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THE APPLICATION OF THE
WAVEFRONT SHEARING OPTICAL INTERFEROMETER TO DIFFUSION
MEASUREMENTS.

Thesis submitted for the degree of Doctor of Philosophy
in the Faculty of Engineering of the University of London.

EDWARD M^CKILLOP NICHOLL,
Chemical Engineering Department,
Battersea College of Technology,
London.

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ABSTRACT.

A wavefront shearing optical interferometer has been built in this laboratory, and its use for diffusion measurements is described.

In Part I of this work, the application of the interferometer to diffusion in liquid-liquid systems is discussed. Using a flowing-junction cell in conjunction with the interferometer, the following systems were investigated and diffusion coefficients reported over a range of concentrations,--

sucrose-water ; monoethanolamine-water ; diethanolamine-water ; and triethanolamine-water .

A new method for calculating the diffusivities of liquid-liquid systems has been proposed, and is used to obtain the diffusion coefficients for the above systems. A Ferranti Sirius computer is used to handle the calculations.

The diffusion coefficients obtained in this investigation were examined in comparison with existing diffusional theories and semi-empirical equations. It is shown that these theories are inadequate, and it is also shown that the large deviations between the predicted diffusivities of the ethanolamines and the observed values are due, a) in part to the inadequacy of the equations,

and b) in part to molecular irregularities of the ethanolamines in solution.

By explaining the molecular irregularities of the ethanolamines in solution on the basis of a hydration effect, and calculating an approximate hydration number, a better agreement between the predicted and observed diffusivities is obtained.

In Part II of this work, the application of the wavefront shearing interferometer to gas-liquid diffusion is described. The gas cell built in this laboratory and the experimental technique is also described. Results for the systems CO_2 -water, and CO_2 into dilute monoethanolamine are reported. In the latter system, the presence of a reaction zone is experimentally illustrated, and calculations are made explaining the movement of this reaction zone.

It is believed that this is the first time ever that a) the presence of this reaction zone has been shown experimentally, and b) that the movement of the zone has been plotted.

At the moment, the application of this interferometer to gas-liquid diffusion is novel and needs improvement. When a fully successful experimental technique has been evolved, the possibilities for further work in this field are considerable.

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NOTATION.

Note: Numbers in parenthesis refer to a particular use of the symbol . i.e. A,-- Arnold's equation const.(36), refers to A's use in equation 36 only.

Where no number follows the description, the use is general.

PART I

A	;	area	cm^2
	;	Arnold's equation constant(36)	
B	;	Arnold's equation constant 36)	
b	;	displacement between wavefronts	
	;	Van der Waals volume(57)	
C	;	Concentration	g/cm^3
D	;	Mutual Diffusion Coefficient	cm^2/sec
D*	;	Self Diffusion Coefficient	cm^2/sec
E_μ, E_D	;	Activation energies for viscosity & diffn.	$\text{cals}/\text{g.mol}$
ΔE_{vap}	;	energy of vaporisation	
F	;	Force opposing motion of particle (18)	
	;	Semi-empirical factor, Arnold's equation(36)	
G	;	Magnification factor	
ΔH_{vap}	;	Heat of vaporisation	$\text{cals}/\text{g.mol}$
J	;	Diffusional flux	$\text{g.mols}/\text{sec.cm}^2$
K	;	Boltzmann's constant (18)	
		External ionic force (44)	

L	; Latent heat of evaporation	cal/s/g.mol
M	; Molecular weight	
	Total mass flow (12)	g.mols/cm ²
N	; Avogadro's number (= 6.023×10^{23})	
	Total number of observations (93)	
n	; Refractive index	
	; Number of ions (43)	
P	; Vapour pressure	mm.Hg
R	; Gas constant	
	; Radius of particle (19)	
r	; Intermolecular spacing(39)	
r_G	; Refractivity (Gladstone) (95)	
r_L	; Refractivity (Lorenz-Lorentz) (96)	
S	; Area factor (= $V_A^{1/3} + V_B^{1/3}$)	cm
s	; Standard error of estimate of $(2x)^2$ on t	
T	; Absolute temperature	°K
t	; time	secs
t_i	; time of inflexion of Gaussian curve	
Δt	; Zero-time correction factor	
U	; Absolute velocity of cation (51)	
u	; Cation valency (51)	
	velocity of particle (18)	
V	; Absolute velocity of anion (51)	
	; Molecular volume at normal boiling point	cm ³

v	; anion valency (51)	
	; partial molecular volume (4)	
w	; mass	gms
x	; distance, length	cm
	; mol. fraction (52)(97)	
	; Association parameter (64)	
Δx	; shear (= b)	cm
$2x$	; distance apart of fringe pairs	cm
Δz	; optical path difference	
γ	; activity coefficient	
ϵ	; parameter describing the geometrical configuration of the solute/solvent molecular structure (37)	
λ	; wavelength of light	$\text{\AA}$
	; characteristic molecular distance (37)	
μ	; viscosity	cp
	; chemical potential (44)	
ρ	; density	gm/cm ³
	; coefficient of ionic friction	
ν	; No. of ions (45)	
ϕ	; hydration number	
ω	; ionic mobility (44)	
∇	; Laplacian operator	

PART II

a	; optical path length thro' cell	cm
c	; concentration	g.mols/cm ³
c _{Al}	; interfacial concentration of gas in liquid	
c _{Bo}	; initial concentration of solute in liquid	
D	; gas-liquid diffusion coefficient	cm ² /sec
H	; Henry's law constant	
K _L ^o	; liquid film coefficient (physical absorp.)	cm/sec
K _L	; Liquid film coefficient (with reaction)	
K _G	; gas film coefficient	
k	; reaction velocity constant	cm ³ /g.mol.sec
M	; dimensionless group, $kD_A c_{Bo} / (K_L^o)^2$	
N	; rate of mass transfer	g.mols/sec
n	; refractive index	
p	; partial pressure	
q	; $= c_{Bo} / c_{Al}$	
r	; $= D_B / D_A$	
t	; time	
x	; length, distance (general)	cm
x _L	; thickness of liquid film	cm
x'	; distance from interface to reaction zone	cm
x''	; distance from reaction zone to edge of liquid film	cm

α ; integration constant (equation 27)

θ ; time

λ ; wavelength of light

$$\sigma ; = \left(\frac{\alpha}{D} \right)^{\frac{1}{2}}$$

ϕ ; $= K_L / K_L^o$, ratio of mass transfer with and without reaction.

PART I

The Application of the Wavefront Shearing Interferometer

to

Liquid-Liquid Diffusion.

INTRODUCTION.

In many branches of chemical engineering a knowledge of diffusivity is of importance where liquid diffusion is rate-controlling in the mass transfer process. Examples include absorption, adsorption, liquid-liquid extraction, and dialysis. On the pure science side, the diffusion process is one of the aspects of liquid behaviour which must be described by a satisfactory liquid-state theory, and hence diffusion rates are of importance in formulating and testing such theories. At the present moment, there is a distinct lack of precise diffusional theory, since the accurate measurement of diffusion rates is only a comparatively recent achievement.

Diffusion studies were first made in this laboratory by Furzer (1) and Thomas (2). The Gouy interferometer, - an accurate optical technique, was used by the above workers to study the diffusion rates of the ethanolamines (mono-, di-, and tri-) in water. The ethanolamines were chosen for investigation since they are widely used industrially in gas absorption (CO_2 removal, natural gas sweetening), and a knowledge of their diffusional properties is valuable in correlating mass

transfer rates to absorption theory. Subsequent to Thomas and Furzer publishing their results, however, a criticism on their findings was made by Ibrahim and Kuloor (3). It was intimated that the disagreement between the experimental results and the theoretical predictions could be due to one of three causes, i.e.

- 1) Inaccurate work.
- 2) Inadequate diffusional theory.
- 3) Association or hydration of the ethanolamines in solution (though this cause was less favoured).

It was therefore of some importance that a re-investigation be made of diffusion in the ethanolamine-water system, in order to examine Ibrahim and Kuloor's criticisms.

A highly accurate and sensitive interferometer was described by Bryngdahl (4), and it was realised that the capabilities of this , the wavefront shearing interferometer, surpassed those of any existing interferometer. It would thus be possible to make diffusion measurements of the greatest accuracy, and, as an added advantage, in very dilute solutions.

With this in mind, and the need to re-examine the diffusion rates in the ethanolamine-water systems,

the wavefront shearing interferometer was constructed in this laboratory.

The scope of the first part of this work therefore takes the following form:

A review of the existing diffusion theories; a review of experimental techniques, and a brief survey of the sensitivities of these methods; a description of the theory, apparatus, and technique for the wavefront shearing interferometer; a report on the investigation, using the wavefront shearing interferometer, into the diffusion rates of the systems ethanolamine-water; a critical appraisal of the accuracy of the results obtained, and a comparison with the work of Thomas and Furzer; an assessment of the applicability of the diffusion theories to the experimental results; a study of the physical chemistry of the amines in order to attempt an explanation of the disagreement between the theoretical and observed diffusivities.

From this work it is hoped to make a recommendation for the future use of semi-empirical equations in predicting diffusivity.

I. THEORY OF DIFFUSION IN LIQUID SYSTEMS

Progress in the study of diffusion in liquid systems is only comparatively recent. Although the first measurements of diffusion were made in 1850, limitations due to inaccurate experimental equipment have kept the data in the literature down to an insufficiently small amount. Also, there is as yet no really clear understanding of diffusion in the liquid state, so that the available methods for estimating diffusion in liquid systems are not at all reliable.

Several theories of diffusion have been advanced, and using these theories semi-empirical correlations have been proposed. Many reviews have been made of both the existing theories and the experimental methods for the determination of the diffusion coefficient. Of particular note are those by Johnson and Babb (5), Nienow(6), Tyrell (7), Lightfoot and Cussler (8), Kamal and Canjar (9).

The purpose of this section is to give a background to the existing theories of diffusion and the available experimental methods. Having illustrated the present state of knowledge on the matter, it is proposed to show the importance of diffusion in mass-transfer operations (e.g. absorption, liquid-liquid extraction and dialysis).

The diffusion coefficient will first be defined as a function of the concentration gradient in a diffusing system, and then the theories will be presented to show

how the diffusion coefficient may be predicted as a function of the various physical properties of liquid systems.

I(a). The Diffusion Coefficient.

For Uni-directional diffusion, Fick (1855) established the simple relationship

$$J = -D \frac{\partial c}{\partial x} \quad (1)$$

now known as Fick's First Law. In words, this states that the rate of mass transfer is proportional to the concentration gradient at constant temperature and pressure. The minus sign indicates that the flow is opposite in sense to the direction of the concentration gradient.

In a system consisting of components A and B, the diffusional flow of one component due to the concentration gradient must be balanced by that of the other. Writing the diffusion equation for each substance

$$J_A = -D_A \frac{\partial C_A}{\partial x} \quad (2)$$

$$J_B = D_B \frac{\partial C_B}{\partial x} \quad (3)$$

The volume transfer will be equal to

$$D_A v_A \left(\frac{\partial C_A}{\partial x} \right) \quad \text{and} \quad D_B v_B \left(\frac{\partial C_B}{\partial x} \right)$$

where v_A and v_B are partial molar volumes

For a constant volume system

$$D_A v_A \left(\frac{\partial C_A}{\partial x} \right) + D_B v_B \left(\frac{\partial C_B}{\partial x} \right) = 0 \quad (4)$$

The quantity of A per unit volume overall is $v_A C_A$ and that of B is $v_B C_B$

$$\therefore v_A C_A + v_B C_B = 1 \quad \dots \dots (5)$$

differentiating (5),

$$v_A \left(\frac{\partial C_A}{\partial x} \right) + v_B \left(\frac{\partial C_B}{\partial x} \right) = 0 \quad \dots \dots (6)$$

For equations (4) and (5) to be true it follows that

$$D_A \equiv D_B$$

Hence, in the standard binary systems to be considered, the diffusion coefficient measured will be the one common to both components, D_{AB} .

If the mass transfer is considered over an elemental

$$\begin{aligned} \text{volume } \delta V &= A \cdot \delta x, \text{ the diffusional flow at } x + \delta x \\ &= J + \left(\frac{\partial J}{\partial x} \right) \cdot \delta x \quad \dots \dots (7) \end{aligned}$$

$$\text{and } \frac{\partial}{\partial t} (J) = - \frac{\partial}{\partial x} (J) \delta x \quad \dots \dots (8)$$

$$\delta x \cdot \left(\frac{\partial C}{\partial t} \right) = \frac{\partial}{\partial x} \left(D \cdot \frac{\partial C}{\partial x} \right) \delta x \quad \dots \dots (9)$$

$$\frac{\partial C}{\partial t} = D \cdot \frac{\partial^2 C}{\partial x^2} \quad \dots \dots (10)$$

This equation is known as Fick's Second Law.

The Second Law is almost exclusively employed in the experimental determination of D_{AB} , since it is far easier to measure concentrations than molecular flux.

Solutions of the equation $\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2}$ have been

developed by Fourier series analysis, and are necessary for an evaluation of D_{AB} . Crank (10) and Jost (11) present the solutions for different boundary conditions.

Solution of Fick's Second Law for a uniform cross-section cylinder of infinite length (extended initial distribution) :-

$$\begin{aligned} \text{at } t = 0, \quad C &= C_0, & x < 0 \\ C &= 0, & x > 0 \end{aligned}$$

By differentiating $\frac{\partial C}{\partial t} = D \cdot \frac{\partial^2 C}{\partial x^2}$, a solution (for the above conditions) is obtained as

$$C = \frac{A}{\sqrt{t}} \cdot \exp \left(- \frac{x^2}{4Dt} \right) \dots \dots (11)$$

where A is an arbitrary constant.

(Please see appendix)

If the total amount of material diffusing

$$= M = \int_{-\infty}^{\infty} C \cdot dx$$

and writing $\frac{x^2}{4Dt} = Z^2$, $dx = 2\sqrt{Dt} \cdot dZ$

$$\text{then } M = 2A\sqrt{D} \int_{-\infty}^{\infty} \exp(-Z^2) dZ = 2A\sqrt{\pi D} \dots \dots (12)$$

$$\text{But } A = \frac{C\sqrt{t}}{\exp(-\frac{x^2}{4Dt})} \dots \dots (13)$$

Substituting (13) into (12)

$$C = \frac{M}{2\sqrt{\pi Dt}} \exp(-\frac{x^2}{4Dt}) \dots \dots (14)$$

Hence the concentration distribution at time t is

$$\frac{\partial C}{\partial x} = \frac{\Delta C}{2\sqrt{\pi Dt}} \exp(-\frac{x^2}{4Dt}) \dots \dots (15)$$

where $\Delta C = C_0 - C$

If it is assumed that the refractive index is linearly related to the concentration, then

$$\frac{\partial n}{\partial x} = \frac{\Delta n}{2\sqrt{\pi Dt}} \exp\left(-\frac{x^2}{4Dt}\right) \quad \dots \dots (16)$$

This relationship, derived from a solution of Fick's second law is used almost exclusively where optical techniques are used to measure the diffusion coefficient.

It will be shown later how equation (16) is used to evaluate D from a knowledge of the refractive index gradient of the diffusion system.

Crank (10) gives a particularly thorough study of the other possible solutions of Fick's second law.

Solutions include:

- Semi-infinite cylinder,
- finite cylinder,
- diffusion in a sphere,
- diffusion with a moving boundary etc.

If D_{AB} is dependant on concentration, then there might be experimental errors in the determination of D_{AB} if the concentration difference between the two solutions is significant. Strictly speaking, D_{AB} , as calculated by the Fick equation, is for a point condition only.

With this criterion in mind, two types of diffusion coefficient can be defined:-

1) Differential Diffusion coefficients, in which diffusion occurs between two solutions of only differential concentration difference.

2) Integral diffusion coefficients, in which diffusion occurs between two solutions of significant concentration difference.

The integral coefficient is related to the differential coefficient, D_{AB} , by the expression

$$\bar{D}_{AB} = \frac{1}{C_1 - C_2} \int_{C_2}^{C_1} D \cdot dC \quad (17)$$

Since the differential coefficient is the one needed for any examination of the physical properties of the solution, then it is desirable to make the concentration difference as small as possible when measuring D_{AB} , - and the coefficient is thus taken as measured at the mean concentration.

Theories of Diffusion

In this section the principal theories of diffusion are discussed, in which the diffusion coefficient is related to the physical properties of the solution.

The theories may be categorised as below:-

a) <u>Non-electrolytes</u>	b) <u>Electrolytes</u>
Hydrodynamic theories	
Kinetic theories	

I(b) Stokes-Einstein Hydrodynamic Theory

Tyrell discusses the hydrodynamic theories in detail, but the essentials of what is known as the Stokes-Einstein theory are adequately described by Gainer and Metzner (12) Tuwiner (13) and Glasstone (14).

Although the hydrodynamic theory has some value for the diffusion of large molecules (e.g. colloids), its use is not suggested at all generally. The derivation of the theory is due independently to Sutherland and Einstein. The Nernst-Einstein equation is intermediate, i.e.

$$D_{AB} = k.T. \frac{u_A}{F_A} \quad (18)$$

where k = Boltzmanns constant

T = absolute temperature

u_A = velocity of particle

F_A = force opposing motion of particle A

The diffusion flow is regarded as a balance between a driving force and a resistance to flow which leads to a constant average diffusion velocity.

For a particle moving through a liquid the Stokes drag is given by

$$F_A = 6 \pi \mu_B \cdot u_A \cdot R_A \quad (19)$$

where μ_B = viscosity of the solvent

R_A = radius of the diffusing particle

On substitution into (18) the Stokes-Einstein equation is obtained

$$D_{AB} = \frac{k.T.}{6 \pi \mu_B \cdot R_A} \quad (20)$$

R_A may be computed from

$$M_A = \frac{4}{3} \pi R_A^3 \rho_B N \quad (21)$$

where M_A = molecular weight

ρ_B = density

N = Avogadro's number

Originally the driving force was considered to be the gradient of osmotic pressure, but nowadays it is taken as the gradient of chemical potential of the diffusing species. Thus an activity correction term should be included with equation (20).

$$\text{i.e.} \quad D_{AB} = \frac{k.T.}{6 \pi \mu_B R_A} \left[1 + \left(\frac{\partial \ln \gamma_A}{\partial \ln c_A} \right)_{T,P} \right] \quad (22)$$

where γ = activity

c = molar concentration

For ideal solutions this activity term is unity.

For diffusion in water the Stokes-Einstein equation is only applicable where the solute molecular weight exceeds 300, and as with all other theories to be discussed applies only to dilute solutions.

I(c) Kinetic Theories of Diffusion

There are two main kinetic theories of diffusion, Arnold's and Eyring's.

Arnold's Kinetic Theory (15)

Arnold applied the kinetic theory of gases, which had been successful in interpreting the mutual diffusion coefficients of gaseous systems, to liquid systems. Many of the reviews of liquid diffusion only summarise Arnold's theory since its use is limited in applicability due to the presence of three empirical constants. However, to understand Arnold's approach to liquid diffusion the development of the theory will be given here.

As mentioned above the classical kinetic theory for gaseous diffusion is applied to liquid systems, making allowances for the difference in the packing of the molecules.

From eqn. (1), Fick's First Law,

$$J = \frac{dM}{dt} = D.A. \frac{dc}{dx} \quad (23)$$

where M = total mass flow

If the net forward velocity of a molecule in the diffusion stream is represented by u, then

$$\frac{dM}{A.dt} = C.u \quad (24)$$

It is assumed that the acceleration of the diffusing molecule is negligible.

The driving force $\frac{dc}{dx}$ is used solely to overcome the

resistance to diffusion, measured in terms of the momentum transferred from the diffusing molecule to the solvent. This momentum transfer is equal to the product of the total number of collisions of unlike molecules by the momentum loss per collision.

From gas theory, the number of collisions per second is proportional to

- 1) Concentration of each type of molecule.
- 2) Average cross-sectional area.
- 3) Root mean square velocity.

$$\text{i.e. } c_1 \cdot c_2 \cdot S^2 \cdot \sqrt{u_1^2 + u_2^2} \dots\dots\dots (25)$$

$$\text{where } S = V_1^{1/3} + V_2^{1/3} \dots\dots\dots (26)$$

(V = molecular volume)

At constant temperature all molecules have the same kinetic energy. Since $mu^2 = \text{constant}$, then (25) becomes

$$c_1 \cdot c_2 \cdot S^2 \sqrt{\frac{1}{M_1} + \frac{1}{M_2}} \dots\dots\dots (27)$$

For forceless spheres, the momentum loss per collision is

$$= \frac{2}{3} \cdot \frac{M_1 \cdot M_2}{M_1 + M_2} \cdot (u_1 + u_2) = \frac{2}{3} \cdot \frac{(u_1 + u_2)}{\frac{1}{M_1} + \frac{1}{M_2}} \dots\dots (28)$$

Assuming no volume change on mixing,

$$c_1 V_1 u_1 - c_2 V_2 u_2 = 0 \dots\dots\dots (29)$$

$$\text{Since } c_1 V_1 + c_2 V_2 = 1 \dots\dots\dots (30)$$

Combining (29) and (30),

$$(u_1 + u_2) = u_1 / c_2 \cdot V_2 \quad \dots\dots\dots (31)$$

From (27), (28), and (31) the resistance to diffusion is proportional to

$$\frac{c_1 \cdot c_2 \cdot s^2 \cdot u_1}{c_2 \cdot V_2 \cdot \sqrt{1/M_1 + 1/M_2}} \quad \dots\dots\dots (32)$$

From (23) and (24), $\frac{dc_1}{dx} = \frac{c_1 u_1}{D} \quad \dots\dots\dots (33)$

Solving for D,

$$D = B \cdot \frac{\sqrt{1/M_1 + 1/M_2} \cdot V_2}{s^2} \quad \dots\dots\dots (34)$$

where B is a proportionality constant.

Equation (34) fails on three main assumptions used in its derivation, the assumptions being that

i) all collisions are binary; ii) the collision rate is unaffected by the molecular volumes; and iii) that intermolecular forces are negligible.

These assumptions cannot be allowed in liquid diffusion. Arnold overcame these objections by bringing in the semi-empirical factor F into equation (34). For dilute systems, F is essentially a function of the solvent properties only, and is proportional to the square

root of the solvent viscosity.

When either solvent or solute or both are associated, association factors A_1 and A_2 are included in the expression for F .

$$\text{Writing } F = A_1 A_2 V_2 \sqrt{\mu_2} \quad (35)$$

$$\text{we get } D = B \cdot \sqrt{\frac{\frac{1}{M_1} + \frac{1}{M_2}}{A_1 A_2 S^2 \sqrt{\mu_2}}} \quad (36)$$

For water, $A_2 = 4.7$ and $B = 0.0108$ at 25°C

Eyring's Theory

Eyring and co-workers applied absolute rate theory to diffusion, and this was presented in a number of papers. A review of all this work is given by Glasstone et al, (16) and Kincaid et al (17). The theory is also summarised in other references, notably by Tyrell (7), Johnson and Babb (5), and Gainer and Metzner (12).

The Eyring theory attempts to explain the diffusion process on the basis of a cell model for the liquid, in which molecules move from a given position to an adjacent hole in the liquid structure. Eyring assumed that the energy of activation for the diffusion process is that energy required to form the extra space in the liquid to allow the molecules to move. A similar argument was applied to viscous flow.

An equation in which the diffusion coefficient is considered as a function of both the activation energy for diffusion and the activation energy for viscous flow was arrived at,

i.e.

$$D = \frac{K.T}{\epsilon \cdot \mu_B} \cdot \left(\frac{\lambda_a}{\lambda_b \lambda_c} \right) \frac{\lambda_1^2}{\lambda_2^2} \exp \left(\frac{E_{\mu B} - E_{D(AB)}}{RT} \right) \quad \dots (37)$$

where K = Boltzmann's constant

E_{μ} = activation energy for viscosity

E_D = " " " diffusion

$\lambda_1^2 / \lambda_2^2$ = ratio of partition functions for molecules in the equilibrium and activated states.

ϵ = parameter describing the geometrical configuration of the solute/solvent molecular structure

$\lambda_a, \lambda_b, \lambda_c$ = characteristic distances as below .

Migrating entities, represented by white circles, are moving in viscous flow under the influence of shearing forces.

The equation may be simplified by putting

$$1) \lambda_1^2 / \lambda_2^2 = 1$$

$$2) \left(\lambda_a / \lambda_b \lambda_c \right) = (N/V_B)^{1/3}$$

Where N = Avogadro's number

Thus we may write the equation for the diffusion coefficient

$$D = \frac{K.T.}{E_{\mu_B}} \left(\frac{N}{V_B} \right)^{1/3} \exp. \left(\frac{E_{\mu(B)} - E_{D(AB)}}{R.T.} \right) \dots (38)$$

Although Eyring and co-workers assumed that $E_{\mu} = E_D$, this is only an approximation that is applicable to self diffusion.

Gainer and Metzner (12) have made a useful analysis of the Eyring theory based on viscosity and diffusivity cage models. They have put forward an equation for the calculation of

$$E_{\mu(B)} - E_{D(AB)},$$

$$\begin{aligned} \text{i.e. } E_{\mu(B)} - E_{D(AB)} = & \frac{E_{\mu(B)}}{2} - \left(\frac{E_A}{E_B} \right) \left\{ \sqrt{\frac{r_{AA}}{r_{AB}} \cdot \frac{E_{\mu(A-H)}}{2} \cdot \frac{r_{BB}}{r_{AB}} \cdot \frac{E_{\mu(B-H)}}{2}} \right. \\ & \left. + \sqrt{\left(\frac{r_{AA}}{r_{AB}} \right)^{1/2} \frac{E_{\mu(A-D)}}{2} \cdot \left(\frac{r_{BB}}{r_{AB}} \right)^{1/2} \frac{E_{\mu(B-D)}}{2}} \right\} \dots (39) \end{aligned}$$

r_{AA} , r_{BB} , r_{AB} are intermolecular spacings,

$$\text{i.e. } r_{AA} = \left(\frac{V_A}{N} \right)^{1/3}, \quad r_{BB} = \left(\frac{V_B}{N} \right)^{1/3}, \quad r_{AB} = \frac{r_{AA} + r_{BB}}{2}$$

$E_{\mu}(A-H)$, $E_{\mu}(B-H)$ are the activation energies due to hydrogen bonding.

$E_{\mu}(A-D)$, $E_{\mu}(B-D)$ are the activation energies due to dispersion effects.

The above two energies are taken on the assumption that the total activation energy may be divided into two parts for a compound in general. They are calculated on the basic assumption that the total heat of vaporisation of a compound is formed of two parts,

i.e.

$$\begin{array}{llll} \Delta H_{\text{vap}} & = & \Delta H_{\text{vap}} & + \quad \Delta H_{\text{vap}}(x-H) \\ \text{at } T_R & & \text{of Hydrocarbon} & \text{due to} \\ & & \text{homologue at } T_R & \text{hydrogen} \\ & & & \text{bonding} \end{array}$$

$$\therefore \frac{E_{\mu}(x-H)}{E_{\mu}(x)} = \frac{\Delta H_{\text{vap.}}(x-H)}{\Delta H_{\text{vap.}}(x)} \quad \dots (40)$$

$$\text{and} \quad E_{\mu}(x-D) = E_{\mu}(x) - E_{\mu}(x-H) \quad \dots (41)$$

This calculation may be done quite easily for say, alcohols, which have a homologue, and Gainer and Metzner refer to the method. But the whole of the above calculation is somewhat invalidated when no homologue can be found (as with the amines).

$E_{\mu}(x)$ is calculated from

$$E_{\mu}(x) = RT \ln \left[\frac{\mu v^{2/3} \Delta E_{\text{vap}}}{(1.09 \times 10^{-3}) M^{1/2} T^{3/2}} \right] \quad \dots (42)$$

The parameters ϵ_A, ϵ_B have been taken by Gainer and Metzner to be 6 for all the compounds that they considered, apart from ethyl and methyl alcohols to which they ascribed the value 8.

In actual fact the variation of this parameter is quite considerable from compound to compound, so that it effectively becomes a semi-empirical constant which introduces a factor of inaccuracy.

I(d) Diffusion of Electrolytes

A comprehensive description of the theory of the diffusion of electrolytes is given by Harned and Owen (16), and Tyrell (7). Tuwiner (13) presents a fairly basic description that is of use for a general understanding of the principles involved.

Obviously, the treatment of diffusion of electrolytes must differ fairly radically from that of non-electrolytes due to the formation of ion pairs in solution. As a requirement of electrical neutrality, the anions and the cations must move at an equal rate. Thus the mobility is intermediate between that of the component ions when these are free of electric forces.

Theory of Diffusion of a Simple Electrolyte

For an electrolyte solution containing two types of ions,

$$\begin{array}{ll}
 u_1 = u_2 = u & J_1 = n_1 u \\
 \text{(ionic velocity)} & J_2 = n_2 u \quad \dots (43) \\
 & \text{(flow of ions)}
 \end{array}$$

At low concentrations, interaction between the ions may be neglected, and

$$u = K_1 \omega_1 = K_2 \omega_2 = -\omega_1 \nabla \mu_1 = \omega_2 \nabla \mu_2 \quad \dots (44)$$

K = external forces on the ions

ω = mobility of the ions

∇ = Laplacian operator

μ = chemical potential

If μ is the chemical potential of a molecule which breaks up into ν_1 anions and ν_2 cations, then

$$K = \nu_1 K_1 + \nu_2 K_2 = -\nabla \mu \quad \dots (45)$$

From (44) and (45)

$$K_2 = \left(\frac{\omega_1}{\omega_2} \right) K_1 = \left(\frac{\rho_2}{\rho_1} \right) K_1 \quad \dots (46)$$

where ρ = coefficient of friction of the ions)

$$K_1 = - \frac{\rho_1}{\nu_1 \rho_1 + \nu_2 \rho_2} \cdot \nabla \mu = - \frac{\omega_2}{\nu_1 \omega_2 + \nu_2 \omega_1} \nabla \mu \quad \dots (47)$$

$$\text{and } u = - \frac{\omega_1 \omega_2}{\nu_1 \omega_2 + \nu_2 \omega_1} \cdot \nabla \mu \quad \dots (48)$$

If the solution is ideal

$$\nabla \mu = (\nu_1 + \nu_2) kT \frac{\nabla n}{n} \quad \dots (49)$$

and consequently

$$J = nV = - \frac{(\nu_1 + \nu_2) \omega_1 \omega_2}{\nu_1 \omega_2 + \nu_2 \omega_1} kT \nabla n \quad \dots (50)$$

This expression is known as Nernst's Law of diffusion.

Written in a simplified form, Nernst's Law may be expressed as

$$D = 8.314 \times 10^{-7} \cdot \frac{UV}{U+V} \left\{ \frac{1}{u} + \frac{1}{v} \right\} \cdot T \quad . . . (51)$$

where U and V are absolute velocities of cation and anion respectively under a force of 1 dyne at infinite dilution. u and v are the valencies of the cation and anion.

This equation is not applicable to weak electrolytes where solutions consist of a mixture of ions and large numbers of undissociated molecules.

Tables may be found in the literature for U and V, but are mostly given only for strongly ionised salts. Where values of U and V are given, the equation is most useful for engineering purposes.

However, since the electrolyte moves in one direction, and the solvent by replacing it moves in the opposite direction, an "electrophoretic" effect exists. This electrophoretic effect is allowed for in two expressions developed by Onsager and Fuoss (19).

Together with a thermodynamic term, - which allows for the activity coefficient of an electrolyte varying throughout the diffusing system, the two electrophoretic terms may be combined with the Nernst equation to give a comprehensive expression for the diffusion coefficient of an electrolyte in solution.

Harned and Owen give the development of this expression. It is not intended to give the development

here since it is somewhat lengthy, and the final results (although given here) are more of use to a pure physical chemist.

The full equation is

$$D = (v_1 + v_2) \cdot 1000 R.T \left(1 + c \cdot \frac{\partial \ln y_{\pm}}{\partial c} \right) \times \left(1.0741 \times 10^{-20} \cdot \frac{\lambda_1^0 \lambda_2^0}{v_1 |z_1| \Lambda^0} + \frac{\Delta M'}{c} + \frac{\Delta M''}{c} \right) \dots (A)$$

where $\Delta M'$ and $\Delta M''$ are the electrophoretic effect terms given by

$$-\Delta M' = \frac{(|z_2| \lambda_1^0 - |z_1| \lambda_2^0)^2}{(\Lambda^0)^2} \left\{ \frac{3.132 \times 10^{-19}}{7_0 (dT)^{1/2}} \right\} \cdot \frac{c \sqrt{\eta}}{(1 + xa)} \dots (B)$$

$$-\Delta M'' = \frac{(|z_2|^2 \lambda_1^0 - |z_1|^2 \lambda_2^0)}{(\Lambda^0)^2} \left\{ \frac{9.304 \times 10^{-13}}{7_0 \cdot (dT)^2} \right\} c^2 \phi(xa) \dots (C)$$

$$\text{where } \phi(xa) = e^{2xa} \cdot E_i(2xa) / (1 + xa)^2 \dots (D)$$

The term $\left(1 + c \cdot \frac{\partial \ln y_{\pm}}{\partial c} \right)$ is the thermodynamic term which allows for the variation of the activity coefficient throughout the diffusing system. The nomenclature for equations A to E (additional to nomenclature already used) is given below:-

Nomenclature for equations A to E;-

R = Gas constant

T = Absolute temperature

c = molecular concentration

$\gamma_{\pm}$ = mean molar activity coefficient of the electrolyte

$\left. \begin{matrix} \lambda_1^{\circ} \\ \lambda_2^{\circ} \end{matrix} \right\}$ = limiting equivalent conductance of the ions
indicated, at infinite dilution.

$\left. \begin{matrix} z_1 \\ z_2 \end{matrix} \right\}$ = valencies

Λ_0 = limiting equivalent conductance of the electrolyte
at infinite dilution.

η_0 = viscosity of the solvent.

d = dielectric constant of the solution.

Γ = ional concentration.

x = reciprocal of average radius of the ionic
atmosphere.

a = activity

$E_1()$ = exponential integral function.

I(e). The Influence of Concentration on the Diffusion Coefficient.

As mentioned above, all the above theories, - and all the semi-empirical equations to be discussed further on, predict the diffusivity of a system at high dilution only.

For systems of concentrations greater than a few percent by weight, the prediction of diffusivity becomes even more confused and unreliable. The influence of concentration on diffusivity is discussed below for a) non-electrolytes and b) electrolytes.

Non-Electrolytes.

For ideal solutions of non-electrolytes, Powell et al (20) and Wilke (21) propose the relationship

$$\left(\frac{D \cdot \mu}{T} \right)_{A,B} = x_A \left[\left(\frac{D \cdot \mu}{T} \right)_{B_0} - \left(\frac{D \cdot \mu}{T} \right)_{A_0} \right] + \left(\frac{D \cdot \mu}{T} \right)_{A_0} \dots (52)$$

where x_A = mol fraction of A in mixture

subscripts: A_B , diffusion of A in B at concn. x_A
 A_0 , " " A " B (very dilute A)
 B_0 , " " B " A (very dilute B)

For non-ideal solutions the right-hand side of the equation must also be multiplied by an activity correction factor

$$\text{i.e.} \left(1 + \frac{\partial \ln \gamma_A}{\partial \ln x_A} \right) \dots (53)$$

where γ_A = activity of component A.

Garner and Marchant (22) on investigating the diffusivities of several associated solutes in water reported that the above relationship gave fairly satisfactory agreement with experimental results.

Caldwell and Babb (23) investigated three systems which were close to being ideal , and found that equation 52 satisfactorily described the variation in diffusivity with concentration.

Obviously, one limitation of the above relationship is the necessity to have values for the diffusivities at the two concentration extremes.

Unfortunately, apart from the references quoted above, there seems to be little evidence to support the use of the expression.

Caldwell and Babb also claimed that the group $D \cdot \mu / T$ varied linearly with mol fraction, which should be the case for ideality. However, inspection of their figures shows that the linearity is not very satisfactory. It would seem that it is not very good practice to correlate the variation in diffusivity with concentration through the group $D \cdot \mu / T$, even if the solutions are assumed to be ideal. Mullin et al (24) tried to use this group, with poor results.

Thus, for ideal non-electrolytes , equation 52 appears to be the most adequate for describing the variation in diffusivity with concentration

Dullien and Shemilt (25) investigated the system ethanol-water over the entire concentration range but did not attempt to use the above equation. Instead they reported the variation in diffusivity with concentration in terms of the Schmidt number ($\frac{\mu}{\rho D}$), without any conclusive results.

Strictly speaking, equations 52 and 53 should only be used for diffusion of liquid into liquid. For the diffusion of solid into liquid (i.e. sucrose-water) the equation proposed by Gordon (26) should be used.

$$\text{i.e. } D = D_0 \left(1 + \frac{\partial \ln \gamma}{\partial \ln x} \right) \frac{\mu_0}{\mu} \quad \dots (54)$$

English and Dole (27) studied the diffusion of sucrose in water in supersaturated solutions, and Gosting and Morris (28) studied the diffusion of sucrose in dilute solutions.

Gosting and Morris found that the Gordon relationship was followed and thus proposed that the diffusion of sucrose in dilute solutions was a true diffusional process.

English and Dole showed, however, that as the concentration increased, the agreement between the observed diffusion coefficients and those predicted by the Gordon equation decreased. This they attributed to a) the greater dependence on viscous flow and b) the influence of hydration on the sucrose molecule.

Electrolytes

With concentrated solutions of electrolytes, effects to be considered that will reduce the diffusivity include

- 1) Thermodynamic effect
- 2) Electrophoretic effect
- 3) Viscosity
- 4) Hydration

In the Nernst-Onsager-Fuoss equation these effects are considered so that corrections should not be necessary.

However, a relationship between D and D_0 was put forward by Stokes et al (29) for concentrated solutions of 1:1 electrolytes

$$\text{i.e.} \quad \frac{D}{D_0} = \left(1 + m \cdot \frac{\partial \ln \gamma}{\partial m}\right) (1 - 0.018 \phi m) \left[1 + 0.018 m \left(\frac{v D^*}{D_0}\right)^{-n}\right] \quad \dots (55)$$

where m = molality

ϕ = hydration number (mols water/mol salt)

D^* = self-diffusion coefficient for water

v = no. of ions formed by one stoichiometric molecule of salt

I(f) Semi-Empirical Equations for Predicting the Diffusion Coefficient

A good review of the semi-empirical correlations available is given by Gambill (30) and Sherwood and Reid (31).

The correlations are all based on the theories already outlined above and are an attempt to predict the diffusivities of solutions using readily available physical data. It should be noted at this stage that all the main correlations are intended for systems of non-electrolytes, but examination of the data on which these correlations are based reveals that electrolyte systems have been fairly widely used in the data. Attention will be drawn to these cases in the discussions on individual correlations.

Three early correlations that are quite inaccurate are summarised below

Thovert (32)

$$D \cdot \mu_B \cdot \sqrt{M_A} = \text{const.} \quad . . . (56)$$

Herzog (33)

$$D = \frac{2RT}{6 \pi N^{0.67} \mu_B} (V_A - b)^{0.33} \quad . . . (57)$$

b = Van der Waals volume

N = Avogadro's number

Olson and Walton (34)

Curves are plotted of D against $\frac{\Delta \sigma}{c_A}$ with σ as parameter (where σ = surface tension and $\frac{\Delta \sigma}{c_A}$ = slope of surface tension lowering curve at concn. c_A).

$$\frac{\Delta \sigma}{c_A} = \frac{10^{\frac{E}{1318}} - 1}{0.695}$$

where $E = E_0 + 0.625 n$

E_0 = potential energy contribution of chemical type

(Olson and Walton tabulate values)

n = number of carbon atoms in molecule

Olson and Walton put forward their correlation on the basis of results given by only 11 organic compounds.

Wilke (21) was the first to make an important step forward in proposing a usable correlation.

Wilke's correlation is derived from the Stokes-Einstein and Eyring theories and employs the use of the group

$$F = \frac{T}{D \cdot \mu} \quad . . . (58)$$

F is plotted against solute molal volume, V_A , for a number of solutes diffusing in water, benzene, and methyl alcohol.

Of the 45 solutes considered diffusing into water, 7 are gases. Of the remainder, almost all exhibit some form of hydrogen bonding or ionisation in solution

(examples, - acetamide, acetic acid, acetonitrile)

This immediately makes the correlation and subsequent improvements suspect.

Also, as pointed out in the discussion on the Stokes-Einstein theory, an activity correction term should be included if the solutions are not ideal. This has not been done, and thus it

is more than likely that errors will be present in the Wilke correlation.

Scheibel (35) expressed the graphical correlation of Wilke by the equation

$$F = 1.22 \times 10^7 \left\{ \frac{V_A^{1/3}}{1 + \left(\frac{3V_B}{V_A} \right)^{2/3}} \right\} \dots (59)$$

$$\text{or } D = 8.2 \times 10^{-8} \cdot \frac{T}{\mu} \left\{ \frac{1 + \left(\frac{3V_B}{V_A} \right)^{2/3}}{V_A^{1/3}} \right\} \dots (60)$$

From the published data, this equation appears to represent the behaviour of large molecules diffusing through a solvent of small molecules, and appears to be correct for the effect of solvent volume with a solute volume as much as twice the solvent volume.

In the above equation

T = absolute temp., $^{\circ}\text{K}$

μ = viscosity of solution, cp.

V_A, V_B = molecular volume (solute, solvent)

The same provisos as were noted for the Wilke correlation must also apply here.

Othmer and Thakar (36)

The correlation is derived from Eyring's theory, using the relationship

$$\log D = - \frac{E_0}{E_\mu} \cdot \log \mu + C \quad . . . (61)$$

Thus a plot of $\log D$ against $\log \mu$ should give a straight line.

For solvent water the slope of this line has been computed to have an average value of -1.1 and the correlation

$$D \times 10^5 = \frac{14}{\mu_W^{1.1}} V_A^{0.6} \quad . . . (62)$$

for diffusion in water has been derived.

For solvents other than water, the general equation for diffusion has been given as

$$D \times 10^5 = \frac{14}{\mu_W^{1.1} \left(\frac{L_S}{L_W} \right)} V_A^{0.6} \cdot \mu_S^0 \quad . . . (63)$$

where L_S and L_W are the latent heats of vaporisation of solvent and water respectively.

$$\mu_S^0 = \text{Viscosity of solvent.}$$

Of the 5 solutes diffusing in water considered by Othmer and Thakar, one is calcium chloride (a strong electrolyte).

The others are :- water (self-diffusing), phenol (a fairly strong acid), mannitol and saccharose (possible hydrogen bonding in solution). Some doubt is thus expressed as to the validity of the correlation.

Wilke and Chang (37)

This is the most widely used correlation and appears to have found general acceptance. The correlation is a development of the earlier work by Wilke, and is based on diffusion data for a large number of organic liquid systems.

The group $F = \frac{T}{D\mu}$ is again used, being correlated with the solute molal volume, V_A . However, in this correlation the "association parameter" for diffusion in various solvents is considered, - the association parameter, x , introduced to define the effective molecular weight of the solvent with respect to the diffusion process.

The correlation for both associated and non-associated liquids is given by

$$D = 7.4 \times 10^{-8} \frac{(xM)^{\frac{1}{2}} \cdot T}{\mu \cdot V_A^{0.6}} \quad . . . (64)$$

Some Values of x are given below:-

		x
water	;	2.6
methyl alcohol	;	1.9
ethyl alcohol	;	1.5
non-associated liquids	;	1.0

Although an association parameter has been included in the correlation, the same criticisms made of the Wilke correlation will apply.

Ibrahim and Kuloor

Subsequent to a diffusional study of the ethanolamines made by Thomas and Furzer (2), Ibrahim and Kuloor (3) proposed two correlations, - partly in an attempt to explain the large differences between the observed diffusion coefficients and those predicted by previous correlations.

The first correlation was a calculation based on gas kinetics, and subsequent communication with Ibrahim (38) has revealed that this was quite irrelevant to any liquid-liquid diffusion case.

The second correlation proposed was subsequently further explained (39), and is based on a modification of Wilke and Chang's correlation. This involves changing $V^{0.6}$ to $V^{0.5}$ and including terms for the latent heat of evaporation of the solute and solvent.

Thus

$$D = 5.4 \times 10^{-8} \left[\frac{M_A^{\frac{1}{2}} L_B^{\frac{1}{3}} T}{\mu_B V_A^{0.5} L_A^{0.3}} \right]^{0.93} \dots (65)$$

115 organic liquid systems were considered. Again, amongst these systems were some such as:-

acetic acid - water, diethylamine - water etc. and also several gases diffusing into water.

There is thus the inevitability that the correlation is based on a large percentage of systems in which a degree of non-ideality is present.

King et al.

A recent correlation by King et al is based on the observation that $\frac{D_{12}}{T}$ is nearly constant for self diffusion. However, the correlation obtained had a 19.5% standard deviation with their accumulated data. Since this is twice as bad as the correlations of Wilke and Chang etc. then it may be assumed that the correlation is insufficiently accurate to be considered here.

Atomic and Molecular Volumes

In the above correlations, the molecular volumes are calculated from the figures due to Le Bas and given by Wilke and Chang (37). The molecular volume is defined as being the volume, ccs., of one gm.mol. at the normal boiling point.

Atomic Volumes for Complex Molecules (the molecular volume being additive):-

Bromine	27	Nitrogen (2 ary amine)	12
Chlorine	24.6	Oxygen (except as below)	7.4
Iodine	37	Oxygen (methyl esters)	9.1
Carbon	14.8	Oxygen (ethyl esters)	9.9
Hydrogen	3.7	Oxygen(ethers,other esters)	11
Nitrogen (double bond)	15.6	Oxygen (acids)	12
Nitrogen (lary amine)	10.5	Sulphur	25.6

For 3-membered ring,	deduct	0.6
4- " " , "		8.5
5- " " , "		11.5
Pyridine " , "		15
Benzene " , "		15
Napthalene " , "		30
Anthracene " , "		47.5

Molecular Volumes :-

H ₂	14.3	O ₂	25.6	N ₂	31.2		
air	29.9	CO	30.7	CO ₂	34	SO ₂	44.8
NO	23.6	D ₂ O	20.0	N ₂ O	36.4	NH ₃	25.8
H ₂ O	18.9	COS	51.5	Cl ₂	48.4	Br ₂	53.3
I ₂	71.5						

Some Comments on the above Theories and Correlations

Unfortunately, none of the above described theories or correlations are in the least bit satisfactory for general engineering purposes. On the one hand, the theories and correlations for non-electrolytes are distinctly hit-and-miss, and on the other hand the theory for electrolytes is too unwieldy for anyone but a pure scientist interested in one system only.

It is as well to quote Wilke and Chang as to the validity of their correlation, since this observation applies equally to all the other equations and puts them in their true perspective.

".... It must be recognised that special structural features of molecules and other molecular interactions may be important in certain cases and that therefore the proposed relationship (correlation) is at best an oversimplification utilised to obtain a practical result".

When diffusion in the systems ethanolamines-water is discussed later on, with practical results as illustration, it will be seen just how insufficient these correlations are.

None of the correlations can be relied upon to predict a D value much better than 10%.

Sherwood and Reid (31) give tables to show calculated and observed values of D, using the empirical correlations. The deviations have been calculated for each system. Summaries are given below.

Diffusion in water

	<u>Wilke-Chang</u>	<u>Scheibel</u>	<u>Othmer</u>
Average error %	11	9	8
Maximum error %	+30	+25	+25
	(pyrogallol)	(alloxan)	
	+33	+23	+23
	(alloxan)	(mannitol)	

Diffusion in Methanol

Average error %	11	12
Maximum error %	+32	+30
	(chloral hydrate)	
	+29	+35
	(lactic acid)	

Diffusion in Benzene

Average error %	12	10	15
Maximum error %	+30	+27	-30
	(chloracetic acid)	(acetyl diphenylamine)	(CBr ₄)

Again, it will be noticed that in the above systems that produce the maximum deviations, solutes that are ionised or hydrated in solution have been considered.

In view of the inclusion of such systems in developing the correlations, it would appear that a far better approach would have been to have developed the correlations using systems that are as near to ideal as possible, and then introduce a term or terms that would account for any deviations due to molecular irregularity etc. However, since the correlations have been developed using irregular systems, then it seems inevitable that large inaccuracies will occur.

II THE EXPERIMENTAL DETERMINATION OF DIFFUSION COEFFICIENTS

The reviews of the past and present methods for the measurement of the diffusion coefficient are numerous. Amongst the most useful general reviews are those by Tyrell (7), Jost (11), Nienow (6), and Johnson and Babb (5). Jost lists a further 30 monographs and review articles (all pre-1951), so that a general background may easily be obtained.

The measurement of D may be grouped under three headings:-

- 1) Steady State methods
- 2) Restricted Diffusion
- 3) Free Diffusion

II (a) Steady State Methods

Diffusion is allowed to occur within a column of solution such that a steady (time-invariant) state is set up within the column. Material is supplied to the base and removed from the top, and the concentration at each point within the column remains constant and independent of time.

The diffusion coefficient found by this method is the integral coefficient.

Fick, in 1855, used observations from this method to put forward his laws of diffusion.

Clack (1908) used this method to study diffusion and later improved on accuracy by analysing the solution in the column by refractive index measurements.

Nowadays the most commonly used steady state method is the use of a sintered glass diaphragm cell. In this method, diffusion takes place through a horizontal glass diaphragm separating the two solutions of different composition. Magnetic stirrers are rotated on the upper and lower faces of the diaphragm, and the rate of stirring is such that the diffusion process within the diaphragm may be treated as a steady state phenomenon.

The classical diaphragm cell method is due to Northrop and Anson (*J.Gen.Physiol.* 12. 543. 1929), and improvements were made by Stokes (41). A good description of a cell and the technique used is given by Dullien and Shemilt (25).

The big disadvantage with the steady state methods is the time factor involved, which may be several days, during which time, of course, the whole system must be kept free of all vibrations and thermal disturbances.

Another disadvantage is that the diffusion coefficients obtained are relative coefficients. The cell has to be calibrated using a known system since there are several unknown factors in the cell, the principal one being the volume of the porous diaphragm.

However, accurate results have been obtained using

diaphragm cells, particularly the results of Harned and Nuttall (42) who used conductivity measurements to obtain the diffusion coefficient of potassium chloride at low concentrations. These figures are frequently used for the calibration of diaphragm cells.

II (b) Restricted Diffusion.

A sharp diffusion boundary is allowed to form within the vertical diffusion cell. Mutual diffusion takes place and the concentration on either side of the boundary changes with time. After sufficient time has elapsed the concentration at each end of the cell begins to change, and the process is thereafter called restricted diffusion.

The principle was first described by Graham in 1861, who introduced a concentrated solution beneath a column of more dilute solution. When the concentration had changed throughout the column, layers were drawn off and analysed. The method was improved by subsequent workers, the most important modification being the application of a shearing cell, by means of which a sharp interface could be formed.

Disadvantages of the method include the length of time for diffusion (days) and the disruption of the system for analysis. Also, the coefficients obtained by the layer analysis method are strictly neither integral nor differential coefficients. The only accurate results

using restricted diffusion appear to be those of Cohen and Bruins (Z.Phys.Chem. 103. 337. 1923) and Harned and French (Ann.N.Y.Acad.Soc. 44. 267. 1945). Harned and French introduced platinised electrodes into the upper and lower walls of a sheared boundary cell and obtained accurate results for the diffusion of various dilute electrolytes.

II (c) Free Diffusion

As with restricted diffusion, a sharp diffusion boundary is allowed to form within a vertical diffusion cell. Mutual diffusion takes place and the concentration on either side of the boundary changes with time. It is in the early stages of diffusion, during which time the concentrations at the extremities of the cell are at their initial values, that the process may be termed free diffusion.

Free diffusion measurements are nowadays the prime means of investigating diffusion, and the analysis of the diffusing system is exclusively optical. One or two workers have analysed the diffusing column by absorption spectra or by photometry, but nearly all methods now employ the variation in refractive index throughout the column. It will be remembered (equation 16) that the refractive index gradient is proportional to the concentration gradient. It is this basic assumption that is the essential feature of all optical methods.

Muller (43) gives a comprehensive review of optical techniques for the study of diffusional mass transfer, with an extensive list of references (about 100). The review is not quite complete, at least two major developments passing unnoticed, but the best known techniques are well covered. Tyrell (7) has also made a good review of optical techniques.

A brief review will be given here of the principal means of optically determining diffusion coefficients, before a detailed description of the interferometer constructed for this work is given. Thus the salient features of these optical techniques may be compared.

FIG.1 The TOEPLER Scanning System.

II (d) Optical techniques for the study of diffusional mass transfer.

The optical techniques for the study of diffusional mass transfer may be classified into two groups,

- a) Schlieren methods
- b) Interferometric methods

Schlieren Methods are based on the curvature of the light path due to the refractive index gradient in the diffusion column. Arrangements are included to transform the angular deflection into an intensity variation, so that a "shadow-graph" record of the refractive index gradient is obtained. The Toepler Scanning Method does this by putting a knife edge in the image plane of the light source, thus preventing all or part of the undeflected light from contributing to the image of the object. The arrangement is shown in Fig.1. A photographic plate at the image plane E is driven horizontally across, whilst the knife edge is moved vertically at a related speed. The recording of a typical concentration gradient obtained by this means is illustrated in Fig.2.

The Philpot-Svensson Diagonal Slit Method is a variation on the Toepler system. A diagonal slit is used instead of the knife-edge; the cell image is focussed in the vertical direction and the slit image is focussed horizontally by a plano-cylindrical lens.

FIG. 2

A Typical Schlieren
record of the c
concentration
gradient during
diffusion

FIG. 3.

Interference fringes as
recorded by a Mach Zender
during diffusion.

Interferometric Methods

Interferometric methods have now superseded schlieren methods, since the data obtained is far more readily interpreted and the methods are generally more sensitive.

The basis of interferometric methods is the introduction of a phase difference to the light passing through the cell due to different propagation rates. The phase may be detected by interference with another wave, which may be a reference beam or another part of the same beam.

Since a shift of one interference fringe corresponds to a change in refractive index, Δn , of λ/a (where a = cell length, λ = wavelength of light source), which is equal to 5.461×10^{-5} for a 1 cm. cell using the mercury green line, it follows that interference methods are very sensitive. It is this that makes interferometry so useful for diffusion measurements.

Numerous interferometers have been used for diffusion measurements, of which the following are listed:-
Jamin; Michelson; Lebedeff; Multiple Beam; Phase Contrast; Mach Zender; Gouy; Rayleigh; and the Wavefront Shearing Interferometer (which has been constructed in this laboratory and is the subject of this work).

For the purposes of comparison, and for an idea as to the principal interferometers used so far by research workers in the field of diffusion, three interferometers

FIG. 4

The MACH ZENDER Interferometer

listed above will be briefly described below. They are the Mach Zender, Gouy, and Rayleigh interferometers.

The Mach Zender Interferometer is illustrated in Fig.4.

By careful alignment of the mirrors M1 - M4 the light paths are made sufficiently different for interference fringes parallel to the axes of rotation of the four mirrors to be produced. A real image of the cell (placed between mirrors M1, M2) is formed at plane E.

The fringes produced in the Mach Zender are as in Fig.3. and give the relationship between refractive index of a plane in the diffusion column and its distance from the optic axis.

Amongst the big disadvantages of the Mach Zender is the difficulty in aligning the mirrors, and the high cost (about £15,000), since the Mach Zender is usually bought as a pre-made unit (construction being difficult for anyone other than an optical expert).

Descriptions of the Mach Zender and its application to diffusion measurements are given by Caldwell et al (45), and Harvey and Smith (46). A description of the instrument may also be had by reading the technical literature supplied by Carl Zeiss and Co.

The sensitivity of the Mach Zender is best illustrated by the results of several workers who have used it.

a) Caldwell et al (45) describe the use of a Mach Zender for determining mutual diffusion coefficients in binary liquid systems. For calibration a 0.6003 % (by weight) solution of sucrose in water was used. For this, $\Delta n \approx 7 \times 10^{-4}$.

b) Caldwell and Babb (23) studied the diffusion of ideal binary liquid systems. Examples of concentration differences used, with the weight % difference in brackets, are:-

0.022	mol fraction	C_6H_6	in	CCl_4	(1.4%)
0.033	"	"		C_6H_5Cl in C_6H_5Br	(2.4%)
0.0133	"	"		$C_6H_5CH_3$ in C_6H_5Cl	(1.1%)

The above concentration differences correspond to refractive index differences of the order of 1×10^{-3} .

Caldwell and Babb give as their criterion for obtaining workable fringes a figure of $\Delta n = 3 \times 10^{-2}$.

c) Bidlack and Anderson (47) studied diffusion in non-ideal binary systems. Their concentration differences, and hence Δn 's, were similar to those of Caldwell and Babb.

d) Mullin et al (24) using a Zeiss diffusion interferometer, which is similar to a Mach Zender,

stated that the maximum and minimum refractive index differences that could be accommodated were 4×10^{-3} and 6×10^{-4} respectively.

The Gouy Interferometer

Strictly speaking, the principle of the Gouy interferometer is a hybrid between schlieren effects and interferometry. The Gouy interferometer is illustrated in Fig.5, and consists basically and simply of light focussed through the diffusion cell by means of the Biconvex lens L 2.

When a concentration gradient is formed in the cell, the light is bent through progressively greater angles according to the change in refractive index. Since the refractive index gradient is symmetrical about the plane containing the optic axis, planes of the same refractive index gradient are disposed symmetrically above and below this axis. Light transmitted by the cell in these conjugate planes is brought to a focus at D, but the two beams differ in optical path length and their phase difference may be such that destructive or constructive interference occurs. Thus, a set of horizontal fringes is obtained, the total number being proportional to the refractive index difference between the top and bottom of the column. By following the movement of these fringes (having registered them photographically at various time intervals) the diffusion coefficient may be computed.

FIG. 5 The GOUY Interferometer

FIG. 6. Plan View of RAYLEIGH
Interferometer.

Although Gouy described this interferometer in 1880, it was not until much later (circa 1947) that its application was extended to diffusion measurements. Longworth (48) was the first to apply the interferometer to diffusional studies and describe them, and in an accompanying paper Kegeles and Gosting (49) developed the necessary theory. Many other workers have since used the Gouy interferometer, notably so Thomas and Furzer (1)(2) in this laboratory for a diffusional study of the ethanalamines.

The concentration differences used by Thomas and Furzer were of the same order as those quoted above for the Mach Zender, i.e. $\Delta n_{\min} \approx 6 \times 10^{-4}$.

The Rayleigh Interferometer is illustrated in Fig.6 (plan view). Parallel light from L2 is passed through a double slit B and the double cell C. L3 focusses the entrance slit A in the horizontal plane, whilst the plano-cylindrical lens forms a vertical image of A at E.

The interference fringes formed during diffusion by this arrangement are similar to those illustrated in Fig. 4 for the Mach Zender, and having the same meaning. It is not proposed to give an account here of the optics required for the formation of these fringes (as this would involve quite a bit of detail), but a good account of both the

theory and the experimental details for the use of the Rayleigh interferometer is given by Svennson (50)(51)(52).

Typical concentration differences used by Svennson are of the order of 0.5 weight %, with one figure of 0.2 weight % (for sucrose-water). This latter figure corresponds to a $\Delta n \approx 2 \times 10^{-4}$.

Of necessity, only brief descriptions of optical methods for diffusional studies have been given above. It is important to note the concentration differences that are manageable with these interferometers, for although the theoretical sensitivity is given by λ/a (refractive index change), none of these interferometers are operated anywhere near this sensitivity. This is due almost solely to the lack of optical resolution inherent in the systems. The theoretical treatment necessary to explain resolution limiting stops is definitely the work of an optical physicist, e.g. Svennson (53). No attempt will be made here at explanation; suffice to say that the resolution is limited in the above described interferometers.

It is this question of sensitivity that has prompted the construction of a wavefront shearing interferometer in this laboratory, since this system has been shown to differentiate between concentration differences of as low as 0.01 weight % ($\Delta n \approx 1 \times 10^{-5}$). This interferometer contains no resolution limiting stops.

This sensitivity is the prime reason for choosing to construct the wavefront shearing interferometer, for not only is the accuracy of the differential diffusion coefficient increased by a decrease in the concentration difference, but the application of interferometry to fields other than liquid-liquid diffusion is immediately suggested (i.e. gas-liquid diffusion).

A detailed description of the wavefront shearing interferometer is given in the next section.

III THE WAVE-FRONT SHEARING INTERFEROMETER

In 1930, Lebedeff (54) described an interferometer which would appear to be the fore-runner of the wave-front shearing interferometer. In the Lebedeff interferometer, polarised light passes through a birefringent crystal plate and is separated into an ordinary and an extraordinary ray. These rays then pass through a half wave-plate before being rejoined by a second birefringent crystal plate. The light finally passes through a second polariser.

Lebedeff used this interferometer in conjunction with a microscope to study the growth of crystals. Interference microscopes using this optical arrangement are still in use to-day.

Although the Lebedeff interferometer appears remarkably similar to the wave-front shearing interferometer, very little reference to it appears to have been made over the past thirty-five years.

The wave-front shearing interferometer was first described by Bryngdahl (4). The theory of the interferometer is presented by Bryngdahl (55), Bryngdahl and Ljunggren (56) and Ingelstam (57) together with accounts of its basic features. Thomas and Nicholl (58) have described the interferometer, the flowing junction cell used for the diffusional processes, and the means of obtaining diffusion coefficients in binary liquid systems.

FIG. 7. The SAVART Plate

Showing how the incident light ray is split up into an extraordinary/ordinary (E/O) and an ordinary/extraordinary(O/E) ray. E/O and O/E are perpendicularly polarised to each other.

III (a) Theory

The principle of the wave-front shearing interferometer is the use of polarised light in conjunction with a Savart plate (a birefringent crystal plate). The Savart plate consists of two uniaxial quartz crystals cemented together with their optic axes at 90° to each other, at 90° to the beam direction, and at 45° with respect to the plane of the paper. (see Fig.7).

Parallel light passes through the first polariser and is polarised such that the oscillation plane bisects the two principal planes of the Savart plate. Thus, the wavefront is divided into two equally strong coherent wavefronts polarised perpendicularly to each other. By means of the second polariser, set at 45° in relation to the principal planes of the crystal plates, the two wavefronts are caused to interfere.

The displacement between the wavefronts (E/O and O/E) b , is given by the relationship

$$b = e \sqrt{2} \cdot \frac{n_e^2 - n_o^2}{n_e^2 + n_o^2} \dots\dots\dots(66)$$

where e = thickness of each part of the optical plate

n_e, n_o = principal refractive indices

(path difference)

(interference
pattern)

FIG. 8.

Interference Fringe

Formation

The Savart plates used in this laboratory have $e = 10$ mm, and $b = 84.2 \mu$. If in the diffusion process to be examined a plane wavefront is passed through a diffusion cell (of rectangular cross section with plane parallel glass windows), the wavefront is distorted in accordance with the concentration of the solution. By passing this distorted wavefront through the Savart plate, as described above, the wave-front is split into two parts ($\frac{E}{O}$ and $\frac{O}{E}$) separated from each other by a small distance $\Delta x (= b)$.

In Fig.8, the two laterally displaced wave-fronts are shown. If the axes of the polarisers are perpendicular to each other, then interference occurs when the path difference, $\Delta z = \frac{M\lambda}{2}$ ($M = \text{whole number}$)

$\lambda = \text{wavelength of light used,}$
cell length)

When the derivative curve is so low that $\Delta z < \lambda/2$, then no fringes are obtained.

The interference pattern produced, a series of horizontal fringe pairs, is related to the Gaussian curve representing the ideal concentration gradient.

The movement of these fringe pairs is utilised to calculate the diffusion coefficient. The relationship between the distance apart of the fringe pairs and time is obtained from the following considerations:-

Before shearing, any one point on the wave-front a

distance x from the interface and corresponding to an optical path length $f(x)$, has a gradient $\Delta z / \Delta x$.

After shearing, two points corresponding to the original one are formed a vertical distance Δx apart, where

$$\Delta x = (x + b/2) - (x - b/2) \dots\dots\dots(67)$$

Their corresponding optical path lengths are now

$$f(x + b/2) \text{ and } f(x - b/2)$$

The path difference introduced is given by

$$z = f(x + b/2) - f(x - b/2) \dots\dots\dots(68)$$

The gradient is given by

$$\left(\frac{\Delta z}{\Delta x} \right)_{\Delta x = b} = \frac{f(x + b/2) - f(x - b/2)}{b} \dots\dots\dots(69)$$

Referring back to equation (16), which is derived from a solution of Fick's Second Law applicable to the free diffusion case being studied, we have

$$\frac{\partial n}{\partial x} = \frac{\Delta n}{2\sqrt{\pi Dt}} \cdot \exp\left(-\frac{x^2}{4Dt}\right)$$

Since z is a function of n ,

$$\left(\frac{\Delta z}{\Delta x} \right)_{\Delta x = b} = \left(\frac{\Delta n}{\Delta x} \right)_{\Delta x = b} = a \dots\dots\dots(70)$$

Expanding equation (69), $\left(\frac{\Delta z}{\Delta x} \right)_{\Delta x = b}$, by a Taylor

series (see appendix),

$$\left(\frac{\Delta n}{\Delta x} \right)_{\Delta x=b} = \frac{\partial n}{\partial x} \left\{ 1 + \frac{1}{2^2 \cdot 3!} \cdot \frac{b^2}{2Dt} \cdot \frac{x^2 - 2Dt}{2Dt} + \frac{1}{2^4 \cdot 5!} \cdot \frac{b^4}{4D^2 t^2} \cdot \frac{x^2 - 12x^2 Dt + 12D^2 t^2}{4D^2 t^2} \right\} \dots\dots\dots(71)$$

Substituting (16) and (71) into (70), taking the first term in brackets only of (71),

$$a = \frac{\Delta n}{2\sqrt{\pi Dt}} \left(1 + \frac{b^2}{48Dt} \cdot \frac{x^2 - 2Dt}{2Dt} \right) \exp \left(-x^2/4Dt \right) \dots\dots\dots(72)$$

$$\text{or } \exp \left(\frac{x^2}{4Dt} \right) = \frac{\Delta n}{2_a \sqrt{\pi Dt}} \left(1 + \frac{b^2}{48Dt} \cdot \frac{x^2 - 2Dt}{2Dt} \right) \dots\dots\dots(73)$$

If due regard is paid to the value of t in equation (19), a "zero-time correction factor" Δt must be introduced, so that

$$t' = t + \Delta t \dots\dots\dots(74)$$

(true time) (measured time)

substituting in 16, and rearranging as above,

$$\exp. \left(\frac{x^2}{4D(t + \Delta t)} \right) = \frac{\Delta n}{2a\sqrt{\pi D(t + \Delta t)}} \cdot \left(1 + \frac{b^2}{48Dt} \cdot \frac{x^2 - 2Dt}{2Dt} \right) \dots\dots\dots(75)$$

Taking logs on both sides and rearranging

$$\frac{(2x)^2}{t + \Delta t} = C - 8D \ln. \left(\frac{t + \Delta t}{t_0} \right) + \frac{b^2}{3t} \cdot \frac{x^2 - 2Dt}{2Dt} \dots\dots\dots(76)$$

$$\text{where } C = 8D \left(1 + \ln. \frac{t_1}{t_0} \right) \dots\dots\dots(76a)$$

t_1 is the time of inflexion of the Gaussian curve; t_0 is an assumed time unit. In the above rearrangement, the assumption $\ln(1 + x) \approx x$ has been taken.

$$\left(\frac{b^2}{3t} \cdot \frac{x^2 - 2Dt}{2Dt} \right) \text{ is very small}$$

For small Δt values, (76) may be rearranged to

$$\frac{(2x)^2}{t} \left(1 - \frac{\Delta t}{t} \right) = C - 8D \ln \frac{t}{t_0} - 8D \frac{\Delta t}{t} + \frac{b^2}{3t} \cdot \frac{x^2 - 2Dt}{2Dt} \dots\dots\dots(77)$$

Simplifying,

$$\frac{(2x)^2}{t} = C - 8D \ln. \frac{t}{t_0} + \frac{1}{t} \left(\frac{(2x)^2}{t} - 8D \right) \left(\frac{b^2}{24D} + \Delta t \right) \dots\dots\dots(78)$$

Putting $\left. \begin{aligned} \eta &= (2x)^2/t \\ \phi &= \ln t/t_0 \end{aligned} \right\} \text{ we get}$

$$\eta = C - 8D\phi + \frac{\eta - 8D}{t} \left(\frac{b^2}{24D} + \Delta t_e \right) \dots\dots\dots(79)$$

Thus, the deviation caused by $\Delta n/\Delta x$ in the first approximation, appears as a constant contribution to the zero time correction.

$$\Delta t_e = \Delta t_w + b^2/24D \dots\dots\dots(80)$$

(e = apparent, w = real)

When the correct zero time correction is applied to (79) the equation representing the movement of the fringe pairs reduces to

$$\eta = C - 8D\phi \dots\dots\dots(81)$$

$$\text{or } (2x)^2 = 8Dt. \left(1 + \ln \frac{t_i}{t} \right) \dots\dots\dots(82)$$

If therefore, the distance apart of any one fringe pair, (2x), is followed with respect to time, t, the diffusion coefficient may be obtained. There are several methods of calculation, all of them determining both the zero time correction factor, Δt , and the diffusion coefficient.

The zero-time correction factor is very important, since it has quite a significant effect on the diffusion coefficient. In practice, it is impossible to obtain an

initially sharp interface, since there is always some initial mass transfer between solutions. This has the effect of displacing a plot of $(2x)$ against t towards the left.

It is this displacement, Δt , that has to be determined before the true D may be calculated.

The methods of calculation are discussed below.

III (b) Calculation of D , and Δt

The first four methods to be described are due to Bryngdahl. The fifth method is entirely new, and has been developed in this laboratory.

(i) From equation (82) the relationship

$$\left(\frac{2x}{t}\right)^2 = C' - 8D \ln \frac{t_1}{t} \quad \text{may be derived.}$$

If $\left(\frac{2x}{t}\right)^2$ is plotted against $\ln t$ for any one fringe pair, repeatedly adding a small time increment to the t -values before plotting the curve, then, theoretically, at the stage when the correct Δt has been applied the curve should be a straight line of slope $-8D$. In practice it has been found that the method is very insensitive, and is not sufficiently accurate to be of any use.

(ii) In runs where more than one fringe pair is observed and recorded, these are plotted on a graph of $(2x)^2$ against t . A straight line is drawn connecting the maxima of the curves. This line is of slope $8D$, and from the point where it cuts the t -axis, Δt may be determined. This method, again, is limited in accuracy, and only gives approximate results.

(iii) In a method of calculation due to Lamm, from a plot of $(2x)^2$ against t for any one fringe pair D may be calculated from the expression

$$D = \frac{(2x)^2 \left(\frac{1}{t_1} - \frac{1}{t_2} \right)}{8 \ln \frac{t_2}{t_1}} \quad \dots\dots\dots(83)$$

Here, t_1 and t_2 are two time-values corresponding to any one value of $(2x)^2$. However, Bryngdahl has shown that the true D is related to the calculated D , D' , by the expression

$$D = \frac{D'}{1 + \Delta t \cdot \mathcal{V}} \quad \dots\dots\dots(84)$$

where $\mathcal{V} = \frac{t_1 + t_2}{t_1 t_2} - \frac{1/t_1 - 1/t_2}{\ln t_2/t_1} \quad \dots\dots\dots(85)$

If, then, D is calculated for any one value of $(2x)^2$ and the corresponding t_1 and t_2 values using equation (83), and plotted against $\mathcal{V}$, a straight line is obtained of slope $D \cdot \Delta t$, cutting the ordinate axis at D . Using this method D may be calculated to 3 significant figures (i.e. $5.21 \times 10^{-6} \text{ cm}^2/\text{sec.}$). It is not, therefore, all that accurate, and it was found more convenient in practice to only use this method as a check before using the fourth method.

(iv) The fourth method of calculation is the most accurate of the methods mentioned so far. D is calculated by equation (83), and is plotted against $(2x)^2$, with Δt as a parameter. This is done by first calculating D with no correction applied to the time, for a set of values of $(2x)^2$, t_1 , t_2 . Then a small time-increment is added to the t -values and the calculations are repeated. This is

continued until the value of D becomes constant when plotted against $(2x)^2$. At this point, the correct value of D is obtained, together with the zero-time correction, i.e.

By this method, D may be calculated to four significant figures.

A fault common to all the four methods outlined above, is that the accuracy of the calculation is dependant upon readings taken from a smooth curve drawn through the experimental points on a $(2x)^2$ vs. t plot. The method developed in this laboratory, overcomes this difficulty. It thus becomes less sensitive to error than any of the above methods, especially when a slight scatter of points

on the experimental curve of $(2x)^2$ vs. t cannot be avoided. In practice, it has also become apparent that this new method is much more convenient to use, and is highly accurate (so that the accuracy of the determination of D is limited by the apparatus rather than the calculation).

III (C) New Method for Calculating D

The method of calculation uses equation (82) in which the movement of one fringe-pair with respect to time is represented. The feature of the calculation, however, is the use of the method of least squares. The sequence of steps in the method will now be described.

Least Squares Curve Fitting

Consider the linear equations

$$\begin{aligned} y_1 &= (ax_1)_1 + (bx_2)_1 + \dots + (\Sigma x_k)_1 \\ y_n &= (ax_1)_n + (bx_2)_n + \dots + (\Sigma x_k)_n \end{aligned} \quad \dots (86)$$

in which there are 'n' sets of observations of y and x .

(y values are dependant variables, x values are independant variables, $a, b, \dots, \Sigma$ values are constants.

If the true values of $a, b, \dots, \Sigma$ are $A, B, \dots, \Sigma$, the true values of $y_1, y_2, \dots$ are $Y_1, Y_2, \dots$, and the differences between the true and observed values of y are $\phi_1, \phi_2, \dots$ then

$$\begin{aligned}\phi_1 &= Y_1 - y_1 \\ &= (Ax_1)_1 + (Bx_2)_1 + \dots + (Bx_k)_1 - y_1\end{aligned}$$

$$\begin{aligned}\phi_2 &= Y_2 - y_2 \\ &= (Ax_1)_2 + (Bx_2)_2 + \dots + (Bx_k)_2 - y_2\end{aligned}$$

Then, ϕ_1, ϕ_2 are errors whose chances are given by a normal distribution curve. The assignment of values to a, b, to minimise the inconsistency which is assumed to be due to imperfect measurement of the 'x' values is obtained by finding those values of A, B, which make $\phi_1^2 + \phi_2^2 + \dots$ a minimum. The conditions for this are that

$$\frac{f(\phi_1, \phi_2, \dots)}{A} = \frac{f(\phi_1, \phi_2, \dots)}{B} = 0 \quad \dots (88)$$

It may be shown that the normal equations satisfying this condition (for $k = 2$), are given by

$$\left. \begin{aligned}A \sum x_1^2 + B \sum x_1 x_2 &= \sum x_1 y \\ A \sum x_1 x_2 + B \sum x_2^2 &= \sum x_2 y\end{aligned} \right\} \dots (89)$$

whose simultaneous solution enables A, B, to be found.

The simultaneous solution of two such equations is most easily done by use of a matrix of the form

$$\begin{bmatrix} \sum x_2 y \\ \sum x_1 y \end{bmatrix} = \begin{bmatrix} A \\ B \end{bmatrix} \begin{bmatrix} \sum x_2^2 & \sum x_1 x_2 \\ \sum x_1 x_2 & \sum x_1^2 \end{bmatrix} \dots (90)$$

$$\text{or } \begin{bmatrix} Y \end{bmatrix} = \begin{bmatrix} C \end{bmatrix} \begin{bmatrix} V \end{bmatrix}$$

$$\text{so that } \begin{bmatrix} C \end{bmatrix} = \begin{bmatrix} Y \end{bmatrix} \begin{bmatrix} V \end{bmatrix}^{-1} \quad \dots\dots(91)$$

When a set of observations of $(2x)^2$ against t are made to satisfy equation (82), the x , y values and constants in (90) will correspond as below (including Δt in time measurements).

$$\begin{aligned} y &: (2x)^2 \\ x_1 &: 8(t + \Delta t) - 8(t + \Delta t) \ln(t + \Delta t) \\ x_2 &: 8(t + \Delta t). \\ A &: D \\ B &: D \ln t_1 \end{aligned}$$

Using appropriate matrix subroutines (to satisfy equation (91)), a computer may be programmed to calculate the best D and t_1 to fit a set of experimental values of $(2x)^2$ and t . In this laboratory, a Ferranti Sirius computer was used and details of the calculation are given below.

Application of the Method of Least Squares to Calculate D

When no Δt is applied to the experimental points, it will be remembered that a true Gaussian curve drawn through these points cuts the t -axis to the left of the origin. This displacement in t is equivalent to the zero-time correction, Δt .

However, when solving the normal equations for a set of $(2x)^2$, t -values, the point $(0,0)$ is automatically included. The least squares fit does not take into account any displacement of the experimental points. Thus, the curve of

$$(2x)^2 = 8Dt(1 + \ln \frac{t_1}{t}) \quad (\text{equation 82})$$

as calculated from the best fitting D and t_1 for the experimental points (using the method of least squares), - and hereafter referred to as the Regression Curve of $(2x)^2$ on t , will be as with curve A, below:-

With no Δt applied to the experimental points, the regression curve (A) of $(2x)^2$ on t has a greater "peakiness" to it, as above.

If now a Δt is applied, thus effectively shifting the experimental points to the right, the regression curve will not be as "peaked" as originally,

As repeated Δt increments are added to the experimental time values, the agreement in shape and position of the regression curve and the experimental points becomes closer. Eventually, when the correct Δt has been applied to the experimental points, the two curves are coincidental.

If too great a Δt is applied to the experimental points, it will be seen that the regression curve becomes less peaked than the experimental curve.

Thus, a criterion must be established whereby the agreement between the regression curve and the experimental points is judged to be best. At this point, the correct Δt has been applied to the experimental points, and hence the D-value may be obtained.

A simple criterion is to compare the maxima of the two curves. The maximum of the experimental curve, $(2x)_{iB}^2$, is found from the experimental points. The maximum of the regression curve, $(2x)_{iA}^2$ is given by the equation

$$(2x)_i^2 = 8Dt_i \dots\dots\dots(92)$$

Equation (92) is derived from (82) by putting $t = t_i$.

When $t_{\text{applied}} < t_{\text{true}}$, $(2x)_{iA}^2 > (2x)_{iB}^2$

$t_{\text{applied}} > t_{\text{true}}$, $(2x)_{iA}^2 < (2x)_{iB}^2$

$t_{\text{applied}} = t_{\text{true}}$, $(2x)_{iA}^2 = (2x)_{iB}^2$

Thus, a print-out of $(2x)_{iA}^2$ on the computer output will enable a comparison of the two $(2x)_i^2$ values, so that when they are equal it may be judged that the correct Δt has been applied.

A more accurate criterion is to calculate the scatter of the experimental points from the least squares regression curve of $(2x)^2$ on t . This scatter is termed the Standard Error of Estimate of $(2x)^2$ on t , and is defined by

$$S = \sqrt{\frac{\sum [(2x)_B^2 - (2x)_A^2]^2}{N}} \dots\dots\dots(93)$$

Thus, for each Δt value applied to the experimental points, the standard error of estimate, S , between the experimental points and the regression curve of $(2x)^2$ on t is calculated. As the Δt is increased, S decreases until a minimum value is reached. At this minimum, the two curves are in agreement, and thus it may be judged that the correct Δt has been applied.

The correct D is thus found, since the D calculated by the method of least squares for the experimental points, is the true D when the correct Δt has been applied.

L : Lenses	SP : Savart Plate
MV : Mercury Lamp	M : Image Plane
F : Filters	
S : Slit	
C : Cell	
P : Polarisers	

FIG.9. THE WAVEFRONT SHEARING INTERFEROMETER

This method of calculation is illustrated in the section dealing with the experimental results.

This method of calculation gives an exact value of D , and is accurate to four significant figures (e.g. $5.221 \times 10^{-6} \text{ cm}^2/\text{sec}$). The method has been repeatedly used in this laboratory, and is very convenient in use. It is essential of course, if this method of calculation is to be wholly successful, that the experimental points are fairly complete and that they are "weighted" equally to either side of the maximum. However, this condition applies equally well to any other method of calculation. The true advantage of the method is that a slight scatter of experimental points is permissible, without deterring from the accuracy of the calculation.

III (d) Apparatus

The arrangement of the wavefront shearing interferometer is shown in Fig.9. The complete optical system is contained in a constant-temperature (thermostatically controlled) darkroom. The temperature of the room can be maintained to $\pm 0.1^\circ\text{C}$ (most experiments being conducted at 25°C).

The optical components are mounted on a 3-metre long optical bench, of triangular section, resting on two 10-ft long steel girders bolted to three concrete pillars. The

whole assembly, weighing over 1000 lbs, is separated from the floor by rubber blocks. The various components in the optical system are attached to the bench by adjustable saddle stands, fitted with clamping screws.

A 250-W high pressure mercury vapour lamp (MV), operated in a vertical position provides a source of monochromatic light (at $5461 \overset{\circ}{\text{Å}}$). The narrow discharge from the lamp is focussed through a short focal length condensing lens, L1, through infrared and green filters on to a horizontal adjustable slit operated from 5μ to 10μ .

To reduce the effect of stray light, the lamp, condenser, filters and slit are housed in a light-proof structure (which is adequately ventilated).

By means of the plano-convex lens L2, parallel light is passed through the diffusion cell, C. By L3 and L4, the image from the cell is collimated through the Savart Plate (SP). Polarisers, P1 and P2, are placed before and after the Savart plate. The image formed after the Savart plate is rather small, and it is convenient to magnify the final image by means of the lens L5.

Details of the lenses used are given below:-

L1 : Biconvex condenser lens, 100 mm dia.
 $f = 100 \text{ mm.}$

L2,L3 : Plano-convex lenses, 102 mm dia. Corrected for spherical and chromatic aberrations.

L4,L5 : Biconvex lens, 20 mm dia. $f = 75$ mm

The diffusion occurring in the cell, with the resultant interference fringes, is recorded photographically in image plane M. The camera used is a 35 mm Robot-Recorder camera mounted on the bench with a Robot Kuli Universal camera holder. The camera is fitted with a 30-ft film magazine, and an electric booster motor (for continuous wind-free transportation of the film). The camera is coupled to a Steuergerat IIA electromechanical time-control set. By means of this set, the camera exposure and the interval between exposures may be set anywhere in the range 0.15 secs to 3 hrs. The film used is Kodak R.55 recording film, developed in DX-80 developer ($2\frac{1}{2}$ minutes development at 24°C , 1 + 3 dilution).

R.55 recording film was chosen after trials with other high speed film (i.e. Ilford HP3, Kodak Tri-X), since it has both a high speed and a maximum sensitivity to light between $5400 \text{ \AA}$ and $5700 \text{ \AA}$ (59). The use of R.55 film is further enhanced by its insensitivity to red light, thus making its handling very simple (the film may be loaded and developed in light from a Kodak Wratten 1A filter, with a 15-W bulb).

The Diffusion cell was constructed by Furzer (1) in this laboratory, and is of the flowing-junction type. The cell is shown in Fig.10 (photograph) and the principle of its construction and operation is diagrammatically shown in

Fig.10. The Flowing-Junction Cell.

FIG. II. Principle of the
Flowing-Junction Cell.

Fig.11. For clarity, the cell has been shown with one chamber only, though in actual fact it has two chambers. The second chamber was originally intended as a reference chamber (for Rayleigh fringes), but now serves as a reserve.

The cell is constructed throughout in stainless steel. Sections are bolted together to form the two chambers, and the ends are ground plane and parallel. The optical path length through the cell is 63 mm. Optical glass flats ($\frac{3}{8}$ " thick) are pressed into contact with the cell ends by ten spring-held pressure screws. A polythene gasket smeared with silicone grease separates the glass flats from the steel faces and copper and rubber gaskets distribute the screw pressure on the glass flats.

In the centre of the cell, running horizontally, is the flowing-junction slit (set at 150 μ). In operation, the two solutions of differing density meet and flow out of this slit, the exit being a capillary tube.

The solutions are contained in two reservoirs, which are connected to the cell by a manifold with suitable taps. A mercury reservoir, of variable height, provides the head necessary for the solution and solvent to flow into the cell.

III (e) Experimental Technique

The cell is cleaned and flushed with distilled water and air, before being finally flushed with solvent. The liquid reservoirs are cleaned, flushed, and filled with solvent and solution. The solution strength found to be most convenient to work with in the interferometer was about 0.06 weight % difference. (Hence, as an example, for determining the diffusivity in a very dilute solution, one reservoir will contain pure solvent and the other will contain a solution of 0.6 g/litre. For the diffusivity in, say, a 100 g/litre solution, one reservoir is filled with 100 g/litre solution and the other with 100.6 g/litre solution.)

When the cell and reservoirs have been filled up, the thermostat for the room is set at 25°C. The cell is then left set up on the optical bench for about 12 - 14 hours (i.e. overnight). This will ensure thermal equilibrium between the two solutions. The establishment of thermal equilibrium is most important, for it must be appreciated that small differences in temperature or slight mechanical vibrations transmitted to the cell can cause much more rapid mixing of the diffusing substances than the pure diffusion process itself. A temperature difference of 0.1°C between solutions is quite sufficient to completely alter the shape of the concentration - distribution curve

as recorded by this interferometer.

Once thermal equilibrium has been established, the solution (or denser solution) is admitted to the bottom of the cell. The solvent (or less dense solution) is admitted to the top of the cell. The mercury reservoir is used for the necessary head to provide the flow of solutions, and a fine control tap on the mercury inlet adjusts the rate of flow. When the solutions are admitted to the cell, the sidestream (from the flowing-junction slit) is started. By careful control of the liquid flowrates the two solutions are caused to meet and flow out at the slit, forming a sharp interface.

A very careful control of the flowrate is necessary to obtain a sharp interface. Practical experience in operating the cell determines this rate, for it varies with the viscosity of the solutions being used. As a rough guide, a flowrate out of the exit slit of about 20-40 drops a minute is needed.

Once the interface is formed, it is left for about 20 minutes to sharpen and establish itself. In the meantime the mercury vapour lamp has been switched on (about 20 minutes is needed before maximum intensity is reached) and the camera magazine is loaded.

Visual inspection of the interface is made by examining the image on a ground-glass screen (with magnifying lens

1 mm.

$t = 170$ secs.

$t = 310$ secs.

FIG. 12. Actual Photograms of Interference

Fringes (0.0578% MEA).

Time (seconds) from start of diffusion.

Fig.13. Interference Fringes, (0.0578% MEA-water)

attached).

Before starting the recording of the diffusion process, the camera is placed in position (the cell image is projected directly on to the film). The time control unit is set for 5 second exposures at 30 second intervals. As soon as the first exposure is taken (of the interface) the relevant taps on the cell are shut, thus stopping the side-stream discharge and starting the diffusion process in the cell.

Photographic recording of the diffusion process is continued until inspection of the image reveals that the next-to-outermost fringe pair has merged. With a 0.06% concentration difference, this will occur after about 60 exposures (depending on the diffusion coefficient).

The movement of the fringe-pairs as recorded photographically is measured primarily by a Joyce-Loebl double beam recording microdensitometer. This instrument translates the intensity variations on the film (due to the fringes) into graphical representations (photograms).

A typical series of fringe pairs is shown in Fig.13, and associated photograms are shown in Fig.12.

The distance between fringe peaks is readily determined from the photograms, and hence ($2x$) for any one fringe pair is measured. (The accuracy of the measurement is about ± 0.002 mm overall).

Where the microdensitometer is limited in resolution (as, for example, when a number of fringe-pairs are very closely spaced together), a cathetometer is used to measure $(2x)$, (to an accuracy of ± 0.005 mm).

From these measurements, therefore, a recording of the experimental values of $(2x)^2$ against t may be made, and the diffusion coefficient evaluated by using one of the calculation methods described.

IV. EXPERIMENTAL RESULTS.

IV(a). Example of the Calculation of Diffusivity.

An example of the calculation of diffusivity from the fringe movement recorded by the wavefront shearing interferometer for diethanolamine-water is illustrated below.

Run No. DEA 8.

Temperature	: 25.3°C
Concentration of DEA solutions	: 462.5 g/litre
Concentration difference between solutions	: 0.8 g/litre
Fringe pair observed	: FP.4
Magnification factor of interferometer	: 1.2482

(Thus, $2x(m)$, - the fringe spacing measured on the film, must be divided by 1.2482 to obtain the true $2x$).

The fringe-pair movement is tabulated in table 1.

With $\Delta t = 0$, the best D and t_i to fit these experimental points are calculated. From this D and t_i , $(2x)_{iB}^2$ is calculated, and the regression curve of $(2x)^2$ on t is drawn in comparison with the experimental points (Fig.15). The standard error of estimate between the two

curves, s , is calculated by equation 93.

Δt is then increased by repeated 10 second increments, and the best-fitting D and t_1 are recorded, together with the calculated $(2x)_{iB}^2$ and s . For the diffusion of 462.5 g/litre DEA - water, these figures are given in table 2. The calculation is illustrated graphically in Fig.14.

From the plot of s against Δt , the curve passes through a minimum at $\Delta t = 89$ secs (the possible error in estimating Δt here is about ± 2 secs. Δt can, of course, be determined extremely accurately if necessary, by altering the Δt increments in the computer programme).

A curve drawn through the experimental points gives a $(2x)_{iA}^2$ value of 2.074 mm. The values of $(2x)_{iB}^2$ at each

Δt are compared with this value, and at $\Delta t = 89$ secs $(2x)_{iA}^2 = (2x)_{iB}^2$.

Thus Δt is calculated to be 89 secs. From this value of Δt , D is found to be 3.184×10^{-6} cm²/sec.

The regression curve of $(2x)^2$ on t , for $D = 3.181 \times 10^{-6}$ and $\Delta t = 90$ secs is compared with the experimental points in Fig.16. It can be seen that there is good agreement between the experimental points and this regression curve.

Table 1.

Fringe-Pair (FP.4) movement recorded during Diffusion
of 462.5 g/litre DEA-water.

t secs	2x(m) mm.	(2x) ² mm. ²	t secs	2x(m) mm.	(2x) ² mm. ²
170	1.398	1.2544	905	1.773	2.0177
240	1.580	1.6023	940	1.758	1.9837
275	1.633	1.7116	975	1.740	1.9433
310	1.665	1.7793	1010	1.740	1.9433
345	1.690	1.8332	1045	1.720	1.8988
380	1.720	1.8988	1080	1.715	1.8878
415	1.733	1.9277	1115	1.690	1.8332
450	1.765	1.9995	1150	1.670	1.7900
485	1.755	1.9769	1185	1.650	1.7474
520	1.780	2.0336	1220	1.645	1.7369
555	1.790	2.0565	1255	1.620	1.6845
590	1.795	2.0680	1290	1.605	1.6534
625	1.795	2.0680	1325	1.585	1.6125
660	1.793	2.0634	1360	1.560	1.5620
695	1.795	2.0680	1395	1.545	1.5321
730	1.798	2.0750	1430	1.520	1.4829
800	1.790	2.0565	1465	1.483	1.4116
835	1.788	2.0519	1500	1.455	1.3588
870	1.780	2.0336	1535	1.430	1.3125

Table 2.

Calculation to determine D and t_i (462.5 g/litre DEA-water).

Δt	Calculated by method of least Squares to best fit Exptl. points			Standard Error of Estimate $s(x10^2)$
	D $cm^2/sec \times 10^6$	t_i	$(2x)_{iB}^2$	
0	3.5443	747.77	2.1203	6.955
10	3.4994	755.27	2.1143	6.293
20	3.4559	762.73	2.1087	5.696
30	3.4134	770.21	2.1032	5.169
40	3.3722	777.66	2.0979	4.715
50	3.3316	785.16	2.0927	4.341
60	3.2926	792.59	2.0877	4.053
70	3.2542	800.06	2.0829	3.854
80	3.2167	807.54	2.0781	3.746
90	3.1806	814.96	2.0737	3.724
100	3.1451	822.42	2.0693	3.779
110	3.1108	829.80	2.0651	3.899
120	3.0770	837.24	2.0609	4.070
130	3.0443	844.62	2.0570	4.281

FIG. 14

Graphs of S & $(2x)_{iB}^2$
against Δt , (DEA 8)

The accuracy of the calculation is determined by considering the estimation of Δt (± 2 secs). The variation in D (calculated by least squares curve-fitting) per sec. (Δt) = $0.0036 \times 10^{-6} \text{ cm}^2/\text{sec}$.

$$\therefore \text{Accuracy of determination of } D = \pm 0.007 \times 10^{-6} \text{ cm}^2/\text{sec} \\ = \underline{\underline{0.2 \%}}$$

IV(b). Diffusional Measurements for the Systems

Sucrose-Water , and Ethanolamines- Water.

Diffusion coefficients were measured for four dilute sucrose-water solutions as a preliminary calibration of the interferometer. The following values for the diffusion coefficient of very dilute sucrose-water solutions were obtained (at 25°C);-

$$\begin{aligned} \text{Run S1 , } D &= 5.221 (\pm 0.011) \times 10^{-6} \text{ cm}^2/\text{sec} \\ \text{S2 , } D &= 5.205 (\pm 0.015) \quad " \quad " \\ \text{S3 , } D &= 5.216 (\pm 0.012) \quad " \quad " \end{aligned}$$

In run S3, a low value of D ($= 5.13 \times 10^{-6}$) was obtained, with only limited accuracy. This was almost certainly due

to an electrical failure , which interfered with the thermostatic control of the experiment. However, the values obtained in runs S1, 2, and 4 agree very well with the accepted values for sucrose-water as obtained by previous workers (28)(60)(61).

Diffusion coefficients for the systems mono-ethanol-amine/water, diethanolamine/water, and triethanolamine/water were measured over a range of concentrations.

A summary of these measurements is given in table 3. Detailed fringe measurements are given in section (c).

The diffusivity-concentration curves for the amines, as measured, are shown in Fig.17.

FIG. 17

Diffusivity / Normality
for
MEA, DEA, TEA.

Table 3

Diffusion Coefficients for Sucrose, MEA, DEA, TEA - Water

Run. No.	Concn of Solute (g/litre)	Normality	D $\text{cm}^2/\text{sec} \times 10^6$	Accuracy +/-	Δt secs	G. Mag. factor	t $^{\circ}\text{C}$
s1	0.472	0	5.221	0.011	87	0.563	25.5
2	0.472	0	5.205	0.015	22	0.563	25.2
3	0.637	0	5.13	Limited	87	0.563	25
4	0.993	0	5.215	0.012	64	0.563	25.3
MEA 1	0.578	0	10.400	0.1	58	0.563	25.3
2	85.5	1.400	9.116	0.02	36	1.925	25.3
3	122.2	2.001	8.575	0.01	22	0.563	25.3
4	244.3	4.003	6.729	0.009	18	0.563	25.3
5	151.85	2.486	8.101	0.02	119	1.925	25.3
6	305.6	5.003	5.770	0.01	153	1.925	25.3
DEA 1	0.60	0	6.624	0.009	7	0.563	25.3
2	54.5	0.518	5.377	0.015	100	0.563	25.3
3	109	1.036	4.877	0.015	60	0.563	25.3
4	154.5	1.470	4.635	0.010	52	1.30244	25.3
5	256	2.435	4.181	0.01	160	1.30244	25.3
6	347.15	3.302	3.736	0.009	40	1.2482	25.3
7	347.15	3.302	3.731	0.008	46	1.2482	25.3
8	462.5	4.399	3.185	0.007	89	1.2482	25.3
9	480.9	4.574	3.089	0.006	142	1.2482	25.3
TEA 1	0.54	0	6.422	0.01	62	1.30244	25.3
2	0.54	0	6.446	0.01	63	1.30244	25.3
3	200.36	1.344	4.452	0.008	72	1.30244	25.3
4	200.36	1.344	4.564	0.008	44	1.30244	25.3
5	308.95	2.071	3.385	0.006	295	1.30244	25.3

IV(c). Tabulated Results.

Run No.s ; S1 to S4
 MEAL to MEA6
 DEAL to DEA9
 TEAL to TEA5

The results are tabulated in the following form:-

- 1) Concentration of diffusing solution.
- 2) Temperature.
- 3) Fringe-pair observed (outermost = 1).
- 4) Tabulated measurements of fringe-pair movement.
 - a) time of exposure (film frame).
 - b) Measured value of $2x$ (on the film).
 - c) Actual value of $(2x)^2$.
- 5) Magnification factor, G .
- 6) Diffusion Coefficient calculated, D .
- 7) Accuracy of measurement of D .
- 8) Zero-time correction factor, Δt .

RUN NO. S/1

0.0472 WT. PCT. SUCROSE WATER

T = 25.5 DEG. C

F.P. 2

T (SECS)	2X(M) (MM)	2X SQD (MM) ²
99	0.721	1.6384
132	0.740	1.7292
165	0.771	1.8769
198	0.781	1.9238
231	0.799	2.0164
264	0.821	2.1258
297	0.821	2.1258
330	0.835	2.1993
363	0.839	2.2231
396	0.850	2.2801
429	0.850	2.2801
462	0.856	2.3104
495	0.856	2.3104
528	0.850	2.2801
561	0.839	2.2231
594	0.833	2.1904
627	0.816	2.1025
660	0.806	2.0506
693	0.790	1.9684
726	0.785	1.9460
759	0.766	1.8496
792	0.744	1.7450
825	0.732	1.6900
858	0.714	1.6078
891	0.676	1.4400
924	0.651	1.3363
957	0.587	1.0878

CALCULATED.....

G = 0.56300
D (CM²/SEC X 10⁻⁶) = 5.2217
ACCURACY, +/- = 0.011
DELTA T (SECS) = 87

RUN NO. S/2

0.0472 WT.PCT. SUCROSE WATER

T = 25.2 DEG.C

F.P.2

T (SECS)	ΔX (M) (MM)	ΔX SQD (MM) ²
65	0.660	1.63759
100	0.684	1.4762
135	0.712	1.6002
170	0.739	1.7240
205	0.761	1.8252
240	0.780	1.9182
275	0.800	2.0192
310	0.812	2.0794
345	0.836	2.2052
380	0.838	2.2172
450	0.852	2.2892
485	0.859	2.3356
555	0.861	2.3409
590	0.856	2.3234
625	0.856	2.3234
660	0.850	2.2801
730	0.836	2.2052
765	0.833	2.1237
800	0.821	2.0794
835	0.812	2.0794
870	0.801	2.0221
905	0.794	1.9881
940	0.775	1.8934
975	0.766	1.8523
1010	0.760	1.8225
1045	0.740	1.7292
1080	0.723	1.6582
1115	0.701	1.5500
1150	0.681	1.4641

CALCULATED.....

G 0.56300
D (CM²/SEC X 10⁻⁶) 5.205
ACCURACY ± / - 0.025
DELTA T (SECS) 22.00

RUN NO. S/3

0.0667 WT.PCT. SUCROSE WATER

T = 25* DEG.C

FP 2

T (SECS)	2X(H) (MM)	2X SQD (MM) ²
100	0.827	2.1580
135	0.853	2.2952
170	0.880	2.4430
205	0.913	2.6276
240	0.935	2.7556
310	0.974	2.9929
345	0.997	3.1329
380	1.019	3.2761
415	1.036	3.3856
450	1.044	3.4410
485	1.061	3.5532
520	1.073	3.6290
555	1.081	3.6864
590	1.087	3.7249
625	1.095	3.7830
660	1.092	3.7636
695	1.109	3.8809
730	1.118	3.9402
765	1.118	3.9402
800	1.120	3.9601
835	1.118	3.9402
870	1.108	3.8730
905	1.109	3.8809
940	1.108	3.8730
975	1.108	3.8730
1010	1.095	3.7830
1195	1.070	3.6100
1380	1.049	3.4708
1575	0.960	3.9070
1760	0.867	2.3716

CALCULATED.....

G = 0.56300
 D (CM²/SEC X 10⁻⁶) = 5.130
 ACCURACY, +/- = 0.100
 DELTA T (SECS) = 87

RUN NO. S/4

-104-

0.0993 WT. PCT. SUCROSE WATER

T = 25.3 DEG. C

F.P. 2

T	2X(M)	2X SQD	T	2X(M)	2X SQD
SECS	(MM)	(MM) ²	(SECS)	(MM)	(MM) ²
528	1.329	5.5696	2238	1.903	11.4244
561	1.374	5.9536	2421	1.925	11.6964
594	1.441	6.5536	2605	1.925	11.6964
627	1.453	6.6564	2788	1.925	11.6964
660	1.486	6.9696	2971	1.909	11.4921
693	1.498	7.0756	3154	1.903	11.4244
726	1.531	7.3984	3337	1.875	11.0889
759	1.543	7.5076	3520	1.875	11.0889
792	1.576	7.8400	3703	1.835	10.6276
825	1.588	7.9524	3886	1.802	10.2400
858	1.576	7.8400	4069	1.785	10.0489
891	1.599	8.0656	4242	1.768	9.8596
924	1.616	8.2369	4425	1.713	9.2346
957	1.644	8.5264	4608	1.695	9.0601
1140	1.689	9.0000	4791	1.633	8.4100
1323	1.745	9.6100	4974	1.616	8.2369
1506	1.802	10.2400	5157	1.543	7.5076
1689	1.824	10.4976	5340	1.486	6.9696
1872	1.864	10.9561	5523	1.441	6.5536
2055	1.903	11.4244	5706	1.327	5.4756

CALCULATED.....

G = 0.56300
D (CM²/SEC X 10⁻⁶) = 5.216
ACCURACY, +/- = 0.012
DELTA T (SECS) = 64

RUN NO. MEA/1

0.0578 WT.PCT. MEA WATER

T = 25.3 DEG.C

F.P.O.

T (SECS)	ΔX(M) (MM)	ΔX SQD (MM) ²
65	0.0780	0.006084
100	0.0873	0.007621
135	0.0899	0.008082
170	0.0923	0.008519
205	0.0951	0.009044
240	0.0959	0.009186
275	0.0967	0.009351
310	0.0961	0.009235
345	0.0959	0.009186
380	0.0947	0.008968
425	0.0938	0.008798
450	0.0918	0.008427
485	0.0896	0.008028
520	0.0859	0.007379
555	0.0834	0.006956

CALCULATED.....

G
D (CM³/SEC X 10⁻⁵)
ACCURACY, ± %
DELTA T (SECS)

0.56300
1.040
0.100
58

RUN NO. MEA/2

85.5 G./LITRE MEA WATER

T = 25.3 DEG.C

F.P.

T (SECS)	ΔX(M) (MM)	ΔX SQD (MM) ²
65	1.883	0.9568
100	2.360	1.5030
135	2.475	1.6531
170	2.575	1.7893
205	2.625	1.8595
240	2.650	1.8951
275	2.650	1.8951
310	2.650	1.8951
345	2.628	1.8638
380	2.535	1.7342
415	2.498	1.6839
450	2.345	1.4840
485	2.248	1.3537
520	2.070	1.2563
555	1.893	0.9670

CALCULATED.....

G (GMS/SEC X 10⁻⁶) =
 ACCURACY, ±% =
 DELTA T (SECS) =

1.92500
 9.116
 0.020
 1.36

RUN NO. MEA/3

Run No. MEA/3

122.2 G./LITRE MEA WATER

T = 25.3 DEG.C

F.P. 2

T (SECS)	2X(M) (MM)	2X SQD (MM) ²
275	1.140	4.1001
310	1.193	4.4902
345	1.208	4.6038
380	1.233	4.7963
415	1.268	5.0725
450	1.300	5.3318
485	1.313	5.4389
520	1.315	5.4555
555	1.310	5.4141
590	1.318	5.4804
625	1.320	5.4971
660	1.343	5.6903
730	1.348	5.7328
765	1.358	5.8181
800	1.365	5.8783
870	1.365	5.8783
975	1.365	5.8783
1045	1.362	5.8534
1080	1.360	5.8353
1115	1.345	5.7073
1150	1.338	5.6480
1185	1.338	5.6480
1220	1.313	5.4389
1255	1.295	5.2908
1290	1.285	5.2094
1325	1.280	5.1690
1360	1.250	4.9295
1395	1.263	5.0326
1430	1.235	4.8119
1465	1.210	4.6191
1500	1.118	3.9434
1535	1.163	4.2672

CALCULATED.....

G	=	0.56300
D (CM ² /SEC X 10 ⁻⁶)	=	8.575
ACCURACY, % +/-	=	0.040
DELTA T (SECS)	=	22

RUN NO. MEA/4

244.5 G./LITRE MEA WATER

T = 25.3 DEG.C

F.P.3

T (SECS)	2X(M) (MM)	2X SQD (MM) ²
205	0.861	2.3388
240	0.884	2.4654
275	0.900	2.5555
310	0.929	2.7228
345	0.929	2.7228
380	0.945	2.8174
415	0.960	2.9075
450	0.959	2.9015
485	0.954	2.8713
520	0.960	2.9075
555	0.960	2.9075
590	0.958	2.8954
625	0.950	2.8473
660	0.942	2.7995
765	0.912	2.6241
800	0.887	2.4822
835	0.885	2.4710
870	0.874	2.4099
905	0.864	2.3551
940	0.847	2.2633
975	0.838	2.2155
1010	0.805	2.0444

CALCULATED.....

G = 0.56300
D (CM²/SEC X 10⁻⁶) = 6.729
ACCURACY, +/- = 0.009
DELTA T (SECS) = 18

RUN NO. MEA/5

151.85 G./LITRE MEA WATER

T = 25.3 DEG.C

F.P. 3

T (SECS)	2X(M) (MM)	2X SQD (MM) ²
0	2.525	1.7205
30	2.768	2.0676
65	3.010	2.4450
100	3.145	2.6692
135	3.260	2.8680
170	3.303	2.9441
205	3.355	3.0376
240	3.388	3.0976
275	3.423	3.1619
310	3.425	3.1656
345	3.440	3.1934
380	3.425	3.1656
415	3.410	3.1380
450	3.395	3.1104
485	3.370	3.0648
520	3.355	3.0376
555	3.318	2.9709
590	3.270	2.8856
625	3.245	2.8416
660	3.230	2.8154
695	3.125	2.6354
730	3.080	2.5600
765	3.028	2.4743
800	2.925	2.3088
835	2.840	2.1766
870	2.675	1.9310

CALCULATED.....

G = 1.92500
D (CM²/SEC X 10⁻⁶) = 8.101
ACCURACY: +/- = 0.020
DELTA T (SECS) = 119

RUN NO. MEA/6

305.6 G./LITRE MEA WATER

T = 25.3 DEG. C

F. P. 3

T	2X(M)	2X SQD	T	2X(M)	2X SQD
SECS	(MM)	(MM) ₂	(SECS)	(MM)	(MM) ₂
0	2.800	2.1157	695	3.835	3.9689
30	2.855	2.1996	730	3.830	3.9585
65	2.983	2.4013	765	3.830	3.9585
100	3.080	2.5600	800	3.830	3.9585
135	3.175	2.7204	835	3.823	3.9441
170	3.255	2.8592	870	3.830	3.9585
205	3.328	2.9889	905	3.793	3.8824
240	3.390	3.1013	940	3.765	3.8253
275	3.450	3.2120	975	3.735	3.7646
310	3.530	3.3627	1010	3.685	3.6645
345	3.570	3.4393	1045	3.685	3.6645
380	3.623	3.5422	1080	3.643	3.5814
415	3.670	3.6347	1115	3.605	3.5071
450	3.710	3.7144	1150	3.550	3.4009
485	3.755	3.8050	1185	3.510	3.3247
520	3.785	3.8661	1220	3.488	3.2832
555	3.800	3.8968	1255	3.425	3.1656
590	3.820	3.9379	1290	3.380	3.0830
625	3.825	3.9482	1325	3.335	3.0014
660	3.830	3.9585	1360	3.290	2.9210

CALCULATED.....

G	=	1.92500
D (CM2/SEC X 10-6)	=	5.770
ACCURACY, +/-	=	0.010
DELTA T (SECS)	=	153

RUN NO. DEA/1

0.060 WT.PCT. DEA WATER

T = 25.3 DEG.C

F.P. 2

T (SECS)	ΔX(M) (MM)	ΔX SQD (MM) ²
170	0.833	0.6939
205	0.855	0.7310
240	0.894	0.7992
275	0.919	0.8444
310	0.936	0.8760
345	0.960	0.9216
380	0.963	0.9274
415	0.986	0.9722
450	0.996	0.9920
485	0.999	0.9980
520	1.011	1.0221
555	1.008	1.0161
590	1.012	1.0241
660	1.010	1.0201
695	1.008	1.0161
730	1.000	1.0000
765	0.998	0.9960
800	0.988	0.9761
835	0.988	0.9761
870	0.968	0.9370
905	0.958	0.9176
940	0.945	0.8930
975	0.925	0.8556
1080	0.885	0.7832

CALCULATED.....

G = 0.56300
D (CM³/SEC X 10⁻⁶) = 6.624
ACCURACY, +/− = 0.009
DELTA T (SECS) = 7

RUN NO. DEA/2

54.5 G./LITRE DEA WATER

T = 25.3 DEG.C

F.P. 2

T (SECS)	2X(M) (MM)	2X SQD (MM)²
0	0.580	1.00613
35	0.626	1.02363
50	0.640	1.02922
65	0.664	1.03910
100	0.687	1.04890
135	0.708	1.05814
170	0.723	1.06491
205	0.730	1.06812
240	0.732	1.06905
275	0.732	1.06905
310	0.736	1.07090
345	0.734	1.06997
380	0.728	1.06720
415	0.722	1.06446
450	0.711	1.05949
485	0.692	1.05108
520	0.680	1.04588
555	0.656	1.03577
590	0.635	1.02721
625	0.620	1.02127
660	0.600	1.01358
695	0.580	1.00613
730	0.559	0.98558
765	0.542	0.9268

CALCULATED.....

G = 0.56300
D (CM²/SEC X 10-6) = 5.377
ACCURACY, ± = 0.015
DELTA T (SECS) = 100

RUN NO. DEA/3

109 G./LITRE DEA WATER

T = 25.3 DEG.C

F.P.2

T (SECS)	2X(M) (MM)	2X SQD (MM) ²
170	0.689	1.4977
205	0.713	1.6038
240	0.734	1.6997
275	0.736	1.7090
310	0.741	1.7323
345	0.747	1.7605
380	0.744	1.7463
415	0.743	1.7416
450	0.742	1.7370
485	0.744	1.7463
520	0.730	1.6812
555	0.712	1.5993
590	0.704	1.5636
625	0.702	1.5547
660	0.680	1.4588
695	0.674	1.4332
730	0.643	1.3044
765	0.625	1.2324
800	0.608	1.1662
835	0.591	1.1019
870	0.574	1.0395
905	0.536	0.9064
940	0.500	0.7887
975	0.472	0.7029

CALCULATED.....

G = 0.56300
D (CM²/SEC X 10⁻⁶) = 4.877
: ACCURACY $\pm$ = 0.005
DELTA T (SECS) = 60

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RUN NO. DEA/4

154.5 G./LITRE DEA WATER

T = 25.3 DEG.C

F.P. 2

T	2X(M)	2X SQD	T	2X(M)	2X SQD
SECS	(MM)	(MM) ²	(SECS)	(MM)	(MM) ²
100	1.980	3.9204	1220	2.928	5.0539
135	2.135	4.5592	1255	2.945	5.1128
170	2.260	5.1076	1290	2.920	5.0263
205	2.335	5.4502	1325	2.933	5.0712
240	2.440	5.9536	1360	2.900	4.9577
275	2.518	6.3403	1395	2.893	4.9338
310	2.555	6.5280	1430	2.875	4.8726
345	2.615	6.8782	1465	2.838	4.7480
380	2.693	7.2522	1500	2.838	4.7480
415	2.710	7.3581	1535	2.888	4.9168
450	2.745	7.5450	1570	2.888	4.9168
485	2.758	7.6066	1605	2.833	4.7313
520	2.803	7.8572	1640	2.840	4.7547
555	2.808	7.8849	1675	2.780	4.5559
590	2.825	7.9606	1710	2.753	4.4678
625	2.840	8.0256	1745	2.723	4.3710
660	2.867	8.2189	1780	2.728	4.3871
695	2.883	8.3115	1815	2.720	4.3614
730	2.920	8.5264	1850	2.678	4.2277
765	2.915	8.4972	1885	2.620	4.0466
800	2.920	8.5264	1920	2.600	3.9850
835	2.920	8.5264	1955	2.573	3.9027
870	2.940	8.6436	1990	2.535	3.7883
905	2.948	8.6903	2025	2.500	3.6844
1045	2.928	8.5731	2060	2.503	3.6932
1080	2.938	8.6318	2095	2.465	3.5819
1115	2.943	8.6602	2130	2.323	3.1811
1150	2.918	8.5147	2270	2.235	2.9447
1185	2.943	8.6602	2305	2.143	2.7073

CALCULATED.....

G = 1.30244
D (CM²/SEC X 10⁻⁶) = 4.635
ACCURACY, +/- = 0.010
DELTA T (SECS) = 52

RUN NO. DEA/5

256 G./LITRE DEA WATER

T = 25.3 DEG.C

F.P.3

T	2X(M)	2X SQD	T	2X(M)	2X SQD
SECS	(MM)	(MM) ²	(SECS)	(MM)	(MM) ²
135	1.924	2.1821	905	2.320	3.01729
170	1.958	2.2600	940	2.315	3.01593
205	2.035	2.4413	975	2.315	3.01593
240	2.033	2.4365	1010	2.315	3.01593
275	2.115	2.6370	1045	2.295	3.01049
310	2.140	2.6997	1080	2.285	3.00779
345	2.155	2.7377	1115	2.280	3.00645
380	2.210	2.8792	1150	2.270	3.00376
415	2.225	2.9184	1185	2.270	3.00376
450	2.250	2.9943	1220	2.263	3.00189
485	2.252	2.9897	1255	2.250	2.99443
520	2.254	2.9950	1290	2.255	2.99976
555	2.254	2.9950	1325	2.245	2.99711
590	2.300	3.1185	1360	2.203	2.86610
660	2.330	3.2003	1395	2.160	2.7504
695	2.325	3.1866	1430	2.090	2.5750
730	2.325	3.1866	1465	2.063	2.5089
765	2.330	3.2003	1500	2.030	2.4293
800	2.335	3.2141	1535	1.993	2.3415
835	2.340	3.2279	1570	1.980	2.3311
870	2.335	3.2141	1605	1.935	2.2072

CALCULATED.....

G = 1.30244
D (CM²/SEC X 10⁻⁶) = 4.181
ACCURACY: +/- = 0.010
DELTA T (SECS) = 160

RUN NO. DEA/6

347.15 G./LITRE DEA WATER

T = 25.3.DEG.C

F.P.3

T	2X(M)	2X SQD	T	2X(M)	2X SQD
SECS	(MM)	(MM) ²	(SECS)	(MM)	(MM) ²
170	1.765	1.9995	1220	2.575	4.2558
205	1.815	2.1144	1255	2.575	4.2558
240	1.905	2.3293	1290	2.588	4.2989
275	1.980	2.5163	1325	2.585	4.2890
310	2.033	2.6528	1360	2.600	4.3389
345	2.088	2.7983	1395	2.590	4.3056
380	2.115	2.8711	1430	2.570	4.2393
415	2.150	2.9669	1465	2.598	4.3322
450	2.193	3.0868	1500	2.585	4.2890
485	2.218	3.1576	1535	2.585	4.2890
520	2.255	3.2638	1570	2.570	4.2393
555	2.275	3.3220	1605	2.548	4.1671
590	2.315	3.4398	1640	2.550	4.1736
625	2.343	3.5235	1675	2.540	4.1409
660	2.355	3.5597	1710	2.540	4.1409
695	2.383	3.6449	1815	2.530	4.1084
730	2.395	3.6817	1850	2.515	4.0598
765	2.425	3.7745	1990	2.510	4.0437
800	2.435	3.8057	2025	2.487	3.9715
835	2.465	3.9000	2060	2.425	3.7745
870	2.475	3.9000	2095	2.425	3.7745
905	2.505	4.0076	2130	2.440	3.8213
940	2.510	4.0437	2165	2.423	3.7682
975	2.530	4.1084	2200	2.410	3.7279
1010	2.530	4.1084	2235	2.410	3.7279
1045	2.543	4.1507	2270	2.400	3.6970
1080	2.545	4.1573	2305	2.390	3.6663
1115	2.548	4.1671	2340	2.380	3.6357
1150	2.555	4.1900	2375	2.338	3.5085
1185	2.565	4.2229	2445	2.328	3.4785

CALCULATED.....

G = 1.24820
 D (CM²/SEC X 10⁻⁶) = 3.736
 ACCURACY, +/- = 0.009
 DELTA T (SECS) = 40

347.15 G./LITRE DEA WATER

T = 25.3 DEG.C

F.P.4

T (SECS)	2X(M) (MM)	2X SQD (MM) ²
240	1.650	1.7474
275	1.678	1.8072
310	1.723	1.9055
345	1.750	1.9657
380	1.758	1.9837
415	1.798	2.0750
450	1.820	2.1261
485	1.820	2.1261
520	1.835	2.1612
555	1.860	2.2205
590	1.875	2.2565
625	1.895	2.3049
660	1.880	2.2685
695	1.883	2.2758
730	1.890	2.2927
765	1.890	2.2927
800	1.893	2.3000
835	1.890	2.2927
870	1.880	2.2685
905	1.875	2.2565
940	1.858	2.2158
975	1.840	2.1730
1010	1.835	2.1612
1045	1.820	2.1261
1080	1.790	2.0565
1115	1.770	2.0108
1150	1.755	1.9769
1185	1.750	1.9657
1220	1.720	1.8988
1255	1.705	1.8659
1290	1.688	1.8288
1325	1.635	1.7158
1360	1.625	1.6949
1395	1.590	1.6227
1430	1.550	1.5420
1465	1.485	1.4154
1500	1.455	1.3588
1535	1.410	1.2761

CALCULATED.....

G = 1.24820
D (CM²/SEC X 10⁻⁶) = 3.731
ACCURACY, +/- = 0.008
DELTA T (SECS) = 46

RUN NO. DEA/8

462.5 G./LITRE DEA WATER

T = 25.3 DEG. C

F.P. 4

T SECS	2X(M) (MM)	2X SQD (MM) ²	T (SECS)	2X(M) (MM)	2X SQD (MM) ²
170	1.398	1.2544	905	1.773	2.00177
240	1.580	1.6023	940	1.758	1.9837
275	1.633	1.7116	975	1.740	1.9433
310	1.665	1.7793	1010	1.740	1.9433
345	1.690	1.8332	1045	1.720	1.8988
380	1.720	1.8988	1080	1.715	1.8878
415	1.733	1.9277	1115	1.690	1.8332
450	1.765	1.9995	1150	1.670	1.7900
485	1.755	1.9769	1185	1.650	1.7474
520	1.780	2.0336	1220	1.645	1.7369
555	1.790	2.0565	1255	1.620	1.6845
590	1.795	2.0680	1290	1.605	1.6534
625	1.795	2.0680	1325	1.585	1.6125
660	1.793	2.0634	1360	1.560	1.5620
695	1.795	2.0680	1395	1.545	1.5321
730	1.798	2.0750	1430	1.520	1.4829
800	1.790	2.0565	1465	1.483	1.4416
835	1.788	2.0519	1500	1.455	1.3588
870	1.780	2.0336	1535	1.430	1.3125

CALCULATED.....

G = 1.24820
D (CM²/SEC X 10⁻⁶) = 3.185
ACCURACY = +/- 0.007
DELTA T (SECS) = 89

***480.9 G./LITRE DEA WATER

T = 25.3 DEG.C

F.P. 3

T SECS	2X(M) (MM)	2X SQD (MM) ²	T (SECS)	2X(M) (MM)	2X SQD (MM) ²
170	1.670	1.7900	1430	2.460	3.08842
205	1.755	1.9769	1465	2.455	3.08684
240	1.840	2.1730	1500	2.448	3.08464
275	1.905	2.3293	1535	2.450	3.08527
310	1.985	2.5290	1570	2.450	3.08527
345	2.015	2.6060	1605	2.438	3.08150
380	2.080	2.7769	1640	2.438	3.08150
415	2.110	2.8576	1675	2.453	3.08621
450	2.170	3.0024	1710	2.465	3.09000
485	2.190	3.0784	1745	2.430	3.07900
520	2.235	3.2062	1780	2.450	3.08527
555	2.245	3.2349	1815	2.450	3.08527
590	2.285	3.3512	1850	2.425	3.07745
625	2.295	3.3806	1885	2.410	3.07276
660	2.320	3.4547	1920	2.388	3.06602
695	2.335	3.4995	2025	2.385	3.06510
730	2.360	3.5748	2060	2.388	3.06602
765	2.355	3.5597	2095	2.365	3.05900
800	2.380	3.6357	2130	2.363	3.05839
835	2.385	3.6510	2165	2.340	3.05145
870	2.395	3.6817	2235	2.320	3.04547
905	2.410	3.7279	2305	2.315	3.04398
940	2.410	3.7279	2340	2.310	3.04250
975	2.420	3.7589	2375	2.278	3.03307
1010	2.435	3.8057	2410	2.275	3.03220
1045	2.435	3.8057	2445	2.273	3.03161
1080	2.440	3.8213	2480	2.265	3.02928
1115	2.435	3.8057	2515	2.240	3.02205
1150	2.435	3.8057	2550	2.230	3.01918
1185	2.445	3.8370	2585	2.220	3.01633
1255	2.455	3.8684	2620	2.215	3.01490
1290	2.460	3.8842	2655	2.190	3.00784
1325	2.463	3.8937	2690	2.160	2.99946
1360	2.465	3.9000	2725	2.153	2.99752
1395	2.465	3.9000	2760	2.133	2.99202

CALCULATED.....

G = 1.24820
D (CM²/SEC X 10⁻⁶) = 3.089
ACCURACY, +/- = 0.006
DELTA T (SECS) = 142

RUN NO. TEA/1

0.054 WT.PCT. TEA WATER

T = 25.3DEG.C

F.P.2

T (SECS)	2X(N) (MM)	2X SQD (MM)2
30	1.320	1.0271
65	1.490	1.3088
100	1.605	1.5186
135	1.680	1.6638
170	1.755	1.8157
205	1.780	1.8678
240	1.805	1.9206
275	1.810	1.9313
310	1.810	1.9313
345	1.805	1.9206
380	1.800	1.9100
415	1.795	1.8994
450	1.760	1.8260
485	1.745	1.7950
520	1.735	1.7739
555	1.678	1.6598
590	1.628	1.5624
635	1.548	1.4126
660	1.467	1.2687
695	1.365	1.0984

CALCULATED.....

G = 1.30244
D (CM2/SEC X 10-6) = 6.422
ACCURACY, +/- = 0.010
DELTA T (SECS) = 62

RUN TEA/2

0.054 WT. PCT. TEA WATER

T = 25.3 DEG. C

F.P. 2

T (SECS)	ΔX(M) (MM)	ΔX SQD (MM)²
30	1.430	1.3055
65	1.610	1.5280
100	1.725	1.7541
135	1.835	1.9850
170	1.900	2.1281
205	1.950	2.2416
240	1.995	2.3462
275	2.035	2.4413
310	2.060	2.5016
345	2.065	2.5138
380	2.070	2.5260
415	2.075	2.5382
450	2.065	2.5138
485	2.065	2.5138
520	2.053	2.4846
555	2.043	2.4605
590	2.030	2.4293
625	1.993	2.3415
660	1.965	2.2762
695	1.938	2.2141
730	1.903	2.1348
765	1.863	2.0460
800	1.853	2.0241
835	1.795	1.8994
870	1.718	1.7399

CALCULATED.....

G = 1.30344
D (CM²/SEC X 10-6) = 6.446
ACCURACY, +/- = 0.010
DELTA T (SECS) = 63

* RUN NO. TEA/3

200.56 G./LITRE TEA WATER

T = 25.3 DEG.C

F.P.3

T	2X(M)	2X SQD	T	2X(M)	2X SQD
SECS	(MM)	(MM) ²	(SECS)	(MM)	(MM) ²
135	1.855	2.0285	1185	2.670	4.2025
170	1.930	2.1958	1220	2.660	4.1711
205	2.025	2.4173	1255	2.650	4.1398
240	2.105	2.6121	1290	2.655	4.1554
275	2.160	2.7504	1325	2.635	4.0930
310	2.205	2.8662	1360	2.635	4.0930
345	2.255	2.9976	1430	2.655	4.1554
380	2.295	3.1049	1465	2.655	4.1554
415	2.345	3.2417	1500	2.625	4.0620
450	2.380	3.3392	1535	2.625	4.0620
485	2.415	3.4381	1570	2.610	4.0157
520	2.465	3.5819	1605	2.585	3.9392
555	2.485	3.6403	1640	2.585	3.9392
590	2.515	3.7287	1675	2.585	3.9392
625	2.540	3.8032	1710	2.575	3.9088
660	2.555	3.8483	1745	2.530	3.7733
695	2.570	3.8936	1780	2.508	3.7080
730	2.610	4.0157	1815	2.470	3.5965
765	2.625	4.0620	1850	2.430	3.4809
800	2.635	4.0930	1885	2.405	3.4097
835	2.650	4.1398	1920	2.385	3.3532
870	2.660	4.1711	1955	2.370	3.3112
905	2.660	4.1711	1990	2.335	3.2141
940	2.665	4.1868	2025	2.330	3.2003
975	2.675	4.2182	2060	2.315	3.1593
1010	2.670	4.2025	2095	2.295	3.1049
1115	2.675	4.2182	2130	2.255	2.9976
1150	2.675	4.2182	2165	2.205	2.8662

CALCULATED.....

G = 1.30244
 D (CM²/SEC X 10⁻⁶) = 4.452
 ACCURACY, +/- = 0.008
 DELTA T (SECS) = 72

RUN NO. TEA/4

200.56 G./LITRE TEA WATER

T = 25.3 DEG.C

F.P.4

T (SECS)	2X(M) (MM)	2X SQD (MM) ²
135	1.565	1.4438
170	1.640	1.5855
205	1.715	1.7339
240	1.755	1.8157
275	1.800	1.9100
310	1.830	1.9742
345	1.835	1.9850
380	1.855	2.0285
415	1.890	2.1058
450	1.895	2.1169
485	1.900	2.1281
520	1.915	2.1618
555	1.915	2.1618
590	1.915	2.1618
625	1.910	2.1506
660	1.915	2.1618
695	1.905	2.1393
730	1.890	2.1058
765	1.885	2.0946
800	1.850	2.0176
835	1.835	1.9850
870	1.805	1.9206
905	1.780	1.8678
940	1.745	1.7950
975	1.710	1.7238
1010	1.645	1.5952
1045	1.655	1.6147
1080	1.605	1.5186
1115	1.530	1.3800
1150	1.485	1.3000
1185	1.938	2.2139
1220	1.405	1.1637
1255	1.370	1.1064

CALCULATED.....

G = 1.30244
D (CM²/SEC X 10⁻⁶) = 4.564
ACCURACY, +/- = 0.008
DELTA T (SECS) = 44

RUN NO. TEA/5

308.95 G./LITRE TEA WATER

T = 25.3 DEG.C

F.P. 3

T	2X(M)	2X SQD	T	2X(M)	2X SQD
SECS	(MM)	(MM) ²	(SECS)	(MM)	(MM) ²
170	2.170	2.7759	1010	2.400	3.3955
205	2.195	2.8402	1045	2.390	3.3673
240	2.240	2.9579	1115	2.380	3.3392
275	2.280	3.0645	1150	2.383	3.3476
310	2.305	3.1320	1185	2.350	3.2555
345	2.325	3.1866	1220	2.350	3.2555
380	2.333	3.2086	1255	2.338	3.2224
415	2.345	3.2417	1290	2.330	3.2003
450	2.380	3.3392	1325	2.330	3.2003
485	2.385	3.3532	1395	2.320	3.1729
520	2.388	3.3617	1430	2.315	3.1593
555	2.388	3.3617	1465	2.305	3.1320
590	2.413	3.4324	1500	2.305	3.1320
625	2.413	3.4324	1535	2.290	3.0914
695	2.415	3.4381	1570	2.280	3.0645
730	2.415	3.4381	1605	2.263	3.0189
765	2.415	3.4381	1640	2.260	3.0109
800	2.415	3.4381	1675	2.250	2.9843
835	2.415	3.4381	1710	2.220	2.9053
905	2.410	3.4239	1745	2.215	2.8922
940	2.410	3.4239	1780	2.180	2.8015

CALCULATED.....

G = 1630244
 D (CM²/SEC X 10⁻⁶) = 3.385
 ACCURACY, ±/ = 0.006
 DELTA T (SECS) = 295

IV(d). Comparison of Results Obtained Using the Wavefront
Shearing Interferometer, and those Obtained by the
Gouy Method.

Thomas and Furzer (1)(2) investigated the diffusion coefficients for the same systems as in this study. However, their results provoked critical interest from Ibrahim and Kuloor (3) , who doubted the discrepancy between the experimental D-values and theoretically predicted values as being due to physico-chemical effects in the ethanolamine-water systems. There are two implications in Ibrahim and Kuloor's criticisms;-

- a) that Thomas and Furzer's D-values are suspect,
- and b) that the semi-empirical equations applied do not adequately describe the ethanolamine-water diffusion process.

The latter topic will be discussed in some detail further on.

A comparison between Thomas and Furzer's results and the results obtained in this study will serve as a check on the accuracy of the former.

Although most of the error in the work of Thomas and Furzer would appear to be due to the inherent

inaccuracies of the Gouy interferometer itself, there are several criticisms that can be made.

As an example, calibration runs using sucrose-water did not show a very great accuracy (e.g. a figure of $D = 5.13 \times 10^{-6} \text{ cm}^2/\text{sec}$ for one sucrose-water run is quoted without any indication of suspected inaccuracy).

On a more detailed examination of the results, no Δt correction has been applied in any one case. Since an estimate of the Δt , and the resulting corrected D-value, is of interest, Thomas and Furzer's ethanolamine-water results were recalculated to include a Δt . A summary of these calculations is given, together with graphs comparing the corrected and uncorrected D-values with those obtained in this study.

Zero Time Correction Applied to the Gouy Calculations.

In Thomas and Furzer's calculations for the Diffusion coefficients of MEA, DEA, and TEA - water, the following approach was taken:-

The relationship,

$$D = \frac{(j_m \cdot \lambda \cdot b)^2}{4 \pi c_t^2 \cdot t}$$

is used, where

j_m = total number of fringes in the pattern,

λ = wavelength of light used.

b = path length thro' diffusion cell.

$c_t = Y / e^{-z^2}$, where Y is the fringe displacement.

e^{-z^2} is obtained from a table of $f(z), e^{-z^2}$,

$f(z)$ being calculated from $f(z) = \frac{j + \frac{1}{4}}{j_m}$

Displacement measurements are taken for the fringes in the fringe-pattern (with the Gouy interferometer, the fringe pattern consists of a number of horizontal fringes moving downwards.).

$f(z)$, e^{-z^2} , and C_t are then calculated for each of the fringes, assuming a value for j_m . When the standard deviation of the C_t values is a minimum, then the corresponding value of j_m is used.

Naturally, j_m should be constant throughout any one experiment(fringe displacements being measured at regular time intervals).

D is thus calculated for several values of t.

However, as with the wavefront shearing interferometer, a zero-time correction, Δt , must be applied to the observed time, t. (This being due to initial mixing at the interface).

The relationship $D' = D \left(1 + \frac{\Delta t}{t} \right)$,

where D is the corrected value of the diffusion coefficient, is used by Longworth (48). Thus a plot of D' against $1/t$ should yield a straight line of slope $D \cdot \Delta t$.

Thomas and Furzer did not employ this relationship, but drew instead the best straight line through plots of

- 1) j_m vs. t
- 2) $1/c_t^2$ vs. $1/t$

the intercepts yielding j_m and $1/c_t^2$ respectively, and from these values D was calculated.

For the purpose of determining the accuracy of the Gouy results, Longworth's method for calculating D and Δt was applied to Thomas and Furzer's results. These calculations are summarised in table 4.

Thomas and Furzer's results, with a) no Δt applied, and b) Δt considered, are compared graphically with the results obtained using the wavefront shearing interferometer in Figs. 18, 19, and 20.

Table 4.

Calculation of Δt for Thomas and Furzer's Results.

Run. No.	Solute Concn.		D' cm^2/sec $\times 10^6$	D cm^2/sec $\times 10^6$	t secs
	ml/litre	N			
MEA 1	7	0.12	10.8	10.08	94
2	40	0.67	10.2	10.04	9
3	100	1.67	8.52	8.17	89
4	200	3.34	5.11	4.65	738
DEA 1	40	0.42	5.67	5.54	241
2	100	1.05	4.64	4.74	170
3	200	2.10	3.82	3.79	248
4	400	4.19	2.81	2.26	1067
5	500	5.42	2.28	2.22	497
TEA 1	4	0.03	7.07	8.38	42
2	20	0.15	6.57	6.24	106
3	200	1.52	4.22	3.93	239
4	400	3.04	1.70	1.42	1339

FIG. 18

Diffusivity / Normality
of MEA

FIG. 19

Diffusivity / Normality of DEA

FIG. 20

Diffusivity / Normality of TEA

Conclusions from a Comparison of Gouy and Wavefront
Shearing Interferometer Results.

When a Δt is applied to the Thomas and Furzer' results, a large variation is observed.

i.e. for TEA 1 , $\Delta t = \sim 42$ secs.

" TEA 4 , $\Delta t = 1339$ secs.

There are also three other results (MEA 4, DEA 4 , & 5) where the Δt is inordinately large . The implication of this is that there is either quite a substantial inherent inaccuracy in the Gouy interferometer, or that Thomas and Furzer did not obtain a sharp interface before diffusion started. There is also the possibility that too many fringes were obtained (the concentration difference between the solutions being too great), so that too much information is presented. As an example, in run TEA 4 , j_M (the total number of fringes) is of the order 75 - 79, whereas the ideal number of fringes should be less than 10.

The inaccuracy factor of the Gouy results is further highlighted by an examination of j_M values. Ideally, the j_M value should be constant throughout each experiment, but this does not appear to have been so. As an example, for the run TEA 4, the j_M values calculated by Thomas and Furzer

are tabulated below:-

t(secs)	1740	2520	3060	3780	4440	5040
j_M	79.0	77.9	77.3	76.9	76.4	75.5

It is not proposed to discuss in detail how inaccuracy is introduced into the results from the Gouy interferometer, suffice to say that when compared with those of the wavefront shearing interferometer, they appear to be considerably inferior. It should thus be taken that the results of this study are the more accurate.

From the graphs on which the comparisons are made, it would appear that although the Gouy results do differ, the shapes of the curves are approximately the same. The Gouy results for monoethanolamine have one point (at 3.34 N) which is widely different, and this point effectively throws the whole curve out of any agreement with the wavefront shearing interferometer results.

One important observation to be made is that the diffusivity values at low concentrations are very similar. It was these D-values on which Ibrahim and Kuloor were most critical. Since Thomas and Furzer's results are almost the same as those in this study, it would therefore appear that a radical re-appraisal of the application of the semi-empirical equations to ethanolamine diffusion is called for.

V. THE APPLICATION OF THE SEMI-EMPIRICAL
EQUATIONS TO ETHANOLAMINE-WATER DIFFUSION .

The second critical implication of Ibrahim and Kuloor mentioned earlier, i.e. that the semi-empirical equations applied do not adequately describe the ethanolamine-water diffusional process , will now be examined in detail. As well as examining the semi-empirical equations, the limitations of the theories of diffusion will be assessed. Starting with the theories of diffusion, the following comments may be made;-

1) The Stokes-Einstein Equation (eqn.20 & 22) is only applicable for solutes with a molecular weight of > 300 . For the ethanolamines, $M_{MEA} = 61.08$; $M_{DEA} = 105.14$; $M_{TEA} = 149.2$. Thus, there can be no correlation between the experimental results for the ethanolamines and this theory.

2) Arnold's Kinetic Theory is of little use for predicting diffusivity in any system, since three empirical constants are involved in Arnold's equation (eqn.36). Two of these constants are known for common solvents (e.g. water at 25°C) but the third constant, relating to the solute, is somewhat arbitrary. The Arnold equation has been applied

to the diffusion of ethanolamines in this study, with the intention of relating this third constant to the apparent molecular volume of the solute in solution.

3) Eyring's Theory is represented by equation 33, - this equation being a simplification of equation 37. There are two important drawbacks to the use of this theory; a) the inclusion of an empirical parameter describing the geometrical configuration of the solute/solvent molecular structure, and b) the assumption that the activation energies for viscosity and diffusion are equal. Reported results on the application of the Eyring theory to various systems showed wide deviations from the experimental results. In view of these considerations, no attempt has been made to correlate the Eyring theory with the experimental results for the ethanolamines.

Gainer and Metzner's improvement on the Eyring theory is of little use in this case. The parametric empirical constants are still present, but the main difficulty with Gainer and Metzner's treatment is that the heat of evaporation of a hydrocarbon homologue must be calculated. With the ethanolamines this calculation is not possible.

4) Nernst's Law (equation 51) is applicable to the diffusion of a strongly ionised electrolyte, where the ionic

mobilities of the cation and anion are known. Since this information is not available for the ethanolamines, the equation cannot be applied in this case.

5) The Nernst-Onsager-Fuoss theory is too complex for a study of the nature conducted in this laboratory. The theory is only of use in a detailed physico-chemical study.

Thus, for the systems ethanolamines-water the prediction of diffusivity is limited to the semi-empirical equations. Bearing in mind the objections raised to these equations (as discussed previously), - one primary demerit being the failure to allow for molecular irregularities, it is not surprising that comparatively large deviations between prediction and observation will occur.

The four semi-empirical equations that will be examined relative to the ethanolamine diffusivity measurements are;-

- a) Wilke-Chang.
- b) Scheibel.
- c) Othmer-Thakar.
- d) Ibrahim-Kuloor.

The molecular volumes, calculated from the atomic volumes due to Le Bas, are;-

- i) MEA , $V_A = 73.4$
- ii) DEA , $V_A = 126.7$
- iii) TEA , $V_A = 180.0$

and these molecular volumes will be used in all calculations relating to the semi-empirical equations.

(As an example of the calculation of V_A , consider diethanolamine , $\sim \text{NH}(\text{CH}_2\text{CH}_2\text{OH})_2$

$$\begin{array}{rcl}
 4 \times C & = & 4 \times 14.8 = 59.2 \\
 11 \times H & = & 11 \times 3.7 = 40.7 \\
 2 \times O & = & 2 \times 7.4 = 14.8 \\
 1 \times N & = & 1 \times 12.0 = 12.0 \\
 & & \hline
 & & 126.7
 \end{array}$$

Taking the above values for V_A , and substituting into the semi-empirical equations, the predicted diffusivities are obtained; these diffusivities are given in Table 5. Also tabulated are the calculated molecular volumes(V_A^i) which would bring the predicted diffusivities into agreement with the observed values. On the assumption that the discrepancies between predicted and observed values are entirely due to hydration of the solute , a hydration factor, ϕ , has been calculated . i.e.

$$\phi = \frac{V_A^i - V_A}{V_{\text{water}}} \dots\dots\dots (94)$$

The hydration factor is also tabulated. The assumption of hydration of the solute will be explained in the following section.

A comparison has also been made between the solute empirical constant necessary to satisfy Arnold's equation if this is to give the observed diffusivity, and this is compared with the ratio $\frac{V_A^i}{V_A}$.

Sample calculations for monoethanolamine follow, and the complete calculations are summarised in table 5.

Specimen Calculation of the Application of the
Semi-Empirical Equations to Dilute MEA-water.

a) Wilke-Chang. $D_o = 7.4 \times 10^{-8} \frac{(xM)^{\frac{1}{2}} \cdot T}{\mu \cdot V_A^{0.6}}$

$$V_A^{0.6} = (73.4)^{0.6} = 13.16$$

$$\mu = 0.8897 \text{ cp}$$

$$T = 298^\circ\text{K}$$

$$(xM)^{\frac{1}{2}} = (2.6 \times 18.016)^{\frac{1}{2}} = 6.85$$

whence $D_o = 12.89 \times 10^{-6} \text{ cm}^2/\text{sec.}$

for $D_o = 10.40 \times 10^{-6}$

$$(V_A')^{0.6} = 12.89 / 10.4 \times (V_A)^{0.6}$$

$$\therefore V_A' = 105.$$

$$\text{and } V_A' / V_A = 1.43.$$

b) Scheibel.

$$D_o = 8.2 \times 10^{-8} \cdot \frac{T}{\mu} \left[\frac{1 + \left(\frac{3V_B}{V_A} \right)^{2/3}}{V_A^{1/3}} \right]$$

$$\left(\frac{3V_B}{V_A} \right)^{2/3} = \left(\frac{3 \times 18.9}{73.4} \right)^{2/3} = 0.9131$$

$$V_A^{1/3} = 4.187$$

$$\therefore \underline{D_o = 12.55 \times 10^{-6} \text{ cm}^2/\text{sec}}$$

Put $V_A' = 100$, $D_o = 9.972 \times 10^{-6}$

Put $V_A' = 90$, $D_o = 10.64$ "

when $V_A' = 93.5$, $D_o = 10.4 \times 10^{-6}$

$$\therefore V_A' / V_A = 1.27$$

c) Othmer and Thakar. $D_o = \frac{14.0 \times 10^{-5}}{\mu^{1.1} V_A^{0.6}}$

$$\therefore D_o = \frac{14.0 \times 10^{-5}}{(0.8895)^{1.1} (73.4)^{0.6}} = \underline{12.10 \times 10^{-6}}$$

For $D_o = 10.4 \times 10^{-6}$, $(V_A')^{0.6} = \frac{12.1}{10.4} (V_A)^{0.6}$

$$\therefore V_A' = 94 \quad \text{and} \quad \frac{V_A'}{V_A} = 1.28$$

d) Arnold's Equation. $D_o = \frac{B \cdot \sqrt{\frac{1}{M_1} + \frac{1}{M_2}}}{A_1 \cdot A_2 \sqrt{\mu_2} (V_1^{1/3} + V_2^{1/3})^2}$

For solvent water at 25°C , $B=0.0108$
 $A_2=4.7$

$$\therefore A_2 = \frac{0.0108 \sqrt{\frac{1}{18.016} + \frac{1}{61.08}}}{(10.4 \times 10^{-6})(4.7)(0.8897)^{\frac{1}{2}}(18.9^{1/3} + 73.4^{1/3})^2}$$

$$\therefore \underline{A_1 = 1.338}$$

Table 5

Summary of the Semi-Empirical Equations Calculations.

		MEA	DEA	TEA
Experimental D_o ($\text{cm}^2/\text{sec} \times 10^6$)		10.40	6.624	6.422
D-values calculated by the semi-empirical equations	D_W	12.89	9.285	7.521
	D_S	12.55	8.668	7.115
	D_O	12.10	8.714	7.058
	D_I	9.865	8.549	8.468
Molecular Vol. (Le Bas),	V_A	73.4	126.7	180.0
Molecular Vols. to correlate exptl. D_o to equations (V_A^i)	W	105	224	235
	S	93.5	206.5	218
	O	94	201	211
ϕ	W	1.67	5.15	2.91
	S	1.06	4.2	2.01
	O	1.12	3.92	1.64
V_A^i/V_A	W	1.43	1.77	1.31
	S	1.27	1.64	1.21
	O	1.28	1.59	1.17
Constant A_1 in Arnold's eqn.		1.338	2.514	1.370

As may be seen from the calculations summarised in table 5, there is a significant discrepancy between the diffusion coefficients predicted by the semi-empirical equations and the values obtained experimentally. In an attempt to correlate the agreement between the equations and the experimental results, two viewpoints may be taken;—

- i) The equations are not sufficient in themselves to predict diffusivity, — assuming that V_A and V_B are correct.
- ii) The value of V_A as calculated from Le Bas is in error, due to molecular irregularities of the solute in solution.

The first viewpoint is substantiated by the section "...comments on the...theories and correlations", Ch.I(f), in which it was pointed out that none of the semi-empirical equations could be relied upon to predict a D-value to much better than 10% . Some substantial deviations were illustrated.

However, one system serves to illustrate the generally poor level of prediction of these equations, — the system being sucrose-water. Sucrose-water is a standard system for diffusion measurement calibrations, the value of D being confirmed as $D_0 = 5.22 \times 10^{-6} \text{ cm}^2/\text{sec}$ at 25°C . In solution, though, sucrose forms a hydrate.

Scatchard (62) reviews previous determinations of the hydration of sucrose, and supplements them with his own accurate measurements from the vapour pressure of sucrose solutions. From these, the average degree of hydration of sucrose in very dilute solutions was found to be 6 (i.e. Sucrose = $C_{12}H_{22}O_{11} \cdot 6H_2O$). Taking the molecular volume of anhydrous sucrose as $V_A = 340.4$, and the molecular volume of the hexahydrate as $V_A^1 = 453.8$, the following diffusion coefficients in dilute solutions were predicted by the semi-empirical equations;—

	$C_{12}H_{22}O_{11}$	$C_{12}H_{22}O_{11} \cdot 6H_2O$
Wilke-Chang	5.131	4.319
Scheibel	5.124	4.467
Othmer-Thakar	4.816	4.054

(all the above D-values in $cm^2/sec \times 10^6$)

If Arnold's equation is applied(using $V_A = 340.4$), and putting $D_0 = 5.22 \times 10^{-5}$,

$$A_1 = 1.29$$

It is interesting to note that if the anhydrous molecular volume of 340.4 is multiplied by a factor of 1.29,

$$V_A^1 = 440$$

This is not very different from the calculated molecular volume for the hexahydrate.

The errors of prediction of the equations for the sucrose-water system are,

$$\begin{array}{llll} \text{a) } V_A = 340.4 & 1.5\% & ; & 1.75\% & ; & 7.5\% \\ \text{b) } V_A^i = 453.8 & 17.\% & ; & 15\% & ; & 22\% \end{array}$$

It is thus seen that the semi-empirical equations are not really sufficient in themselves in the prediction of diffusivity. The first viewpoint taken above, therefore, is justified to a large extent. With the ethanolamines, however, the assumption that the inaccuracy of prediction is increased (over the inaccuracy due to the insufficiency of the equations) by the wrong determination of V_A is also valid.

In the following section it will be shown that the ethanolamines are irregular in solution. This irregularity is clearly evident from several considerations, but attempts at calculating the degree of irregularity were not wholly successful. The simplest explanation is to assume the ethanolamines to be hydrated in solution, and to calculate an approximate hydration number in an attempt to correlate the experimental results with the predictions a little more successfully.

VI. THE PHYSICAL CHEMISTRY OF THE ETHANOLAMINES IN SOLUTION.

Ibrahim and Kuloor (3) made the doubtful and unsupported statement that " all the physical properties of the ethanolamines, except freezing point and specific heat, show a simple gradation from mono- to tri-." This statement was made in an attempt to say that diethanolamine should not be much more irregular in solution than either mono- or triethanolamine ; even though Thomas and Furzer's results (1)(2) had first indicated this to be so.

From table 6, an examination of the tabulated physical properties of the pure amines (i.e. not in solution) shows that there is an apparent simple gradation in all properties apart from the freezing point. (note that, contrary to Ibrahim and Kuloor , the specific heat DOES show a simple gradation). The first indication of irregularity is apparent, however, when curves of the vapour pressures of pure amines against temperature are compared. These curves are shown in Fig.21. Below a temperature of 130°C , DEA has a lower total vapour pressure than TEA, whereas above this point the reverse is so.

Table 6

Properties of Pure Ethanolamines(99.9% +).(63)

	MEA	DEA	TEA
Mol.Wt.	61.08	105.14	149.2
Boiling pt., °C	170.3	268.4	338.8
Freezing pt., °C *	10.31	27.95	21.57
Density, gm/ml at 40°C	0.9989	1.0828	1.1116
Viscosity, cps, at 40°C	10.06	196.4	208.1
Refractive index, n_D^{40}	1.4474	1.4720	1.4798
Specific heat, 30°C, cal/gm	0.561	0.531	0.497
Flash point, °F	200	295	380
Heat of fusion, cal/mol ²	4900	6000	6500
Heat of vap. , cal/mol ²	12,150	15,590	16,127

* triethanolamine tends to supercool.

In solution, however, there is abundant evidence of irregularity in physical properties. Thus Ibrahim and Kuloor should have considered the properties in solution rather than the properties of pure amines. The simplest demonstration of this irregularity is shown by viscosity measurements of the amines in solution, where DEA shows a markedly anomalous behaviour. Viscosity measurements were made in this laboratory of MEA, DEA, and TEA solutions at 25°C. These measurements have been amalgamated with the data of Leibush and Shneerson (65), the Shell Chemical Co. (64) and Dow (63). The viscosities of amine solutions at 25°C are tabulated in table 7, and the curves are shown in Fig.22.

A further indication of the anomalous behaviour of DEA, is the variation of the product $D \cdot \mu$ against concentration. Values for $D \cdot \mu$ for MEA, DEA, and TEA are tabulated in table 8, and the curves of $D \cdot \mu$ against concentration are shown in Fig.23.

FIG. 22

Viscosities of
Ethanolamine Solutions.
(25°C)

Table 7.

Viscosities of Ethanolamine Solutions at 25°C (cps).

Concn. wt. %	MEA	DEA	TEA
0	0.8897	0.8897	0.8897
10	1.17	1.28	1.23
20	1.66	1.93	1.75
30	2.42	3.10	2.58
40	3.52	5.47	4.08
50	5.23	10.2	7.09
60	7.55	22.4	14.28
70	11.08	49.2	30.7
75	13.4	69.8	49.2
80	15.1	98.9	79.1
90	17.4	199	206
100	18.9	395	614

FIG. 23

D_{μ} / Concentration
for
the Ethanolamines
(25°C)

Table 8.

The Product $D \cdot \mu$ for the Ethanolamines at 25°C.

	Concn. wt. %	D $\text{cm}^2/\text{sec} \times 10^6$	μ cps	$D \cdot \mu$ $\times 10^6$
MEA	0	10.40	0.8897	9.26
	8.6	9.116	1.110	10.12
	12.22	8.575	1.252	10.72
	15.19	8.101	1.388	11.23
	24.45	6.729	1.960	13.18
	30.56	5.770	2.470	14.24
DEA	0	6.624	0.8897	5.89
	5.45	5.377	1.073	5.77
	10.90	4.877	1.323	6.45
	15.45	4.635	1.591	7.37
	25.6	4.181	2.49	10.4
	34.72	3.733	4.02	14.98
	46.25	3.185	8.00	25.5
	48.09	3.089	8.95	27.7
TEA	0	6.422	0.8897	5.71
	0	6.446	0.8897	5.74
	20.06	4.452	1.75	7.80
	20.06	4.564	1.75	7.98
	30.9	3.385	2.715	9.19

From the viscosity data for ethanolamine solutions at 25°C, it can be seen that in aqueous solutions below about 90% (by weight) DEA has a higher viscosity than TEA.

From the curves of the product $D.\mu$ against concentration, the DEA curve is very steep compared to the MEA and TEA curves, -which are approximately parallel.

The above considerations indicate that aqueous diethanolamine solutions are anomalous in behaviour, and that therefore there is some form of association of diethanolamine in solution. Thus, if there is a hydration effect with all three amines, DEA will tend to exhibit greater irregularities in other physico-chemical measurements than will MEA and TEA.

Trotman-Dickenson (66) made a qualitative study of the importance of hydration effects on the basic strength of amines. Condon (67) presented a general theory for the influence of hydration on the base strength of amines. Both these workers, however, limited their remarks to mainly qualitative assessments of the structure of the amines in solution. Furthermore, the ethanolamines have not been included in their work, due to the presence of additional hydrophilic groups. It is clearly evident, however, from the work of Trotman-Dickenson and Condon that the ethanolamines

will be hydrated in solution, and to quite a significant effect.

For "regular" amines the hydration by hydrogen bonding is schematically shown below, i.e.

However, as mentioned above, the ethanolamines contain hydrophilic groups (the C_2H_4OH groups). Thus as well as the hydration illustrated above, the hydration due to the presence of the alkanol groups must also be considered.

Although it is qualitatively certain that the ethanolamines are hydrated in solution, the extent of hydration is by no means clear. Correspondence with

Professor Condon in fact established that the present state of knowledge on the hydration of amines is wholly inferential, - that is, based on the effect it produces.

On considering Trotman-Dickenson and Condon's work, therefore, the only conclusion to be drawn is that the ethanolamines are hydrated in solution, and with appreciable effect. The deviation of the experimental diffusivities of the ethanolamines from predicted values is explainable on a basis that the molecular volumes concerned are effectively increased by the hydration effect. The greatest difference in values, shown by diethanolamine, is understandable on consideration of the irregularities shown by DEA in solution (e.g. viscosity). All this is in addition to the conclusion that the semi-empirical equations are unsatisfactory in any case.

An attempt was made, through calculations based on hygroscopicity, refractive index measurements, and vapour pressure data, to estimate the hydration effect quantitatively. The calculations were made on the basis of a hydration number, n , as defined previously, to estimate the increase in V_A . These calculations are summarised in the next section.

I(a). Estimation of Hydrate Formation in Ethanolamines
from Hygroscopicity Measurements.

All three ethanolamines are markedly hygroscopic. If, then, the asymptotic values of maximum hygroscopicity are taken from the curves of increase in weight (due to water pick-up) against time, a pointer will be given as to of what order the maximum possible hydration will be.

The data used is taken from Shell (64). It should be noted that Shell recommend that the curves be only used as approximate guides, since the results were affected by the greater volatility of monoethanolamine, and by the absorption of the ethanolamines by other specimens being tested at the same time.

Monoethanolamine. Weight gain = 95% (1400 hrs.)

$$\therefore \phi = 3.2$$

Diethanolamine. Weight gain = 68% $\therefore \phi = 4$

Triethanolamine. Weight gain = 50% $\therefore \phi = 4.2$

VI(b) Estimation of Hydration of Diethanolamine
from Refractive Index Measurements.

Refractivities of Solutions.

Use has been made of refractive index measurements of diethanolamine solutions to test the variation of the experimental values from refractive indices predicted from theoretical considerations.

Partington (69) reviews the equations applicable to refractive indices in solution.

A simple formula was proposed by Beer, Gladstone, and Dale (Phil.Trans., 148, 88, 1858) in which the refractivity of a gas or liquid over a temperature range is connected by the formula

$$\frac{n - 1}{\rho} = \text{constant} = r_G \dots\dots\dots(95)$$

A little later, Lorenz(Ann.Phys.,11,70,1880)and Lorentz (Ann.Phys.,2,641,1880) proposed the most commonly used refractivity formula;-

$$\frac{n^2 - 1}{(n^2 + 2) \cdot \rho} = \text{const} = r_L$$

where r_L and r_G = molar refractivities

n = refractive index

ρ = density

For liquid mixtures and solutions the refractivity is considered to be additively composed of proportions by weight. It has also been found by numerous workers that the Lorenz-Lorentz equation is more suitable for many systems. Thus, in molar terms, the following relationship between the refractivity of the solution and the refractivity of the components (1 and 2) is derived;-

$$\left(\frac{M}{\rho} \right) \left[\frac{n^2 - 1}{n^2 + 2} \right]_{1,2} = x_1 \left(\frac{M}{\rho} \right)_1 \left[\frac{n^2 - 1}{n^2 + 2} \right]_1 + x_2 \left(\frac{M}{\rho} \right)_2 \left[\frac{n^2 - 1}{n^2 + 2} \right]_2 \quad \dots (97)$$

where M = mol.wt., and x = mol fraction.

The above equation is sometimes written,

$$[R]_{1,2} = x_1 [R]_1 + x_2 [R]_2 \quad \dots (98)$$

The above equation has been employed to determine whether refractive index measurements can give any indication as to the molecular abnormality of diethanolamine solutions.

Consider a solution made up of an ethanolamine, subscript E, and water, subscript W. Assuming no hydration, then if wt. of ethanolamine = w_E

and wt. of water = w_W

$$\text{then, mols ethanolamine} = \frac{W_E}{M_E} = x_E$$

$$\text{mols water} = \frac{W_W}{18.016} = x_W$$

However, if Z mols water combine with x_E mols ethanolamine, the following equation is obtained by substituting into the Lorenz-Lorentz equation;

$$\begin{aligned} [R]_{1,2} &= \left[\frac{x_E + Z}{x_E + x_W} \right] \left[\frac{M_E + \frac{Z}{x_E} \cdot M_W}{\rho_E} \right] r_E \\ &+ \left[\frac{x_W - Z}{x_E + x_W} \right] \left[\frac{18.016}{W} \right] r_W \dots\dots (99) \end{aligned}$$

The main assumption that has been taken above is that the density of hydrated amine solution is the same as that for pure amine.

Solving for Z in the above a quadratic is obtained:

$$\begin{aligned} \left[\frac{18.016 \cdot r_E}{x_E \cdot \rho_E} \right] Z^2 + \left[\frac{r_E M_E}{\rho_E} + \frac{r_E \cdot 18.016}{\rho_E} - r_W \cdot 18.016 \right] Z \\ + \left[\frac{r_E x_E M_E}{\rho_E} + r_W x_W M_W - R_{1,2} (x_E + x_W) \right] = 0 \end{aligned} \dots(100)$$

and from Z, ϕ may be found.

The Refractive Index of DEA Solutions.

The refractive index of 12 diethanolamine solutions was measured at 25°C , using a Pulfrich refractometer. A brief description and explanation of the method is given.

In the Pulfrich refractometer, the liquid under test is put in a small quartz cell in contact with a prism. Monochromatic light from a low pressure sodium lamp is focussed through the cell and the angle of refraction is measured by rotating the refractometer telescope and centerring the cross-wires on the emergent sodium D-line. i.e.

For a 60° prism the general equation applicable is

$$n = \sin 60^\circ \sqrt{N^2 - \sin^2 B} - \cos 60^\circ \sin B \dots (101)$$

where n = refractive index of the sample

N = refractive index of the prism

$\angle B$ = angle of emergence (with respect to the normal)

N is determined by measuring B with the cell empty.

Substituting $n = 1$ (refractive index of air) in the general equation, and putting $\angle \phi = \angle B$,

$$N^2 - 1 = \left[\frac{\sin \phi + \cos 60^\circ}{\sin 60^\circ} \right]^2 \dots\dots\dots (102)$$

Using the Pulfrich, the refractive index of a sample may be measured to an accuracy of ± 0.00002 .

All measurements were made at a constant temperature of 25°C , the cell and prism being jacketed by a water bath.

Of the 12 solutions tested, two are in obvious error when the refractivities are plotted against concentration. These are 9.5% and 47% DEA. All the other points are accurate. The refractivity measurements are given in table 9.

Using the experimental results and also refractivity values published by Shell(64), the possible degree

TABLE 9 - Refractive Index Measurements (Pulfrich) for DEA solutions at 25°

TABLE FOR READING GONIOMETER (FULL) FOR DEA SOLUTIONS at 22										
Soln No.	(wt %) DEA CONCL.	ϕ_i °	ϕ_r "	$\sin \phi$	θ °	"	$\sin \theta$	N	n	
	0.0	47°	54"	39"	18°	19"	4"	0.31428703	1.748454	1.332399
	1.0	47°	55"	14"	4°	15"	7"	0.07414233	1.748562	1.475866
1	0.045773	47°	54"	45"	17°	46"	1"	0.30514594	1.748473	1.338411
2	0.09498	47°	55"	5"	17°	17"	56"	0.29735636	1.748534	1.343539
3	0.186862	47°	55"	0"	15°	56"	37"	0.27469118	1.748519	1.358113
4	0.290262	47°	54"	42"	14°	32"	32"	0.25104645	1.748463	1.373001
5	0.397326	47°	54"	59"	12°	59"	36"	0.22483768	1.748516	1.389294
6	0.471402	47°	55"	42"	10°	54"	56"	0.18936203	1.748648	1.410787
7	0.587947	47°	55"	20"	10°	7"	16"	0.17572946	1.748580	1.418784
8	0.756752	47°	55"	11"	7°	37"	10"	0.13259277	1.748553	1.443635
9	0.839037	47°	55"	24"	6°	25"	56"	0.11202779	1.748593	1.455201
10	0.915069	47°	54"	44"	5°	23"	40"	0.09401178	1.748473	1.465023

of hydration was calculated as above. The theoretical refractive index of the solutions (assuming no hydration) was also calculated. The results are shown in table 10.

Table 10

Calculation of DEA Hydration from refractivity Data.

DEA Concn. wt. %	n_{exp}	$n_{theor.}$	$n_{exp} - n_{th.}$	ϕ
DEA Solutions at 25°C (experimental)				
4.58	1.33841	1.33827	0.00014	0.05
18.69	1.35811	1.35675	0.00136	0.02
29.03	1.37300	1.37020	0.00280	0.02
39.73	1.38929	1.38545	0.00384	0.02
58.79	1.41878	1.41267	0.00611	0.02
75.68	1.44364	1.43781	0.00583	0.01
83.90	1.45520	1.45044	0.00476	0.01
91.51	1.46502	1.46233	0.00269	0.01
DEA Solutions at 60°C (Shell)				
25	1.36380	1.35958	0.00422	0.07
50	1.39850	1.39315	0.00535	0.03
75	1.43500	1.42864	0.00636	0.02
90	1.45470	1.45092	0.00378	0.01
95	1.46050	1.45851	0.00199	0.00

Comments on the Refractive Indices of DEA.

In both the Shell data and the experimental results the difference between the experimental and the calculated refractive indices is appreciable (maximum of 0.0064 in 1.435). However, calculations to determine the possible hydration using the Lorenz-Lorentz equation showed insignificant changes in the constitution of the ethanolamine (maximum possible hydration of 0.07 mols water to 1 mol DEA).

Further calculations were made to see what effect an appreciable degree of hydration should have on the experimental refractive index if the Lorenz-Lorentz equation was strictly true. (i.e. the molecularity of the solution components being of relevance).

Using the figures for 25% DEA at 60°C (these indicating the greatest molecular deviation) the refractive index that would be observed if the equation were true was calculated for two cases;

Assuming 1) 0.25 mols water to 0.2377782 mols DEA ($\phi=1.05$)

2) 0.5 " " " " " " ($\phi=2.1$)

(since 25% DEA = 0.237782 mols DEA, 4.1629662 mols H₂O)

The refractive indices that would satisfy the equation were

calculated to be 1) 1.51858 $\therefore n_{\text{ex.}} - n_{\text{th.}} = 0.15900$

2) 1.75814 $\therefore n_{\text{ex.}} - n_{\text{th.}} = 0.39856$

$n_{\text{ex.}} - n_{\text{th.}}$ being 40 and 90 times greater respectively than the observed values.

Calculations were then made to see whether an associated molecule would be indicated by the experimental refractive index. Again, for the 25% solution, the increased molecular weight that would account for the deviation was insignificant, - being 108.9 ($M_{\text{DEA}} = 105.14$).

It is apparent, then, that the measurement of the refractive indices of a range of solutions is not a valid method of determining molecular irregularity in solution.

This could be due to several reasons, such as the inaccuracy of the Lorenz-Lorentz equation. One factor that seems very probable is that the refractive index is an additive function of the pure components only. Thus, hydration and association, which are physical and not chemical changes, would not influence the refractive index to any great extent. i.e. if we have X mols DEA, Y mols H_2O , and the DEA hydrates with Z mols of this water, then the refractive index is not influenced by this movement of Z to X at all, - being a function only of X and Y.

VI(c) Estimation of the possible Hydration of the
Ethanolamines from Vapour Pressure Data.

The total vapour pressure of a binary solution is related to the mol.fraction of its components by the expression,

$$x P_1 + (1 - x) P_2 = \pi \quad \dots\dots(103)$$

where P_1 is the partial pressure of component 1, of concentration x mol fraction; P_2 is the partial pressure of component 2, of concentration $(1 - x)$ mol fraction; and π is the total pressure.

The total vapour pressures of 10% MEA, 10% DEA, and 20% DEA solutions are taken from the data of the Shell Chemical Co. (70). The total vapour pressures (π) are tabulated in table 11 , together with the vapour pressures of water (P_W) and ethanolamine (P_E). The vapour pressure of water is taken from Perry (71) and the vapour pressures of the ethanolamines are calculated from the data of McDonald et al (72). The Antoine coefficients to satisfy the relationship $\log_{10} P_E = A - \frac{B}{t + C}$

are	$A = 7.738$	} MEA	$A = 8.13968$	} DEA
	$B = 1732.11$		$B = 2328.56$	
	$C = 186.215$		$C = 174.399$	

Using the relationship

$$x = \frac{\frac{E\%}{M_E} + Z}{\frac{E\%}{M_E} + \frac{100 - E\%}{M_W}} \dots\dots\dots (104)$$

and $\phi = \frac{Z}{E\%/M_E} \dots\dots\dots (105)$

where $E\%$ = % ethanolamine by weight ; M_E = molecular wt. of ethanolamine ; M_W = mol.wt. of water .

determining x from

$$xP_E + (1 - x)P_W = \pi$$

the hydration number was calculated . The results are tabulated in table 11.

Table 11.

Possible Hydration of Ethanolamines from Vap. Press. Data.

	T°C	π	P _W	P _E	Z	ϕ
10% MEA	25	21.793	23.756	0.3445	0.2489	1.520
	27	24.494	26.739	0.4113	0.2762	1.687
	41	53.025	58.340	1.303	0.3171	1.937
	49.5	81.779	90.24	2.453	0.3335	2.037
	51.6	90.672	100.6	2.848	0.3603	2.201
	69.7	208.54	230.7	9.346	0.3529	2.155
	69.8	209.44	231.7	9.380	0.3526	2.154
	88.1	443.36	488.0	26.53	0.3354	2.048
	90.5	486.23	535.82	30.09	0.3421	2.090
	98.8	662.50	727.98	45.78	0.3315	2.025
	99.8	686.97	754.58	48.08	0.3300	2.016
10% DEA				(x10 ²)		
	24.3	20.202	22.785	0.0263	0.4809	5.056
	25	21.047	23.756	0.0290	0.4842	5.091
	30.9	29.503	33.503	0.0627	0.5115	5.377
	45.6	64.726	74.12	0.359	0.5489	5.771
	48.6	75.298	86.28	0.499	0.5522	5.806
	64.9	163.27	186.72	2.564	0.5431	5.711
	84.2	371.81	420.16	13.66	0.4898	5.150
10% TEA	25	20.969	23.756	0.029	0.3534	1.858
	30.8	29.245	33.312	0.0619	0.3751	1.972
	43.6	58.196	66.86	0.287	0.3999	2.102
	66.6	174.48	201.41	3.003	0.4291	2.256
	85.4	383.15	440.61	15.03	0.4139	2.176
	99.0	642.33	733.24	41.94	0.3842	2.020

The calculations to estimate a degree of hydration from hygroscopicity, refractive index measurements, and vapour pressure data were not entirely successful. However, using the hydration numbers calculated from hygroscopicity and the vapour pressure data, it will be of interest to compare the diffusion coefficients predicted (from the semi-empirical equations) using a V_A which includes a hydration number with those coefficients previously predicted. The ϕ -values from vapour pressure data for MEA and DEA will be taken as 2 and 5 respectively. Thus the recalculated molecular volumes, V_A' , will be as in table 12.

Table 12.

Estimated Hydration Numbers and Related Molecular Volumes.

	V_A	From Hyg. data		From v.p. data	
		ϕ	V_A'	ϕ	V_A'
MEA	73.4	3.2	133	2	111
DEA	126.7	4	202	5	221
TEA	180.0	4.2	260		

Using these V_A' values, the diffusion coefficients predicted by the Wilke-Chang, Scheibel, and Othmer-Thakar equations will be as in table 13.

Table 13.

Predicted Diffusivities Using Estimated Hydration Numbers.

		No. Hydr.		from hydr.		from v.p.	
		D x10 ⁶	%error	D x10 ⁶	%error	D x10 ⁶	%error
MEA	Wilke	12.89	+28	9.13	-12	10.0	-4
	Sch.	12.55	+21	8.41	-19	9.35	-10
	Oth.	12.10	+16	8.55	-18	9.42	-10
DEA	Wilke	9.285	+40	7.01	+6	6.64	+0.25
	Sch.	8.668	+31	6.67	+0.7	6.36	-4
	Oth.	8.714	+32	6.60	0	6.24	-5.5
TEA	Wilke	7.521	+17	6.13	-4.5		
	Sch.	7.115	+11	5.84	-9		
	Oth.	7.058	+9.9	5.74	-10.5		

(all D-values above in cm²/sec)

From table 13, it can be seen that the inclusion of a hydration number in the calculation of the ethanolamine molecular volume brings the diffusivities predicted by the semi-empirical equations into much better agreement with the experimental diffusivities. In view of this improved correlation, it would appear that where abnormalities are known to occur in solution, an allowance should be made for this when calculating the molecular volumes for use in the semi-empirical equations. This is somewhat of a stop-gap measure, for the semi-empirical equations would appear to be unreliable in any case.

It is hoped that in the future, with an increasing volume of accurate diffusion measurements to hand, an accurate semi-empirical equation can be formulated which allows for molecular irregularities in solution. In the meantime, it is suggested that for any known molecular irregularity, allowance for this should be made in calculating the molecular volumes for use in the semi-empirical equations.

VII. SUMMARY

The wavefront shearing optical interferometer, as constructed in this laboratory, has proved to be a highly accurate and sensitive instrument. A new method of computation has been devised, based on the method of least squares, and necessitating the use of a computer, which has facilitated the calculation of diffusivity (with increased accuracy).

The programme of investigation of diffusivity in liquid-liquid systems, using the wavefront shearing interferometer, involved the systems ethanolamines-water (MEA, DEA, and TEA - water). The accuracy of the interferometer was established by determining the diffusion coefficient for dilute sucrose-water solutions, this giving a satisfactory comparison with established results. Diffusion coefficients for the ethanolamine-water systems were measured over a range of concentrations.

The diffusivities of the ethanolamines, as measured in this work, were then compared with the values obtained by Thomas and Furzer (1) (2) using a Gouy interferometer. Their calculations were checked, and it was established that their results were only of limited accuracy.

However, the diffusivity values for dilute ethanolamine solutions as measured by the above workers were almost identical with those obtained in this study. Also, the diffusivity-concentration curves for DEA and TEA are similar in the two cases.

It is important to note that the diffusivities of the dilute ethanolamine solutions are in agreement, for it was these values that excited critical comment from Ibrahim and Kuloor (3). In view of this criticism, the application of diffusional theory (especially the existing semi-empirical equations) to the ethanolamine-water systems was thoroughly examined. From this appraisal, two definite conclusions may be drawn;~

a) the semi-empirical equations are in themselves highly unsatisfactory. The average accuracy of the equations is in no case better than 10% , and reported deviations are as high as 30% in error in predicting diffusivity. The failings of these equations were pointed out, ~ one of the chief weaknesses being the inclusion of many electrolytic and non-ideal systems for formulating the equations, yet without making allowances for molecular irregularities in solution.

b) the ethanolamines are hydrated in solution to

an appreciable extent. Diethanolamine, in particular, exhibits anomalous behaviour (as shown by viscosity measurements). In an attempt to ascertain the degree of hydration, calculations were made using hygroscopicity, refractive index, and vapour pressure data for the ethanolamines in solution. No definite hydration number was determined, but the hydration numbers calculated were used in recalculating the molecular volumes for use in the semi-empirical equations.

It was shown that by accounting for molecular irregularities (by increasing the molecular volume) when applying the semi-empirical equations, a much more satisfactory agreement is obtained between predicted and observed diffusivity values.

A possible indication of the necessary increase in the molecular volume is shown by the constant A_1 in Arnold's equation. This fact may be coincidental, but deserves a slightly less cursory investigation.

It is suggested that, in future, when the semi-empirical equations are used to predict diffusivity, that some consideration be made as to any molecular irregularities in solution. A far more satisfactory outcome would be a complete re-examination of the theories of diffusion in liquids, with the supplementing of these semi-

empirical equations by equations based on ideal systems which take into account any molecular irregularities.

VII(a) Suggestions for Further Work.

The optical arrangement of the wavefront shearing interferometer is perfectly satisfactory, and needs no alteration. Likewise, the recording and measurement of the fringe pairs, and the calculation of the diffusivity need no improvement.

The only experimental improvement that could be made, though it is not essential, is the redesign of the flowing-junction cell. The following improvements could be made with the cell;-

i) Inclusion of a baffle chamber between the mercury reservoir and the liquid reservoirs. This would eliminate any vibration transmitted by the mercury when turning off the mercury tap at the start of diffusion.

ii) Retention of the present double chamber arrangement, but the inclusion of two adjustable exit slits in each chamber. The adjustable slits would be engineered from knife-edges vertically movable by micrometer

screw-threads. This arrangement would enable an extremely sharp interface to be obtained.

iii) Fabrication of all the glasswork in a pressure tight "Quick-fit" type arrangement. At the moment, cleaning the glasswork is laborious and not very efficient since all the glasswork is in one unit. However, if the reservoirs and taps could individually be quickly removed, the setting up of the cell for experimentation would be greatly facilitated.

The possibilities of the application of the wavefront shearing interferometer to liquid-liquid systems is endless. Even today, diffusional investigations are being made (73) using diaphragm cells, which are considerably less convenient and accurate to use than this interferometer. With the superiority of the interferometer, a wealth of useful data could be rapidly accomplished.

The wavefront shearing interferometer also has great potential use for thermal diffusion measurements.

Bryngdahl (74) has pioneered the interferometer's use for this purpose, and Gustafsson et al (75) have recently started work in this field .

One main project which exploits the novel use of the wavefront shearing interferometer is already under way.

This is the application of the wavefront shearing interferometer to gas-liquid diffusion. Because of the superior sensitivity of the instrument, this is the first time that an interferometer has been used in this field with any measure of success. This application, which has immensely exciting possibilities, is described in Part II of this work.

Other recent developements include the micro-wedge interferometer (76) (77) and Moiré interferometry(78) (79), both of which it is hoped to investigate in this laboratory at a later date.

There is one other field of investigation that is not being studied yet, but which must be thoroughly examined in the future. This is the subject of liquid diffusion theory, - and in particular the formulation of a new semi-empirical equation which will enable diffusivity to be predicted a little more successfully than at present. It is suggested that the basis of this work take the form of,

- a) amassing diffusivity data for systems as near to ideal as possible,
- b) formulating an equation from these carefully vetted systems, and then
- c) introducing a molecular irregularity factor into

this equation that would account for deviations in abnormal liquid systems.

As mentioned above, the wavefront shearing interferometer is being applied in this laboratory to gas-liquid diffusion. This quite novel developement will now be described in Part II of this work.

PART II.

THE APPLICATION OF THE WAVEFRONT SHEARING INTERFEROMETER

to

GAS-LIQUID DIFFUSION MEASUREMENTS.

INTRODUCTION.

With the wavefront shearing interferometer built, and proved as being a highly accurate and sensitive instrument for liquid-liquid diffusion measurements, it is a natural progression to apply the interferometer to gas-liquid diffusion.

Firstly, for the physical absorption of a gas into a liquid, the possibility of measuring D_A (the diffusion coefficient of the gas into the liquid) by an interferometric technique is an attractive proposition. The most convenient existing methods for the determination of diffusion coefficients of gases in liquids involve the measurement of mass transfer rates under unsteady-state conditions, and suffer from the inherent disadvantage of requiring flowing systems. The laminar jet technique which has been used in this laboratory by Thomas and Adams (80)(81) is an accurate means of determining mass transfer rates, but a degree of error is introduced by the presence of entry and end effects.

Thus, if it were possible to absorb a gas into a liquid (with no reaction) and to calculate D_A from interferometric measurements of the concentration profiles

made "in situ", and without necessitating an extensive knowledge of the physical properties of the system, then a useful technique would be evolved.

Secondly, for absorption of a gas into a liquid accompanied by a chemical reaction, it would again be highly desirable to be able to make measurements "in situ". In absorption accompanied by a rapid second-order irreversible reaction, all existing theories account for the formation and movement of a "reaction zone". The movement of this reaction zone is related to the physical properties of the system, and by calculating this movement the mass transfer rate may be predicted. Previous investigations, using such apparatus as the laminar jet, have produced good agreement between experimental results and theory. Using the wavefront shearing interferometer, it may be possible to observe the actual movement of this reaction zone in a stagnant system, since a modification to the interferometer enables a direct observation of concentration profiles to be made. Thus, the presence of the reaction zone can be confirmed by direct observation, and a possible means is formulated of relating theory to practice.

There are limits to the applicability of interferometry to gas-liquid absorption. The first consideration

is the sensitivity of the interferometer in relation to the system under investigation. This will be discussed in some detail further on. Another consideration is the presence of heat effects associated with the absorption of a gas into a liquid. The elimination of these effects will be to a large degree experimental, and this again will be discussed in the relevant section.

A survey of the theories relevant to physical absorption and absorption accompanied by a rapid second-order irreversible reaction follow.

In the experimental investigations so far undertaken in this laboratory, the following two systems have so far been investigated:-

- 1) Carbon Dioxide into water(physical absorption).
- 2) Carbon Dioxide into dilute monoethanolamine solution(absorption with fast 2nd order reaction)

The results of these investigations are reported.

I. THEORY OF GAS-LIQUID DIFFUSION.

I(a) Gas Absorption Without Reaction.

The theories for the absorption of a gas by a liquid without chemical reaction may be broadly classified under

1) Film theory

2) Penetration Theory.

Film Theory

Whitman (82) proposed the two-film concept, whereby at the interface between a gas and a liquid it could be assumed there were two films adjacent to the interface. (see Fig.1)

The rate of mass transfer is defined by the following equations

$$N_A = K_L^O (c_{Ai} - c) = K_G (p - p_i) \dots\dots(1)$$

and the liquid film mass transfer coefficient is defined by

$$K_L^O = \frac{D_A}{x_L} \dots\dots\dots(2)$$

FIG. 1

FIG. 2

(A)

(B)

Penetration Theory.

Higbie (83) showed that the Whitman film mechanism was only true if the penetration of the liquid film by the gas continued uninterrupted until steady flow could be assumed (see Fig. 2).

The dotted lines in Fig.2 represent the concentration profile of A and B in the initial penetration process.

From a solution of Fick's second law for the appropriate boundary conditions, Higbie obtained

$$\frac{c}{c_{Ai}} = \frac{1}{\sqrt{\pi Dt}} \int_x^{\infty} e^{-x^2/4Dt} dx \quad \dots\dots(3)$$

which is $\frac{c}{c_{Ai}} = \text{erfc}(x/2\sqrt{Dt}) \quad \dots\dots\dots(4)$

A similar solution is given by Crank (10).

From this, K_L^0 is defined by

$$K_L^0 = 2\sqrt{\frac{D_A}{\pi t}} \quad \dots\dots\dots(5)$$

I(b) . Gas Absorption With Reaction.

The monograph by Sherwood and Pigford (84) gives an account of the theories applicable to absorption with reaction. There are two theoretical bases for the theoretical discussion of the kinetic theory of simultaneous diffusion and chemical reaction;

a) assuming a physical film of negligible capacity but finite resistance (film theory).

b) assuming unsteady state molecular diffusion of the solute (penetration theory).

Rapid second order reactions only will be considered in this section.

Film Theory, -2nd Order Reaction (Hatta).

A dissolves and reacts with B at the phase boundary; the product AB begins to diffuse towards the main boundary of the liquid; as B is depleted near the interface, A diffuses further into the bulk of the liquid to meet B diffusing in the opposite direction. Thus the reaction zone moves away from the interface, until after a short while the zone reaches its equilibrium position (see Fig.3).

FIG. 3

Hatta Film Theory.

FIG. 4

Curves of
 ϕ vs $\sqrt{M}$

For the gas film,

$$N_A = K_G (p - p_i) \dots\dots\dots(6)$$

also
$$N_A = K_L^O (c_{Ai} - 0) = \frac{D_A}{x_L} (c_{Ai} - 0) \dots\dots(7)$$

and
$$-N_B = \frac{D_B}{x''} (c_{Bo} - 0) \dots\dots\dots(8)$$

By assuming Henry's Law, $p_i = Hc_{Ai}$, combining equations 6,7,&8, and eliminating gas phase concentrations,

$$N_A = \frac{c_{Ai} + (D_B/D_A) c_{Bo}}{x_L/D_A} \dots\dots\dots(9)$$

and hence,
$$K_L = \frac{D_A}{x_L} \left[1 + (D_B/D_A) \left(\frac{c_{Bo}}{c_{Ai}} \right) \right]$$

or,
$$\phi = \frac{K_L}{K_L^O} = 1 + (D_B/D_A) \left(\frac{c_{Bo}}{c_{Ai}} \right) \dots\dots(10)$$

$$= 1 + r \cdot q \dots\dots\dots(11)$$

where ϕ is the ratio between the mass transfer coefficients with and without reaction, and

$$r = \left(\frac{D_B}{D_A} \right), \quad q = \left(\frac{c_{Bo}}{c_{Ai}} \right) \dots\dots(12)$$

By dimensional analysis, Van Krevelen and Hoftyzer(85)(86) related ϕ to the dimensionless products

$$\sqrt{M} = \frac{(k D_A c_{Bo})^{\frac{1}{2}}}{K_L^O} \quad \text{and} \quad q$$

where k is the reaction velocity constant in

$$-\frac{dA}{dt} = -\frac{dB}{dt} = k.AB \quad \dots\dots\dots(13)$$

Brian (87) has shown that the film theory predicts that

ϕ is a unique function of $\sqrt{M}$, and $r.q$, and shows that the film theory solution may be approximated by

$$\phi = \frac{\sqrt{M} \sqrt{1 - \frac{\phi - 1}{rq}}}{\tanh \sqrt{M} \sqrt{1 - \frac{\phi - 1}{rq}}} \quad \dots\dots\dots(14)$$

$$\tanh x = \frac{e^x - e^{-x}}{e^x + e^{-x}}, \text{ and for } x > 2, \tanh x \approx 1$$

This relationship between ϕ , $\sqrt{M}$, and rq is described by Gilliland et al (88), Brian et al (89), and Thomas(81), who have plotted ϕ against $\sqrt{M}$ with $1 + r.q$ as parameter (see Fig.4).

From the curves relating ϕ to $\sqrt{M}$ the following points may be observed;

a) at low values of $\sqrt{M}$ (small k), ϕ tends to unity. Thus a slow reaction will not increase the mass transfer coefficient.

b) At large values of $\sqrt{M}$ (k is large) , ϕ approaches an asymptote for each $r.q$ value. This asymptote corresponds to an infinitely rapid reaction region, and is given by

$$\phi_a = 1 + r.q \quad \dots\dots\dots(15)$$

c) For any fixed value of $\sqrt{M}$, ϕ approaches an asymptote for large values of $r.q$. As this asymptote is approached, c_{Bo} is essentially constant throughout the liquid phase and the reaction becomes pseudo first order. The curve of the asymptote is closely approximated to by the equation

$$\phi = \sqrt{M} \quad \dots\dots\dots(16)$$

$$\text{whence } K_L = \sqrt{k \cdot D_A \cdot c_{Bo}} \quad \dots\dots\dots(17)$$

Penetration Theory, - Rapid 2nd order Irreversible Reaction.

The derivation for the theory for unsteady state absorption with rapid second order reaction is described adequately by Sherwood and Pigford (84).

The model for the diffusion of A into B, with

reaction $A + B \rightarrow AB$, is similar to the film theory model of Hatta. As A is absorbed, B molecules near the interface are consumed in the reaction and are replenished by diffusion of additional B molecules from the main body of the liquid. Since the reaction velocity is assumed infinite, the assumption follows that reaction is instantaneous when A and B are brought together, and thus the point where A and B meet each other will move further away from the interface. The rate of absorption of A therefore grows progressively smaller as the molecules have to diffuse further into the liquid in order to react.

Since A does not react with B at a distance $0 < x < x'$ (where $x' =$ distance of the reaction zone from the interface), and B does not react at $x' < x < \infty$, then the diffusion of A and B are governed by

$$D_A \cdot \frac{\partial^2 c_A}{\partial x^2} = \frac{\partial c_A}{\partial \theta} \dots\dots\dots (18)$$

$$D_B \cdot \frac{\partial^2 c_B}{\partial x^2} = \frac{\partial c_B}{\partial \theta} \dots\dots\dots (19)$$

where $\theta =$ time.

In Fig.5, concentration profiles for A and B are shown at times θ and $\theta + d\theta$, the reaction zone having moved dx' in time $d\theta$.

FIG. 5

Penetration Theory Model for
Absorption + Fast 2nd order Reaction.

From the geometry of the triangles MNP and MPO (Fig.5),

$$MN = \frac{\partial c_A}{\partial \theta} \cdot d\theta = - \frac{\partial c_A}{\partial x} \cdot dx' \dots\dots\dots(20)$$

$$OP = - \frac{\partial c_B}{\partial \theta} \cdot d\theta = \frac{\partial c_B}{\partial \theta} \cdot dx' \dots\dots\dots(21)$$

From 20 and 21,

$$dx'/d\theta = - \frac{\partial c_A}{\partial \theta} / \frac{\partial c_A}{\partial x} = - \frac{\partial c_B}{\partial \theta} / \frac{\partial c_B}{\partial x} \dots\dots(22)$$

Solutions of equations 18 and 19 to satisfy the necessary boundary conditions are ;=

$$c_A = A_1 + B_1 \operatorname{erf} \frac{x}{2\sqrt{D_A \theta}} \dots\dots\dots(23)$$

$$c_B = A_2 + B_2 \operatorname{erf} \frac{x}{2\sqrt{D_B \theta}} \dots\dots\dots(24)$$

$$\text{where } \operatorname{erf} z = \frac{2}{\sqrt{\pi}} \int_0^z e^{-t^2} dt \dots\dots\dots(25)$$

Differentiating 23 and 24 with respect to x and θ ,
substituting into 22, and putting $x = x'$, we get

$$\frac{dx'}{d\theta} = \frac{x'}{2\theta} \dots\dots\dots (26)$$

On integrating

$$\underline{x' = 2\sqrt{\alpha} \sqrt{\theta}} \dots\dots\dots (27)$$

where $2\sqrt{\alpha}$ is the integration constant.

Equation 27 therefore relates the movement of the reaction zone to time.

The constant $\sqrt{\alpha}$ is determined by considering the boundary conditions .

i.e. 1./ $c_A = c_{Ai}$, $x = 0$, $\theta > 0$.

2./ $c_B = c_{Bo}$, $x = \infty$, $\theta \geq 0$.

3./ $c_B = c_{Bo}$, $\theta = 0$, $x > 0$.

4./ $c_A = 0$, $c_{Bo} = 0$, when $x = x'$, $\theta > 0$.

5./ $D_A \frac{\partial c_A}{\partial x} + D_B \frac{\partial c_B}{\partial x} = 0$, when $x = x'$

Applying the boundary conditions to equations 22, 23, 24, 26, and 27 to solve for the constants A_1 , A_2 , B_1 , B_2 and α ,

$$A_1 = c_{Ai} \dots\dots\dots (28)$$

$$A_2 + B_2 = c_{Bo} \dots\dots\dots (29)$$

$$A_1 + B_1 \operatorname{erf}\left(\frac{\alpha}{D_A}\right)^{\frac{1}{2}} = 0 \dots\dots(30)$$

$$A_2 + B_2 \operatorname{erf}\left(\frac{\alpha}{D_B}\right)^{\frac{1}{2}} = 0 \dots\dots(31)$$

$$B_1 \sqrt{D_A} e^{-(\alpha/D_A)} + B_2 \sqrt{D_B} e^{-(\alpha/D_B)} = 0 \dots(32)$$

Solving eqns. 28 to 32

$$\left(\frac{D_B}{D_A}\right)^{\frac{1}{2}} \left(\frac{c_{Bo}}{c_{Ai}}\right) e^{(\alpha/D_A)(1-D_A/D_B)} \operatorname{erf}\left(\frac{\alpha}{D_A}\right)^{\frac{1}{2}} + \operatorname{erf}\left(\frac{\alpha}{D_B}\right)^{\frac{1}{2}} = 1$$

.....(33)

$$\text{or, } \sqrt{r} e^{\sigma_A^2(1-1/r)} \operatorname{erf} \sigma_A + \operatorname{erf} \sigma_A (1/\sqrt{r}) = 1 \dots(33a)$$

$$\text{where } \sigma_A = \frac{\sqrt{\alpha}}{\sqrt{D_A}} \text{ and } r = \frac{D_B}{D_A}$$

Thus the integration constant $\sqrt{\alpha}$, from eqn.27, describing the movement of the reaction zone with time, is given by the implicit function described by equation 33

Dankwerts (90) has presented a similar equation to 33, but without any discussion or mathematical developement. The equation Dankwerts gives is,

$$\left(\frac{c_{Ai}}{\sqrt{D_B}}\right) e^{\sigma_B^2} \operatorname{erfc} \sigma_B - \left(\frac{c_{Bo}}{\sqrt{D_A}}\right) e^{\sigma_A^2} \operatorname{erf} \sigma_A e^{\sigma_A^2} = 0 \quad \dots (34)$$

Rearranging this equation by putting

$$\sigma_B = \sigma_A \sqrt{r}$$

$$\text{and } \operatorname{erfc} z = 1 - \operatorname{erf} z$$

the same result is obtained as with equation 33

The rate of mass transfer, N_A , is given by

$$N_A = -D_A \left(\frac{dc_A}{dx} \right)_{x=0} \quad \dots (35)$$

From equations 23, 28, and 30, this is equal to

$$N_A = \frac{c_{Ai}}{\operatorname{erf}\left(\frac{\alpha}{D_A}\right)^{\frac{1}{2}}} \cdot \left(\frac{D_A}{\pi \theta}\right)^{\frac{1}{2}} \quad \dots (36)$$

and the average rate of absorption up to time θ is given by

$$(N_A)_{av} = \frac{c_{Ai}}{\operatorname{erf}\left(\frac{\alpha}{D_A}\right)^{\frac{1}{2}}} \cdot 2\left(\frac{D_A}{\pi \theta}\right)^{\frac{1}{2}} \quad \dots (37)$$

If the liquid film mass transfer coefficient, K_L , is defined on the basis of a driving force ($c_{Ai} - 0$), we get

$$K_L = \frac{2}{\sqrt{\pi}} \cdot \frac{(D_A/\theta)^{\frac{1}{2}}}{\text{erf } \sigma_A} \dots\dots\dots (38)$$

This same result is given by Dankwerts also, but without any developement.

Brian (87) has predicted from the penetration theory that ϕ is a unique function of the variables $\sqrt{M}$, r , and q . From the preceding section, it will be remembered that for the film theory ϕ is a function of $\sqrt{M}$, and $r \cdot q$.

For the penetration theory there is no mathematical solution relating ϕ , $\sqrt{M}$, r , and q when $r \neq 1$, $k \neq \infty$.

As an approximation,

$$\text{putting } \phi_a - 1 = r \cdot q \dots\dots\dots (39)$$

$$\text{where } \phi_a = 1 / \text{erf } \sigma_A \dots\dots\dots (40)$$

$$\text{and } q \sqrt{r} = \frac{1 - (\frac{\sigma_A}{\sqrt{r}})}{\text{erf } \sigma_A e^{\sigma_A^2 (1 - 1/r)}} \dots\dots\dots (41)$$

$$\text{then } \phi = \frac{\sqrt{M} \sqrt{1 - \frac{\phi - 1}{\phi_a - 1}}}{\tanh \sqrt{M} \sqrt{1 - \frac{\phi - 1}{\phi_a - 1}}} \dots\dots\dots (42)$$

The curves relating ϕ to $\sqrt{M}$, with $\phi_a - 1$ as parameter, are as in Fig. 4, and the same observations to these curves apply as with the film theory.

II. THE EXPERIMENTAL INVESTIGATION OF GAS-LIQUID DIFFUSION.

II(a). Sensitivity of the Wavefront Shearing Interferometer.

As mentioned in the introduction, the sensitivity of the wavefront shearing interferometer will be a prime consideration if the interferometer is to be successful for a particular system. Generally speaking, the refractive index of a liquid saturated with a moderately soluble gas is negligibly different from that of the pure liquid. The penetration theory for physical absorption, eqn 4, gives that

$$\frac{c}{c_{Ai}} = \operatorname{erfc} \left(\frac{x}{2\sqrt{Dt}} \right)$$

Assuming, again, that the refractive index/concentration relationship is a straight line, then,

$$\frac{n}{n_{Ai}} = \operatorname{erfc} \left(\frac{x}{2\sqrt{Dt}} \right) \dots\dots\dots(43)$$

Theoretically, with the wavefront shearing interferometer using a 6.3 cm cell and the mercury green line of 5461 Å, the minimum refractive index difference

measurable, $\Delta n_{\min} = 9 \times 10^{-6}$

Thus, for any gas-liquid system the refractive index difference introduced by contact between the gas and the liquid must be above this figure. For physical absorption, $n_{\text{solvent}} - n_{\text{Ai}}$ must be above this minimum. In absorption with reaction, due to the presence of reaction products, only experience will show if $\Delta n_{\min}$ is attained.

Although the figure of $\Delta n_{\min} = 9 \times 10^{-6}$ is a theoretical figure for this interferometer, it can be shown that this limit was approached when examining mutual diffusion in liquid systems. For instance, the average concentration difference employed was 0.06%. For diethanolamine, $\Delta c = 0.06\% \equiv \Delta n = 9 \times 10^{-5}$. Although the Δn is relatively high in this case, the concentration difference used was only chosen because about 8 fringe pairs (a convenient number) were formed at the start of diffusion. It was quite feasible to work at a lower concentration(and hence refractive index) difference.

It had been decided to first apply the interferometer to the physical absorption of carbon dioxide into water. Thus, as an illustration of the criterion of sensitivity applied to a system, the preliminary investigations will be described here.

The only data that exists on the refractive index of CO_2 in water is reported by Watson (91). The study made by Watson is only for dilute CO_2 solutions, from which he gives

$$- 4.6 \Delta n = 5.1 \times 10^4 \cdot c \quad \dots\dots\dots (44)$$

$$\text{where } \Delta n = (n_{\text{water}} - n_{\text{solution}}) \times 10^7$$

$$c = \text{CO}_2 \text{ concn., mols/litre}$$

If this relationship is applied to CO_2 -saturated water ($c = 3.31 \times 10^{-2}$ g.mols/litre) then,

$$\Delta n \simeq 3 \times 10^{-5}$$

Thus the refractive index difference should be very close to Δn_{min} .

A check on the refractive index of water saturated with CO_2 was attempted in this laboratory. Seven solutions were prepared by bubbling CO_2 through 100ml water at a rate of $20 \text{ cm}^3/\text{min}$ for 14-15 hrs. The refractive indices were measured using a Pulfrich refractometer, which has an accuracy of ± 0.00002 . Some difficulty was experienced with temperature control, so that one or two figures obtained are suspect.

The refractive indices measured in this laboratory for CO_2 - saturated water are listed below. Fixing the

first four significant figures at 1.332 , the variation in the fifth and sixth significant figures was;

45,67,27,45,39,51,and45

The average value for $n_D^{26} = 1.33245$ (refractive indices being measured at 26°C).

Accepted values for the refractive index of pure water (92) are listed below:-

$t^{\circ}\text{C}$	n_D
20	1.33299
22	1.33281
24	1.33262
26	1.33241
28	1.33219

It is thus evident that the refractive index difference between CO_2 - saturated water and pure water is not accurately measurable by a Pulfrich refractometer, but can be expected to be of the order 10^{-5} . Thus the interferometer will be working close to its limit.

One point which should be noted is the refractive index change of water with temperature. The change per $^{\circ}\text{C}$ is approximately 0.0001. Thus using the wavefront

FIG.6: Modification to the
w/s Interferometer.

shearing interferometer (and a cell of path length 6.3 cm.), a temperature difference of only 0.09°C will be enough to produce fringes. This illustrates the importance of temperature control and the necessity of guarding against heat effects during absorption.

II(b). Description of the Apparatus.

The wavefront shearing interferometer has been fully described in Part I of this work.

However, an important modification to the optical arrangement, as shown in Fig.6, was made to enable a direct recording of the refractive index (concentration) gradient.

This modification was first described by Bryngdahl and Ljunggren (93) and Bryngdahl (94). The modification consists of introducing a second Savart plate, SP2, after SP1 . Polariser P2 is then put after SP2.

Strictly speaking, the gradient recorded is not in Cartesian co-ordinates (x,y) but in curvilinear co-ordinates (x,u) , where $u = y(1 - \frac{\phi x}{h})$. Here, h = distance between L5 and M , and ϕ is given by

$$\phi = \frac{1}{n_e^2} \left(\frac{1}{n_e^2} - \frac{1}{n_o^2} \right)^{-\frac{1}{2}}$$

where n_e and n_o are the principal refractive indices of the Savart plate.

In the system used in this laboratory, $h=600$ mm., and $\phi = 0.3$. To all intents and purposes, therefore, the gradients recorded by the interferometer are in Cartesian co-ordinates.

The Gas-Liquid Cell is diagrammatically shown in Fig.7 , and a photograph (Fig.8) shows the external appearance.

The cell is constructed throughout of stainless steel, and the dimensions are based on the flowing junction cell which was used successfully in the liquid-liquid diffusion experiments. The optical path length through the cell is 6.3 cm., and the interfacial area between the gas and the liquid is 32 cm² . Optical glass flats, 10 mm thick, are clamped parallel to the precision machined faces of the cell by 12 spring held screws. Copper and rubber gaskets ($\frac{1}{16}$ " and 2 mm thick respectively) distribute the screw pressure.

Gas is admitted through one of the ports ($\frac{3}{16}$ " o.dia.) and is deflected by the baffle. Distribution over the liquid surface is aided by the stainless steel gauze (200

① Gas Ports	⑤ Gauze
② Optical Flats	⑥ Knife-Edge
③ 12 Screws	⑦ Liquid Ports
④ Baffle	⑧ Copper/Rubber Gaskets

FIG. 7.

The Gas-Liquid Cell.

Fig.8. The Gas-Liquid Cell.

① Gas Cell

② Burette

③ Cell Base

④ Optical Bench

⑤ Wash Bottle

⑥ Gas Rotameters

FIG.9. Arrangement of Cell on Bench

mesh/inch).

The liquid is admitted via. a burette, so that a careful control of the liquid level can be effected. This is necessary, since an ingenious device has been incorporated into the cell to eliminate the meniscus (thus making identification of the interface more accurate). This device consists of a silver knife-edge, $\frac{5}{1000}$ " thick, projecting 1 mm round the walls of the cell. The engineering of this knife-edge is a matter of some delicacy, but once accomplished the result is highly successful.

The cell is mounted on a circular base, attached in turn to an H-shaped base with four adjustable screws in the legs. The circular base may be rotated by means of a screw device, so that the axis of the cell may be aligned with the optic axis.

The admission of gas to the cell for contacting with a solution is in itself a technique (since it is so essential to minimise all heat effects).

The first arrangement tried for admitting gas to the cell is shown in Fig.9 . Two 5-litre aspirators contained CO_2 and nitrogen , - the CO_2 being maintained over a concentrated magnesium sulphate solution. The gas (concentrated, or diluted with nitrogen) is metered through

two rotameters (range 0 - 25 ml/min) and passed through a sintered glass disc (porosity 1) wash bottle. This permits a visual check on the gas rate and ensures additional saturation of the gas. However, this arrangement is not very successful, since the passage of gas over the liquid introduces either evaporation or condensation, - heat effects being apparent by the formation of fringes even when pure nitrogen is passed over.

A second arrangement which is almost entirely successful is shown in Fig.10. One of the cell gas ports is connected to the CO₂ aspirator, and the other to the N₂ aspirator. Tap B is closed, so that the cell is under a slight pressure equal to that in the N₂ aspirator, which in turn is equal to that in the CO₂ aspirator (approx. 8 mm Hg. gauge). Before contacting the gas with the liquid, the N₂ aspirator gas jar is elevated about 7 cm (thus introducing a pressure difference between the CO₂ and N₂ aspirators of about 7 cm water). Shortly afterwards, tap B is opened. CO₂ is thus brought into contact with the liquid whilst equalising the pressure in the system. Negligible physical changes are introduced by this method.

However, a disadvantage of the method is that gas concentrations are not easily controllable. A proposed

FIG. 10.

FIG. 10A

Fig.11. General View of Optical Bench & Gas Cell.

Fig.12. The Camera, Time-Recorder, and Viewer.

modification is to introduce a third aspirator as in Fig.10A, with careful metering of the gas flows.

The optical bench, with the gas cell fitted up as in Fig.10, is shown in the photograph in Fig.11. The camera, time recorder, and viewer are shown in Fig.12. It will be noticed in Fig.12 that in front of the viewer, in place of which the camera is mounted during runs, is a hinged mirror and ground glass screen. This is for inspection of the image during photographic registration.

II(c). Experimental Technique.

The gas cell is thoroughly cleaned, taking care not to damage the knife-edge, before the glass flats are screwed into position and the whole unit is centered on the optical bench. The cell is purged with nitrogen.

Using the burette, the cell is filled with the solution to be contacted with the gas. As explained

previously, the cell is filled via. the burette so that the liquid level can be controlled. If this is done, it is simple to reduce the meniscus to a very fine depth by means of the knife-edge. Thus, identification of the interface is facilitated.

The gas cell is connected up to the aspirators, which have been filled with their respective gases, as in Fig. 10. The aspirators are at equal pressures.

The complete unit is then left overnight in the thermostatically controlled constant temperature room (maintained at $25 \pm 0.1^{\circ}\text{C}$).

When about to start a run, the Robot Recorder camera is loaded with Kodak R.55 recording film, and the timing unit is set for 1 sec. exposures every 4 seconds. The 250w mercury vapour lamp is started up, and after inspection of the image (to verify that the fringes are all vertical, - any bending indicates preliminary mass transfer or thermal imbalances) the camera is placed in position.

The gas jar of the nitrogen aspirator is raised about 7 cm., - thus effectively lowering the pressure in the gas cell and aspirator by about 7 cm. water. Tap B, from the carbon dioxide aspirator, is opened, and at this

instant the timing of the photographic registration is started.

After about 60 seconds the image is inspected (using the hinged mirror and ground glass screen). With absorption of CO_2 into dilute monoethanolamine, it is quite possible that by this time cumulative heat effects will be disturbing the solution sufficiently to make further photographic registration unnecessary (this will be illustrated later on). However, if careful control of concentrations is effected, it may be possible to eliminate these heat effects and to continue photographic registration for a considerable time further. With physical absorption these heat effects are not apparent, and inspection and recording of the fringes continues until the fringes are nearly vertical.

The exposed R.55 recording film is developed in Kodak DX.80 developer for 2 minutes at 25°C .

Measurement of the concentration profiles is effected by projecting the photographic image onto a frosted screen (at a magnification of about 60x), and tracing the profiles or reaction zone position. It does not appear that a recording microdensitometer can be applied in this case.

III. EXPERIMENTAL RESULTS.

III(a). Physical Absorption of CO₂ into Water.

Several repeated runs were made for the diffusion of CO₂ into water, and a photograph of a typical refractive index (concentration) gradient recording from one of the runs is shown in Fig.13. The exposure shown is for t = 720 seconds.

In table 1, measurements for concentration gradients recorded at t = 205 and t = 720 seconds for one run are given. Also tabulated are the values of the diffusion coefficient which would satisfy the curves at each point.

In Fig.14, the theoretical concentration profiles for the diffusion of CO₂ into water are given. These have been calculated for t = 20, 90, and 720 seconds, using equation 4. Values of erfc x have been computed and tabulated by the author , between x = 0.0000 and x = 2.3000 (at intervals of 0.0001).The algebraic expansion

$$\text{erfc } x = \frac{2}{\sqrt{\pi}} \int_x^{\infty} e^{-t^2} .dt$$

$$\text{or, } \operatorname{erfc} x = 1 - \frac{2}{\sqrt{\pi}} \left[x - \frac{(-1)^n x^{2n-1}}{(n-1)!(2n-1)} \right] \dots\dots(45)$$

was used, where n is the number of terms in the series expansion. The series was expanded as follows;-

x	no.of terms
0 to 1	9
1 " 1.2	14
1.2 " 1.4	16
1.4 " 1.6	18
1.6 " 1.8	20
1.8 " 2.0	24
2.0 " 2.3	32

A value of $D = 19.5 \times 10^{-6} \text{ cm}^2/\text{sec}$ for the diffusion coefficient of CO_2 into water (80)(95) was taken in computing the theoretical concentration gradients.

The experimental concentration gradient for $t = 720 \text{ secs}$ has been plotted together with the theoretical curves for comparison.

From table 1, and also from a comparison of the theoretical and experimental concentration profiles in Fig.14, it is apparent that the experimental diffusivity

Fig.13. CO_2 - water refractive index gradient recording.

FIG. 14
THEORETICAL CONCENTRATION PROFILES FOR
 $\text{CO}_2 \rightarrow \text{H}_2\text{O}$ DIFFUSION

Table 1. Experimental Diffusion of CO₂ into water.

Concentration Gradients recorded.

G = 55.8

	x^i	$x = x^i/G$ (mms)	c/c_{Ai}	D, to satisfy point (cm ² /sec x 10 ⁶)
t = 205 secs	4	0.0717	0.898	7.69
	8	0.143	0.711	3.65
	12	0.215	0.560	3.33
	16	0.287	0.403	2.88
	20	0.359	0.280	2.70
	24	0.430	0.207	2.84
	30	0.538	0.126	3.00
	40	0.717	0.0560	3.45
	50	0.896	0.0187	3.56
t = 720 secs	4	0.0717	0.905	2.51
	8	0.143	0.813	2.54
	12	0.215	0.718	2.47
	16	0.287	0.625	2.40
	20	0.359	0.535	2.32
	24	0.430	0.460	2.35
	30	0.538	0.360	2.40
	40	0.717	0.220	2.39
	50	0.896	0.141	2.57
	60	1.076	0.0950	2.89
	70	1.255	0.0575	3.03

of CO_2 into water is too low by a factor of about 8, and as such is unreal. It must be emphasised here that these runs were repeated many times, and the recorded concentration profiles were all similar in their apparent D values to the two profiles reproduced in table 1.

The main conclusion that may be postulated from these repeated failures at measuring the correct diffusion coefficient, is that the interferometer is working at its absolute limit of sensitivity. This is supported by an examination of the recorded concentration profiles.

In Fig.13 it will be noticed that the maximum "bending" of the gradients is only equal to (or slightly less than) the equidistant spacing apart of the fringes. Since this spacing is equivalent to an optical path length of λ/a (4), it would appear that the refractive index difference between CO_2 -saturated water and pure water is only about 9×10^{-6} .

(In the discussion on the sensitivity of the interferometer, it will be remembered that the refractive index difference was expected to be of the order 10^{-5} .)

Since the refractive index difference is so apparently low, then there is a good possibility that distortion of the recorded gradients will occur. It may

well be ,then, that there is not a sufficient refractive index difference present initially to enable any accurate measurements to be made of the diffusion of CO_2 into water. If this is so, then re-examination and re-appraisal of previous workers' results using interferometers to study diffusion of CO_2 into water will be necessary.

Harvey and Smith (46) used a Mach Zender interferometer to determine the interfacial resistance in a liquid film to the absorption of CO_2 . Now, since a Mach Zender is a good deal less sensitive than a wavefront shearing interferometer , $\Delta n_{\min} = 6 \times 10^{-4}$ being quoted by Mullin et. al (24), then it is unlikely that their observed concentration gradients were true mass transfer gradients. Also, a feature of Harvey and Smith's experimental technique was the sudden changing in pressure of the system from vacuum to atmospheric. Since this will undoubtedly have caused marked physical changes in the system and introduced large heat effects, their technique and results need very careful reconsideration.

Recently, Jepsen et. al (96) reported on the effect of wave-induced turbulence on the rate of absorption of gases in falling liquid films. One of the basic features of this work was the use of a Mach Zender interferometer

to determine concentration profiles for the diffusion of carbon dioxide into water films. Although Jepsen describes the close temperature control of the water he uses, there is no account of any attempt to control the temperature and humidity of the gases. Since Jepsen used a flowing system, then it is quite probable that thermal imbalances were introduced, so that, again, it is quite probable that the gradients observed were not true mass transfer gradients.

Although the wavefront shearing interferometer has not produced any accurate profiles for the physical absorption of CO_2 into water, there is no reason why it should not yield true gradients where a more soluble gas is concerned.

III(b). Absorption of CO_2 into dilute Monoethanolamine.

Using a 1 g/litre MEA solution (0.0166 N) several runs were repeated for the absorption of CO_2 into dilute monoethanolamine solution. Other concentrations of MEA were used, but due to an initial lack of experimental technique these runs were of little value. Only when experience had been gained, and the interpretation of the

FIG. 15 Diagrammatic Detail of Fig. 16

FIG. 16 CONCENTRATION PROFILES OBSERVED DURING
ABSORPTION OF CO_2 BY 0.0166 N MEA .

photographic recordings was accomplished, did any consistency appear in the results. Thus, only two runs, both using 0.0166 N MEA, are recorded here.

It will be remembered from the theory of absorption accompanied by a fast 2nd order irreversible reaction, that a reaction zone is formed in such a case, - the reaction zone moving away from the interface. In Fig.16 a detail of the photographic recording of this reaction zone is shown for CO₂ diffusing into 0.0166 N MEA after 57 seconds. In Fig.15 the main features of this photograph are drawn, so that the principal regions and dimensions may be identified. Note the scale of the photograph (approx. 60x mag.factor).

These features will now be described;-

1) The top, totally dark, region is the meniscus. (In this photograph, as well as in Figs.17A to D, a deep meniscus is apparent. This is due to the knife-edge not being used, having been damaged earlier on. The presence of a meniscus does not in any way prejudice the results)

2) Beneath this dark region is an apparent narrow white band. The top of this band has been identified as the interface.

3) Beneath the interface, a set of lines run

slightly downwards from right to left. These lines represent the steep concentration gradient of CO_2 diffusing through the reaction products solution.

4) Meeting the CO_2 -diffusion gradient lines are a set of lines sloping upward from left to right. These lines have been taken to represent the concentration gradient of MEA diffusing upwards (and possibly also the downward diffusion of the reaction products).

5) Where the two sets of lines meet, the reaction zone is assumed to lie.

6) The lower edge of the lower white band is taken as the extremity of the liquid film.

The above interpretations of the photographic recordings of the absorption of CO_2 by dilute MEA, taken using the wavefront shearing interferometer, is tentative. It must be remembered that this is the first time that the presence of the reaction zone, in absorption with fast 2nd order reaction, has been illustrated. Previously an entirely theoretical concept, it is now possible to actually observe this reaction zone and its movement.

A series of photographs illustrating the movement of this reaction zone are shown in Figs. 17A to D.

Figs. 17A to 17D.

Photographs showing movement of the Reaction Zone in absorption of CO_2 by 0.0166 N MEA. The times of exposure were as follows;

3 secs(A) ; 21 secs (B) ; 33 secs (C) ; 51 secs(D).

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FIG. 17A

FIG. 17B

FIG. 17C

FIG. 17D

In Fig.18 is shown a photograph of turbulence in the liquid film, taken about 65 seconds after admission of CO_2 to the cell (containing 0.0166 N MEA). In Fig.19, eddy diffusion and turbulence in the bulk of the liquid is clearly visible,- this exposure being taken about 80 secs after the admission of CO_2 .

It must be emphasised that in Figs. 18 and 19 the turbulence is due almost entirely to a lack of control over the phase concentrations,- particularly the CO_2 . The CO_2 was almost 100% pure on admission , and it is a fair surmise that the lowering of the CO_2 partial pressure would eliminate this turbulence. A few test runs, using a gas burette to meter the CO_2 into the cell, seem to bear this out. However, this is a refinement of the experimental technique that will need investigating in the future.

The cause of the turbulence is a matter for conjecture. Possibly, the heat of reaction between CO_2 and amine may be dissipated at a somewhat greater rate than the mass transfer process. The turbulence encountered, however, would indicate a build-up of thermal energy which is only dissipated after a fair length of time.

The effect of this turbulence is not of any great importance in the particular system studied. All the

Fig.18. Turbulence in the Liquid Film.

Fig.19. Turbulence in the Bulk of the Liquid.

information necessary regarding the movement of the reaction zone is registered in about 35 seconds, and the turbulence does not follow until about 30 seconds later. However, turbulence may be an important consideration with other systems.

In table 2 are recorded measurements taken in two runs for the absorption of CO_2 in 0.0166 N MEA. Following this table are calculations relating the experimental observations to the film and penetration theories outlined earlier on.

Calculation of $\sqrt{\alpha}$ from graphs of x^i against $\sqrt{\theta}$.

From the penetration theory it follows that

$$x^i = 2\sqrt{\alpha} \sqrt{\theta} \quad (\text{eqn.27})$$

Thus the slope of the graph of x^i against $\sqrt{\theta}$ should be $2\sqrt{\alpha}$.

In Fig.21, plots of x^i , $\sqrt{\theta}$ have been made for runs I and II. From which,

$$\text{Run I, } \sqrt{\alpha} = 0.059$$

$$\text{Run II, } \sqrt{\alpha} = 0.070$$

Table 2. Absorption of CO₂ into 0.0166 N MEA.

	θ (secs)	$\sqrt{\theta}$	x' (mm)	$x_L = x' + x''$ (mm)	x'' (mm)
Run I	3	1.732	0.140	0.686	0.546
	9	3.00	0.322	0.876	0.554
	15	3.87	0.438	0.992	0.554
	21	4.59	0.479	1.100	0.621
	27	5.20	0.578	1.200	0.622
	33	5.74	0.628	1.258	0.630
	39	6.25	0.636	1.327	0.691
	45	6.71	0.661	1.327	0.666
	51	7.15	0.628	1.298	0.670
	57	7.55	0.645	1.290	0.645
	63	7.94	0.661	1.290	0.629
Run II	5	2.24	0.158		
	10	3.16	0.288		
	15	3.87	0.379		
	20	4.48	0.458		
	25	5.00	0.537		
	30	5.48	0.616		
	35	5.91	0.663		
	40	6.32	0.679		
	45	6.71	0.695

FIG. 20

Graphs of x' & x'' vs θ
(RUN 1).

FIG. 21

Graphs of x' vs. $\sqrt{\theta}$

If $(x' + x'')$ is plotted against $\sqrt{\theta}$, the slope gives

$$\sqrt{\alpha} = 0.0728 \quad (\text{Run I})$$

In the graphs of x' against $\sqrt{\theta}$ it will be noticed that the line cuts the $\sqrt{\theta}$ -axis at a positive value of $\sqrt{\theta}$; this gives an indication of the error of the timing of the photographic recording. As an estimate of the time-error,

$$\Delta\theta = 0.6 \text{ secs (Run I)}$$

$$\Delta\theta = 1.2 \text{ secs (Run II)}$$

If the θ values are incorrect, and also the position of the "interface" for measuring x' , then a plot of $(x'_a - x'_b)$ against $(\sqrt{\theta}_a - \sqrt{\theta}_b)$ should give the true $\sqrt{\alpha}$. On this basis, by applying a least squares fit, $\sqrt{\alpha}$ was calculated for runs I and II.

$$\text{For a line } Y = A + B.X \dots\dots\dots(46)$$

the best slope is given by

$$B = \frac{N \sum XY - \sum X \sum Y}{N \sum X^2 - (\sum X)^2} \dots\dots\dots(47)$$

where N is the number of points (X,Y). In table 3, a sample calculation to calculate $\sqrt{\alpha}$ by the above method is given for run II. The first 7 points are used.

Table 3. Calculation of from Least Squares fit to

$$(\bar{x}_a^i - \bar{x}_b^i), (\sqrt{\theta}_a - \sqrt{\theta}_b).$$

Points.	$(\sqrt{\theta}_a - \sqrt{\theta}_b)$		$(x_a^i - x_b^i)$	
	X	X^2	Y	XY
1,2	0.92	0.8464	0.130	0.11960
2,3	0.71	0.5041	0.091	0.06461
3,4	0.61	0.3721	0.079	0.04819
4,5	0.52	0.2704	0.079	0.04108
5,6	0.48	0.2304	0.079	0.03792
6,7	0.43	0.1849	0.047	0.02021
1,3	1.63	2.6569	0.221	0.36023
1,4	2.24	5.0176	0.300	0.67200
1,5	2.76	7.6176	0.359	0.99084
1,6	3.24	10.4976	0.458	1.48392
1,7	3.67	13.4689	0.505	1.85335
2,4	1.32	1.7424	0.170	0.22440
2,5	1.84	3.3856	0.249	0.45816
2,6	2.32	5.3824	0.328	0.76096
2,7	2.75	7.5625	0.375	1.03125
3,5	1.13	1.2769	0.158	0.17854
3,6	1.61	2.5921	0.237	0.38157
3,7	2.04	4.1616	0.284	0.57936
4,6	1.00	1.0000	0.158	0.15800
4,7	1.43	2.0449	0.205	0.29315
5,7	0.91	0.8281	0.126	0.11466
Σ	33.56	71.6434	4.638	9.87200

$$\text{From this, } B = \frac{21(9.872) - (33.56)(4.638)}{21(71.6434) - (33.56)^2}$$

$$\therefore 2\sqrt{\alpha} = 0.13658$$

$$\therefore \underline{\sqrt{\alpha} = 0.0683}$$

From Run I, N = 31	} whence $\sqrt{\alpha} = 0.0659$
$\sum X = 36.83$	
$\sum X^2 = 59.5613$	
$\sum Y = 4.854$	
$\sum XY = 7.85038$	

Using the x_L values in Run I,

N = 15	} whence $\sqrt{\alpha} = 0.0725$
$\sum X = 27.36$	
$\sum X^2 = 65.84112$	
$\sum Y = 3.940$	
$\sum XY = 9.9495888$	

$\sqrt{\alpha}$ in the six calculations has been calculated to be
 0.059 : 0.07 : 0.0728 : 0.0683 : 0.0659 : 0.0725.

Taking the average value,

$$\underline{\underline{\sqrt{\alpha} = 0.0681}}$$

This value of $\sqrt{\alpha}$ will be used in all subsequent calculations.

From the penetration theory, σ_A is defined by

$$\sigma_A = \frac{\sqrt{\alpha}}{\sqrt{D_A}}$$

Using $\sqrt{\alpha} = 0.0681$, and $D_A = 19.5 \times 10^{-4} \text{ mm}^2/\text{sec}$ (since $\sqrt{\alpha}$ has been calculated on a millimetric basis)

$$\underline{\underline{\sigma_A = 1.54}}$$

Using this value of σ_A , it will now be shown what agreement exists between the experimental results obtained, and the film and penetration theories for absorption accompanied by a rapid 2nd order reaction.

1./ Taking $D_A = 19.5 \times 10^{-4} \text{ mm}^2/\text{sec}$
 $D_B = 10.4 \times 10^{-4} \text{ mm}^2/\text{sec}$
 $c_{Ai} = 3.31 \times 10^{-5} \text{ g.mols/cm}^3$
 $c_{Bo} = 1.66 \times 10^{-5} \text{ g.mols/cm}^3$

What σ_A value is needed to fit equation 33,

i.e. $\left(\frac{D_B}{D_A}\right)^{\frac{1}{2}} \left(\frac{c_{Bo}}{c_{Ai}}\right) e^{(\sigma_A^2)(1 - \frac{1}{r})} \text{erf } \sigma_A + \text{erf}\left(\frac{\sigma_A}{\sqrt{r}}\right) = 1$

(note: D_B is taken as the diffusion coefficient of 0 N MEA, as measured by the author. c_{Ai} is the equilibrium solubility of CO_2 in water)

$$r = D_B/D_A = 0.539 ; \sqrt{r} = 0.734 ; (1 - \frac{1}{r}) = -0.858$$

$$q = c_{Bo}/c_{Ai} = 0.5 ; q\sqrt{r} = 0.367$$

Sample calculation;-

Put $\sigma_A = 1$

$$\therefore e^{-0.858} = 0.424 ; \operatorname{erf} 1 = 0.8427 ; \operatorname{erf} \frac{1}{0.734} = 0.9461$$

Substituting in eqn.33,

$$\text{L.H.S.} = 1.077 \quad (\text{R.H.S.} = 1)$$

$\therefore \sigma_A$ does not satisfy the equation

Substituting σ_A values from 0.6 to 3 , it is apparent that there are two values of σ_A that satisfy the equation for the above r and q .

i.e.

A	LHS - RHS
0.6	-0.0856
0.7	-0.0138
0.74	+0.0083
0.8	+0.0331
1.0	+0.0770
1.2	+0.0765
1.4	+0.0581
1.6	+0.0373
2.0	+0.0116
2.2	+0.0057
3.0	+0.0002

FIG. 23

Experimental &
Theoretical.

x' vs. θ Curves.

The solution to equation 33, using the above q and r , is shown in Fig.22. From Fig.22 and the table above, the two σ_A values that satisfy the equation are

$$\sigma_A = 0.72 \quad (\text{real})$$

$$\sigma_A \approx 3 \quad (\text{unreal})$$

whence, $\sqrt{\alpha} = 0.0318$ (real) and > 0.1325 (unreal).

The theoretical movement of the reaction zone, from eqn.27, for the above $\sqrt{\alpha}$'s is shown in Fig.23; and these curves are compared with the experimental points for runs I and II.

2./ From the film theory,

$$\phi_a = \frac{K_L}{K_L^0} = \frac{1}{\text{erf } \sigma_A} = 1 + r \cdot q$$

Taking $r = 0.539$, $q = 0.5$, then $r \cdot q = 0.2695$

whence $\sigma_A = 0.883$ (and $\sqrt{\alpha} = 0.0389$)

It is thus quite obvious from calculations 1 and 2 that the experimental values obtained for $\sqrt{\alpha}$ and σ_A differ widely from the theoretical values for the system CO_2 into 0.0166 N MEA, using the known values of D_A , D_B , c_{A1} , and c_{B0} to satisfy the equations. Taking c_{A1} and c_{B0} to

be correct, the problem, then, is to assess whether an alteration to the value of either D_A (not very likely) or D_B (more likely) will satisfy the film and penetration theories for the experimental σ_A value.

3./ What is D_A to satisfy $\frac{1}{\text{erf } \sigma_A} = 1 + r.q$?

Taking $\sqrt{\alpha} = 0.0681$, $q = 0.5$, and $D_B = 10.4 \times 10^{-4} \text{ mm}^2/\text{sec}$

$$\therefore \frac{1}{\text{erf} \left(\frac{0.0681}{\sqrt{D_A}} \right)} = 1 + 0.5 \left(\frac{10.4 \times 10^{-4}}{D_A} \right)$$

Solving in the above equation, D_A must have to have a value of about $38 \times 10^{-4} \text{ mm}^2/\text{sec}$.

4./ What is D_A to satisfy

$$q\sqrt{r} e^{(\sigma_A^2)} (1 - 1/r) \text{erf } \sigma_A + \text{erf } \sigma_A / \sqrt{r} = 1,$$

taking the above $\sqrt{\alpha}$, q , and D_B values ?

Solving in the above equation ,

$D_A (x 10^4)$	LHS-RHS
20	+0.026
40	+0.0052
45	+0.0037
50	+0.0026
70	+0.0003

Thus, to explain the $\sqrt{\alpha}$ value obtained experimentally, assuming D_B , c_{Ai} , and c_{Bo} to be correct, D_A would have to be about $38 \times 10^{-4} \text{ mm}^2/\text{sec}$ (film theory, calc. 3) or greater than $70 \times 10^{-4} \text{ mm}^2/\text{sec}$ (penetration theory, calc. 4). Since the only means of increasing D_A by this extent would be a temperature rise of a good 20 to 30°C, it would appear that D_B needs re-examination (assuming this time that D_A is correct).

5./ What is D_B to satisfy $\frac{1}{\text{erf } \sigma_A} = 1 + r \cdot q$?

taking $\sigma_A = 1.54$, $q = 0.5$.

$$r = \left(\frac{1}{\text{erf } 1.54} - 1 \right) \div 0.5 = 0.06$$

whence $D_B = 1.73 \times 10^{-4} \text{ mm}^2 / \text{sec.}$

6./ What is D_B to satisfy eqn 33, as in calculation 4?

Solving, using the σ_A and q values as in calculation 5,

$D_B (\times 10^4)$	LHS - RHS
10.4	6×10^{-2}
5	1×10^{-4}
4	9×10^{-6}
2	4×10^{-11}

From calculations 5 and 6, it can be seen that by lowering D_B to a value of around $2 \times 10^{-4} \text{ mm}^2/\text{sec}$, the experimental $\sqrt{\alpha}$ value is verified to an extent.

It would appear then that the reaction zone observed in the runs described above gives rise to an artificially low value of $\sqrt{\alpha}$, the likeliest explanation of which is a lowering of D_B .

There is a fair amount of justification in making this statement, -- certainly in view of the long contact time employed, and this will be discussed in the following section.

One point remains in clarifying the above calculations. Presuming the interface had been wrongly identified, and simultaneously the timing of the photographic recording was incorrect by about 2 seconds (large error), would this have much effect on $\sqrt{\alpha}$? As a test of this particular case, a theoretical curve was drawn, and was then displaced by appreciable increments in x' and θ . On plotting x' against $\sqrt{\theta}$ the effect is to shift the curve sufficiently to cut the θ -- axis at a negative value when $x' = 0$. By comparing this displaced curve and the experimental curves, it is quite evident that the interface has been fairly accurately identified. Also $\sqrt{\alpha}$ is not altered much by displacing the curve.

FIG. 24

POSSIBLE
CHLORINE/FERROUS CHLORIDE
ABSORPTION MODEL.

FIG. 25

POSSIBLE
CO₂ - MEA
ABSORPTION MODEL.

The Reduction of D_B in the Absorption of CO_2 by MEA.

In an experimental investigation of the absorption of chlorine by ferrous chloride in hydrochloric acid, Gilliland et al (88) concluded that the effective diffusivity of the ferrous ion was only 59% that of the salt diffusivity of ferrous chloride. The overall reaction may be expressed as

However, this reaction may be broken down into three stages,

Stage 2 is slow relative to stages 1 and 3.

Thus, a fairly complex ionic reaction model is formulated, and it becomes evident that D_B is no longer merely the diffusion coefficient for the ferrous salt diffusing towards the reaction zone. Instead , D_B must take into account the complex ionic counterdiffusion occurring as the reaction proceeds.

Using the Hatta film theory model, the absorption of chlorine by ferrous chloride may thus probabaly be represented by Fig.24.

For the absorption of CO_2 by MEA, the rate is governed by three main simultaneous reactions.

A possible representation of the absorption, based on the Hatta model, would be as in Fig.25.

As with Fig.24, Fig.25 is only a representational diagram. However, it can be seen that the diffusion of the amine is very probably countered by the diffusion of the reaction products. With the absorption of chlorine by ferrous chloride, the controlling reactions are strongly ionic, and the maintenance of electrical neutrality will govern the diffusional processes. With the absorption of CO_2 by MEA, the reactions are not strongly ionic, but it is very likely that significant forces of interaction are present, as with the plain diffusion of amine in water.

With the experimental technique employed in observing the diffusion of CO_2 in MEA, comparatively large contact times are employed. There is a strong possibility, therefore, that the reaction products formed in this time

will interfere with the diffusion of the amine to a far greater extent than that observable in, say, the laminar jet with a contact time of the order of 0.005 seconds. As a possible indication of this, it can be seen in Fig. 23 that the position of the experimentally observed reaction zone after 5 seconds is not very different from that of the theoretical reaction zone position for $D_B = 10.4 \times 10^{-4} \text{ mm}^2/\text{sec}$. Only at the longer contact times does the experimental curve differ widely from the curve for $D_B = 10.4 \times 10^{-4}$.

It would thus appear that the counterdiffusion of the amine and the reaction products (formed in the reaction between CO_2 and MEA) will significantly affect the value of D_B at long contact times.

A further insight into the influence on D_B of ionic counterdiffusion is given by Sherwood and Wei (97). However, in the systems they examined, - HCl in NaOH, and acetic acid in NaOH, the value of D_B is increased. For the absorption of HCl in NaOH, a rigorous treatment of the ionic counterdiffusion occurring leads to a prediction of a doubling of the mass transfer rate over that predicted by the simple film theory.

Further experimental observations are needed to validate the decrease in D_B for the absorption of CO_2 in

amine . However, it can be safely assumed at this stage that D_B is decreased due to the counterdiffusion of the amine and reaction products at the long contact times employed.

IV. SUMMARY

To summarise the study made of the application of the wavefront shearing interferometer to gas-liquid diffusion, the following observations are made;—

1) Having proved the wavefront shearing interferometer as being a highly accurate and sensitive instrument for the measurement of mutual diffusion rates in binary liquid systems, a new diffusional cell was designed and constructed for gas-liquid contacting. An experimental technique was evolved for admitting the gas to the cell, for contacting with the liquid, with the minimum change in the physical conditions of the system. Since only a very slight thermal imbalance is detectable by the interferometer, it is essential that the physical conditions in the cell remain as stable as possible.

2) The first gas-liquid system investigated using the wavefront shearing interferometer was the diffusion of CO_2 into water. It was expected from the outset that there would not be a great enough refractive index difference present to make any accurate measurements possible. A preliminary check on the refractive index of CO_2 -saturated

water indicated that the detection of the absorption of CO_2 by water was at the limit of the sensitivity of the interferometer. The experimental results confirmed this expectation. Thus, the wavefront shearing interferometer can only have a limited application for diffusion measurements with a gas of sparing solubility in a solution. In the light of this, the results of previous workers who who used less sensitive interferometers to study mass transfer in the CO_2 -water system, may be said to need critical re-examination. There is no reason to doubt, however, that the wavefront shearing interferometer could not be employed with success with a more soluble gas.

3) The second system to be investigated was the absorption of CO_2 by dilute monoethanolamine solution, - the diffusion of CO_2 in this case being accompanied by a fast 2nd order reaction. After a number of trial and error runs, in which a successful experimental technique was finally evolved, a major success was accomplished. This consisted of the showing experimentally, for the first time, of the existence of a distinct reaction zone in the liquid film. The movement of this reaction zone was recorded photographically.

4) Measurements taken of the reaction zone movement observed in the absorption of CO_2 by dilute MEA, indicated that the value of D_B ,-- the diffusion coefficient for the amine, was only about 20% of its true value. This has been explained as being caused by counterdiffusion of amine and the reaction products at the large contact time employed.

5) In view of the successful illustration of diffusion with reaction in the liquid film, there is every possibility that a completely new field of interferometric experimental investigation in mass transfer is opened up. A good deal more experience is called for, and also a re-appraisal of the experimental technique involved.

Suggestions for Further Work.

In the immediate future, improvement in the experimental technique for operating the gas-liquid cell is of first priority. These improvements may be itemised as below;-

1) Control of the gas concentrations on admission, such that the heat of reaction is minimised. The experimental

arrangement shown in Fig. 10A is a first step towards this.

2) Increase the intensity of the illumination, so that the photographic registration (at short exposure times) can be made of the initial diffusional process (say, within the first 5 seconds). Arrangements are being made at the moment to put this matter in hand.

3) Improve the image measurement. The use of an instrument as accurate as the recording microdensitometer is suggested for measuring the movement of the reaction zone.

4) Although not as vital as the above suggestions, a re-appraisal of the gas-liquid cell design is called for. The present dimensions , 6.3 cm path length x 5 cm wide x 4 cm deep could possibly be changed to advantage. A cell 2 cm wide would be quite sufficient, and would make the engineering of the knife-edge easier. Also, an alteration of the path length might increase the sensitivity, though providing no optical aberrations are introduced.

5) A further series of runs on the absorption of CO_2 in dilute MEA is desirable. The use of di- and tri-ethanolamines as solvents could also be profitably studied. Other systems, with slower reaction rates, are also of interest.

APPENDIX I

Solution to Fick's 2nd Law.

APPENDIX I.

Solution to Fick's Second Law.

It can be shown by dimensional analysis that a solution

of

$$\frac{\partial c}{\partial t} = D \cdot \frac{\partial^2 c}{\partial x^2} \dots\dots\dots (A)$$

is obtained as

$$C = \frac{A}{\sqrt{t}} \exp\left(-\frac{x^2}{4Dt}\right) \dots\dots\dots (B)$$

The derivation is lengthy, however, so that in this work it will be shown that equation (B) is a solution of (A).

Differentiating (B) with respect to t,

$$\begin{aligned} \frac{\partial c}{\partial t} &= A \left[e^{-x^2/4Dt} \left(-\frac{1}{2}\right) t^{-3/2} + \frac{1}{\sqrt{t}} \left(\frac{x^2}{4Dt^2} \right) e^{-x^2/4Dt} \right] \\ &= A \cdot e^{-x^2/4Dt} \cdot t^{-3/2} \left[\left(-\frac{1}{2}\right) + t \cdot \left(\frac{x^2}{4Dt^2} \right) \right] \\ &= \frac{A}{2} \cdot e^{-x^2/4Dt} \cdot t^{-3/2} \left[\frac{x^2}{2Dt} - 1 \right] \dots\dots\dots (C) \end{aligned}$$

Differentiating (B) with respect to x,

$$\frac{\partial c}{\partial x} = \frac{A}{\sqrt{t}} \left(-\frac{2x}{4Dt} \right) \cdot e^{-x^2/4Dt} \dots\dots\dots (D)$$

$$\begin{aligned} \therefore \frac{\partial^2 c}{\partial x^2} &= \frac{A}{\sqrt{t}} \left[\left(\frac{2x}{4Dt} \right)^2 \cdot e^{-x^2/4Dt} - \frac{2}{4Dt} \cdot e^{-x^2/4Dt} \right] \\ &= \frac{A}{t} \cdot e^{-x^2/4Dt} \cdot \frac{1}{2Dt} \left[\frac{x^2}{2Dt} - 1 \right] \dots\dots (E) \end{aligned}$$

Multiply (E) by D (diffusivity),

$$D \cdot \frac{\partial^2 c}{\partial x^2} = \frac{A}{2} \cdot e^{-x^2/4Dt} \cdot t^{-3/2} \left[\frac{x^2}{2Dt} - 1 \right]$$

$$\therefore D \cdot \frac{\partial^2 c}{\partial x^2} = \frac{\partial c}{\partial t}$$

And therefore $C = \frac{A}{\sqrt{t}} \cdot e^{-x^2/4Dt}$ is a solution to this equation.

APPENDIX II

The Taylor Series Expansion of

$$\left(\frac{\Delta z}{\Delta x} \right)_{\Delta x = b}$$

APPENDIX II

The Taylor Expansion (98).

Taylor's theorem determines the law for the expansion of a function of the sum of two variables into series of ascending powers of one of the variables.

$$\text{Assume } u = f(x + y) = A + By + Cy^2 + Dy^3 \dots \quad (1)$$

Let $A', B', C' \dots$ be the respective values of $A, B, C, \dots$ in (1) when $x = a$ ($a = \text{an arbitrary value}$).

$$\therefore u' = f(a + y) = A' + B'y + C'y^2 + D'y^3 \dots \quad (2)$$

Putting $z = a + y$ $\therefore y = z - a$,

$$u' = f(z) = A' + B'(z-a) + C'(z-a)^2 + D'(z-a)^3 \dots \quad (3)$$

Differentiating with respect to z ,

$$\frac{\partial u'}{\partial z} = f'(z) = B' + 2C'(z-a) + 3D'(z-a)^2 \dots$$

$$\frac{\partial^2 u'}{\partial z^2} = f''(z) = 2C' + 2.3D'(z-a) + 3.4E'(z-a)^2 \dots$$

$$\frac{\partial^3 u'}{\partial z^3} = f'''(z) = 2.3.D' + 2.3.4E'(z-a) \dots$$

Putting $z = a$, and $\therefore y = 0$,

$$f(a) = A^1 ; f'(a) = B^1 ; f''(a) = 2C^1 ; f'''(a) = 2.3D^1 ;$$

$$\therefore C = \frac{1}{2}f''(a) \text{ and } D = \frac{1}{2.3}f'''(a) \dots\dots\dots(4)$$

Substituting (4) into (2),

$$u^1 = f(a+y) = f(a) + \frac{f'(a).y}{1!} + \frac{f''(a).y^2}{2!} + \frac{f'''(a).y^3}{3!} \dots\dots\dots(5)$$

But if a is any value of x,

$$u = f(x+y) = f(x) + \frac{f'(x).y}{1!} + \frac{f''(x).y^2}{2!} + \frac{f'''(x).y^3}{3!} \dots\dots\dots(6)$$

And similarly,

$$u = f(x-y) = f(x) - \frac{f'(x).y}{1!} + \frac{f''(x).y^2}{2!} - \frac{f'''(x).y^3}{3!} \dots\dots\dots(7)$$

Equations (6) and (7) are the Taylor Series expansions of $f(x+y)$ and $f(x-y)$ respectively.

$$\text{Expansion of } \left(\frac{\Delta z}{\Delta x} \right)$$

$$\left(\frac{\Delta z}{\Delta x} \right)_{\Delta x = b} = \frac{f(x+b/2) - f(x-b/2)}{b}$$

expanding,

$$f(x+b/2) = f(x) + \frac{f'(x).b}{1! \cdot 2} + \frac{f''(x).b^2}{2! \cdot 4} + \frac{f'''(x).b^3}{3! \cdot 8} \dots\dots\dots(8)$$

$$f(x-b/2) = f(x) - \frac{f'(x) \cdot b}{1! \cdot 2} + \frac{f''(x) \cdot b^2}{2! \cdot 4} - \frac{f'''(x) \cdot b^3}{3! \cdot 8} \dots \dots \dots (10)$$

$$\therefore \frac{f(x+b/2) - f(x-b/2)}{b} = \frac{1}{b} \left[f'(x) \cdot b + \frac{2f'''(x) \cdot b^3}{3! \cdot 8} + \frac{2f^{(V)}(x) \cdot b^5}{5! \cdot 64} \dots \dots \dots \right] \quad (11)$$

$$\text{Now } f'(x) = \frac{\partial n}{\partial x} = A \cdot e^{-x^2/B} \dots \dots \dots (12)$$

$$\text{where } A = \frac{\Delta n}{2\sqrt{\pi Dt}} \quad \text{and } B = 4Dt.$$

$$\therefore f''(x) = -\left(\frac{2x}{B}\right) \cdot A \cdot e^{-x^2/B}$$

$$\therefore f''(x) = -\left(\frac{2x}{B}\right) \cdot f'(x) \dots \dots \dots (13)$$

$$\begin{aligned} f'''(x) &= \left[-\frac{2}{B} \cdot f'(x) \right] + \left[\left(-\frac{2x}{B}\right) \left(-\frac{2x}{B}\right) \cdot f'(x) \right] \\ &= \frac{2}{B^2} \cdot f'(x) \left[2x^2 - B \right] \dots \dots \dots (14) \end{aligned}$$

$$f^{IV}(x) = \left[\left(\frac{2}{B^2} \cdot f''(x)\right) (2x^2 - B) \right] + \left[\frac{2}{B^2} \cdot f'(x) \cdot 4x \right]$$

$$\therefore f^{IV}(x) = \frac{2}{B^3} \cdot f'(x) \cdot \left[6xB - 4x^3 \right] \dots \dots \dots (15)$$

$$f^V(x) = \left[\frac{2}{B^3} \left(-\frac{2x}{B} \right) f^I(x) \cdot (6xB - 4x^3) \right] + \left[\frac{2}{B^3} \cdot f^I(x) (6B - 12x^2) \right]$$

$$\therefore f^V(x) = \frac{4}{B^4} \cdot f^I(x) \left[4x^4 - 12x^2B + 3B^2 \right] \dots\dots(16)$$

Substituting 12, 14, and 16 into 11,

$$\begin{aligned} \left(\frac{\Delta z}{\Delta x} \right)_{\Delta x=b} &= \left\{ f^I(x) + f^I(x) \cdot \frac{2}{B^2} \cdot \frac{(2x^2-B)}{3!} \left(\frac{b}{2} \right)^2 \right. \\ &\quad \left. + f^I(x) \cdot \frac{4}{B^4} \cdot \frac{(4x^4 - 12x^2B + 3B^2)}{5!} \cdot \left(\frac{b}{4} \right)^4 \dots \right\} \\ &= f^I(x) \left[1 + \frac{2}{B^2} \cdot \frac{(2x^2-B)}{3!} \left(\frac{b}{2} \right)^2 \right. \\ &\quad \left. + \frac{4}{B^4} \cdot \frac{(4x^4 - 12x^2B + 3B^2)}{5!} \cdot \left(\frac{b}{4} \right)^4 \dots \right] \end{aligned}$$

Substituting $B = 4Dt$ and putting $f^I(x) = \frac{\partial^n}{\partial x}$,

$$\begin{aligned} \left(\frac{\Delta z}{\Delta x} \right)_{\Delta x=b} &= \frac{\partial^n}{\partial x} \left\{ 1 + \frac{1}{2^2 \cdot 3!} \left(\frac{b^2}{2Dt} \right) \left(\frac{x^2 - 2Dt}{2Dt} \right) \right. \\ &\quad \left. + \frac{1}{2^4 \cdot 5!} \left(\frac{b^2}{2Dt} \right)^2 \left(\frac{x^4 - 12x^2Dt + 12D^2t^2}{4D^2t^2} \right) \dots \right\} \quad (17) \end{aligned}$$

APPENDIX III

Computer Programme (Sirius Autocode) for the
Calculation of D (least squares curve fitting).

N
COMPUTATION OF DIFFUSION COEFFICIENT.

BEST D AND T(INFL.) FOUND BY THE METHOD OF LEAST SQUARES,
APPLYING EXPERIMENTAL DATA.

TIME INCREMENT ADDED BEFORE CALCULATING D.
INITIAL DELTA T = 0SECS, WITH 10SEC INCREMENTS REPEATED.

IDEAL CURVE TO FIT BEST D AND T ALSO CALCULATED.
ALSO VARIANCE OF EXPTL. FROM THEORETICAL POINTS.

V=1507

T5

J05

ALL

L

S615-15

S616-16

S617-17

T5

J01

V901=TAPE0

V1202=TAPE0

V1=TAPE0

V101=TAPE0

N12=70

V1000=0

N10=0

TEXT

POSSIBLE RANGE OF 2X SQD MAX EXPTL.

I

II

III

IV

V

V908=V901/1.025

V909=V908XV908

V910=V902/1.025

V911=V910XV910

V906=V903/1.025

V907=V906XV906

V912=V904/1.025

V913=V912XV912

V914=V905/1.025

V915=V914XV914

PRINTV909,1024

PRINTV911,1024

PRINTV907,1024

PRINTV913,1024

PRINTV915,1024

PRNN

PN

```

1) V(101+N10)=V(101+N10)/1.925
V(101+N10)=V(101+N10)*V(101+N10)
N10=N10+1
→1, N10=N12
N10=0
20) PRINT V(1+N10), 3080
PRINT V(101+N10), 4024
N10=N10+1
→20, N10=N12
5) N10=0
TEXT

```

DELTA T

D

T

AX SQD

```

PRINT V1000, 3062
4) V(1001+N10)=V(1+N10)+V1000
N10=N10+1
→4, N10=N12
N10=0
2) V(201+N10)=LOG V(1001+N10)
V(1101+N10)=V(1001+N10)*8
V(201+N10)=V(201+N10)*V(1101+N10)
V(201+N10)=V(1101+N10)-V(201+N10)
V(801+N10)=V(101+N10)*V(201+N10)
V(401+N10)=V(101+N10)*V(1101+N10)
V(501+N10)=V(201+N10)*V(1101+N10)
V(601+N10)=V(1101+N10)*V(1101+N10)
V(701+N10)=V(201+N10)*V(201+N10)
N10=N10+1
→2, N10=N12
V321=0
V322=0
V323=0
V324=0
V326=0
N10=0
3) V321=V321+V(801+N10)
V322=V322+V(401+N10)
V323=V323+V(701+N10)
V324=V324+V(501+N10)
V326=V326+V(601+N10)
N10=N10+1
→3, N10=N12

```

```

V335=V334
N0=0
N1=2
N2=3
N3=323
N4=327
+SR17
N1=327
N2=328
N3=338
N4=2
N5=
N6=2
N7=1
+SR16
V333=V332/V332
V333=EXP V333
PRINT V333, 2026
PRINT V333, 2062
V331=8X V331
V350=V331X V333
PRINT V350, 2026
XV1000=V1000+5
XV1000=V1000+5
N10=0
V1249=V331
6) V(1250+N10)=V(1202+N10)XV1249
N10=N10+1
+6, N10#25
N10=0
7) V(1300+N10)=V333/V(1202+N10).
N10=N10+1
+7, N10#25
N10=0
8) V(1350+N10)=LOG V(1300+N10)
N10=N10+1
+8, N10#25
N10=0
9) V(1350+N10)=V(1350+N10)+1
N10=N10+1
+9, N10#25
N10=0
10) V(1400+N10)=V(1350+N10)XV(1250+N10).
N10=N10+1
+10, N10#25
N10=0

```

TEXT

T : 2X SQD

```
11) PRINTV(1202+N10),3080
PRINTV(1400+N10),4024
N10=N10+1
→11,N10≠25
N10=0
```

```
12) V(1600+N10)=V(1001+N10)XV1249
V(1700+N10)=V333/V(1001+N10)
V(1700+N10)=LOGV(1700+N10)
V(1700+N10)=1+V(1700+N10)
V(1700+N10)=V(1700+N10)XV(1600+N10)
V(1800+N10)=V(1700+N10)-V(101+N10)
V(1800+N10)=V(1800+N10)XV(1800+N10)
N10=N10+1
→13,N10≠N12
N10=0
V1900=0
15) V1900=V1900+V(1800+N10)
N10=N10+1
→15,N10≠N12
N10=0
V1950=N12
V1900=V1900/V1950
V1900=SQRTV1900
```

TEXT

DEVIATION OF EXPTL. FROM THEORETICAL CURVE

S =

PRINTV1900,1028

→5,V1000≠1000
(→0)

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The Application of the Wavefront Shearing Optical Interferometer to Diffusion Measurements

W. J. Thomas and E. McK. Nicholl

The measurement of diffusion coefficients in dilute solutions of electrolytes can be effectively and accurately carried out using birefringence. An interferometer utilizing birefringence has been constructed by the authors and is described. A flowing-junction cell is also used. The four available methods for the calculation of the diffusion coefficient are discussed. A Ferranti Sirius computer has been programmed to handle the calculations. Diffusion coefficients for the systems sucrose-water, monoethanolamine-water, and diethanolamine-water are reported.

Introduction

The determination of diffusion coefficients by an examination of concentration distributions and concentration gradients across a liquid-liquid interface by optical methods is well known. Among the most useful methods are those due to Lamm, Rayleigh, and Gouy.¹⁻³ The latter has recently been examined in this laboratory by Thomas and Furzer.^{4,5} The Mach-Zender interferometer falls into the same group of optical methods and is also well known.

All the above methods for determining diffusion coefficients rely on the formation of interference fringes. Other optical methods exist, viz., the schlieren scanning and Svernnson's diagonal (the slit method), but methods using interference fringes are the most sensitive. Since a shift of one fringe corresponds to a change in refractive index of 5.461×10^{-5} for a 1-cm cell ($= \lambda/a$ for the mercury green line), it follows that it is possible to detect extremely small changes in refractive index.

However, a recent development by Ingelstam and Bryngdahl⁶⁻⁹ is an interferometer with an appreciably greater sensitivity to changes in refractive index than any of the above methods. Bryngdahl has shown that concentrations of as low as 0.01% can be used. It appears, therefore, that this is the only optical method which can be applied to very dilute electrolyte solutions. It has also been shown that this particular method is capable of giving greater accuracy than previous methods, due to the decrease in the concentration range.

The principal features of the method described by Ingelstam and Bryngdahl are the use of polarized

light and a Savart plate to form interference fringes. The Savart plate consists of two uniaxial quartz crystals cemented together, with their optic axes at 90° to each other, at 90° to the beam direction, and at 45° with respect to the plane of the paper (see Fig. 1).

Parallel light passes through the first polarizing plate and is polarized such that the oscillation plane bisects the two principal planes of the Savart plate. Thus, the wavefront is divided into two equally strong coherent wavefronts polarized perpendicularly to each other. By means of the second polarizer set at 45° in relation to the principal planes of the crystal plates, the two wavefronts are caused to interfere.

A complete description of the mechanics of the interference is given by Bryngdahl.⁷

The interference pattern itself consists of a set of horizontal fringe pairs (Fig. 2).

Description

The Optical System

The complete optical system, as shown in Fig. 3 is contained in a constant-temperature (thermostatically controlled) darkroom. The temperature of the room can be maintained to $\pm 0.1^\circ\text{C}$.

The optical bench is of steel, of triangular section, 3 m long, resting on two 10-ft (3.05-m) long steel girders bolted to three concrete pillars. (The whole assembly, weighing over 450 kg, is separated from the floor by rubber blocks.) The various components in the optical system are attached to the bench by adjustable saddle stands, fitted with clamping screws.

A 125-W mercury vapor lamp operated in a horizontal position provides a source of monochromatic light (at 5461 Å). The narrow discharge from the lamp is focused through a short focal length condensing lens, L_1 , through infrared and green filters onto a horizontal adjustable slit operated from 5 μ to 10 μ .

The authors are with the Department of Chemical Engineering, Battersea College of Technology, London, England.

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Fig. 1. The Savart plate, showing how the incident light ray is split up into an extraordinary/ordinary (E/O) and an ordinary/extraordinary (O/E) ray. E/O and O/E are perpendicularly polarized to each other.

135 170 205 275 310 415
Time (sec) from start of diffusion

Fig. 2. Photographs of interference fringes recorded during diffusion of 0.0578% monoethanolamine into water.

To reduce the effect of stray light, the lamp, condenser, filters, and slit are housed in a light-proof structure (which is adequately ventilated).

By means of the similar lenses L_2 , L_3 , the light is collimated through the flowing-junction cell and also by lens L_4 . Parallel light is, thus, passed through the Savart plate.

Polarizers P_1 and P_2 are placed before L_4 and after the Savart plate.

The image formed after the Savart plate is rather small, and it is convenient to magnify the final image by means of the lens L_5 .

The diffusion occurring in the cell is recorded photographically by a 35-mm Robot Recorder camera placed in the image plane, M . The lens is removed from the camera so that the image is projected directly onto the film. The camera is coupled to an automatic time-control unit, by means of which the exposure time and time intervals between exposures may be accurately set.

The Flowing-Junction Cell

The diffusion cell is of the flowing-junction type and was constructed in the laboratory workshops.

Figure 4 shows the cell with solution reservoirs.

The cell is constructed by bolting together several pieces of ground stainless steel, and grinding the ends plane and parallel. The flowing-junction slit is set at 150μ . Optical glass plates are pressed into contact with the ends of the cell by ten pressure screws. A polythene gasket smeared with silicone grease separates

the glass cell ends from the steel flats, while a copper gasket separates the pressure screws from the glass. The optical path length through the cell is 630 mm.

The solution and solvent reservoirs are connected to the cell by a manifold with suitable taps. A mercury reservoir, of variable height, provides the head necessary for the solution and solvent to flow into the cell.

Experimental Technique

The cell is cleaned and flushed with distilled water and air, before finally being flushed with solvent. The liquid reservoirs are cleaned, flushed, and filled with solvent and solution.

The thermostatic control for the room is set at 25°C , and the cell and reservoirs are left, set up on the optical bench, for about 12 h (i.e., overnight). It is important that thermal equilibrium is established when a run is started, for it must be appreciated that small differences in temperature or slight mechanical vibrations transmitted to the cell can cause much more rapid mixing of the diffusing substances than the pure diffusion process itself.

When this is done, the solvent is admitted to the top of the cell and the solution is admitted to the bottom, using the mercury reservoir for the necessary head. The sidestream is then started, and the denser solution slowly rises in the cell chamber so that eventually a sharp interface is formed between solvent and solution at the slit exit. The rate of discharge of the sidestream is critical in establishing an interface, varying between twenty and forty drops per minute depending on the solution used.

Once established, the interface is maintained for about 15 min in order to be certain that it is quite stable.

Meanwhile the Robot Recorder camera is loaded with a length of Kodak R.55 recording film. A ground glass screen with a magnifying viewer placed in the image plane (for ready inspection of the interface and, later on, the fringes), is removed and the camera is substituted in its place. The automatic time-control unit is set for 5-sec exposures at 30-sec intervals and is switched on. As soon as the first exposure is taken (of the interface), the relevant taps on the cell are shut, thus stopping the sidestream discharge and starting the diffusion process in the cell.

Photographic recording of the diffusion process is continued until inspection of the image reveals that the

Fig. 3. The wavefront shearing optical interferometer. MV, mercury vapor lamp; F, green and ultraviolet filters; HS, Hilger slit; C, cell; P, polarizers; and L, lenses.

Fig. 4. The flowing-junction cell.

next-to-outermost fringe pair has merged. Depending on the concentration difference between solvent and solution (0.6% is convenient) this could occur after about forty exposures.

The exposed film is developed in Kodak DX.80 at a dilution of 1:4.

Several high-speed films and developers were tried before it was decided to use the R.55 film and DX.80 developer. R.55 film is sensitive to ultraviolet, blue, and green light—the maximum sensitivity lying between 5400 Å and 5700 Å.¹⁰ The use of R.55 film is further enhanced by its insensitivity to red light, thus making film handling very easy.

The movement of the fringe pairs as recorded photographically is measured primarily by a recording microdensitometer. Photograms of the fringe pairs are obtained using this instrument, and the distance between the fringe pair peaks can then be measured. Where the recording microdensitometer is limited in accuracy in differentiating the fringe pairs, a cathetometer is used to measure the distance between respective fringe pairs.

Although the movement of several fringe pairs may be observed during the course of a run, it is convenient to follow only one, namely the next to outermost, in order to calculate the diffusion coefficient.

A typical series of fringe pairs is shown in Fig. 2, and associated photograms in Fig. 5.

Calculation of the Diffusion Coefficient

The calculation of the diffusion coefficient is based on the basic diffusion equation for the free diffusion case

with the diffusion coefficient independent of concentration, i.e.,

$$\frac{\partial c}{\partial z} = \frac{c}{2\sqrt{\pi Dt}} \cdot \exp\left(\frac{-z^2}{4Dt}\right) \quad (1)$$

or,

$$\frac{\partial n}{\partial z} = \frac{\Delta n}{2\sqrt{\pi Dt}} \cdot \exp\left(\frac{-z^2}{4Dt}\right) \quad (2)$$

Equation (2) follows from Eq. (1), since there is a linear relationship between c and n , where

- c = concentration of solute diffusing into solvent,
- z = distance from original boundary in diffusion cell,
- t = time,
- n = refractive index of liquid,
- Δn = difference in refractive index between initial concentrations of the upper and lower solution in the cell.

Equations (1) and (2) are symmetrical about the origin and have the same form as the Gaussian error curve. The method used here for the evaluation of D is due to Lamm and Bryngdahl,⁷ and the equations used are derived from Eq. (2).

The interference pattern produced is related to the Gaussian curve which represents the ideal concentration gradient, as above, and D is deduced from the rate at which the fringe pattern changes. Following a definite fringe pair with respect to time, we find then the curve representing the movement of this one fringe pair is given by

$$(2x)^2 = 8Dt(1 + \ln t/t_i) \quad (3)$$

where

- $2x$ = distance between fringe pairs
- t_i = time corresponding to the maximum distance between fringes.

When $t = t_i$,

$$(2x)_i^2 = 8Dt_i \quad (4)$$

The diffusion coefficient, D , is obtained from values of $(2x)^2$ and its corresponding times t_1 and t_2 by the expression

$$D = \frac{(2x)^2 (1/t_1 - 1/t_2)}{8 \cdot \ln t_2/t_1} \quad (5)$$

Fig. 5. Actual photograms of interference fringes (0.0578% monoethanolamine/water).

Fig. 6. Graph of $(2x)^2$ against t , -0.0578% monoethanolamine-water (next-to-outermost fringe pair). ($\Delta t = 58$ sec added to original t values.)

A typical curve of $(2x)^2$ against t is shown in Fig. 6.

The calculation of D , however, is complicated by the fact that the experimental curve obtained is not the true curve.

Due to the experimental impossibility of obtaining an infinitely sharp interface in the diffusion cell, the experimental curve of $(2x)^2$ against t is, in effect, displaced toward zero along the t axis. It is necessary, therefore, to introduce a zero-time correction factor to Eqs. (3), (4), and (5) in order to calculate the correct value of D [the zero-time factor effectively displacing the curve of $(2x)^2$ against t to its true position, thus enabling the correct value of D to be calculated]. Thus, the equation of the curve will become:

$$(2x)^2 = 8D(t + \Delta t)[1 + \ln(t_1 + \Delta t)/(t + \Delta t)]. \quad (6)$$

The calculation of Δt , the zero-time correction factor, may be done by four separate methods as outlined by Bryngdahl.^{7,11} Two of the methods are only very limited in accuracy, but the other two methods have proved to be quite acceptable and have been used in the experimental work undertaken in this laboratory. A new technique for calculating D and Δt is being perfected by the authors, and this has proved to be considerably more convenient and as accurate as the previous methods. Since a large number of repetitive calculations are involved in the calculation of D , use was made of the College's Ferranti Sirius computer. Descriptions of the methods of calculation and associated computer programs are given below.

1. In runs where more than one fringe pair is observed and recorded photographically, these are plotted on a graph of $(2x)^2$ against t . A straight line is drawn connecting the maximum points of the curves. The line is of slope $8D$, and, from the point where it cuts the t axis, Δt may be determined. This method is limited in accuracy and has not been used beyond an initial trial.

2. From the basic diffusion equations the logarithmic relationship

$$(2x)^2/t = C - 8D \ln t_1/t \quad (7)$$

may be derived.

If $(2x)^2$ is plotted against $\ln t$ for any one fringe pair, repeatedly adding a small time-increment to the t values before plotting the curve, then, theoretically, at the stage when the correct Δt is reached the curve should be a straight line of slope $-8D$. In practice, it has been found that the method is very insensitive and is even less accurate than the method outlined above.

3. Bryngdahl has shown that the true D is related to the calculated D , D' , by the expression

$$D = D'/(1 + \Delta t \cdot \nu) \quad (8)$$

where

$$\nu = \frac{t_1 + t_2}{t_1 t_2} - \frac{1/t_1 - 1/t_2}{\ln t_2/t_1}. \quad (9)$$

If then D is calculated for any one value of $(2x)^2$ and the corresponding t_1 and t_2 values using Eq. (5), and plotted against ν , a straight line is obtained of slope $D \cdot \Delta t$ cutting the ordinate axis at D . There are limitations to this method, but it is accurate to the third significant figure. This method has been found most useful as a guide to the accuracy of the experimental points before calculating D using the fourth and most accurate method.

4. The fourth method for calculating D is the most accurate of the four methods outlined here. D is calculated by Eq. (5) and is plotted against $(2x)^2$, with Δt as a parameter. This is done by first calculating D with no correction applied to the time, for a set of

Fig. 7. Graph of D against $(2x)^2$, Δt as parameter (0.0578% monoethanolamine-water).

Table I. Diffusion Coefficients Measured Using the Wavefront Shearing Optical Interferometer^a

Run No.	Solute concn. in diffusing solution (wt. %)	Average concn. (wt. %)	Temp. (°C)	D ($\text{cm}^2/\text{sec} \times 10^6$)	Δt (sec)
S/1	0.0472	0.0236	25.5	5.221 ± 0.011	87
S/2	0.0472	0.0236	25.2	5.205 ± 0.015	22
S/3	0.0667	0.0334	24.8	5.13	87
S/4	0.0993	0.0497	25.3	5.216 ± 0.012	64
MEA/1	0.0578	0.0289	25.3	10.400 ± 0.100	58
MEA/3	2 g mol/liter		25.3	8.575 ± 0.066	22
MEA/4	4 g mol/liter		25.3	6.729 ± 0.044	18
DEA/1	0.03259	0.0163	25.5	6.624 ± 0.040	8

^a Runs S/1-4 for sucrose-water, runs MEA/1, 3, and 4 for monoethanolamine-water, and run DEA/1 for diethanolamine-water. Magnification factor of the interferometer = 0.563.

values of $(2x)^2$, t_1 , t_2 . Then a small time increment is added to the t values and the calculations are repeated. This is continued until the value of D becomes constant when plotted against $(2x)^2$. At this point the correct value of D is obtained together with the zero-time correction.

The method of calculation is illustrated by Fig. 7 with actual experimental results. It may be seen that D becomes constant at $\Delta t = 62$ sec and has a value of $10.400 \times 10^{-6} \text{ cm}^2/\text{sec}$ at this stage.

The only drawback to this method is the sheer volume of repetitive calculations if done by hand. To eliminate this a Ferranti Sirius Autocode computer was programmed to handle the calculations.

The program tape is headed off with the calculation method outlined in paragraph 3 above. As stated previously, this calculation serves as a guide to the accuracy of the points calculated by the fourth method.

The flow diagrams for the two computer programs used by the authors are not given here, but would be available on request.

Experimental Results and Discussion

The interferometer was calibrated using dilute solutions of sucrose-water before further runs were undertaken to investigate the diffusion coefficients of the ethanolamines over a range of concentrations. The sucrose-water results, together with three monoethanolamine- and one diethanolamine-water results are given in Table I. Complete data for the diffusivities of the mono-, di-, and triethanolamines are being accumulated at the moment in these laboratories and will be presented later. Thus the results given in Table I are only a representative sample.

The values of D obtained for sucrose-water agree well with previous experimental values,^{7,12-14} obtained by Bryngdahl using a similar interferometer and other workers using the Gouy interferometer; they illustrate the accuracy obtainable and the concentration range in which this interferometer is capable of working.

In run S/3 it can be seen that an inconsistent value of D was obtained. In this run, thermal equilibrium was not established due to an electrical failure. It was decided to continue with the run, nevertheless, to see what effect this would have on the value of D . Since the resulting coefficient is undoubtedly inconsistent, it is most important that thermal equilibrium be established before any run takes place.

The authors have had several opportunities to examine the accuracy obtainable using this interferometer, and to compare the work with that done on the Gouy interferometer in the same laboratory by Furzer.⁵ It is their firm opinion that the wavefront shearing interferometer is superior both in accuracy and convenience of use. The calculation of the results, particularly, is simpler.

The accuracy of the interferometer, naturally, is increased by the quality of the optical components used, and it is essential that the best quality lenses be used in order to utilize the inherent accuracy. There are few problems in the setting up of the interferometer that a basic knowledge of optics will not resolve, so that it is, in fact, an extremely useful instrument for the type of work discussed above.

Appendix: a New Method of Calculating the Diffusion Coefficient for Liquid-Liquid Systems

The design of a wavefront shearing optical interferometer and its use for the measurement of diffusion coefficients in dilute electrolyte solutions has been described in the foregoing sections.

Four methods of calculating the diffusion coefficient were examined, each involving a zero-time correction factor. Such a factor is necessary as the infinitely sharp interface required for the rigorous application of the Fick equation cannot be realized in practice. It was found from direct calculations based on experimental results that of the four methods the iteration method was the most acceptable and accurate. The large volume of repetitive calculations involved in this method was handled by a Ferranti Sirius computer.

However, a fault common to all four methods is that the accuracy of the calculations is dependent upon readings taken from a smooth curve drawn through the experimental points on a $(2x)^2$ vs t plot. A slight scatter of points is difficult to avoid experimentally, and this obviously affects the true position of the curve when drawn by hand.

A new method for calculating D is proposed which is less sensitive to error than any of the previously described methods, especially when a slight scatter of points on the experimental curve of $(2x)^2$ vs t cannot be avoided due to limitations of the optical equipment. The new method is also as accurate as the previously mentioned iteration method, and is possibly more convenient to use.

The Method

The equation for the ideal movement of one fringe pair, as given by Bryngdahl,⁷ is used for the calcula-

Fig. 8. The ideal curve describing the movement of one fringe pair with respect to time.

Fig. 9. Theoretical curve (A) as obtained from the best D and t_i calculated by the method of least squares to fit the experimental points (B). No zero-tide correction applied to B curve.

tions. A fringe pair in the interference pattern (the next to outermost is generally the most convenient to use) is followed with respect to time, and the experimental values of $2x$ are found. $(2x)^2$ against t is plotted as shown in Fig. 8.

The equation of the curve in Fig. 8 is given by

$$(2x)^2 = 8Dt[1 + \ln(t_i/t)] \quad (\text{A-1})$$

where t_i is the time corresponding to $(2x)_i^2$. When $t = t_i$,

$$(2x)_i^2 = 8Dt_i. \quad (\text{A-2})$$

As mentioned before by the authors, a degree of non-ideality is introduced to this equation by the zero-time correction factor, Δt . Thus the practical equation to be used is

$$(2x)^2 = 8D(t + \Delta t) \left[1 + \ln \frac{(t_i + \Delta t)}{(t + \Delta t)} \right]. \quad (\text{A-3})$$

Consider now a set of linear equations

$$\begin{aligned} y_1 &= (Z_1 k_1)_1 + (Z_2 k_2)_1 \\ \text{to } y_n &= (Z_1 k_1)_n + (Z_2 k_2)_n \end{aligned} \quad (\text{A-4})$$

in which there are n sets of observations of y and Z values (k values being constants). It can be shown that the normal equations to determine values for k_1, k_2 that best correlate a set of data $(y_1, \dots, y_n, x_1, \dots, x_n)$, where $Z_1, Z_2 = f(x)_1, f(x)_2$, are:

$$k_1 \sum Z_1^2 + k_2 \sum Z_1 Z_2 = \sum Z_1 y, \quad (\text{A-5})$$

$$k_1 \sum Z_1 Z_2 + k_2 \sum Z_2^2 = \sum Z_2 y. \quad (\text{A-6})$$

Values for k are obtained by the simultaneous solution of the normal equations.

Thus for a set of readings of the movement of one fringe pair, the two applicable normal equations to solve for D , and $(t_i + \Delta t)$ are:

$$\begin{aligned} D \sum (8t + \Delta t)^2 + D \cdot \ln(t_i + \Delta t) \sum (8t + \Delta t) \\ \times [(8t + \Delta t) - (8t + \Delta t) \cdot \ln(t_i + \Delta t)] = \sum (2x)^2 \cdot D, \quad (\text{A-7}) \\ D \cdot \sum (8t + \Delta t) [(8t + \Delta t) - (8t + \Delta t) \cdot \ln(t_i + \Delta t)] \\ + D \cdot \ln(t_i + \Delta t) \sum [(8t + \Delta t) - (8t + \Delta t) \cdot \ln(t_i + \Delta t)]^2 \\ = \sum (2x)^2 [(8t + \Delta t) - (8t + \Delta t) \cdot \ln(t_i + \Delta t)] \quad (\text{A-8}) \end{aligned}$$

The simultaneous solution of these two equations is best obtained by the use of an algebraic matrix of the form

$$\begin{bmatrix} \sum Z_2 \cdot y \\ \sum Z_1 \cdot y \end{bmatrix} = \begin{bmatrix} k_1 \\ k_2 \end{bmatrix} \begin{bmatrix} \sum Z_2^2 & \sum Z_1 Z_2 \\ \sum Z_1 Z_2 & \sum Z_1^2 \end{bmatrix}. \quad (\text{A-9})$$

The authors programmed the College's Ferranti Sirius computer to handle the large volume of calculations entailed.

Starting with a value of $\Delta t = 0$, the best D and t_i are calculated for a set of experimental points. The calculation is repeated for $\Delta t = 5, 10, 15, \dots$ sec.

It will be found that, when $\Delta t = 0$, the curves calculated from the D and t_i that best fit the experimental points will be of the same shape as curve A in Fig. 9, i.e., the calculated curve is somewhat more peaked than the curve drawn through the experimental points.

When too large a Δt has been applied the calculated curve is less peaked than the experimental curve. Comparing the two values of $(2x)_i^2$ i.e., the experimental and the value for the calculated curve, as the calculation proceeds, we find when they coincide that the two curves are identical and the correct value of D and Δt may be established.

The authors have used this method of calculation extensively in their work, and the accuracy has proved to be equal to that of the previously mentioned iteration method. However, the method is very much more convenient to use due to its essential simplicity, and is, in fact, quite a rapid method.

Possibly the only limitation to the use of this method is the fact that a fairly complete experimental curve must be obtained which should not be weighted too much to any one side of its peak. This condition, however, would apply just as much to any other method of calculation.

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