mathfrak{D}_{12}\eta_2}{kT}\left(\frac{V_{01}}{N_{\text{A}}}\right)^{1/3} = \frac{1}{2}\left(1 - \frac{\tau}{\sigma}\right) \qquad \text{(Eq. 47)}$$

Equation 47 agrees with Eq. 44 if

$$\frac{2\sigma}{\sigma - \tau} \cong 2\pi$$

which is true when the structure in the liquid is the simple cubic packing for which $\sigma = 6$ and $\tau = 4$.

E. ACTIVATED RATE PROCESS ANALYSIS OF DIFFUSION

Eyring (41) postulated that diffusion arose from the jumping of molecules from one equilibrium neighboring site to another under a force arising from the gradient of the chemical potential. Although the equation based on this hypothesis yielded results of the correct order of magnitude for many systems, it failed to predict correctly diffusivities in nonideal systems of aqueous solutions.

The chief use of Eyring's approach arises when it is combined with Eyring's expressions for viscosity. One form of the resulting expression has been given by Olander (92) as

$$\frac{D_{12}\eta}{T} = \left(\frac{\lambda_1}{\lambda_2\lambda_3}\right)\left(\frac{k}{\xi}\right) \exp\left\{\frac{\Delta F_\eta^* - \Delta F_D^*}{RT}\right\} \qquad \text{(Eq. 48)}$$

The λ's arise from the absolute rate theory of viscosity and are independent of the solute species. In the original Eyring theory, ξ was considered to be unity but in ref. 92 the empirical value of 5.6 was employed, a value based on mutual diffusion experiments. If the relation between molar volume and the molecular size parameters is introduced into Eq. 48

$$\frac{V_0}{N_A} = \lambda_1\lambda_2\lambda_3 \qquad \text{(Eq. 49)}$$

as well as the experimental fact that $\lambda_1 = \lambda_2\lambda_3$, Eq. 48 becomes

$$\frac{D_{12}\eta}{T} = \left(\frac{V_0}{N_A}\right)^{-1/3}\left(\frac{k}{5.6}\right) \exp\left\{\frac{\Delta F_\eta^* - \Delta F_D^*}{RT}\right\} \qquad \text{(Eq. 50)}$$

When the concentration of the diffusing solute is small

$$(\Delta F_\eta^*)_{\text{solution}} \cong (\Delta F_\eta^*)_{\text{solvent}}$$

The relation between the free energy of activation for viscous flow and the absolute viscosity of the liquid is

$$\eta = \frac{hN_A}{V_0} \exp\left(\frac{\Delta F_\eta^*}{RT}\right) \qquad \text{(Eq. 51)}$$

Olander (92) subdivided each of the free energies of activation in Eq. 50 into two parts, the hole-making and the bond-breaking contributions. When the concentration of the diffusing solute is small, the moving solute molecule can be considered to be completely surrounded by solvent molecules; hence the hole-making contribution for diffusion should be the same as that for viscous flow. Therefore for the diffusion of dilute species 1 in species 2

$$\Delta F_\eta^* - \Delta F_D^* = \Delta F_{22}{}^j - \Delta F_{12}{}^j \qquad \text{(Eq. 52)}$$

where the superscript j refers to the bond-breaking contributions and the subscripts refer to the molecular species between which the interaction exists. The bond-breaking contribution $\Delta F_{22}{}^j$ constitutes a fraction of the total free energy of activation for viscous flow $(\Delta F_\eta^*)_2$. The ratio between these two, defined as

$$\epsilon = (\Delta F_{22}{}^j)/(\Delta F_\eta^*)_2 \qquad \text{(Eq. 53)}$$

is not the same for all pure substances and it may even vary with temperature for a given substance. A rough estimation proposed by Olander is to assume ϵ to be a constant for all pure substances, with its value estimated to be about 0.5. To estimate $(\Delta F_\eta^* - \Delta F_D^*)$ for nonliquid solutes (in their pure state), Olander's method requires some estimate of solute viscosity as a liquid, which is a hypothetical value for a solute gas.

Tang (129), assuming binary diffusion coefficients were known either theoretically or experimentally, extended these concepts to the diffusion of dilute component 1 through a mixture of two solvents. The derivation was a crude approximation; nevertheless it appeared to have good predictive ability both for gases dissolved in liquids and dilute liquids in liquids. Two alternate expressions were given for the effective diffusion coefficient

$$D_{i\text{m}}\eta_{\text{m}}{}^{1/2} = x_2D_{12}\eta_2{}^{1/2} + x_3D_{13}\eta_3{}^{1/2} \qquad \text{(Eq. 54)}$$

$$\log\,(D_{i\text{m}}\eta_{\text{m}}{}^{1/2}) = x_2 \log\,(D_{12}\eta_2{}^{1/2}) + x_3 \log\,(D_{13}\eta_3{}^{1/2}) \qquad \text{(Eq. 55)}$$

with Eq. 54 preferred. In a test of six systems for which diffusivity data were available, Eq. 54 and 55 alone gave reasonable predictions for diffusivities in nonideal solvent mixtures, such as ethanol–water combinations.

The most recent version of Eyring's theory (113) reduces to the following relation.

$$D_{12}\frac{\eta}{T} = \frac{k}{(\xi\lambda_1)(k''/k')}\frac{\partial \ln a}{\partial \ln c} \qquad \text{(Eq. 56)}$$

The quantities ξ and k''/k' are peculiar to each type of solvent and solute, depending on the interaction between molecules. ξ ranges from about 4 to 9 for self-diffusion of liquids (the value 6 or 5.6 is commonly used as an average) while k''/k' is approximately 1 unless there is a strong interaction, such as in water, in which case the ratio cannot be predicted *a priori*, but may range up to 3, 4, or more. Equation 56 requires specification of both ξ and k''/k'; consequently, it falls in the same category as the Arnold equation in ability to predict diffusivities of dissolved gases.

Panchenkov (97), based on an analysis of self-diffusion by kinetic theory, postulated the following relation for mutual diffusion

$$D_{12} = A \exp\left[-\frac{2L}{\lambda RT} - \frac{\epsilon^\circ}{2RT}\right]\left[\frac{\epsilon^\circ}{2RT} + 1\right] \qquad \text{(Eq. 57)}$$

where

$$A = \frac{4(3)^{1/3}(2R)^{1/2}V_0{}^{1/3}T^{1/2}}{(4\pi N_A)^{1/3}\pi^{1/2}M^{1/2}}$$

and

$$\epsilon^\circ = \epsilon^\circ{}_{11}x_1{}^2 + 2\epsilon^\circ{}_{12}x_1x_2 + \epsilon_{22}{}^\circ x_2{}^2$$

Although all the quantities which characterize the molecular properties of Eq. 57, namely, V_0, M, and L, must be taken as mean values for the system, for dilute dissolved gases these will essentially prove to be properties of the solvent. The coordination number, λ, must be developed from empirical correlations, but is fixed as zero at the critical point and at the appropriate value for the solid state at the melting point. Equation 57 has not been tested for dissolved gases to date.

F. RANDOM WALK INTERPRETATION OF DIFFUSION

There are ways of examining molecular diffusion in liquids which reformulate the microscopic equations and definitions presented in the Introduction, and result in a somewhat different mathematical description. Molecular diffusion is usually explained in terms of large numbers of collisions of molecules during any small time interval in which transfer takes place. An accompanying premise is that the entire process is highly random in character; successive elementary displacements of an individual molecule are completely uncorrelated. This type of model when stated mathematically is expressed in the form of parabolic partial differential equations. Various types of partial differential equations can be derived corresponding of different sets of assumptions about the mechanism to molecular diffusion. For example, Goldstein (42) and Taylor (131) have shown that modification of the basic assumptions of the model of diffusion results in a hyperbolic (rather than parabolic) partial differential equation known as the Telegrapher's equation. Consider these special cases of the molecular transport process.

1. No Correlation in Motion of a Particle. Isotropic Media

With these assumptions, Fick's law can be shown to evolve from the random walk problem if the net flux is assumed to be linearly dependent on the local concentration gradient. Then one obtains as the one-dimensional equation for molecular diffusion

$$\frac{\partial c}{\partial t} = D_{12}\frac{\partial^2 c}{\partial y^2} \qquad \text{(Eq. 58)}$$

Equation 58 implies that the molecules move with an infinite velocity; *i.e.*, the individual displacements are very rapid compared with the diffusion coefficient D multiplied by some characteristic time for the macroscopic process. Another way of looking at Eq. 57 is that the displacement in time t is greater than the region affected by the diffusion in the same time.

2. Perfect Correlation. Isotropic Medium

If the individual displacements occur at a finite velocity, then one obtains the wave equation

$$\frac{\partial^2 c}{\partial t} = v_y^2\frac{\partial^2 c}{\partial y^2} \qquad \text{(Eq. 59)}$$

3. Partial Correlation. Isotropic Medium

These assumptions lead to the Telegrapher's equation

$$\frac{\partial^2 c}{\partial t^2} + \frac{1}{A}\frac{\partial c}{\partial t} = v_y^2\frac{\partial^2 c}{\partial y^2} \qquad \text{(Eq. 60)}$$

The Telegrapher's equation was suggested by Goldstein as representing a diffusion process in which the motions are continuous in time and the correlations become significant. Equation 60 is more apropos to turbulent than molecular diffusion.

4. Anisotropic Diffusion. Partial Correlation

For the most general case, one assumes partial correlations and a directional preference for movement. A number of possible sets of assumptions can be made depending on the order of terms retained, etc. The physical significance of the equations developed is not as clear as in previous cases, but a typical equation might be (90)

$$\frac{\partial^2 c}{\partial t^2} + 2\left(\frac{1}{A} + \frac{1}{B}\right)\frac{\partial c}{\partial t} + 2\frac{v_y}{E}\frac{\partial c}{\partial y} - v_y^2\frac{\partial^2 c}{\partial y^2} = 0 \qquad \text{(Eq. 61)}$$

Equation 61 is a hyperbolic partial differential equation and shares the characteristic wave solutions of the wave and Telegrapher's equation. By suitable transformation of variables, Eq. 61 can be written in the form of the Telegrapher's equation.

Another interpretation of the random walk problems provides some additional insight into the process of diffusion. Michelson (90) shows that the local rate of increase of concentration is given by a conservation equation

$$\frac{\partial c}{\partial t} = \frac{\delta}{\tau}\frac{\partial \phi}{\partial y} \qquad \text{(Eq. 62)}$$

The usual assumption which leads to Fick's law is that the flux is proportional to the concentration gradient (or the gradient of chemical potential)

$$\phi = \delta\frac{\partial c}{\partial y} \qquad \text{(Eq. 63)}$$

so that

$$\frac{\partial c}{\partial t} = \frac{\delta^2}{\tau}\frac{\partial^2 c}{\partial y^2} \qquad \text{(Eq. 64)}$$

$$= D_{12}\frac{\partial^2 c}{\partial y^2} \qquad \text{(Eq. 65)}$$

if

$$\lim_{\tau \to 0}\frac{\delta^2}{\tau} \rightarrow D_{12} \qquad \text{(Eq. 66)}$$

Now, for the case of perfect correlation of movement in an isotropic media, if with a finite velocity

$$\lim_{\tau \to 0}\frac{\delta}{\tau} \rightarrow v_y \qquad \text{(Eq. 67)}$$

it can be shown that

$$\frac{\partial \phi}{\partial t} = v_y\frac{\partial c}{\partial y} \qquad \text{(Eq. 68)}$$

Combining Eq. 62 and 68, one obtains the wave equation, Eq. 59.

Similar analysis applied to the other basic assumptions leads to the following successively more generalized relations between concentration (c) and flux (ϕ)

Diffusion equation

$$v_v \frac{\partial c}{\partial y} = \frac{v_v \phi}{k} \qquad \text{(Eq. 69)}$$

Wave equation

$$v_v \frac{\partial c}{\partial y} = \frac{\partial \phi}{\partial t} \qquad \text{(Eq. 70)}$$

Telegrapher's equation

$$v_v \frac{\partial c}{\partial y} = \frac{\partial \phi}{\partial t} + \frac{1}{A}\phi \qquad \text{(Eq. 71)}$$

Michelson's equation

$$v_v \frac{\partial c}{\partial y} = \frac{\partial \phi}{\partial y} + \left(\frac{1}{A} + \frac{1}{B}\right)\phi + \frac{1}{B}c \qquad \text{(Eq. 72)}$$

It is easy to see that direct expression of the flux in terms of time, distance, and concentration is inconvenient for the more complicated models.

G. RELATIONS BETWEEN MUTUAL AND SELF-DIFFUSION COEFFICIENTS

Up to this point nothing has been said about the relation between binary and "self-diffusivities." That such a relation might exist was indicated early by Meyer (89) who developed an analogy based on the kinetic theory of gaseous diffusion that indicated the dissipation of a concentration gradient by molecular transfer would give rise to the existence of "intrinsic diffusion coefficients," D_A and D_B, which were unrelated to each other because the rate of transfer of component A across a boundary need not be the same as that for component B.

A number of expressions (in addition to Eq. 29) have been proposed to relate a binary diffusion coefficient to the appropriate self-diffusion coefficients.

Darken (25)

$$D_{12} = (x_1 D_2 + x_2 D_1)\frac{\partial \ln a}{\partial \ln x} \qquad \text{(Eq. 73)}$$

Lamm (77)

$$D_{12} \cong \frac{x_2\left[1 + \frac{\partial \ln f_2}{\partial \ln x_2}\right]}{\frac{1}{D_{1,x_2}} - \frac{C_1 V_{01}}{D_1}} \qquad \text{(Eq. 74)}$$

where D_{1,x_2} represents the self-diffusion coefficient at mole fraction x_2.

Gordon (43)

$$D_{12} = D_1^{\infty}\left(1 + \frac{\partial \ln f_1}{\partial \ln c_1}\right)\left(\frac{\eta_2}{\eta}\right) \qquad \text{(Eq. 75)}$$

Horrocks and McLaughlin (55)

$$D_{12} = D_1^{\infty}\left(1 + \frac{\partial \ln \gamma_1}{\partial \ln x_1}\right)\left(\frac{\eta_2}{\eta}\right)\left[x_1 \frac{V_{01}}{V_{02}} + x_2\right] \qquad \text{(Eq. 76)}$$

Hartley and Crank (48)

$$D_{12} = kT\left(\frac{x_1}{\sigma_2 \eta} + \frac{x_2}{\sigma_1 \eta}\right)\left(1 + \frac{\partial \ln \gamma_1}{\partial \ln x_1}\right) \qquad \text{(Eq. 77)}$$

Bearman (8) shows that when the molar volumes are additive

$$\left(1 + \frac{\partial \ln f_1}{\partial \ln c_1}\right) = \left(1 + \frac{\partial \ln \gamma_1}{\partial \ln x_1}\right)\left(\frac{x_1 V_{01} + x_2 V_{02}}{V_{02}}\right) \qquad \text{(Eq. 78)}$$

Substituting Eq. 28, 30, and 78 into Gordon's equation, one obtains Darken's equation. Moreover, both Crank (20) and Carman and Stein (14) have shown that Hartley and Crank's equation can be reduced to Darken's equation without assuming equal molar volumes for the two components. Therefore, in spite of the differences in appearance, Eq. 73, 75, 76, and 77 may be considered essentially the same.

One difficulty in testing these relations is that the dissolved gas is normally very dilute so that the effect of the activity coefficient correction and the portion of the sum contributed by the term containing x_1 (the gas mole fraction) are quite small. For example, in Darken's equation D_{12} would be approximated by D_1 while in Gordon's, D_{12} would be approximated by D_1^{∞}. Furthermore, the physical meaning of the "self-diffusion" coefficient for a dissolved gas is not clear. Nevertheless, it may eventually prove possible on an empirical basis to employ hypothetical self-diffusion coefficients for the solute gas in equations of the type of 73 to 78.

Longuet-Higgins and Pople (81) developed theoretical expressions for the viscosity and self-diffusivity from which the self-diffusivity could be expressed in terms of a single empirical parameter, the radius of the molecule.

$$D_i \eta = \frac{2r^2}{5}\frac{N_A kT}{V_0} \qquad \text{(Eq. 79)}$$

McCall, Douglass, and Anderson (87) suggested calculating the molecular radius from

$$r = (0.297 V_0)^{1/3} 10^{-8} \qquad \text{(Eq. 80)}$$

Using a modified rate-theory approach to self-diffusion, McLaughlin (88) tested Eq. 44 in which the diffusivity became a self-diffusion coefficient and the effective radius r was equal to $\sigma_{12}/2$. Values of σ_{12} were taken from ref. 53 or estimated by $\sigma_{12} = (3V/\pi N_A)^{1/3}$. By further analysis he arrived at the following relation for a liquid composed of spherically symmetrical molecules.

$$D_i = \left(\frac{kT}{2\pi M}\right)^{1/2} \frac{\alpha^2}{V_f} \exp\left[\frac{-\left(\frac{\epsilon^*}{k}\right)\left(\frac{V_0^m}{V^m}\right)^4}{T}\right] \exp[-e_0/kT] \qquad \text{(Eq. 81)}$$

The value of α can be estimated from various models, such as the cell models of the liquid, and the free volume is equal to $V_f = 2\pi\sqrt{2}G(V_0/N_A)$. ϵ^*/k and G are well-known tabulated functions, and e_0 can be approximated by

$$e_0 \cong \left[1.2045\left(\frac{V_0^m}{V^m}\right)^2 - 0.5055\left(\frac{V_0^m}{V^m}\right)^4\right]/3 \qquad \text{(Eq. 82)}$$

Equations 79 and 81 have not been tested as to their ability to predict hypothetic self-diffusion coefficients for dissolved gases in liquids, but Eq. 81 does seem to give reasonable results for self-diffusivities of condensed gases near their normal boiling points.

H. DIFFUSION IN INHOMOGENEOUS MEDIA

If the liquid is not homogeneous but holds an emulsion or suspension of solids, the diffusivity may vary from point to point in a random manner. Prager (101) suggests that effective diffusion coefficients be calculated from statistical descriptions of the media. Certain simple exact cases were discussed and a number of approximate expressions also given.

III. DESCRIPTION AND EVALUATION OF SEMI-EMPIRICAL CORRELATIONS OF DIFFUSIVITY

Because of the difficulty of predicting diffusion coefficients from molecular considerations, considerable use has been made in correlating diffusivities of the form of the theoretical equations modified by introducing empirically determined parameters. Several useful semi-empirical correlations are described below.

A. ARNOLD CORRELATION

Arnold (3) applied the classical kinetic theory for gaseous diffusivity to liquid systems. By making three major assumptions concerning the collision rate: (1) that all collisions are binary, involving only two molecules, (2) that the collision rate is unaffected by the volume occupied by the molecules, (3) that intermolecular forces are not present, he developed a relation for diffusivity in liquids at 20°.

$$D_{12} = \frac{0.010\sqrt{\frac{1}{M_1} + \frac{1}{M_2}}}{(V_1^{1/3} + V_2^{1/3})^2} V_2 \qquad \text{(Eq. 83)}$$

None of the above assumptions can be considered valid in the treatment of liquid diffusion, but Arnold corrected Eq. 83 by inserting a factor $(A_1 A_2 V_2 \eta_2^{1/2})$ in the denominator of the equation. Typical abnormality factors A_1 (for the solute) and A_2 (for the solvent) are:

Substance	A_1	A_2	Solutes in water	A_1
Acetone		1.15	CO_2 (10°)	1.33
Nitrobenzene		1.35	CO_2 (25°)	1.03
Acetic acid	1.38		CO_2 (50°)	0.71
Methyl alcohol	1.19	2.00	O_2 (25°)	0.94
Ethyl alcohol	1.24	2.00	N_2 (25°)	1.10
Phenol	1.21		SO_2 (25°)	0.94
Aniline	1.23			
Water		4.70		

For conversion of D_{12} to other temperatures than 20°, Arnold gave the empirical correlation

$$D_{12} = D_{20°}[1 + b(T - 273)] \qquad \text{(Eq. 84)}$$

where $b = 0.02(\eta V^{2/3})^{1/2}$.

Unless the abnormality factors are known in advance (from empirical data), Eq. 83 and 84 are not especially useful in predicting diffusivities of dissolved gases.

B. WILKE CORRELATION

Wilke's (141, 142) correlation (in 1949) was based on relations suggested by the Eyring theory of absolute reaction rates and the Stokes–Einstein equation. The correlation was made through the group $F = T/(D_{12}\eta)$. Within the limits of the available experimental data, F was essentially independent of temperature for a given system, but was a function of the molal volume of the solute. Experimental data from 178 experiments were reproduced with an average deviation of 10%.

In 1955 Wilke and Chang (143) performed several experiments and obtained data to supplement that used by Wilke in 1949. Their data indicated that F was a smooth function of the solute molal volume having a slope of about 0.7 at low molal volumes and apparently merged with the Stokes–Einstein equation at high molal volumes. Over the middle range of molal volumes, the curve may be represented by a line of slope = 0.6; therefore, they assumed that $D_{12}\eta/T$ was proportional to $V_{01}^{0.6}$. (Plots of log $D\eta/T$ and log $D\eta$ *vs.* log V_{01} indicate this assumption is approximately correct.)

To determine the effect of solvent properties on diffusivity, a wide variety of variables such as solvent molal volume, heat of vaporization, molecular weight, etc., were examined. Of these, the solvent molecular weight appeared to correlate the data most successfully. Although there is considerable scattering of data, a line of slope = $^1/_2$ correlates each system fairly well on a plot of log $D_{12}\eta/T$ *vs.* M_2. (This appears to be strictly an eyeball choice.)

From the above results Wilke concluded that an equation for unassociated liquids of the form

$$D_{12} = (\text{constant})\frac{TM_2^{1/2}}{\eta V_{01}^{0.6}} \qquad \text{(Eq. 85)}$$

would successfully include the interaction of solvent and solute; the constant was determined empirically to be 7.4×10^{-8}.

For H_2O and other associated liquids the plot of log D_{12}/T *vs.* log $\eta V_{01}^{0.6}/M_2^{1/2}$ fell above the line for unassociated liquids. By assigning a molecular weight to H_2O of 2.6 times the nominal weight, the curve was brought into agreement with the curve for unassociated liquids. (A similar procedure for other associated solvents gave the same result.) Thus the general correlation was

$$D_{12} = 7.4 \times 10^{-8}\frac{T(xM_2)^{1/2}}{\eta V_{01}^{0.6}} \qquad \text{(Eq. 86)}$$

where the viscosity of the mixture is in centipoise. Typical values for x, the association parameter, are: $x_{H_2O} = 2.6$, $x_{CH_3OH} = 1.9$, $x_{C_2H_5OH} = 1.5$.

The average deviation for H_2O as a solvent was 6%; for CH_3OH as the solvent, 11%. As can be seen from

Fig. 7–11, Eq, 86 gives reasonable predicted values of diffusivity, especially if the experimental values of V_0 for the solute rather than the Le Bas values are used. Nevertheless, the equation cannot be used indiscriminately without experimental testing because for some gases, such as hydrogen and helium in water, the predicted values vary widely from the experimental ones.

C. SCHEIBEL CORRELATION

Scheibel's (120) method is essentially a correction to Wilke's original correlation. It is possible to express Wilke's correlation without the solvent factor as

$$D_{12} = 8.2 \times 10^{-8} \frac{[1 + (3V_{01}/V_{02})^{2/3}]T}{\eta V_{01}^{1/3}} \qquad \text{(Eq. 87)}$$

where η is in centipoise.

When $V_{01} < V_{02}$, better agreement is obtained by the following rules in these solvents:

Water	if $V_{01} < V_{02}$,	use $V_{01} = V_{02}$
Benzene	if $V_{01} < 2V_{02}$,	use $V_{01} = 2V_{02}$
Methanol	if $V_{01} < 1.5V_{02}$,	use $V_{01} = 1.5V_{02}$
Miscellaneous	if $V_{01} < 2.5V_{02}$,	use $V_{01} = 2.5V_{02}$

The error limits and remarks at the end of section B (for water as the solvent) also apply to the Scheibel correlation.

D. OTHMER AND THAKAR CORRELATION

Their method (96) follows the principle used effectively to correlate many other properties of matter: plotting logarithmically the property of one material against the same property of another on a scale based on the vapor pressure of a reference substance. If diffusivity is expressed as a rate process which varies exponentially with the temperature, by introduction of the Clausius–Clapeyron equation it can be shown that

$$\log D_{12} = \frac{E_D}{L} \log P^* + \text{constant} \qquad \text{(Eq. 88)}$$

This suggested that a log plot of D_{12} *vs.* the vapor pressure of a reference substance at equal temperatures would give a straight line of slope E_D/L. Othmer and Thakar made this plot, but when the solvent was H_2O, a definite break occurred at 30°. A similar break occurred when the viscosity of water *vs.* the vapor pressure was plotted in the above manner. (This similarity in behavior supported the view of Eyring that the mechanisms of viscosity and diffusion were similar. Eyring further proposed that $E_D = E_V$ for dilute solutions.) A plot of log D_{12} *vs.* log of the viscosity essentially eliminated the break.

The equation which best represented the data for water as the solvent was

$$D_{12}^w = \frac{14.0 \times 10^{-5}}{\eta_w^{1.1} V_{01}^{0.6}} \qquad \text{(Eq. 89)}$$

where the viscosity of water is in centipoise. As can be seen in section V, the validity of Eq. 89 is roughly the same as the Wilke equation and the Othmer–Thakar relation.

E. METHOD OF INNES AND ALBRIGHT

For rate processes such as viscosity and diffusion, Innes and Albright (63) suggested the use of a three-constant Arrhenius equation (4). Excluding temperatures within 25° of the freezing point, viscosity data of liquids can be correlated accurately over large temperature ranges by such an equation. Thus, for liquid diffusivities one might expect a similar empirical form

$$D_{12} = AT^n e^{-B/T} \qquad \text{(Eq. 90)}$$

where A, B, and n are constants.

This equation was tested by Innes and Albright for self-diffusion data and it agreed well with experimental values (2–3% deviation); n may be considered as primarily a function of the solvent, while A and B are functions of the solute. To date Eq. 89 has not been tested on the diffusivities of dissolved gases, and consequently no values have been assigned to n, A, and B.

F. LONGSWORTH CORRELATION

Generally, even for large molecules in dilute solution, the radius calculated from the Stokes–Einstein equation, Eq. 45, is larger than the radius obtained from experimental molal volumes.

$$r = \left(\frac{3V_0}{4\pi N_A}\right)^{1/3} \qquad \text{(Eq. 91)}$$

This is due to asymmetry and hydration of the molecules. However, unless there is extreme asymmetry, the product $D_{12}V_{01}^{1/3}$ is roughly constant for large molecules, whereas for smaller ones Polson (100) noted a decrease in the product $D_{12}M_1^{1/3}$ with increasing molecular weight. Longsworth (83) proposed the relation

$$D_{12} = \frac{A'}{M_1^{1/3}} + \frac{B'}{M_1^{2/3}} + \frac{C'}{M_1} \qquad \text{(Eq. 92)}$$

Actually, the simpler relation

$$D_{12} = \frac{A}{M_1^{1/3} - B} \qquad \text{(Eq. 93a)}$$

fits his data almost as well. In terms of molal volumes, the expression is

$$D_{12} = \frac{A''}{V_{01}^{1/3} - B''} \qquad \text{(Eq. 93b)}$$

Thus, molal volume seems to be a more significant property for the interpretation of the diffusion results than the molecular weight.

None of the Eq. 91 to 93 have been tested for gases in liquids.

G. IBRAHM AND KULOOR CORRELATION

These authors (61) contended that the group $\eta_g V_{01}/D_{12}$ plotted *vs.* M_1 gave a straight line (inorganic and organic gases gave lines of different slope). This correlation was checked at 20° for the diffusion of N_2, N_2O, CO_2, O_2, NH_3, H_2, and CO_2 in water. Excluding N_2, these gases were found to form a fairly straight line. The diffusion coefficients used were obtained from the Wilke and Chang correlation in order to have some type of consistency.

Based on the above correlation and previous equations, it was felt that a plot of D_{12} *vs.* $\eta_g V_{01} T/(\eta_w M_1)$ should give parallel straight lines. This calculation was carried out for N_2, CO_2, O_2, and H_2 using the experimental data of Cullen and Davidson (23) (in order to have internal consistency of the diffusion values). Again N_2 failed to correspond to a linear plot.

IV. DESCRIPTION AND EVALUATION OF EXPERIMENTAL METHODS OF MEASURING THE DIFFUSION OF DISSOLVED GASES

The most widely used techniques to determine molecular diffusion coefficients of dissolved gases are (a) to measure the transfer of gas into or out of a liquid phase, or (b) to measure concentration gradients in a diffusing system. Both of these general experimental methods fulfill the requirements of a simplified mathematical description based on Eq. 1. The major problems are the accurate measurement of the transport of very small quantities of gas and the prevention of convection currents in the diffusion cell from thermal or density variations, or other cause.

A. DIAPHRAGM CELLS (POROUS DISKS)

A diaphragm cell is simply a porous glass or metal disk sealed in a cylinder (see Fig. 1). The gas diffuses through the pores from a solution of high concentration to one of lower concentration. When the volume of the solution on either side of the diaphragm is sufficiently large and is stirred by magnetic bars A and B at the proper rate to keep the concentrations uniform, the transfer conditions across the disk, for all practical purposes, are steady state. Changes in concentration can be measured on each side of the disk by what is called the Northrop–Anson method; a good evaluation of the method is given by Gordon (44).

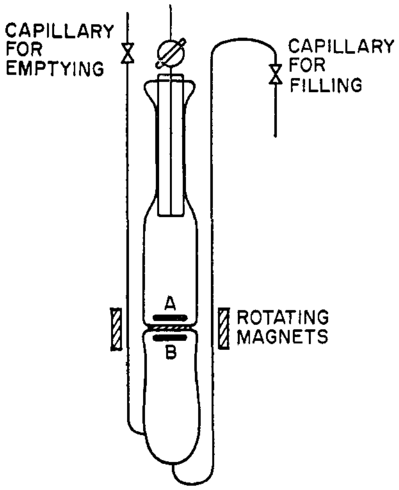

Fig. 1.—Diaphragm cell.

Since neither the area nor length of the diffusion path can be determined by direct measurement, it is necessary that each individual cell be calibrated, using a solute of known diffusivity. For water solutions, KCl has almost always been chosen for this purpose since its diffusivity as a function of concentration is well known (49); but for other solutions, because the cell constant is a function of viscosity, as well as concentration, the calibration must be carried out in a liquid of approximately the same viscosity as the one to be used in the investigation. Another problem inherent with sparingly soluble gases is the difficulty of measuring small concentration changes in solution and the danger of loss of gas on sampling from the solution. Finally, it is never certain to what extent surface effects within the pores of the disk are likely to affect the rate of mass transfer and how these effects might change with concentration and solvent.

In spite of these difficulties, Peaceman (98) and others have used this technique. As can be seen from section V, Peaceman's value for the diffusivity of CO_2 at 30° is perhaps 7% higher than the best current estimate of diffusivity; his experimental error was approximately ±10% for CO_2. Another idea of the reproducibility of the data which can be obtained from diaphragm cells is given by the data of Scriven (121) for runs ranging from 101 to 156 hr. For three successive runs at 25°, in cell I, D was 1.85, 1.94, and 1.83; in cell II, 1.80, 1.84, and 1.94; in cell III, incorrect values were obtained because of poor mixing (all values are times 10^5 cm.²/sec.).

What results from diaphragm cell measurements is the integral coefficient of diffusion, not the differential coefficient. In many cases these coefficients may be the same, but in principle the following relations hold (44).

$$\frac{\overline{D}_{12}}{D_{12}{}^{\infty}} = 1 + \frac{\displaystyle\int_{\Delta c_f}^{\Delta c_0} \gamma \mathrm{d} \ln (\Delta c)}{\ln (\Delta c_0/\Delta c_f)} \qquad \text{(Eq. 94)}$$

$$D_{12}{}^{\infty}\ \Delta c = (1+\gamma)\int_{(R^*c_0{}''-\Delta c)/(R^*+1)}^{(R^*c_0{}''+\Delta c)/(R^*+1)} D_{12}\mathrm{d}c \qquad \text{(Eq. 95)}$$

In the above equations, $\Delta c = c'' - c'$, γ is defined by Eq. 95, and $''$ stands for the upper chamber, while $'$ is for the lower chamber. Dullien and Shemilt (28) suggested simplified methods of retrieving the differential diffusion coefficient from the experimental data by graphical methods, and Olander (93) described the necessary corrections to take into account volume changes in mixing.

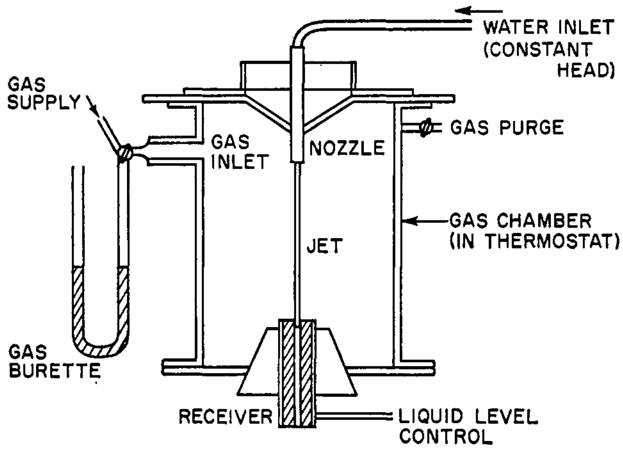

Fig. 2.—Liquid jet and test chamber.

B. GAS ABSORPTION IN STEADY-STATE LAMINAR FLOW SYSTEMS (JETS, SPHERES, ETC.)

The absorption of gases in liquids involves three steps, *i.e.*, the diffusion in the gas phase, the diffusion in the liquid phase, and the "interfacial resistance," if any. When the gas is a pure component or is only slightly soluble, the "resistance" in the gas phase is negligible. This has been confirmed for the CO_2–water system by Woods (144). Reports of previous authors (22, 50, 121) on the same system also indicate that, in the absence of surface active agents, the interfacial resistance need not be considered. Under these conditions, the gas absorption process becomes a diffusion-controlled process in the liquid phase. For gases such as Cl_2 and N_2O_4 which react with the solvent water significantly, Eq. 1 must include an appropriate chemical reaction term.

In the absorption of slightly soluble gases in liquids, the concentration of the solute gas in the liquid phase is so small that the density and viscosity of the liquid phase are practically the same as those of the pure solvent. For an isothermal, steady-state flow system in the laminar regime, the diffusion equation in the absence of chemical reactions becomes

$$\mathbf{v} \cdot \nabla c = \nabla \cdot (D \nabla c) \qquad \text{(Eq. 96)}$$

with the boundary conditions $c = c_0$ at the inlet and $c = c^*$ on the free boundary of the liquid. Equation 96 has been simplified for liquid jets by several authors (22, 50, 121) for the case of constant D. When D varies with c, Eq. 96 is nonlinear. To obtain an analytic solution to this problem is, except for a few special cases, very difficult. For the case where the variation of D with c is small, a perturbation method derived by Tang (129) may be used to obtain an approximate solution.

The absorption of gas into a liquid jet, such as shown in Fig. 2, is widely used to determine diffusion coefficients for a number of reasons (15, 22, 29, 50, 52, 76, 85, 91, 94, 102, 121, 136, 144, 145). Jets are simple in design, have freedom from ripples, have small end effects, are stable, and have such short contact time that surface active agents do not have time to adsorb on the surface. Above all they are rapid. Most of the investigators have treated their data by applying the penetration theory.

If we temporarily assume that the depth of penetration of the solute gas in the liquid is small and neglect the curvature of the jet, the problem can be expressed as

$$v_s \frac{\partial c}{\partial z} = \frac{\partial}{\partial x}\left(D_P \frac{\partial c}{\partial x}\right) \qquad \text{(Eq. 97)}$$

where, v_s, the surface velocity is assumed to be constant. The boundary conditions are

$$\begin{aligned} c &= c^* \quad \text{at} \quad x = 0,\ z > 0 \\ c &= c_0 \quad \text{at} \quad \begin{cases} x \to \infty,\ z > 0 \\ z = 0,\ x > 0 \end{cases} \end{aligned} \qquad \text{(Eq. 98)}$$

This is the problem of diffusion in a semi-infinite medium. Equations 97 and 98 lead to the penetration solution when D_P is a constant.

$$D_P = \frac{N^2}{16(c^* - c_0)^2 qH} \qquad \text{(Eq. 99)}$$

A more exact analysis of the same problem shows that the penetration theory gives a higher absorption rate with a given value of D_{12} by about 1%, but that end corrections reduce D_{12} by about 1.5% so that these two types of corrections partly cancel each other out. To calculate the diffusion coefficient by the penetration theory without corrections, as is commonly done, would give a value only one-half of 1% too high. The above comments were based on the assumption that the jet nozzle is designed to provide an initial uniform velocity profile at the jet tip, and the calculations were based on a tip of 0.400 cm. and a liquid flow rate of 600 cm.^{3}/sec. Nozzles of other shapes and smaller nozzles involve more substantial corrections. Non-Newtonian fluids require special treatment (5).

Jets are very suitable for obtaining values for industrial work (±5%), and with more care, data of ±1% precision can be obtained. The precision of the total gas absorbed, N, the liquid flow rate, q, and the jet length, H, can be about ±1%. However, as can be seen from Eq. 99, the accuracy of the calculated value of the binary diffusion coefficient depends greatly upon the accuracy of the available solubility data. An error of 1% in the latter would introduce an error of about 2% in the calculated diffusion coefficient. Since considerable divergence is usually found in reported solubility data for slightly soluble gases, it is impossible to make general statements concerning the accuracy of calculated diffusion coefficients.

Other types of steady-state flow apparatus of known geometry which have occasionally been used to de-

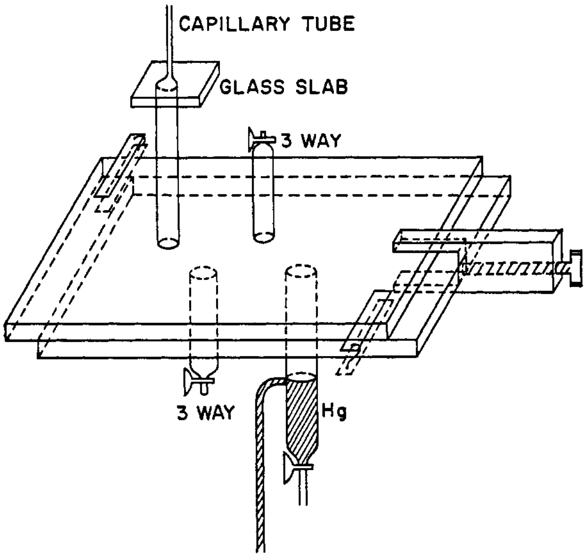

Fig. 3.—Apparatus of Carlson.

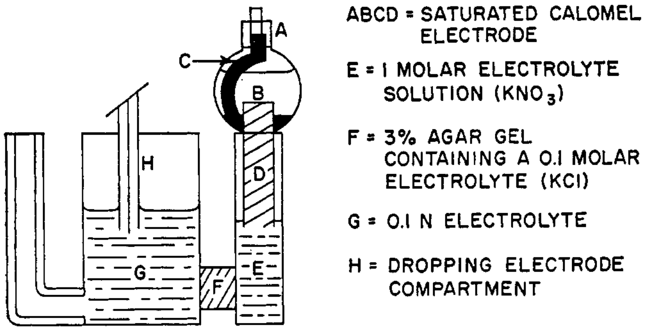

Fig. 4.—Dropping mercury electrode apparatus.

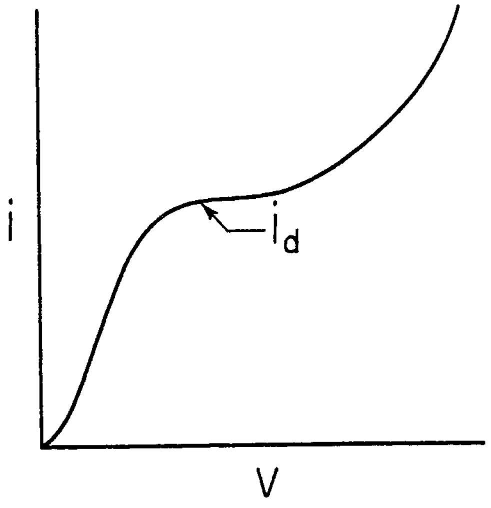

Fig. 5.—Location of plateau in current–voltage curve.

termine diffusion coefficients are shown in Table I. They are not as satisfactory to use as laminar jets and consequently will not be discussed here.

TABLE I

STEADY-STATE FLOW APPARATUS USED TO DETERMINE DIFFUSION COEFFICIENTS

	Reference
Wetted wall columns	27, 34, 91
Wetted sphere	24
Stirred flask	11
Two-phase flow in rectangular duct	130
Rotating drum	71

C. GAS ABSORPTION IN UNSTEADY-STATE QUIESCENT SYSTEMS

One of the earlier workers to use this method was Carlson (12). A sketch of the apparatus is shown in Fig. 3. The diffusion experiments were carried out in the following manner. The upper cylinder, and its matching section in the lower slab, was filled with air-

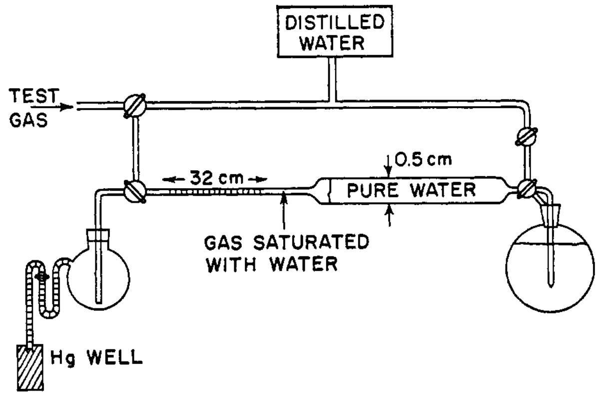

Fig. 6.—Modified Ringbom apparatus.

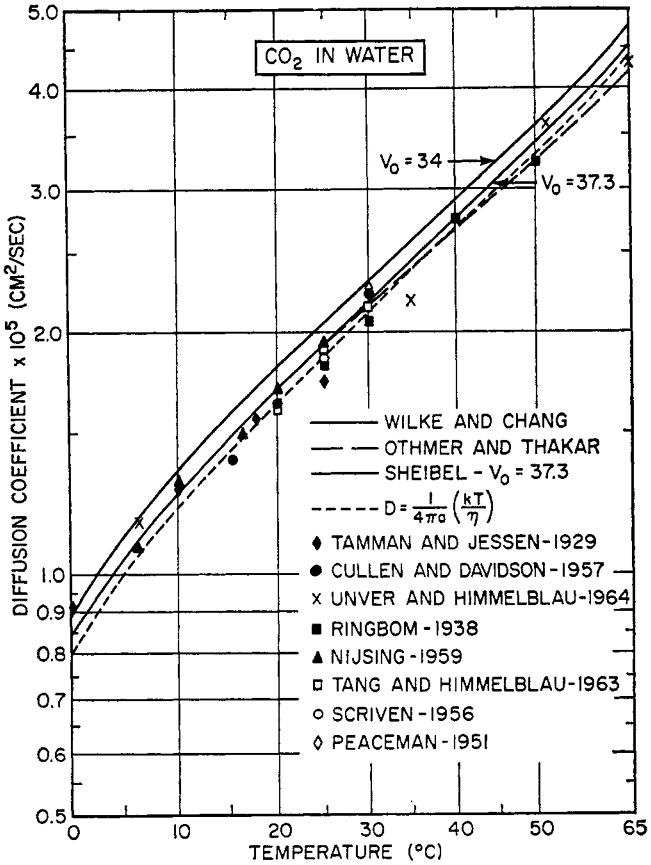

Fig. 7.—Comparison of predicted and experimental diffusivities: carbon dioxide in water.

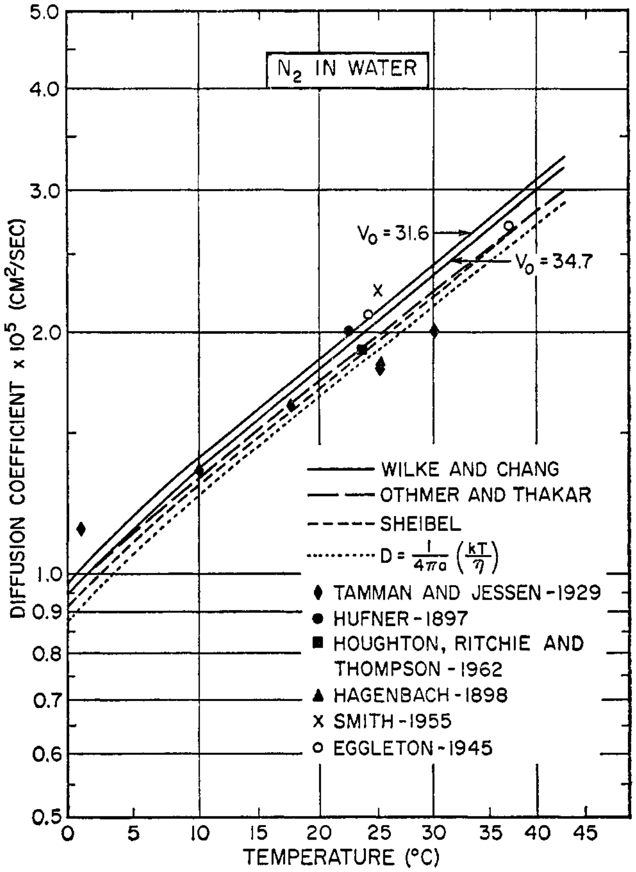

Fig. 8.—Comparison of predicted and experimental diffusivities nitrogen in water.

free, distilled water which was allowed to run upwards through the cylinder from the bottom for 15 to 20 min. Afterwards the cock was closed and the capillary tube shut off. At the same time a 1% KCl solution (the KCl was added to prevent convection currents) in which O_2, or CO_2, had previously been dissolved, was made to run through the lower cylinder by means of a glass tube which opened on the surface of the mercury. When the cylinders had been filled in this manner, the front part of the upper glass slab was pushed above the filled portion of the lower cylinder. The whole apparatus was set up in a thermostat on a firm base with the cylinders in a vertical position free from the possibility of vibration. After a certain number of days, the cylinders were pushed past each other till the cock in the upper slab stood exactly above the lower cylinder, and the liquid was displaced by Hg and analyzed.

For this experimental setup the diffusion coefficient could be determined from the unsteady-state solution to Eq. 1 in an initially solute-free solvent of semi-infinite extent, which for moderate times is equivalent to

$$N_T = 2c^*S\sqrt{D_{12}t/\pi} \qquad \text{(Eq. 100)}$$

The internal consistency of Carlson's work was excellent; for example, at 18.2 ± 0.2°

Time, days	D_{12} for CO_2, cm.^{2}/sec. × 10^5	Time, days	D_{12} for O_2, cm.^{2}/sec. × 10^5
7	1.704	6	1.971
5	1.721	6	2.019
9	1.697	5.9	1.983

From Fig. 7-11, it can be seen that Carlson's work is in reasonable agreement with more recent results, although perhaps a bit high for CO_2.

To prevent convection currents during the long time required for experiments of this type, some workers put gel in the liquid. For example, Hagenbach (47) used a 20% gelatin solution. Hagenbach stated that the gelatin offered greater resistance to the diffusing gas molecule than pure water although his values for CO_2 in a 20% gel solution are quite satisfactory. Possibly the high values obtained by Hagenbach for O_2 represent a measurement of the amount diffused plus the amount of O_2 absorbed by the gelatin or chemically used in oxidation of the gelatin.

Another method of eliminating convection during diffusion is to conduct the experiment in capillary tubes of diameter sufficiently small that convection currents are prevented. It was by such small tubes (of less than 1 mm. in diameter) that Stefan (126) demonstrated the validity of Fick's law of diffusion for gases in liquids. Since Stefan's time, only a few in-

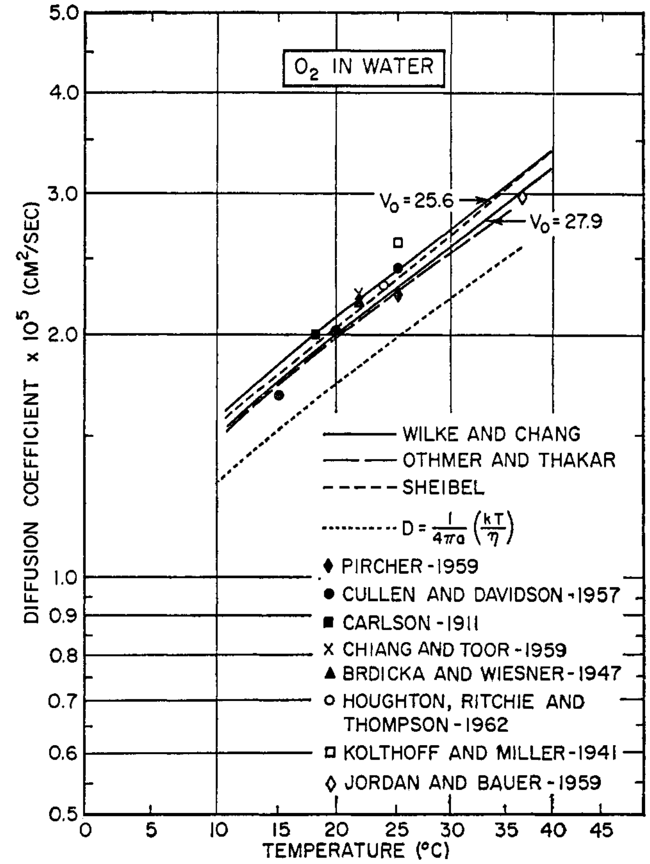

Fig. 9.—Comparison of predicted and experimental diffusivities: oxygen in water.

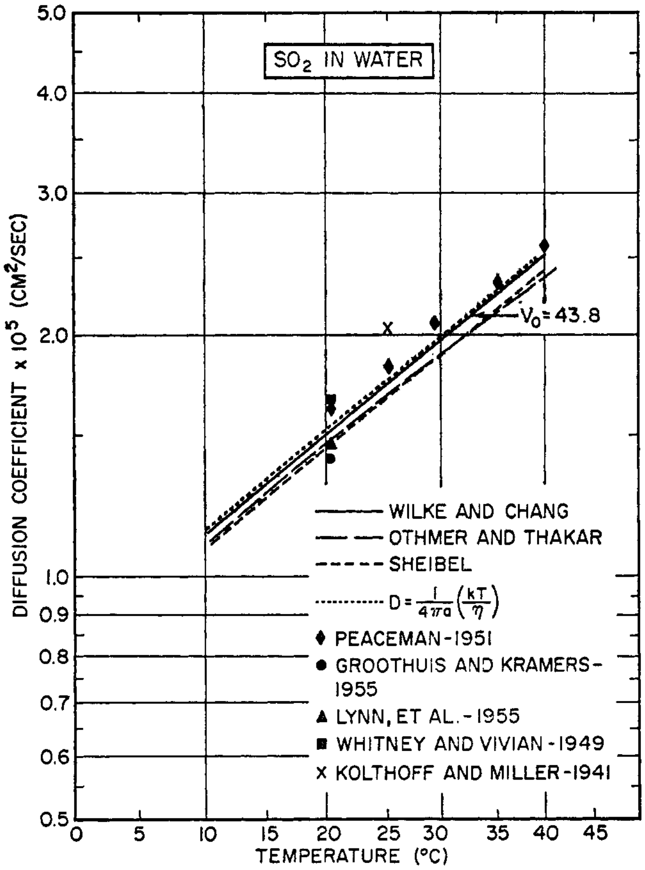

Fig. 10.—Comparison of predicted and experimental diffusivities: sulfur dioxide in water.

vestigators have used the capillary method. Ringbom (see below) used an improved form of apparatus designed to overcome some of the disadvantages and sources of error of Stefan's method. The capillary method suffers the disadvantage that the area of the interface is uncertain if it has a meniscus and the proper mixing conditions are needed at the upper end of the capillary to provide a clear-cut boundary condition. A good description of the modern approach to this technique including the influence of volume changes on mixing is given by Shim (123).

D. DROPPING MERCURY ELECTRODE

A typical dropping mercury electrode apparatus was that used by Kolthoff and Miller (74) as shown in Fig. 4. The saturated calomel electrode was placed into the salt solution just before the experiments were carried out. The magnitude of the surface of the Hg in the saturated half-cell was about 8 cm.^{2} so that the electrode remained almost completely depolarized during the determination of the current–voltage curves.

The diffusion coefficient can be calculated from the experimental results by the Ilkovic equation (62)

$$i_d = 0.63nFc_1m^{2/3}t^{1/6}D_{12}^{1/2} \qquad \text{(Eq. 101)}$$

where t is the drop time.

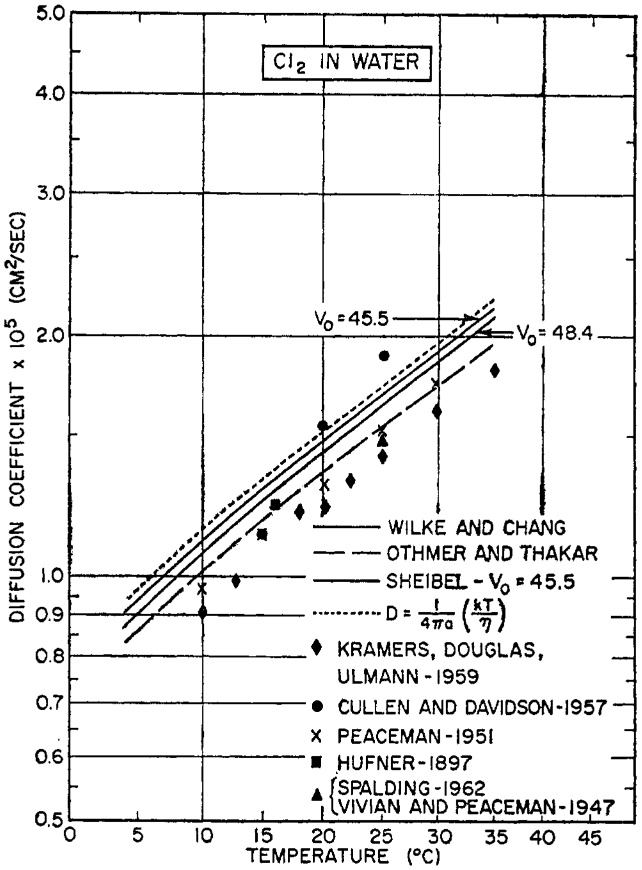

Fig. 11.—Comparison of predicted and experimental diffusivities: chlorine in water.

According to the theory of Ilkovic, the limiting currents caused by nonelectrolytes tend to a constant value, denoted as the diffusion current. This "diffusion current" is due entirely to the diffusion of the nondissociated molecules through the solution and is independent of the "indifferent electrolyte" so long as the electrolyte is not concentrated enough to affect the viscosity of the solution. These diffusion currents are observed as horizontal portions of the current–voltage curves (Fig. 5). Ilkovic's test of Eq. 101 showed a precision of about ±4% and a discrepancy of 5–10%

Table II

Molar Volumes of Gases (cm.^{3}/g. mole)

Gas	Le Bas[a]	Exptl.[b]	Gas	Le Bas[a]	Exptl.[b]
Ar		29.2	H_2S	32.9	35.2
C_2H_2	37.0	42.0	He		31.9
C_2H_4	44.2	50.5	N_2	31.6	34.7
C_3H_6	66.3	69.0	NH_3	28	24.5
C_4H_8[c]	87.8	89.5	N_2O	36.4	36
CH_3Cl	48	50.6	NO_2		31.7
Cl_2	48.8	45.5	O_2	25.6	27.9
CO_2	34.0	37.3	SO_2	42.2	43.8
H_2	14.3	28–29			

[a] Estimated from G. Le Bas, "The Molecular Volumes of Liquid Chemical Compounds," Longmans, Green and Co., Ltd., London, 1915. [b] Selected molar volumes at the normal boiling point for liquids. [c] Butene-1.

TABLE III

EXPERIMENTAL DIFFUSIVITIES OF DISSOLVED GASES IN WATER[a]

Temp., °C.	D	Ref.	Temp., °C.	D	Ref.
	Acetylene			Chlorine[c]	
0	1.10	128	10	0.91 ± 6%	76
10	1.50	128		0.97	98
17.5	1.69	128	12	1.41[b]	35
30	2.19	128	13	0.98 ± 6%	76
	Ammonia[c]		15	1.14	98
4.0	1.23	119		1.13	23
8.0	1.09	59	16.3	1.27	59
10.8	1.16	59	18.3	1.20 ± 6%	76
12.0	1.64	4	20.0	1.22 ± 6%	76
13.9	1.22	59	25	1.42 ± 6%	76
15	1.29	59		1.51	98
15.2	1.78	1		1.89	23
17.0	1.84	47		1.48[g]	125
	2.23	36		1.48	137
20	1.46	138	30	1.74	98
	Argon			1.62 ± 6%	76
21.7	2.0 ± 10%	57	35	1.81 ± 6%	76
25	1.46 ± 10%	124		Helium	
	Carbon Dioxide		22.1	5.8 ± 10%	57
0	0.960	128		Hydrogen	
6.2	0.891[b]	47	0	1.96[d]	128
6.5	1.08	91	10	4.34	60
10	1.17	23		2.80	128
	1.28[d,e]	23	13	6.72	36
10.2	1.30	91	14	3.41	47
	1.44[d]	60	15	2.49[b]	64
15	1.37	23	16	4.73	59
	1.40	47	17	5.15	23
15.2	1.58[d]	60	17.5	3.40[d]	128
15.8	1.49	91	21	5.15	60
16	1.57	128	23	3.85	2
	1.63	126	24.5	4.9	57
	1.60[f]	13	25	3.37	64
16.4	1.57	59		7.07	23
17.5	1.56[d,e]	128		3.49	64
18.2	1.71 ± 1%[f]	12	25.5	4.08[d]	128
20	1.77	94	30	4.49[d]	128
	1.60 ± 5%	130	35	4.22[b]	64
	1.63	23	45	5.69[b]	64
	1.69[d,e]	91	100	23.2[b]	64
20.4	1.85	59		Hydrogen Sulfide	
23	2.35[b]	40	15.5	1.43	47
24.8	1.94	91	16.0	1.77	36
25	1.82	118	25.0	1.36	69
	1.91	23		Methyl Chloride	
	1.74	128	22.1	1.39 ± 4%	15
	1.87 ± 3%	121		Neon	
	1.9 ± 8%	144	22.2	2.8 ± 10%	57
	1.90 ± 5%	130		Nitrogen	
	1.92	114	1.0	1.134[d]	128
	1.85	135	10	1.34[d]	128
29	2.71[b]	40	15	1.94	36
30	2.06[e]	118	17.5	1.62[d]	128
	2.29 ± 10%	98	21.7	2.00	59
	2.25	23	23.5	1.9 ± 10%	59
	1.75[b]	128	24	2.10[d]	30
	2.15 ± 5%	130	25	1.80[d]	128
35.0	2.26	91		1.83	47
	2.18	135		2.25 ± 5%	124
37	3.13[b]	40	30	2.00[d]	128
40	2.75[e]	118	37	2.70[d]	30
50	3.24[e]	118		Nitrogen Dioxide[c]	
52.0	3.61	135	20	1.23 ± 10%	75
65.0	4.30	135	30	1.59 ± 10%	75

TABLE III (*Continued*)

Temp., °C.	D	Ref.
	Nitrous Oxide	
14	0.73	47
15	1.62	23
16.2	1.56	60
20	2.11	23
25	2.57	23
	Oxygen	
1.0	$1.23^{b,d}$	128
10	$1.82^{b,d}$	128
14	$7.48^{b,d}$	47
15	2.21^{b}	36
	1.67	23
16	1.87	60
17.5	$2.45^{b,d}$	128
18.2	1.99	12
20	2.01	23
21.7	1.87	60
22	2.25	15
	2.22	10
2.38	2.3 ± 10%	57
25	2.60	74
	1.90^{b}	78
	1.87^{b}	122
	2.42	23
	$3.54^{b,d}$	128
	2.12	66
	2.25	99
37	3.0	76
	Sulfur Dioxide[c]	
20	1.40	46
	1.46	84
	1.66	140
	1.62	98
25	2.04	73
	1.83	98
30	2.08	98
35	2.33	98
40	2.59	98

[a] All values are $D_{12} \times 10^5$ cm.²/sec. [b] Value is probably incorrect. [c] Substantial reaction takes place on dissolution in water. [d] Diffusion measured in agar media. [e] Recalculated for modern solubility data. [f] KCl added to solution. [g] 0.1 N HCl added to solution.

between experiment and theory (62). The original Ilkovic equation has been rederived in the more general form as

$$i_d = 607nm^{2/3}t^{1/6}D_{12}^{1/2}(1 + Km^{-1/3}t^{1/6}D_{12}^{1/2}) \quad \text{(Eq. 102)}$$

Jordan and Ackerman have studied this equation and the original, and they contend the above equation gives diffusion coefficients some 10% less than those calculated from the original Ilkovic equation (66).

The dropping Hg electrode as shown in Fig. 4 or in some modification has been used by several other researchers in determining diffusion coefficients. Some typical results of Brdicka and Wiesner (10) for O_2 at 22° ranged from 2.16 to 2.46 ($D \times 10^5$ cm.²/sec.) with a mean of 2.30 ± 0.20 (for 95% confidence limits).

E. RINGBOM APPARATUS

A modified Ringbom apparatus as described in ref. 124 is occasionally used for measuring the diffusion of gases in liquids; examine Fig. 6. In this apparatus a gas-saturated and a gas-free water column (introduced from either end into a capillary tube) are separated by a pure gas phase. With the gas-saturated water connected to a large reservoir and the pure water fixed as a dead-end column of sufficient length, the volume of gas moving into the pure water is measured by observing the movement of the gas-saturated water column into the displaced gas space. The rate at which this displacement occurs gives a measure of the diffusion coefficient of the gas through the water, provided the tube diameter is small enough to minimize convection, and assuming that suitable temperature control is maintained.

Under these conditions the solution to the diffusion equation results in the following equation for the diffusion coefficient

$$D_{12} = (\pi/4a^2S^2)(\Delta V/\sqrt{t + \Delta t} - \sqrt{t})^2 \quad \text{(Eq. 103)}$$

where ΔV is the volume of gas displaced in time Δt.

Smith gave the results at 25° for twelve trials for N_2; he obtained $D_{12} = 2.245 \pm 0.106 \times 10^{-5}$ cm.²/sec. Eleven trials for argon gave $D_{12} = 1.463 \pm 0.138 \times 10^{-5}$ cm.²/sec. Figure 8 for N_2 compares Smith's value with the work of others. Ringbom's values for CO_2 are fairly good (1.82 at 25° *vs.* 1.92 × 10^{-5} cm.²/sec. estimated as the best value).

F. INTERFEROMETRIC TECHNIQUES

Interferometric measurements take place in an unsteady-state absorption process during which the concentration gradient is evaluated as a function of time. Although interference phenomena were first considered by Gouy (45) in 1880, it was not until 1947 that the theory of fringe spacing was presented by Kegeles and Gosting (70) and was used by Longworth (82). In the Gouy method, the progress of diffusion of the gas into the liquid is followed and recorded by the change of refractive index of the liquid as a function of distance and time. Monochromatic light is used to illuminate a fine slit which is focused by a lens through the diffusion boundary into a photographic plate. The optical theory and methods of calculating the diffusion coefficients are far too complex to detail here, but the interested reader can refer to ref. 21, 39, 50, 65, 132, 139. Interferometry is a delicate technique and requires expensive equipment, with the result that it has not been widely used for gases dissolved in liquids, but, when used properly, can achieve high precision.

TABLE IV

DIFFUSIVITY OF OXYGEN IN AQUEOUS SUCROSE SOLUTIONS AT 1 ATM. PRESSURE (67)

$D \times 10^5$,[a] cm.²/sec., at 37°	$D \times 10^5$,[a] cm.²/sec., at 80°
3.0(0)	0.50(0)
3.5(9.6)	0.71(15)
3.7(21)	0.91(31)
2.4(40)	0.89(41)
2.1(47)	1.16(50)
	1.48(60)
	1.50(69)
	2.4 (75)
	4.7 (89)

[a] Values in parentheses are weight per cent sucrose.

TABLE V

DIFFUSIVITY OF AMMONIA IN SALT SOLUTIONS[a] (51)

$D \times 10^5$, cm.²/sec. at 20°	$D \times 10^5$, cm.²/sec. at 20°
1.65 (0)[b]	1.60 (0.11)[c]
1.55 (0.55)[b]	1.57 (0.27)[c]
1.43 (1.13)[b]	1.50 (0.45)[c]
	1.57 (0.52)[c]

[a] In agar media. [b] Millimoles of ammonium acetate/gram of agar × 10³. [c] Millimoles of acetic acid/gram of agar × 10³; reaction taken into account.

TABLE VI

DIFFUSIVITY OF CARBON DIOXIDE IN SALT SOLUTIONS AT 25° AND 1 ATM. (103)

Electrolyte	$D \times 10^5$, cm.²/sec.	g. mole/l.	Electrolyte	$D \times 10^5$, cm.²/sec.	g. mole/l.
Pure H_2O	1.92	0			
NaCl	1.73	1.041	$MgCl_2$	1.80	0.377
	1.61	1.939		1.70	0.512
	1.50	2.754		1.65	0.695
	1.30	3.776		1.43	1.262
$NaNO_3$	1.76	1.076	$Mg(NO_3)_2$	1.85	0.215
	1.70	1.452		1.73	0.791
	1.59	2.697		1.64	1.219
	1.34	3.602			
Na_2SO_4	1.74	0.318	$MgSO_4$	1.84	0.195
	1.62	0.546		1.80	0.278
	1.60	0.582		1.70	0.338
	1.63	0.662		1.63	0.475
	1.50	0.898		1.54	0.692
				1.28	0.969

TABLE VII

DIFFUSIVITY OF CARBON DIOXIDE AT 18° AND 1 ATM. IN AQUEOUS NON-NEUTONIAN FLUIDS (5)

Fluid	Weight %	$D \times 10^5$, cm.²/sec.	Flow characteristic[a]
Water		1.75	1.00
Clay slurry	5.10	2.40	0.73
Clay slurry	5.01	2.02	0.83
Clay slurry	3.80	1.91	0.94
CMC[b]	1.50	2.44	0.52
CMC	0.75	2.06	0.74
CMC	0.37	1.72	0.89

[a] Indication of rheological characteristics of fluid. [b] Carboxymethylcellulose.

V. DIFFUSION DATA AND ANALYSIS

A shortage of reliable diffusion data exists which makes it difficult to evaluate proposed correlations for diffusivity or determine the effect of temperature, pressure, concentration, etc., on diffusivity. Figures 7 through 11 present the experimental diffusivities of CO_2, N_2, O_2, SO_2, and Cl_2 in water compared with theoretical predictions by Eq. 86, 87, 89, and 44 combined with 46. These systems represent the only gas–liquid systems studied by several investigators for more than a modest temperature range. It is easily seen that considerable additional experimental work is needed in this field before anything more than tentative conclusions can be drawn.

Table II gives the values of the molal volumes of the gases used in Eq. 86 (Wilke), 87 (Scheibel), 89 (Othmer and Thakar), and 44 plus 46 (modified Stokes–Einstein). Both the Le Bas and the experimental values of V_0 were used in Wilke's correlation and the predicted values of D are indicated by the two solid lines in the figures. For the Othmer and Thakar correlation, only the Le Bas values of V_0 were employed. In the Scheibel correlation only the experimental values of V_0 were used; in two cases the Scheibel predictions coincided with those from Wilke's equation. The modified Stokes–Einstein relation with the molecular radius "a" ($a = r_1$) given by Eq. 46 (using experimental values of V_0) has been added to the figures as a matter of interest.

Tables III through IX present a summary of the available experimental data for diffusivities of gases in water, aqueous solutions, and nonaqueous solvents. The data of Table IX for hydrocarbon gases in hydrocarbons represent only a brief outline of what is available since the actual reported results are quite extensive, and the interested reader should refer to the appropriate references for the details. It is easily observed that the bulk of the experimental work has been concerned with diffusion in water.

A. EFFECT OF TEMPERATURE ON DIFFUSIVITY

The theoretical and semitheoretical equations of sections II and III do not clearly indicate the temperature dependence of the diffusivity because either they involve temperature-dependent parameters or they involve temperature-dependent variables such as the viscosity. Since the experimental data are so scattered, even for CO_2, it is also difficult to draw conclusions concerning the temperature dependence of diffusion coefficients from empirical evidence.

Two alternate choices were examined in considering the temperature scale to be used in Fig. 7 through 11. One choice was to use the inverse of the absolute temperature, and the other was to employ an Othmer temperature scale (95). The latter was selected since it appeared that the predicted diffusivities were

TABLE VIII

DIFFUSIVITY OF VARIOUS GASES IN NONAQUEOUS SOLUTIONS

$D \times 10^5$, cm.²/sec.	Temp., °C.	Remarks
	Isobutylene in Dinonyl Phthalate (56)[a]	
0.026	0	All pressures in range 20–30 mm.
0.055	15	
0.088	25	
0.25	50	
0.61	75	
	Methane in Liquid Propylene (86)[a]	
0.095 (0–3)	−183.0	Pressure range 8–24 mm. Values in parentheses represent mole % methane in the propylene
0.085 (4–6)		
0.074 (12–14)		
0.068 (16–19)		
0.063 (25–27)		
	Nitrogen in Liquid Oxygen (6)	
1.07	−205.4	±5%; pressure range 80–100 mm.
	Argon-37 in Liquid Nitrogen (16)	
2.1	−200.2	
1.9	−201.5	
	Argon in Liquid Nitrogen (17)	
2.41	75.62	
2.26	75.52	
2.38	74.74	
2.00	74.73	
2.10	71.47	
1.75	70.18	
1.59	68.94	
1.57	66.94	
	Tritium in Liquid Nitrogen (17)	
3.69	72.82	
3.40	71.20	
2.88	70.20	
3.16	70.08	
2.81	67.40	

Sulfur Dioxide at 20° (46)

Solvent	$D \times 10^5$, cm.²/sec.
n-Heptane	2.7
n-Nonane	2.5
n-Decane	2.4
n-Dodecane	2.0
n-Hexadecane	1.4

[a] Estimate of precision given in original article.

TABLE IX

DIFFUSION OF HYDROCARBON GASES IN LIQUID HYDROCARBONS

System	Ref.	Temp. range, °C.	Pressure range, atm.	*D*-range $\times 10^{-5}$, cm.²/sec.
Methane in propane	108	4.4–71	25–66	18.2–62.5
Methane in butane	106	−12.2–104	18–85	12.7–28.7
Methane in *n*-hexane	123	25	1–5000	9.5–2.6
Methane in *n*-heptane	107	4.4–171	23–207	4.08–23.7
Methane in decane	104	4.4–138	23–300	1.06–18.2
Methane in cyclohexane	110	38–138	27–240	5.0–15.8
Methane in white oil	105	4.4–138	23–121	10.1–41.4
Methane in crude oil	109	4.4–138	1–280	1.14–11.2
Ethane in *n*-pentane	112	4.4–138	4–46	12.8–361
Ethane in white oil	111	4.4–204	5–41	0.88–13.4

slightly more linear in the middle temperature range using the Othmer scale than $1/T$ on the abscissa. Also, Othmer plots have been widely used with success to correlate vapor pressures, thermodynamic properties, and other transport coefficients besides diffusivity. Relying solely on Fig. VII for CO_2, for which the most data exist, one can conclude that a linear relation on such a plot does not appear to be inconsistent with the experimental evidence.

In extrapolating and interpolating diffusivities analytically instead of graphically, a simple relation such as the following should be effective over moderate temperature ranges.

$$\log D_{12} = \frac{A}{T} + B \qquad \text{(Eq. 104)}$$

As a working hypothesis, the slopes of the curves in Fig. 7 to 11 seem to be approximately the same, and consequently the slope A in equation 104 may prove with further study to be the same for all solutes in a single solvent such as water.

Experimental diffusivities of isobutylene into dinonyl phthalate in the range 0 to 75° were correlated by ref. 56 as

$$D_{12} = 0.64e^{-8000/RT} \qquad \text{(Eq. 105)}$$

The experimental diffusion coefficients were also compared with Eyring's and Wilke's relations. Both of these latter relations predicted values 20 to 100 times smaller than the experimental ones, perhaps due to difficulties in determining the molar volume of the solute. Longuet-Higgins and Pople's equation (81) for *self-diffusion* as modified by McCall, Douglass, and Anderson (87) gave values that were larger than the experimental values; however, the temperature dependence was much less than that observed experimentally.

Finally, although considerable experimental data has accumulated (refer to Table IX) for diffusivities of hydrocarbon gases in hydrocarbon liquids, the separate influences of temperature, pressure, and concentration are not yet apparent for such systems.

B. EFFECT OF PRESSURE ON DIFFUSIVITY

The effect of pressure on diffusivities of dissolved gases is a topic which remains virtually untouched by theoretical analysis. Some empirical relations can be found in the references of Table IX.

C. EFFECT OF CONCENTRATION ON DIFFUSIVITY

Since the concentration of the dissolved gas in the liquid phase is very low under normal conditions, the viscosity of the solution should be essentially the same as that of the pure solvent. Under these circumstances, as mentioned in section IIG, theory predicts that the diffusion coefficient does not vary significantly with concentration.

Ratcliff and Holdcroft (103) amassed considerable data (see Table VI) on the effect of electrolytes on the diffusivity of carbon dioxide. They suggested a number of semi-empirical relations to correlate their data; the simplest of these was

$$D = D_0(1 - Ac) \qquad \text{(Eq. 106)}$$

where D_0 was the diffusivity in the pure solvent and was a constant which could be related to the viscosity. Equation 106 fit the experimental data very well, even for concentrated solutions. An equation of this form should be applicable to other gases dissolved in electrolytes.

Table IV lists the data of Jordan and Bauer (67) for the diffusivity of O_2 in sucrose solutions; the behavior is different at 37° from that at 80°. Table V gives some brief data from ammonia absorption studies in ammonium salts.

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