TEMPERATURE AND CONCENTRATION DEPENDENCE
OF
LIQUID PHASE DIFFUSION COEFFICIENTS

by

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To my dearest wife "Dr. Mya Lay Thant" for her
love and understanding.

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ABSTRACT

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A study of experimental techniques for the determination of diffusion coefficients for binary mixtures and a study of the existing relationships for these coefficients were carried out.

A new three-compartment diffusion cell was developed capable of measuring diffusion coefficients at temperatures up to the normal boiling point (24). By means of this cell, diffusion coefficients were measured for the systems ethanol-water, acetone-water and acetone-chloroform for a range of temperatures up to the normal boiling points. Thus diffusion coefficients for the above mixtures including those at boiling points and at infinite dilution are presented.

A relationship was developed to relate diffusion coefficients with temperature and concentration (equation 3-1.21) in binary systems. It agrees better with the experimental data for the associated systems than some literature correlations.

By application of parachors a new equation (3-2.4) was developed for the prediction of diffusion coefficients at infinite dilution (201). This equation, because of the ease of calculating parachors, is more convenient to use than other equations based on the Stokes-Einstein equation.

An additive method for the prediction of self-diffusion coefficients was introduced and a correlating equation (3-3.4) was developed. The bond and structural contributions to the constant of the equation were calculated on the basis of a limited amount of experimental data. Despite this the correlation gives reasonable predictions for the temperature range between melting point and boiling point.

boiling points and at infinite dilution are presented.

Another correlation for the prediction of self-diffusion coefficients was developed (203) (equation 3-3.6) by modifying an existing equation. This was possible by applying the relationship between the molal volume at the boiling point and the critical molal volume developed in this work (202). The new equation is more convenient to use.

The correlating property of the critical temperature was used to devise a relationship between diffusion coefficients, critical temperature and the working temperature. The two correlating equations (3-4.6) and (3-4.7) can predict diffusion coefficients at various temperatures if one value of the diffusion coefficient at a single temperature is known.

PART 1 INTRODUCTION

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A knowledge of diffusion coefficients is required in the design of chemical engineering equipment in which mass transfer or simultaneous heat transfer and mass transfer take place. So far the most reliable diffusion coefficients in the liquid phase are derived experimentally. Most of the methods available for the experimental determination of diffusion coefficients are designed for work at ambient temperature and atmospheric pressure. Since chemical engineering processes occur mainly at temperatures higher than ambient, there is a need for a reliable method for the experimental determination of mass diffusion coefficients at elevated temperatures. In this work a three-compartment diaphragm cell was developed for experimental determinations of diffusion coefficients at elevated temperatures, up to the normal boiling point. Using this diaphragm cell, diffusion coefficients for three binary liquid systems i.e. ethanol-water, acetone-water and acetone-chloroform were determined for various temperatures up to the neighbourhood of their normal boiling points over the complete concentration range. The values of diffusion coefficients at normal boiling points for these binary systems were obtained by interpolation and extrapolation. The diffusion coefficients at infinite dilution for these mixtures were also obtained by extrapolation.

Experimental methods of obtaining diffusion coefficients are tedious. Therefore many attempts have been made by research workers to develop methods for predicting diffusion coefficients as a function of temperature and concentration. Out of many such correlations available those of Leffler and Cullinan (111), of Vignes (210) and of Gainer (61) are promising. A new correlation of this type is developed in this work and it appears that this correlation gives better predictions for associated binary systems.

Literature correlations for the prediction of diffusion coefficients at infinite dilution and self-diffusion coefficients are usually difficult to use because of the lack of physical properties available. It was found that the most reliable correlations in this group are those of Wilke and Chang (219), of King et al (104) and of Sitaraman et al (182). In this work an effort was made to devise a new correlation employing parachors instead of such properties as latent heats of vaporisation etc. The advantage of this equation is in the fact that parachors are easier to obtain from literature.

Self-diffusion coefficients are important as they are used in many correlations in the same way as other physical properties of liquids. Hence many empirical correlations for the prediction of self-diffusion coefficients are available. Those of Dullien (43) and of Vadovic and Colver (206) have the reputation of giving reasonable predictions. Their equations, to be used, require a knowledge of critical molal volume and molal volume at melting point respectively. In this work the Dullien equation is modified so that molal volume at the boiling point can be used.

In this work an attempt is made to develop an additive method for the prediction of self-diffusion coefficients. A large number of experimental self-diffusion coefficients are needed to define accurately the bond contributions. So far these contributions are determined on the basis of 46 available experimental self-diffusion coefficients. The correlation developed gives predictions comparable with experimental coefficients.

Transport properties of liquids are strongly temperature dependent. It appears from a literature search that this temperature dependence can be correlated by introducing the critical temperature. This method is applied, in this work, to develop one empirical equation for the prediction of self-diffusion coefficients and another for the prediction of diffusion coefficients at infinite dilution at other temperatures when a single value of the coefficient at one temperature is available.

PART 2 LITERATURE SURVEY

2 - Literature Survey

The various theories for diffusion in liquids may be listed as (a) Hydrodynamic theory (b) Statistical-Mechanical theory (c) Irreversible Thermodynamics theory (d) Eyring's (absolute reaction rate) theory and (e) Lamm-Dullien theory. Each theory is based on a specific structural model. The basis of the structural models of liquids are briefly described below.

None of the theories is described in detail except those on which the correlations of Leffler and Cullinan (111), Vignes (210) and Gainer and Metzner (60) are based. When discussing these correlations the relevant theory will be referred to.

2-1 Structural models of liquid phase

The theory of the liquid state is only partially developed when compared to the well established theories of the gaseous and solid states. The theoretical knowledge of gases and solids is more advanced because the gaseous state exhibits complete molecular disorder, and the solid state possesses a regular crystalline structure.

In the case of liquids neither the complete randomness of gases, nor the rigid geometrical structure of solids is observed. There is no definite structural description for liquids other than the very gross explanation that the properties of liquids lie between those of gases and solids. However, taking advantage of the latter explanation, attempts have been made to formulate a theory of liquid state from the presumption that liquids are either condensed gases or disordered solids. The theories developed from the assumption of condensed gases are called "distribution function" theories (10), because they are described by certain distribution functions specifying the probability of finding sets of molecules in particular configurations. The theories developed from the assumption of disordered solids are known as "lattice" theories (10), because they assume a certain structure which bears some relation to the regular lattice structure of a crystalline solid.

Both of these approaches are useful in describing the liquid state properties, there is no 'a priori' reason to suppose that either approach is more correct or more fundamental than the other. However, the lattice theories are usually more convenient to use as they involve less complex mathematics than do the distribution function theories.

A brief description of a few theories, based on the lattice structure of the liquid phase, will be given below.

2-1.1 : The cell model (10, 159, 93, 87)

In this model each molecule in the liquid may be regarded as confined to a comparatively restricted region, designated as a 'cell' or a 'cage', formed by its surrounding molecules. According to this view the main difference between a solid and a liquid is that a molecule in a cell has a little more freedom of movement in the liquid than in the solid, due to the increase in volume on melting.

In developing this cell model the molecules are assumed to move entirely independently of one another within their cells, i.e. the positions of neighbouring molecules remain fixed while the central molecule moves around. This assumption involves a paradox as any molecule may be regarded either as a neighbouring molecule or a central molecule. All the cells are assumed to be identical and each contains just one central molecule, usually called a "wanderer". The molecules are assumed to behave as hard, non-attracting, spheres. During the melting process the lattice is assumed to expand uniformly.

With this structural model it is difficult to suggest the mechanism of a solute molecule moving through the solvent molecules.

2-1.2 The "hole model" (69, 57)

The hole model of the structure of the liquid phase pictures the configuration of molecules as a cubical lattice structure. In this structure there are missing random molecules and the vacant spaces are called "holes". The location of the holes is not permanent, they are supposed to be moving as a vapour bubble in a liquid. This theory explains the diffusional motion and viscous motion in a liquid quite well. The process of jumping of a molecule from the neighbouring layer into that hole constitutes the process of diffusion. The sliding motion of a row of molecules to occupy the vacated space represents the process of viscous motion. The hole theory is very suitable as a foundation for the theories stating that diffusion and viscosity are two interlinked processes.

2-1.3 The significant structure theory model (53)

As in the hole theory the lattice structure is assumed but the molecules are divided at least into two groups. One group consists of solid-like molecules possessing vibrational motion and the other group of molecules is supposed to exhibit translational motion like molecules in a gas phase. The lattice structure is subject to expansion and contraction on changes in temperatures. These are the main differences between the hole model and the significant structure theory. The significant liquid structure theory constitutes a better basis for various theories of fluid physical properties.

2-1.4 The tunnel model (10)

This model attempts to picture the structure of the liquid phase more realistically. The molecules are imagined as behaving as beads on long strings. These strings are supposed to move in parallel and a sufficient space is available between the neighbouring strings to make the motion possible. Each string of molecules behaves like a single cell in the cell model.

2.1-5 Other models

Most of the other structural models are modifications of the models mentioned above and have been described comprehensively in the following references: (10, 53, 57, 69, 87, 93, 129, 159).

2-2 Self-diffusion in Liquids

Self-diffusion is diffusion in a single component fluid i.e. diffusion of molecules through an assembly of molecules of the same species. Self-diffusion coefficients are obtained experimentally in the same way as the mutual diffusion coefficients except that radio active tracers are used to mark the diffusing molecule. A large number of mathematical models and empirical equations for the prediction of self-diffusion coefficients have been developed. Some of these equations are summarised in Table 2-2.1. One group of these correlations is based on the Stokes-Einstein equation, which is a result of the Einstein-Sutherland hydrodynamic theory of diffusion. The other group of correlations is based on the Eyring theory of absolute reaction rate. Some of the correlations, particularly those of a mainly empirical nature, are based partly on the hydrodynamic theory and partly on the Eyring theory. It can be seen from Table 2-2.1 that very few of these correlations were checked with experimental data, therefore there is no basis for recommending any of these equations.

No one has yet attempted to predict self-diffusion coefficients from the group additive properties; this method was tried successfully in the calculation of molecular volumes e.g. Le Bas method (109), in the prediction of surface tension by means of parachors (188) and in the prediction of viscosity by rheochors (58, 59).

Table 2-2.1 Equations for estimating self-diffusion coefficients

Author, year and reference	Equation	Liquids tested	% error	Equation number
Einstein-Sutherland, 1905 (49, 189)	$D^* = \frac{kT}{f}$ where $f = 6\pi\mu r \left[\frac{2\mu + r\beta}{3\mu + r\beta}\right]$, viscous resistance per molecule or frictional coefficient β = coefficient of sliding friction between molecules.	-	-	2-2.1
Stokes-Einstein, 1905 (187, 49)	$D^* = \frac{kT}{4\pi r \mu}$ (modification of eq.(2-2.1)by introducing the value of 'f' with $\beta = 0$).	34	10	2-2.2
Ottar, 1935 (149)	$D^* = RT \rho V^{\frac{2}{3}} / (4\sqrt{2}\ \mu M)$ (a modification of Eyring's theory).	-	16	2-2.3
Stern et al, 1940 (184)	$D^* = \frac{\lambda^2}{V_f^{\frac{1}{2}}} \left(\frac{RT}{2\pi M}\right)^{\frac{1}{2}} \exp\left(-\frac{\Delta E_D}{RT}\right)$ (derived from absolute reaction rate theory).	-	-	2-2.4
Eyring, 1941 (69)	$D^* = \frac{\lambda_1}{\lambda_2 \lambda_3} \quad \frac{kT}{\mu}$ (derived from absolute reaction rate theory).	-	poor	2-2.5
Gierer-Wirtz, 1953 (68)	$D^* = \frac{1}{6\pi r g} \quad \frac{kT}{\mu}$ where $g = 0.16 + 0.4 \left(\frac{r}{r_B}\right)$ r = radius of the solute molecule r_B = radius of the solvent molecule.	-	-	2-2.6
Li-Chang, 1955 (115)	$D^* = \frac{1}{2}(1 - \frac{\xi}{Z}) \quad \frac{kT}{\mu} \left(\frac{N}{V_b}\right)^{\frac{1}{3}}$ where ξ = number of nearest neighbours in one plane	-	12	2-2.7

Table 2-2.1 (continued)

Author, year and reference	Equation	Liquids tested	% error	Equation number
	z = number of all nearest neighbours (developed from the hydrodynamic and Eyring's theory).			
Longuet-Huggins -Pople, 1956 (119)	$D^* = \frac{\lambda}{2}\left(\frac{\pi kT}{M}\right)^{\frac{1}{2}}\left(\frac{P\bar{V}}{RT} - 1\right)^{-1}$	-	-	2-2.8
Mackenzee-Hillig, 1958 (126)	$D^* = 1.29 \times 10^{-14} \left(\frac{V_b}{\lambda}\right)^{\frac{2}{3}} \left(\frac{T_m}{M}\right)$ where T_m = melting point temperature, ^oK.	-	-	2-2.9
Longuet-Huggins -Valleau,1958 (120)	$D^* = \frac{2\varrho}{32}\sqrt{\frac{RT}{\pi M}}\left[\lambda_1 a_1^2 + \lambda_2 a_2^2 z\right]^{-1}$ for notation see ref. (51).	-	-	2-2.10
Panchenkov, 1958 (150)	$D^* = 4\left(\frac{3V}{4\pi N}\right)^{\frac{1}{3}}\left(\frac{2RT}{\pi M}\right)^{\frac{1}{2}}\left[\frac{\epsilon_0}{2RT} + 1\right] x$ $\exp\left[-\frac{2\,\Delta E}{\gamma RT} - \frac{\epsilon_0}{2RT}\right]$ where ϵ_0 = the energy of one bond between the liquid molecules per mole γ = co-ordination number of the liquid at T ΔE = ΔH-RT, energy of vaporization.	-	-	2-2.11
Cohen-Turnbull, 1959 (28)	$D^* = g\,\sigma\sqrt{\frac{3kT}{M}}\quad\exp\left[-\frac{\gamma V^*}{V_f}\right]$ where g = geometric factor σ = molecular diameter V_f = free volume γV^* = approximately equal to molecular volume.	-	-	2-2.12
Swalin, 1959 (190)	$D^* = \frac{CT^2}{\Delta H \alpha^2} \approx C^1\,T^2$ where α = thermal expansion coefficient C, C^1 = constants.	-	-	2-2.13

Table 2-2.1 (continued)

Author, year and reference	Equation	Liquids tested	% error	Equation number
McLaughlin, 1959 (129)	$D^* = \left(\frac{kT}{2\pi M}\right)^{\frac{1}{2}} \frac{\lambda^2}{V_f^{\frac{1}{2}}} \left(\frac{n_h}{N}\right) \exp\left[-\frac{\Phi_o}{3NkT}\right]$ where n_h = number of holes in a gmole of liquid Φ_o = lattice energy defined in ref. (129).	6	10	2-2.14
Douglass-McCall, 1959 (41)	$D^* = \frac{2\lambda^2 kT}{5\bar{V}\mu}\left[\frac{P^*\bar{V}}{RT} - 1\right]^{-1}$ where $\lambda = 0.56\ (V/N)^{\frac{1}{3}}$ P^* = thermal pressure defined as $T\left(\frac{\partial P}{\partial T}\right)_V$.	-	-	2-2.15
Eyring-Ree, 1961 (54)	$D^* = \frac{\lambda_1}{\xi_{\iota}\lambda_2\lambda_3} \frac{kT}{\mu}$.	-	12	2-2.16
Houghton, 1964 (91)	$D^* = \frac{RT\rho}{6\mu M}\left(\frac{V_b}{N}\right)^{\frac{2}{3}}$.	25	9	2-2.17
Walls-Upthegrove, 1964 (213)	$D^* = \frac{kT}{2\pi\hbar\ (2b+1)\mu}$ where b = ratio of atomic radius to intermolecular distance.	-	- 10	2-2.18
van Geet-Adamson, 1965 (208)	$\log D^* = \left[-3.28 - \frac{\Delta E_D}{2.3R}\left(\frac{10^3}{T} - 0.82\right)\right] \times 10^3$.		-	2-2.19
Adam-Gibbs, 1965 (1)	$D^* = A \exp\left[\frac{-B}{T - To}\right]$ where A, B = constants To = temperature at which the configurational entropy vanishes, °K.	-	-	2-2.20

Table 2-2.1 (continued)

Author, year and reference	Equation	Liquids tested	% error	Equation number
Macedo-Litovitz, 1965 (125)	$D^* = A \exp\left[-\frac{\Delta E_v}{RT} - \frac{\gamma V^*}{V_f}\right]$ where ΔE_v = activation energy at constant volume $V^* \approx$ approximately equal to van der Waals volume of molecule γ = constant $A \propto T^{\frac{1}{2}}$.	-	-	2-2.21
Ravdel'-Poraikoshits, 1967 (165)	$D^* = 1.246 \times 10^{-15} \frac{T}{\mu R_D^{\frac{1}{3}}}$ where R_D = molecular refraction.	12	5	2-2.22
Ascarelli-Paskin, 1968 (9)	$D^* = 0.28\, b_m \sqrt{\frac{\pi kT}{M}\left(\frac{\xi_m}{\xi}\right)} \left[\frac{10T_m\rho}{T\rho_m} - 1\right]^{-1}$ where m = subscript indicating melting point temperature ρ = density ξ = packing fraction $b_m = \left[\left(\frac{3}{4\pi}\right) V_m\right]^{\frac{1}{3}}$. (based on the ideal gas diffusion theory using Enskog high density correction (9) for liquid. Good for liquid metals).	-	-	2-2.23
Panchenkov et al, 1970 (150)	$D^* = \frac{1}{A}\frac{RT}{\mu}\frac{\rho V_b}{M}^{\frac{2}{3}} = \frac{1}{A}\frac{RT}{\mu}\frac{\rho^{\frac{1}{3}}}{M^{\frac{1}{2}} N^{\frac{2}{3}}}$ when A = 1/6 error ± 11.2% A = 1/4√2 error ± 6.0% (a modification of Stokes-Einstein equation).	-	-	2-2.24

Table 2-2.1 (continued)

Author, year and reference	Equation	Liquids tested	% error	Equation number
D'yakonov, 1970 (47)	$D^* = 4.21 \times 10^{-14}\left[\left(\frac{T}{M}\right)^{\frac{1}{2}} \exp\left(\frac{Sq}{R}\right)\right] \Big/ R\sigma_x^2$ where $\frac{Sq}{R}$ = the number of states of the "microcanonic ensemble" as defined in ref. (47). R = gas constant in J/Kg°K σ_x = in cm.	-	-	2-2.25
Dullien, 1972 (43)	$D^* = 0.124\times10^{-16}\left(\frac{RT}{\mu\bar{V}}\right)V_c^{\frac{2}{3}} = 0.129\times10^{-16} \times \sigma^2 (\Omega_D \Omega_\mu)\left(\frac{RT}{\mu\bar{V}}\right)T_c^{\frac{1}{2}}$ where σ = Lennard-Jones distance parameter $\Omega_D \Omega_\mu$ = generalised collision potentials for diffusion and for viscosity $R = 8.314 \times 10^7$	31	4	2-2.26
Vadovic-Colver, 1972 (206)	$D^* = 0.219 \times 10^{-8}\,\frac{T}{\mu\bar{V}}\,V_m^{\frac{2}{3}}$	20	6	2-2.27
Ertl-Dullien, 1973 (50)	$D^* = \frac{RT}{\mu\bar{V}}\left(\frac{d}{d_{min}}\right)^2\left(-1.42 + 0.152\,V_c^{\frac{2}{3}}\right)$ where $\frac{d}{d_{min}} = \left[0.179 + 0.35\,T_r + \left(2.55\times10^{-3}\,T_r^{-4}\right)\right]$ $T_r = \frac{T}{T_c}$ (a modification of Dullien's eq. (2-2.26) to include the temperature dependence of the molecular diameter).	31	4	2-2.28

Table 2-2.1 (continued)

Author, year and reference	Equation	liquids tested	% error	Equation Number
Collings, 1973 (29)	$D^* = \frac{kT}{\xi_i^H + \xi_i^S}$ where $\xi_i^H = \frac{8 \rho \sigma^2}{3V} (\pi mkT)^2 \; g(\sigma)$ and $\xi_i^S = \frac{8 \rho \sigma^2}{3V} (\pi mkT)^2 \left[\frac{\epsilon}{kT} \times \int_0^\infty F(r) \left\{ g(r) - 1 \right\} \right]$ (the nomenclature is given in ref. (29)).	-	-	2-2.29
Dymond, 1974 (48)	$D^* = 2.306 \times 10^{-5} \left(\frac{T}{M}\right)^{\frac{1}{2}} \left[\frac{V_b - 1.384\ Vo}{V_o^{\frac{2}{3}}}\right]$ where $V_o = N \frac{\pi^3}{\sqrt{2}}$, hard sphere closed packed volume (based upon Enskog's theory (87) of dense fluid).	-	-	2-2.30
This work (203)	$D^* = 0.229 \times 10^{-8} \left(\frac{T}{\mu \bar{V}}\right) V_b^{0.636}$ (similar to eq. (2-2.26) and V_c is replaced by V_b).	31	4.8	3-3.6
This work	$D^* = T \left[\frac{\breve{V}}{[M]}\right]^{7.7}$ where $[M]$ is a constant and may be estimated by summing the bond contributions given in Table (3-3.2) of this work. Symboles used in this Table are explained in the section "Nomenclature" unless otherwise specified.	48	12	3-3.4

2-3 Diffusion coefficient at infinite dilution

A number of correlations from the literature are presented in Table 2-3.1. The majority of these correlations can be classified into two groups, on the basis of their theoretical background:

(a) those developed from Stokes-Einstein equation and

(b) those developed from Eyring's theory of absolute reaction rate.

In group (a) the expression ($D^o_{AB}\mu_B/T$) is usually correlated with the relative size of the molecules, i.e.

(i) For colloidal solutions where $V_A \gg V_B$

$$\frac{D^o_{AB}\mu_B}{T} = f \text{ (size of the solute molecule, A)}$$

(ii) For ideal liquid mixtures where the sizes of the molecules are of the same order of magnitude

$$\frac{D^o_{AB}\mu_B}{T} = f \text{ (ratio of the dimensions of the pure components)}$$

(iii) For non-ideal and associated mixtures

$$\frac{D^o_{AB}\mu_B}{T} = f \text{ (ratio of the dimensions of the pure components and correction factor for association)}$$

The correction factor for association is introduced to account for the changes in the sizes of the molecules due to association. In group (b) the variation of activation energy for diffusion with temperature constitutes the basis of the Eyring theory. Diffusion coefficients, according to this theory, vary exponentially with the energy of activation and the temperature. Correlations based on the Eyring theory are more suitable for systems in which the sizes of solute and solvent molecules are of the same order of magnitude.

Table 2-3.1 Equations for estimating diffusion coefficients at infinite dilution

Author, year and reference	Equation	Systems tested	% error	Equation Number
Einstein-Sutherland, 1905 (49,189)	$D^o_{AB} = \frac{kT}{f}$ where f = viscous resistance per molecule or frictional coefficient (derived from hydrodynamic theory of liquid).	-	-	2-3.1
Stokes-Einstein, 1905 (187,49)	$D^o_{AB} = \frac{1}{6\pi r_A}\left(\frac{3\mu_B + r_A\beta}{2\mu_B + r_A\beta}\right)\cdot\frac{kT}{\mu_B}$ $D^o_{AB} = \frac{1}{4\pi r_A}\;\frac{kT}{\mu_B}$ when $\beta = 0$ $D^o_{AB} = \frac{1}{6\pi r_A}\;\frac{kT}{\mu_B}$ when $\beta = \infty$ where β = coefficient of sliding friction between the solute molecule and the solvent molecules.	-	-	2-3.2
Herzog, 1930 (84)	$D^o_{AB} = \frac{2RT}{6\pi N^{0.67}\mu_B (V_A - b)^{0.33}}$ where b = van der Waal's volume constant.	-	-	2-3.4
Arnold, 1930 (8)	$D^o_{AB} = \frac{[(M_A+M_B)/M_A M_B]^{0.5} \times 10^{-3}}{A_A A_B \mu_B^{0.5} (V_A^{0.33} + V_B^{0.33})^2}$ where A_A, A_B = 'abnormality factors' which correct for association and abnormal intermolecular forces in liquid (developed by extending the kinetic theory of gases to liquids. Its application is limited to a temperature of 20°C and to relatively low boiling solvents).	-	15	2-3.4a
Eyring, 1936 (52)	$D^o_{AB} = \frac{\lambda_1}{\lambda_2 \lambda_3}\;\frac{kT}{\mu_B}$ where μ_B = in poises (based on the absolute reaction rate theory).	-	-	2-3.5

Table 2-3.1 (continued)

Author, year and reference	Equation	Systems tested	% error	Equation Number
Powell et al, 1941 (155)	$D^{o}_{AB} = \frac{kT}{a(2\lambda_A)\mu_B}$ where $a = 3\pi$ for spherical solute molecules $a = 2\pi$ for cylindrical solute molecules μ_B = in poises (modification of Stokes-Einstein equation, applicable only for $V_A \gg V_B$).	-	-	2-3.6
Wilke, 1949 (218)	$D^{o}_{AB} = \frac{1}{F}\ \frac{T}{\mu_B}$ where $F \propto V_A^{\frac{1}{3}}$ μ_B = in poises (derived from Stokes-Einstein equation and Eyring's theory).	-	-	2-3.7
Polson, 1950 (168)	$D^{o}_{AB} = 2.74 \times 10^{-5}\ M_A^{-\frac{1}{3}}$ (obtained empirically for systems where water is the solvent and $M_A > 1000$).	-	-	2.3.8
Olson-Walton, 1951 (146)	A plot of D^{o}_{AB} or $\frac{(D^{o}_{AB}\ \mu_B)}{T}$ vs $\left(\frac{\Delta\sigma}{\Delta C_A}\right)$ with surface-tension of pure solutes as parameters, where $\frac{\Delta\sigma}{\Delta C_A}$ = slope of the curve from the plot of surface tension against the molar concentration σ = in dynes/cm C_A = in g-moles/litre.	11	5	2-3.9
Longsworth, 1952 (117)	$D^{o}_{AB} = \frac{A}{M_A^{1/2}} + \frac{B}{M_A^{2/3}} + \frac{C}{M_A}$ where A, B, C = characteric constants for the solute	-	-	2-3.10
Sherwood-Pigford, 1952 (177)	$D^{o}_{AB} = 4 \times 10^{-7}\ \frac{T}{\mu_B(V_A^{1/3} - C)}$ where μ_B = in centipoises T = in ^{o}R C = 2 for the solvent, water C = 2.46 for the solvent, methanol C = 2.84 for the solvent, benzene.	125	15	2-3.11

Table 2-3.1 (continued)

Author, year and reference	Equation	Systems tested	% error	Equation Number
Othmer-Thaker, 1953 (148)	$D^{o}_{AB} = 14\times10^{-5}\left[V_A^{0.6}\mu^{o}_{B}\mu_W^{(1.1\Delta H_B/\Delta H_w)}\right]^{-1}$ where μ^{o}_{B} = viscosity of solvent at 20°C, in centipoises μ_W = viscosity of water at T, centipoises $\Delta\bar{H}_B, \Delta\bar{H}_w$ = latent heats of vaporization of the solvent and of water at T, cal/gmole.	50	28	2-3.12
	For dilute aqueous solutions eq.(2-3.12) reduces to $D^{o}_{AB} = \frac{14\times10^{-5}}{V_A^{0.6}\mu_W^{1.1}}$.	40	13	2-3.12a
Coulson-Richardson, 1954 (33)	$D^{o}_{AB} = 7.7\times10^{-10}\frac{T}{\mu_B\,(V_A^{1/3} - K^{\frac{1}{3}})}$ where μ_B = in poises K = 8 for the solvent, water K = 14.9 for the solvent, methanol K = 22.8 for the solvent, benzene.	125	15	2-3.13
Scheible, 1954 (178)	$D^{o}_{AB} = 8.2\times10^{-8}\frac{T}{\mu_B}\frac{1+(3V_B/V_A)^{\frac{2}{3}}}{V_A^{\frac{1}{3}}}$ (a modification of Wilke's equation (2-3.7)). It simplifies for special cases to: $D^{o}_{AB} = \phi\frac{T}{\mu_B V_A^{\frac{1}{3}}}$ where ϕ = 25.2, when water is the solvent and $V_A < V_B$ ϕ = 18.9, when benzene is the solvent and $V_A < 2V_B$ ϕ = 17.5, for all other solvents and $V_A < 2.5V_B$ μ_B = in centipoises.	50	11-27	2-3.14
Collins-Raffel, 1955 (32)	$D^{o}_{AB} = \frac{kT}{\langle\varsigma_{AB}\rangle}$ where $\varsigma_{AB} = \frac{3\left[\frac{\pi}{2}\left(\frac{M_A M_B}{M_A+M_B}\right)kT\right]\omega}{\pi\sigma_{AB}\left[1-\left(\frac{V}{V_{1A}}\right)^{\frac{1}{3}}\right]}$ $\omega = 1+\left(\frac{M_A+M_B}{M_A}\right)-\left[\left(\frac{M_A}{M_A+M_B}\right)\Big/\left(\frac{M_B}{M_A+M_B}\right)\right]^{\frac{2}{3}}\ln\left[\frac{1+\left(\frac{M_B}{M_A+M_B}\right)^{\frac{1}{2}}}{\left(\frac{M_A}{M_A+M_B}\right)^{1/2}}\right]$	-	-	2-3.15

Table 2-3.1 (continued)

Author, year and reference	Equation	Systems tested	% error	Equation Number
Collins-Raffel, 1955 (32) continued	σ_{AB} = collision diameter, cm $\left(\frac{V}{V_i}\right)_A$ = ratio of molecular and incompressible volumes estimated from velocity of sound.			
Wilke-Chang, 1955 (219)	$D^o_{AB} = 7.4 \times 10^{-8} \frac{(x_B M_B)^{\frac{1}{2}} T}{\mu_B V_A^{0.6}}$ (a modification of Wilke's equation (2-3.7)) where μ_B = in centipoises x_B = association parameter used to define the effective molecular weight of solvent with respect to the diffusion process. Recommended values for x_B: x_B Non-associated solvent = 1 Water as solvent = 2.6 Methanol as solvent = 1.9 Ethanol as solvent = 1.5 Otherwise the following empirical equation is recommended (3) to estimate the value of x_B for associated solvents:	535	16.5	2-3.16
	$x_B = \left(\frac{\Delta H_B}{\Delta H_B^*}\right)^{0.6}$ where ΔH_B^* = the latent heat of vaporization of the homomorph** of the solvent. (**the homomorph is the compound where "-OH" group is replaced by "-CH_3" group).	–	–	2-3.16a
Li-Chang, 1955 (115)	$D^o_{AB} = \frac{1}{2} \left(1 - \frac{\xi_{AB}}{\mathcal{Z}_{AB}}\right) \frac{kT}{\mu_B \left(\frac{V_A}{N}\right)^{\frac{1}{3}}}$ where μ_B = in poises ξ_{AB} = number of nearest neighbours in the same plane. $\mathcal{Z}_{AB}$ = number of all nearest neighbours. (developed from the hydrodynamic theory and Eyring theory)	–	–	2-3.17

Table 2-3.1 (continued)

Author, year and reference	Equation	Systems tested	% error	Equation Number
Innes-Allbright, 1957 (95)	$D^{o}_{AB} = A\,T^{n}\,\exp\left[-\frac{B}{T}\right]$ where n = constant depending on solvent A,B = characteristic constants for the solute.	30	10	2-3.18
Panchenkov, 1958(150)	$D^{o}_{AB} = 4\left(\frac{3VA}{4N}\right)^{\frac{1}{3}}\left(\frac{2RT}{\pi M_{B}}\right)^{\frac{1}{2}}\left[\frac{Eo}{2RT}+1\right]\exp\left[-\frac{2\Delta E}{\gamma RT}-\frac{Eo}{2RT}\right]$ where γ = co-ordination number Eo = the energy of a single bond between the molecules in the liquid ΔE = $\Delta H - RT$, energy of vaporization.		-	2-3.19
Ree-Eyring, 1958 (167)	$D^{o}_{AB} = \frac{\lambda_1}{\xi_{AB}\lambda_2\lambda_3}\;\frac{kT}{\mu_B}$ where μ_B = in poises ξ_{AB} = number of nearest neighbours in one plane. (modification of Eyring (2-3.5)).	-	-	2-3.20
Thomaes-Itterbreek, 1959 (194)	$D^{o\prime}_{AB} = D^{o}_{RB}\left(\frac{\epsilon_{A,R}}{\epsilon_A}\right)^{\frac{1}{2}}\left(\frac{M_{A,R}}{M_A}\right)\left(\frac{r_A}{r_{A,R}}\right)T$ where R = subscript indicating the reference solute diffusing into the same solvent ϵ_A = Lennard-Jones force constant r_A = distance at which the minimum in Lennard-Jones' potential curve occurs.	-	-	2-3.21
Adamson-Irani, 1960 (2)	$D^{o}_{AB} = \frac{\lambda^2}{V_B\left[1+\frac{V_B}{V_A}\right]}\;\frac{kT}{h}\;\exp\left[\frac{-\Delta G_D}{RT}\right]$ (developed from Eyring's absolute reaction rate theory).	-	-	2-3.22
Tyrell, 1960 (204)	$D^{o}_{AB} = \frac{kT}{\mu_B\alpha}$ where μ_B = in poises α = a parameter having a dimension of length (modification of eq. (2-3.1) where 'f' is separated into α and μ_B).	-	-	2-3.23

Table 2-3.1 (continued)

Author, year and reference	Equation	Systems tested	% error	Equation Number
Ibrahim-Kuloor, 1960 (94)	$Sc' = \dfrac{\mu_B V_B}{D_{AB}} = aM + b$ where Sc' = modified Schmidt number a, b = parameter related to the properties of the solvent and may be estimated from surface tension.	4	10	2-3.24
Wilke-Chang-Olander, 1961 (145)	$D^o_{AB} = 7.4 \times 10^{-8} \dfrac{(x_B M_B)^{\frac{1}{2}} T}{\mu_B (4V_A)^{0.6}}$ where μ_B = in centipoises x_B = association parameter of solvent. (a modification of Wilke-Chang eq. (2-3.16) for systems where water is the solute).	-	16	2-3.25
Kamal-Canjar, 1962 (100)	$D^o_{AB} = B\ f(\Delta H)$ where $B = 1.2021 \times 10^{-8} \left(\dfrac{RT}{\pi \cdot M}\right)^{\frac{1}{2}} V_B^{\frac{1}{3}} A$ $A = \left[1.6\bar{V}_B + 2.56(\bar{V}_B)^2 \left\{1 + 2.5\bar{V}_B + 4.5864(\bar{V}_B)^2\right\}\right] (\bar{V}_B)^{-\frac{2}{3}}$ $\bar{V}_B = V_B/V_{Bi}$, ratio of molecular volume to incompressible volume. $f(\Delta H) = \dfrac{RT}{24\Delta H_A - 39RT}$	56	12	2-6.26
Sitaraman et al, 1963 (182)	$D^o_{AB} = 5.4 \times 10^{-8} \left[\dfrac{M_B^{\frac{1}{2}} (\Delta L_B)^{\frac{1}{3}} T}{\mu_B V_A^{0.5} (\Delta L_A)^{0.3}}\right]^{0.93}$ where μ_B is in centipoises, ΔL_A and ΔL_B in cal/gm. (modified Wilke – Chang eq. (2-3.16) by replacing the empirical constant 'x_B' (i.e. association parameter) by the ratio of the latent heats of vaporization of solvent and solute).	499	16	2-3.27
Olander 1963 (144)	$D^o_{AB} = \left(\dfrac{N}{V_B}\right)^{\frac{1}{3}} \dfrac{k\ \ T}{5.6\mu_B} \exp\left[\dfrac{\Delta G_{\mu, AB} - \Delta G_{D^o AB}}{RT}\right]$ where $\Delta G_{\mu, AB} \approx \Delta G_{\mu, B}$, μ_B in poises. (derived from Eyring's absolute reaction rate theory).	40	15	2-3.28

Table 2-3.1 (continued)

Author, year and reference	Equation	Systems tested	% error	Equation Number
King et al 1965 (104)	$D^o_{AB} = 4.4 \times 10^{-8} \left(\frac{V_B}{V_A}\right)^{\frac{1}{6}} \left(\frac{\Delta H_B}{\Delta H_A}\right)^{\frac{1}{2}} \frac{T}{\mu_B}$ where μ_B is in centipoises.	499	15	2-3.29
Gainer- Metzner, 1966 (60)	$D^o_{AB} = \frac{kT}{\xi \mu_B} \left(\frac{N}{V_B}\right)^{\frac{1}{3}} \exp\left[\frac{\Delta E_{\mu,B} - \Delta E_{D,AB}}{RT}\right]$ where μ_B is in poises. (a modification of Eyring's absolute reaction rate theory; recommended for high viscosity solvents).	19	18	2-3.30
Reddy- Doraiswamy, 1967 (166)	$D^o_{AB} = \phi \frac{M_B^{\frac{1}{2}} T}{\mu_B V_A^{\frac{1}{3}} V_B^{\frac{1}{3}}}$ where $\phi = 10 \times 10^{-8}$ when $\frac{V_B}{V_A} < 1.5$ $\phi = 8.5 \times 10^{-8}$ when $\frac{V_B}{V_A} > 1.5$ μ_B = in centipoises. (a modification of Wilke-Chang eq. (2-3.16)).	23	18	2-3.31
Pratap- Doraiswamy, 1967 (157)	$D^o_{AB} = 2.015 \times 10^{-3} \quad u_l V_A^{\frac{1}{3}} \left[\frac{M_A + M_B}{M_A \ M_B}\right] T^{\frac{1}{2}} \exp\left[\frac{1 \times 10^7}{\Delta H_B T}\right]$ where u_l = velocity of sound in liquid (derived from Eyring's theory).	9	25	2-3.32
Ravdel' Porai-Koshits, 1967 (165)	$D^o_{AB} = \frac{kT}{A \mu_B \pi r_A}$ where A is a constant and estimated empirically from $A = 5.98 \times 10^{-15} \quad \frac{T}{D_B^* \mu_B (R_D)_B^{\frac{1}{3}}}$ where R_D = molecular refraction μ_B = in poises (for non-polar liquids $A \approx 4.8 \pm 0.2$).	-	-	2-3.33

Table 2-3.1 (continued)

Author, year and reference	Equation	Systems tested	% error	Equation Number
Lusis-Ratcliff, 1968 (123)	$D^o_{AB} = 8.52\times10^{-10} \dfrac{1}{V_B^{\frac{1}{3}}} \left[1.4\left(\dfrac{V_B}{V_A}\right)^{\frac{1}{3}} + \left(\dfrac{V_B}{V_A}\right)\right] \dfrac{T}{\mu_B}$ where μ_B = in poises.	8	16	2-3.34
Loflin-McLaughlin, 1969 (116)	$\dfrac{2\left(D^*_B/D^o_{AB}\right)^2}{1+\left(D^*_B/D^o_{AB}\right)} = \left(\dfrac{\epsilon_B}{\epsilon_A}\right)^{\frac{1}{2}} \left(1+\dfrac{\sigma_B}{\sigma_A}\right)\left[\dfrac{M_B}{M_A+M_B}\right]$ where ϵ and σ are Lennard-Jones parameters.	–	–	2-3.35
Laddha-Smith, 1969 (108)	$D^o_{AB} = 1.892\text{X}10^{-9} \dfrac{(V_B/V_A)^{0.1604}}{V_A^{\frac{1}{3}}} \dfrac{T}{\mu_B}$ where μ_B = in poises.	26	38	2-3.36
Mitchells, et al,1971 (135)	$D^o_{AB} = \dfrac{kT}{\xi_{l_B} h} \left[\dfrac{(2)^{\frac{1}{2}} V_B}{h}\right]^{\frac{2}{3}} \exp\left[-\dfrac{\Delta G_D}{RT}\right]$	6	13	2-3.37
Hiranuma, 1971 (86)	$D^o_{AB} = 7.4 \times 10^{-8} \dfrac{(x_B M_B)^{\frac{1}{2}}}{(x_A V_A)^{0.6}} \dfrac{T}{\mu_B}$ where μ_B = in centipoises x_A, x_B = association parameters for the solute and the solvent respectively. (a modification of Wilke-Chang eq. (2-3.16) by introducing additional association parameter, x_A, for the solute molecule).	-	-	2-3.38
Lusis, 1971 (122)	$D^o_{AB} = \dfrac{kT}{6\pi(r_A + r_B)\mu_B}$ where μ_B = in poises.	–	–	2-3.39

Table 2-3.1 (continued)

Author, year and reference	Equation	Systems tested	% error	Equation Number
Lusis-Ratcliff, 1971 (123)	$D^{o}_{AB} = \frac{1}{1+K} D_{A_1} + K D_{A_1 B_1}$ where $K = \frac{1-\gamma^{\circ}_{A}}{\gamma^{\circ}_{A}}$ $\gamma^{\bullet}_{A}$ = activity coefficient at infinite dilution DA_1 and $D_{A_1B\,1}$ are found from $\frac{Di\,\mu_s}{T} = 8.52 \times 10^{-8} \frac{1}{V^{\frac{1}{3}}} \left[1.4R_i^{\frac{1}{3}} + R_i\right]$ where $R_i = \frac{V_B}{V_A}$ if $i = A_1$ $R_i = \frac{V_B}{V_A+V_B}$ if $i = A_1B_1$ μ_B = in poises (recommended for complex forming substances defined in ref. (123)).	-	6	2-3.40
Hayduk-Cheng, 1971 (81)	$D^{o}_{AB} = m\mu_B^{\,n}$ where m and n are constants applying to the solute.	-	18	2-3.41
Nir-Stein, 1971 (142)	$D^{o}_{AB} = \left[D^{o}_{AB,fl} \exp\left(\frac{-\Delta G_{D,fl}}{RT}\right)\right] + \left[D^{o}_{AB,lat.} \exp\left(\frac{-\Delta G_{D,lat}}{RT}\right)\right]$ where subscripts fl = indicates the contribution due to the flow mechanism of the matrix and lat. = indicates the contribution due to the mechanism of lattice diffusion as defined in ref. (142) (a modification of Eyring's absolute reaction rate theory).		-	2-3.42

Table 2-3.1 (continued)

Author, year and reference	Equation	Systems tested	% error	Equation number
Akgerman-Gainer, 1972 (3)	$D^{o}_{AB} = \frac{kT}{\xi \mu_B} \left(\frac{N}{V_B}\right)^{\frac{1}{3}} \left(\frac{M_B}{M_A}\right)^{\frac{1}{2}} \exp\left[\frac{\Delta E_{\mu,B} - \Delta E_{D,AB}}{RT}\right]$ where μ_B = in poises. (a modification of Gainer-Metzner eq. (2-3.30), recommended for the estimation of diffusion coefficients of gases into liquids) (* gas-liquid system; **liquid-liquid system).	52* 7**	15 33	2-3.43
Vadovic-Colver, 1973 (206)	$D^{o}_{AB} = 0.103\text{x}10^{-6} \left(\frac{V_{Bc}}{V_{Bc}}\right)^{\frac{2}{3}} \left(\frac{M_A+M_B}{2M_A}\right)^{\frac{m}{2}} \text{x}$ $V_{Bc}^{\frac{2}{3}} \left(\frac{\rho_B\ T}{\mu_B\ M_B}\right)$ where μ_B = in centipoises V_{Ac}, V_{Bc} = critical volume of pure A and B respectively, cm^3/gmole. m = 1, for non-associated systems. m = 0, for associated systems. For the systems where water is the solvent, the constant ($1.08 \text{ x } 10^{-6}$) is to be used in the place of ($0.103 \text{ x } 10^{-6}$).	50	9	2-3.44
This work (201)	$D^{o}_{AB} = 8.93\text{x}\,10^{-8} \frac{V_A^{1/6}}{V_B^{1/3}} \left(\frac{[P_B]}{[P_A]}\right)^{0.6} \frac{T}{\mu_B}$ where μ_B = in centipoises $[P_A]$, $[P_B]$ = parachors of pure A and B respectively. (for the development of this equation see section 3-3). Symboles used in this Table are explained in the section "Nomenclature" unless otherwise specified.	535	12	3-2.4

2-4 Concentration dependence of diffusion coefficient

Correlations available for the prediction of diffusion coefficients for concentrated binary mixtures originate mainly from hydrodynamic theory, theory of absolute reaction rate, or a combination of the two theories. A few have purely empirical origins, however.

Table 2-4.1 gives a list of the more common correlations.

Only the equation of Vignes (210) and equation of Leffler and Cullinan (111) were found to agree reasonably well with experimental data. The equation of Vignes (210) is regarded as one of the experimentally derived equations, however, Cullinan (36) showed that this equation can be derived from the principles of the Eyring absolute reaction rate theory (69). Leffler and Cullinan (111) applied the Eyring absolute reaction rate theory to diffusion in concentrated solution making a number of assumptions. As the derivation of the Leffler and Cullinan equation (2-4.16) has a considerable amount of theoretical concepts some of these assumptions are listed and discussed below.

(1) Leffler and Cullinan assume the following relationship between the free energy of activation for a mixture and those for diffusion at infinite dilution.

i.e. $$\Delta G_{D,AB} = x_A \Delta G_D^{o}{}_{,BA} + x_B \Delta G_D^{o}{}_{,AB}$$

This relationship is linear and therefore should be correct for an ideal solution but not for solutions departing from ideality.

(2) Leffler and Cullinan (111) adopted the expression for the mixture viscosity of Glasstone et al (69)

i.e. $$\mu_{AB} = \frac{h}{\lambda_\mu^2}\left(\frac{\lambda_1}{\lambda_2 \lambda_3}\right)_{AB} \exp\left[\frac{\Delta G_{\mu,AB}}{RT}\right]$$

in the derivation of their correlation and then assumed that the various distances appearing in the group $\left(\frac{\lambda_1}{\lambda_2 \lambda_3}\right)$ are the same

i.e. $\lambda_1 = \lambda_2 = \lambda_3$.

This assumption is reasonable only if the group $\left(\frac{\lambda_1}{\lambda_2 \lambda_3}\right)$ contains the number of nearest neighbours, ξ. This group should have the form $\left(\frac{\lambda_1}{\xi \lambda_2 \lambda_3}\right)$ as was found by Li and Chang (115), Ree and Eyring (167) and Olander (144).

(3) The distance between successive equilibrium positions for the diffusional process in a binary mixture will be related to those of the pure components, Glasstone et al (69) used the following equation to define this distance

i.e. $\lambda_{D,AB} = x_A \lambda_{D,A} + x_B \lambda_{D,B}$.

Leffler and Cullinan (111) found that if the '$\lambda_{D,AB}$' is defined as

$$\lambda_{D,AB} = \left(\lambda_{D,A}\right)^{x_A} \cdot \left(\lambda_{D,B}\right)^{x_B}$$

the resulting correlation agrees better with the experimental data.

(4) Most of the theories of transport properties of the liquid state, such as Eyring's absolute reaction rate theory (69), the significant liquid structure theory (53) and others (20, 87, 168) indicate some inter-relationship between diffusional flow and viscous flow, in addition experimental evidence (38) confirms the prediction of the above theories. Leffler and Cullinan (111) therefore introduced the viscosity of the mixture and of the individual components into their correlation. This may be the reason that their correlation gives better agreement, in most cases, with experimental data than the equation of Vignes (210).

(5) Leffler and Cullinan (111), in the course of the derivation of their equation, obtained an exponential term in which the exponent is

$$\left(\Delta G_{\mu,AB} - \Delta G_{D,AB}\right).$$

They assumed that this expression does not vary with the composition of a binary mixture. This assumption allows them to eliminate this term from their correlation , which is an over-simplification as this assumption is approximately correct for an ideal solution only. In case of non-ideal solutions this assumption is incorrect, as shown by Anderson et al (6).

Table 2-4.1 Some of the equations defining the concentration dependence of diffusion coefficients in liquid binary mixtures.

Author, year and reference	Equation	Equation Number
Stearn et al, 1940 (184)	$D_{AB} = \dfrac{kT}{6\pi \mu_{AB} r_A} \left[\dfrac{x_A \bar{V}_A + x_B \bar{V}_B}{x_B \bar{V}_B^2} \right] \alpha_A$	2-4.1
Powell, et al 1941 (155)	$D_{AB} = D^o_{AB} \alpha_A$	2-4.2
Gordon, 1945 (70)	$D_{AB} = D^o_{AB} \dfrac{\mu_B}{\mu_{AB}} \alpha_A$	2-4.3
Darken, 1948 (37)	$D_{AB} = (D^*_A x_A + D^*_B x_B) \alpha_A$	2-4.4
Hartley-Crank, 1949 (78)	$D_{AB} = \dfrac{RT}{\mu_{AB} N} \left[\dfrac{x_B}{\sigma_A} + \dfrac{x_A}{\sigma_B} \right] \alpha_A$	2-4.5
Wilke, 1949 (218)	$\dfrac{D_{AB}\mu_{AB}}{T} = \left\{ \left[\left(\dfrac{D^o_{BA}\mu_A}{T} \right) - \left(\dfrac{D^o_{AB}\mu_B}{T} \right) \right] x_A + \left(\dfrac{D^o_{AB}\mu_B}{T} \right) \right\} \alpha_A$	2-4.6
Prager, 1953 (156)	$D_{AB} = D^*_A \alpha_A$	2-4.7
Carman-Stein, 1956 (26)	$D_{AB} = (D^o_{BA} \mu_A x_A + D^o_{AB} \mu_B x_B) \dfrac{\alpha_A}{\mu_{AB}}$	2-4.8
Bearman, 1961 (13)	$D_{AB} = \dfrac{D^o_{AB}\mu_B}{\mu_{AB}} \left[1 - \left(\dfrac{\bar{V}_A}{\bar{V}_B} - 1 \right) \right] \alpha_A$	2-4.9
Pyun-Fixman, 1964 (160)	$D_{AB} = \dfrac{RT}{6\pi \mu_B N r_A} \left[\alpha_A - 7.16 \phi_A + (\phi_A^2) \right]$ where ϕ_A = volume fraction	2-4.10

Table 2-4.1 (continued)

Author, year and reference	Equation	Equation Number
Rathbun-Babb, 1966 (164)	$D_{AB} = \left(D^o_{AB}\, x_B + D^o_{BA}\, x_A\right) \alpha_A^S$ where S = 0.6 for binary systems containing an associated component and a non-polar component. or S = 0.3 for binary systems with negative deviation from Raoult's law.	2-4.11
Vignes, 1966 (210)	$D_{AB} = \left(D^o_{BA}\right)^{x_A} \left(D^o_{AB}\right)^{x_B} . \ \alpha_A$	2-4.12
Schroff, 1968(179)	$\ln\left(\dfrac{D_{AB}}{\alpha_A}\right) = x_A \ln D^o_{BA} + x_B \ln D^o_{BA} + x_A x_B \ln D'$ where $D' = \left[\exp\left\lvert D^o_{BA} - D^o_{AB}\right\rvert\right] - \frac{1}{2}\left(D^o_{AB} + D^o_{BA}\right)$	2-4.13a
	$D_{AB} = \dfrac{RT}{\mu_{AB} N} \left[\dfrac{x_A}{\sigma_B} + \dfrac{x_B}{\sigma_A}\right] \alpha_A^{0.6}$ where σ_A, σ_B = friction coefficients of pure A and B respectively.	2-4.13b
Vasenin, 1969 (209)	$D_{AB} = D^*_A \left[1 - \left(1 - \dfrac{\bar{V}_A}{\bar{V}_B}\right) C_A \bar{V}_A - 2\,\omega\, C_A C_B \bar{V}_A \bar{V}_B\right]$	2-4.14a
	or $D_{AB} = D^*_B \left[1 - \left(1 - \dfrac{\bar{V}_A}{\bar{V}_B}\right) C_B \bar{V}_B - 2\omega C_A C_B \bar{V}_B^{\,2}\right]$ where C_A, C_B = concentrations, gm/cm^3 $\omega = \dfrac{\Delta E}{kT}$, energy parameter as defined in ref (209).	2-4.14b
Loflin-McLaughlin, 1969 (116)	$D_{AB} = \dfrac{\left(D_B^* x_A + D_A^* x_B\right)\alpha_A}{\left(\dfrac{x_A \sigma_{AB}}{x_A \sigma_{AB} + x_B \sigma_{BB}} + \dfrac{x_B \sigma_{AB}}{x_A \sigma_{AA} + x_B \sigma_{AB}}\right)}$ where σ_{AB} = friction coefficient of the binary mixture σ_{AA}, σ_{BB} = friction coefficients of pure A and B respectively.	2-4.15

Table 2-4.1 (continued)

Author, year and reference	Equation	Equation number
Leffler-Cullinan, 1970 (111)	$D_{AB} = \left(D^{o}_{BA}\mu_A\right)^{x_A} \left(D^{o}_{AB}\mu_B\right)^{x_B} \dfrac{\alpha_A}{\mu_{AB}}$	2-4.16
Gainer, 1970 (61)	$D_{AB} = D^{o}_{AB}\left(\mu_A\right)^{x_A}\left(\mu_B\right)^{x_B} \left(K\right)^{x_A} \dfrac{\alpha_A}{\mu_{AB}}$ where $K = \left(\dfrac{\mu_B}{\mu_A}\right)^{\frac{1}{2}} \left(\dfrac{M_B}{M_A}\right)^{\frac{1}{2}} \cdot \left(\dfrac{\Delta E_A}{\Delta E_B}\right)^{\frac{1}{2}}$ ΔE_A , ΔE_B = energy of vaporization for pure A and B respectively.	2-4.17
Haluska-Colver, 1971 (75)	$D_{AB} = \dfrac{\mu_A\mu_B \; RT \left(V_A x_A + V_B x_B\right)}{\left(x_A \mu_A \sigma^{o}_{BA} + x_B \mu_B \sigma^{o}_{AB}\right)} \dfrac{\alpha_A}{\mu_{AB}}$ where $\sigma^{o}_{AB}, \sigma^{o}_{BA}$ = friction coefficients at infinite dilution of A and B respectively.	2-4.18
This work	$D_{AB} = \left(D^{*}_{A}\mu_A\right)^{x_A} \left(D^{*}_{B}\mu_B\right)^{x_B} \dfrac{\alpha_A}{\mu_{AB}} \times \exp\left[\dfrac{\Delta G_{\mu,AB} - \Delta G_{D,AB}}{RT}\right].$	3-1.21
	Symboles used in this Table are explained in the section "Nomenclature" unless otherwise specified.	

2-5 Temperature dependence of diffusion coefficient

Experimental data on diffusion coefficients, as reported in the literature, are usually given at ambient temperatures. There are a few reports giving diffusion coefficients at elevated temperatures (19, 21, 55, 131, 135, 175). Experimental data on the diffusion coefficients at normal boiling points are very scarce (25, 183).

A brief review of the experimental data for binary liquid diffusion coefficients of non-electrolytes at elevated temperatures has been given in reference (200). Only a few methods of predicting the diffusion coefficients at elevated temperatures will be discussed here.

Generally, all correlations for the prediction of diffusion coefficients contain temperature as a variable, therefore they can be used for the calculation of diffusion coefficients at specific temperatures. To this class of correlations belong all those given in Tables (2-2.1) (2-3.1) (2-4.1) and (2-6.1). Some of these equations can be adapted for the calculation of diffusion coefficients at varying temperatures provided that experimental values of the coefficient for a given concentration, at one or more temperatures, are available.

(1) Thus it is usual to transform the Stokes-Einstein equation (2-3.2) into the following form;

$$\left[D^o_{AB}\right]_2 = \left[\frac{D^o_{AB}\,\mu_B}{T}\right]_1 \left[\frac{T}{\mu_B}\right]_2 \qquad (2\text{-}5.1)$$

in which 1 and 2 indicate the properties at different temperatures. This equation was tested for various systems and gives an average accuracy of $\pm$ 10% (218).

(2) The group $(D^o_{AB}\,\mu_B/T)$ however varies slightly with temperature and Marinin (20) used this fact to improve equation (2-5.1).

He devised the following relationship

$$\frac{D^{o}_{AB}\mu_B}{T} = A + B\mu_B \qquad (2\text{-}5.2)$$

To find the constants A and B experimental values of the diffusion coefficients at two temperatures at least should be known.

(3) It may be deduced from the Eyring absolute reaction rate theory that for a given binary mixture the following relationship holds

i.e. $$D_{AB} = A\,e^{\frac{-B}{T}} \qquad (2\text{-}5.3)$$

where A and B are constants.

From this relationship it follows that a plot of ln D_{AB} vs $\frac{1}{T}$ should give a straight line. Equation (2-5.3) requires at least two experimental points in order to use it.

(4) Inns and Albright (95) modified equation (2-5.3) to the form

$$D^{o}_{AB} = A\,T^{n}\,e^{-\frac{B}{T}} \qquad (2\text{-}3.18)$$

where A, B and n are constants.

These authors regard this relationship as an improvement on the equation (2-5.3) but in order to use it at least three experimental values are needed.

(5) Arnold (8) suggested the following empirical correlation for estimation of the temperature dependence of the diffusion coefficient over short temperature ranges:

$$\left[D^{o}_{AB}\right]_{t} = \left[D^{o}_{AB}\right]_{20^{o}C}\left[1 + b\,(t - 20)\right] \qquad (2\text{-}5.4)$$

where $b = 0.02\,\mu_B^{\frac{1}{2}}\,\rho_B^{\frac{1}{3}}$

t = temperature in ^{o}C

μ_B = solvent viscosity at 20^{o}C, c.p.

ρ_B = solvent density at 20^{o}C, gm/cc

(6) Kincaid, Eyring and Stearn (103) pointed out that a plot of specific volume vs either (D^{o}_{AB}/T) or$(D^{o}_{AB}/T^{1.5})$ displays good linearity. These relationships have not been thoroughly tested. Of these two, the latter i.e. $(D_{AB}/T^{1.5})$ is probably preferable (63).

2-6 Diffusion coefficient and viscosity

In 1858 Wiedemann (217) observed that solutes show low values of diffusivity in highly viscous solvent and proposed the relationship

$$D^{o}_{AB} \propto \frac{1}{\mu_B} \tag{2-6.1}$$

The relationship between the diffusion coefficient and viscosity is more complicated than equation (2-6.1) suggests. It is better defined by the Stokes-Einstein equation and the equations resulting from other theories of diffusion in the liquid phase.

There are a relatively large number of various empirical equations relating diffusion coefficient to viscosity. These equations are not universally valid. Some examples of these equations are given in Table (2-6.1).

Table 2-6.1 Some of the empirical equations defining the relationship between the diffusion coefficient and viscosity.

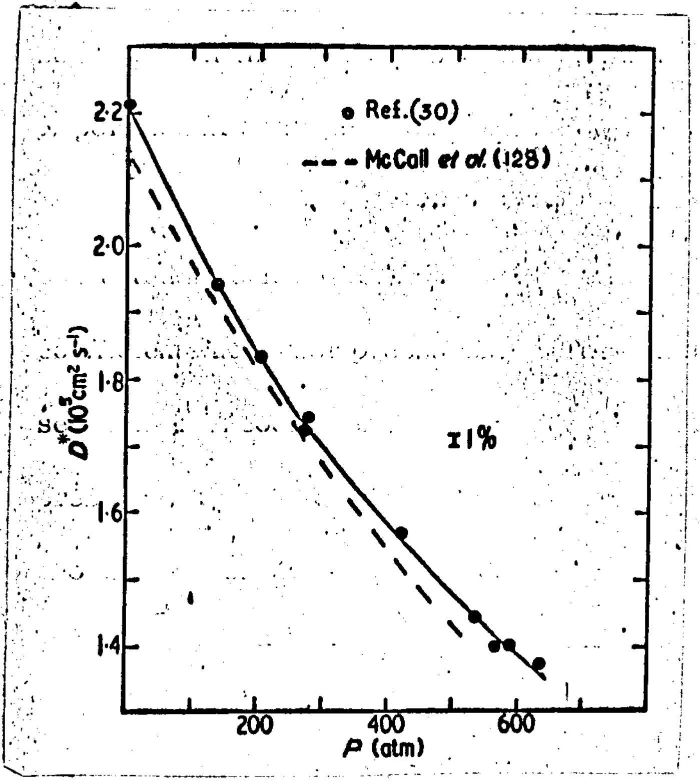
Author, year and reference	Equation	Equation number
Wiedemann, 1858 (217)	$D^{o}_{AB} \propto \frac{1}{\mu_B}$	2-6.1
Othmer-Thakar, 1953 (148)	$D^{o}_{AB} = 14.0 \times 10^{-5} \frac{1}{V_A^{0.6}\ \mu_B^{1.1}}$ where μ_B = in centipoises (recommended for systems in which water is the solvent).	2-6.2
Sitaraman et al, 1962 (182)	$D^{o}_{AB} = 1.37 \times 10^{-5} \frac{1}{\mu_B}$ where μ_B = in centipoises (recommended for diffusion of water in organic solvents).	2-6.3

Table 2-6.1 continued

Author, year and reference	Equation	Equation number
Hayduck-Cheng, 1971 (81)	$D^o_{AB} = m \mu_B^n$ (separate constants m and n apply to each diffusion substance).	2-6.4
Lusis, 1972 (121, 122)	$D^o_{AB} = 5.2 \times 10^{-10} \frac{T}{\mu_B} \left(\frac{\mu_B \; \Delta \bar{H}_B}{\mu_A \; \Delta \bar{H}_A} \right)^{\frac{1}{4}}$ where μ_B in poises. (for diffusing of hydrogen bonding solutes in viscous associated solvents, especially the mono- and poly-hydroxy alcohols).	2-6.5
(ibid)	$D^o_{AB} = 7.5 \times 10^{-14} \frac{T}{\mu_B^{0.6}}$ where μ_B in poises (for diffusion in unassociated solvents if no solute-solvent complex are formed and for $V_A > 80$ cc/gmole).	2-6.6
Hayduck et al, 1973 (82)	$D^o_{AB} = 0.591 \times 10^{-10} \mu_B^{-0.545}$ where μ_B in poises (for diffusion of propane in n-hexane, n-heptane, n-octane, hexadecane, n-butanol and chlorobenzene at 0^oC to 50^oC).	2-6.7
McManamey-Woolen, 1973 (130)	$D^o_{AB} = 1.41 \times 10^{-10} \mu_B^{-0.47}$ where μ_B in poises (for diffusion of CO_2 into organic liquids from 25^oC to 50^oC).	2-6.8
Hiss-Cussler, 1973 (88)	$D^o_{AB} \mu_B^{\frac{2}{3}} = \text{constant}$ (for diffusion of n-hexane and naphthalene in high viscosity liquids, 0.5 to 5000 centipoises).	2-6.9
	Symboles used in this Table are explained in the section "Nomenclature" unless otherwise specified.	

2-7 Pressure dependence of diffusion coefficients

The liquid phase is,to a certain extent,compressible and therefore increased pressure tends to reduce the intermolecular distances. This suggests the pressure will slow down diffusional motion. Experimental evidence shows that below a pressure of 1000 atm the effect of pressure on the mechanism of diffusion is negligible (40). Barton and Speedy (11) conducted a review of experimental methods for determination of diffusion coefficients at higher pressures , they also listed the references in which self-diffusion coefficients in pure liquids and binary liquid mixtures at high pressures may be found. From this review it may be deduced that at least two patterns of pressure dependence are observed.



Self-diffusion in benzene

P atm	$\frac{D_1^*}{D_p^*}$ 25°C
200	1.201
400	1.394
600	1.589

where D_1 = diffusion coefficient at 1 atm.

D_p = diffusion coefficient at p atm

Fig. 2-7.1 Dependence of diffusion coefficient on pressure for benzene (30)

Diffusion coefficients for hydrocarbon systems decrease approximately linearly with increase in pressure,as illustrated in Fig. 2-7.1.

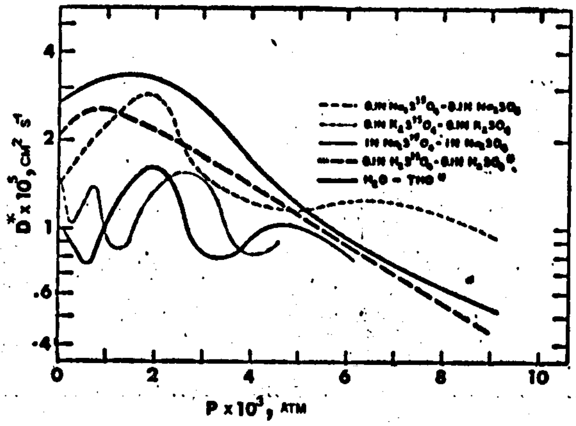


Fig. 2-7.2 Pressure dependence of self-diffusion coefficients in aqueous sulphate solutions.(35).

Diffusion coefficients of salt solutions, on the otherhand, vary irregularly with increase in pressure,as illustrated in Fig. 2-7.2. Some of the equations relating self-diffusion coefficients with pressure found in the literature are shown in Table 2-7.1.

Table 2-7.1 Some of the equations defining the relationship between diffusion coefficient and pressure

Author, year and reference	Equation	Equation number
Koeller-Drickamer, 1953 (105)	$\frac{D^*p}{D^*o} = \frac{\mu_o}{\mu_p} \left(\frac{V_o}{V_p}\right)^{\frac{1}{3}}$ where D*p = diffusion coefficient at pressure p D*o = diffusion coefficient at reference pressure. (based on the Stokes-Einstein eq. (2-2.2))	2-7.1
Koeller-Drickamer, 1953 (105)	$\frac{D^*p}{D^*o} = \left(\frac{\mu_o}{\mu_p}\right)^{\frac{1}{2}} \left(\frac{V_o}{V_p}\right)^{\frac{1}{3}}$ (based on the Arnold eq. ref. 8).	2-7.2
Koeller-Drickamer, 1953 (105)	$\frac{\partial \ln D^*}{\partial P} = \frac{2}{3} \frac{1}{\bar{V}} \frac{\partial V}{\partial P} - \frac{\partial \Delta G_D}{RT \partial P}$ or $\frac{\partial \ln D^*}{\partial P} = \frac{2}{3} \frac{1}{\bar{V}} \frac{\partial V}{\partial P} - \frac{\Delta V_D^{\ddagger}}{RT}$. ΔG_D = free energy of activation $\Delta V_D^{\ddagger}$ = activation volume interpreted as the local volume change associated with motion.	2-7.3
Longuet-Higgin-Pople, 1956 (119)	$D^* = \frac{r}{2} \left(\frac{\pi kT}{M}\right)^{\frac{1}{2}} \left[\frac{P\bar{V}}{RT} -1\right]^2$	2-2.8
Nachtrieb-Petit, 1956 (138)	$\log_e D^* = 4.7889-9.637 \times 10^{-6} P$ empirical equation valid only for liquid mercury up to 8366 Kg/cm^2.	2-7.4

2-8 Diaphragm cell methods (66, 99, 134, 170, 199, 209)

One of the most popular methods of experimental determination of diffusion coefficient is the diaphragm cell method. Generally, diaphragm cells consist of two compartments, one containing the more concentrated liquid and the other the dilute liquid. The diffusion takes place through the pores of the diaphragm in which the liquid is supposed to be stationary. The liquid concentration in the two compartments, on the otherhand, is maintained uniform by various methods.

In the earlier cells a density stirring method was used. This was effected by placing the heavier liquid in the upper cell and the lighter liquid in the lower cell. This resulted in mixing by the bulk flow of the two liquids. In the most recent diaphragm cells mixing is achieved by special stirrers placed one in each cell and bulk flow through the diaphragm is no longer present.

Table 2-8.1 lists, chronologically, the diaphragm cells used from Graham (71) onwards and shows the most important features of each cell. The earliest cells reported in the literature employed animal bladders, intestines or parchment papers as the diaphragm, Figs. (2-8.1), (2-8.2) and (2-8.14). In the most recent diaphragm cells sintered glass diaphragms are employed, Figs. (2-8.3) and (2-8.4).

Despite the efforts of many workers, the precise measurement of the diffusion coefficient was still not possible before the mid-1940's. The first diaphragm cell which gave reasonable results was developed by Stokes (185). This diaphragm cell, Fig. (2-8.8), consists of two almost identical compartments divided by the sintered glass diaphragm. The homogeneity of the compartment solutions is maintained by magnetic stirring. The lighter liquid is placed in the upper compartment while the heavier liquid occupies the lower one. Procedures for diffusion measurements,as well as the calibration method outlined by Stokes (185), have now become standard. This contribution of Stokes to the diaphragm cell method constitutes a landmark in the historical evolution of the diaphragm cell (134).

The latest designs are modifications of Stokes' two-compartment diaphragm cell in order to satisfy particular conditions. One such modification of Stokes' cell is to adapt it for measurements at elevated temperatures. In this case the design must allow for thermal expansion of the liquid and must prevent boiling. Calus and Tyn (25) modified Stokes' two-compartment cell, Fig. (2-8.18), by employing pressure to prevent the boiling of test liquids during experiments at elevated temperatures. One weak point of their design is that the bulk flow of the test liquid during the preheating period cannot be prevented. Another modification of Stokes' cell for higher temperature measurements was due to Sanni and Hutchison (175). They introduced a third compartment to store one of the test liquids during the preheating period. One disadvantage of their design is that it cannot be used for measurements at or near the boiling point of the test liquids due to boiling effects.

Table 2-8.1 Some of the diaphragm diffusion cell designs employed by various authors

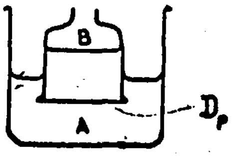
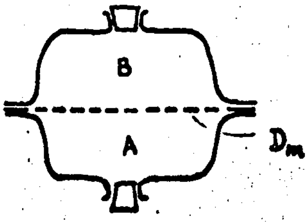
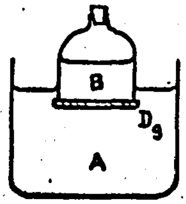
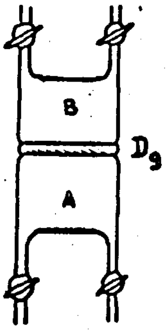
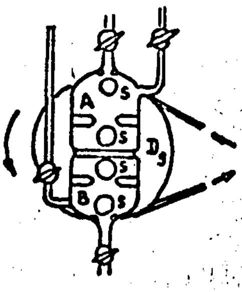
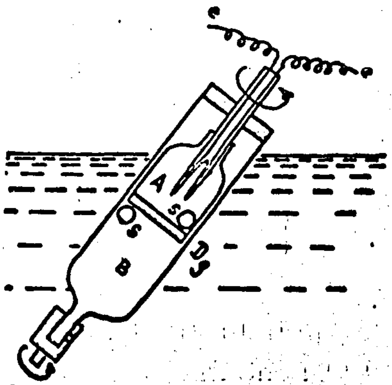
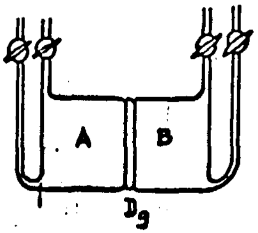
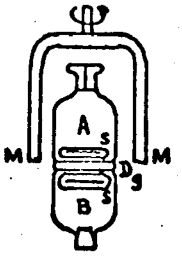
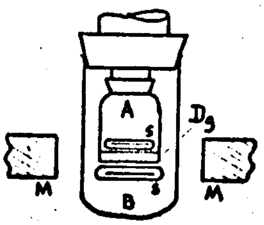
 2-8.1: Graham,1854 (71)	A = Compartment with lighter solution B = Compartment with heavier solution D_p = Paper diaphragm D_m = Membrane diaphragm D_g = Sintered glass diaphragm D_n = Platinum sintered diaphragm M = Magnets for rotating the stirrers S = Stirrers e = Electrode for measuring the concentration of the upper liquid "in situ".	
 2-8.2: Thoms,1917 (199)	 2-8.3: Northrup-Anson,1929 (143)	 2-8.4: McBain-Dawson, 1935(127)
 2-8.5: Mouquin-Cathcart, 1935(136)	 2-8.6: Hartly-Runnicles, 1938(79)	 2-8.7: Trevoy-Drickamer, 1949(198)

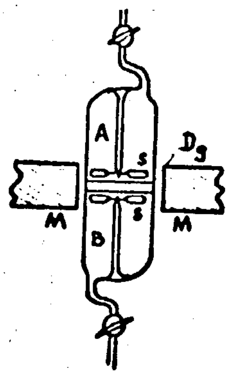
Table 2-8.1 (contd.)



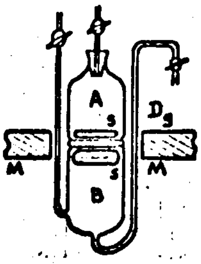
2-8.8: Stokes,1950 (185)



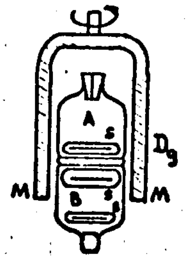
2-8.9: Smith-Storrow,1952 (183)



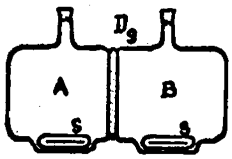
2-8.10 : Lewis,1955 (113)



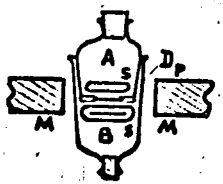
2-8.11: Dullien-Shemilt, 1961(45)



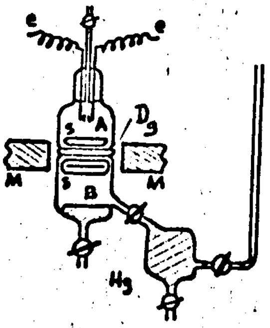
2-8.12: Henrion,1964 (83)



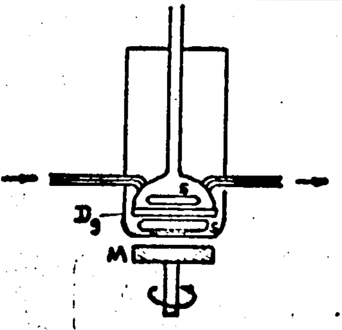
2-8.13: Holmes,1965 (89)



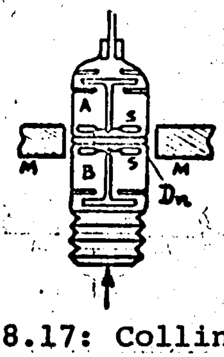
2-8.14: Hashitani, 1967(80)



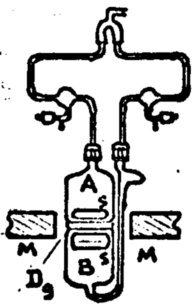
2-8.15: Sanni-Hutchison, 1968(175)



2-8.16: Rao-Bennet, 1971(162)



2-8.17: Colling et al, 1971(30)



2-8.18: Calus-Tyn, 1973(25)

PART 3 DEVELOPMENT OF CORRELATIONS

3-1 Diffusion coefficients for concentrated binary liquid mixtures

The most recent mathematical models for diffusion in non-ideal and non-associating binary liquid mixtures were developed by Vignes (210) and by Leffler and Cullinan (111). They agree reasonably well with experimental data. Gainer and Metzner (60) developed another model which they recommend for dilute solutions. The latter model is fairly complicated as it allows for the variation of the free energies of activation for viscosity and diffusivity. However, this model does not agree with the experimental data for solutions of higher concentration, as was expected. The correlation of Leffler and Cullinan is based on the mathematical model of viscosity, which was found by Li and Chang (115) and Eyring and Jhon (53) to contain a faulty definition of the shear stress area between neighbouring layers of molecules. In this work the correlation of Leffler and Cullinan is modified by incorporating the corrected model for viscosity and including the free energies of activation for viscosity and diffusivity.

Before this, a physical model of the liquid structure, on which all the above models are based, is briefly described.

3-1.1 A physical model for diffusive and viscous processes in the liquid phase

In considering the mechanism of diffusive and viscous flows the model of the liquid structure proposed by Eyring (69) will be assumed. This model assumes the liquid to have a quasi-crystalline structure, i.e. molecules are arranged in layers of fairly regular configuration. The irregularities are due to the existence of 'holes' of approximately molecular size. This model, together with the notation assumed to describe the distances between molecules, is shown in Fig. 3-1.1.

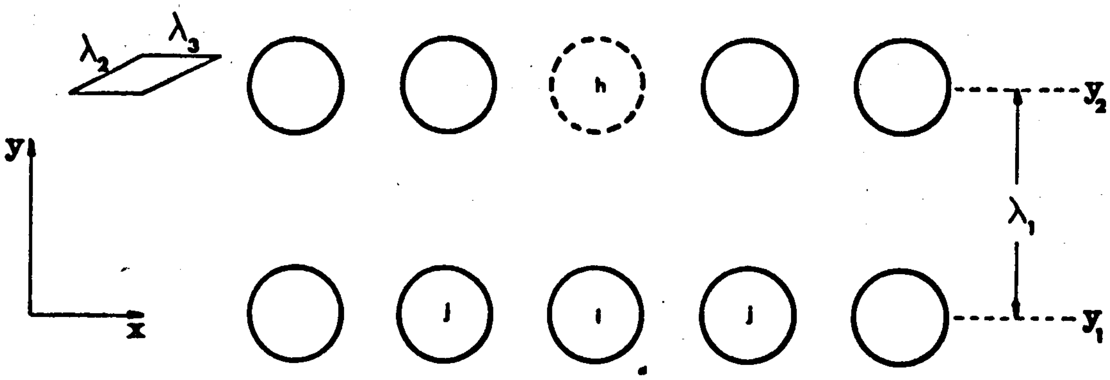


Fig. 3-1.1 Notation in the model representing a lattice type of structure of the liquid phase.

The molecular structure in Fig. 3-1.1, with all the molecules being of the same size, represents a pure liquid. It can be used to illustrate self-diffusion and viscous flow. To illustrate a mutual diffusion the lattice in Fig. 3-1.1 must be composed of two types of molecules but the mechanism of the diffusive and viscous flows will be the same. The distances between the layers are considered to be larger than the size of the molecules. Thus the process of jumping, e.g. of the molecule "i", into the vacant space "h" represents the diffusion or self-diffusion process. On the other hand the sliding action of the whole layer of molecules in the y_1 row to fill the position vacated by the molecule "i" represents the viscous flow.

3-1.2 Viscosity of binary liquid mixtures

The equation of viscosity for a binary mixture used by Leffler and Cullinan (111) and presented by Eyring (69) is

$$\mu_{AB} = \frac{h}{\lambda_{\mu}^{2}} \left(\frac{\lambda_1}{\lambda_2\lambda_3}\right)_{AB} \exp\left[\frac{\Delta G_{\mu,AB}}{RT}\right] \qquad (3\text{-}1.1)$$

In this equation the length parameter $\left(\frac{\lambda_1}{\lambda_2\,\lambda_3}\right)_{AB}$ is not correct, and the derivation of eq. (3-1.1) is repeated here to introduce a correct value for this parameter.

Following a diffusive jump, Fig. 3-1.1, of 'i' from the row y_1 to y_2 the layer of molecules in the row y_1 will move to occupy the vacated space. This motion requires a force in x-direction. Eyring and Jhon (53) and Li and Chang (115) defined the surface area on which this force is acting as

$$A = \xi\,\lambda_2\,\lambda_3 \qquad (3\text{-}1.2)$$

Thus the shear stress in the x-direction is

$$f_x = \frac{F_x}{\lambda_2\,\lambda_3\,\xi} \qquad (3\text{-}1.3)$$

where F_x is the force acting on the area A. Eq. (3-1.2) denotes the surface area, this includes some of the space between the neighbouring molecules in the plane of the motion which was not taken into account by earlier investigators. The symbol ξ denotes here the number of nearest molecule-neighbours in the plane of motion. In this model Newton's Law of viscosity is also applicable which applied to this geometry it gives

$$f_x = -\mu\,\frac{du_x}{dy} = -\mu\,\frac{\Delta u_x}{\lambda_1} \qquad (3\text{-}1.4)$$

where Δu_x is the difference in the velocity between the two neighbouring layers of molecules, Fig. 3-1.1.

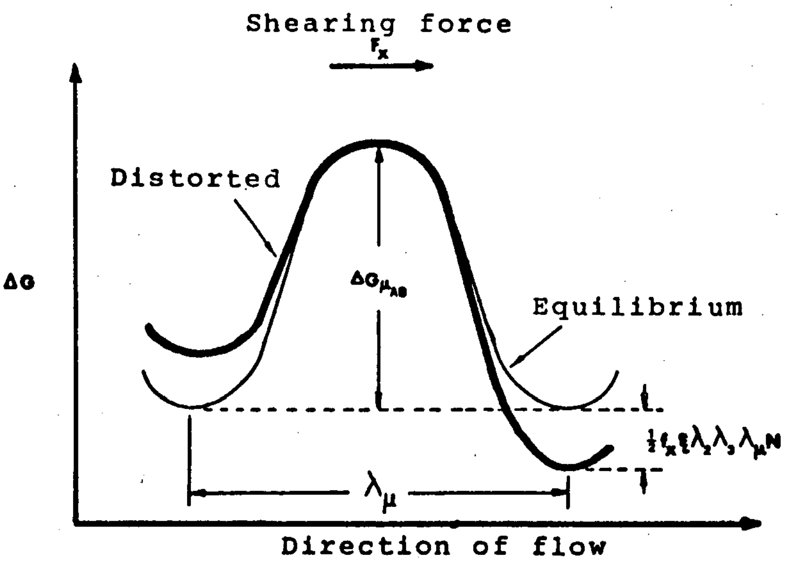


Fig. 3-1.2 Potential energy barrier for viscous flow, with and without shearing force.

The various energies concerned with viscous motion are shown in Fig. 3-1.2. Equations (3-1.5) and (3-1.6) below represent the free energies of activation for the forward and backward movements of the individual molecule, respectively

i.e. $$\frac{\Delta G^{+}_{\mu,AB}}{N} = \frac{\Delta G_{\mu,AB}}{N} - \tfrac{1}{2} f_x \xi \lambda_2 \lambda_3 \lambda_\mu \qquad (3\text{-}1.5)$$

and $$\frac{\Delta G^{-}_{\mu,AB}}{N} = \frac{\Delta G_{\mu,AB}}{N} + \tfrac{1}{2} f_x \xi \lambda_2 \lambda_3 \lambda_\mu \qquad (3\text{-}1.6).$$

These equations (3-1.5) and (3-1.6) are written on the basis of a single molecule.

The frequencies of forward and backward motions of a molecule are given by (69)

$$\nu^{+} = \frac{kT}{h} \exp\left(-\frac{\Delta G^{+}_{\mu,AB}}{RT}\right) \qquad (3\text{-}1.7)$$

and $$\nu^{-} = \frac{kT}{h} \exp\left(-\frac{\Delta G^{-}_{\mu,AB}}{RT}\right) \qquad (3\text{-}1.8)$$

The change of velocity is the product of the distance between two equilibrium positions in the direction of motion of the moving molecule and the difference in the two frequencies

i.e. $$\Delta u_x = \lambda_\mu \left(\nu^+ - \nu^- \right) \qquad (3\text{-}1.9)$$

Rearranging equations (3-1.5) and (3-1.6)

i.e. $$\Delta G^{+}_{\mu,AB} = \Delta G_{\mu,AB} - \tfrac{1}{2} f_x \xi \lambda_2 \lambda_3 \lambda_\mu N \qquad (3\text{-}1.5a)$$

and $$\Delta G^{-}_{\mu,AB} = \Delta G_{\mu,AB} + \tfrac{1}{2} f_x \xi \lambda_2 \lambda_3 \lambda_\mu N \qquad (3\text{-}1.6a)$$

and bombining them with equations (3-1.7) and (3-1.8) we obtain

$$\nu^+ = \frac{kT}{h} \exp\left[-\frac{\Delta G_{\mu,AB}}{RT} + \frac{\frac{1}{2} f_x \xi \lambda_2 \lambda_3 \lambda_\mu N}{RT} \right] \qquad (3\text{-}1.7a)$$

and $$\nu^- = \frac{kT}{h} \exp\left[-\frac{\Delta G_{\mu,AB}}{RT} - \frac{\frac{1}{2} f_x \xi \lambda_2 \lambda_3 \lambda_\mu N}{RT} \right] \qquad (3\text{-}1.8a)$$

These equations combined with eq. (3-1.9) gives

$$\Delta u_x = \lambda_\mu \frac{kT}{h} \left[\exp \left(\frac{-\Delta G_{\mu,AB}}{RT} \right) \right] \left[\exp \left(\frac{\frac{1}{2} f_x \xi \lambda_2 \lambda_3 \lambda_\mu N}{RT} \right) - \exp \left(\frac{-\frac{1}{2} f_x \xi \lambda_2 \lambda_3 \lambda_\mu N}{RT} \right) \right] \qquad (3\text{-}1.10)$$

By expansion of the last two exponential terms in eq. (3-1.10) and neglecting insignificant groups we get

$$\Delta u_x = \lambda_\mu^2 \left(\frac{k}{R} \right) \left(\frac{N}{h} \right) f_x \xi \lambda_2 \lambda_3 \exp\left(\frac{-\Delta G_{\mu,AB}}{RT} \right) \qquad (3\text{-}1.11)$$

but $\frac{k}{R} = \frac{1}{N}$ and therefore

$$\Delta u_x = \lambda_\mu^2 \frac{f_x \xi \lambda_2 \lambda_3}{h} \exp\left(\frac{-\Delta G_{\mu,AB}}{RT} \right) \qquad (3\text{-}1.12)$$

Combining eq. (3-1.12) with Newton's law of viscosity, i.e. eq. (3-1.4), and rearranging we get

$$\mu_{AB} = \frac{h}{\lambda_\mu^2} \left(\frac{\lambda_1}{\xi \lambda_2 \lambda_3}\right)_{AB} \exp\left(\frac{\Delta G_{\mu,AB}}{RT}\right) \quad (3\text{-}1.13)$$

where subscript 'AB' indicates a binary mixture.

Equation (3-1.13) will now replace eq. (3-1.1) in developing a correlation for the diffusion in binary liquid mixtures.

3-1.3 Development of the correlation

Equation (3-1.13) developed, in the previous section, contains a length parameter for a binary liquid mixture $\left(\frac{\lambda_1}{\xi \lambda_2 \lambda_3}\right)_{AB}$.

This is made up of the length parameters of the two pure components and it will be assumed that the binary parameter will be, in some way, related to the two parameters of the pure components. Cullinan's(36) method of estimating a parametric mean value will be applied here. Therefore

$$\left(\frac{\lambda_1}{\xi \lambda_2 \lambda_3}\right)_{AB} = \left(\frac{\lambda_1}{\xi \lambda_2 \lambda_3}\right)_{A}^{x_A} \left(\frac{\lambda_1}{\xi \lambda_2 \lambda_3}\right)_{B}^{x_B} \quad (3\text{-}1.14)$$

Next a relationship between the length parameter and the self-diffusion coefficient for a single component liquid, established by Eyring and Jhon (53), will be applied

i.e. $$\left(\frac{\lambda_1}{\xi \lambda_2 \lambda_3}\right)_{A} = \frac{D^*_A \mu_A}{kT} \quad (3\text{-}1.15)$$

and $$\left(\frac{\lambda_1}{\xi \lambda_2 \lambda_3}\right)_{B} = \frac{D^*_B \mu_B}{kT} \quad (3\text{-}1.16)$$

The length parameter for the binary mixture is then obtained by combining equations (3-1.14), (3-1.15), and (3-1.16) giving

$$\left(\frac{\lambda_1}{\xi\lambda_2\lambda_3}\right)_{AB} = (D^*_A\,\mu_A)^{x_A}\,(D^*_B\,\mu_B)^{x_B}\,\frac{1}{kT} \qquad (3\text{-}1.17)$$

This value of the length parameter is inserted into equation (3-1.13) to transform it into the following form

$$\mu_{AB} = \frac{1}{\lambda_\mu^2}\,\frac{h}{kT}\,(D^*_A\,\mu_A)^{x_A}\,(D^*_B\,\mu_B)^{x_B}\,\exp\left(\frac{\Delta G_{\mu,AB}}{RT}\right)$$

$$(3\text{-}1.18)$$

On the basis of the absolute reaction rate theory Leffler and Cullinan (111) obtained the following equation for the binary diffusion coefficient

i.e. $$\frac{D_{AB}}{\alpha_A} = \frac{kT}{h}\,\lambda_D^{\,2}\,\exp\left(-\frac{\Delta G_{D,AB}}{RT}\right) \qquad (3\text{-}1.19)$$

Now combining equation (3-1.19) with equation (3-1.18) we have

$$\frac{D_{AB}\,\mu_{AB}}{\alpha_A} = \left(\frac{\lambda_D}{\lambda_\mu}\right)^2 \left(D^*_A\,\mu_A\right)^{x_A} \left(D^*_B\,\mu_B\right)^{x_B}$$

$$\times\exp\left[\frac{\Delta G_{\mu,AB} - \Delta G_{D,AB}}{RT}\right] \qquad (3\text{-}1.20)$$

in which λ_D and λ_μ are the distances between the successive equilibrium positions in the diffusional and viscous processes respectively. It will be assumed that λ_D and λ_μ are approximately equal and therefore equation (3-1.20) simplifies to

$$\frac{D_{AB}\,\mu_{AB}}{\alpha_A} = \left(D^*_A\,\mu_A\right)^{x_A} \left(D^*_B\,\mu_B\right)^{x_B} \exp\left[\frac{\Delta G_{\mu,AB} - \Delta G_{D,AB}}{RT}\right]$$

$$(3\text{-}1.21)$$

Evaluation of $\left[\Delta G_{\mu,AB} - \Delta G_{D,AB}\right]$

The exponential term in equation (3-1.21) was already present in the original correlation of Leffler and Cullinan (111), but they dropped it on account of that, for non associated mixtures, it is almost constant. Gainer and Metzner (60), on the other hand, made an attempt to evaluate this quantity, in doing so they assumed that their correlation would be used for dilute solutions only. In this work an attempt has been made to modify Leffler and Cullinan's(111) and Gainer and Metzner's(60) results so that the resulting correlation will be suitable for the prediction of the diffusion coefficient for associated binary mixtures of any concentration.

In the evaluation of the term, $\left[\Delta G_{\mu,AB} - \Delta G_{D,AB}\right]$ most of the assumptions of the previous workers (60, 111, 144) will be taken to be correct. Thus the free energy of activation for viscous flow consists of a part required to form a "hole" and another part for "jumping" stage so that for a binary mixture we have

$$\Delta G_{\mu,AB} = \Delta G^{h}_{\mu,AB} + \Delta G^{j}_{\mu,AB} \tag{3-1.22}$$

A similar relationship may be written for the free energy of activation for the diffusive process

i.e. $$\Delta G'_{D,AB} = \Delta G^{h}_{D,AB} + \Delta G^{j}_{D,AB} \tag{3-1.23}$$

Gainer and Metzner (60) and Leffler and Cullinan (111) assume that for the viscous process the 'hole making' and 'jumping' stages need the same amount of energy. Therefore

$$\Delta G^{h}_{\mu,AB} = \Delta G^{j}_{\mu,AB} = \tfrac{1}{2}\Delta G_{\mu,AB} \tag{3-1.24}$$

The same authors assume that the hole making process requires the same amount of energy whether the flow is viscous or diffusive. Therefore

$$\Delta G^{h}_{\mu,AB} = \Delta G^{h}_{D,AB} = \tfrac{1}{2}\Delta G_{\mu,AB} \qquad (3\text{-}1.25)$$

It may be deduced from equations (3-1.24) and (3-1.25) that

$$\Delta G_{\mu,AB} - \Delta G_{D,AB} = \tfrac{1}{2}\Delta G_{\mu,AB} - \Delta G^{j}_{D,AB}$$

(3-1.26)

It remains now to establish the method of computation for the quantities $\Delta G_{\mu,AB}$ and $\Delta G^{j}_{D,AB}$ in order to use equation (3-1.21).

Free energy of activation for the viscous flow, $\Delta G_{\mu,AB}$

Glasstone et al (69) recommended the following relationship for the calculation of the free energy of activation for viscous flow

i.e. $$\Delta G_{\mu,AB} = x_A \Delta G_{\mu,A} + x_B \Delta G_{\mu,B} + \Delta G_{m}$$

(3-1.27)

in which $\Delta G_{\mu,A}$, $\Delta G_{\mu,B}$ are free energies of activation for pure components A and B respectively. ΔG_{m} is the excess free energy of mixing. Glasstone et al (69) reported the following relationships between the free energy of activation for viscous flow and the latent heats of vaporisation of the pure components.

i.e. $$\Delta G_{\mu,A} = \frac{\Delta E_A}{2.45} = \frac{\Delta \bar{H}_A - RT}{2.45} \qquad (3\text{-}1.28)$$

and $$\Delta G_{\mu,B} = \frac{\Delta E_B}{2.45} = \frac{\Delta \bar{H}_B - RT}{2.45} \qquad (3.1.29)$$

Dumas et al (46) recommended the following equation for the calculation of the excess free energy of activation for mixing

i.e. $$\Delta G_m = RT \left[\ln \mu_{AB} - \left(x_A \ln \mu_A + x_B \ln \mu_B\right)\right] \qquad (3\text{-}1.30)$$

The last three equations (3-1.28), (3-1.29) and (3-1.30) are sufficient to calculate the $\Delta G_{\mu, AB}$ term in equation (3-1.27).

Free energy of activation of $\Delta G^j_{D,AB}$

The method for estimating $\Delta G^j_{D,AB}$ used by Gainer and Metzner (60) gave good results when tested by them on dilute solutions , but when tested on concentrated solutions of ethanol and water by this author the agreement was unsatisfactory. Therefore,a different approach is used in this work for estimation of $\Delta G^j_{D,AB}$. In agreement with Gainer and Metzner (60) it is assumed that the free energy of activation for the jumping stage in the diffusive process may be split into the jumping stage in breaking the hydrogen bonding and the jumping stage in resisting the dispersion forces. The dispersion forces are assumed to be the dominant component of the intermolecular forces. Thus the other intermolecular forces are ignored in this derivation as insignificant. Therefore

$$\Delta G^j_{D,AB} = \Delta G^j_{D,AB-H} + \Delta G^j_{D,AB-I} \qquad (3\text{-}1.31)$$

The activation energy for the jumping stage will be found from the activation energies of the pure components using the simple mixing rule recommended by Glasstone et al (69). Therefore

$$\left[\sqrt{\Delta G^{j}_{D,AB-H}}\right] \propto \left[x_A \sqrt{\Delta G^{j}_{D^*,A-H}} + x_B \sqrt{\Delta G^{j}_{D^*,B-H}}\right] \qquad (3-1.32)$$

$$\left[\sqrt{\Delta G^{j}_{D,AB-I}}\right] \propto \left[x_A \sqrt{\Delta G^{j}_{D^*,A-I}} + x_B \sqrt{\Delta G^{j}_{D^*,B-I}}\right] \qquad (3-1.33)$$

According to Gainer and Metzner (60) the potential energy between molecules for hydrogen bonding varies inversely as the first power of the intermolecular distance. Therefore equation (3-1.32) may be written as follows

$$\sqrt{\Delta G^{j}_{D,AB-H}} = x_A \sqrt{\delta_A \, \Delta G^{j}_{D^*,A-H}} + x_B \sqrt{\delta_B \Delta G^{j}_{D^*,B-H}} \qquad (3-1.34)$$

In this equation (3-1.34) δ_A and δ_B are the intermolecular distances defined by the following equations

$$\delta_A = \frac{2 \mathcal{R}_A}{\mathcal{R}_A + \mathcal{R}_B} \qquad (3-1.35)$$

$$\delta_B = \frac{2 \mathcal{R}_B}{\mathcal{R}_A + \mathcal{R}_B} \qquad (3-1.36)$$

$$\mathcal{R}_A = \left(\frac{\bar{V}_A}{N}\right)^{\frac{1}{3}} \text{ and } \mathcal{R}_B = \left(\frac{\bar{V}_B}{N}\right)^{\frac{1}{3}} \qquad (3-1.37)$$

According to Gainer and Metzner (60) the dispersion forces are inversely proportional to the twelfth power of the intermolecular distance. This exponent gives a correlation which does not agree with the experimental results for ethanol-water mixtures (24, 45, 76). After lengthy trial and error calculation it has been found empirically that the exponent should be "two". Therefore the equation for $\Delta G^{j}_{D,AB-I}$ takes the form

$$\sqrt{\Delta G^{j}_{D,AB-I}} = x_A \sqrt{\left(\frac{1}{\delta_A}\right)^2 \Delta G^{j}_{D^*-I}} + x_B \sqrt{\left(\frac{1}{\delta_B}\right)^2 \Delta G^{j}_{D,*B-I}}$$

(3-1.38)

Computation of $\Delta G^{j}_{D^*,X-H}$ and $\Delta G^{j}_{D^*,X-I}$

By analogy to equation (3-1.31) we can write,for the pure component X

$$\Delta G^{j}_{D^*,X} = \Delta G^{j}_{D^*,X-H} + \Delta G^{j}_{D^*,X-I} \qquad (3\text{-}1.39)$$

$$\Delta G^{j}_{\mu,X} = \Delta G^{j}_{\mu,X-H} + \Delta G^{j}_{\mu,X-I} \qquad (3.1.39a)$$

Rewriting equation (3-1.24) for a single component and combining it with equation (3-1.39a) results in the following relationship

$$\Delta G^{j}_{\mu,X} = \Delta G^{j}_{\mu,X-H} + \Delta G^{j}_{\mu,X-I} = \tfrac{1}{2}\Delta G_{\mu,X}$$

(3-1.40)

Glasstone et al (69), Gainer and Metzner (60) and Olander (144) establish that the free energy of activation of the jumping stage in a single component liquid is the same for the diffusional process as for the viscous process. Therefore

$$\Delta G^{j}_{D^*,X} = \Delta G^{j}_{\mu,X} = \tfrac{1}{2}\Delta G_{\mu,X} \qquad (3\text{-}1.41)$$

An assumption is made here,that,in a single component liquid,the hydrogen bond contribution to the free energy of activation is the same for the diffusional process as for the viscous process:

i.e. $$\Delta G^{j}_{D^*,X-H} = \Delta G^{j}_{\mu,X-H} = \tfrac{1}{2}\Delta G_{\mu,X-H} \qquad (3\text{-}1.42)$$

$\Delta G_{\mu,X-H}$ is the hydrogen bond contribution to the free energy of activation for viscosity and the computation of it was suggested by Olander (144) in the following relationship

$$\frac{\Delta G_{\mu,X-H}}{\Delta G_{\mu,X}} = \frac{\Delta \bar{H}_{X-H}}{\Delta \bar{H}_{X}} \qquad (3\text{-}1.43)$$

In this equation (3-1.43) $\Delta G_{\mu,X}$ is the total free energy of activation of viscosity for a single component liquid X and $\Delta \bar{H}_{X-H}$ is the difference between the heat of vaporisation of the pure liquid X and the heat of vaporisation of its homomorph. This difference is found by the method recommended by Bondi and Simkin (18). The above equations (3-1.42), (3-1.41) and (3-1.39) make it possible to calculate $\Delta G^{j}_{D^{*}X-H}$, $\Delta G^{j}_{D^*,X}$ and $\Delta G^{j}_{D^*,X-I}$ respectively. With the help of equations (3-1.34), (3.1.38) and (3-1.31) $\Delta G^{j}_{D,AB}$ is finally calculated.

Correction factor to $\Delta G^{j}_{D,AB}$

In the calculation of the free energy of activation for the jumping stage in the diffusive flow, $\Delta G^{j}_{D,AB}$, only the dispersion forces are taken into account. The other intermolecular forces such as electrostatic, induction and resonance forces are relatively small, as indicated by Hirschfelder et al (87), but they are not negligible. To account for these forces in the correlation analytically is not possible, on the account of the complexity of the problem. Gainer and Metzner (60), in their paper limited to dilute solutions, used the argument that the number of A-B bonds broken during the diffusional process is probably not the same as the number of B-B bonds broken in the viscous process. They suggested that this assumption calls for a correction factor consisting of a ratio of the number of nearest neighbours in the pure A, ξ_A, to the number of nearest neighbour in the pure B, ξ_B. They were satisfied that this correction factor i.e. (ξ_A / ξ_B) correlated their data for dilute solutions. In this work, however, there was no agreement between the correlation and the experimental data for the full range of concentration of binary mixture.

It was decided, in this work, to obtain a bond breaking factor, f_{AB}, which is made up of the bond breaking factors for the pure components. It is suggested that f_{AB} is related to the pure component factors f_A and f_B by the type of relationship recommended by Cullinan (36).

i.e. $$f_{AB} = \left(f_A^{x_A} \cdot f_B^{x_B}\right) \qquad (3\text{-}1.44)$$

The bond breaking factor f_{AB} is used as a multiplier to the free energy of activation for the jumping stage in the diffusive flow $\Delta G^j_{D,AB}$. The individual bond breaking factors f_A and f_B are obtained as follows. For the factor f_A equation (3-1.21) is rewritten for an infinite dilution of component B and the correction factor f_A included. The modified equation (3-1.21) is combined with equation (3-1.26) to obtain

$$D^o_{BA} = D^*_A \exp\left[\frac{\frac{1}{2}\Delta G_{\mu,A} - f_A \Delta G^j_{D^o,BA}}{RT}\right] \qquad (3\text{-}1.45a)$$

This equation (3-1.45) rearranged gives

$$f_A = \frac{1}{\Delta G^j_{D^o,BA}}\left[\frac{1}{2}\Delta G_{\mu,A} - RT \ln\left(\frac{D^o_{BA}}{D^*_A}\right)\right] \qquad (3\text{-}1.46a)$$

in which

$$\Delta G^j_{D^o,BA} = \delta_A \Delta G^j_{D^*,A\text{-}H} + \left(\frac{1}{\delta_A}\right)^2 \Delta G^j_{D^*,A\text{-}I} \qquad (3.1.47a)$$

Equation (3-1.47a) is obtained by combining equations (3-1.34), (3-1.38) with equation (3-1.31).

In a similar way we get

$$D^o_{AB} = D^*_B \exp\left[\frac{\frac{1}{2}\Delta G_{\mu,B} - f_B \Delta G^j_{D^o,AB}}{RT}\right] \qquad (3\text{-}1.45b)$$

from which

$$f_B = \frac{1}{\Delta G^{j}_{D^o,AB}} \left[\frac{1}{2} \Delta G_{\mu,B} - RT \ \ln \left(\frac{D^o_{AB}}{D^*_B} \right) \right] \qquad (3\text{-}1.46b)$$

where

$$\Delta G^{j}_{D^o,AB} = \delta_B \Delta G^{j}_{D^*,B\text{-}H} + \left(\frac{1}{\delta_B} \right)^2 \Delta G^{j}_{D^*,B\text{-}I}$$

(3-1.47b)

Thus equation (3-1.26) with the bond breaking factor f_{AB} included takes the form

$$\Delta G_{\mu,AB} - \Delta G_{D,AB} = \frac{1}{2} \Delta G_{\mu,AB} - f_{AB} \Delta G^{j}_{D,AB}$$

(3-1.26a)

Concluding remarks

It may be seen from this derivation that,in order to use equation (3-1.21) for the prediction of the diffusion coefficient of a binary mixture the following physical properties are required : self-diffusion coefficients of the pure components, mutual diffusion coefficients at infinite dilution, molal volumes, latent heat of vaporisation of pure components, the hydrogen bond contribution to the latent heat of vaporisation, viscosity of the pure components and of mixtures of them, and the isothermal vapour-liquid equilibrium data. Before equation (3-1.21) is used all the information required in it is obtained from equations (3-1.28), (3.1.29), (3-1.30), (3-1.27), (3-1.41), (3-1 .43), (3-1.42), (3-1.39), (3-1.37), (3-1.35), (3-1.36), (3-1.34), (3-1.38), (3-1.31), (3-1.47a), (3-1.47b), (3-1.46a), (3-1.46b), (3-1.44) and (3-1.26a) which are listed in the order in which they are required for computation. An example of using equation (3-1.21) is given in Appendix (7-3.1).

The comparison of the values of diffusion coefficients predicted by equation (3-1.21),and by the equations of Vignes (210) and Leffler and

Cullinan (111),with the experimental data of this work are given in the section 7-3.1 under the heading "Discussion".

3-2.1 Diffusion coefficients at infinite dilution

Inspection of the Stokes-Einstein relationship and of the equations based on it i.e.

$$\frac{D^{o}_{AB}\,\mu_B}{T} = \frac{1}{6\,\pi\,r_A} \qquad (2\text{-}3.2)$$

$$\frac{D^{o}_{AB}\,\mu_B}{T} = 7.4 \times 10^{-8}\ \frac{(X_B\ M_B)^{\frac{1}{2}}}{V_A^{\,0.6}} \qquad (2\text{-}3.16)$$

$$D^{o}_{AB} = 5.4 \times 10^{-8} \left[\frac{M_B^{\frac{1}{2}}\ \Delta L_B^{\frac{1}{3}}\ T}{\mu_B\ V_A^{0.5}\ \Delta L_A^{0.3}}\right]^{0.93} \qquad (2\text{-}3.27)$$

$$\frac{D^{o}_{AB}\,\mu_B}{T} = 4.4 \times 10^{-8} \left[\frac{V_B}{V_A}\right]^{\frac{1}{6}} \left[\frac{\Delta H_B}{\Delta H_A}\right]^{\frac{1}{2}} \qquad (2\text{-}3.29)$$

leads to the following conclusions:

(1) The Stokes-Einstein equation itself agrees well with experimental data obtained with liquid phase systems answering the description of the physical model assumed in the derivation of (2-3.2). The size of the solute molecules is an important variable in (2-3.2) and the solvent is treated as a continuum.

(2) For most of the binary systems the size of the solute and solvent molecules is of the same order of magnitude. Thus any attempt to adapt the Stokes-Einstein equation would make it necessary to introduce the size of the solvent molecules as an additional variable. This could take the form of such ratios as ($r_A^{\,e}/r_B^{\,g}$) or ($V_A^{\,s}/V_B^{\,q}$).

(3) An association factor, which is different for every polar solvent and almost certainly temperature dependent, was introduced in eq (2-3.16). In equation (2-3.27) and (2-3.29) a ratio of the latent heats of vaporisation was introduced in the belief that it would account for the association phenomenon.

Unfortunately these equations do not show any marked improvement over eq. (2-3.16) as demonstrated in Table 3-2.1 .

Ibrahim and Kuloor (94) and Olson and Walton (146) indicated that a relationship exists between the property of surface tension and the intermolecular forces. It is suggested that the relationship between surface tension and diffusion coefficient be examined. Surface tension reflects the strength of the intermolecular forces, probably better than the latent heats of vaporisation, if it is considered as a component of a parachor. A parachor is a secondary derived function dependent on the primary properties of surface tension, density and molecular weight (161). It can be regarded as a sum of constants characteristic of the individual atoms or groups within the molecule (87). According to Sugden (188) a parachor is in some degree a measure of the effect of the forces due to molecular attraction on the molecular volumes. There are a number of quantitative definitions of the parachor which reflect the above features. Thus in Hirschfelder et al (87) it is defined as

$$[P] = 7.1 \times 10^{23} \quad \epsilon^{\frac{1}{4}} \quad \delta^{5/2} \qquad (3\text{-}2.1)$$

Quayle (161) also defines parachors as molecular volumes at corresponding states of the same value of surface tension and suggests the following definition:

$$[P] = \sigma^{\frac{1}{4}} \bar{V} \qquad (3\text{-}2.2)$$

According to Hirschfelder et al (87) the parachor for any given substance remains nearly independent of temperature over a wide temperature range. The last property makes it possible to use the parachor in conjunction with the group $(D^{\circ}_{AB}\,\mu_B/T)$. Thus it is obvious that parachors are more dependent on molecular structures and sizes than the latent heats of vaporisation and would be expected to be more sensitive indicators of the intermolecular forces, particularly with polar compounds. It is therefore suggested that the correlating equation should assume the form:

$$\frac{D_{AB}\mu_B}{T} = K \; \frac{V_A^{s}}{V_B^{q}} \left[\frac{[P_B]}{[P_A]}\right]^{m} \qquad (3\text{-}2.3)$$

This equation was tested with a large variety of literature experimental data in order to evaluate the constant K and the exponents s, q and m. The optimisation routine NELM (140) and an ICL 1904A computer were used. With a total of 883 data points at infinite dilution and 113 data points for self-diffusion (see Appendices 3-2.1 and 3-2.2) the constants were established, giving the following correlation:

$$\frac{D_{AB}\mu_B}{T} = 8.93 \times 10^{-8} \; \frac{V_A^{1/6}}{V_B^{1/3}} \left[\frac{[P_B]}{[P_A]}\right]^{0.6} \qquad (3\text{-}2.4)$$

The constant of the equation has dimensions and therefore the set of units defined in the nomenclature should be used with eq. (3-2.4).

Table 3-2.1 gives a summary of the binary systems used to establish the constant and the exponents in eq. (3-2.4). The parachors required in eq. (3-2.4) were obtained either from Quayle (161) or were calculated by the Sugden (188) additive method. Also the deviations of the diffusivities predicted by equations (2-3.16), (2-3.27), (2-3.29) and (3-2.4) from the experimental values are reported. A comparison of the values predicted by eq. (3-2.4) with the experimental values is made in Fig. (3-2.1). It follows from Table 3-2.1 that eq. (3-2.4) compares favourably with equations (2-3.16), (2-3.27) and (2-3.29).

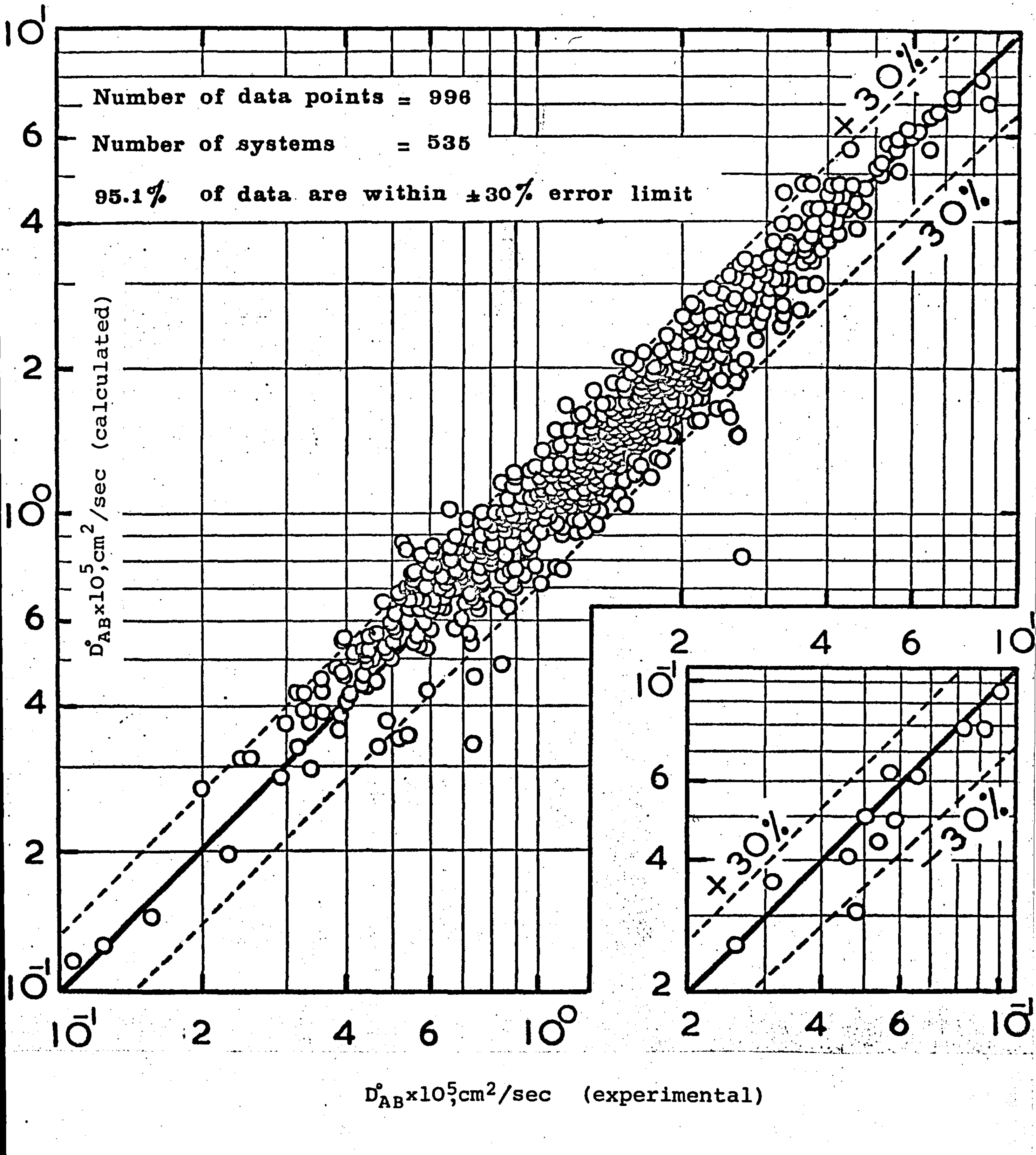


Figure 3-2.1 Comparison of experimental diffusion coefficients with the coefficients predicted by eq.(3-2.4)

Table 3-2.1 Comparison of correlations for estimating diffusion coefficients at infinite dilution, $D^\circ_{AB} \times 10^5$ cm^2/sec

No.	Solvent	Temp. range ($^\circ$C)	Number of systems **	Number of data points **	% Error* in D°_{AB} estimated by			
					This work eq(3-2.4)	W-C† eq(2-3.16)	King eq(2-3.29)	Sitar. eq(2-3.27)
1	Water	0-70	91(75)	287(253)	13.1	10.3	19.4	12.9
2	Methanol	5-55	90(79)	104(93)	14.0	17.2	13.1	13.3
3	Ethanol	7-65	27(26)	43(42)	18.1	25.8	18.5	16.7
4	n-Propanol	15-30	10	11	12.2	32.9	24.8	22.6
5	i-Propanol	30	5	5	5.3	24.6	36.7	29.9
6	n-Butanol	25-45	11(9)	13(11)	11.2	21.7	14.8	15.5
7	i-Butanol	20-30	7	8	19.1	33.7	19.0	19.0
8	n-Pentanol	25	3	3	11.7	48.6	48.0	51.5
9	Heptanol	25	3	3	12.3	47.3	44.3	51.1
10	iso-Amyl alcohol	19	1	1	35.0	77.2	46.6	45.2
11	n-Hexane	0-80	25	35	9.3	11.5	13.9	18.8
12	n-Heptane	7-100	7	32	7.7	10.7	13.2	22.2
13	n-Octane	0-100	5	24	4.4	11.5	15.2	16.8
14	n-Decane	20-25	2	3	12.9	14.0	12.2	20.8
15	n-Dodecane	25	5	5	16.5	14.5	11.6	19.7
16	n-Tetradecane	25	2	2	25.3	18.4	9.1	23.1
17	n-Hexadecane	25	4	4	27.2	22.1	17.4	26.6
18	Benzene	5-85	59(53)	110(108)	10.1	12.2	10.8	17.8
19	Toluene	6-110	23	50	8.9	17.1	10.0	17.5
20	Cyclohexane	7-100	7	28	11.6	10.5	12.1	16.1
21	Methylcyclohexane	10-60	5	11	10.0	15.5	13.0	11.8
22	Acetone	6-55	11	19	6.4	11.9	12.9	10.8
23	Methylethylketone	25	1	1	13.5	15.9	26.0	14.3
24	Methylisobutylketone	25	1	1	23.5	39.3	44.9	29.6
25	Cyclohexanone	25-90	2	4	9.7	15.6	5.2	17.9
26	Carbontetrachloride	6-60	48	78	10.1	32.5	10.7	14.1
27	Chloroform	10-40	11	15	9.6	27.8	9.7	11.3
28	Bromoform	20-25	4	4	11.4	66.3	16.5	15.4
29	Methylene chloride	7.5	1	1	13.0	58.4	26.9	47.6
30	Ethylene chloride	7.3	1	1	1.8	22.2	7.9	26.1
31	Tetrachloroethane	50	1	1	11.9	51.3	25.2	60.6
32	Chlorobenzene	10-40	3	7	8.3	11.4	10.4	10.8
33	Bromobenzene	7-40	4	8	10.0	21.2	2.2	10.7
34	Ethylbenzene	7.3	1	1	1.1	8.0	10.5	6.7
35	Nitrobenzene	17-20	4	4	9.4	12.3	4.1	7.2
36	Ethylbenzoate	15-20	4	4	17.5	9.0	9.5	16.8
37	m-Xylene	7-25	2	3	18.7	44.9	20.7	43.9
38	Methyl acetate	30	1	1	14.6	14.9	17.8	6.9
39	Ethyl acetate	20-30	8	9	12.9	24.2	16.4	16.4
40	iso-Propyl acetate	30	1	1	20.3	31.5	31.0	2.5
41	Butyl acetate	20-30	4	4	11.6	31.7	22.1	13.7
42	Ethyl ether	7-25	5	6	29.5	30.0	25.0	17.1
43	Aniline	20-60	5	7	27.5	25.0	21.2	23.2
44	Mesitylene	7.3	1	1	6.5	17.5	21.9	15.4
45	Tetralin	7	2	2	10.9	20.7	24.2	29.4
46	Transdecalin	7-25	3	3	12.6	11.4	9.0	12.9
47	Dioxane	25	2	2	2.6	13.4	9.0	24.2
48	m-Cymene	7.3	1	1	22.9	11.9	11.4	14.7
49	Acetic acid	20	1	1	32.4	3.2	3.4	35.2
50	Anisole	20	1	1	11.0	16.6	12.3	22.3

Table 3-2.1 (continued)

No.	Solvent	Temp. range ($^\circ$C)	Number of systems **	Number of data points **	% Error* in D°_{AB} estimated by			
					This work eq.(3-2.4)	W-C † eq(2-3.16)	King eq(2-3.29)	Sitar. eq(2-3.27)
51	Methylnaphthalene	7.5	1	1	11.8	2.6	2.2	9.8
52	Carbon disulphide	16-19	2	2	6.2	15.9	20.4	21.1
53	Ethyleneglycol	25-40	2	7	12.2	8.7	19.5	20.8
54	Diethyleneglycol	25-40	2	6	5.6	9.7	13.3	18.7
55	Propyleneglycol	25-50	2	7	13.7	10.3	23.3	24.1
Overall absolute average % error					12.0	16.5	15.2	15.9
Percentage of data points within ±30% accuracy limit					95.1%	83.2%	87.8%	87.2%

The total number of data points = 996(946) and

the total number of systems = 535(499).

* % Error = (Calculated - Experimental) x 100 / Experimental

† The Wilke and Chang association parameter x_B was assumed to be 2.6 for water, 1.9 for methanol and 1.5 for other alcohols. All the other solvents were allocated unity as the association parameter. Water was treated as a tetramer in eq.(2-3.16) when diffusing in organic solvents.

** The quantities in the brackets indicate the data points and the systems used with eqs.(2-3.29) and (2-3.27).

3-2.2 Limitations of equation (3-2.4)

Highly viscous solvents

All the equations tested (Table 3-2.1) underpredict the diffusion coefficients in highly viscous solvents, such as glycerol, chrysene , hendecane and others of similarly high viscosity. The predicted coefficients were up to 80% below the experimental ones. Thus equation (3-2.4) is not recommended for this type of binary system. Of the solvents in Table 3-2.1 propyleneglycol has the highest viscosity of 43 centipoises at 25°C. The upper limit of solvent viscosity for which eq. (3-2.4) may be used is probably higher if a larger deviation than 13.7% in the predicted coefficient can be tolerated.

Diffusion of water in organic solvents

Equation (3-2.4) predicts coefficients within ± 10% accuracy limits for these systems provided that water molecules are treated as dimers, i.e. a double molal volume ($2V_A$) and double parachor ($2P_A$) is used in eq. (3-2.4).

Acids diffusing in organic solvents

The best results were obtained if the acid solutes, such as acetic acid, formic acid, benzoic acid and similar acids were treated as dimers (123, 117) when diffusing in such solvents as benzene, toluene, carbontetrachloride, acetone, ethanol and others. But an exception should be made for acids diffusing in water, methanol and butanol, when the acids should be treated as monomers (123).

Diffusion of inert solutes in monohydroxy solvents

For the diffusion of such inert solutes as benzene and carbontetrachloride in monohydroxy alcohols all the equations predict coefficients about 45% lower than the experimental ones. This is ascribed to the association of the solvent molecules. For these systems an empirical formula was devised (see Fig. 3-2.2) for the estimation of the association factor

$$n = 8\,\mu_B \qquad (3\text{-}2.5)$$

where the viscosity of the solvent is in centipoises. The factor n is used in eq. (3-2.4) as a multiplier to the molal volume and to the parachor of the solvent. The application of this association factor reduced the prediction error from 45% to 10% for the appropriate systems in Table 3-2.1.

With these limitations eq. (3-2.4) predicts diffusion coefficients at infinite dilution and self-diffusion coefficients which are slightly more accurate than those predicted by equations (2-3.16), (2-3.27) and (2-3.29). This is demonstrated in Table 3-2.1. Moreover Fig. (3-2.1) shows that 95.1% of the data points fall within the ± 30% accuracy lines. The corresponding percentages for the other equations are : 83.2% for the Wilke and Chang eq(2-3.16), 87.2% for the Sitaraman et al eq. (2-3.27) and 87.8% for the King et al eq. (2-3.29).

Equation (3-2.4) besides giving more accurate predictions, is also more convenient to use on account of the ease of estimating the parachors. These can be obtained by means of such relationships as those given by equation (3-2.2) or by the addition of the parachors of the individual atoms and groups of a given compound (188).

It is sometimes not possible to use equations (2-3.27) and (2-3.29) for the prediction of diffusion coefficients because some solutes do not form a liquid phase and therefore their latent heat of vaporisation cannot be defined uniquely. This difficulty does not arise with eq. (3-2.4) as it employs parachors instead which can be defined uniquely.

Out of the total of 996 data points in Table 3-2.1, 113 represent self-diffusion coefficients. The values predicted by eq. (3-2.4) are more accurate because the molal volumes of the solute and the solvent are fitted with different exponents.

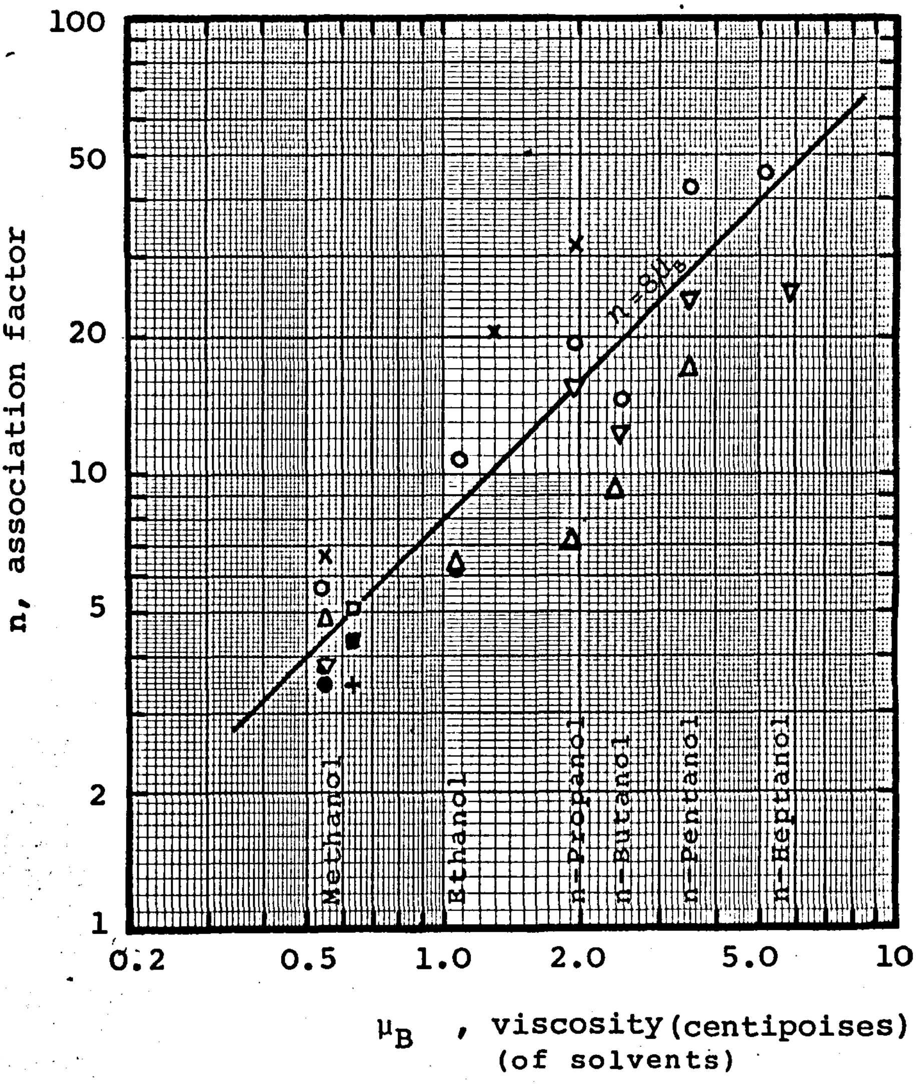


Fig. 3-2.2 Correlation of viscosity of monohydroxy alcohol solvents with association factor, n, for eq. (3-2.4),

Inert solutes:

o Benzene
× Toluene
● Carbontetrachloride
△ Biphenyl
▽ p-dichlorobenzene
□ Ethyl bromide
■ Ethyl iodide
+ Bromobenzene

3-3 Self-diffusion coefficients

3-3.1 An additive method for estimating self-diffusion coefficient

By analogy to the concept of parachor and rheochor an additive method of estimating self-diffusion coefficient is developed below. As a starting point the Dullien (44) equation for self-diffusion coefficient determination is used:

i.e. $$\frac{D^*\mu\bar{V}}{T} = \left(\frac{R}{2}\right)\delta^2 \qquad (3\text{-}3.1)$$

in which $$\delta = \left(\frac{0.6}{N^{\frac{1}{3}}}\right)(\bar{V})^{\frac{1}{3}} \qquad (3\text{-}3.2)$$

where D* is the self-diffusion coefficient in cm^2/sec, μ the viscosity in poises, $\bar{V}$ molal volume in cm^3/gmole, T the absolute temperature in $^\circ$K and δ the mean distance of momentum transfer in cm.

Combining equations (3-3.1) and (3-3.2) gives

$$\frac{D^*\mu\bar{V}}{T} = K\,(\bar{V})^{\frac{2}{3}} \qquad (3\text{-}3.3)$$

where $K = \dfrac{0.18R}{N^{\frac{1}{3}}}$

The viscosity term in equation (3-3.3) will be replaced by the rheochor [Rh], defined by Friend (58) as $\mu^{\frac{1}{8}}\,\bar{V}$.

With this substitution equation (3-3.3) can be rearranged as follows:-

$$\left(\frac{T}{D^*}\right)^{\frac{3}{23}}\bar{V} = \frac{[Rh]^{\frac{24}{23}}}{K^{\frac{3}{23}}} = [M]$$

or $$\left(\frac{T}{D^*}\right)^{0.13}\bar{V} = [M] \qquad (3\text{-}3.4)$$

Where [M] is approximately constant for an individual liquid for temperatures ranging from above the melting point to below the normal boiling point.

To prove experimentally that the value of [M] is constant 46 pure liquids, for which the experimental self-diffusion coefficients and experimental molal volumes are known, were used. An example of these calculations is given in Table 3-3.1 for pure methane and pure benzene and it can be seen that the variation in the value of [M] with temperature is very low. Methane and benzene were chosen for this illustration as their experimental self-diffusion coefficients and molal volumes are regarded as most reliable (43, 50). The list of pure compounds in the liquid phase which were used in proving that the value of [M] is approximately constant is given in Table 3-3.3.

By analogy with the procedure adopted by Sugden (188) the value of the constant [M] is compared with the critical molal volume

i.e. $[M] = \phi \; V_c$. (3-3.5)

By reference to Table 3-3.3 it is obvious that ϕ is approximately constant for the various groups of chemical compounds in the liquid phase. But the average value for each group of chemical species differ slightly. The average value of ϕ for paraffins is fairly well established because it is based on a large number of hydrocarbon compounds. The other groups of chemical compounds are not so well represented.

The close relationship between the critical molal volume and the constant [M] and also the constancy of the value of [M] for such isomerics as C_5H_{12} and C_6H_{14} (Table 3-3.3) suggest that the constant [M] is a constitutive property in a similar way as the parachor and the rheochor. On this assumption trial and error calculations were performed to obtain the "bond contribution" and "structural contribution" components to the value of [M] . For these trial and error calculations the values of [M] from equation (3-3.4), obtained by using experimental molal volumes and

Table 3-3.1 Values of [M] for liquid methane and benzene obtained from equation (3-3.4)

Liquid	T ^oK	D* x 10^5 (exper.)		$\bar{V}$ (exper.)		[M]	%deviation*	D*, calculated @	
		$cm^2/sec.$	ref.	$cm^3/gmole$	ref.	eq. (3-3.4)	from [M] avg.	$cm^2/sec.$	%erro
Methane	90.7	2.60	43	35.24	43	55.93	0.2	2.57	-1.0
	95.2	3.05	43	35.74	43	55.90	0.1	3.01	-1.4
	100.0	3.70	43	36.29	43	55.71	0.0	3.55	-3.9
	106.1	4.45	43	37.06	43	55.96	0.2	4.43	-0.4
	110.5	5.45	43	37.65	43	55.68	-0.3	5.21	-4.4
	111.1	5.23	48	37.74	43	56.14	0.5	5.32	1.8
	Average value of [M], i.e. $[M]_{avg.}$					55.84	0.22		2.2
Benzene	283.2	1.65	150	87.81	196	171.41	+1.3	1.84	11.4
	288.2	1.87	43	88.34	43	170.05	+0.5	1.96	4.8
	288.2	1.88	129	88.34	43	169.93	+0.4	1.96	4.3
	298.2	2.22	43	89.40	43	169.05	-0.1	2.22	0.0
	298.2	2.15	129	89.40	43	169.75	+0.3	2.22	3.3
	308.2	2.59	43	90.51	43	168.48	-0.4	2.53	-2.4
	308.2	2.40	129	90.51	43	170.15	+0.6	2.53	-5.4
	313.2	2.58	150	91.08	196	169.97	0.5	2.69	4.5
	318.2	3.01	31	91.66	43	168.00	-0.7	2.88	-4.4
	318.2	3.04	43	91.66	43	167.78	-0.8	2.88	-5.3
	318.2	2.67	129	91.66	43	170.58	0.8	2.88	7.9
	328.2	3.50	43	92.87	43	167.58	-1.0	3.28	-6.2
	338.2	4.03	43	94.12	43	167.41	-1.1	3.75	-7.0
	353.2	4.37	150	95.90	196	169.75	0.3	4.51	3.2
	373.2	6.15	43	98.50	43	167.97	-0.7	5.87	-4.6
	Average value of [M], i.e. $[M]_{avg.}$					169.20	0.60		5.0

@ Calculated from eq. (3-3.4) by using the values of [M] from Table 3-3.2

$$\% \text{ deviation} = \left[\frac{[M] - [M]_{avg.}}{[M]_{avg.}}\right] \times 100$$

experimental self-diffusion coefficients, were used. The results are reported in Table 3-3.2. It is to be noted that only 46 species, the same as shown in Table 3-3.3, were used to obtain Table 3-3.2. The scarcity of experimental self-diffusion coefficients and molal volumes does not allow for a better accuracy in Table 3-3.2.

After Table 3-3.2 has been completed the values of bond contributions in it were used to predict the constant [M]. These calculated constants are compared with the experimental values of [M], i.e. calculated from equation (3-3.4), and the deviations from the experimental values are reported in column 10 of Table 3-3.3. For 90% of these compounds the deviations are within ± 3% accuracy limits.

The values of the constant [M] as determined from Table 3-3.2 were tested by predicting self-diffusion coefficients from equation (3-3.4) and comparing them with the experimental coefficients. Both the calculated and the experimental D* are reported in Appendix 3-3.1b, and the average percentage deviation for each compound is also given in Table 3-3.3. The average deviation for all the 42 tested liquids is ± 12%. The corresponding deviation for the Stokes-Einstein equation (2-2.2) based on 34 compounds is ± 10%. The Dullien equation (2-2.26) has an accuracy of ± 4% for the liquids other than methanol and ethanol. It was possible to obtain this small deviation (43) by not taking into account the deviations for methanol and ethanol which are 43% and 42% respectively.

The method of calculating self-diffusion coefficients by means of the constant [M] gives quick results but is perhaps not as accurate as the Stokes-Einstein equation. This might be because there is not enough experimental data available from which more accurate values of the bond and structural contributions to the constant [M] could be calculated.

Table 3-3.2 Values of the bond and structural contributions for [M]

Bond	Contribution
C-H (number of n of carbons in chain)	
$n \leqslant 7$	14.0
$12 \geqslant n > 8$	14.5
$n \geqslant 12$	17.5
C-C	7.0
C-C (in alcohols)	17.0
C=C	19.0
O-H	33.0
O-H (in water)	17.0
C-0	9.5
C=0	28.0
C-Cl	48.5
C-Br	58.0
C-I	76.0
C-S (in carbondisulphide)	(53.0)*
N-H (in ammonia)	(14.0)*
Rings: 5 membered	-2.0
6 membered	7.0

* The values given are obtained from a single compound

Table 3-3.3 Comparison of the estimated and experimental values of [M] and the deviation of the calculated D* from the experimental D*.

Liquids	Formulae	Temp. range for D*, ^{o}K	No. of data points for D*	References for D*	Exper. $[M]_{avg.}$ from eq. (3-3.4)	V_c ref. (168)	$\phi = \frac{\text{exper. } [M]}{V_c}$	Calculated [M] from Table (3-3.2)		% error in estimated D* using [M] from Table (3-3.2)
								[M]	% dev.	
1	2	3	4	5	6	7	8	9	10	11
Paraffins:										
Methane	CH_4	90-111	5	43	55.8	99.5	0.56	56	0.3	2.2
Ethane	C_2H_6	103-183	5	150	86.8	148.0	0.59	91	4.9	27.7
n-Pentane	C_5H_{12}	195-309	13	41, 43, 150	193.0	311.0	0.62	196	1.5	18.3
Isopentane	C_5H_{12}	273-298	4	56, 204	197.3	-	-	196	-0.6	9.1
Neopentane	C_5H_{12}	298	1	43	210.6	303.0	0.69	196	-6.7	-
2-Methyl n-butane	C_5H_{12}	298	1	43	198.1	308.0	0.64	196	-1.1	-5.5
n-Hexane	C_6H_{14}	233-353	10	43, 150	231.0	368.0	0.63	231	0.0	6.0
2-Methyl pentane	C_6H_{14}	273-313	6	43, 150	232.3	367.0	0.63	231	-0.6	4.6
3-Methyl pentane	C_6H_{14}	273-313	5	43, 150	231.9	367.0	0.63	231	0.4	2.0
2,2-Dimethyl butane	C_6H_{14}	298	1	43	239.0	359.0	0.67	231	-3.3	29.9
2,3-Dimethyl butane	C_6H_{14}	273-313	6	43, 150	233.9	358.0	0.65	231	-1.2	10.1
n-Heptane	C_7H_{16}	233-369	14	43, 150	269.9	426.0	0.63	266	-1.4	10.0
n-Octane	C_8H_{18}	273-393	18	43, 150	310.5	486.0	0.64	310	-0.2	6.0
n-Nonane	C_9H_{20}	273-373	11	43, 150	349.8	543.0	0.64	346	-1.1	8.6
n-Decane	$C_{10}H_{22}$	273-298	3	43, 150	395.0	602.0	0.67	382	-3.3	45.4
n-Dodecane	$C_{12}H_{26}$	298	1		446.9	718.0	0.62	454	1.6	-11.5
n-Octadecane	$C_{18}H_{38}$	323	1	43	785.1	1100.0	0.71	784	-0.1	1.1
							0.64			10.7

Liquids	Formulae	Temp. range for D*, °K	No. of data points for D*	References for D*	Exper. $[M]_{avg.}$ from eq. (3-3.4)	V_c ref. (168)	$\phi = \frac{\text{exper.}[M]}{V_c}$	Calculated [M] from Table (3-3.2)		% error in estimated D* using [M] from Table (3-3.2)
								[M]	% dev.	
<u>Cycloparaffins</u>										
Cyclopentane	C_5H_{10}	273-313	3	56	173.6	260.0	0.67	173	-0.3	1.5
Cyclohexane	C_6H_{12}	293-353	5	43, 150	217.8	308.0	0.71	217	-0.4	5.0
Methylcyclohexane	C_7H_{14}	273-373	7	150	247.3	344.0	0.72 0.70	252	1.9	15.3 9.1
<u>Aromatics</u>:										
Benzene	C_6H_6	283-373	15	31, 43, 129, 150	169.2	260.0	0.65	169	-0.1	5.0
Toluene	C_7H_8	283-373	6	150	199.8	316.0	0.63 0.64	204	2.1	14.7 7.8
<u>Alcohols</u>:										
Methyl alcohol	CH_3OH	278-298	10	43, 96, 150	76.4	118.0	0.65	74	-1.8	13.7
Ethyl alcohol	C_2H_5OH	280-338	13	43, 72, 96, 106	120.6	167.0	0.72	120	-0.5	21.1
n-Propyl alcohol	C_3H_7OH	288-318	4	43, 152	165.5	218.2	0.76	165	-0.3	12.7
Isopropyl alcohol	C_3H_7OH	288-318	4	43, 152	168.5	220.4	0,76	165	-2.1	22.0
n-Butyl alcohol	C_4H_9OH	298-318	3	152	207.7	274.6	0.75	210	1.4	12.1
tert-Butyl alcohol	C_4H_9OH	308-328	3	152	214-6	274-5	0.78 0.74	210.0	-2.1	25.0 18.0
<u>Organic halides</u>:										
Methyl iodide	CH_3I	270-294	2	106	115.8	190	0.61	117.0	1.9	7.6
Ethyl bromide	C_2H_5Br	296-303	3	72	133.0	215.0	0.62	135.0	1.5	16.0
Ethyl iodide	C_2H_5I	293	1	43	152.3	300.0	0.51	153.0	-0.5	-3.6

Liquids	Formulae	Temp. range for D*, °K	No. of data points for D*	References for D*	Exper. $[M]_{avg.}$ from eq.(3-3.4)	V_c ref. (168)	$\phi = \frac{\text{exper.}[M]}{V_c}$	Calculated [M] from Table (3-3.2)		% error in estimated D* using [M] from Table (3-3.2)
								[M]	% dev.	
Organic halides contd.										
Butyl iodide	C_4H_9I	293	1	26	229.3	-	-	223.0	-2.8	22.9
Chloroform	$CHCl_3$	200-298	3	43	150.2	240.0	0.63	159.0	6.2	29.9
Carbontetrachloride	CCl_4	293-333	23	31,43,129, 150	195.4	276.0	0.71	194	-0.8	5.9
Chlorobenzene	C_6H_5Cl	298	1	147	198.7	308.0	0.65	204	2.7	-18.4
Bromobenzene	C_6H_5Br	298	1	43	217.0	324.0	0.67	213	-1.9	15.6
							0.65			11.8
Ketones:										
Acetone	C_3H_5OH	298-333	3	43,106	127.9	211.0	0.61	126	-1.5	12.4
Ethers:										
Di-ethylether	$C_4H_{10}O$	287-240	3	106	168.0	274.0	0.61	173	2.9	21.6
p-Dioxan	$C_4H_8O_2$	307	1	43	172.7	238.0	0.72	171	-1.0	7.8
1,1-Diethoxy-methane	$C_5H_{12}O_2$	295-333	3	106	226.2	-	-	220	-2.7	23.9
1,2-Dimethoxy ethane	C_3H_8O	293	1	106	189.4	-	-	185	-2.3	19.2
							0.66			20.4
Nitrogen compounds:										
Nitromethane	CH_3NO_2	293	1	43	98.2	173.0	0.57	-	-	-
Ammonia	NH_3	213-287	2	43	40.8	72.5	0.56	-	-	-
Sulphur compounds:										
Carbondi-sulphide	CS_2	273-313	4	105	107.0	170.0	0.63	-	-	-
Acids										
Acetic Acid	$C_2H_4O_2$	290-357	4	106	119.5	171.0	0.69	119.5	1.3	18.3

Table 3-3.3 (contd.)

Liquids	Formulae	Temp. range for D*, °K	No. of data points for D*	References for D*	Exper. $[M]_{avg.}$ from eq. (3-3.4)	V_c ref. (168)	$\phi = \frac{\text{exper.}[M]}{V_c}$	Calculated [M] from Table (3-3.2)		% error in estimated D* using [M] from Table (3-3.2)
								[M]	% dev.	
Miscellaneous:										
Water	H_2O	273-373	38	43	33.5	56.0	0.60	34.0	-	-
Tetrahydrofuran	C_4H_8O	293	1	106	147.4	224.0	0.66	150.0	1.8	-12.8
	Overall % average deviation								1.6	12.0

3-3.2 Modification of Dullien's equation (203)

There are in literature two semi-empirical equations for the prediction of self-diffusion coefficients. Dullien (43) used the molecular-kinetic-model of liquids devised by Lamm and Dullien (44) and the experimental self-diffusion coefficient and viscosity to derive the following relationship

$$\frac{D^{*}\mu\bar{V}}{T} = 0.103 \times 10^{-8} \ V_{c}^{\frac{2}{3}} \qquad (2\text{-}2.26)$$

The units to be used in this equation are D* in cm^2/sec, μ in poises, T in ^oK and $\bar{V}$ and V_c in $cm^3/gmole$. This equation was tested on 29 pure liquids mainly hydrocarbons giving an average deviation of 4% from the experimental self-diffusion coefficients. But this equation gave poor prediction for the self-diffusion coefficients for methanol and ethanol.

Vadovic and Colver (206) based the derivation of their equation on the hard sphere model of Longuet-Higgins and Pople (119). Their equation is of the form

$$\frac{D^{*}\mu\bar{V}}{T} = 0.216 \times 10^{-8} \ V_{m}^{\frac{2}{3}} \qquad (2\text{-}2.27)$$

and the units to be used are the same as in eq. (2.2.26). It may be shown that equations (2-2.26) and (2-2.27) are identical if the following relationship between molal volume at melting point and critical molal volume i.e. $V_m = 0.310 \ V_c$ is assumed (206). These authors tested the equation (2-2.27) with the experimental D* of pure liquids used by Dullien (43) and with a few molten metals and found that the average deviation from the experimental self-diffusion coefficients was $\pm$ 6%. Again this equation also gives poor prediction for ethanol and methanol.

Equations (2-2.26) and (2-2.27) employ critical molal volume and molal volume at melting point respectively. It will be shown that the first of the two equations may be modified by replacing the critical molal volume by the molal volume at normal boiling point. To do this the equation developed in another section

$$V_b = 0.285 \ V_c^{\ 1.048} \qquad (3\text{-}5.2)$$

is used to elimiate V_c from equation (2-2.26).

The resulting correlation is

$$\frac{D^* \mu \bar{V}}{T} = 0.229 \times 10^{-8} \ V_b^{\ 0.636} \qquad (3\text{-}3.6).$$

This equation was tested on the pure liquids used by Dullien (43) and shown in Table 3-3.4. The average deviation of the predicted self-diffusion coefficients, with methanol and ethanol excepted, is 4·8%.

Eq. (3-3.6) is also shown in Fig. 3-3.1.

Eq. (3-3.6) gives predictions of approximately the same accuracy as the other two equations and is convenient to use when no reliable values of V_c and V_m are available.

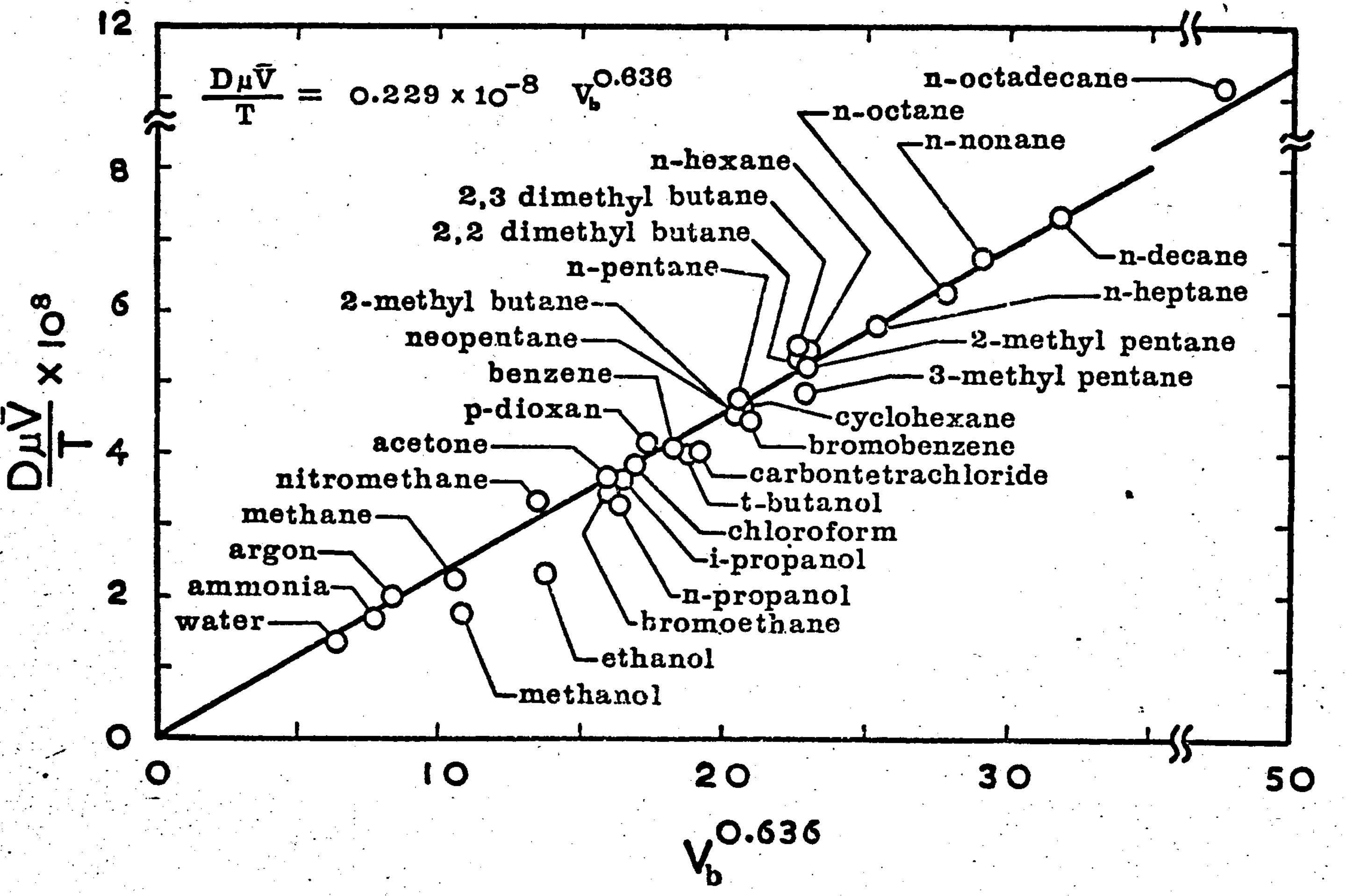


Figure 3-3.1 Correlation of self-diffusion coefficient for pure liquids, eq.(3-3.6)

Table 3-3.4 Percentage deviations of the estimated self-diffusion coefficients of eq. (3-3.6) from the experimental coefficients, D* x 10^5 cm^2/sec.

Liquids	Temp. range °K	Number of data @	% error in D* estimated by eq. (3-3.6)
Argon	84	1	1.7
Methane	90-111	6	11.1
CCl_4	293-333	5	7.2
Chloroform	200-298	2	2.1
n-Pentane	250-309	4	1.1
n-Hexane	298	1	2.7
n-Heptane	250-369	7	2.3
n-Octane	298	1	1.5
n-Nonane	298	1	1.9
n-Decane	298	1	0.7
n-Octadecane	323	1	2.4
2-Methylbutane	298	1	2.2
Neopentane	298	1	0.8
3-Methylpentane	298	1	8.1
2,3-Dimethyl butane	298	1	7.0
p-Dioxan	307	1	5.6
2,2-Dimethyl butane	298	1	3.7
2-Methylpentane	298	1	0.5
Bromoethane	303	1	6.7
Nitromethane	293	1	8.0
Benzene	288-423	8	3.2
Cyclohexane	298	1	3.4
Bromobenzene	298	1	5.5
Acetone	298	1	1.3
Water	273-373	7	9.5
Ammonia	213-287	2	5.2
Methanol	268-328	7	39.9†
Ethanol	280-338	7	41.5†
n-Propanol	288	1	14.5
i-Propanol	288	1	5.9
t-butanol	308	1	9.0
	Average % error		4.8

@ Experimental data are taken from Dullien (43)

† Not included in calculating the percentage average error.

3-4 The effect of temperature on liquid diffusion coefficients

Liquid diffusion coefficients, like other transport properties, are temperature sensitive. Diffusion coefficients in liquids increase with temperature. A literature search shows that the relationship between some of the physical properties and temperature is usually a function of the critical temperature. Table 3-4.1 shows some of these relationships:

Table 3-4.1 Some of the equations defining the relationship between various physical properties of liquids and the critical temperature function $(T_c - T)$.

Author and Reference	Property	Equation	Equation Number
van der Waals (207)	Surface tension	$\sigma = k_s (T_c - T)^{1.2}$	3-4.1
Theisein (193)	Heat of vaporization	$\Delta\bar{H} = k_l (T_c - T)^{0.38}$	3-4.2
Narsimhan (139)	Densities	$(\rho_l - \rho_c) = k_d (T_c - T)^{0.74}$	3-4.3
Pettinelli (154)	Viscosity	$\mu = k_v(\rho^{\frac{2}{3}}/M^{\frac{1}{6}}) (T_c - T)^{0.5}$	3-4.4
		where k_s, k_l, k_d and k_v are constants	

An attempt will be made to find a similar relationship between diffusion coefficients and temperature. The type of relationship reported in Table 3-4.1 is of the form

$$D = k\,(T_c - T)^{-n} \qquad (3\text{-}4.5)$$

This relationship is verified below with respect to the diffusivity in the liquid phase.

3-4.1 Self-diffusion coefficient

In agreement with eq. (3-4.5) self-diffusion coefficients at various temperatures for 26 liquids, found in literature, were plotted on the log-log paper in Figures 3-4.1 (a, b and c). It may be observed from these plots that the diffusion coefficients for each liquid lie fairly close to a straight line and that the liquids can be divided into groups, each having the same slope. Thus three groups can be defined and these are tabulated in Table 3-4.2. The fact that the constant k is different for each liquid makes it possible to adapt eq. (3-4.5) in order to predict self-diffusion coefficients for a given liquid at another temperature if a coefficient at one temperature is available. The modified equation will have the form

$$\frac{D^*_1}{D^*_2} = \left[\frac{T_c - T_2}{T_c - T_1}\right]^n \qquad (3\text{-}4.6)$$

where n is taken from Table 3-4.2.

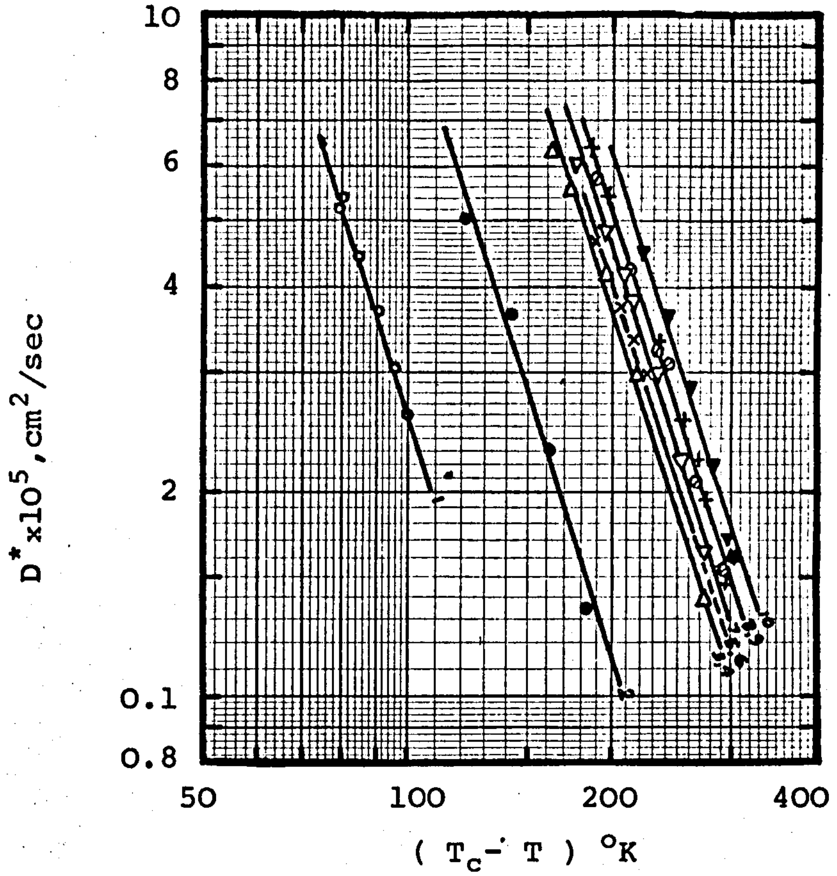


Figure 3-4.1a Correlation of self-diffusion coefficient with critical temperature function; for the group of liquids where the slope n=3

Numbers on lines indicate

1 o Methane
2 ● Ethane
3 Δ Pentane
4 Δ 2,3-dimethylbutane
5 x 2-methylpentane
6 x 3-methylpentane
7 ∇ Hexane
8 ⌀ Heptane
9 + Octane
10 ▼ Nonane

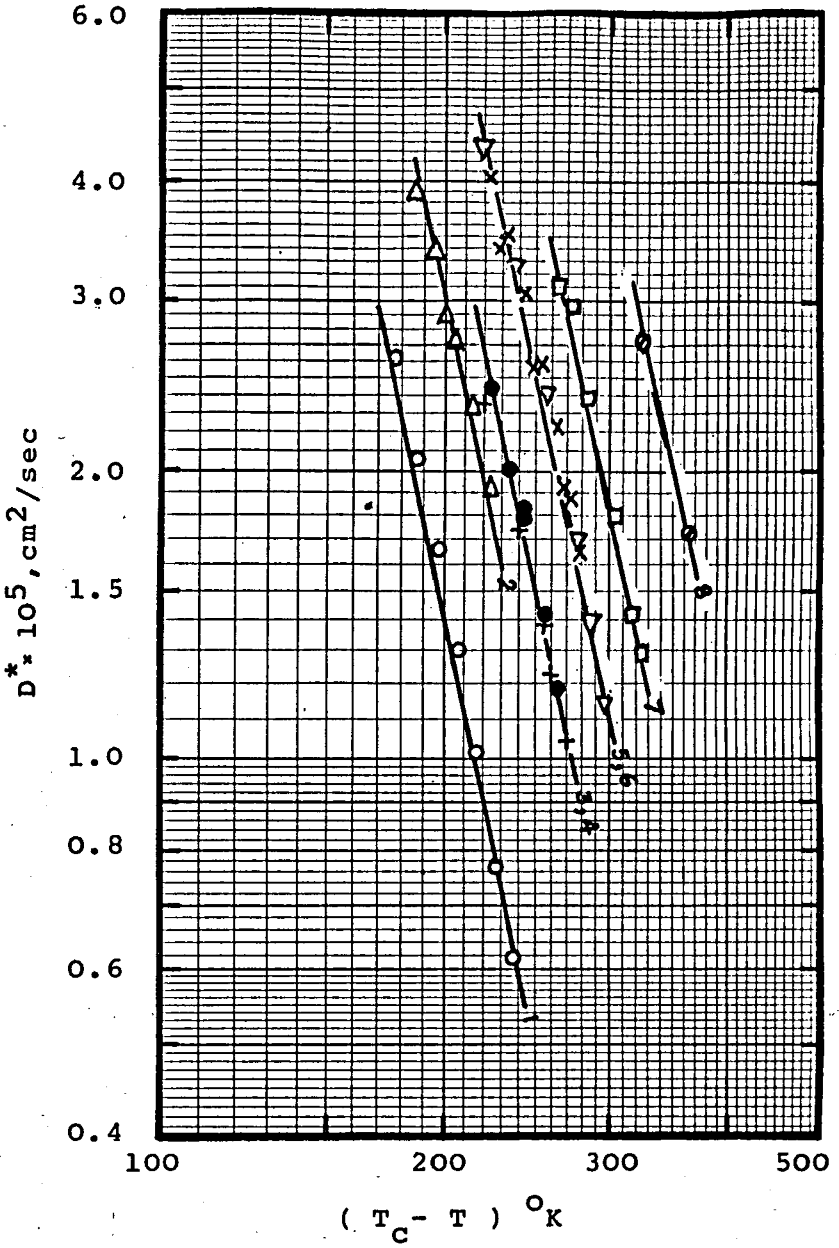


Figure 3-4.1b Correlation of self-diffusion coefficient with critical temperature function; for the group of liquids where the slope n=4

Numbers on lines indicate

1 o Ethanol
2 Δ Methanol
3 ● Carbontetrachloride
4 + Cyclohexane
5 × Benzene
6 ▽ Methylcyclohexane
7 □ Decane
8 ⊘ Dodecane

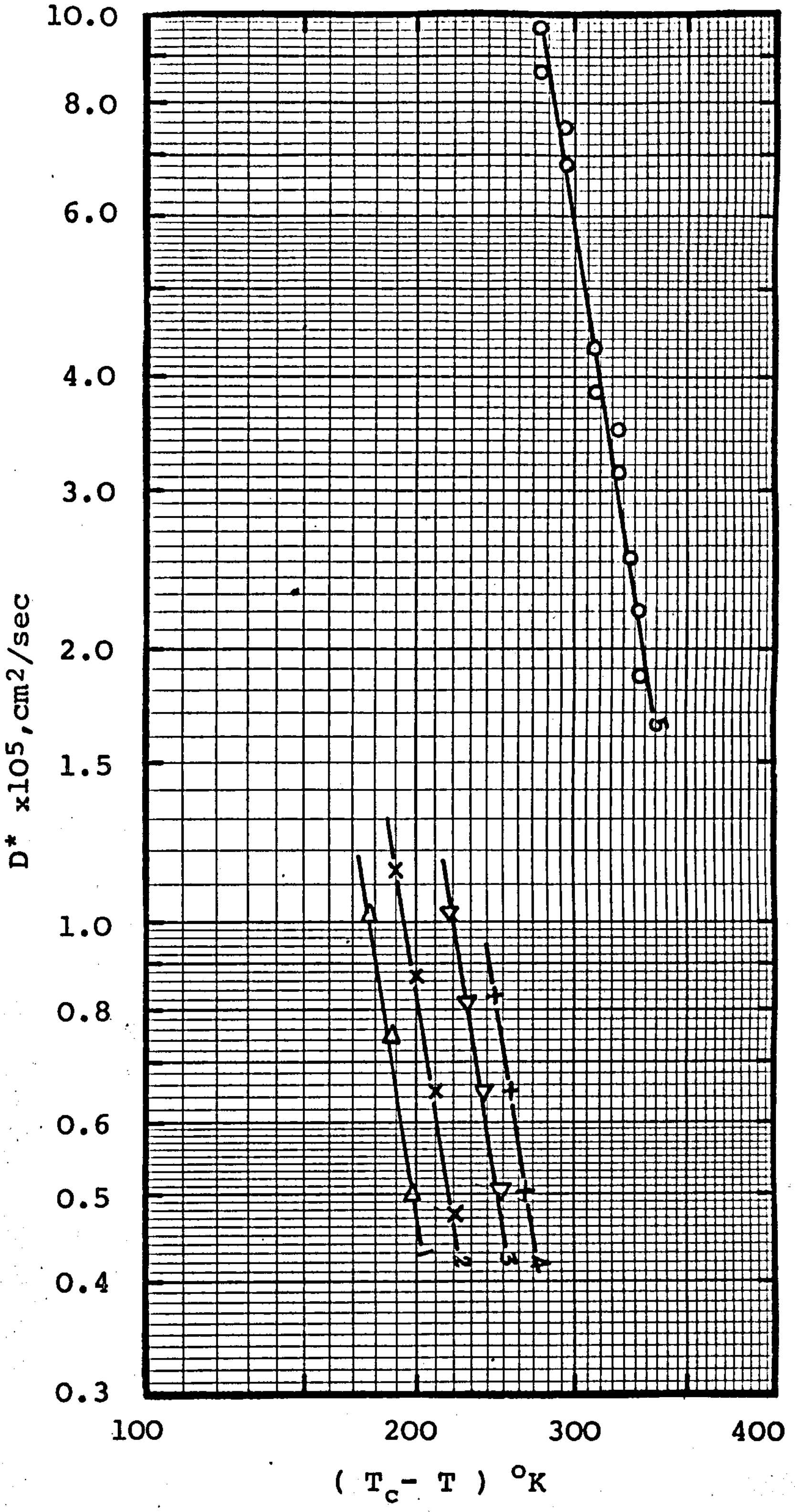


Figure 3-4.1c Correlation of self-diffusion coefficient with critical temperature function; for the group of liquids where n=6

Numbers on lines indicate
1 △ t-Butanol
2 × i-Propanol
3 ▽ n-Propanol
4 + n-Butanol
5 ○ Water

Table 3-4.2 Values of exponent 'n' in eq. (3-4.5) for self-diffusion coefficients.

	Group of compounds	n
I	Lower paraffins (C $\leqslant$9), cyclopentane, chloroform, toluene and acetone.	3
II	Higher paraffins (C$\geqslant$ 10), cyclohexane, methyl cyclohexane, methanol, ethanol, benzene and carbontetrachloride.	4
III	Water, isopropanol, n-propanol, n-butanol and t-butanol.	6

Equation (3-4.6) was used to predict the coefficients for the 26 liquids and the average percentage deviation for each liquid is shown in Table 3-4.3. In the same Table the deviations of the coefficients predicted from the Stokes-Einstein eq. (2-5.1) are shown. The experimental values of self-diffusion coefficient for the 26 liquids in Table 3-4.3 are reported in Appendix 3-3.1b. In using eq. (3-4.6) the reference values of the coefficient were, in most cases, the values at 25^{o}C. The average deviation for the Stokes-Einstein eq. (2-5.1) and eq. (3-4.6) is about the same, but the deviations for the individual liquids are much closer to the average value for eq. (3-4.6). A further advantage of using eq. (3-4.6) is that no knowledge of viscosity is required.

Table 3-4.3: Percentage deviations of the estimated from the experimental values† of liquid self-diffusion coefficients, $(D^* \times 10^5$, cm^2/sec)

Liquids	Value of n ‡	Temp. range (^{o}K)	No. of data	% error in D* estimated by	
				This work eq. (3-4.6)	Stokes-Einstein eq. (2-5.1)
Methane	3	90-111	5	2.78	3.20
Ethane	3	123-183	3	11.40	3.40
n-Pentane	3	195-309	4	7.35	30.60
n-Hexane	3	273-333	4	7.60	3.08
n-Heptane	3	250-369	6	8.80	12.70
n-Octane	3	273-373	6	5.94	6.59
2-3 Dimethyl butane	3	273-313	5	3.78	4.60
2-Methylpentane	3	273-313	5	4.90	2.20
3-Methylpentane	3	273-313	5	3.64	1.90
Acetone	3	238-333	3	7.07	8.90
Toluene	3	283-383	6	3.53	10.57
Cyclopentane	3	273-313	2	4.14	2.70
n-Nonane	4	298-413	6	10.20	1.1
n-Decane	4	293-353	5	10.72	-
CCl$_4$	4	288-333	6	1.88	3.31
Benzene	4	288-338	4	2.15	1.00
Methanol	4	268-328	7	5.20	2.70
Ethanol	4	280-338	6	12.18	6.47
Cyclohexane	4	283-353	5	4.50	6.80
Methylcyclohexane	4	273-373	6	8.10	3.69
Carbondisulphide	4	273-313	2	1.41	11.12
n-Propanol	6	288-318	3	3.39	9.36
i-propanol	6	288-318	3	2.40	3.00
t-butanol	6	308-328	2	6.58	5.40
n-butanol	6	298-318	2	1.29	3.44
Water	6	293-373	5	7.79	1.27
	Total average % error			6.00	5.94

‡ Values of exponent 'n' in eq. (3-4.6)

† Experimental values of D* are found in Appendix 3.3.1b, of viscosity in ref. (20, 42, 168, 196) and of the critical temperature in ref. (168).

3-4.2 Diffusion coefficient at infinite dilution

Equation (3-4.5) was also found to be applicable in estimating the values of the diffusion coefficients of binary liquid mixtures at infinite dilution. The corresponding equation for this case can be written as

$$\frac{\left(D^{o}{}_{AB}\right)_1}{\left(D^{o}{}_{AB}\right)_2} = \left[\frac{T_c - T_2}{T_c - T_1}\right]^{n}_{B} \qquad (3\text{-}4.7)$$

Here the value of exponent 'n' is that of the pure solvent and is taken from Table 3-4.2. It was found that Table 3-4.2 does not apply to toluene for which n = 4 and not '3' as indicated in that Table. The values of T_c in eq. (3-4.7) are those of the pure solvents. An accuracy of eq. (3-4.7) was tested with 44 binary mixtures, involving 10 solvents and 24 solutes and consisting of both associated and non-associated liquids. Table 3-4.4 shows the percentage deviations of the coefficients predicted by eq. (3-4.7) from the experimental coefficients. The corresponding deviations for the coefficients predicted by the Stokes-Einstein eq. (2-5.1) are also reported in Table 3-4.4. It is to be noted that the Stokes-Einstein equation gives slightly better predictions particularly for aqueous binary mixtures, however eq.(3-4.7) is more convenient to use if the values of viscosity are not very reliable.

Equations (3-4.6) and (3-4.7) are valid if used in the temperature range 10°C above the melting point to 10°C below the boiling point. Outside these limits equations (3-4.6) and (3-4.7) give predictions with an average deviation of +20 % for all the liquids tested.

Table 3-4.4 Percentage deviations of the estimated from the experimental values† of binary liquid diffusion coefficients at infinite dilution, ($D^o_{AB} \times 10^5$, cm^2/sec)

Solute (A)	Solvent (B)	Value of * 'n' for solvent	Temp. range (°K)	No. of data	% error in D^o_{AB} estimated by	
					This work eq. (3-4.7)	Stokes-Einstein eq. (2-5.1)
Acetic acid	Acetone	3	288-313	2	1.6	1.0
Water	Acetone	3	298-318	2	12.1	8.0
Benzoic acid	Acetone	3	286-313	2	6.6	3.9
Chloroform	Acetone	3	298-328	2	9.4	3.2
Benzene	Heptane	3	298-358	5	8.7	8.5
Toluene	Heptane	3	280-313	2	2.8	3.9
Acetone	Chloroform	3	298-328	2	1.2	3.4
Acetic acid	Toluene	4	280-298	3	5.7	2.3
Benzene	Toluene	4	298-313	1	3.1	1.4
Cyclohexane	Toluene	4	298-328	2	2.3	2.0
Methylcyclohexane	Toluene	4	298-333	2	2.8	3.5
Aniline	Toluene	4	298-333	2	1.6	3.3
Benzoic acid	Toluene	4	289-313	3	7.3	7.2
Heptane	Benzene	4	298-348	5	7.9	4.8
Toluene	Benzene	4	298-313	1	2.1	0.1
Methanol	Benzene	4	284-313	2	5.7	3.7
Ethanol	Benzene	4	288-313	3	5.2	4.8
Acetone	Benzene	4	313-327	1	10.5	7.6
Benzoic acid	Benzene	4	284-313	2	2.6	5.4
Acetic acid	Carbontetrachloride	4	279-313	3	1.3	5.9
Formic acid	Carbontetrachloride	4	281-298	2	5.5	9.7
Benzene	Carbontetrachloride	4	283-313	3	3.7	2.6
Cyclohexane	Carbontetrachloride	4	298-328	3	3.1	2.6
Carbontetrachloride	Cyclohexane	4	298-328	2	1.3	4.4
Iodine	Cyclohexane	4	288-313	2	1.5	4.8
Benzene	Cyclohexane	4	298-333	3	2.1	4.7
Toluene	Cyclohexane	4	298-328	2	6.0	10.1
Iddine	Methylcyclohexane	4	303-313	1	1.2	1.2
Toluene	Methylcyclohexane	4	298-318	1	2.5	7.5
Iodine	n-Octane	4	288-313	2	4.7	4.5
Iodine	Ethanol	4	281-313	2	4.7	1.6
Water	Ethanol	4	298-346	3	2.6	1.7
Methane	Water	6	293-333	2	11.8	2.4
Ethane	Water	6	293-333	2	14.2	0.9
Propane	Water	6	293-333	2	24.3	11.6

Table 3-4.4 (continued)

Solute (A)	Solvent (B)	Value of* 'n' for solvent	Temp. range (^{o}K)	No. of data	% error in D^{o}_{AB} estimated by	
					This work eq. (3-4.7)	Stokes-Einstei eq. (2-5.1)
Butane	Water	6	293-333	2	23.8	10.9
Pentane	Water	6	293-333	2	20.7	8.2
Cyclopentane	Water	6	293-333	3	17.4	2.7
Cyclohexane	Water	6	283-333	3	14.3	6.8
Butene	Water	6	298-333	2	4.6	6.5
Benzene	Water	6	283-333	4	11.4	5.9
Toluene	Water	6	283-333	3	14.9	3.1
Ethyl benzene	Water	6	283-333	3	12.8	1.5
Methanol	Water	6	288-370	2	10.0	3.1
Ethanol	Water	6	298-346	4	5.9	9.9
Acetone	Water	6	298-346	6	10.5	20.2
					7.8	5.7

* Values of exponent 'n' in eq. (3-4.7)

† Experimental values of D^{o}_{AB} are found in Appendix 3-2.2, of solvents viscosity in ref. (20, 42, 168, 196) and of the critical temperature of solvents in ref. (168).

3-5 Molal volumes at normal boiling points (202)

The molal volume of liquid at the normal boiling point is of practical interest to Chemical Engineers as it is frequently employed in estimating various physical properties, such as diffusion coefficients, latent heat of vaporisation and boiling point temperatures (20, 168), which are essential for the design of chemical engineering equipment.

The experimental liquid volumes at normal boiling point are somewhat scarce and it is customary to estimate this quantity either from the additive method of LeBas (109) or Schroeder (168) or from the empirical equation of Benson (14). Both the additive methods give poorer results than the Benson method as shown in Table 3.5 of reference (168). The failure of the additive methods is due to the fact that most chemical compounds appear in an associated form and the extent of association is a function of temperature. The degree of association at the normal boiling point is still appreciable. As the association effects are negligible at the critical temperature, the critical volume estimated by additive methods is normally reliable (168). Therefore it is not surprising that the estimated values of liquid molal volume at the normal boiling point, V_b (in cm^3/gmole), from the Benson equation

$$\frac{V_c}{V_b} = 0.422 \log_{10} P_c + 1.981 \qquad (3\text{-}5.1)$$

employing the critical volume, V_c (in cm^3/gmole), and critical pressure, P_c (in atm), compare very favourably with both the additive methods. Table 3.5 in reference (168) shows that the average deviation of the predicted volume V_b from the experimental one is 2% for the Benson (14) method, 2.8% for the additive method of Schroeder (168) and 4.7% for the additive method of LeBas (168). All the 34 compounds shown in the table of reference (168) are taken into account in compiling Table 3-5.1 of this work.

3-5.1 Correlation of the literature data

From the fact that the ratio of V_c to V_b is approximately 2.68 (14) for most of the liquids, a simple relationship is expected to exist between V_c and V_b itself without incorporating any other physical properties. Experimental values of the molal volumes at the critical point V_c and at the normal boiling points V_b were found for a number of compounds in references (14, 20, 42, 59, 151, 168). These were plotted on a log-log graph paper as shown in Fig. 3-5.1. A vast majority of the experimental data points is very well correlated by a single straight line. The best (least square method) straight line drawn through these points gave the following relationship

$$V_b = 0.285\ V_c^{1.048} \qquad (3\text{-}5.2)$$

3-5.2 Test of the correlations

To check the accuracy of the correlation the values of V_b, for all the compounds shown in Fig. 3-5.1, were predicted by Benson's equation (3-5.1) and equation (3-5.2) using the critical volumes and critical pressures from references (14, 20, 42, 168). The predicted values were compared with the experimental ones and the average deviations for each class of compounds were calculated and recorded in Table 3-5.1.

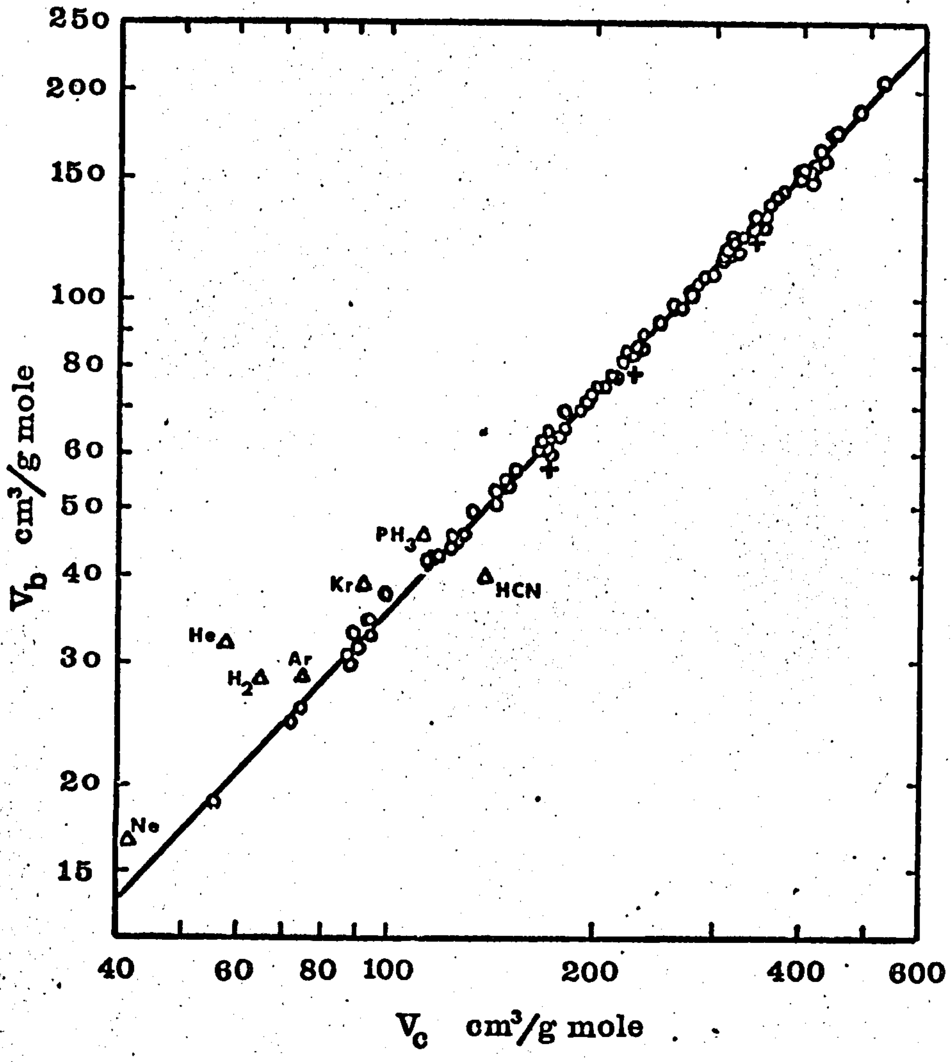


Figure 3-5.1 Relationship between liquid molal volume at normal boiling point and critical volume

+ Nitrils are included in calculating average percentage error

Δ Not included in calculating average percentage error

Table 3-5.1 : Percentage deviations of the estimated from the experimental values of liquid molal volume at the normal boiling point (in cm^3/gmole)

Class of liquid	No. of data	Proposed Eq.(3-5.2) % Error *	Benson Eq. (3-5.1) % Error *
Elements	7	2.65	4.42
Inorganic Compounds	13	2.30	2.37
Organic Compounds:			
Paraffins	10	1.54	0.96
Cycloparaffins	5	0.50	0.32
Olefins	4	3.12	1.12
Ketones	2	1.20	2.15
Organic acids	5	1.10	1.06
Aromatics	5	0.70	0.34
Aldehydes	2	1.45	1.75
Ethers	6	1.20	1.32
Sulphur Compounds	4	1.25	1.32
Nitrogen Compounds	11	4.12	4.20
Esters	17	1.84	2.40
Alcohols	9	1.84	1.54
Organic halides	15	1.22	0.99
Average % error	115	1.88	1.90

* % Error = [(Calculated - Experimental)] x 100/Experimental
Experimental data of V_b obtained from references (14, 20, 42, 59, 151, 168)
** Data of V_c and P_c: 96 experimental values of V_c and 115 experimental values of P_c were found in references (168, 14, 42).
V_c for the remaining 19 compounds were found estimated either by Vowle or Lydersen additive methods (168).

In calculating the deviations for the groups of elements and compounds shown in Table 3-5.1 the following were excluded: Ne, Kr, H_2, He, Ar, hydrogen cyanide and phosphine. The average deviation for this group is about 25%. Benson (14) ascribes this abnormality to "the quantum effect" in the case of the lighter compounds and to association in the case of hydrogen cyanide. The phenomenon of association of the heavier gases could be appreciable even in the neighbourhood of the critical point. In the case of phosphine the deviation could be due to an error in the experimental value of V_b.

Nitriles and nitromethane gave deviations ranging from 6% to 9% from the experimental values and they are included in obtaining the average deviations shown in Table 3-5.1. As similar abnormal deviations are also observed in the other physical properties of nitriles and nitro compounds, such as high dipole moments (14), they are presumed to be a special class of compounds which show abnormalities owing to their unusually large electrostatic forces.

The average deviations shown in Table 3-5.1 are based on 115 compounds. Equations (3-5.1) and (3-5.2) give practically the same results and both considerably better than any of the additive methods, as pointed out earlier.

Equation (3-5.2) is more convenient to use because it requires only one physical property, i.e. the molal volume at the critical point, V_c, to determine the molal volume V_b at the normal boiling point. Equation (3-5.2) is more reliable than equation (3-5.1) if the values of the critical volumes and critical pressures are to be obtained by one of the additive methods. The critical pressure obtained in this way has an error of about 4% (168), thus lowering the accuracy of the value of V_b predicted by equation (3-5.1) considerably.

PART 4 EXPERIMENTAL APPARATUS AND METHODS

PART 4 EXPERIMENTAL APPARATUS AND METHODS (24)

The experimental apparatus employed in this work for operating at elevated temperatures is an adaptation of the two-compartment diaphragm cell used by Stokes (185). An attempt to construct a cell for such a duty was made by Calus and Tyn (25). The cell developed in this work is a further modification of the Calus and Tyn cell and constitutes a considerable improvement.

4-1 Three-compartment diaphragm cell

4-1.1: Requirements for a successful cell :

(1) A provision of space for thermal expansion during the preheating period in which the test liquids are being brought to the required temperature.

(2) Prevention of diffusion and bulk flow due to thermal expansion during the preheating period.

(3) Prevention of evaporation of the test liquids during the run, as this would alter the concentrations.

(4) Establishment of an initial concentration gradient in the diaphragm or to design the cell so that the initial concentration gradient is unimportant.

(5) Prevention of boiling of test liquids, as this would introduce convective mixing in the pores of the diaphragm and vapour-locking of some of the channels in the diaphragm.

In the cell described below the boiling of the test liquids is prevented by carrying out diffusion experiments under a pressure high enough to suppress boiling. The effect of minor changes in pressure on the diffusion coefficient is negligible, as was shown by Doane and Drickamer (40).

The requirements (1) to (4) are taken care of in the design of the cell and in the operating procedure, which are described below.

4-1.2: Description of diaphragm cell

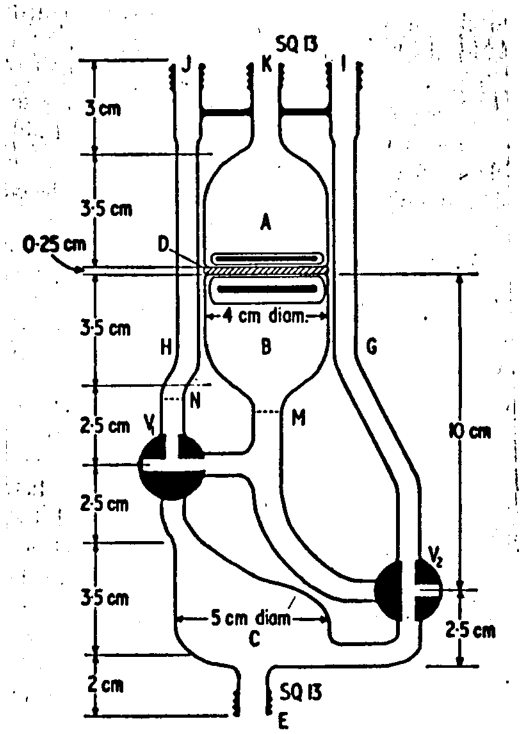


Fig. 4-1.1 Three-compartment diaphragm cell

The three compartment cell finally developed is shown in Fig. 4-1.1 with the valves set as for a normal run carried out at an elevated temperature and at some pressure greater than atmospheric. Compartment A contains about 45 cm^3 of the lighter test liquid, compartment B, down to the mark M, contains exactly the same volume of the heavier test liquid. The space below the mark M, and also below the mark N in the leg H, is occupied by mercury. The level of mercury at N is predetermined in order to balance the columns of test liquids in A and B and the mercury below the mark M.

Compartment C contains mercury which, in the preheating stage, occupied compartment B while the heavier test liquid was being preheated in compartment C. The mercury in compartment C can be expanded into the leg G.

With the dimensions given in Fig. 4-1.1 , the volume of each compartment A and B is approximately 45 cm^3 net plus the volume of the stirrers and the volume of compartment C is about 65 cm^3. The diaphragm is a sintered glass disc, manufactured by Jencons Scientific Limited, 4cm. in diameter with a porosity number of 4 and a pore size range of 5-10 microns. Four cells were used in this work and their individual specifications are given in Table 4-1.1. The initial volume of the pores in the diaphragm varied, from cell to cell, in the range 0.8 to 1.0 cm^3, due to a small variation in cell diameter and, of course, the diaphragm wearing out with time. The ratio of the pore volume to the cell compartment volume was approximately 0.02 which agrees with the recommendation of Holmes (89).

Table 4-1.1 Specifications of the three-compartment diaphragm cells:

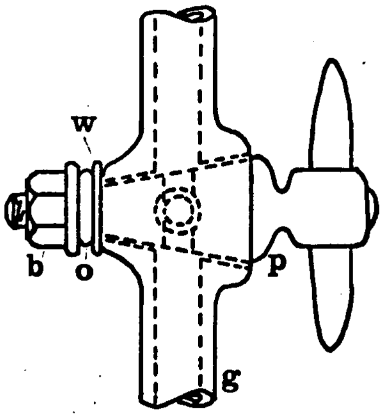
Cell code number	$V_1=V_2$ * (up to mark M) cm^3	$V_D^\dagger$ cm^3	$\lambda = \frac{V_D}{V_1}$
R	46.2	1.100	0.02380
D	44.8	0.890	0.01986
H	41.8	0.850	0.02033
G	45.2	0.920	0.02035

* V_2 is the predetermined volume of lighter test liquid which will have the same volume as V_1 at a given operating temperature.

† V_D is the average volume of the pores of the diaphragm.

The stirrers are made of glass tubes with soft iron wires sealed in them. The upper stirrer is heavy enough to rest on the diaphragm and the lower one is light enough to float on top of the heavier liquid in the lower compartment. Both stirrers are wrapped with a thin PTFE sheet to reduce the rate of attrition of the diaphragm. The stirrers are operated by a pair of magnets fixed to a rotating U-shaped yoke.

The three-way valves, V_1 and V_2, are constructed of glass with the PTFE core and washers secured by a brass nut, as shown in Fig. 4-1.2.



b = Brass nut

w = PTFE washers

o = PTFE O-ring

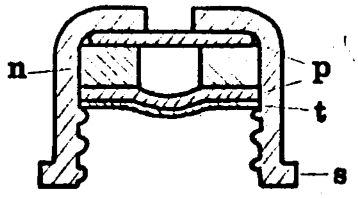
g = Glass casing

p = PTFE core with 4mm. bore

Figure 4-1.2 : Three way valve of type GSTT (manufactured by Fison Scientific Ltd.)

These valves are spring loaded by O-rings and no lubricants are necessary.

The cap E of compartment C is designed to withstand the weight of mercury plus any applied pressure during a run. A detailed drawing of this cap is shown in Figure 4-1.3.



s = knurled screw cap, SQ13

n = Neoprene washer

p = Thick PTFE circular disc

t = Thin PTFE circular disc

Figure 4-1.3 : Details of the cap E for compartment C of diffusion cell.

4-1.3 : Auxiliary Apparatus

The operation of the three-compartment cell requires some auxiliary laboratory equipment and its design will be described in some detail.

Valve openers

The operation of the cell requires precise manipulation of the cell valves (i.e. V_1 and V_2 of Fig. 4-1.1) while the cell is immersed in the hot oil bath. A special valve opening mechanical jig was constructed, as shown in Fig. 4-1.4, for each valve to allow remote manipulation from above the surface of the oil. This valve opener consists of two brass rods, A and B. The rod B has a socket C which can slide and be secured at any position on the rod A. The rod A has a socket on each end and a gear-wheel (Meccano no. 27) is attached to each of these sockets using a brass shaft. A plastic knob E is attached to the upper shaft and a clamp F, with two Terry clips 't' on each end, is attached to the bottom shaft as shown in Fig. 4-1.4. PTFE washers are provided at the connections of these shafts to the rod A for smooth operation. An endless chain H is attached to the gear-wheels G which allows a synchronized

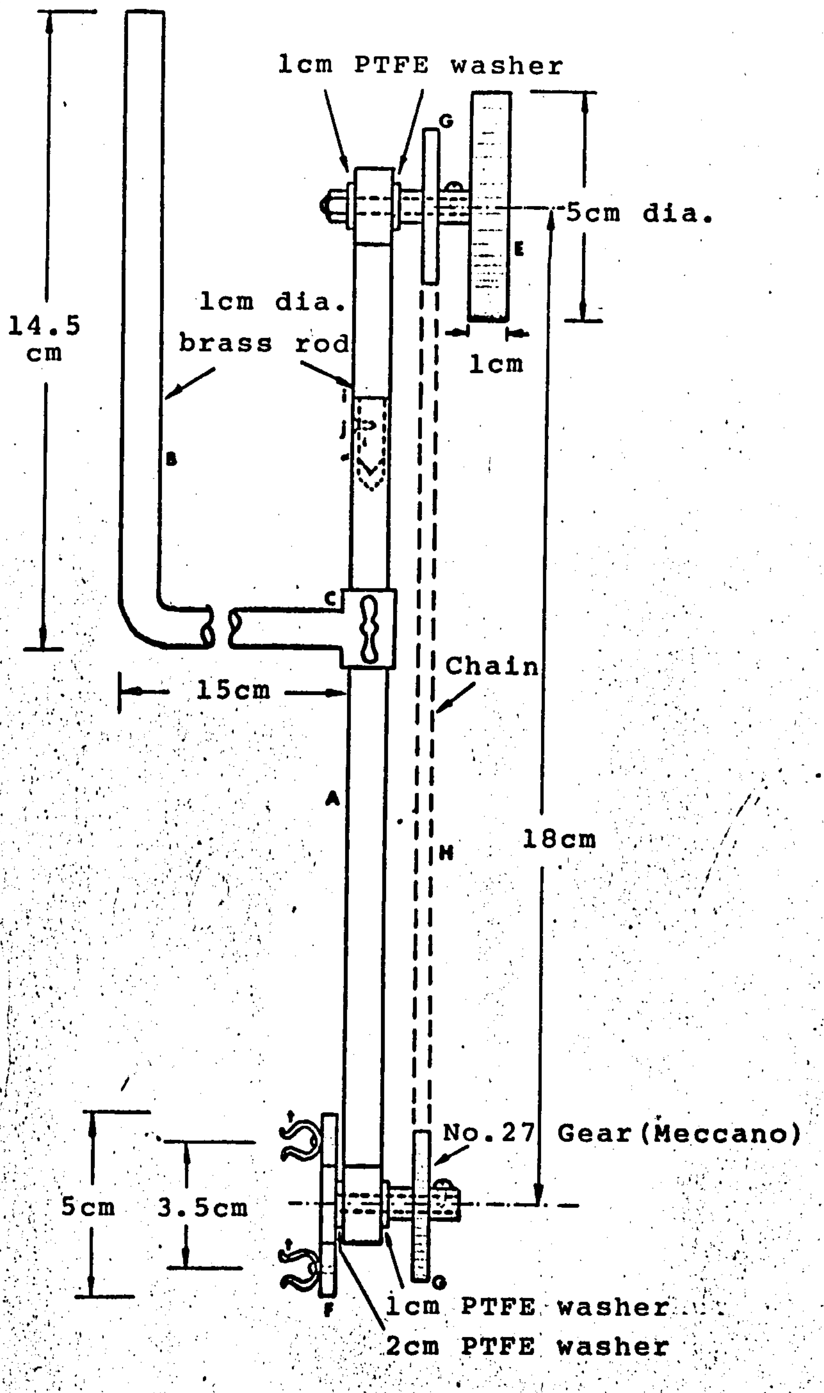
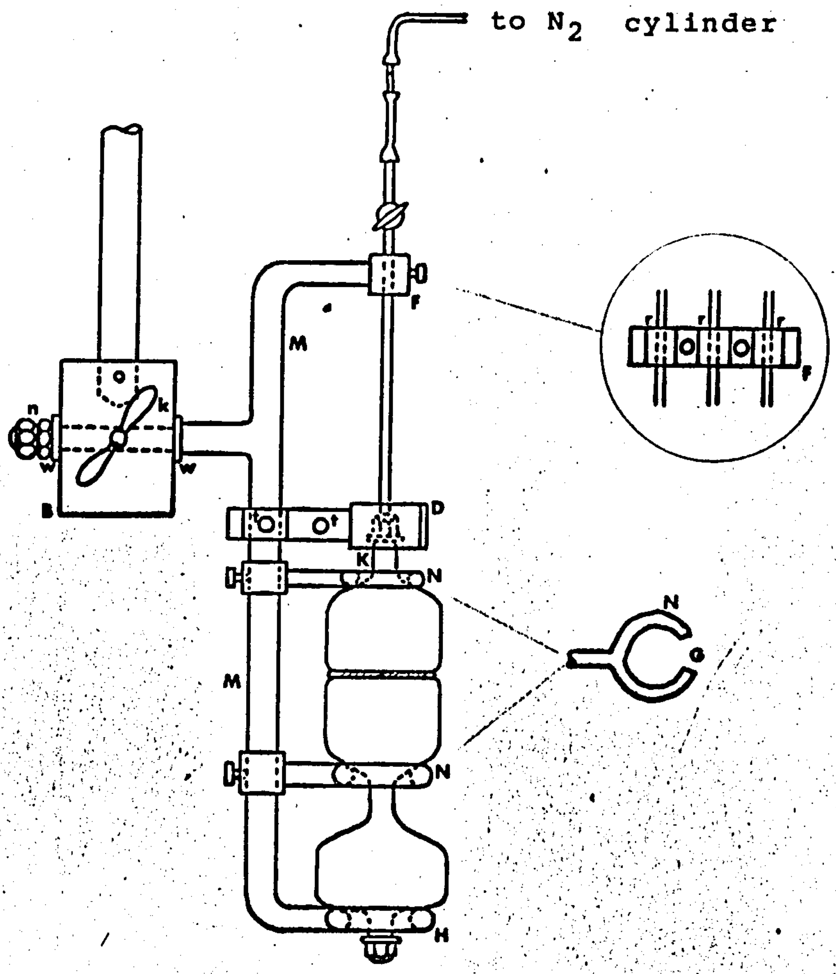


Figure 4-1.4 Valve opener

movement of the knob E and the clamp F. To allow for easy assembly of the whole jig, and also to facilitate adjustment of the tension in the chain, the rod A is made in two sections joined together at i by the screw j. The cell valve is operated by attaching the Terry clips t of the clamp F to the handle of the valve and manipulating the knob E from above the oil surface while the whole jig is secured to the rigid frame using rod B.

Cell clamp

As the cell, with its contents, has to be precisely fixed in position throughout the experimental run and is also required to be able to be turned upside down after the run, a specially designed cell clamp is necessary. Such a clamp is shown in Fig. 4-1.5. The clamp consists of a T-shaped brass rod M with a ring support H at its lower end and a clip F at its upper end. The middle arm of the rod M is attached to the brass block B of the cell support (see Fig. 4-1.6) by the lock nuts n and PTFE washers w. The rod M can rotate within the block B and can be secured at any position by the screw k. Two movable brass ring-supports N are provided which can slide on the rod M and also can be secured at any required position. A gap G is made in each ring N to allow passage of the cell. A clip D, made from brass sheet, is also provided to secure the middle neck of the cell (i.e. K of Fig. 4-1.1) using the screws t. Another clip F, which has three sockets r is used to secure the three capillaries of the pressure connectors (of Fig. 4-1.7). In Fig. 4-1.5 the cell is shown in the position as during a normal run, i.e. with the various supports and clips in the correct locations.



B	Brass block
M	Brass rod with ring support H
N	Movable ring supports with gap G
D	Clip for the neck K of diaphragm cell
F	Clip for pressure connectors
n	Lock nuts
w	PTFE washers

Figure 4-1.5 Cell clamp

Cell support

The starting and terminating operations on the cell for an elevated temperature run require the cell to be handled while it is under pressure. This requirement makes it necessary to design a suitable 'cell-support' which can hold the assembled pressurized cell during these operations.

The cell support consists of a solid metal rod A with a brass block B at its lower end. Its upper end is attached to a counter balance weight of about 2 lb. by a tough nylon string 'S' passing over two pulleys (H and G) as shown in Fig. 4-1.6. The two cylindrical guides C are mounted coaxially with the rod A on the rigid frame, in order to assist the vertical movement of the rod A. The brass block B has a horizontal hole into which the cell clamp (of Fig. 4-1.5) can be fixed. The assembled pressurized cell, accommodated in the cell clamp, can be lowered or raised with ease using this counter-balanced cell-support and its position can be secured at any required place by locking the sliding rod A by the screw 'l' at the lower cylindrical guide C.

Pressure connections

Three pressure connectors, made of 1mm diameter x 15cm long glass capillaries, C are used for applying pressure to the cell. Each of the capillaries has a spring loaded valve near its upper end. The upper terminals of the capillaries are joined onto a single outlet which leads, either to a nitrogen cylinder, or to an aspirator bottle through the long flexible plastic tubing t and the reducing valves p, q, r, as shown in Fig. 4-1.7. The use of the aspirator bottle, for depressurizing the cell, is necessary for two reasons: (1) it can control the rate of release of pressure and (2) the water inside the bottle can absorb the harmful

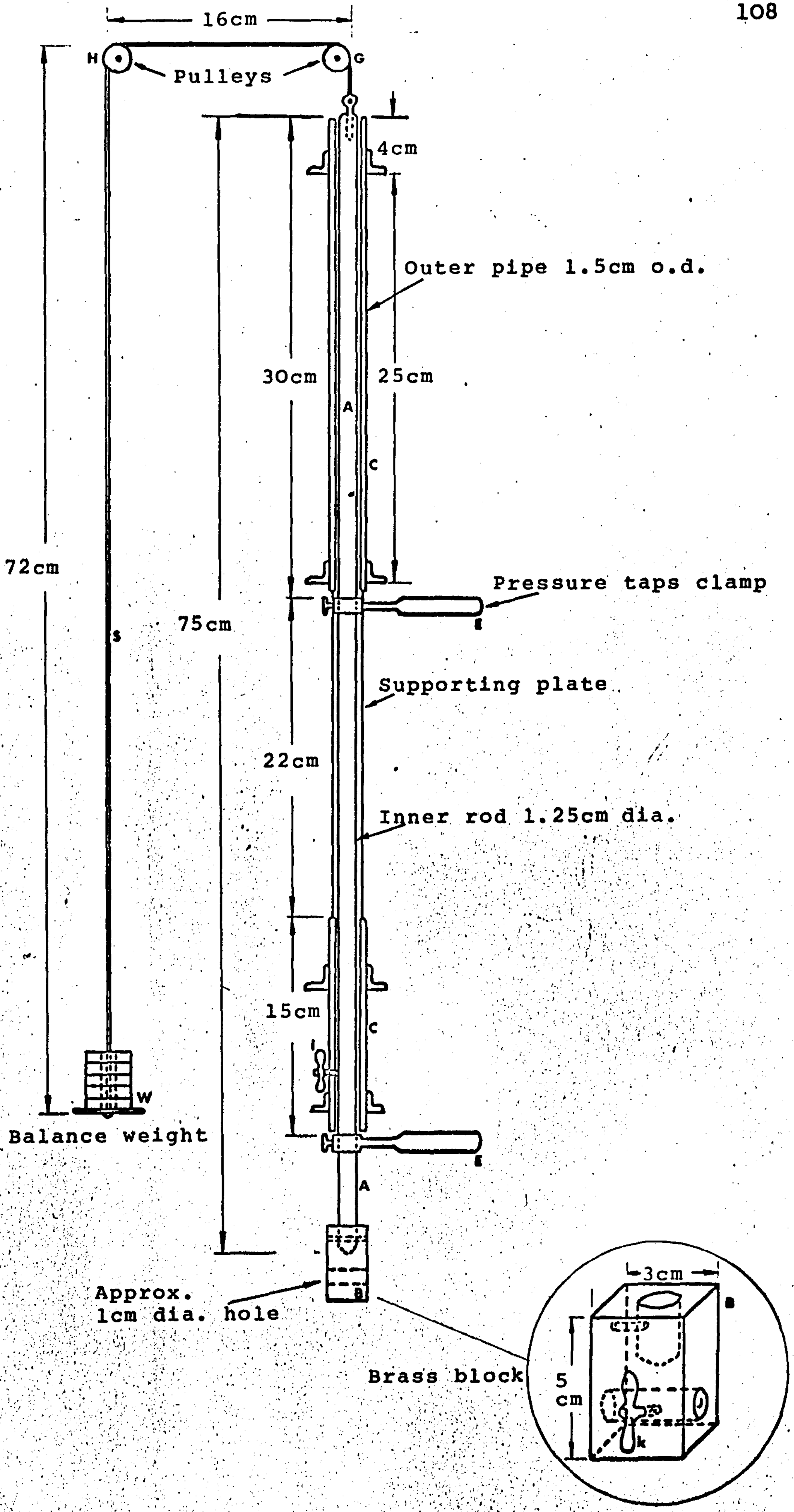
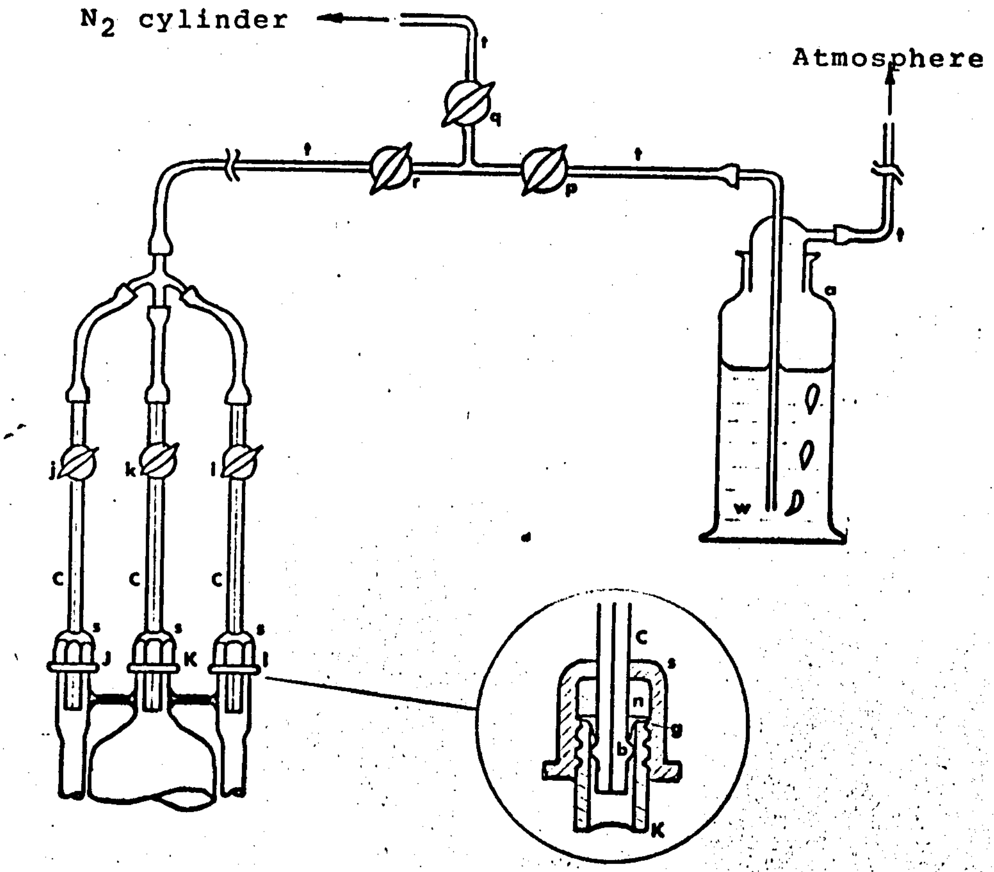


Figure 4-1.6 Cell support



c	Glass capillaries (1mm dia x 15cm)
s	Knurled screw caps, SQ13
i,j,k	Spring loaded valves
I,J,K	Necks of diaphragm cell
p,q,r	Reducing valves
n	Neoprene washer
g	PTFE gasket
b	Glass thickening
a	Aspirator bottle
w	Water

Figure 4-1.7 Pressure connections

mercury vapour that could come out from the cell. Correct manipulation of the reducing valves r,p and q allows either the cell to be pressurised, from the nitrogen cylinder,or the depressurised by means of the aspirator bottle. Each of the three lower terminals of the capillaries has a knurled screw cap s with a neoprene washer n and a PTFE gasket g to secure the capillaries to the three necks, (I, J and K) of the cell (Fig. 4-1.1). A detail of the cap s is also shown in Fig. 4-1.7.

Filling appliance :

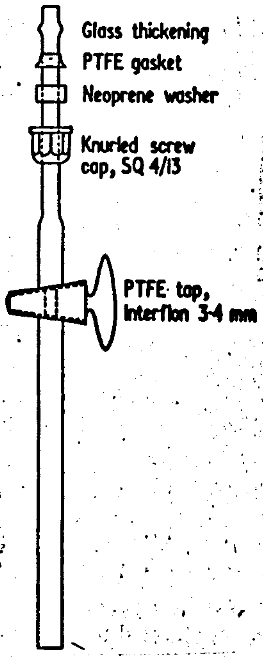


Fig. 4-1.8 Filling appliance for the upper compartment of the diffusion cell.

It is important to degass the pores of the diaphragm properly. Air locking of the diaphragm pores would cause a serious error in the measured diffusion coefficient. A filling appliance, as shown in Fig. 4-1.8,is used to remove the air from the pores of the diaphragm. It consists of a glass tube with a knurled screw cap together with a neoprene washer and PTFE gasket on one end. A PTFE tap is located in the middle of its length.

Magnetic rotating mechanism and oil bath :

The stirrers of the cell are operated by a pair of magnets fixed to a rotating U-shaped yoke. The yoke is operated by an endless chain which is connected to the main gear, driven by a speed controlled motor (manufactured by Allspeeds Ltd., Accrington, England, type MSRZVD and input H.P. 0.25). The yoke, together with the chain and the driven gear, is immersed in a bridge-controlled oil bath (manufactured by Townsen & Mercer Ltd., Croydon, England, Type E-270, major bath) containing a transparent, high boiling point oil (manufactured by Mobil Oil Co. Ltd., England, Type "Whiterex 307"). The temperature of the bath can be controlled to an accuracy of $\pm$ 0.1°C. A general view of the oil bath, together with rotating mechanism, is given in Fig. 4-1.9.

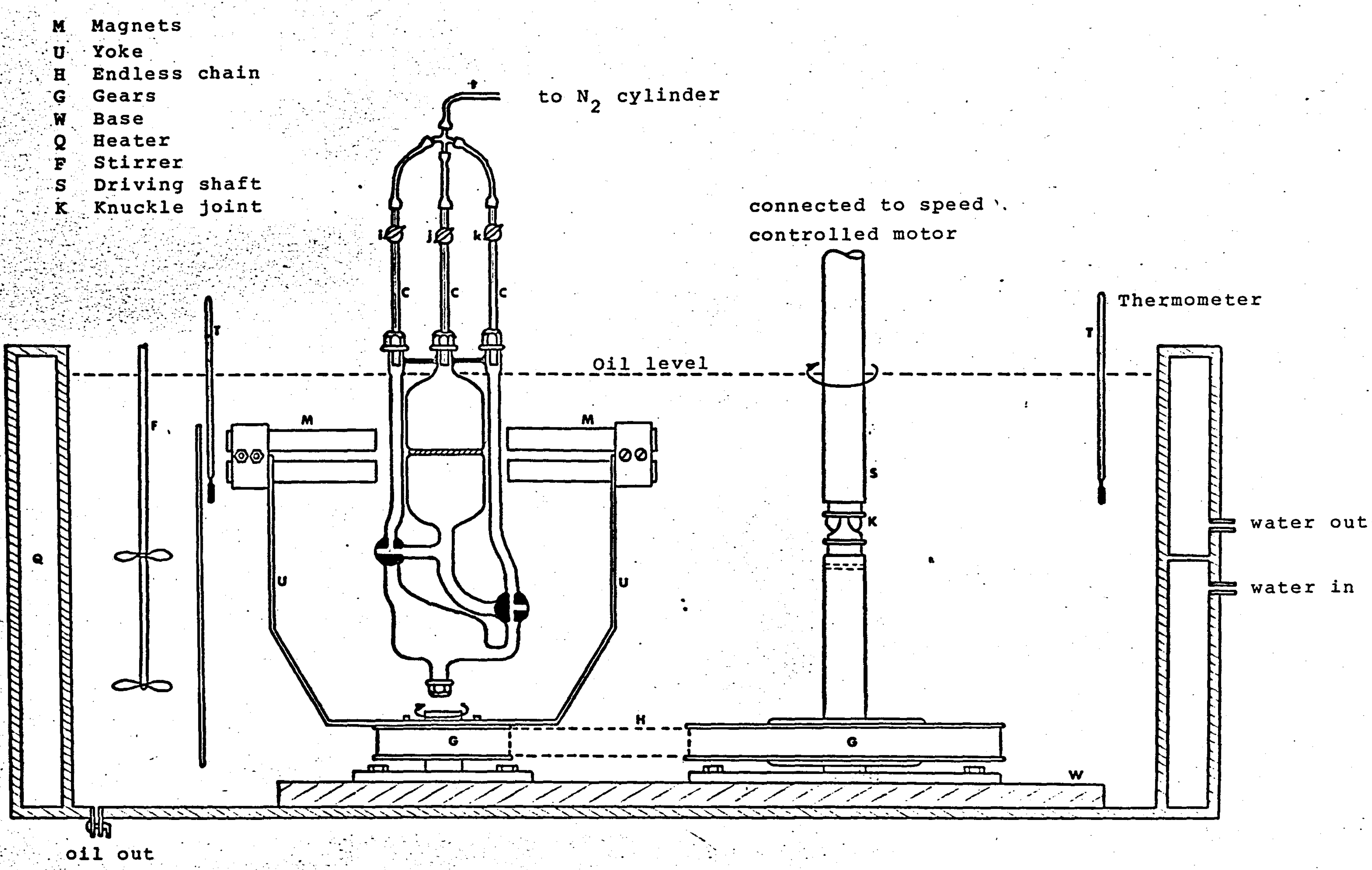


Figure 4-1.9 General assembly of diffusion apparatus

4-2 EXPERIMENTAL PROCEDURE

The design of the cell outlined above requires that the following operating procedure is observed. The procedure is described with the aid of Fig. 4-1.10 and reasons for various actions are also given when appropriate.

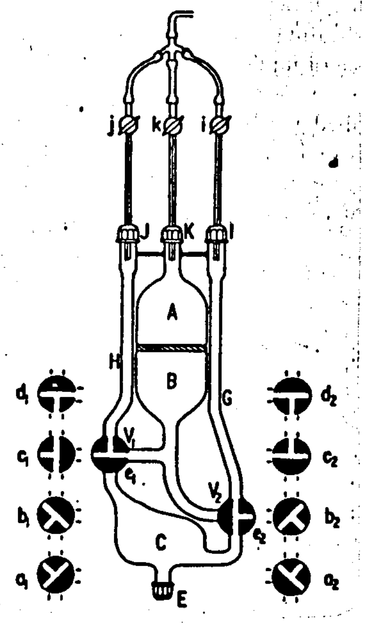
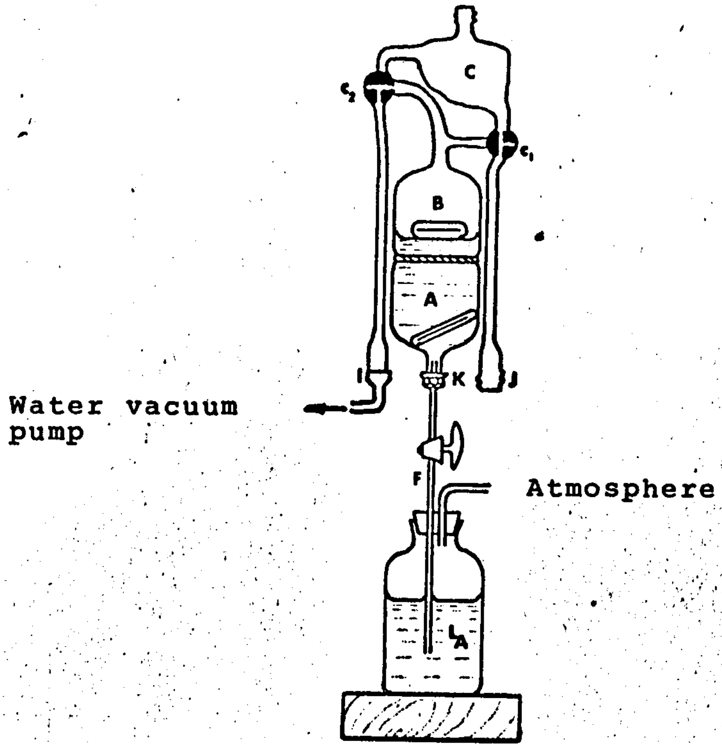


Fig. 4-1.10 General arrangement of the diffusion cell and the operating procedure

4-2.1 Charging the cell with test liquids

The cell is put into an inverted position with the filling appliance attached (as shown in Fig. 4-1.11). The test liquid is sucked into the compartment A and then into approximately $\frac{1}{4}$ of the compartment B. The supply of the liquid L_A is closed and the compartments A and B maintained under vacuum for a few minutes. This procedure should remove any air present in the diaphragm.

The cell is put in the upright position, the filling appliance removed, and then the top K of the compartment A is closed with a cap making sure that no air has been trapped. Then the cell is put again into the inverted position.



L_A Upper compartment solution

F Filling appliance

Figure 4-1.11 Degassing procedure of the diaphragm pores

Approximately $\frac{1}{4}$ of the compartment B is filled with mercury (when the valve V1 connects B with C as in Fig. 4-1.10 (d1). The test liquid L_A is sucked out, by means of a small bore flexible PTFE tube (the inside of the valve V2 is removed to accommodate the flexible tube). To remove the traces of the liquid L_A the compartments B and C and the mercury should be rinsed with the test liquid L_B.

The valve V2 is reassembled and put into the position to connect B and G as in Fig. 4-1.10 (c2). Enough mercury is added to obtain an overflow from V2. Now the space remaining in the compartment C is just enough to accommodate the test liquid L_B with some small excess.

The valves V1 and V2 are closed (Fig. 4-1.10 (a1) and Fig. 4-1.10 (a2)) and the compartment C filled with the test liquid L_B. At this stage the remainder of any air trapped in the valves should be removed. Finally the end E of the compartment C should be sealed without trapping any air. At this stage a sample of the test liquid L_B should be taken.

The cell is put into the upright position. Some liquid L_B is inserted into the tubes G and H to seal the valves V1 and V2. At this stage any air still present in the compartment C should be expelled by opening V1 and V2 to form a U-tube combination of the tubes H, G and the compartment C, Fig. 4-1.10 (c1) and 4-1.10 (e2). More mercury is added into tube G, enough to balance the weight of liquids in the compartments A and B, closing first the valves V1 and V2 as shown in Fig. 4-1.10 (b1) and 4-1.10 (a2).

The compartment A is opened at K, and all the test liquid is removed and replaced with a predetermined volume of the fresh test liquid L_A. This step is necessary because some change in the composition of the test liquid L_A would occur in an earlier stage when a vacuum was applied to remove the air from the diaphragm. At this stage a sample of the test liquid L_A should be taken.

The cell is now placed in its cage above the thermostat bath. The valve V2 is set so that the compartments A and B and the tube G form a U-tube combination, Fig. 4-1.10 (c2), the compartment C being isolated. The valve V1 is set so that the compartment C is vented through the tube H, Fig. 4-1.10 (cl), but the compartments A and B are isolated. Now the outlets J, K and I are connected to the manifold supplying the nitrogen gas. The nitrogen gas pressure is set to the required level and the cage containing the cell is lowered into the bath which had already attained the required temperature.

4-2.2 Transfer of the test liquid L_B to the compartment B

The transfer is made after the test liquids have attained the temperature of the bath. In this operation the valves V1 and V2 are operated by means of two mechanical appliances controlled remotely from above the bath. The following procedure is used. The valve V1 is set as in Fig. 4-1.10 (b1) and the valve V2 is set as in Fig. 4-1.10 (b2). Then V1 is put in a position to connect B and C and to isolate the tube H as in Fig. 4-1.10 (d1). Next V2 is gradually opened to allow a slow flow of mercury into the compartment C while the test liquid L_B takes its place in the compartment B. During this operation tube G is isolated. The valve V2 is closed after the mercury has dropped to a predetermined level at the bottom of the compartment B, as in Fig. 4-1.10 (b2). The volume of the compartment B, down to the mark M shown in Fig. 4-1.10, is known from direct measurement.

Next V1 is set to connect the tube H with the compartment C, the compartment B being isolated as in Fig. 4-1.10 (cl). By means of V2, Fig. 4-1.10 (e2), some of the mercury from the tube G is transferred into the tube H to a predetermined level to balance the liquids in A and B. Once this is obtained V1 is set to form a U-tube combination consisting of H, A and B as in Fig. 4-1.10 (el). Next the valve V2 is set to connect the compartment C and the tube G, the compartment B being isolated as in Fig. 4-1.10 (e2). Now the run is commenced by starting the magnetic stirrers. A stirring speed of 40 r.p.m. is used. The setting of the valves is shown in Fig. 4-1.10 (el) and Fig. 4-1.10 (e2).

4-2.3 Termination of the run

The run may be terminated by one of two methods: one is more suitable for the operation at ambient temperatures and the other for the operation at higher temperatures.

Ambient temperature operation

The stirrers are stopped. The cell is removed from the bath and suspended above it to drain the bath oil and to cool. The cooling is done by passing a fast stream of cooling air. At this stage any condensate that might have collected on the walls of the capillary tube of the compartment A descends into the compartment.

When the test liquids are sufficiently cold the pressure is released, the valves V1 and V2 are set as in Fig. 4-1.10 (al) and Fig. 4-1.10 (b2) i.e. the compartments A and B are isolated from C, G and H. The capillary tubes are removed from the cell terminals J, K and I and replaced by screwed caps.

Three samples of the test liquid L_A are taken from various levels within the compartment A avoiding the liquid in the immediate neighbourhood of the diaphragm.

The valves V1 and V2 are set as shown in Fig. 4-1.10 (b1) and Fig. 4-1.10 (b2) and the cell is put into the inverted position. Any test liquid or mercury, present above the valves, drains from the tubes G and H.

Now the cap E is removed from the compartment C. To transfer the test liquid to C the valve V2 is opened as shown in Fig. 4-1.10 (d2) (B connected to C but G is isolated), with valve V1 as shown in Fig. 4-1.10 (d1), letting the test liquid flow slowly to C. The first few cubic cemtimeters of that liquid are discarded and then three samples taken from the incoming stream.

Elevated temperature operation

The stirrers are stopped. The cell is lifted from the bath and secured above it. The valves V1 and V2 are closed (as in Fig. 4-1.10 (b1) and Fig. 4-1.10 (b2)). The cocks j,k,i on the capillaries (Fig. 4-1.10) are closed and the cell is put in the inverted position. By manipulating the valves V1 and V2, in the manner described earlier, the test liquid L_B is transferred to the compartment C and the valves V1 and V2 are closed again as in Fig. 4-1.10 (b1) and Fig. 4-1.10 (b2).

The cell is returned to the upright position and the valves V1 and V2 to the same position as during the run (Fig. 4-1.10 (e1) and Fig. 4-1.10 (e2)). The cocks j,k,i on the capillaries are opened, the cell is cooled in a stream of cold air. When the test liquids have reached ambient temperature the pressure is released and samples of the test liquids L_A and L_B are taken in the manner described earlier.

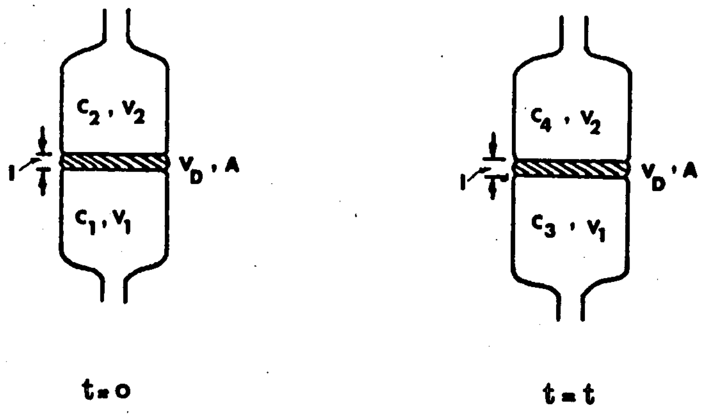
4-2.4 Time scale of the experiments

In the experiments carried out with this cell the following were the approximate times taken for the various steps:

(a)	Charging of the cell with test solutions (washing the compartments, de-aerating the diaphragm, filling the compartments with the test liquids, e.t.c.)	1.00 hrs.
(b)	Preheating to the temperature of the experiment.....	0.50 hrs.
(c)	Run time	24.00 hrs.
(d)	Cooling down after the run	0.25 hrs.
(e)	Sampling	0.25 hrs.
	Total	26.00 hrs.

4-3 Methods for calculating experimental data

The following equation was used to calculate integral diffusion coefficients from the experimental data obtained from the cell, shown diagrammatically in Fig. 4-3.1 (The notation used in the equations below is also given in Fig. 4-3.1)



t=o

t=t

Figure 4-3.1 Initial and final concentrations in the diaphragm cell.

$$\bar{D}_{AB} = \frac{1}{\beta t} \log_{10} \left(\frac{C1 - C2}{C_3 - C_4} \right) \qquad (4\text{-}3.1)$$

where

$$\beta = \frac{A}{l} \left(\frac{1}{V_1} + \frac{1}{V_2} \right) \text{, cell constant} \qquad (4\text{-}3.2)$$

t = time, sec.

C_1, C_2, C_3 and C_4 = concentrations in gm/cm^3 at T^{o}C

A = effective mass transfer area of the diaphragm, cm^2

l = effective length, cm.

V_1 and V_2 = volumes of compartments, cm^3

$\bar{D}_{AB}$ = integral diffusion coefficients, cm^2/sec.

Equation (4-3.1) was derived from Ficks' laws as shown by Mills and Woolf (134).

4-3.1 : Cell constant β

The cell constant β was obtained by calibration using the $KCl-H_2O$ system of known diffusion coefficient and eq. (4-3.1), recommended by Holmes (89),

i.e. $$\beta = \frac{1}{\bar{D}_{AB}t} \log_{10} \left(\frac{C_1 - C_2}{C_3 - C_4} \right) \qquad (4-3.1)$$

(concentrations are in gm/litre at 25°C, t in seconds and $\bar{D}_{AB}$ in $cm^2/sec.$).

The experimental work with 0.1N KCl (in the lower compartment) and double distilled water (in the upper compartment) was carried out at 25°C; the procedure described in section 4-2 being used. The initial and final concentrations of the test solutions were obtained using Mohr's method (212) i.e. by titrating them against 0.05 N $AgNO_3$ standard solution with potassium dichromate solution (4.2 gm. of A.R. potassium chromate and 0.7 gm. of A.R. Potassium dichromate in 100 cm^3 of distilled water) as the indicator.

The integral diffusion coefficient $\bar{D}_{AB}$, to be used in equation (4-3.1),was obtained from

$$\bar{D}_{AB} = \frac{C_B \bar{D}_{CB} - C_T \bar{D}_{CT}}{C_B - C_T} \qquad (4-3.3)$$

where $$C_B = \frac{C_1 + C_3}{2} \quad \text{and} \quad C_T = \frac{C_2 + C_4}{2} \qquad (4-3.4)$$

$\bar{D}_{CB}$ is an integral diffusion coefficient which would be found in a run of vanishingly short duration with the initial concentrations C_B and zero on the two sides of the diaphraghm. $\bar{D}_{CT}$ is defined similarly for the initial concentrations C_T and zero. The values of $\bar{D}_{CB}$ and $\bar{D}_{CT}$ have been calculated from the differential diffusion coefficients and tabulated by Mills and Woolf (134) for a range of concentrations of $KCl - H_2O$

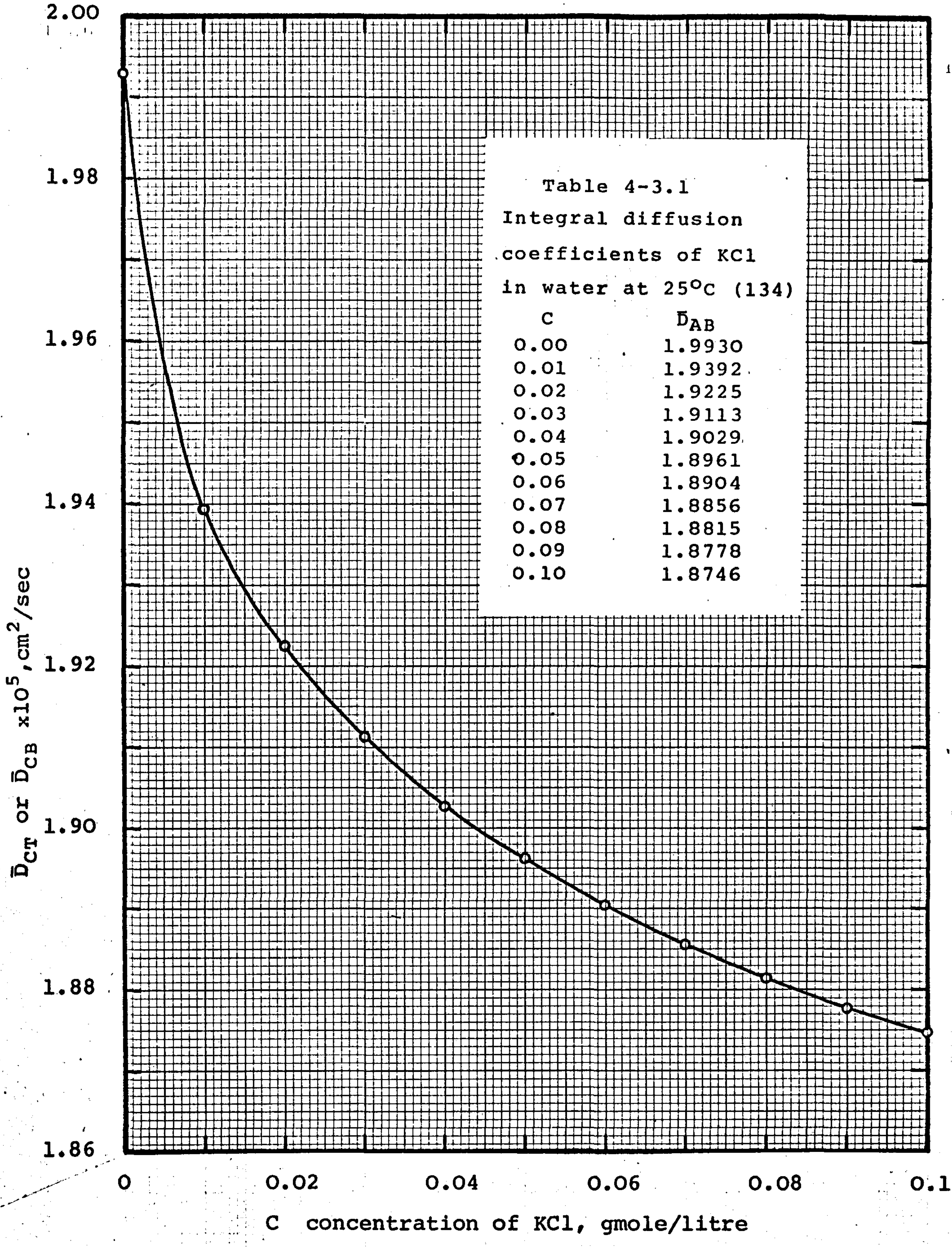


Table 4-3.1
Integral diffusion coefficients of KCl in water at 25°C (134)

C	$\bar{D}_{AB}$
0.00	1.9930
0.01	1.9392
0.02	1.9225
0.03	1.9113
0.04	1.9029
0.05	1.8961
0.06	1.8904
0.07	1.8856
0.08	1.8815
0.09	1.8778
0.10	1.8746

Figure 4-3.2 Integral diffusion coefficients of aqueous KCl solutions at 25°C

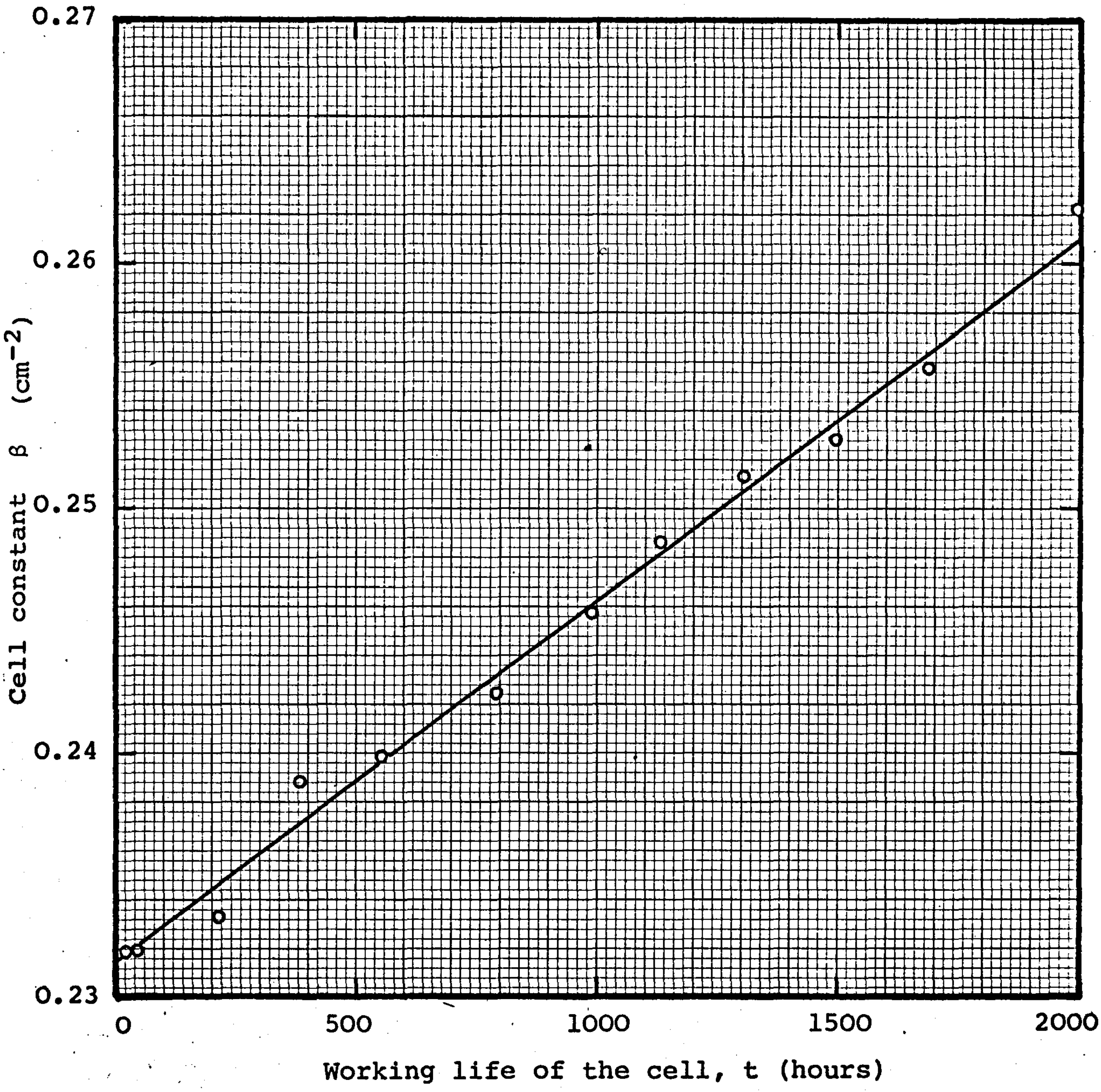


Figure 4-3.3 Wear of the diaphragm of cell 'R' in terms of the cell constant, β.

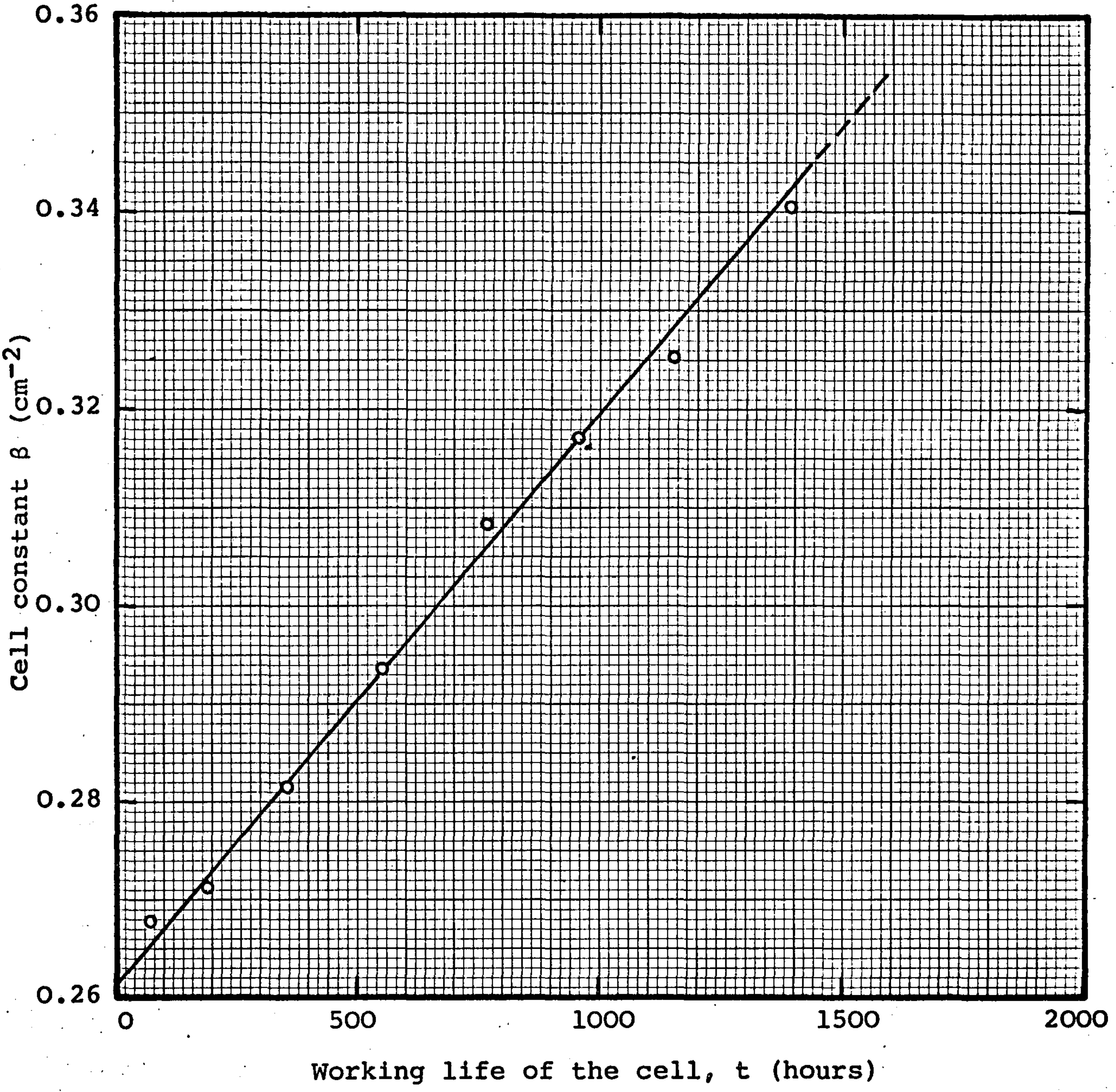


Figure 4-3.4 Wear of the diaphragm of cell 'H' in terms of cell constant β.

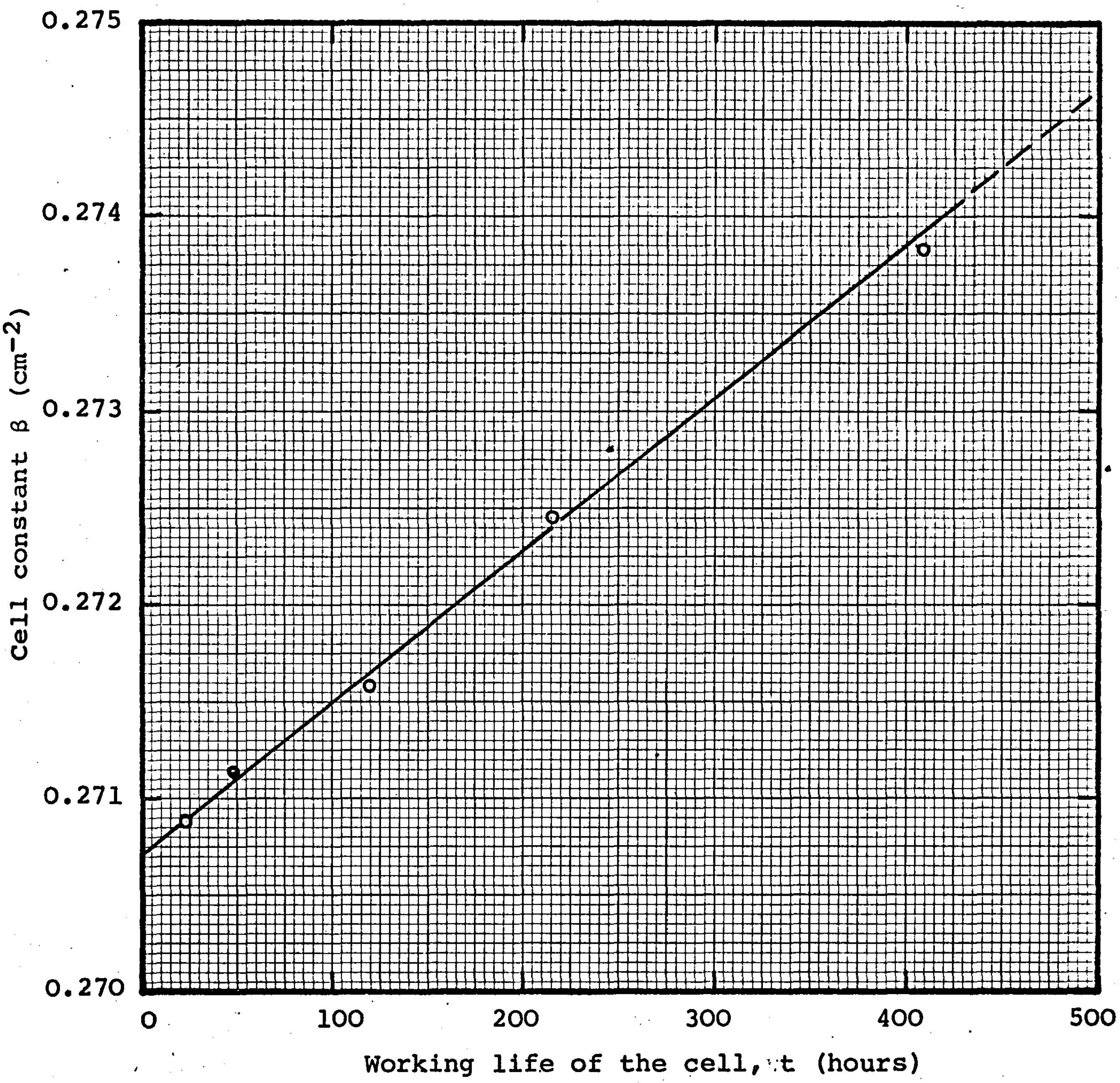


Figure 4-3.5 Wear of the diaphragm of cell 'D' in terms of cell constant β.

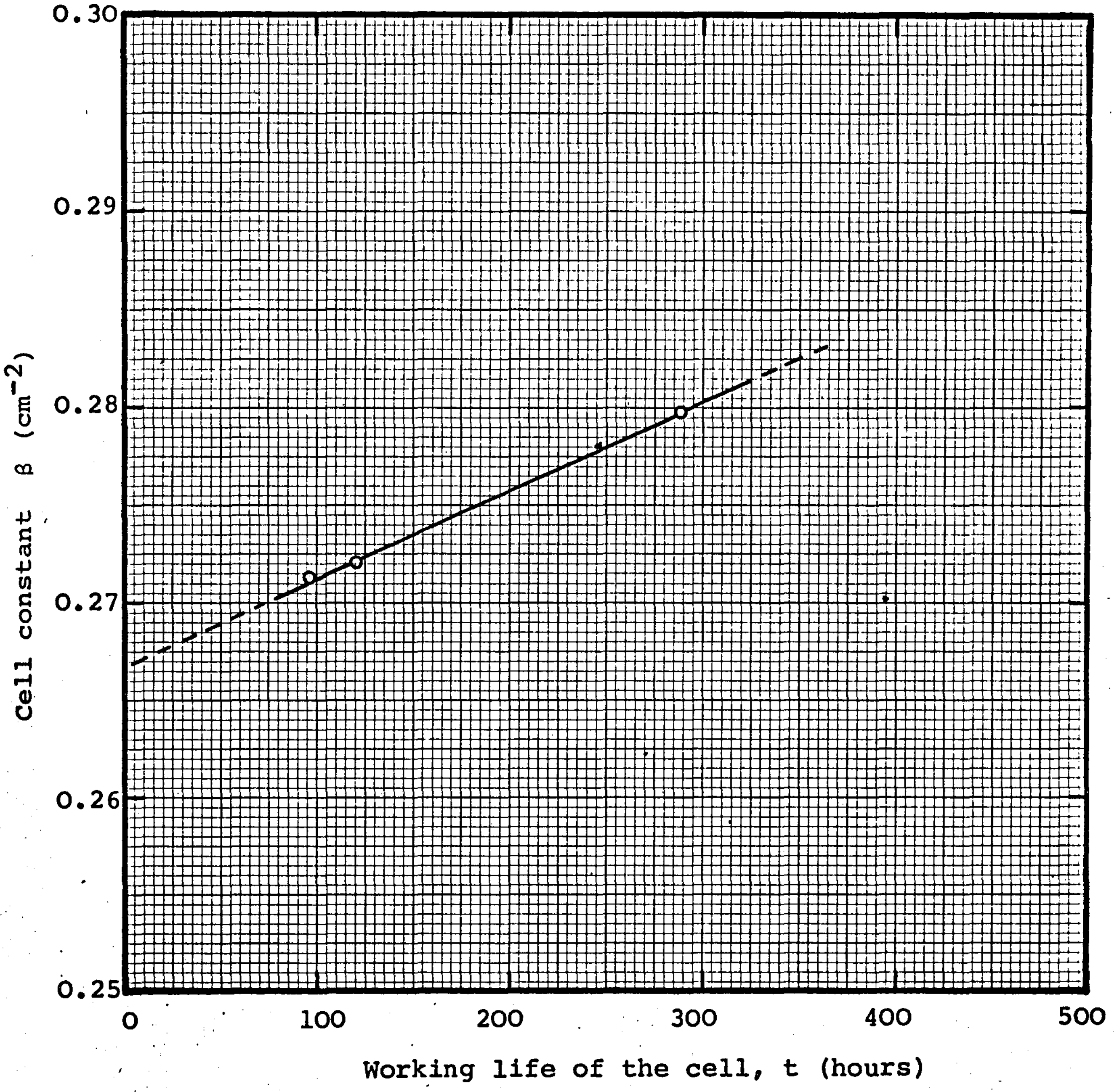


Figure 4-3.6 Wear of the diaphragm of cell 'G' in terms of cell constant β .

system at 25°C. These data are represented in Table 4-3.1 and Figure 4-3.2.

The abrasive action of the stirrers gradually wears out the diaphragm thus causing an increase in the value of the quantity β. This change in β is allowed for by frequent recalibrations of the cell and by the use of a plot of β against the working life of the cell (see Fig. 4-3.3 to 4-3.6); to interpolate the cell constant for each run. This variation of the constant β with time is also tabulated in Table 6-1.5, pg. 188.

From the definition of the cell constant, β, in equation (4-3.2) it is obvious that the temperature dependence of 'β' is due to the variations of V_1 and V_2, as changes in the values of A and l are negligible in comparison.

Since the design of the diaphragm cell developed and the operating procedure outlined above, can maintain constant values of V_1 and V_2, irrespective of temperature, the cell constant β is regarded as constant with temperature. Therefore the values of β at 25°C from Figures (4-3.3 to 4-3.6) are used in calculating the diffusion coefficients of the test liquids for the elevated temperatures.

A sample calculation for β is given in Appendix 4-3.1.

4-3.2 : Integral diffusion coefficient

The integral diffusion coefficients are calculated from equation (4-3.1). The cell constants β corresponding to the working life of the cell are obtained from Figures (4-3.3 to 4-3.6). Here, β is assumed to be independent of temperature as indicated above. The volumetric concentration unit (i.e. gm solute/100cm^3 of solution) is used for C_1, C_2, C_3 and C_4. This type of concentration unit, of course, applies only to a specified operating temperature. Since eq.(4-3.1) is derived from Fick's law (134) i.e. $J = -D_{AB} \frac{\partial c}{\partial t}$ (4-3.5) (where J in gm/cm^2 sec, C in gm/cm^3, t in sec and D_{AB} in cm^2/sec) for a given temperature, it is therefore more appropriate to use the values of C_1, C_2, C_3 and C_4 at the operating temperature.

Analysis of test solutions

The test liquids are analysed by two methods to measure their concentrations. For the ethanol-water and acetone-water systems their densities are measured at 25°C by Lypkin's (5 cc) pycnometer using the method described by Lypkin (124). Then the corresponding weight fraction concentration W_A is read directly from a calibration charts, Fig. (4-3.7 and 4-3.8), for that system. For the acetone-chloroform system the refractive angle of the test solution at 25°C is measured by the Abbe - refractometer and then converted to weight fraction concentration by a calibration chart, Fig. (4-3.9), for that system. Once the weight fraction concentrations of the test solutions are known, the corresponding volumetric concentrations (gm/100cm^3 at T) are read, for the required operating temperature, from the conversion charts i.e. Figures (4-3.10 to 4-3.12).

Material balance equation for C_3 :

It was mentioned earlier that, at the termination of an elevated temperature run, there is a possible bulk flow of test liquid, through the diaphragm, from the upper compartment to the lower one. Therefore the final lower compartment concentration C_3 should be obtained from a

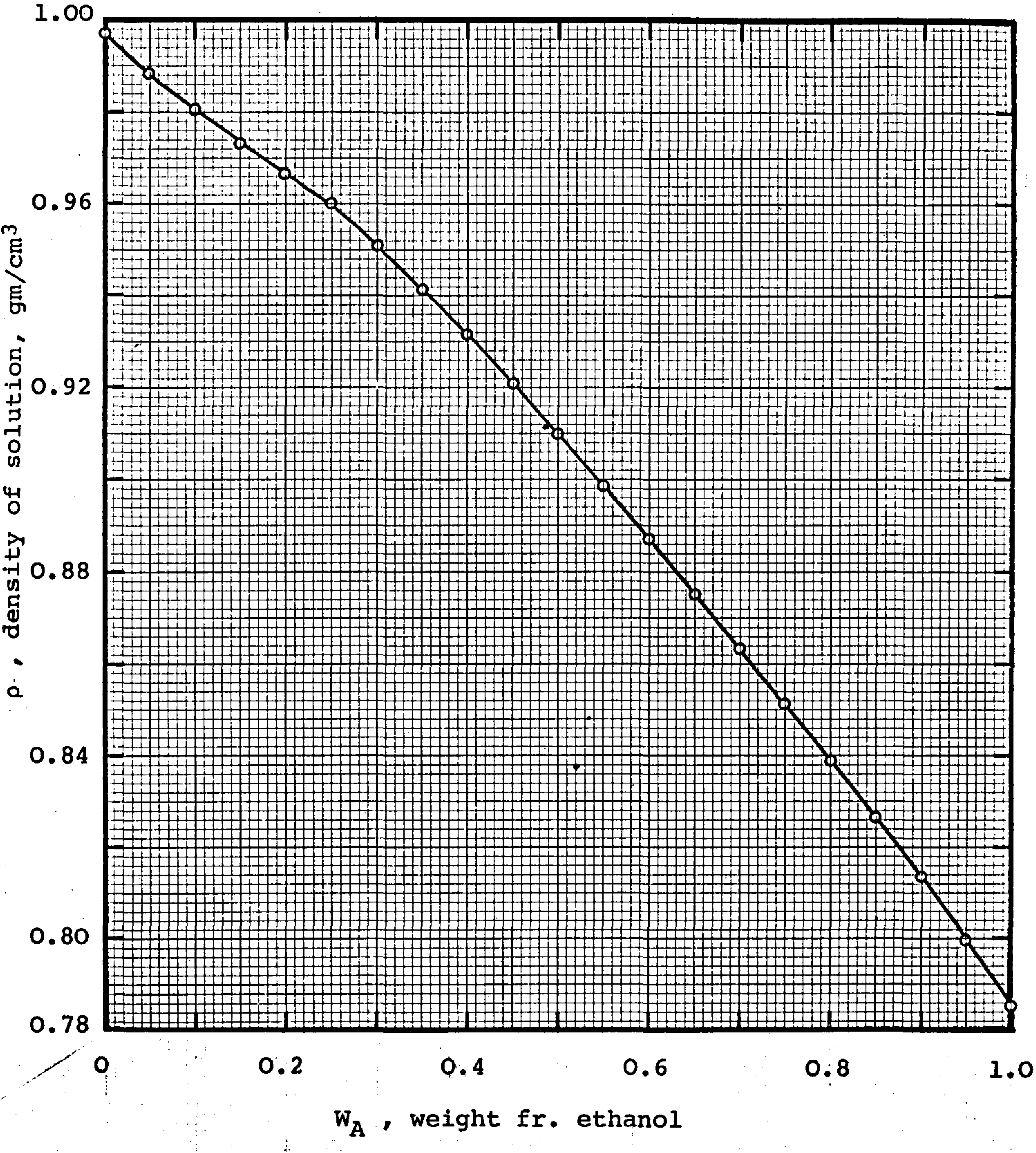


Figure 4-3.7 Density of aqueous ethanol solutions at 25°C (153)

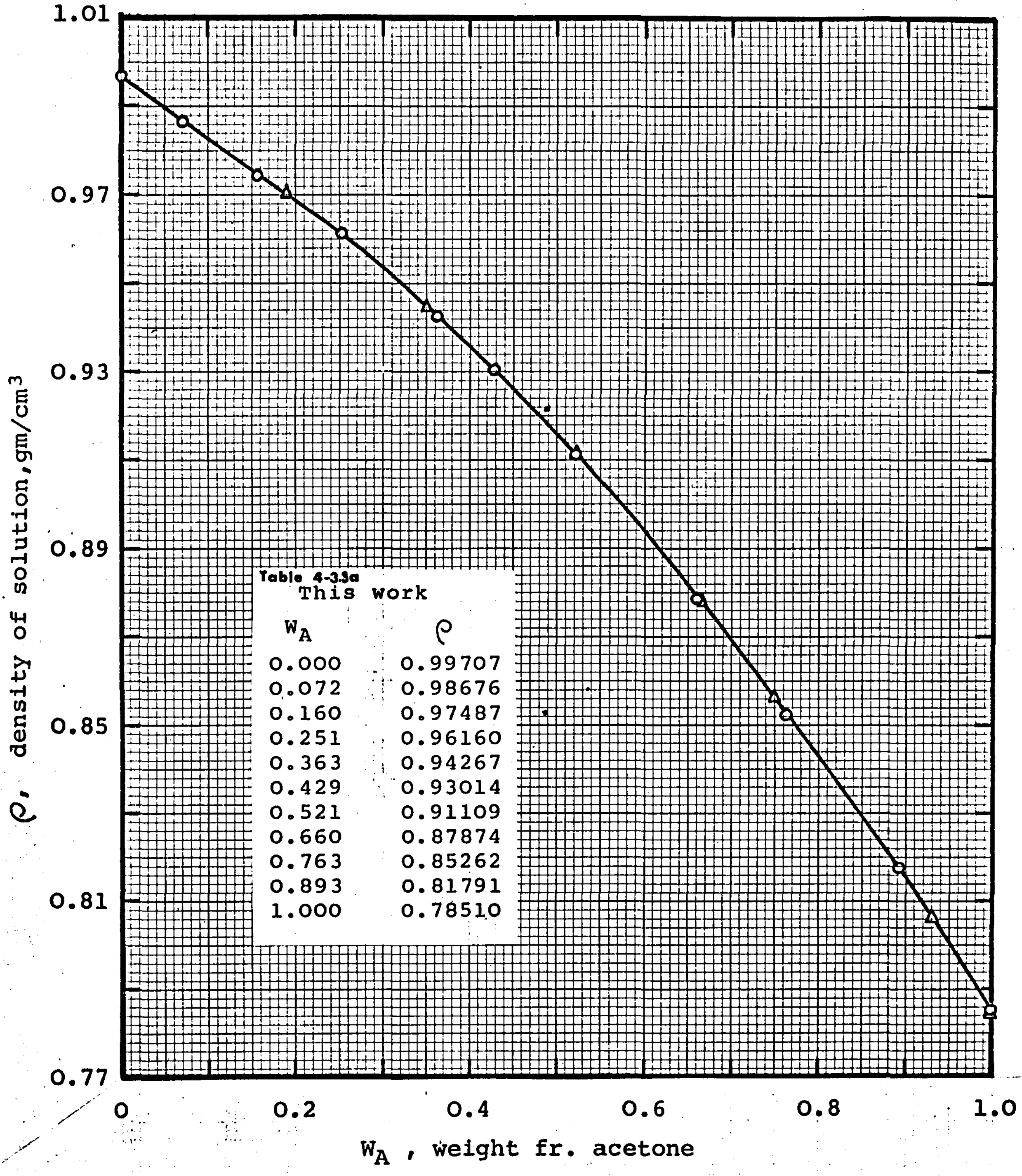


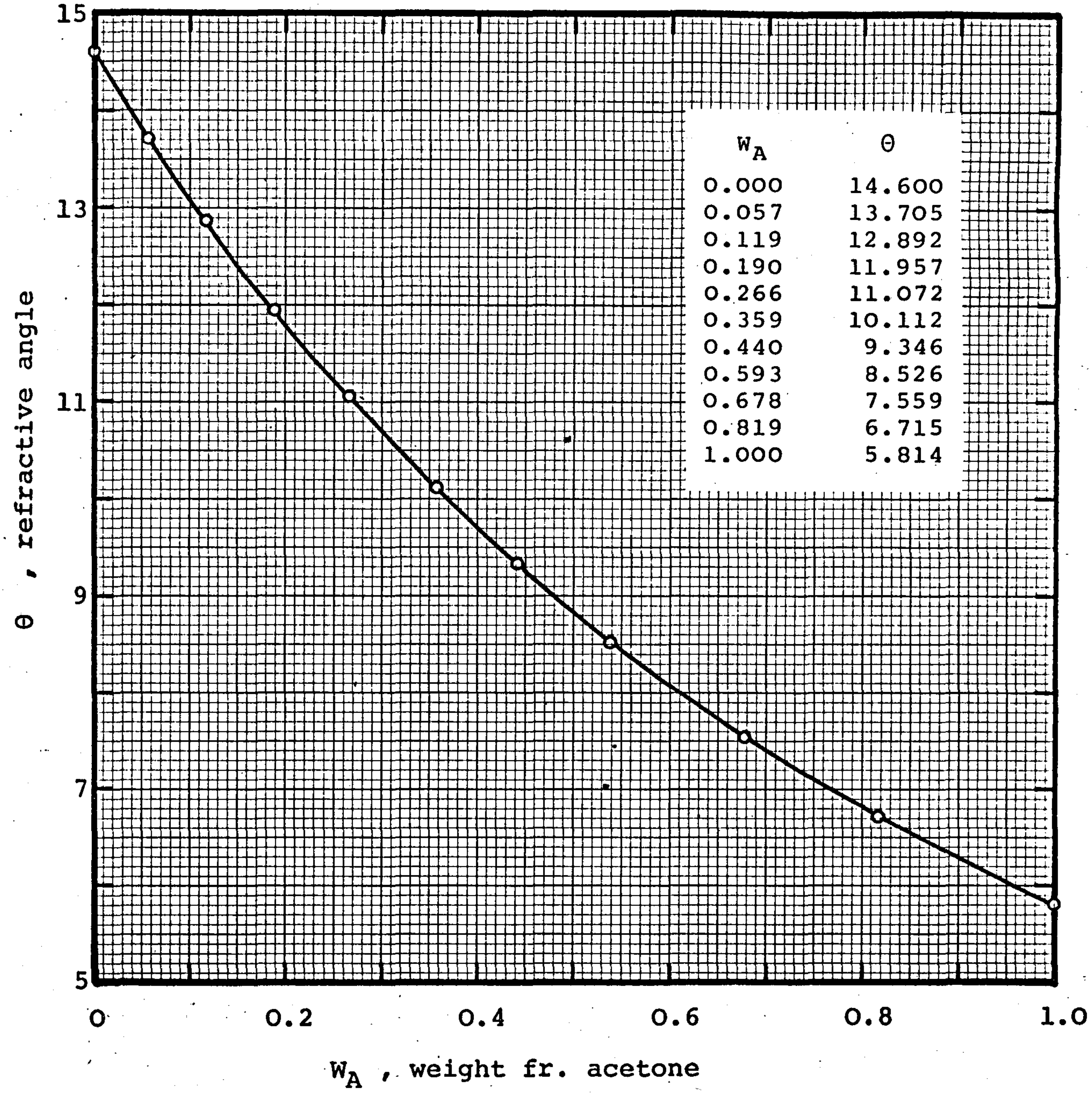
Table 4-3.3a
This work

W_A	ρ
0.000	0.99707
0.072	0.98676
0.160	0.97487
0.251	0.96160
0.363	0.94267
0.429	0.93014
0.521	0.91109
0.660	0.87874
0.763	0.85262
0.893	0.81791
1.000	0.78510

Figure 4-3.8 Density of aqueous acetone solutions at 25°C

△ Thomas and McAllister (195)

o This work



W_A	Θ
0.000	14.600
0.057	13.705
0.119	12.892
0.190	11.957
0.266	11.072
0.359	10.112
0.440	9.346
0.593	8.526
0.678	7.559
0.819	6.715
1.000	5.814

Figure 4-3.9 Refractive angles vs weight fr. concentration for acetone-chloroform mixtures at 25°C

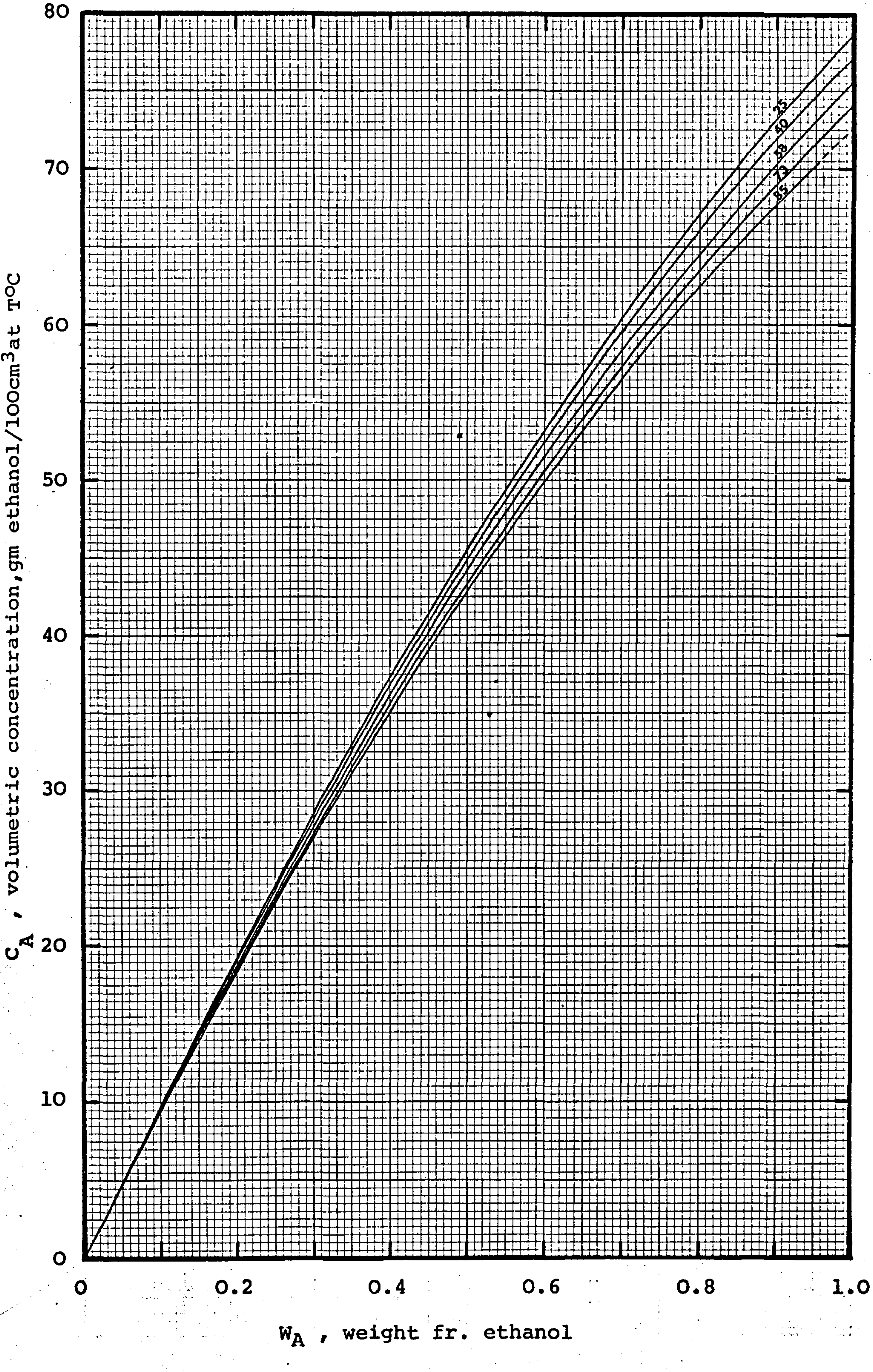


Figure 4-3.10 Conversion chart for aqueous ethanol solutions (Numbers on lines indicate temperature in ^oC)

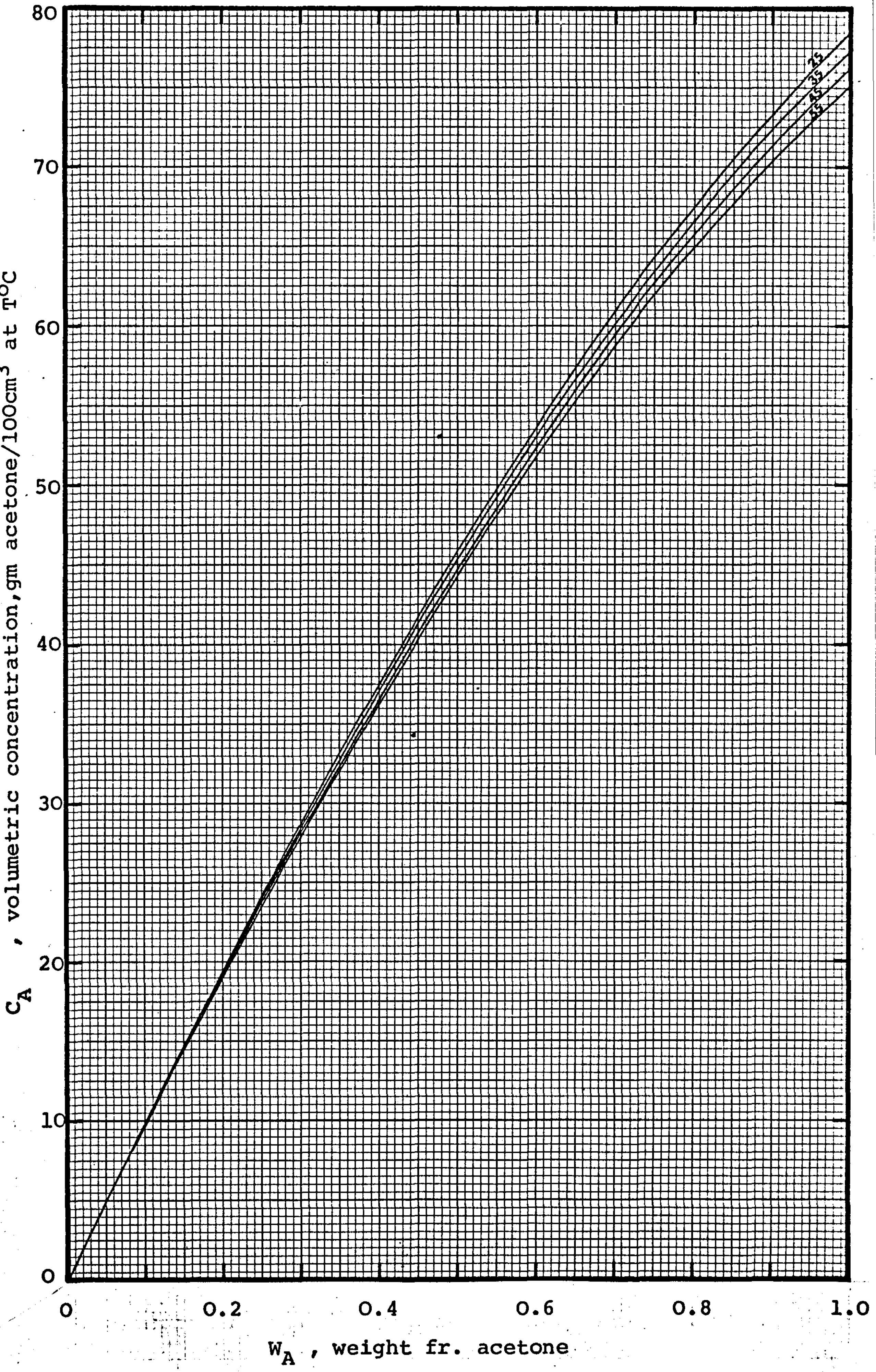


Figure 4-3.11 Conversion chart for aqueous acetone solutions (Numbers on lines indicate temperature in ^{o}C)

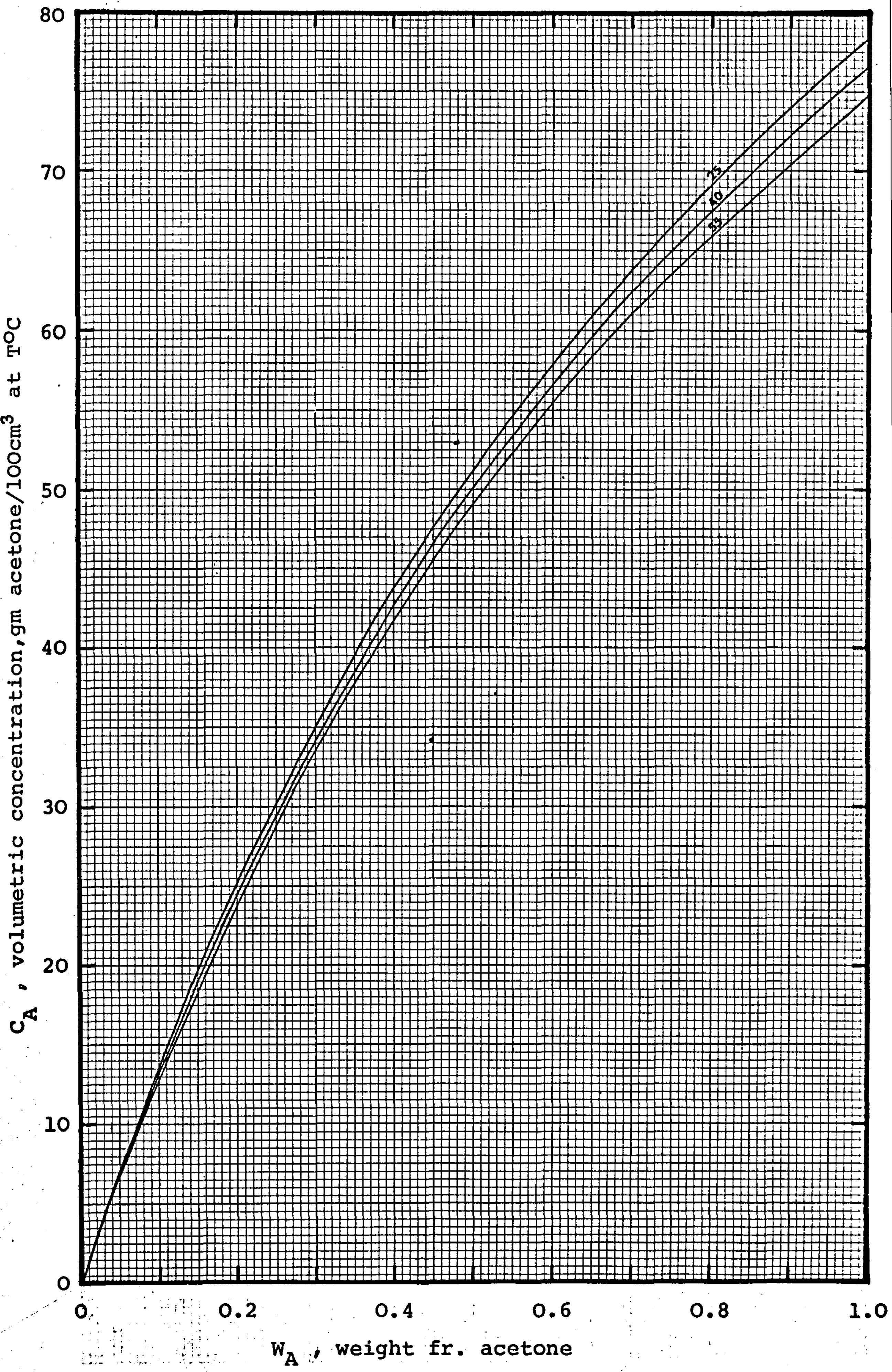


Figure 4-3.12 Conversion chart for acetone-chloroform solutions (Numbers on lines indicate temperature in °C)

Table 4-3.2 Density and volumetric concentration, ethanol-water mixtures, (ρ in $\frac{\text{gm}}{\text{cm}^3}$ and C_A in $\frac{\text{gm solute}}{100\text{cm}^3}$)

Wt. fr. acetone W_A	25°C *		40°C *		58°C **		73°C **		85°C **	
	ρ	C_A	ρ	C_A	ρ	C_A	ρ	C_A	ρ	C_A
0.000	0.9971	0.000	0.9923	0.000	0.9815	0.000	0.9715	0.000	0.9687	0.000
0.050	0.9882	4.941	0.9831	4.916	0.9750	4.865	0.9660	4.820	0.9580	4.780
0.100	0.9804	9.804	0.9748	9.748	0.9660	9.644	0.9575	9.573	0.9500	9.484
0.150	0.9733	14.600	0.9667	14.501	-	-	-	-	-	-
0.165	-	-	-	-	0.9450	15.611	0.9440	15.595	0.9350	15.446
0.195	-	-	-	-	0.9485	18.505	0.9380	18.300	0.9290	18.125
0.200	0.9664	19.328	0.9586	19.171	-	-	-	-	-	-
0.250	0.9600	23.974	0.9499	23.748	-	-	-	-	-	-
0.300	0.9507	28.520	0.9406	28.217	0.9275	27.819	0.9155	27.460	0.9060	27.175
0.350	0.9415	32.9511	0.9305	32.568	-	-	-	-	-	-
0.400	0.9315	37.259	0.9199	36.797	0.9055	36.093	0.8925	35.575	0.8820	35.157
0.450	0.9209	41.438	0.9088	40.898	-	-	-	-	-	-
0.460	-	-	-	-	0.8920	41.039	0.8790	40.441	0.8680	39.935
0.500	0.9099	45.493	0.8975	44.875	0.8823	44.016	0.8690	43.382	0.8580	42.833
0.550	0.8985	49.418	0.8859	48.724	-	-	-	-	-	-
0.596	-	-	-	-	0.8590	51.201	0.8445	50.336	0.8320	49.591
0.600	0.8870	53.219	0.8742	52.450	-	-	-	-	-	-
0.650	0.8753	56.893	0.8623	56.048	-	-	-	-	-	-
0.698	-	-	-	-	0.8340	58.187	0.8200	57.211	0.8080	56.373
0.700	0.8634	60.438	0.8503	59.518	-	-	-	-	-	-
0.750	0.8513	63.851	0.8381	62.857	-	-	-	-	-	-
0.800	0.8391	67.129	0.8258	66.062	-	-	-	-	-	-

Table 4-3.2 Density and volumetric concentration, ethanol-water mixtures, (ρ in $\frac{gm}{cm^3}$ and C_A in $\frac{gm\ solute}{100cm^3}$)
(continued)

Wt. fr. acetone W_A	25°C *		40°C *		58°C **		73°C **		85°C **	
	ρ	C_A	ρ	C_A	ρ	C_A	ρ	C_A	ρ	C_A
0.806	-	-	-	-	0.8076	65.110	0.7925	63.893	0.7800	62.885
0.850	0.8266	70.261	0.8182	69.124	-	-	-	-	-	-
0.899	-	-	-	-	0.7835	70.442	0.7675	69.004	0.7540	67.790
0.900	0.8136	73.226	0.8003	72.025	-	-	-	-	-	-
0.936	-	-	-	-	0.7730	72.314	0.7580	70.911	0.7460	69.788
0.950	0.7999	75.992	0.7867	74.737	-	-	-	-	-	-
1.000	0.7851	78.506	0.7720	77.203	0.7550	75.50	0.7415	74.150	-	-

* Reference (153)

** Data obtained by extrapolation or interpolation of the data of Schwers (1909) from reference (197)

Table 4-3.3 Density and volumetric concentration, acetone-water mixtures (ref. 195) (ρ in $\frac{\text{gm}}{\text{cm}^3}$ and C_A in $\frac{\text{gm acetone}}{100\ \text{cm}^3}$)

Wt. fr. acetone w_A	25°C @		35°C		45°C		55°C	
	ρ	C_A	ρ	C_A	ρ	C_A	ρ	C_A
0.0	0.99707	0.00	0.9942	0.00	0.9905	0.00	0.9860	0.00
0.1	0.9831	9.83	0.9791	9.79	0.9743	9.74	0.9690	9.69
0.2	0.9693	19.39	0.9639	19.28	0.9578	19.16	0.9462	18.92
0.3	0.9537	28.61	0.9473	28.42	0.9400	28.20	0.9325	27.98
0.4	0.9361	37.44	0.9285	37.14	0.9200	36.80	0.9110	36.44
0.5	0.9159	45.80	0.9077	45.39	0.8982	44.91	0.8888	44.44
0.6	0.8941	53.65	0.8846	53.08	0.8742	52.45	0.8638	51.83
0.7	0.8698	60.89	0.8601	60.21	0.8496	59.47	0.8389	58.72
0.8	0.8432	67.46	0.8336	66.69	0.8226	65.81	0.8117	64.94
0.9	0.8155	73.40	0.8055	72.50	0.7939	71.45	0.7820	70.38
1.0	0.78505	78.51	0.7740	77.40	0.7620	76.20	0.7501	75.01

Wt. fr. acetone w_A	65°C		75°C		85°C	
	ρ	C_A	ρ	C_A	ρ	C_A
0.0	0.9805	0.00	0.9743	0.00	0.9684	0.00
0.1	0.9630	9.63	0.9562	9.56	0.9497	9.50
0.2	0.9436	18.87	0.9353	18.71	0.9276	18.55
0.3	0.9250	27.75	0.9181	27.54	0.9111	27.33
0.4	0.9020	36.08	0.8930	35.72	0.8832	35.33

@ = this work

Table 4-3.4 Density and volumetric concentration, acetone-chloroform mixtures. (ρ in $\frac{gm}{cm^3}$ and C_A in $\frac{gm\ solute}{100\ cm^3}$)

Wt.fr. acetone W_A	25°C *		40°C @		50°C @		55°C @	
	ρ	C_A	ρ	C_A	ρ	C_A	ρ	C_A
0.000	1.4787	0.000	1.4450	0.000	1.4172	0.000	1.4114	0.000
0.030	1.4419	4.365	-	-	-	-	-	-
0.062	-	-	1.3693	8.490	1.3463	8.347	1.3369	8.289
0.071	1.3929	9.900	-	-	-	-	-	-
0.112	-	-	1.3156	14.735	1.2934	14.486	1.2843	14.384
0.129	1.3298	17.113	-	-	-	-	-	-
0.137	1.3219	18.065	-	-	-	-	-	-
0.189	-	-	1.2395	23.427	1.21990	23.056	1.2110	22.886
0.209	1.2499	26.098	-	-	-	-	-	-
0.246	1.2166	29.869	-	-	-	-	-	-
0.267	-	-	1.1700	31.238	1.1521	30.760	1.1440	30.543
0.354	-	-	1.1014	38.990	1.0845	38.392	1.0766	38.113
0.357	1.1255	40.150	-	-	-	-	-	-
0.374	1.1130	41.575	-	-	-	-	-	-
0.420	1.0775	45.227	-	-	-	-	-	-
0.450	-	-	1.0343	46.545	1.0183	45.825	1.0115	45.518
0.505	1.0223	51.600	-	-	-	-	-	-
0.520	1.0137	52.605	-	-	-	-	-	-
0.563	-	-	0.9652	54.341	0.9500	53.478	0.943	53.108
0.642	0.9418	60.501	-	-	-	-	-	-
0.687	0.9194	63.153	-	-	-	-	-	-
0.690	-	-	0.8973	61.949	0.8831	60.969	0.8771	60.555
0.803	0.8639	69.346	-	-	-	-	-	-
0.818	-	-	0.8352	68.319	0.8203	67.101	0.8140	66.585
0.838	0.8486	71.107	-	-	-	-	-	-
1.00	0.7840	78.400	0.7670	76.700	0.7555	75.55	0.7496	74.96

* Karr, Bowes and Scheible (1951) (Ref. 197)

@ This work.

material balance. The equation for this material balance is given below.

The initial and final concentration profiles within the diaphragm are shown in Fig. (4-3.13)

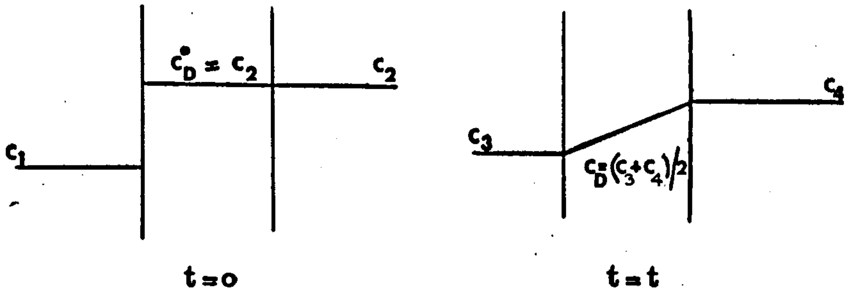


Figure 4-3.13 : Concentration profiles within the diaphragm.

From the principle of conservation of mass the following overall material balance can be made

$$C_1 V_1 + C_2 V_2 + C^o_D V_D = C_3 V_3 + C_4 V_4 + C_D V_D \quad (4\text{-}3.6)$$

The following assumptions are made in the above equation

(1) $V_1 = V_2 = V_3 = V_4 = V_B$

(2) The material balance is made at the operating temperature.

(3) A linear concentration gradient within the diaphragm at the end of the 24 hour diffusion period is assumed,

i.e. $C^o_D = C_2$ and $C_D = \left(C_3 + C_4\right)/2$

According to the above assumptions the concentration C_3 can be calculated from the equation

$$C_3 = \frac{C_1 + C_2(1+\lambda)}{(1 + 0.5\lambda)} - C_4 \quad (4\text{-}3.7)$$

where $\lambda = \frac{V_B}{V_D}$

A sample calculation for the integral diffusion coefficient for the acetone-water system is given in Appendix 4-3.2.

4-3.3 : Conversion of integral diffusion coefficient to differential diffusion coefficient

The integral diffusion coefficients $\bar{D}_{AB}$ obtained from equation (4-3.1) are converted to the differential diffusion coefficients D_{AB} by means of the following relationship

$$\bar{D}_{AB} = \frac{1}{C' - C''} \int_{C''}^{C'} D_{AB}\, dC \qquad (4\text{-}3.8)$$

where $C' = \frac{C_2 + C_4}{2}$, $C'' = \frac{C_1 + C_3}{2}$

The concentrations C_1, C_2, C_3 and C_4 are those shown in Fig. 4-3.1.

The differential diffusion coefficients D_{AB} were obtained from equation (4-3.8) over the complete concentration and temperature range by the graphical method recommended by Dullien and Shemilt (45). In this method the curve of best fit is drawn through the measured integral diffusion coefficients, as shown in Figures 6-1.1, 6-2.1 and 6-3.1. Integral diffusion coefficients were calculated by graphical integration for each run listed in Tables 6-2.1, 6-2.3 and 6-2.5 using equation (4-3.8). Next the average concentration corresponding to this new integral coefficient was found from Figures 6-1.1, 6-2.1, and 6-3.1. The concentration corresponding to this new integral coefficient is the concentration at which the integral coefficients from Tables 6-1.1, 6-1.3, and 6-1.5 become differential coefficients. Thus in Tables 6-2.1, 6-2.2 and 6-2.3 columns 8 and 10 represent differential diffusion coefficients and corresponding concentrations respectively.

4-4 Error analysis

The apparatus described constitutes a new development and therefore it is necessary to point out its strong and its weak points. Knowledge of the latter will make it possible to estimate the experimental error for a given binary system. Experimental errors in the diffusion coefficients have three sources: (i) errors in measurement, (ii) errors inherent in the construction of the cell and in the operating procedure; (iii) errors due to the impurity of the materials and to the inaccuracy of the physical properties reported in the literature.

4-4.1 Errors in measurement

Any errors of measurement such as in the analysis of solutions, in the volumes of test liquids charged and in the setting of the levels in the cell, ultimately contribute to an error in the concentration of the test liquid used. Three methods of determining concentration are used: (a) Mohr's (212) titration method for determination of the concentration of KCl (b) concentrations of ethanol and acetone in mixtures with water are obtained from density measurement at 25°C (c) the concentration of acetone in solution with chloroform was obtained using refractive angle measurements.

The error in the diffusion coefficient may be calculated from the formula :

$$\delta D_{AB} = \frac{D_{AB}}{\log_{10}\left(\frac{\Delta C_i}{\Delta C_f}\right)} \left[\left(\frac{\delta \Delta C_i}{\Delta C_i}\right)^2 + \left(\frac{\delta \Delta C_f}{\Delta C_f}\right)^2\right]^{\frac{1}{2}} \qquad (4\text{-}4.1)$$

where $\delta \Delta C_i = \left[(\Delta C_1)^2 + (\Delta C_2)^2 \right]^{\frac{1}{2}}$

$\delta \Delta C_f = \left[(\Delta C_3)^2 + (\Delta C_4)^2 \right]^{\frac{1}{2}}$

and $\Delta C_i = (C_1 - C_2)$; $\Delta C_f = (C_3 - C_4)$

This method is an application of the principle recommended by Levitt (114). The percentage error in the experimental coefficient as calculated by this method depends on the difference in the concentrations in the two compartments of the cell and on the absolute value of the diffusion coefficient.

(a) Error in the cell constant, β

The error in the constant β was estimated from an equation similar to equation (4-4.1).

i.e.

$$\delta\beta = \frac{\beta}{\log_{10}\left(\frac{\Delta C_i}{\Delta C_f}\right)} \left[\left(\frac{\delta \Delta C_i}{\Delta C_i}\right)^2 + \left(\frac{\delta \Delta C_f}{\Delta C_f}\right)^2 \right]^{\frac{1}{2}} \qquad (4\text{-}4.2)$$

The error in the volume measurement with the burette is about 0.05 cm^3 which gives a maximum error in the concentration of 0.0002 g mole/litre. This in turn would give a maximum error of 2% in the value of β. In the plot of β against time it was found, for a given cell, that the average deviation of experimental values of β from the best line through the data points was 0.7%. A sample calculation of the main error in the value of β is given in Appendix 4-4.1.

(b) Error in D_{AB} resulting from density measurement

In the case of ethanol-water and acetone-water solutions the error originates in weighing the pycnometers. With the analytical balance used the maximum error made in the density determination is $\pm$ 0.00005 gm/cm^3.

Table 4-4.1 Probable experimental error in the diffusion coefficient; ethanol-water mixtures at 25°C

$\frac{1}{2}(C_1+C_2)$ (g/100 cm^3)	$\frac{1}{2}(C_2+C_4)-\frac{1}{2}(C_1+C_3)$ (g/100 cm^3)	$D_{AB}\times10^5$ (cm^2 s^{-1})	$\delta D_{AB}\times10^7$ (cm^2 s^{-1})	% probable error
6·225	9·7055	1·0755	0·4956	0·4608
41·565	12·6060	0·3675	0·3909	1·0637
55·460	12·7840	0·4050	0·4587	1·1327
70·304	3·7520	0·7446	1·1889	1·5968
70·101	3·7240	0·7432	1·1908	1·6020
70·115	3·7805	0·7433	1·3437	1·8080
75·858	1·5660	1·0468	3·4069	3·2545
77·700	1·2800	1·1305	3·7996	3·3610

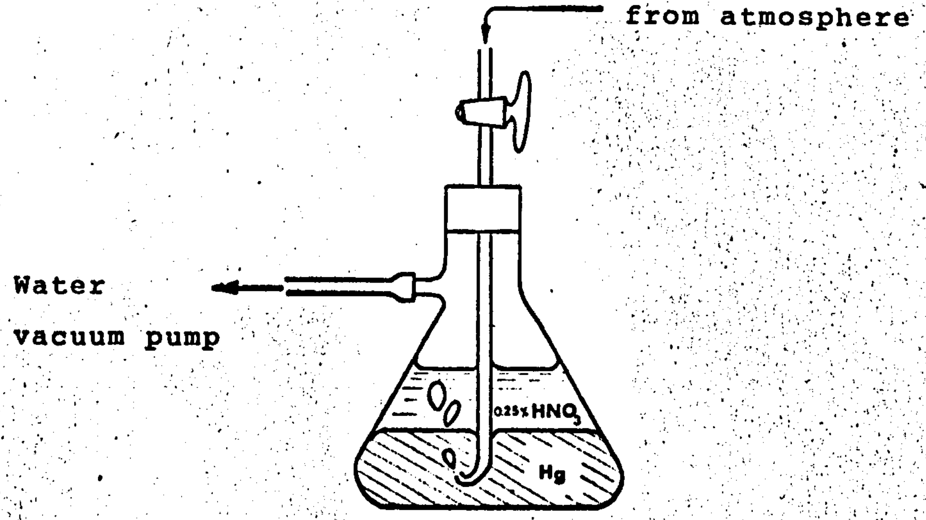


Figure 4-4.1 Purification of mercury

Using this error and applying equation(4-4.1)the error in the diffusion coefficient is calculated. It is easy to deduce that the magnitude of the error calculated by this method depends on the difference in the concentrations in the compartments of the cell and the absolute value of the diffusion coefficient. This is shown in Table 4-4.1. A sample calculation is given in Appendix 4-4.2

(c) Error in D_{AB} due to error in refractive angle measurement

The possible error in a refractive angle measurement is ± 0.001 degrees. This gives a maximum error of 0.00005 gm/cm^3 in the concentration. Using equation(4-4.1)the error in the diffusion coefficient is calculated. This error also depends on the concentrations in the two compartments of the cell and on the absolute value of the diffusion coefficient.

4-4.2 Errors inherent in the design and operating procedure

(a) In the experiments conducted at elevated temperatures some evaporation takes place from the surface of the meniscus in compartment A. Therefore the tube K above meniscus is kept in a stream of cold air in order to condense any vapour produced and to return it to the bulk of the test liquid. At the highest temperature investigated (i.e. 85°C) the hold-up of the condensate in the lower part of the tube K was estimated as 0.05 cm^3. Because of the air cooling no condensate was noticed in the capillary. The condensate hold-up above the meniscus is never lost as,at the end of the run,it is returned to the bulk of the liquid L_A by a gentle swirling motion of the whole cell. Thus the error resulting from this effect can be regarded as negligible.

(b) During the process of diffusion itself some changes in the volume of the test liquids in the two compartments occur. These changes are usually not significant because diffusion is a two-way process: the solute diffusing into one compartment and the solvent diffusing in the opposite direction from that compartment. Figure 4-1.1 shows that tube H provides an expansion space for compartment B and tube K for compartment A. This provision for expansion is necessary but it does not not prevent a small amount of bulk flow through the diaphragm, if the molecular weights of the solvent and the solute differ considerably. It is estimated that for the systems studied in this work this change of volume could amount to approximately 0.05 cm^3 in a 24 hrs. run. As mentioned earlier, the error in the diffusion coefficient due to this bulk flow was approximately 1%.

(c) The most serious error due to the experimental procedure can result if the ambient temperature method of terminating a run is applied to a run conducted at an elevated temperature. In this case a bulk flow of liquid L_A to compartment B can occur during 'after the run' cooling operations. This would not effect the concentration of the test liquid L_A but it could alter the concentration of the liquid in compartment B. In this case the concentration of test liquid L_B (i.e. C_3) should be obtained by a material balance as mentioned earlier and not by methods of chemical analysis. An example of this is given in Appendix 4-4.3 for a run at 85°C with the ethanol-water system where the ambient temperature method of shut-down was used. In the calculation of the diffusion coefficient, the concentrations from specific gravity measurements and from a material balance were used. This resulted in a deviation of 1.3% in the calculated diffusion coefficients. Thus it is advisable to use the material balance equation to obtain the final lower compartment liquid concentration i.e. C_3 when the ambient temperature operation method of terminating was applied to terminate a high temperature run.

(d) To verify the literature information (Doane and Drickamer (40)) that pressure variations up to 25 lb./in^2 gauge have practically no effect on the diffusion coefficient, tests are carried out with the cell described above. The experiments were conducted with a 50 mole % solution of benzene in n-heptane at 25°C (see Table 4-4.2). The experimental coefficient determined at 25 lb./in^2 gauge was 0.06% smaller than that determined at atmospheric pressure. The discrepancy between the two results is not sufficient to class it as being due to the effect of pressure. The experimental error is considerably higher i.e. ± 2%.

(e) It is not recommended that a short pre-run be carried out for the establishment of a steady state concentration gradient in the diaphragm. The reasons for this are given by Holmes (89). This is justified if the following structural features of the cell and the operating conditions are observed: the ratio of the pore volume in the diaphragm to one compartment volume is about 0.02; the ratio $\left(\frac{\Delta C_i}{\Delta C_f}\right)$ is about 2.

Also the determinations of the cell constant β should be carried out under the same operating conditions as those to be used in the subsequent determinations of the diffusion coefficients, the temperature effect being made negligible due to the design of the cell.

(f) The requirement of chemical purity of the test liquids and of mercury used in the operation of a cell is self-evident. In this work the mercury was purified after every run (i) by filtering through filter paper with a pin hole and (ii) first washing with 0.25% nitric acid for 6 hrs. and then with distilled water as shown in Fig. 4-4.1 , p.143.

The other important fact to be pointed out is the requirement of the test liquids to be free of dissolved gases. The slightest trace of air or other inert gas in any of the liquids is sufficient to air-lock the diaphragm pores in operations at elevated temperatures. To avoid this the test liquids must be refluxed, for a sufficiently long period, before the run.

Table 4-4.2

Summary of runs at constant temperature and varying pressures with the cell developed in this work.

Experimental diffusion coefficient of benzene-n-heptane system for the concentration of 50 mole percent at 25°C.

Stirrer speed = 40 r.p.m. ; run time = 24 hrs.

Cell used = D

Run Code	Date	Psig	Concentration @				Cavg., $\frac{gm}{100cm^3}$	x_A m.f.	Elapsed time t (hr.)	β Fig(4-3.5)	$D_{AB} x10^5$ cm²/sec.
			C_1	C_2	C_3	C_4					
D1	12.2.73	0	39.066	28.008	35.212	32.357	33.537	0.5055	72	0.27125	2.5094
D2	20.2.73	25	39.066	28.008	35.0145	32.1597	33.537	0.5055	96	0.27142	2.5079

$$\% \text{ deviation} = \left[\frac{D_{AB} \text{ at 0 Psig} - D_{AB} \text{ at 25 Psig}}{D_{AB} \text{ at 25 Psig}}\right] \times 100 = 0.0593\%$$

@ Concentration in (gm-benzene/100cm³ at 25°C)

PART 5 MATERIALS AND THEIR PHYSICAL PROPERTIES

Materials and their physical properties

5-1 Suppliers of the Chemicals used

The chemicals used were obtained from the sources shown in Table 5-1.1. All chemicals were used without further purification, as all of them were of the "analytical reagent" grade.

Table 5-1.1 Sources and quality of test liquids

Chemical (grade)	Source
Acetone (A.R.)	Fisons Scientific Apparatus Ltd., Loughborough, England.
Ethanol (A.R.)	James Burrough Ltd., 60, Montford Place, London S.E.11.
Chloroform (A.R.)	B.D.H. Chemicals Ltd., Poole, England.
$AgNO_3$ solution (A.R.)	B.D.H. Chemicals Ltd., Poole, England.
KCl (A.R.)	B.D.H. Chemicals Ltd., Poole, England.
Mercury	Harrison, Clark Ltd., Benfleet, London.

5-2 Physical properties of pure liquids

Table 5-2.1 shows some of the physical properties for pure acetone, chloroform, ethanol and water at various temperatures. These properties are self-diffusion coefficients, molal volumes, latent heats of vaporization and latent heats of vaporization due to hydrogen bonding. The sources of the data are indicated by the references also given in this Table.

Table 5-2.1 Physical properties of pure liquids

T °C	$D^* \times 10^5$ cm²/sec.	ref.	$\bar{V}$ cm³/gmole	ref.	$\Delta\bar{H}_x$ cal/gmole	ref.	$\Delta\bar{H}_{x-H}$ cal/gmole	ref.
	Acetone:							
25	4.835	43	74.01	196	7608	196	-	
35	5.380*	-	75.06	196	7498	196	-	
40	5.660*	-	75.75	196	7439	196	-	
45	5.980*	-	76.25	196	7373	196	-	
55	6.750*	-	77.46	196	7245	196	-	
60	7.000	106	78.00	196	7174	196	-	
	Chloroform:							
25	2.580	43	80.75	43	7442	196	-	
40	3.110*	-	82.63	196	7274	196	-	
55	3.700*	-	84.60	196	7100	196	-	
	Ethanol:							
25	1.01	43	58.68	196	10010.0	196	5500	18
40	1.50	43	59.67	196	9905.5	196	5380	18
58	2.25	43	61.02	196	9710.0	196	5180	18
73	3.04*	-	62.13	196	9495.0	196	5100	18
85	3.68*	-	-	-	9300.0	196	5000	18
	Water:							
25	2.236	133	18.07	196	10484.5	196	5250	18
35	2.900	133	18.12	196	10385.6	196	5190	18
40	3.300	43	18.16	43	10338.2	196	5160	18
45	3.680	43	18.19	43	10286.6	196	5140	18
55	4.580	43	18.27	43	10192.0	196	5070	18
58	4.880	43	18.36	43	10161.0	196	5050	18
65	5.500	43	18.37	43	10093.0	196	5000	18
73	6.260	43	18.54	196	10008.0	196	4970	18
75	6.420	43	18.56	196	9989.6	196	4960	18
85	7.410	43	18.60	196	9886.3	196	4900	18

* D^* are estimated from eq. (2-5.1) using the known value of D^* at 25°C

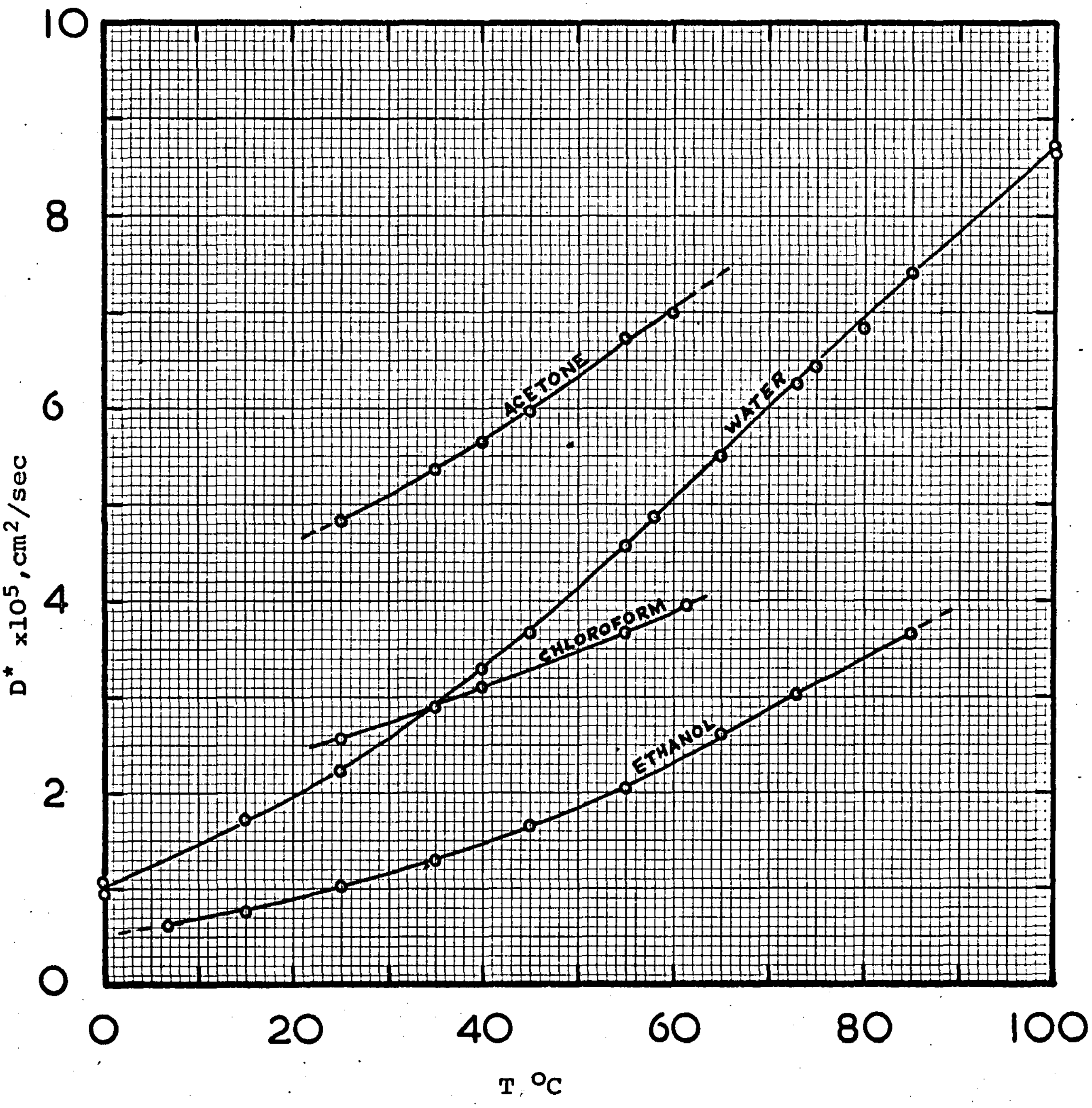


Figure 5-2.1 Self-diffusion coefficients of pure liquids (ref.43,106 and also see Appendix 3-3.1a)

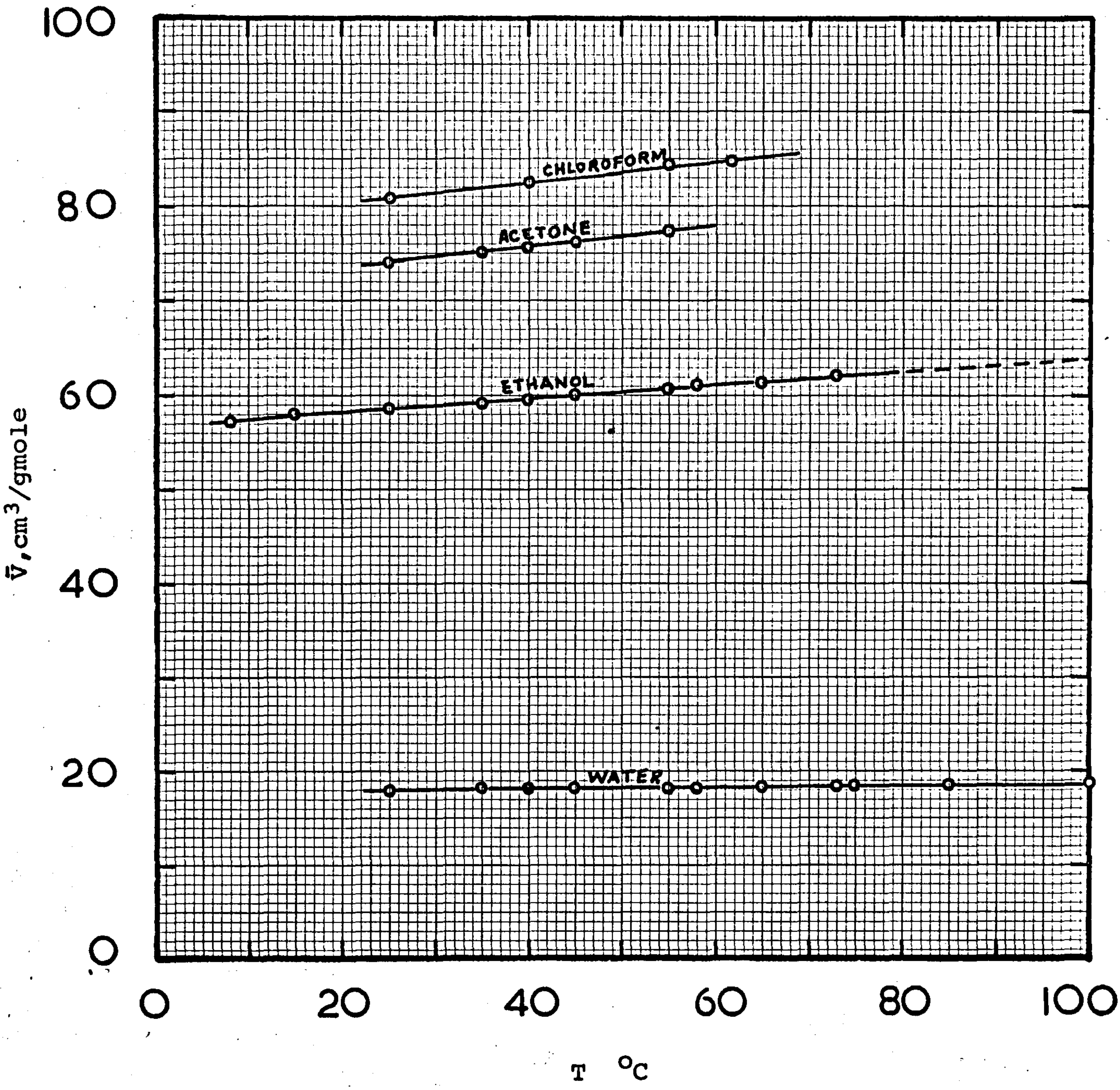


Figure 5-2.2 Molal volume of pure liquids (ref.43,196)

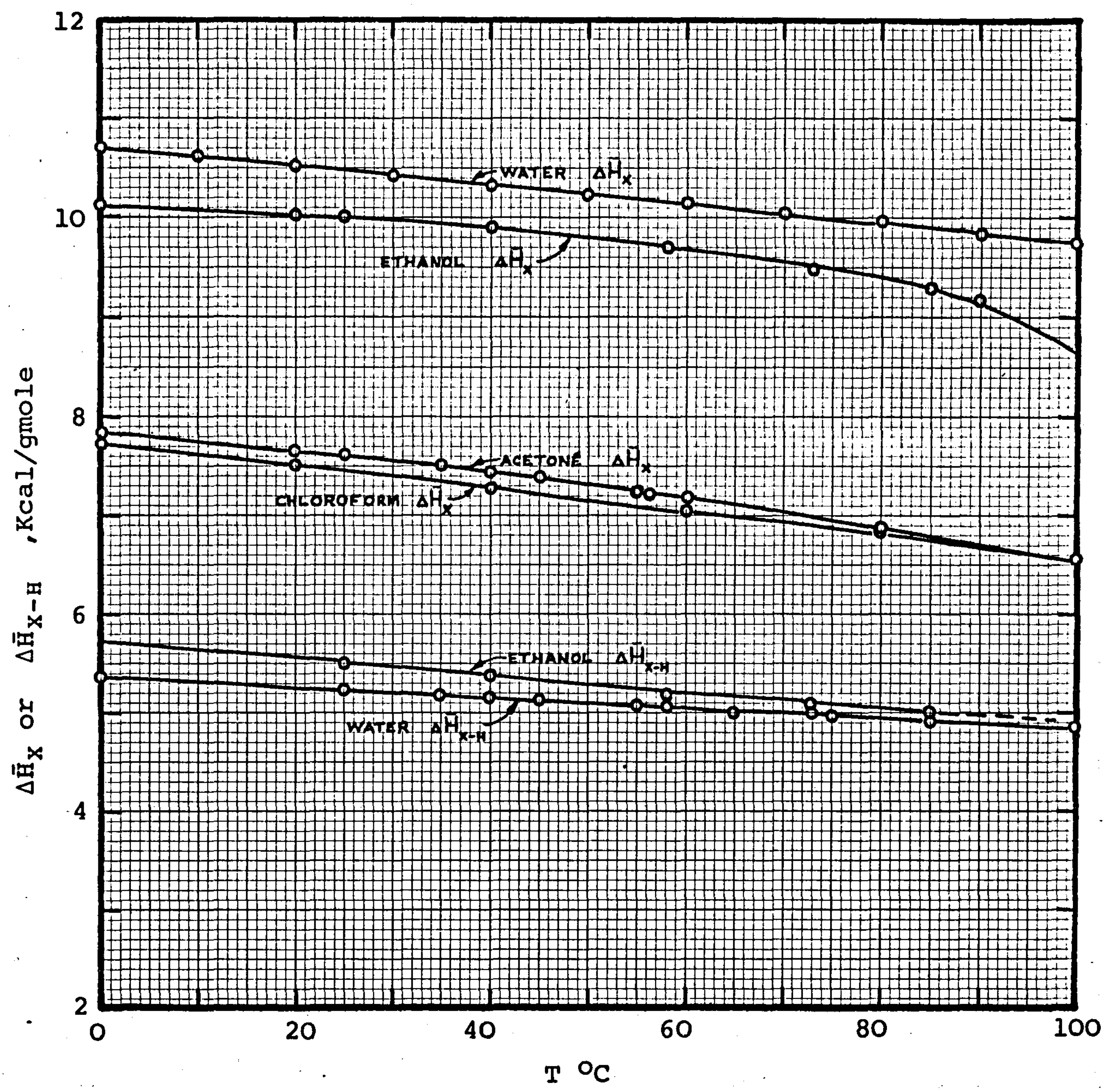


Figure 5-2.3 Heats of vaporisation and heats of vaporisation due to hydrogen bonding for pure liquids (ref.196,153,214, 168 and 18)

5-3 Physical properties of binary mixtures

The physical properties of the binary liquid mixtures studied in this work i.e. ethanol-water, acetone-water and acetone-chloroform, are presented in Tables specified below.

Viscosity : Viscosity data at various temperatures are presented in

Tables 5-3.1a, 5-3.2a, and 5-3.3a, p 162-165.

They were obtained by extrapolation or interpolation of the data found in literature and presented in Figures 5-3.1a, 5-3.2a and 5-3.3a, p 155-157.

Density : Densities for the three binary mixtures for a range of concentrations at various temperatures are reported in Tables 4-3.2, 4-3.3, 4-3.3a, and 4-3.4, p 135-138.

The densities of acetone-water mixtures at 25°C and the acetone-chloroform mixtures at 40°C, 50°C and 55°C were determined experimentally by this author. The densities at other temperatures for these two binary systems and for the ethanol-water system were obtained from the literature.

Thermodynamic factor : The values of the thermodynamic factor for the three binary mixtures and for various temperatures are presented in Tables 5-3.1b, 5-3.2b and 5-3.3b, p 163-166 ; and Figures 5-3.1b, 5-3.2b, and 5-3.3b, p 158-161. The value of the thermodynamic factor for the mixtures of ethanol-water at 25°C was found in the literature (73). The thermodynamic factor for the ethanol-water mixtures as well as the thermodynamic factors for acetone-water mixtures and for acetone-chloroform mixtures for all the temperatures required were calculated from the vapour pressure data or activity coefficients found in the literature. The method of calculation is shown in Table 5-3.1c for ethanol-water at 60^{o}C. The ratio $\left(\frac{\partial \ln \gamma_A}{\partial \ln x_A}\right)$ in each case is obtained graphically from the plot of $\ln \gamma_A$ against $\ln x_A$ as illustrated in Figure 5-2.1c. The sources of vapour pressure data, concentrations in the liquid and vapour phase or of the activity coefficients are given in the appropriate tables.

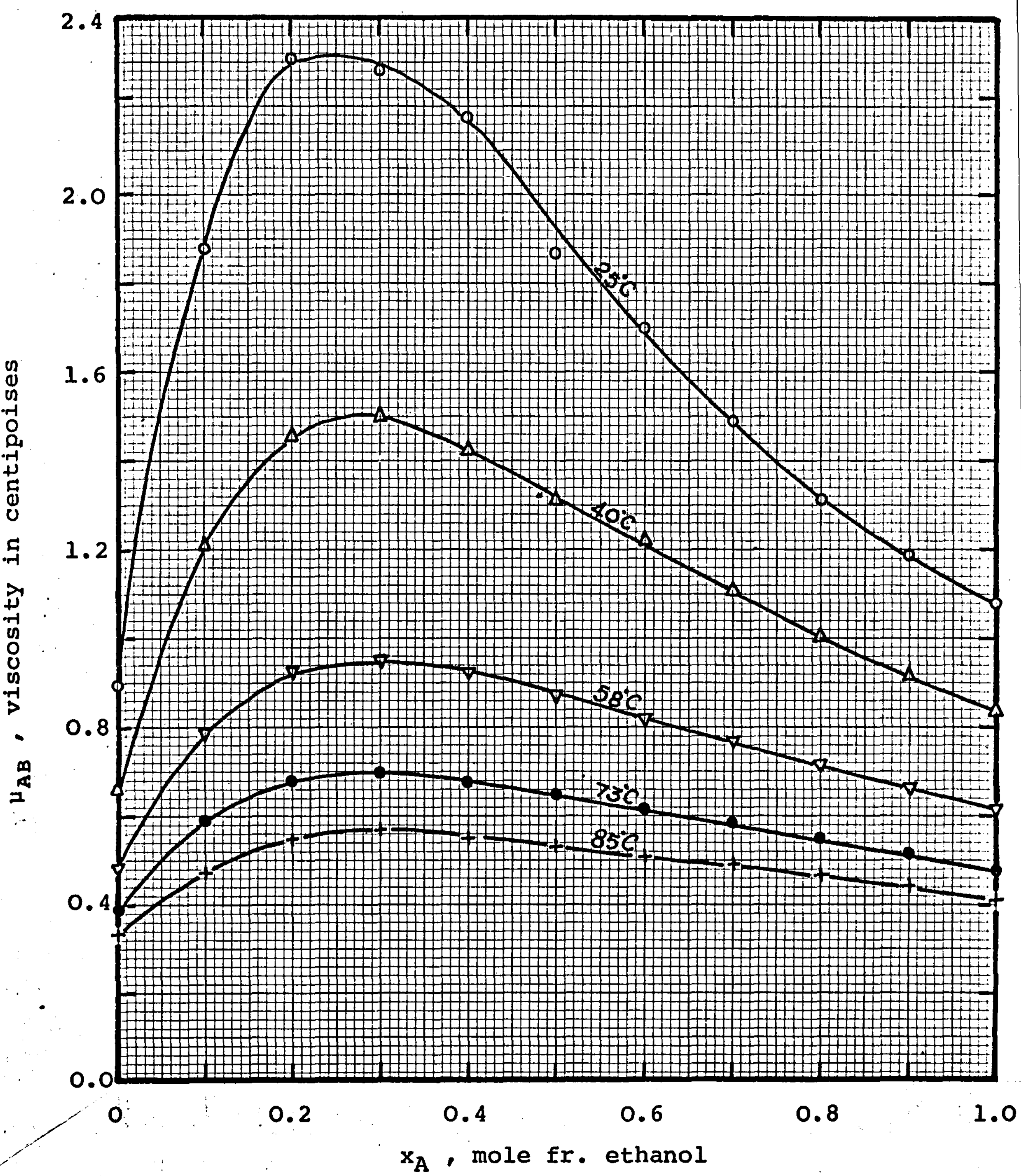


Figure 5-3.1a Viscosity of ethanol-water mixtures (obtained by extrapolation or interpolation from experimental data given in ref.197)

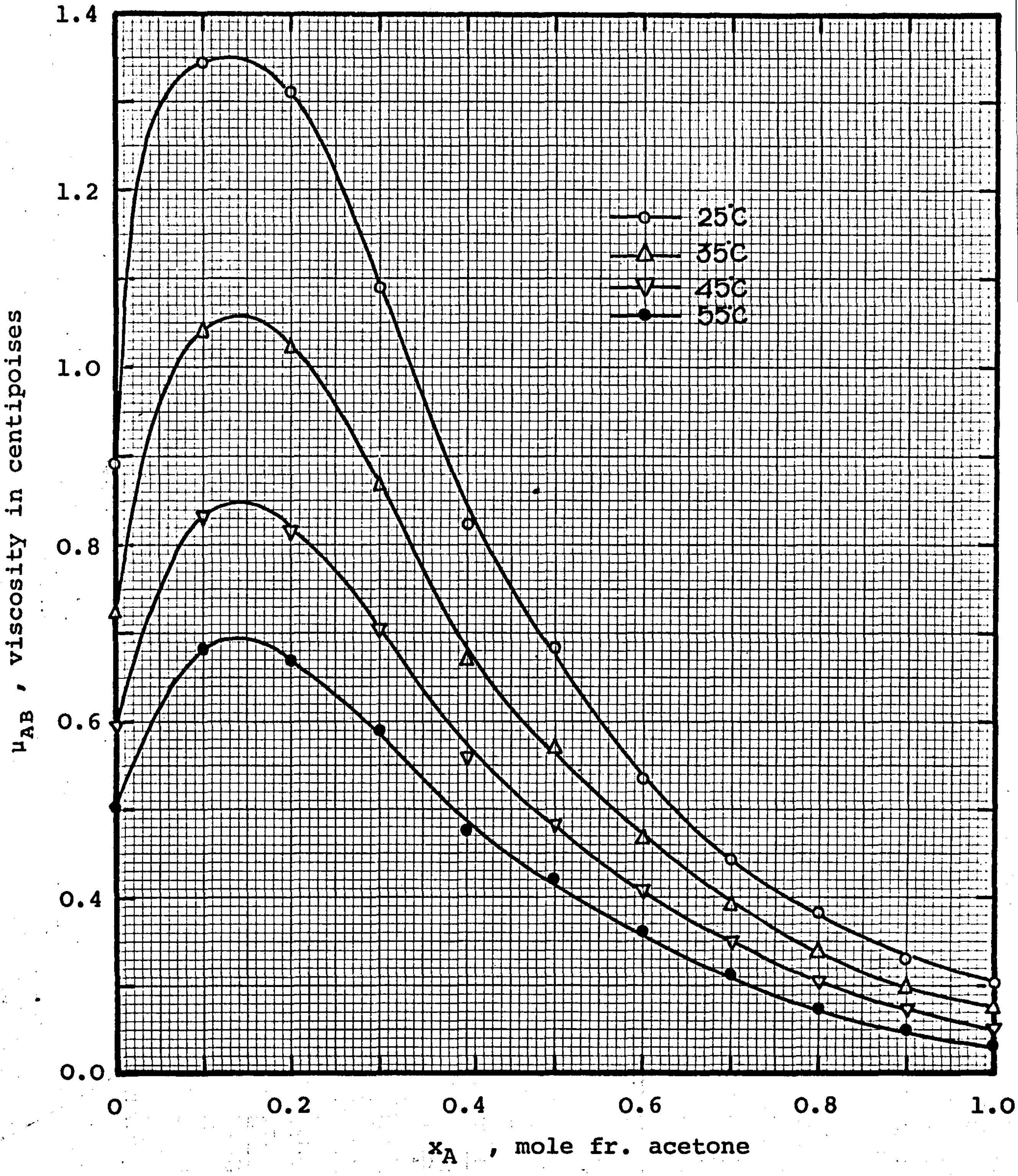


Figure 5-3.2a Viscosity of acetone-water mixtures(ref.92)

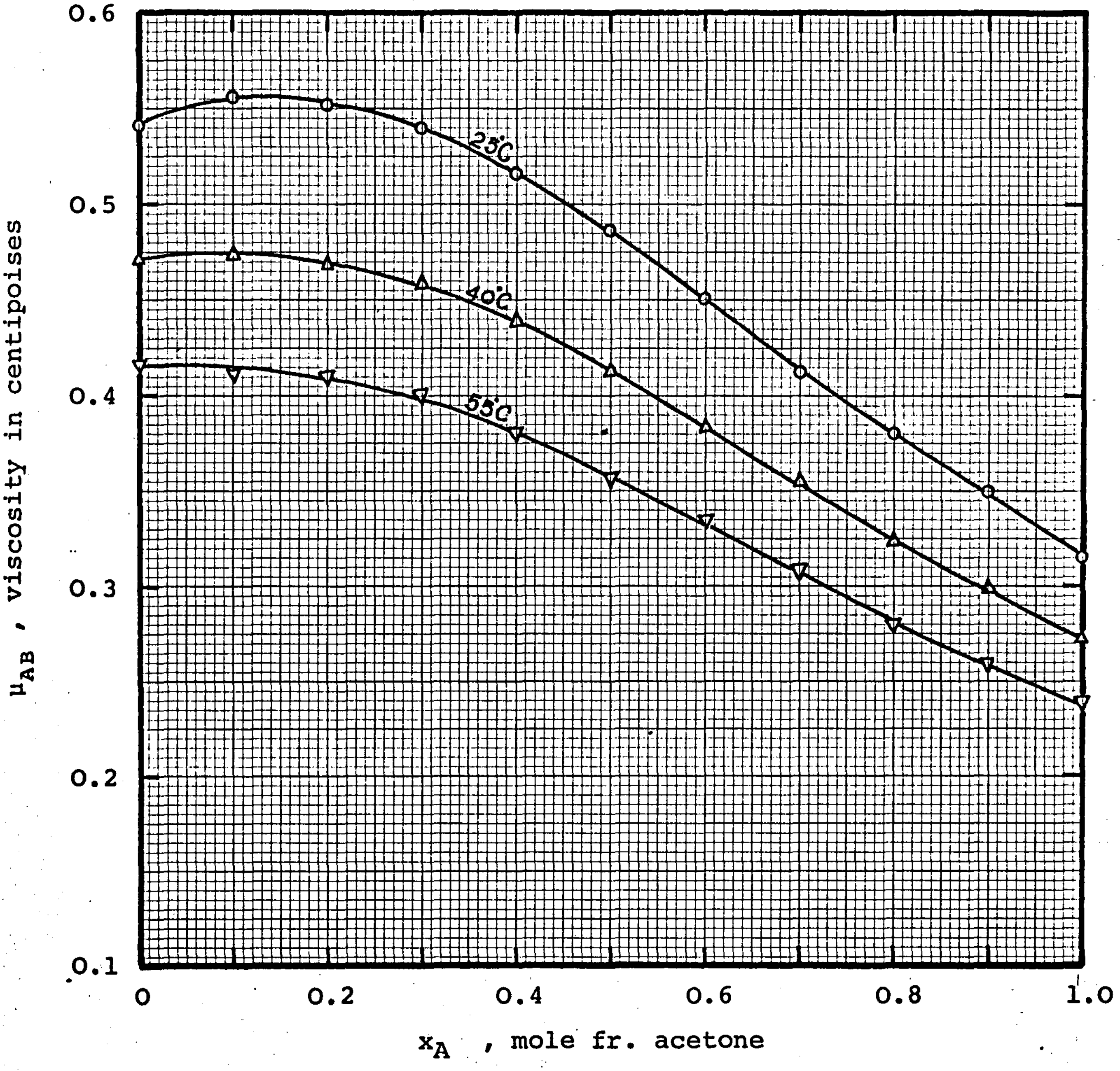


Figure 5-3.3a Viscosity of acetone-chloroform mixtures (6,141)

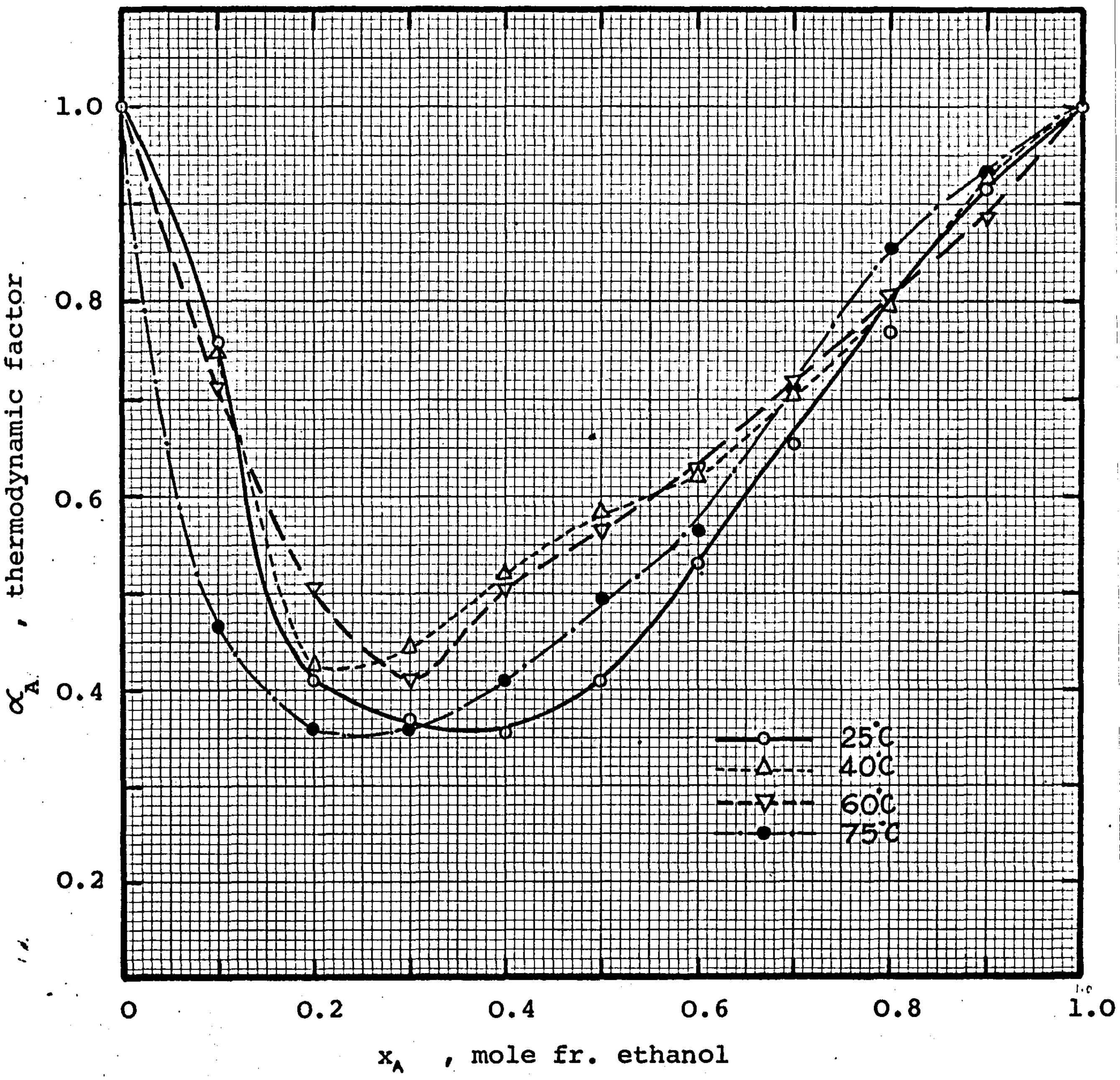


Figure 5-3.1b Thermodynamic factor for ethanol-water mixtures (ref.73,74,98,214)

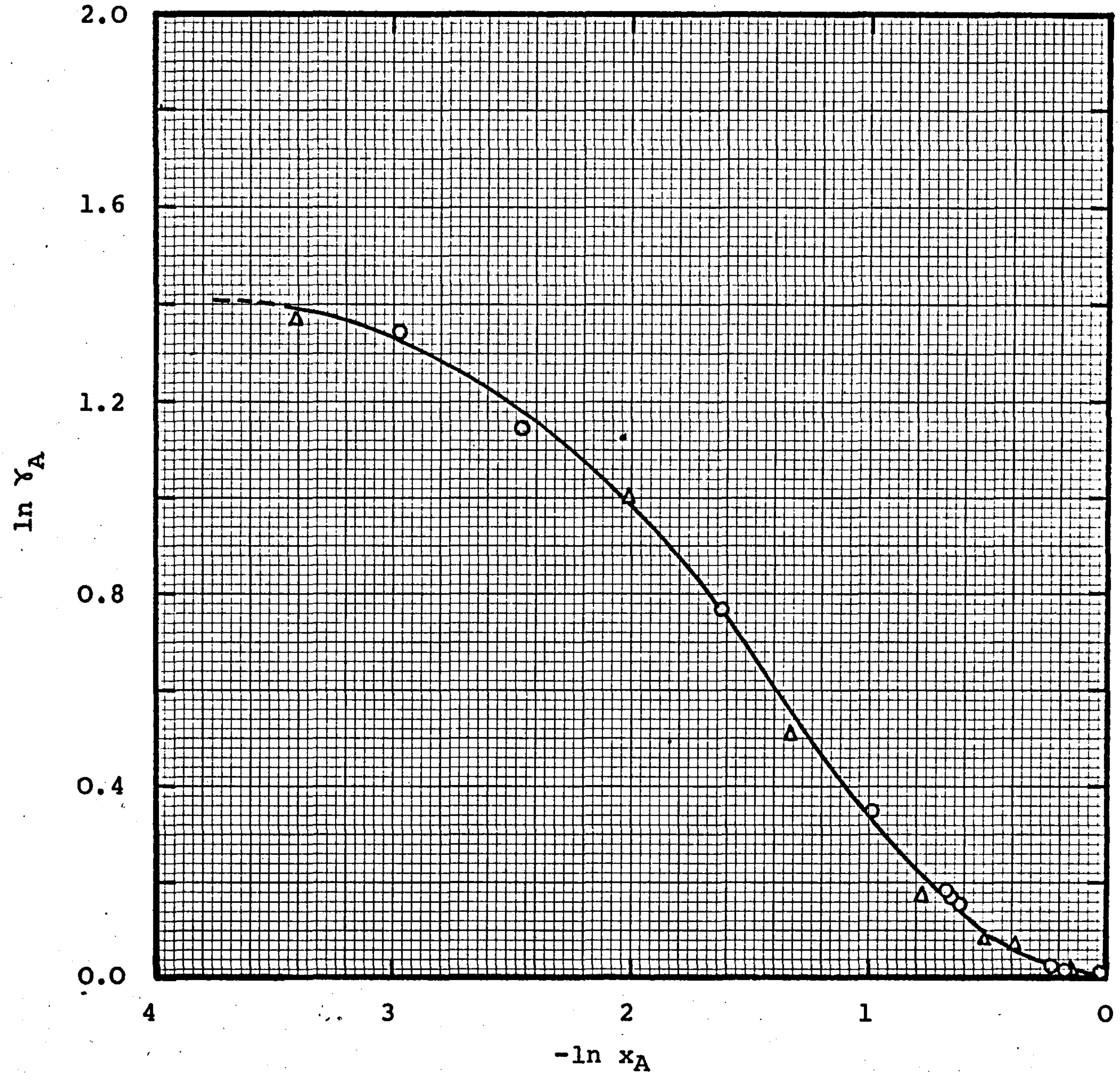


Figure 5-3.1c Calculation of thermodynamic factor for ethanol-water mixture at 60°C

Δ Udovenko, V. V., Fatkulina, L.G.,(1952)(ref.74)

o Jones, C.A., Schoenborn, E.M., Colburn, A.P., (1943) (ref.98)

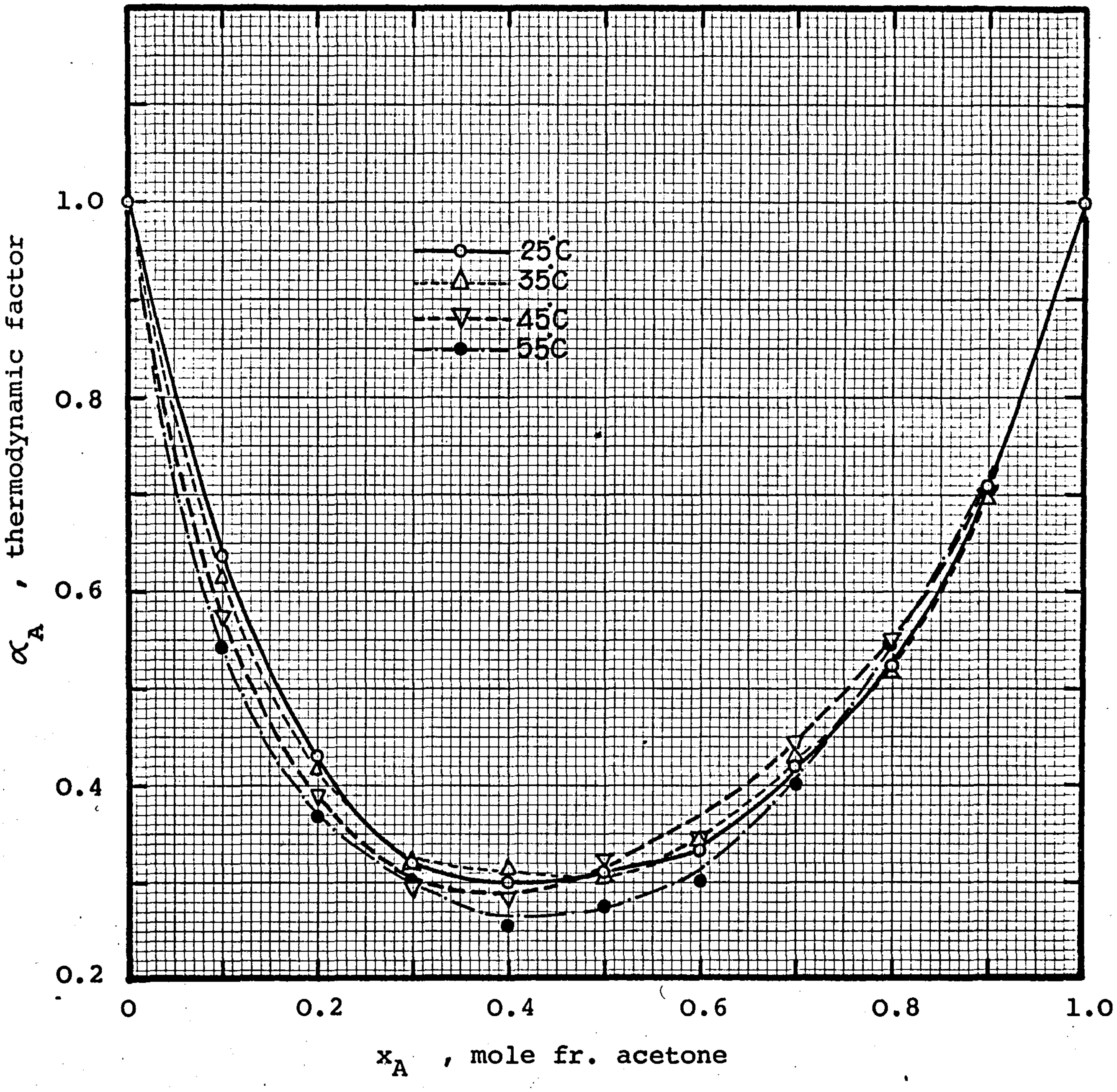


Figure 5-3.2b Thermodynamic factor for acetone-water mixtures (ref.191)

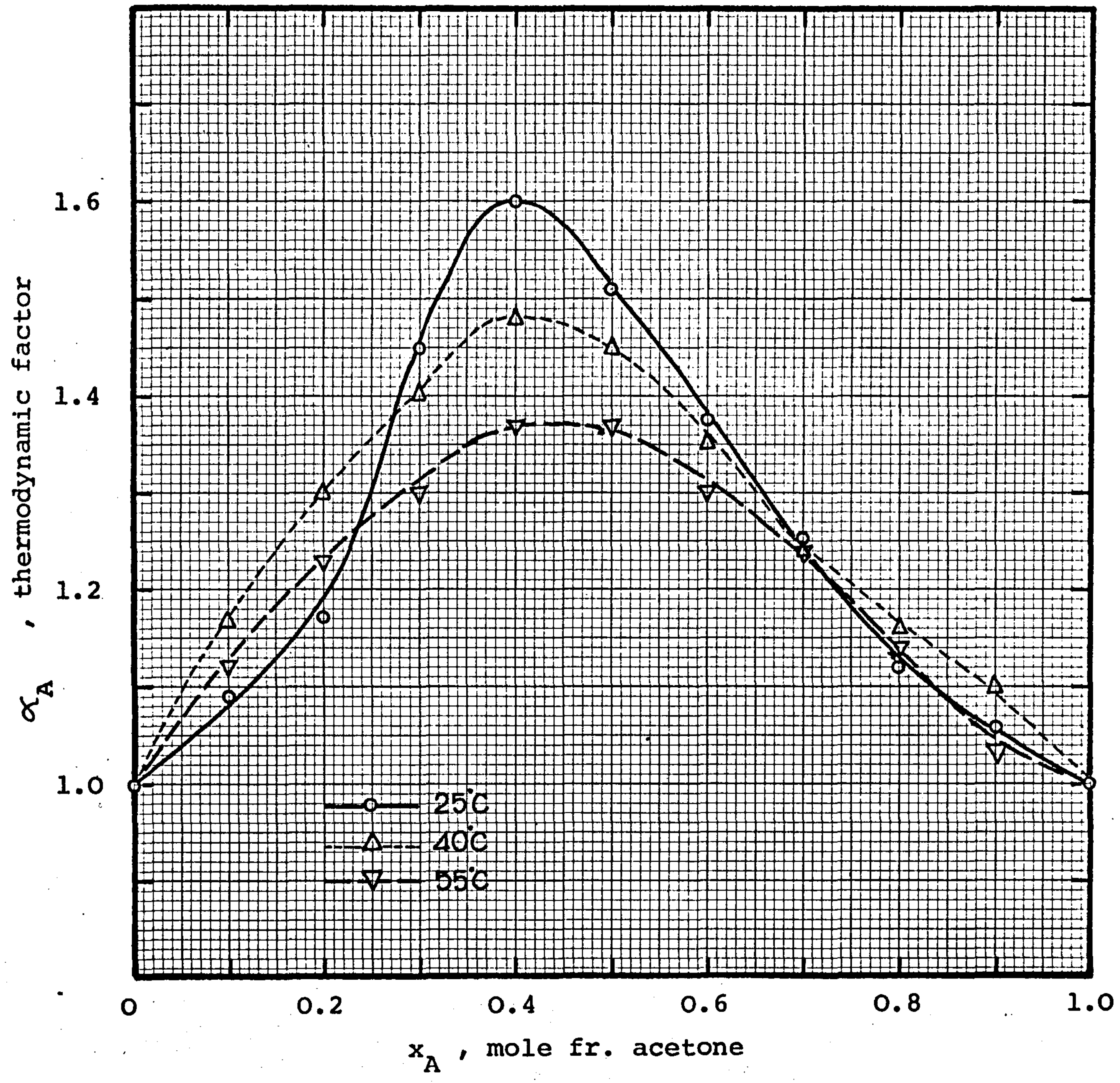


Figure 5-3.3b Thermodynamic factor for acetone-chloroform mixtures (ref.137,172)

Table 5-3.1a Viscosity of ethanol-water mixtures (ref.197)

x_A m.f. ethanol	Viscosity in c.p. at $T^{o}C$ *				
	$25^{o}C$	$40^{o}C$	$58^{o}C$	$73^{o}C$	$85^{o}C$
0.0	0.895	0.6565	0.486	0.390	0.335
0.1	1.880	1.210	0.790	0.590	0.471
0.2	2.310	1.456	0.926	0.680	0.544
0.3	2.280	1.500	0.950	0.696	0.569
0.4	2.180	1.422	0.922	0.678	0.550
0.5	1.870	1.314	0.871	0.650	0.530
0.6	1.700	1.220	0.820	0.616	0.510
0.7	1.490	1.108	0.770	0.586	0.490
0.8	1.310	1.008	0.716	0.551	0.466
0.9	1.190	0.914	0.665	0.516	0.440
1.0	1.080	0.836	0.615	0.479	0.409

* Data obtained from Figure 5-3.1a

Table 5-3.1b Thermodynamic factor for ethanol-water mixtures.

Mole fr. ethanol x_A	α_A				Mole fr. ethanol x_A	α_A			
	* 25°C	** 40°C	** 60°C	** 75°C		* 25°C	** 40°C	** 60°C	** 75°C
0.0	1.00	1.000	1.000	1.000	0.6	0.530	0.620	0.628	0.565
0.1	0.760	0.750	0.713	0.465	0.7	0.655	0.705	0.720	0.715
0.2	0.410	0.425	0.505	0.360	0.8	0.770	0.795	0.800	0.855
0.3	0.370	0.445	0.410	0.360	0.9	0.915	0.925	0.885	0.928
0.4	0.355	0.520	0.505	0.410	1.0	1.000	1.000	1.000	1.000
0.5	0.410	0.585	0.565	0.495					

* α_A at 25°C from reference (73)

** α_A at 40°C, 60°C and 75°C are calculated from the vapour liquid equilibrium data of references (74, 98, 214).

Table 5-3.2a Viscosity of actone-water mixtures (ref. 92).

Mole fr. acetone x_A	μ_{AB} in c.p.				Mole fr. acetone x_A	μ_{AB} in c.p.			
	25°C	35°C	45°C	55°C		25°C	35°C	45°C	55°C
0.0	0.8905	0.721	0.596	0.504	0.6	0.535	0.468	0.407	0.362
0.1	1.346	1.040	0.831	0.682	0.7	0.442	0.392	0.350	0.313
0.2	1.310	1.021	0.816	0.670	0.8	0.381	0.339	0.305	0.275
0.3	1.090	0.867	0.705	0.590	0.9	0.330	0.299	0.274	0.250
0.4	0.822	0.670	0.560	0.475	1.0	0.3012	0.275	0.251	0.2318
0.5	0.683	0.570	0.484	0.422					

Data obtained from Figure 5-3.2a.

Table 5-3.1c Thermodynamic factor for ethanol-water system at 60°C

x_A mole fr. ethanol	$P_A = y_A P$ mm Hg	$\gamma_A = \frac{P_A}{x_A P_A^\circ}$	Ref.	ln x_A	ln γ_A
0.033	45.6	3.926	a	-3.411	1.368
0.051	69.2	3.845	b	-2.976	1.347
0.086	97.9	3.135	b	-2.453	1.143
0.125	120.4	2.736	a	-2.079	1.007
0.197	154.1	2.155	b	-1.625	0.768
0.267	156.6	1.666	a	-1.321	0.511
0.375	193.7	1.421	b	-0.981	0.351
0.459	191.9	1.188	a	-0.779	0.172
0.509	221.6	1.198	b	-0.675	0.181
0.527	227.0	1.181	b	-0.641	0.166
0.545	230.2	1.171	b	-0.607	0.158
0.597	227.8	1.084	a	-0.516	0.081
0.682	257.9	1.074	a	-0.383	0.072
0.808	299.8	1.022	b	-0.213	0.022
0.851	313.8	1.015	b	-0.161	0.015
0.860	317.3	1.010	b	-0.151	0.00995
0.865	309.9	1.018	a	-0.145	0.0176
0.891	316.3	1.0085	a	-0.1154	0.0085
0.928	329.4	1.0084	a	-0.0747	0.0084
0.949	335.9	1.0055	a	-0.0523	0.0055
0.972	351.9	0.998	b	-0.028	-0.002
1.000	352.0	1.000	a	0.00	0.00

x_A mole fr ethanol	ln x_A	$-\frac{\partial \ln \gamma_A}{\partial \ln x_A}$ slope of Fig. 5-3.1c	$\alpha_A = 1 + \frac{\partial \ln \gamma_A}{\partial \ln x_A}$
0.0	-	-	1.000
0.1	-2.303	0.287	0.713
0.2	-1.609	0.495	0.505
0.3	-1.204	0.590	0.410
0.4	-0.916	0.495	0.505
0.5	-0.693	0.435	0.565
0.6	-0.511	0.372	0.628
0.7	-0.357	0.280	0.720
0.8	-0.223	0.200	0.800
0.9	-0.1054	0.115	0.885
1.0	0.0	-	1.00

a Udovenko, V.V., Fatkulina, L.G, (1952), (ref. 74)

b Jones, C.A., Schoenborn, E.M., and Colburn, A.P., (1943), (ref. 98)

P Total pressure

P_A Partial pressure of A

P_A^o Vapour pressure of A

y_A Mole fr. of A in vapour phase

Table 5-3.2b Thermodynamic factor for acetone-water mixtures (ref.191)

Mole fr. acetone x_A	α_A				Mole fr. acetone x_A	α_A			
	25°C	35°C	45°C	55°C		25°C	35°C	45°C	55°C
0.0	1.000	1.000	1.000	1.000	0.6	0.333	0.345	0.345	0.300
0.1	0.637	0.615	0.576	0.545	0.7	0.420	0.430	0.445	0.400
0.2	0.430	0.429	0.390	0.370	0.8	0.525	0.515	0.550	0.547
0.3	0.320	0.320	0.295	0.300	0.9	0.710	0.698	0.700	0.700
0.4	0.300	0.315	0.285	0.255	1.0	1.000	1.00	1.00	1.00
0.5	0.310	0.305	0.325	0.275					

Table 5-3.3a Viscosity of acetone-chloroform mixtures

Mole fr. acetone x_A	μ_{AB} in c.p.			Mole fr. acetone x_A	μ_{AB} in c.p.		
	25°C *	40°C *	55°C **		25°C *	40°C *	55°C **
0.0	0.541	0.472	0.416	0.6	0.450	0.384	0.335
0.1	0.556	0.473	0.410	0.7	0.412	0.355	0.308
0.2	0.552	0.469	0.411	0.8	0.380	0.323	0.280
0.3	0.540	0.458	0.400	0.9	0.350	0.299	0.260
0.4	0.516	0.439	0.381	1.0	0.315	0.272	0.239
0.5	0.486	0.412	0.357				

* Nigham (141)
* Anderson (6)
** Obtained by extrapolation

Table 5-3.3b Thermodynamic factor for acetone-chloroform mixtures.

Mole fr. acetone x_A	α_A			Mole fr. acetone A	α_A		
	25°C*	40°C**	55°C**		25°C*	40°C**	55°C**
0.0	1.00	1.000	1.00	0.6	1.376	1.350	1.30
0.1	1.09	1.166	1.12	0.7	1.253	1.240	1.240
0.2	1.17	1.300	1.23	0.8	1.121	1.160	1.14
0.3	1.45	1.400	1.300	0.9	1.060	1.100	1.03
0.4	1.60	1.480	1.37	1.0	1.000	1.0000	1.000
0.5	1.51	1.45	1.37				

* Mueller & Kearns, 1958 (ref.137)

** Röck & Schröder, 1957 (ref.172)

PART 6 EXPERIMENTAL RESULTS

PART 6-1 Presentation of experimental results

The primary experimental results, together with the experimental integral diffusion coefficients calculated from them, are reported in Tables 6-1.1, 6-1.2, 6-1.3 and 6-1.4. They are also shown graphically in Figures 6-1.1, 6-2.1, 6-3.1. The experimental integral diffusion coefficients were converted into differential diffusion coefficients in Tables 6-2.1, 6-2.3 and 6-2.5 and then plotted in Figures 6-1.2, 6-2.2 and 6-3.2 as differential diffusion coefficients against mole fraction concentrations. These Figures (i.e. 6-1.2, 6-2.2, and 6-3.2) were then used to obtain smoothed differential diffusion coefficients which subsequently were recorded in Tables 6-2.2, 6-2.4, and 6-2.6. The smoothed differential diffusion coefficients were extrapolated or interpolated in order to obtain differential diffusion coefficients at normal boiling points. The interpolation or extrapolation was done in Figures 6-1.3, 6-2.3 and 6-3.3 by plotting $\ln D_{AB}$ against the reciprocal of absolute temperature. This type of plot gives a straight line from which the differential diffusion coefficient is read off from the reciprocal of the boiling point temperature. The differential diffusion coefficients obtained by this method, for all three binary systems, are recorded in Table 6-3.1 and are also shown in Figures 6-1.4, 6-2.4 and 6-3.4.

Figures 6-1.1, 6-2.1 and 6-3.1 were used to obtain, by extrapolation, the diffusion coefficients at infinite dilution. In accordance with the method of Dullien and Shemilt (45) for obtaining differential diffusion coefficients these coefficients at infinite dilution are identical with integral coefficients.

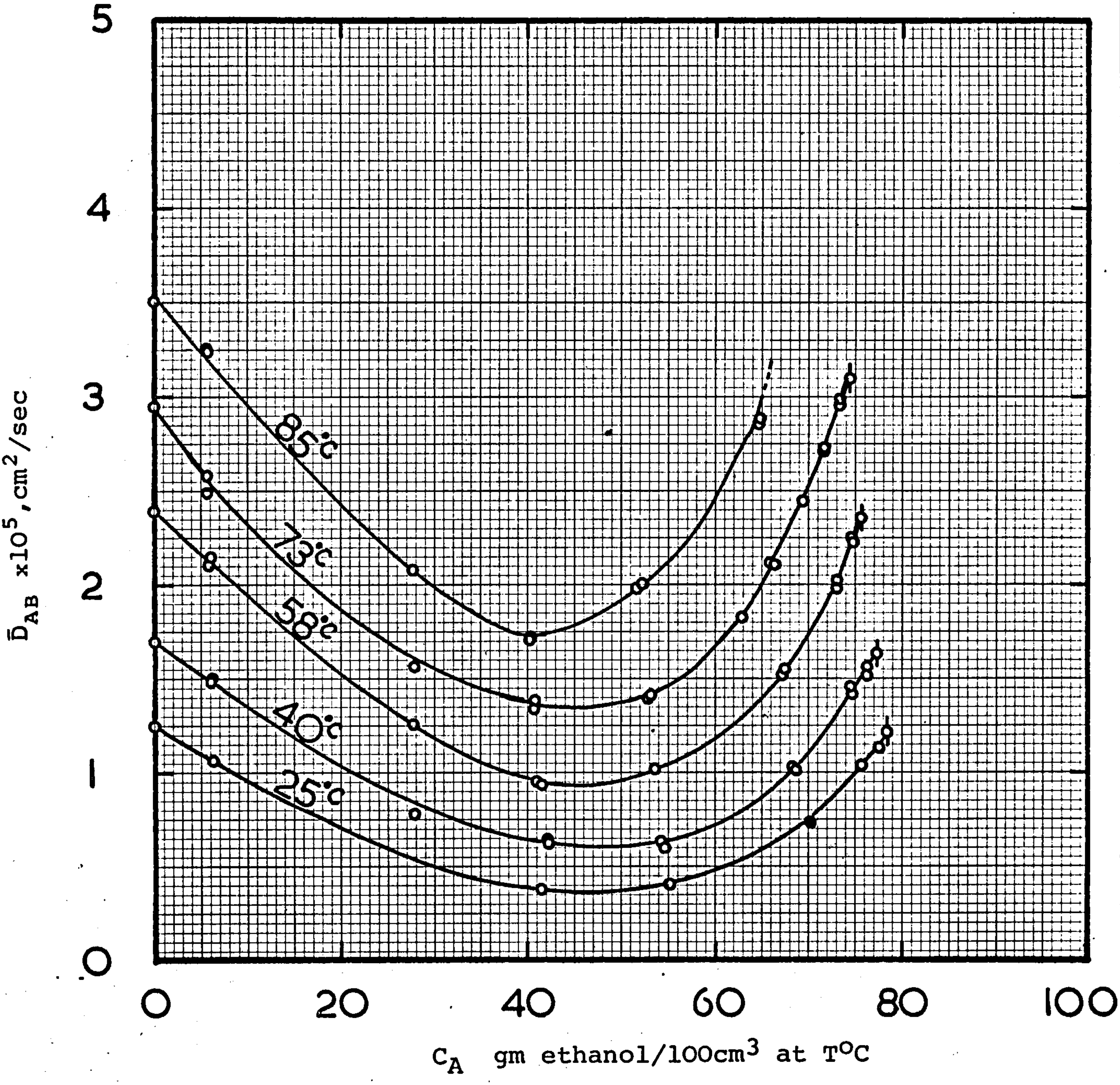


Figure 6-1.1 Integral diffusion coefficients vs volumetric concentration for ethanol-water mixtures

ϕ Value of $\bar{D}_{AB}$ for pure ethanol

● Three data points

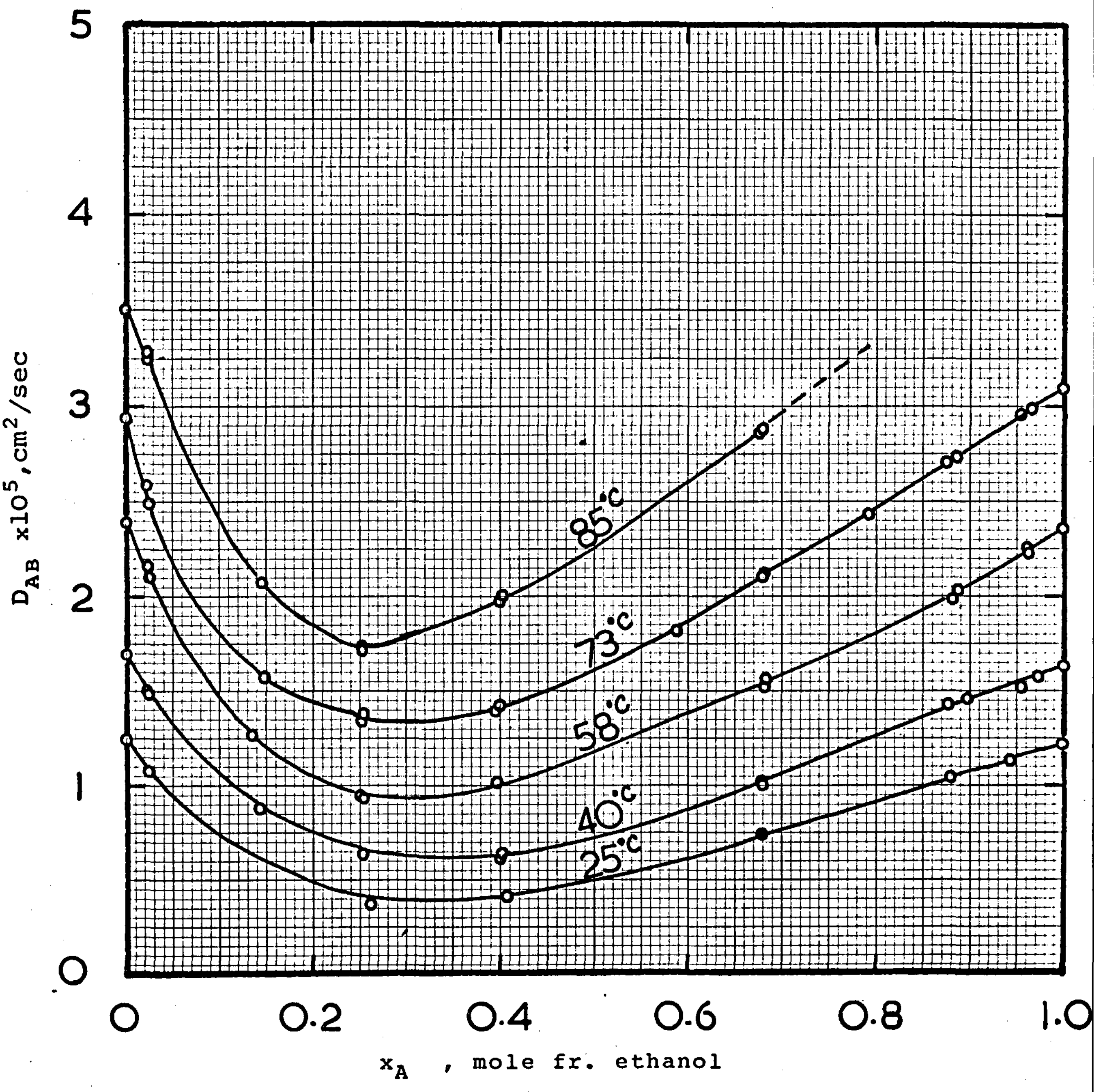


Figure 6-1.2 Differential diffusion coefficients vs mole fr. concentration for ethanol-water mixtures.

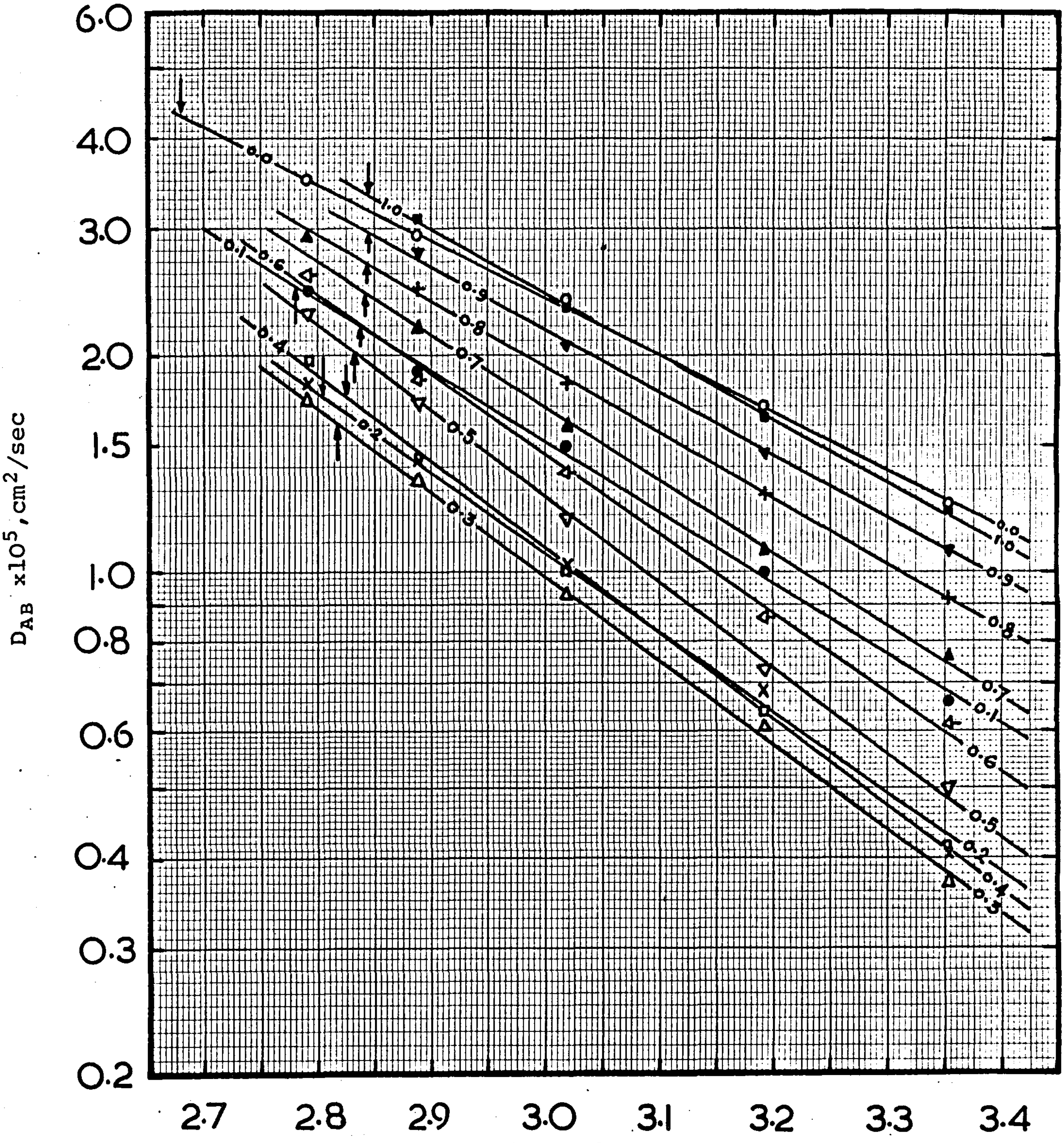


Figure 6-1.3 Variation of $\ln D_{AB}$ with (1/T) for ethanol-water mixtures (data of this work)

↑ ↓ indicate boiling point

Numbers on lines indicate concentration of ethanol, m.f.

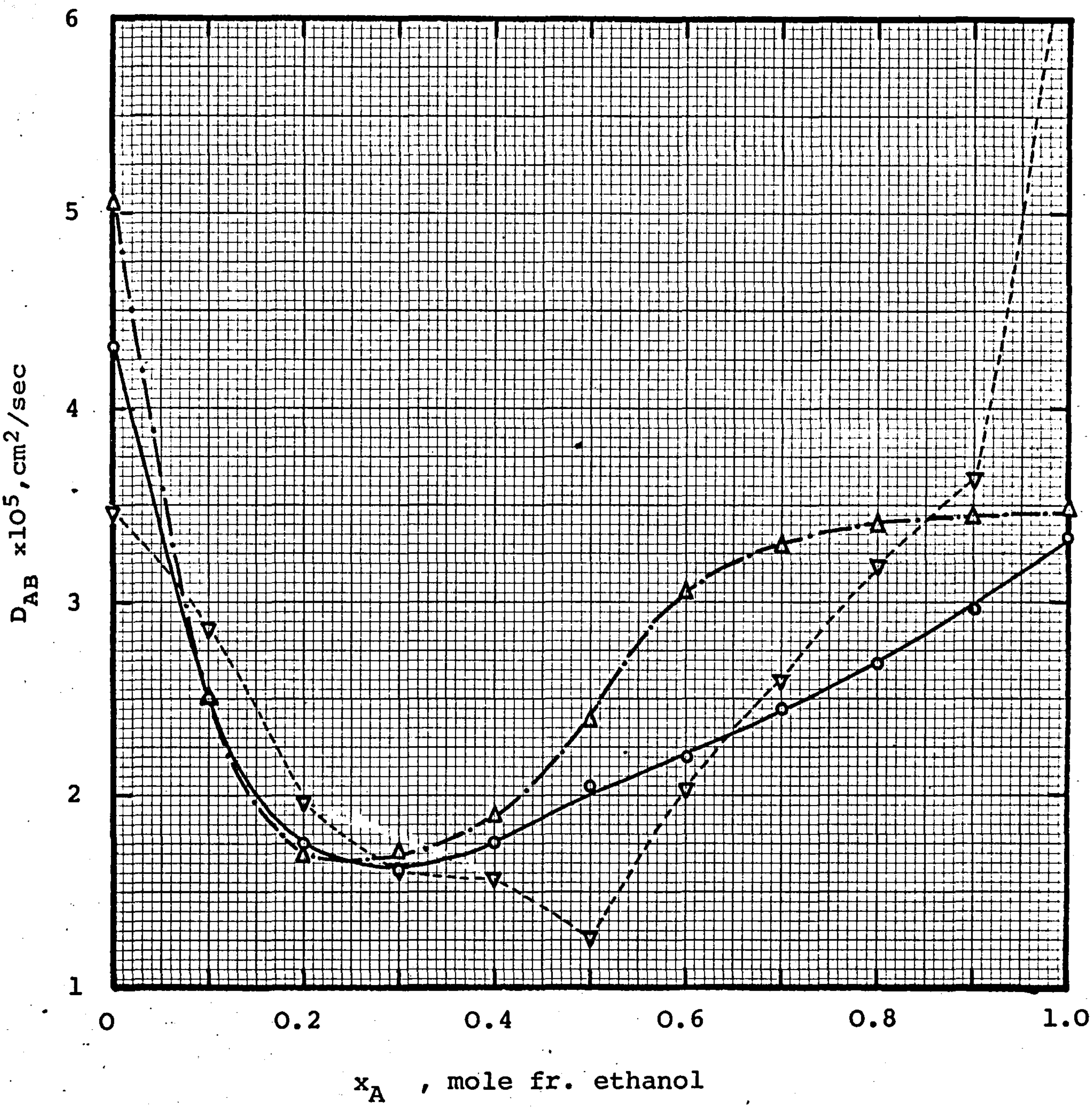


Figure 6-1.4 Differential diffusion coefficients at normal boiling points for ethanol-water mixtures.

o This work

Δ Pratt and Wakeham (158)

∇ Smith and Storrow (183)

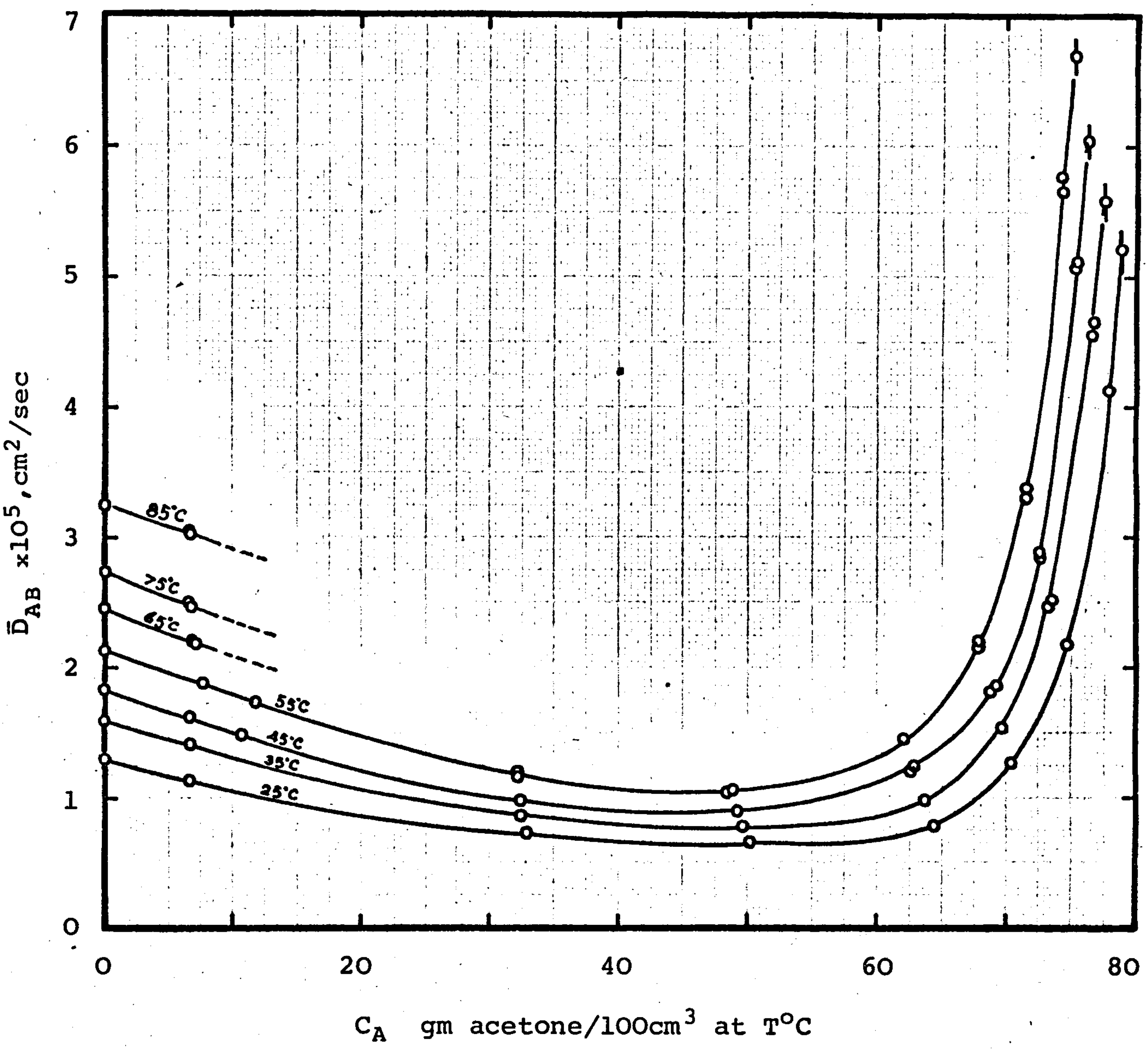


Figure 6-2.1 Integral diffusion coefficients vs volumetric concentration for acetone-water mixtures.

ϕ indicate the value of $\bar{D}_{AB}$ for pure acetone

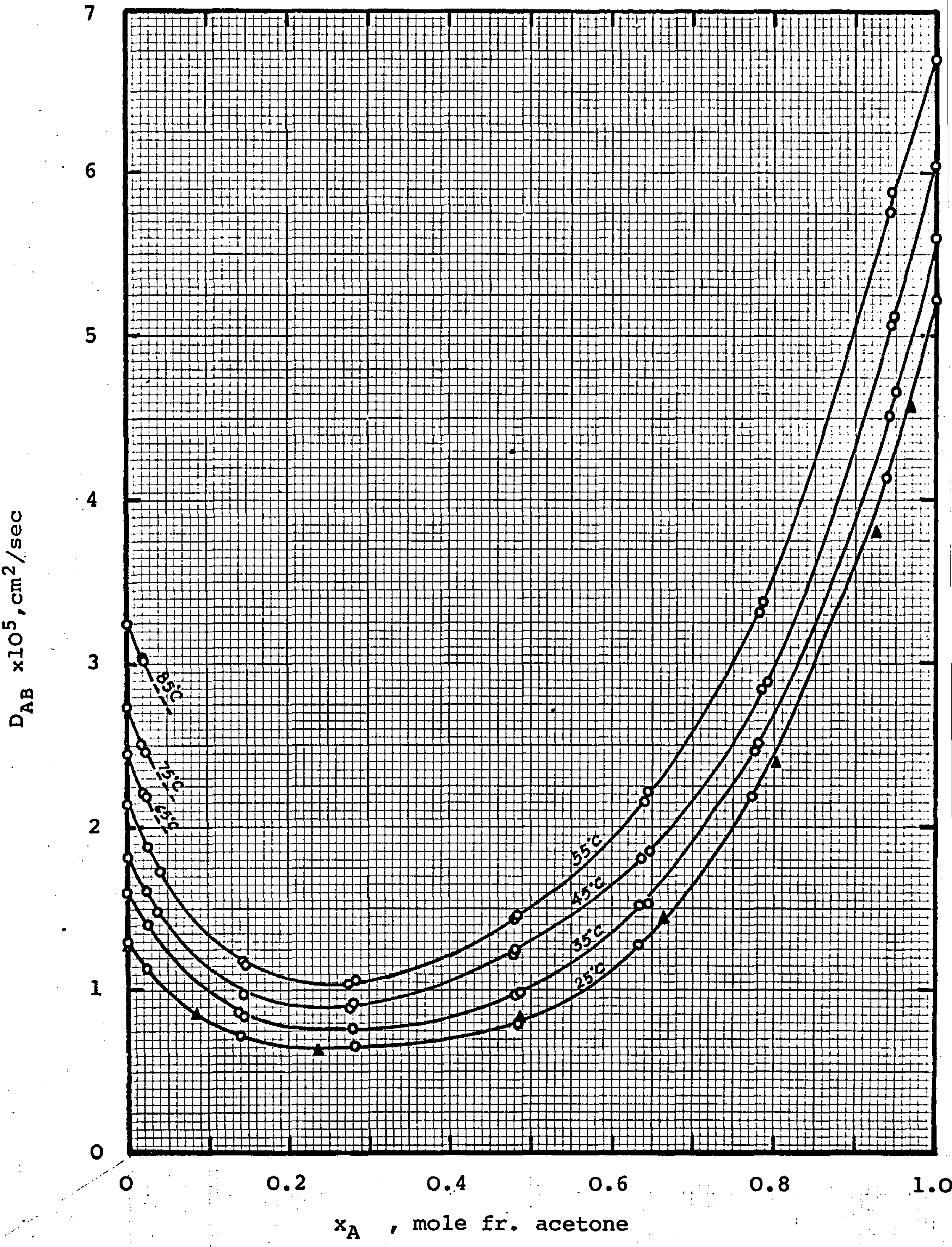


Figure 6-2.2 Differential diffusion coefficients vs mole fr. concentration for acetone-water mixtures.

o This work

▲ Anderson et al (6)

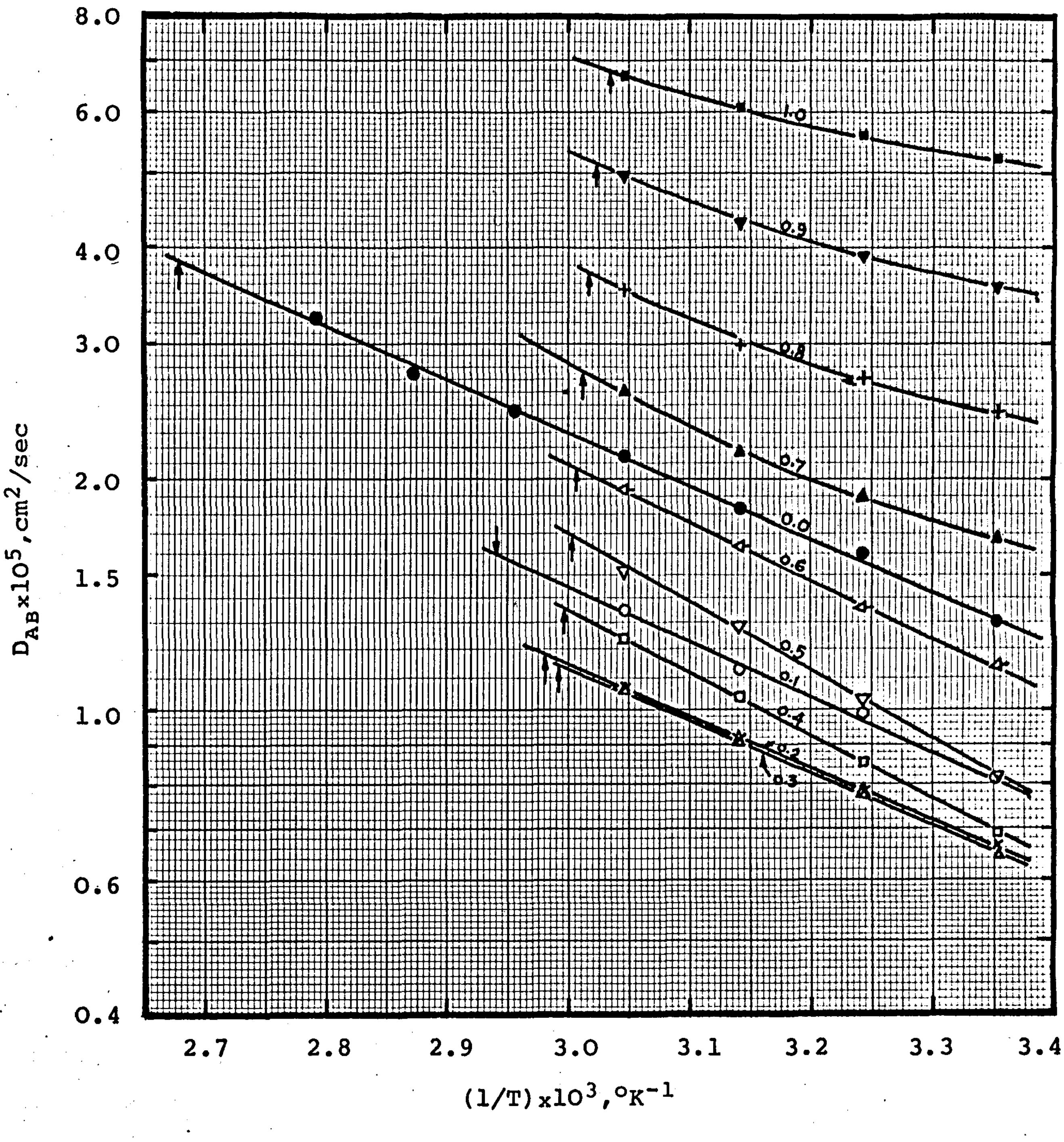


Figure 6-2.3 Variation of ln D_{AB} with (1/T) for acetone-water mixtures

↑ ↓ indicate boiling point

Numbers on lines indicate concentration of acetone in mole fr.

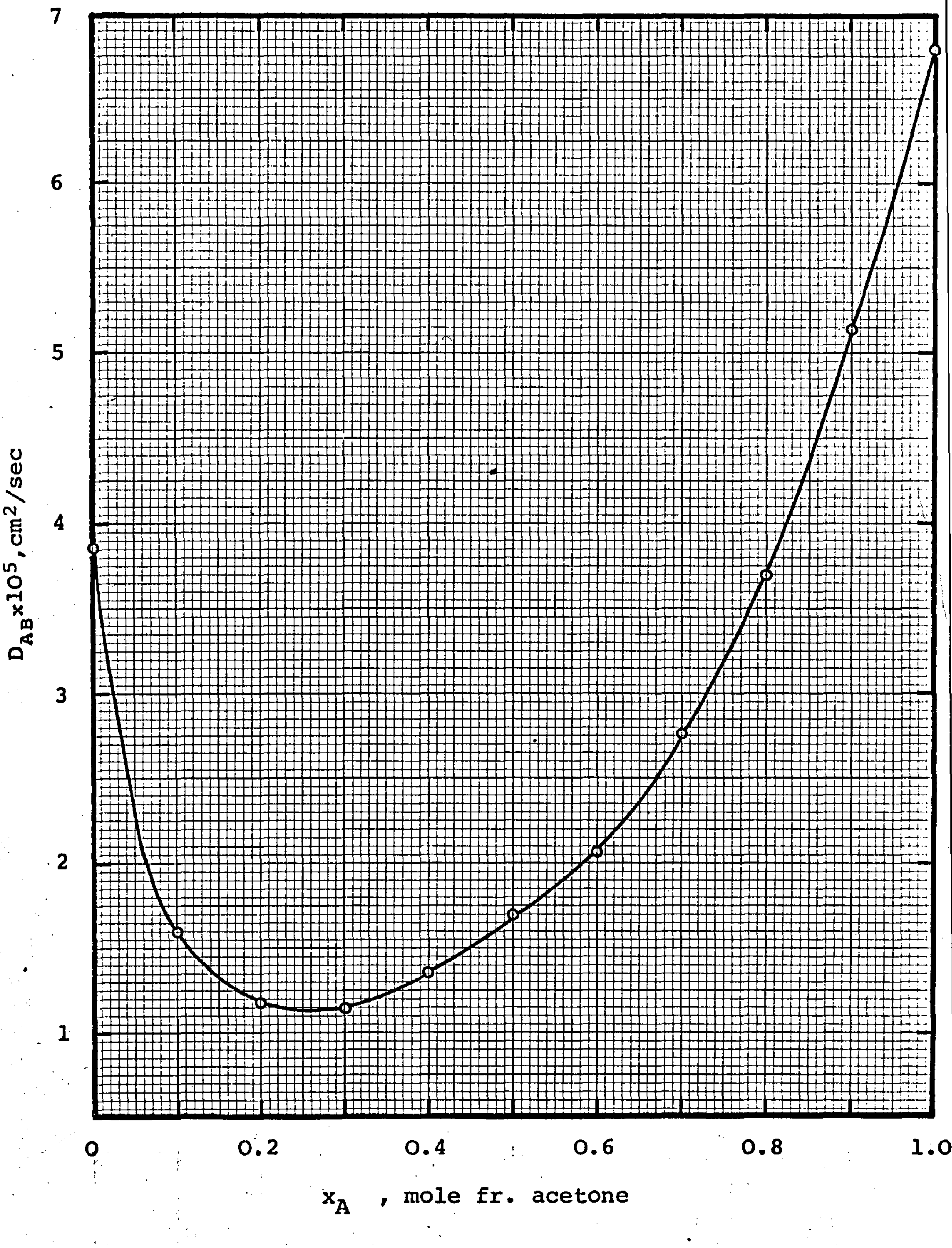


Figure 6-2.4 Differential diffusion coefficients at normal boiling points for acetone-water mixtures.

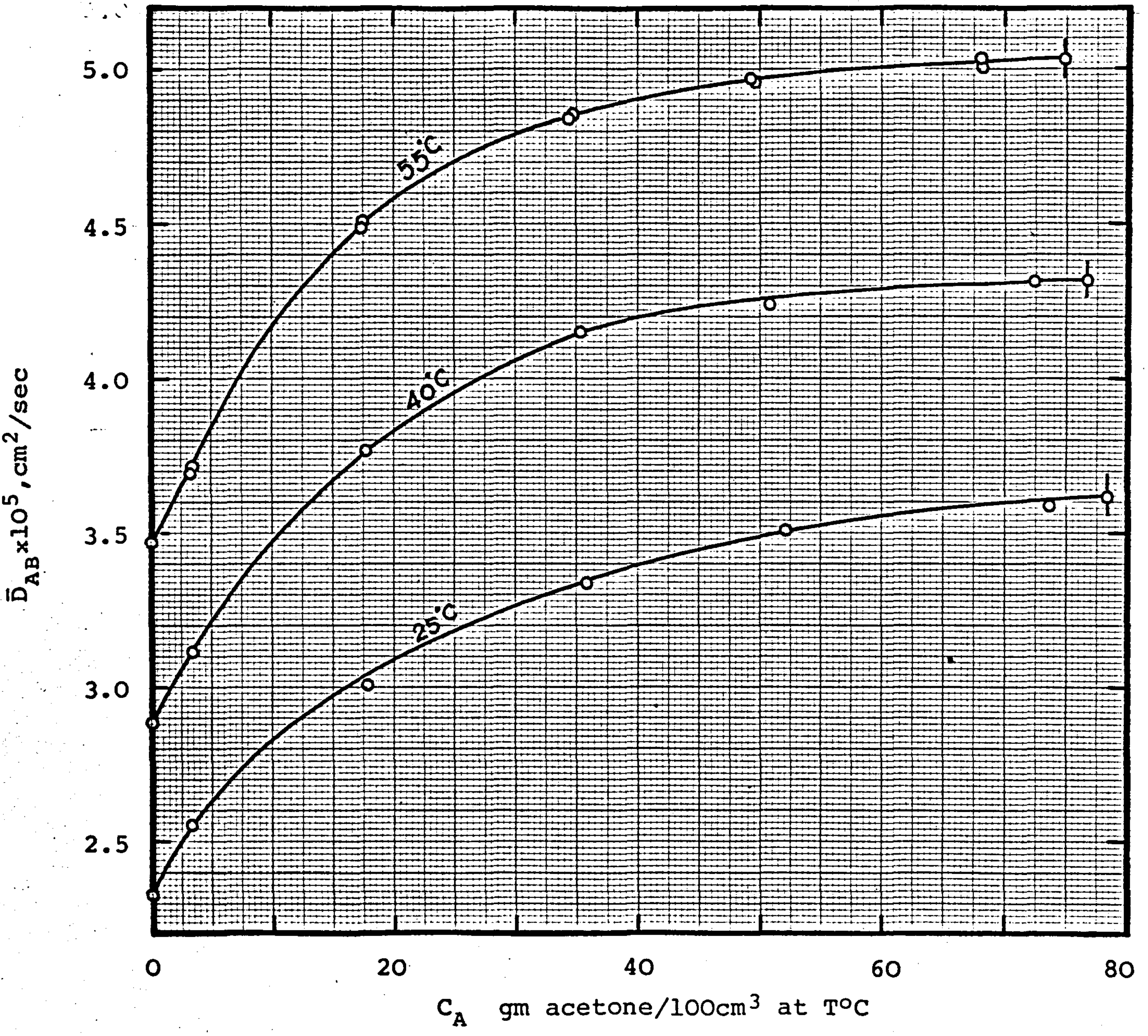


Figure 6-3.1 Integral diffusion coefficients vs volumetric concentration for acetone-chloroform mixtures.

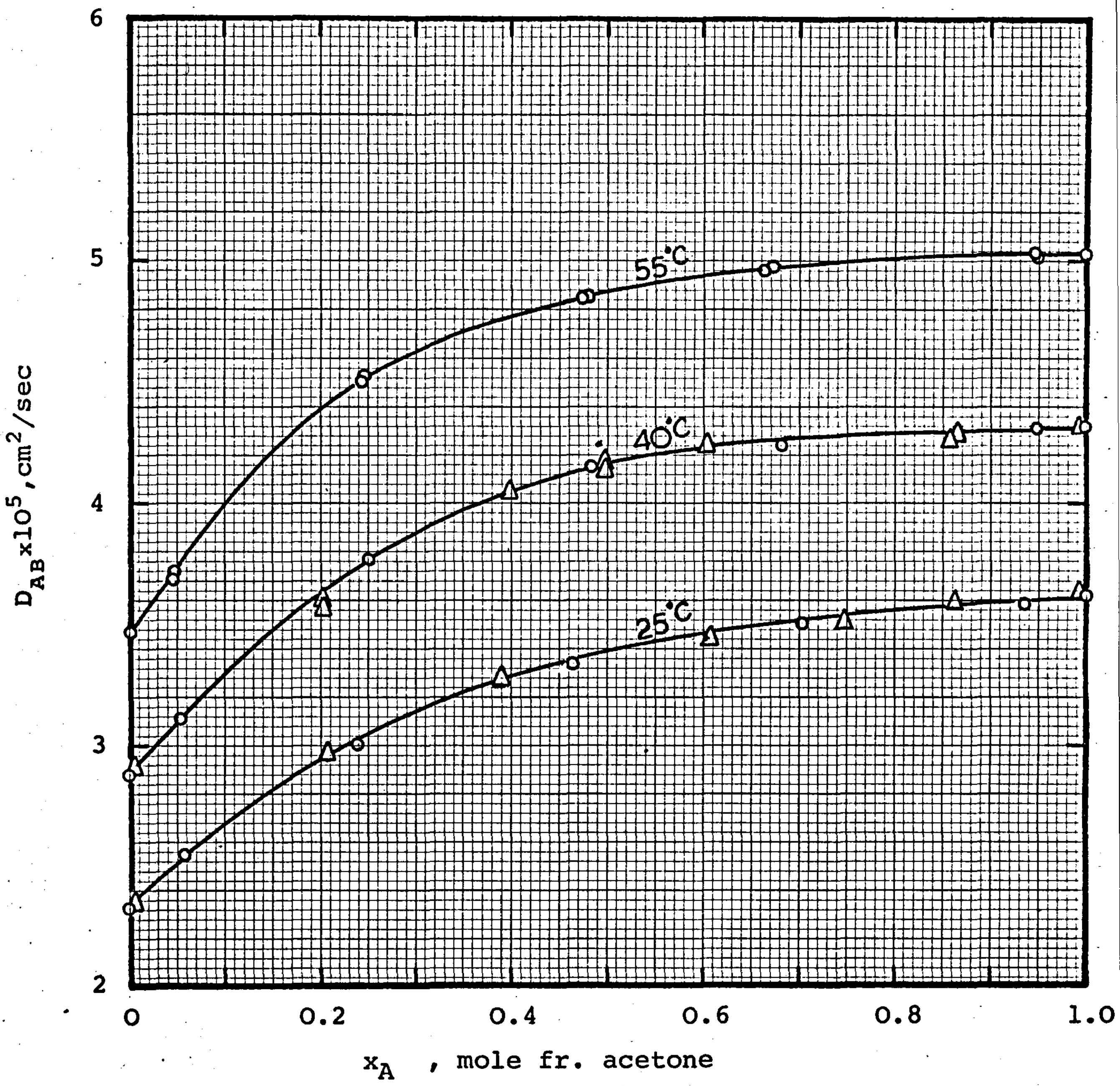


Figure 6-3.2 Differential diffusion coefficients vs mole fr. concentration for acetone-chloroform mixtures.

o This work
Δ Anderson et al (6)

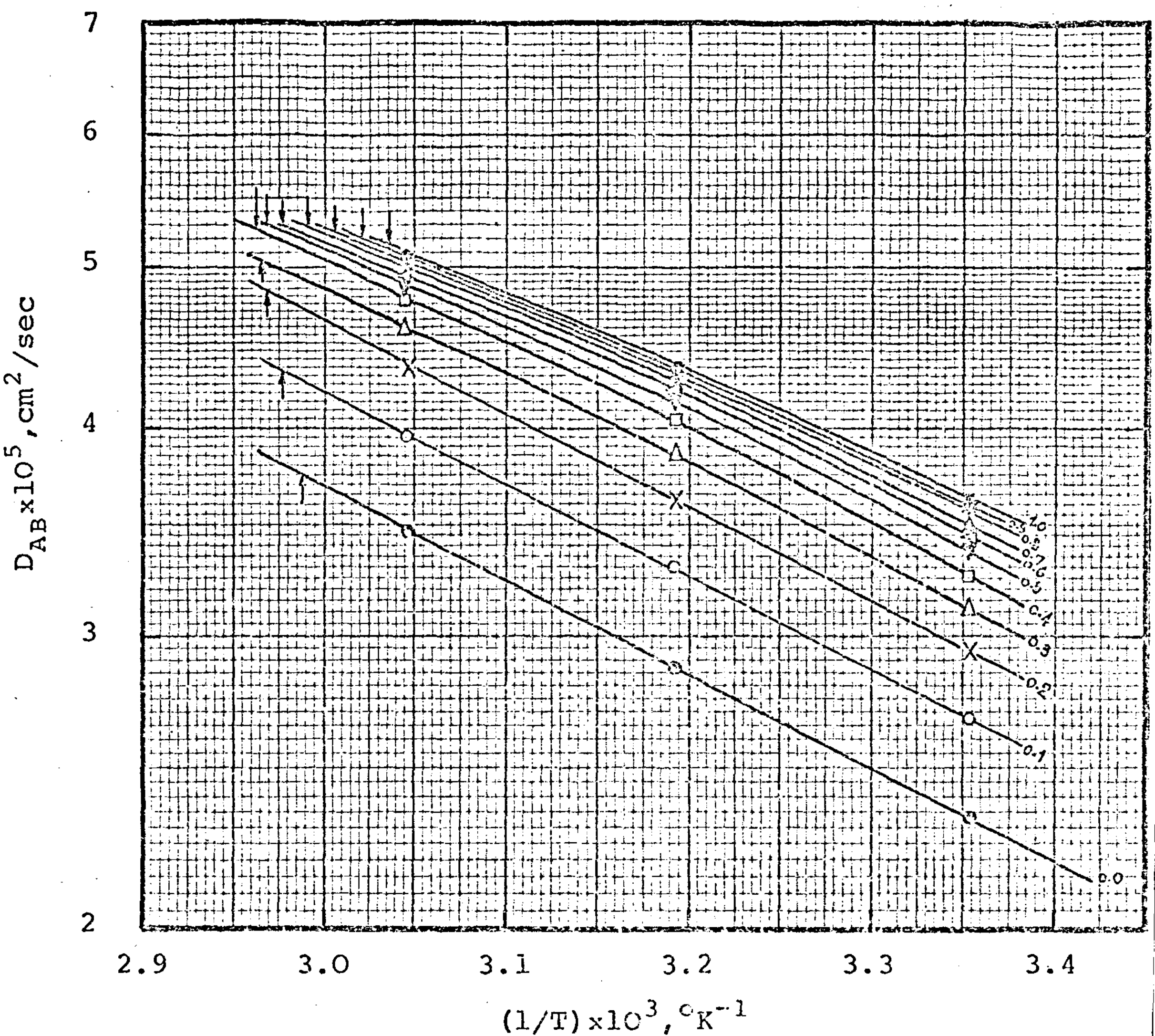


Figure 6-3.3 Variation of ln D_{AB} with (1/T) for acetone-chloroform mixtures

↓ ↑ indicate boiling point

Number on lines indicate concentration of acetone in mole fr.

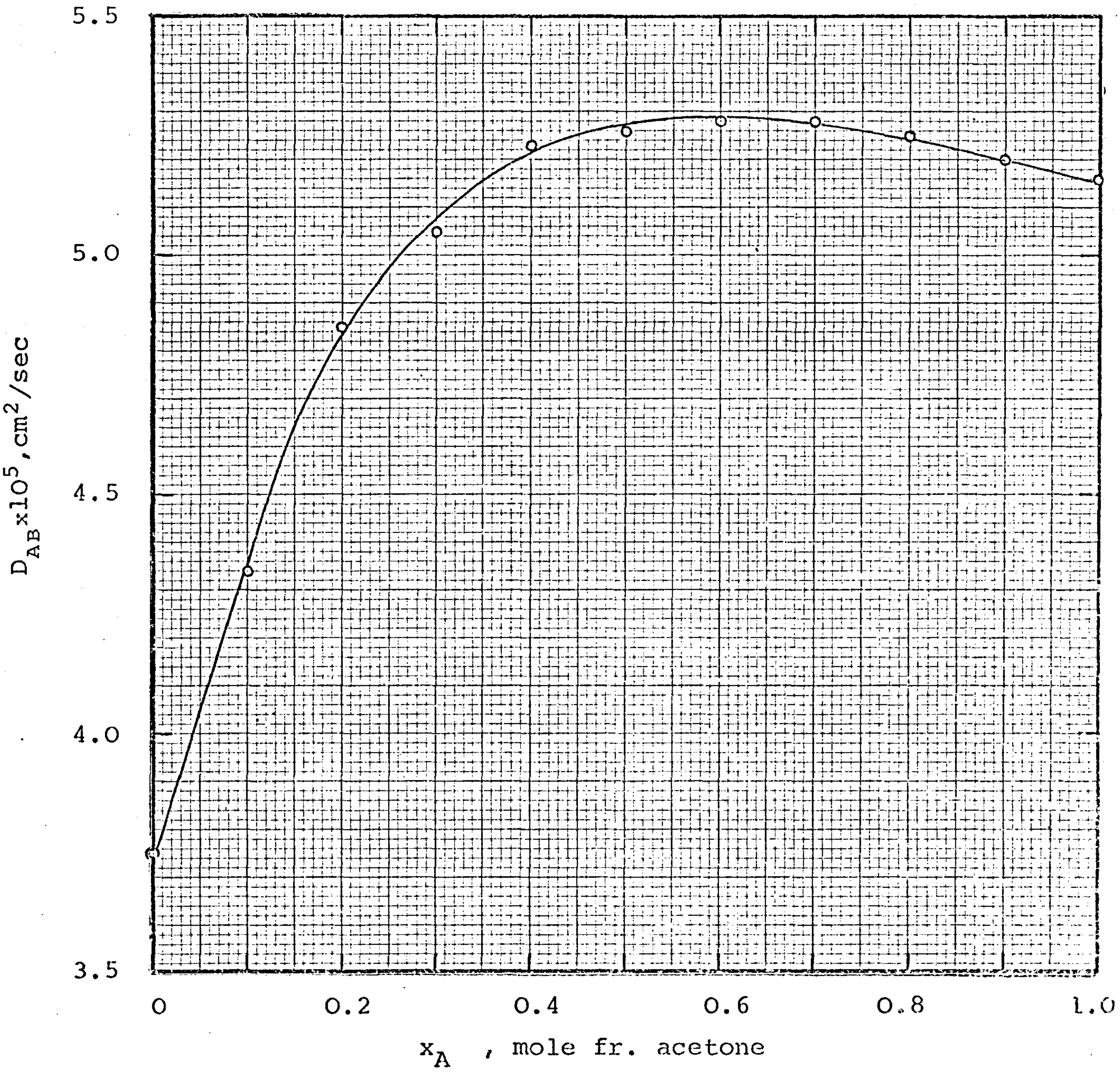


Figure 6-3.4 Differential diffusion coefficients at normal boiling points for acetone-chloroform mixtures.

Table 6-1·1 : Experimental data for diffusion coefficients obtained with the cell 'R'

Stirrer speed = 40 rpm,   Run time for each run = 24 hours

(R1 to R35) and (R73 to R75) = Ethanol - water system.
(R36 to R60) = Acetone - water system.
(R61 to R72) = Acetone - Chloroform system.

Run No.	Date	Concentration (gm solute/100cm^3 at T^{o}C)				P psig	T ^{o}C	Elapsed time hrs.	β, cm^{-2} from Fig. 4-3.3	$\bar{D}_{AB} \times 10^5$ cm^2/sec.
		C1	C2	C3	C4					
	Ethanol - Water System									
R 1	16. 3.73	0.000	12.112	2.875	9.379	0	25	72	0.2327	1.3431
R 2	19. 3.73	0.000	12.300	3.145	9.300	4	40	96	0.2330	1.4935
R 3	21. 3.73	0.000	12.050	3.892	8.300	6	58	120	0.2334	2.1657
R 4	26. 3.73	0.000	11.800	4.250	7.800	6	73	144	0.2337	2.5836
R 5	30. 3.73	0.000	11.850	4.689	7.300	7	85	168	0.2340	3.2496
R 6	2. 4.73	0.000	11.620	4.6067	7.150	7	85	192	0.2344	3.2580
R 7	9. 4.73	0.000	48.723	6.296	43.000	0	25	240	0.2352	0.6054
R 8	12. 4.73	0.000	48.100	8.666	40.000	4	40	264	0.2355	0.9148
R 9	25. 4.73	0.000	46.800	10.050	37.300	6	58	288	0.2358	1.1529
R10	27. 4.73	34.719	48.411	35.805	47.325	0	25	312	0.2362	0.3675
R11	30. 4.73	48.456	62.463	49.771	61.332	0	25	336	0.2365	0.4079
R12	2. 5.73	74.885	76.830	75.300	76.488	0	25	360	0.2369	1.0460
R13	14. 5.73	0.000	46.400	10.346	36.600	6	58	408	0.2376	1.2048
R14	16. 5.73	0.000	44.50	13.850	33.840	7	73	432	0.2380	1.6902
R15	25. 5.73	67.895	72.335	71.645	68.534	0	25	456	0.2383	0.743
R16	30. 5.73	0.00	45.00	15.600	32.200	12	85	480	0.2387	2.100
R17	4. 6.73	47.550	61.80	49.518	60.00	5	40	504	0.2391	0.6450
R18	6. 6.73	46.600	60.60	49.365*	58.00	8	58	528	0.2394	1.0143
R19	9. 6.73	-	-	-	-	-	-	-	SPOILT	RUN
R20	22. 6.73	46.300	59.700	49.707	56.450	10	73	582	0.2404	1.4362

Table 6-1·1 (continued)

Run No.	Date	Concentration (gm solute/100cm^3 at T^{o}C)				P psig	T ^{o}C	Elapsed time hrs.	β, cm^{-2} from Fig.4-3.3	$\bar{D}_{AB}$ x 10^5 cm^2/sec.
		C1	C2	C3	C4					
R21	26. 6.73	45.100	59.000	49.463	54.800	15	85	606	0.2406	2.001
R22	28. 6.73	37.000	47.800	38.477	46.450	5	40	630	0.2409	0.6333
R23	4. 7.73	36.100	47.000	38.128	45.100	10	58	654	0.2413	0.9309
R24	6. 7.73	36.500	45.100	38.500	43.100	9	73	678	0.2416	1.3481
R25	9. 7.73	34.800	45.500	37.876	42.550	13	85	702	0.2420	1.7404
R26	12. 7.73	66.700	70.520	67.465	69.800	7	40	726	0.2423	1.0211
R27	16. 7.73	65.700	69.100	66.620	68.220	9	58	750	0.2427	1.5612
R28	18. 7.73	64.400	67.900	65.540	66.800	13	73	774	0.2430	2.1133
R29	7. 8.73	63.400	66.500	64.586	65.350	15	85	822	0.2438	2.8889
R30	9. 8.73	73.500	75.500	74.023	75.000	10	40	846	0.2440	1.4770
R31	13. 8.73	72.100	73.980	72.702	73.400	13	58	870	0.2444	2.0381
R32	15. 8.73	70.700	72.500	71.371	71.850	15	73	894	0.2448	2.7191
R33	20. 8.73	75.680	77.200	76.098	76.800	10	40	918	0.2451	1.584
R34	22. 8.73	74.000	75.500	74.5076	75.010	14	58	942	0.2455	2.2398
R35	30. 8.73	72.600	74.000	73.200	73.470	15	73	966	0.2459	2.9946
Acetone - Water system										
R36	14. 9.73	0.000	13.500	3.758	9.900	8	45	1014	0.2466	1.6055
R37	16. 9.73	0.000	23.700	6.929	17.050	10	55	1038	0.2469	1.7322
R38	19. 9.73	0.000	14.200	4.767	9.600	12	65	1062	0.2473	2.1907
R39	22. 9.73	0.000	13.600	4.860	8.900	15	75	1086	0.2476	2.4642
R40	25. 9.73	0.000	13.500	5.309	8.350	18	85	1110	0.2480	3.0209
R41	9.10.73	24.500	40.500	27.388	37.800	6	35	1158	0.2487	0.8680
R42	11.10.73	24.500	40.350	27.636	37.400	9	45	1182	0.2491	0.9780
R43	16.10.73	24.200	39.900	27.735	36.550	12	55	1206	0.2493	1.1637

Table 6-1.1 (continued)

Run No.	Date	Concentration (gm solute/100cm^3 at T^{o}C)				P psig	T ^{o}C	Elapsed time hrs.	β, cm^{-2} from Fig.4-3.3	$\bar{D}_{AB} \times 10^5$ cm^2/sec.
		C_1	C_2	C_3	C_4					
R44	18.10.73	40.000	57.650	43.708	54.150	13	55	1230	0.2498	1.0562
R45	23.10.73	40.100	58.350	43.465	55.200	11	45	1254	0.2501	0.8875
R46	25.10.73	40.500	58.950	43.517	56.150	10	35	1278	0.2505	0.7600
R47	2.11.73	59.435	69.211	61.100	67.661	0	25	1326	0.2512	0.7980
R48	6.11.73	58.800	68.600	60.765	66.750	10	35	1350	0.2516	0.9853
R49	8.11.73	58.100	67.500	60.311	65.400	12	45	1374	0.2519	1.2243
R50	12.11.73	57.400	66.700	59.859	64.350	15	55	1398	0.2522	1.4510
R51	15.11.73	66.400	73.250	68.281	71.450	10	35	1422	0.2526	1.5336
R52	19.11.73	65.800	72.350	67.827	70.400	12	45	1446	0.2529	1.8572
R53	21.11.73	64.700	71.200	66.926	69.050	17	55	1470	0.2533	2.2200
R54	28.11.73	72.139	77.447	73.948	75.700	4	25	1518	0.2540	2.1941
R55	4.12.73	70.450	74.600	72.069	73.030	13	45	1542	0.2544	2.8901
R56	7.12.73	69.400	73.600	71.149	71.900	17	55	1566	0.2547	3.3983
R57	14.12.73	76.831	78.505	77.576	77.780	5	25	1590	0.2550	4.1466
R58	17.12.73	75.800	77.400	76.529	76.690	10	35	1614	0.2554	4.5173
R59	19.12.73	74.600	76.200	75.349	75.470	13	45	1638	0.2558	5.1289
R60	1. 1.74	73.600	75.010	74.277	74.350	17	55	1662	0.2564	5.7936
Acetone - Chloroform system										
R61	8. 1.74	0.000	6.950	2.572	4.460	3	255	1710	0.2568	2.5507
R62	12. 1.74	0.000	6.450	2.775	3.750	15	55	1734	0.2572	3.6942
R63	14.1 .74	0.000	6.550	2.827	3.800	15	55	1758	0.2576	3.7209

Table 6-1·1 (continued)

Run No.	Date	Concentration (gm solute/100cm^3 at T^{o}C)				P psig	T ^{o}C	Elapsed time hrs.	β, cm^{-2} from Fig.4-3.3	D_{AB}x10^5 cm^2/sec.
		C_1	C_2	C_3	C_4					
R64	16. 1.74	6.100	28.500	16.313	18.550	15	55	1782	0.2579	4.4909
R65	18. 1.74	6.200	29.200	16.170	19.500	10	40	1806	0.2582	3.7625
R66	21. 1.74	6.000	29.600	15.428	20.45	3	25	1830	0.2586	3.0076
R67	23. 1.74	28.900	41.650	34.600	36.100	10	40	1854	0.2590	4.1534
R68	1. 2.74	28.400	40.650	34.094	35.100	16	55	1878	0.2592	4.84756
R69	5. 2.74	41.250	60.650	49.979	52.150	10	40	1902	0.2596	4.2399
R70	7. 2.74	39.450	59.300	48.733	50.250	17	55	1926	0.2600	4.9720
R71	10. 2.74	68.100	76.500	71.899	72.800	13	40	1950	0.2603	4.3108
R72	12. 2.74	66.300	74.860	70.3107	70.9500	18	55	1974	0.2607	5.0024
<u>Ethanol - Water system</u>										
R73	21. 2.74	19.600	35.800	23.591	32.000	8	58	2022	0.2614	1.2607
R74	23. 2.74	19.700	35.850	25.140	30.600	15	85	2046	0.2617	2.0830
R75	25. 2.74	58.800	66.600	61.242	64.250	17	73	2070	0.2620	1.8280

Table 6-1·2: Experimental data for diffusion coefficients obtained with the cell 'H'

Stirrer speed = 40 r.p.m. Run time for each run = 24 hours.

(H1 to H12)
(H51 to H53) = Ethanol - water system.
(H13 to H41) = Acetone - Water system.
(H42 to H50) = Acetone - Chloroform system.

Run No.	Date	Concentration (gm solute/100 cm^3 at T°C)				P psig	T °C	Elapsed time hrs.	β, cm^{-2} from Fig.4-3.4	$\bar{D}_{AB} \times 10^5$ cm^2/sec.
		C_1	C_2	C_3	C_4					
Ethanol - water system.										
H 1	22. 3.73	0.000	12.000	4.071	8.050	6	58	24	0.2630	2.1097
H 2	28.3. 73	0.000	11.800	4.369	7.550	6	73	48	0.2648	2.4884
H 3	10. 4.73	0.000	48.630	9.720	39.400	4	40	96	0.2672	0.9288
H 4	1. 5.73	67.990	72.550	68.763	71.824	0	25	120	0.2690	0.7446
H 5	3. 5.73	-	-	-	-	-	-	-	-	SPOILT RUN
H 6	10. 5.73	76.870	78.530	77.250	78.150	0	25	166	0.2712	1.1305
H 7	15. 5.73	0.000	46.300	14.550	32.800	7	73	214	0.2750	1.6441
H 8	18. 5.73	0.000	45.400	15.357	30.500	12	85	238	0.2760	1.9997
H 9	26. 5.73	67.912	72.390	68.681	71.652	0	25	262	0.2774	0.7432
H10	1. 6.73	47.600	61.950	49.845	59.850	5	40	286	0.2782	0.65163
H11	5. 6.73	46.600	60.900	49.744	57.900	8	58	310	0.2800	1.0081
H12	7. 6.73	46.000	59.750	49.740	56.100	10	73	334	0.2814	1.3914
Acetone - Water system										
H13	10. 9.73	0.000	13.206	3.218	10.121	0	25	382	0.2841	1.1478
H14	12. 9.73	0.000	13.500	3.786	9.850	0	35	406	0.2858	1.4076
H15	15. 9.73	0.000	21.200	6.163	12.250	8	45	430	0.2870	1.4839

Table 6-1·2 (continued)

Run No.	Date	Concentration (gm solute/100 cm^3 at T^{o}C)				P psig	T ^{o}C	Elapsed time hrs.	β, cm^{-2} from Fig.4-3.4	D_{AB} x 10^5 cm^2/sec.
		C_1	C_2	C_3	C_4					
H16	18. 9.73	0.000	15.700	5.281	10.600	10	55	454	0.2882	1.9161
H17	20. 9.73	0.000	13.900	5.090	8.950	12	65	478	0.2898	2.2220
H18	24. 9.73	0.000	13.500	5.236	8.400	15	75	502	0.2912	2.5040
H19	26. 9.73	0.000	13.200	5.533	7.800	18	85	526	0.2923	3.0296
H20	8.10.73	24.967	40.674	27.770	38.029	0	25	574	0.2952	0.7252
H21	10.10.73	24.500	40.300	27.659	37.300	6	35	598	0.2963	0.8381
H22	15.10.73	40.250	24.700	28.207	36.900	9	45	622	0.2981	0.9806
H23	17.10.73	24.300	39.900	28.357	36.000	12	55	646	0.2998	1.1963
H24	19.10.73	39.700	57.45	43.979	53.350	13	55	670	0.3080	1.0425
H25	22.10.73	39.900	58.300	43.886	54.500	11	45	694	0.3021	0.9154
H26	24.10.73	40.700	59.00	44.185	55.700	10	35	718	0.3036	0.7669
H27	29.10.73	40.832	59.640	44.012	56.650	0	25	742	0.3065	0.65202
H28	5.11.73	58.850	68.550	61.098	66.400	10	35	790	0.3080	0.9859
H29	7.11.73	58.100	67.600	60.696	65.100	12	45	814	0.3092	1.2499
H30	9.11.73	57.450	66.700	60.244	64.000	15	55	838	0.3106	1.5332
H31	13.11.73	67.056	73.897	68.973	72.050	0	25	862	0.3121	1.2870
H32	16.11.73	66.400	73.350	68.571	71.250	10	35	886	0.3134	1.5288
H33	20.11.73	65.600	72.300	67.918	70.050	12	45	910	0.3150	1.8153
H34	22.11.73	64.700	71.250	67.167	68.850	17	55	934	0.3162	2.1599
H35	29.11.73	71.300	75.850	73.147	74.050	10	35	982	0.3186	2.5155
H36	2.12.73	71.300	75.700	73.065	73.980	10	35	1006	0.3201	2.4661
H37	6.12.73	70.500	74.630	72.252	72.920	13	45	1030	0.3218	2.8463
H38	10.12.73	69.500	73.650	71.352	71.840	17	55	1054	0.3232	3.3306
H39	18.12.73	75.900	77.400	76.621	76.695	10	35	1078	0.3244	4.6598
H40	20.12.73	76.200	74.700	75.431	75.485	13	45	1102	0.3260	5.1214
H41	31.12.73	75.010	73.600	74.295	74.330	17	55	1126	0.3274	5.6712

Table 6-1·2 (continued)

Run No.	Date	Concentration (gm solute/100 cm^3 at T^{o}C)				P psig	T ^{o}C	Elapsed time hrs.	β, cm^{-2} from Fig.4-3·4	$\bar{D}_{AB} \times 10^5$ cm^2/sec.
		C_1	C_2	C_3	C_4					
Acetone - Chloroform system										
H42	10. 1.74	0.000	6.850	3.019	3.900	10	40	1174	0.3307	3.1170
H43	15.1. 74	6.300	28.450	16.923	18.050	15	55	1198	0.3320	4.5093
H44	22. 1.74	29.000	42.850	35.240	36.750	3	25	1222	0.3335	3.3400
H45	24 .1.74	-	-	-	-	-	-	-	-	SPOILT RUN
H46	31. 1.74	28.200	40.400	33.123	34.600	15	55	1270	0.3362	4.8471
H47	4. 2.74	42.400	61.950	51.347	53.200	5	25	1294	0.3377	3.5073
H48	6. 2.74	40.200	58.950	49.339	50.000	17	55	1318	0.3390	4.9610
H49	9. 2.74	69.200	77.850	73.950	73.188	5	25	1342	0.3405	3.5859
H50	11. 2.74	66.000	74.650	70.228	70.510	18	55	1366	0.3420	5.0303
Ethanol - Water system										
H51	20. 2.74	19.500	36.300	23.069	32.900	5	40	1414	0.3458	0.7789
H52	22. 2.74	19.500	35.200	24.758	30.100	11	73	1438	0.3460	1.5663
H53	24. 2.74	66.600	72.200	68.907	69.950	16	73	1462	0.3475	2.4311

Table 6-1.3 : Experimental data for diffusion coefficients obtained with the cell 'G'

Stirrer speed = 40 rpm   Run time for each run = 24 hours

Run No.	Date	Concentration (gm solute/100 cm^3 at T^{o}C)				P psig	T ^{o}C	Run time (hr)	Elapsed time (hr)	β, cm^{-2} from Fig.4-3.6	$\bar{D}_{AB}$ x 10^5 cm^2/ sec.
		C_1	C_2	C_3	C_4						
Ethanol - Water system											
G 1	17. 7.73	65.45	69.10	66.490	68.100	8	58	24	24	0.2674	1.5385
G 2	19. 7.73	64.30	67.60	65.436	66.50	10	73	24	48	0.2686	2.1189
G 3	26. 7.73	63.50	66.40	64.652	65.28	13	85	24	72	0.2696	2.854
G 4	10. 8.73	73.85	75.80	73.389	75.285	10	40	24	144	0.2730	1.4311
G 5	14. 8.73	72.00	74.00	72.674	73.35	12	58	24	168	0.2742	1.989
G 6	16. 8.73	70.60	72.55	71.373	71.80	15	73	24	192	0.2754	2.774
G 7	21. 8.73	75.65	77.18	76.0993	76.750	10	40	24	216	0.2765	1.518
G 8	23. 8.73	74.05	75.45	74.558	74.960	13.5	58	24	240	0.2776	2.260
G 9	31. 8.73	72.60	74.00	73.168	73.450	13.5	73	24	264	0.2788	2.953
G10	11. 9.73	13.50	0.00	3.733	9.900	0	35	24	312	0.2810	1.4014

Table 6-1.4 : Experimental data for diffusion coefficients obtained with the cell 'D'

Stirrers speed = 40 r.p.m.   Run time for each run = 24 hours

Ethanol - Water system

D 3	14. 3.73	0.000	12.450	2.750	9.705	0	25	24	144	0.27182 *	1.076
D 4	17. 3.73	0.000	12.600	3.377	9.350	0	35	24	168	0.2720	1.379
D 5	20. 3.73	0.000	12.470	3.545	9.050	2	40	24	192	0.2722	1.510
D 6	25. 6.73	45.250	58.650	49.732	54.300	10	85	24	240	0.2726	1.985

* Fig.4-3.5

Table 6-1·4 (continued)

Run No.	Date	Concentration (gm solute/100cm^3 at T^{o}C)				P psig	T ^{o}C	Run time (hr)	Elapsed time (hr)	β, cm^{-2} from Fig.4-3·5	$\bar{D}_{AB}$ x 10^5 cm^2/sec.
		C_1	C_2	C_3	C_4						
D 7	27. 6.73	36.800	47.800	38.459	42.250	5	40	24	264	0.2728	0.6355
D 8	2. 7.73	36.100	46.050	38.148	44.100	6.5	58	24	288	0.2730	0.9462
D 9	5. 7.73	36.00	46.00	38.700	43.400	8.5	73	24	312	0.2732	1.389
D10	7. 7.73	-	-	-	-	10	85	24	336	-	-
D11	10. 7.73	34.730	45.40	38.036	42.200	10	85	24	360	0.2736	1.729
D12	13. 7.73	67.00	70.60	67.783	69.850	6.4	40	24	384	0.2738	1.0185

Table 6-1·5 : Calibration of the cells : R, H, D and G

Stirrers speed = 40 r.p.m. Run time for each run = 24 hours
Temperature = 25^{o}C

Run No.	Date	Concentration (gm/litre)				Elapsed time (hr)	$\bar{D}_{AB}$x10^5 used Fig.4-3·2	β cm^{-2}
		C_1	C_2	C_3	C_4			
RC 1	8. 2.73	0.09923	0.00	0.070656	0.02876	24	1.86911	0.231896
RC 2	14. 2.73	0.09838	0.00	0.06945	0.02893	48	1.86981	0.231958
RC 3	4. 4.73	0.10048	0.00	0.071333	0.02915	216	1.8687	0.23347
RC 4	8. 5.73	0.101541	0.00	0.071667	0.02987	384	1.86835	0.23887
RC 5	15. 6.73	0.101546	0.00	0.071583	0.029963	558	1.86831	0.239963
RC 6	2. 8.73	0.100998	0.00	0.0710	0.029938	798	1.86829	0.242539
RC 7	3. 9.73	0.101826	0.00	0.07133	0.030493	990	1.86831	0.24579

Table 6-1.5 (continued)

Run No.	Date	Concentration (gm/litre)				Elapsed time (hr)	$\bar{D}_{AB} x10^5$ used Fig.4-3.2	β cm^{-2}
		C_1	C_2	C_3	C_4			
RC 8	4.10.73	0.091083	0.00	0.063583	0.03608	1134	1.8719	0.24864
RC 9	30.10.73	0.09933	0.00	0.069166	0.030166	1302	1.8692	0.25141
RC10	26.11.73	0.09900	0.00	0.06883	0.030166	1494	1.8690	0.25284
RC11	4. 1.73	0.10158	0.00	0.07042	0.0311667	1686	1.8680	0.25588
RC12	14. 2.74	0.10166	0.00	0.0700	0.03166	1998	1.8682	0.26237
HC 1	5. 4.73	0.10041	0.0000	0.06875	0.03166	72	1.8683	0.26794
HC 2	12. 5.73	0.10159	0.0000	0.06933	0.03226	190	1.8681	0.271243
HC 3	8. 9.73	0.10095	0.0000	0.0682	0.03275	358	1.8680	0.28159
HC 4	1.10.73	0.09982	0.0000	0.0666	0.03316	550	1.8684	0.29373
HC5	31.10.73	0.10066	0.0000	0.06633	0.03433	766	1.8680	0.30837
HC 6	27.11.73	0.09942	0.000	0.06500	0.03442	958	1.8685	0.31714
HC 7	3. 1.74	0.09999	0.000	0.06483	0.03500	1150	1.8683	0.32542
HC 8	15. 2.74	0.10033	0.000	0.06433	0.03600	1390	1.8678	0.34060
DC 1	5. 2.73	0.10056	0.000	0.06858	0.031837	24	1.8684	0.270875
DC 2	6. 2.73	0.09999	0.000	0.06833	0.03184	48	1.8685	0.271145
DC 3	22. 2.73	0.09993	0.000	0.06808	0.031671	120	1.86861	0.27159
DC 4	20. 6.73	0.101086	0.000	0.06892	0.03217	216	1.86825	0.27245
DC 5	7. 9.73	0.10140	0.000	0.06900	0.03240	408	1.8704	0.27384
GC 1	31. 7.73	0.09965	0.000	0.06800	0.03165	96	1.8684	0.2713
GC 2	3. 8.73	0.09973	0.000	0.06800	0.03173	120	1.86861	0.27208
GC 3	5. 9.73	0.10110	0.000	0.06842	0.032683	288	1.86806	0.27985

Table 6-2·1 : Conversion of integral diffusion coefficients to differential diffusion coefficients for the mixtures of ethanol and water.

No.	Run No.	P psig	T °C	Concentration, gm EtOH/100cm^3 at T°C			$D_{AB} \times 10^5$, cm^2/sec	$\bar{D}_{AB} = \frac{1}{c''-c'}\int_{c'}^{c''} D_{AB}\,dC$	Cavg.,† $\frac{\text{gmEtOH}}{\text{100cm}^3}$ at T°C	x_A ‡ mole fr. corresp. to Cavg.
				Cavg = $\frac{(C_1+C_2)}{2}$	$C^1 = \frac{(C_1+C_3)}{2}$	$C^{11} = \frac{(C_2+C_4)}{2}$				
1	2	3	4	5	6	7	8	9	10	11
1	-	-	25	0.00	-	-	1.250	-	0.000	0.000
2	D 3	0	25	6.225	1.373	11.078	1.076	1.070	6.400	0.026
3	D 7*	0	25	24.482	3.148	45.862	0.605	-	-	-
4	R10	0	25	41.565	35.262	47.868	0.368	0.325	44.00	0.266
5	R11	0	25	55.460	49.114	61.898	0.405	0.412	56.00	0.408
6	H 4	0	25	70.300	68.411	72.163	0.745	0.720	70.00	0.680
7	H 9	0	25	70.101	68.297	72.021	0.743	0.725	70.00	0.680
8	R15	0	25	70.115	68.215	71.980	0.743	0.717	70.00	0.680
9	R12	0	25	75.858	75.093	76.659	1.047	1.047	75.86	0.880
10	H 6	0	25	77.700	77.060	78.340	1.131	1.130	77.50	0.944
11	-	-	25	78.510	-	-	1.220	-	78.51	1.000
12	-	-	40	0.000	-	-	1.700	-	0.00	0.000
13	R 2	4	40	6.150	1.573	10.800	1.494	1.500	0.62	0.025
14	D 5	4	40	6.235	1.773	10.760	1.510	1.510	0.61	0.024
15	R 8*	4	40	24.050	4.353	44.050	0.917	-	-	-
16	H 3*	4	40	24.315	4.960	44.015	0.929	-	-	-
17	H51	4	40	27.900	21.285	34.600	0.779	0.775	28.10	0.143
18	R22	5	40	42.400	37.739	47.125	0.633	0.630	42.10	0.255
19	D 7	5	40	42.300	37.628	47.025	0.636	0.632	42.00	0.253

Table 6-2.1 (continued)

No.	Run No.	P psig	T °C	Concentration, gm EtOH/100cm^3 at T°C			$D_{AB} \times 10^5$, cm^2/sec	$\bar{D}_{AB} = \frac{1}{c''-c'}\int_{c'}^{c''} D_{AB}\,dC$	Cavg., $\frac{\text{gmEtOH}}{100\text{cm}^3}$ at T°C †	x_A mole fr. corresp. to Cavg. ‡
				Cavg = $\frac{(C_1+C_2)}{2}$	$C^1 = \frac{(C_1+C_3)}{2}$	$C^{11} = \frac{(C_2+C_4)}{2}$				
1	2	3	4	5	6	7	8	9	10	11
20	R17	5	40	54.675	48.534	60.900	0.645	0.640	54.80	0.403
21	H10	5	40	54.775	48.723	60.900	0.636	0.638	54.75	0.402
22	D12	7	40	68.800	67.392	70.225	1.019	1.020	68.80	0.680
23	R26	7	40	68.610	67.083	70.160	1.021	1.020	68.80	0.680
24	R30	10	40	74.500	73.762	75.250	1.477	1.460	75.00	0.898
25	G 4	10	40	74.825	73.620	75.543	1.431	1.435	74.40	0.872
26	G 7	10	40	76.415	75.875	76.965	1.518	1.540	76.20	0.952
27	R33	10	40	76.440	75.885	77.000	1.584	1.570	76.60	0.973
28	-	-	40	77.200	-	-	1.640	-	77.20	1.000
29	-	-	58	0.000	-	-	2.400	-	0.000	0.000
30	R 3	6	58	6.025	1.946	10.175	2.166	2.160	0.580	0.024
31	H 1	6	58	6.000	2.036	10.025	2.110	2.120	0.620	0.025
32	R 9*	6	58	23.400	5.025	42.050	1.153	-	-	-
33	R13*	6	58	23.200	5.173	41.500	1.205	-	-	-
34	R73	8	58	27.700	21.595	33.900	1.261	1.200	27.00	0.136
35	R23	7	58	41.55	27.114	46.050	0.931	0.940	41.50	0.255
36	D 8	7	58	41.075	37.124	45.075	0.946	0.941	41.20	0.252
37	R18	8	58	53.600	48.000	59.300	1.023	1.020	53.60	0.399
38	H11	8	58	53.650	48.300	59.350	1.017	1.020	53.60	0.399
39	R27	9	58	67.400	66.160	68.660	1.561	1.550	67.35	0.682

Table 6-2·1 (continued)

No.	Run No.	P psig	T ^oC	Concentration, gm EtOH/100cm^3 at T^{o}C Cavg = $\frac{(C_1+C_2)}{2}$	C^1 = $\frac{(C_1+C_3)}{2}$	C^{11} = $\frac{(C_2+C_4)}{2}$	$D_{AB} \times 10^5$, cm^2/sec	$\bar{D}_{AB} = \frac{1}{c''-c'}\int_{C'}^{c''} D_{AB}dC$	Cavg., $\frac{\text{gmEtOH}}{100\text{cm}^3}$ at T^{o}C †	x_A mole fr. corresp. to Cavg. ‡
1	2	3	4	5	6	7	8	9	10	11
40	G 1	9	58	67.275	65.970	68.600	1.539	1.540	67.30	0.681
41	R31	13	58	73.040	72.401	73.690	2.038	2.030	73.15	0.888
42	G 5	13	58	73.000	72.337	73.675	1.989	2.00	73.10	0.882
43	R34	14	58	74.750	74.254	75.255	2.240	2.245	74.80	0.962
44	G 8	14	58	74.750	74.300	75.200	2.260	2.250	74.80	0.962
45	L	-	58	75.500	-	-	2.360	-	75.50	1.000
46	-	-	73	0.000	-	-	2.95	-	0.00	0.000
47	R 4	6	73	5.900	2.125	9.800	2.584	2.560	5.700	0.024
48	H 2	6	73	5.900	2.185	9.675	2.488	2.510	6.300	0.025
49	R14*	7	73	22.250	6.925	39.170	1.690	-	-	-
50	H 7*	7	73	23.150	7.275	39.550	1.667	-	-	-
51	H52	7	73	27.350	22.129	32.650	1.566	1.550	28.20	1.48
52	R24	9	73	40.800	37.500	44.100	1.348	1.350	40.70	0.253
53	D 9	9	73	41.000	37.350	44.700	1.389	1.360	40.90	0.255
54	R20	10	73	53.000	48.000	58.075	1.436	1.420	52.80	0.400
55	H12	10	73	52.875	48.050	57.925	1.391	1.400	52.40	0.394
56	R75	13	73	62.700	60.021	65.425	1.828	1.830	62.75	0.589
57	R28	13	73	66.150	65.025	67.350	2.113	2.150	66.00	0.680
58	G 2	13	73	65.950	64.868	67.050	2.119	2.200	66.10	0.684
59	H53	13	73	69.400	67.754	71.075	2.431	2.450	69.30	0.792
60	R32	15	73	71.600	71.060	72.175	2.719	2.720	71.50	0.876

Table 6-2·1 (continued)

No.	Run No.	P psig	T °C	Concentration, gm EtOH/100cm^3 at T°C Cavg. = $\frac{(C_1+C_2)}{2}$	$C^I = \frac{(C_1+C_3)}{2}$	$C^{II} = \frac{(C_2+C_4)}{2}$	$D_{AB} \times 10^5$, cm^2/sec	$\bar{D}_{AB} = \frac{1}{c''-c'}\int_{c'}^{c''} D_{AB}\,dC$	Cavg., gmEtOH/100cm^3 at T°C †	x_A mole fr. corresp. to Cavg. ‡
1	2	3	4	5	6	7	8	9	10	11
61	G16	15	73	71.575	70.987	72.175	2.774	2.750	71.80	0.887
62	R35	15	73	73.300	72.900	73.735	2.995	2.980	73.40	0.966
63	G19	15	73	73.300	72.884	73.725	2.953	2.960	73.20	0.952
64	-	-	73	74.150	-	-	3.100	-	74.15	1.000
65	-	-	85	0.000	-	-	3.503	-	0.000	0.000
66	R 5	7	85	5.925	2.375	9.575	3.250	3.252	5.920	0.025
67	R 6*	7	85	5.810	2.390	9.385	3.258	3.256	5.920	0.025
68	R16*	12	85	22.500	7.800	38.600	2.100	-	-	-
69	H 8	12	85	22.700	7.679	37.950	2.000	-	-	-
70	R74	13	85	27.775	22.420	33.225	2.0830	2.080	27.790	0.147
71	R25	13	85	40.150	36.338	44.025	1.720	1.721	40.10	0.253
72	D11	13	85	40.065	36.383	43.800	1.729	1.724	40.15	0.255
73	R21	15	85	52.050	47.282	56.900	2.001	2.000	52.10	0.403
74	D 6	15	85	51.950	47.491	56.475	1.985	1.990	52.00	0.402
75	G 3	15	85	64.950	64.076	65.840	2.854	2.860	64.80	0.679
76	R29	15	85	64.950	63.993	65.925	2.889	2.880	65.00	0.684
77	R 1	0	35	6.056	1.438	10.746	1.343	-	-	0.024
78	D 4	0	35	6.300	1.688	10.975	1.380	-	-	0.025

† Concentration of ethanol (gm EtOH/100cm^3) at which the integral diffusion coefficient in column 8, equals the differential diffusion coefficient.

‡ Concentration in column 10 converted to mole fraction.

* These points are not included in calculating differential diffusion coefficients as their accuracy is uncertain.

Table 6-2·2 : Smoothed differential diffusion coefficients for ethanol - water system.

x_A Mole fr. EtOH	Differential diffusion coefficient, $D_{AB} \times 10^5$, $cm^2/sec.$				
	25°C	40°C	58°C	73°C	85°C
0.00	1.250	1.700	2.400	2.950	3.503
0.10	0.660	1.000	1.500	1.900	2.470
0.20	0.405	0.680	1.020	1.420	1.835
0.30	0.370	0.610	0.930	1.340	1.740
0.40	0.415	0.640	1.020	1.420	1.980
0.50	0.500	0.730	1.185	1.610	2.285
0.60	0.615	0.865	1.380	1.860	2.600
0.70	0.760	1.060	1.590	2.170	2.930
0.80	0.920	1.275	1.810	2.490	-
0.90	1.070	1.475	2.060	2.800	-
1.00	1.220	1.640	2.360	3.100	-

Table 6-2·3 : Conversion of integral diffusion coefficients to differential diffusion coefficients for the mixtures of acetone-water.

No.	Run No.	P psig	T °C	Concentration, gm acetone/100cm³ at T°C			$D_{AB} \times 10^5$, $cm^2/sec.$	$\bar{D}_{AB} = \frac{1}{c''-c'}\int_{c'}^{c''} D_{AB}\,dC$	Cavg., $\frac{\text{gm AcOH}}{100cm^3}$ at T°C †	x_A ‡ mole fr. corresp. to Cavg.
				Cavg = $\frac{(C_1+C_2)}{2}$	$C^1 = \frac{(C_1+C_3)}{2}$	$C^{11} = \frac{(C_2+C_4)}{2}$				
1	2	3	4	5	6	7	8	9	10	11
1	-	-	25	0.000	-	-	1.300	-	0.000	0.00
2	H13	0	25	6.603	1.609	11.663	1.148	1.140	6.750	0.022
3	H20	0	25	32.820	26.368	39.352	0.725	0.720	32.850	0.140

Table 6-2·3 (continued)

No.	Run No.	P psig	T °C	Concentration, gm acetone/100cm^3 at T°C			$D_{AB} \times 10^5$, cm^2/sec.	$\bar{D}_{AB} = \frac{1}{c''-c'}\int_{c'}^{c''} D_{AB}\,dC$	Cavg., † $\frac{\text{gm AcOH}}{100\text{cm}^3}$ at T°C	x_A ‡ mole fr. corresp. to Cavg.
				Cavg. = $\frac{(C_1+C_2)}{2}$	$C^I = \frac{(C_1+C_3)}{2}$	$C^{II} = \frac{(C_2+C_4)}{2}$				
1	2	3	4	5	6	7	8	9	10	11
4	H27	0	25	50.236	42.422	58.145	0.652	0.649	50.400	0.282
5	R47	0	25	64.323	60.268	68.436	0.798	0.800	64.400	0.482
6	H31	0	25	70.477	68.015	72.974	1.287	1.290	70.520	0.632
7	R54	4	25	74.793	73.044	76.574	2.194	2.200	74.800	0.772
8	R57	5	25	77.668	77.203	78.143	4.147	4.120	77.660	0.939
9	-	-	25	78.505	-	-	5.220	-	78.500	1.00
10	-	-	35	0.00	-	-	1.600	-	0.000	0.000
11	G10	0	35	6.750	1.866	11.700	1.401	1.402	6.740	0.024
12	H14	0	35	6.750	1.893	11.675	1.408	1.406	6.760	0.025
13	R41	6	35	32.500	25.944	39.150	0.868	0.862	32.00	0.139
14	H21	6	35	32.400	26.080	38.800	0.838	0.834	32.80	0.143
15	R46	10	35	49.725	42.009	57.550	0.760	0.761	49.73	0.280
16	H26	10	35	49.850	42.442	57.350	0.767	0.766	49.80	0.281
17	H28	10	35	63.700	59.974	67.475	0.986	0.987	63.80	0.486
18	R48	10	35	63.800	59.783	67.675	0.985	0.983	63.70	0.482
19	R51	10	35	69.825	67.340	72.350	1.534	1.540	69.90	0.644
20	H32	10	35	69.875	67.485	72.300	1.529	1.527	69.60	0.634
21	H35	10	35	73.575	72.223	74.950	2.515	2.513	73.575	0.780
22	H36	10	35	73.500	72.183	74.840	2.466	2.468	73.505	0.779
23	H39	10	35	76.650	76.260	77.048	4.660	4.690	76.680	0.950

Table 6-2·3 (continued)

No.	Run No.	P psig	T °C	Concentration, gm acetone/$100cm^3$ at T°C			$D_{AB} \times 10^5$, cm^2/sec.	$\bar{D}_{AB} = \frac{1}{c''-c'}\int_{c'}^{c''} D_{AB}\,dC$	Cavg., † $\frac{\text{gm AcOH}}{100cm^3}$ at T°C	x_A ‡ mole fr. corresp. to Cavg.
				Cavg. = $\frac{(C_1+C_2)}{2}$	$C^I = \frac{(C_1+C_3)}{2}$	$C^{II} = \frac{(C_2+C_4)}{2}$				
1	2	3	4	5	6	7	8	9	10	11
24	R58	10	35	76.600	76.164	77.045	4.517	4.512	76.58	0.942
25	-	-	35	77.40	-	-	5.600	-	77.40	1.000
26	-	-	45	0.000	-	-	1.820	-	0.00	0.00
27	R36	8	45	6.750	1.879	11.700	1.606	1.604	6.750	0.023
28	H15	8	45	10.600	3.082	18.225	1.484	1.486	10.600	0.036
29	R42	9	45	32.425	26.068	38.875	0.978	0.979	32.430	0.143
30	H22	9	45	32.475	26.454	38.575	0.981	0.983	32.460	0.144
31	R45	11	45	49.225	41.783	56.775	0.887_5	0.889	49.200	0.278
32	H25	11	45	49.100	41.893	56.400	0.915	0.913	49.300	0.280
33	H29	12	45	62.850	59.398	66.350	1.250	1.246	62.850	0.482
34	R49	12	45	62.800	59.205	66.450	1.224	1.222	62.750	0.480
35	R52	12	45	69.075	66.814	71.375	1.857	1.859	69.090	0.647
36	H33	12	45	68.950	66.759	71.175	1.815	1.812	68.800	0.638
37	R55	13	45	72.525	71.259	73.815	2.890	2.900	72.750	0.792
38	H37	13	45	72.565	71.376	73.775	2.846	2.849	72.600	0.785
39	H40	13	45	75.450	75.065	75.843	5.121	5.120	75.450	0.948
40	R59	13	45	75.400	74.974	75.835	5.071	5.070	75.400	0.946
41	-	-	45	76.200	-	-	6.050	-	76.200	1.000
42	-	-	55	0.000	-	-	2.140	-	0.000	0.000
43	R37	10	55	11.850	3.465	20.375	1.732	1.736	11.700	0.040
44	H16	10	55	7.850	2.640	13.150	1.880	1.890	7.770	0.025

Table 6-2·3 (continued)

No.	Run No.	P psig	T °C	Concentration,gm acetone/100cm^3 at T°C			D_{AB} x 10^5, cm^2/sec.	$\bar{D}_{AB} = \frac{1}{c''-c'}\int_{C'}^{c''} D_{AB}dC$	Cavg., † $\frac{\text{gm AcOH}}{100\text{cm}^3}$ at T°C	x_A ‡ mole fr. corresp. to Cavg.
				Cavg. = $\frac{(C_1+C_2)}{2}$	$C^1 = \frac{(C_1+C_3)}{2}$	$C^{11} = \frac{(C_2+C_4)}{2}$				
1	2	3	4	5	6	7	8	9	10	11
45	R43	12	55	32.050	25.967	38.225	1.164	1.160	32.800	0.147
46	H23	12	55	32.100	26.329	37.950	1.196	1.195	32.150	0.143
47	R44	13	55	48.825	41.854	55.900	1.056	1.054	48.800	0.281
48	H24	13	55	48.575	41.840	55.400	1.042	1.048	48.560	0.274
49	H30	15	55	62.075	58.847	65.350	1.458	1.459	62.080	0.484
50	R50	15	55	62.050	58.630	65.525	1.451	1.455	62.060	0.483
51	R53	17	55	67.950	65.813	70.125	2.220	2.228	67.990	0.644
52	H34	17	55	67.975	65.933	70.050	2.160	2.172	67.965	0.641
53	R56	17	55	71.500	70.275	72.750	3.398	3.399	71.550	0.787
54	H38	17	55	71.575	70.426	72.745	3.331	3.336	71.500	0.782
55	H41	17	55	74.350	73.947	74.670	5.671	5.674	74.300	0.944
56	R60	17	55	74.305	73.938	74.680	5.794	5.797	74.32	0.945
57	-	-	55	75.010	-	-	6.700	-	75.01	1.000
58	-	-	65	0.000	-	-	2.4500	-	0.000	0.000
59	R38	12	65	7.100	2.383	11.900	2.191	2.186	7.45	0.024
60	H17	12	65	6.950	2.545	11.425	2.222	2.226	6.850	0.022
61	-	-	75	0.000	-	-	2.740	-	0.000	0.000
62	R39	15	75	6.800	2.430	11.250	2.464	2.460	7.100	0.023
63	H18	15	75	6.750	2.618	10.950	2.504	2.500	6.550	0.021

Table 6-2·3 (continued)

No.	Run No.	P psig	T °C	Concentration, gm acetone/100cm^3 at T°C			$D_{AB} \times 10^5$, cm^2/sec.	$\bar{D}_{AB} = \frac{1}{c''-c'} \int_{c'}^{c''} D_{AB} dC$	Cavg., † $\frac{\text{gm AcOH}}{100\text{cm}^3}$ at T°C	x_A ‡ mole fr. corresp. to Cavg.
				Cavg. = $\frac{(C_1+C_2)}{2}$	C^1 = $\frac{(C_1+C_3)}{2}$	C^{11} = $\frac{(C_2+C_4)}{2}$				
1	2	3	4	5	6	7	8	9	10	11
64	-	-	85	0.000	-	-	3.250	-	0.000	0.000
65	R40	18	85	6.750	2.654	10.925	3.021	3.020	6.700	0.021
66	H19	18	85	6.600	2.767	10.500	3.030	3.030	6.650	0.020

† Concentration of acetone (gm acetone/ 100cm^3) at which the integral diffusion coefficient in column 8, equals differential diffusion coefficient.

‡ Concentration in column 10 converted to mole fraction.

Table 6-2·4 : Smoothed differential diffusion coefficients for acetone-water system.

x_A Mole fr. Acetone	Differential diffusion coefficient, $D_{AB} \times 10^5$ cm^2/sec.						
	25°C	35°C	45°C	55°C	65°C	75°C	85°C
0.00	1.300	1.600	1.820	2.140	2.450	2.740	3.250
0.05	1.000	1.230	1.390	1.655	1.960	2.220	2.730
0.10	0.810	0.990	1.120	1.350	-	-	-
0.20	0.665	0.780	0.910	1.070	-	-	-
0.30	0.650	0.780	0.910	1.060	-	-	-
0.40	0.690	0.858	1.040	1.230	-	-	-

Table 6-2·4 (continued)

x_A Mole fr. Acetone	Differential diffusion coefficient, $D_{AB} \times 10^5$ cm^2/sec.						
	25°C	35°C	45°C	55°C	65°C	75°C	85°C
0.50	0.820	1.025	1.290	1.510	-	-	-
0.60	1.130	1.365	1.640	1.940	-	-	-
0.70	1.680	1.898	2.170	2.600	-	-	-
0.80	2.440	2.700	2.990	3.540	-	-	-
0.90	3.560	3.900	4.310	4.990	-	-	-
1.00	5.220	5.600	6.050	6.700	-	-	-

Table 6-2·5 : Conversion of integral diffusion coefficient to differential diffusion coefficient for the mixtures of acetone-chloroform

No.	Run No.	P psig	T °C	Concentration, gm acetone/100cm^3 at T°C			$D_{AB} \times 10^5$, cm^2/sec.	$\bar{D}_{AB} = \frac{1}{c''-c'} \int_{c'}^{c''} D_{AB} dC$	Cavg., † $\frac{\text{gm AcOH}}{100\text{cm}^3}$ at T°C	x_A ‡ mole fr. corresp. to Cavg.
				Cavg. = $\frac{(C_1+C_2)}{2}$	$C^1 = \frac{(C_1+C_3)}{2}$	$C^{11} = \frac{(C_2+C_4)}{2}$				
1	2	3	4	5	6	7	8	9	10	11
1	-	-	25	0.00	-	-	2.330	-	-	0.000
2	R61	3	25	3.475	1.286	5.705	2.551	2.565	4.300	0.058
3	R66	3	25	17.800	10.714	25.025	3.008	3.022	17.500	0.240
4	H44	3	25	35.925	32.120	39.800	3.340	3.354	35.000	0.465
5	H47	5	25	52.175	46.874	57.575	3.507	3.502	53.500	0.702
6	H49		25	73.523	71.194	75.900	3.586	3.590	72.75	0.935

Table 6-2·5 (continued)

No.	Run No.	P psig	T °C	Concentration, gm acetone/100cm^3 at T°C			$D_{AB} \times 10^5$, cm^2/sec.	$\bar{D}_{AB} = \frac{1}{c''-c'}\int_{c'}^{c''} D_{AB}\,dC$	Cavg., † $\frac{\text{gm AcOH}}{100\text{cm}^3}$ at T°C	x_A ‡ mole fr. corresp. to Cavg.
				Cavg. = $\frac{(C_1+C_2)}{2}$	$C^{1} = \frac{(C_1+C_3)}{2}$	$C^{11} = \frac{(C_2+C_4)}{2}$				
1	2	3	4	5	6	7	8	9	10	11
7	-	-	25	78.400	-	-	3.620	-	78.40	1.000
8	-	-	40	0.000	-	-	2.880	-	-	0.000
9	H42	10	40	3.425	1.509	5.375	3.117	3.110	3.75	0.052
10	R65	10	40	17.700	11.185	24.350	3.763	3.750	18.00	0.250
11	R67	10	40	35.275	31.750	38.875	4.153	4.150	35.270	0.482
12	R69	10	40	50.990	45.615	56.400	4.240	4.255	50.50	0.680
13	R71	13	40	72.300	69.999	74.65	4.311	4.308	72.00	0.947
14	-	-	40	76.700	-	-	4.320	-	76.70	1.000
15	-	-	55	0.00	-	-	3.470	-	-	0.000
16	R62	15	55	3.225	1.388	5.100	3.694	3.700	3.250	0.045
17	R63	15	55	3.275	1.414	5.175	3.721	3.710	3.250	0.046
18	R64	15	55	17.300	14.257	23.525	4.491	4.500	17.350	0.242
19	H43	15	55	17.375	11.612	23.250	4.509	4.512	17.750	0.256
20	H46	15	55	34.300	30.662	37.500	4.847	4.842	33.750	0.473
21	R68	16	55	34.525	31.247	37.875	4.848	4.847	34.300	0.480
22	R70	17	55	49.375	44.092	54.775	4.972	4.970	49.00	0.673
23	H48	17	55	49.575	44.770	54.475	4.961	4.968	48.50	0.667
24	H50	18	55	70.325	68.114	72.580	5.030	5.029	70.320	0.948
25	R72	18	55	70.580	68.305	72.905	5.002	5.025	70.560	0.950
26	-	-	55	74.96	-	-	5.03	-	74.96	1.000

† Concentration of acetone (gm acetone/100cm^3) at which the integral diffusion coefficient D_{AB} in column 8, equals the differential diffusion coefficient.

‡ Concentration in column 10 converted to mole fraction.

Table 6-2·6 : Smoothed differential diffusion coefficients for acetone-chloroform system.

x_A mole fr. acetone	Differential diffusion coefficients, $D_{AB} \times 10^5$, cm^2/sec.		
	25°C	40°C	55°C
0.00	2.330	2.880	3.470
0.10	2.685	3.300	3.965
0.20	2.926	3.624	4.355
0.30	3.110	3.880	4.620
0.40	3.26	4.060	4.779
0.50	3.380	4.160	4.861
0.60	3.448	4.212	4.932
0.70	3.500	4.248	4.988
0.80	3.572	4.282	5.010
0.90	3.582	4.301	5.020
1.00	3.620	4.320	5.030

Table 6-3·1 : Differential diffusion coefficients at normal boiling points obtained in Figs. 6-1.3, 6-2.3, 6-3.3 by interpolation or extrapolation, (D_{AB} x 10^5 cm^2/sec.)

Mole fr. of 'A' x_A	Ethanol (A) - Water (B)			Acetone (A) - Water (B)			Acetone (A) - Chloroform (B)		
	Tb * °C	$\frac{1}{Tb}$ x10^3, °K^{-1}	D_{AB}x10^5 Fig. 6-1.3	T_b ** °C	$\frac{1}{T_b}$ x10^3, °K^{-1}	D_{AB}x10^5 Fig. 6-2.3	T_b *** °C	$\frac{1}{T_b}$ x 10^3, °K^{-1}	D_{AB}x 10^5 Fig. 6-3.3
0.0	100	2.680	4.32	100	2.680	3.86	61.5	2.988	3.75
0.1	86.4	2.781	2.50	66.72	2.941	1.60	62.60	2.978	4.34
0.2	83.2	2.805	1.75	62.20	2.981	1.18	63.60	2.969	4.85
0.3	81.7	2.818	1.61	61.00	2.992	1.14	63.80	2.967	5.05
0.4	80.8	2.825	1.76	60.40	2.997	1.35	64.32	2.963	5.23
0.5	80.0	2.832	2.05	59.80	3.003	1.69	63.55	2.970	5.26
0.6	79.5	2.838	2.20	59.30	3.007	2.06	62.50	2.979	5.28
0.7	79.2	2.842	2.45	58.80	3.012	2.76	61.15	2.991	5.28
0.8	78.8	2.844	2.69	58.20	3.017	3.70	59.50	3.006	5.25
0.9	78.5	2.845	2.97	57.40	3.024	5.13	57.76	3.022	5.20
1.0	78.5	2.845	3.33	56.20	3.035	6.79	56.20	3.036	5.16

* Boiling points from Smith and Storrow (183)

** Boiling points from Thomas and McAlister (195)

*** Boiling points from Reinders and Minjer (1947) taken from ref. (197)

PART 7 DISCUSSION

DISCUSSION

7-1 Comparison of the data of this work with that of other workers

7-1.1 Ethanol-water system

Four previous workers (45, 76, 158, 183) measured diffusion coefficients of ethanol-water mixtures over the complete concentration range: Hammond and Stokes (76) and Dullien and Shemilt (45) at a temperature of 25°C, Smith and Storrow (183) at temperatures 25°C, 40°C, 58°C and 73°C and Pratt and Wakeham (158) at temperatures of 25°C, 35°C, 45°C, 55°C and 65°C. The data of these workers at 25°C are plotted in Fig. 7-1.1 and the best correlating line is drawn. Three data points of Smith and Storrow (183) at high ethanol concentrations deviate so much from the rest of the data that they are not on Fig. 7-1.1 and have not been taken into account in drawing the best line. The deviations from this line of all the experimental data are reported in Table 7-1.1a. Table 7-1.1a shows that the experimental data of this work have the smallest deviations and agree very closely with the data of Dullien and Shemilt (43). The data of Smith and Storrow (183) have an exceptionally large average deviation of 50%.

There are only two reports giving experimental diffusion coefficients for the ethanol-water system at elevated temperatures. The data of Smith and Storrow (183) were obtained at the same temperatures as in this work. The data of Pratt and Wakeham (158) were obtained at temperatures slightly lower which makes the comparison more difficult. To interpolate or extrapolate the latter data to the temperatures used in this work the method of plotting ln D_{AB} against $\frac{1}{T}$ was used in Fig. 7-1.2. These plots are practically straight lines and the extrapolating or interpolating range is very short so that the distortion of the data is negligible. All the experimental data of this work and from these two

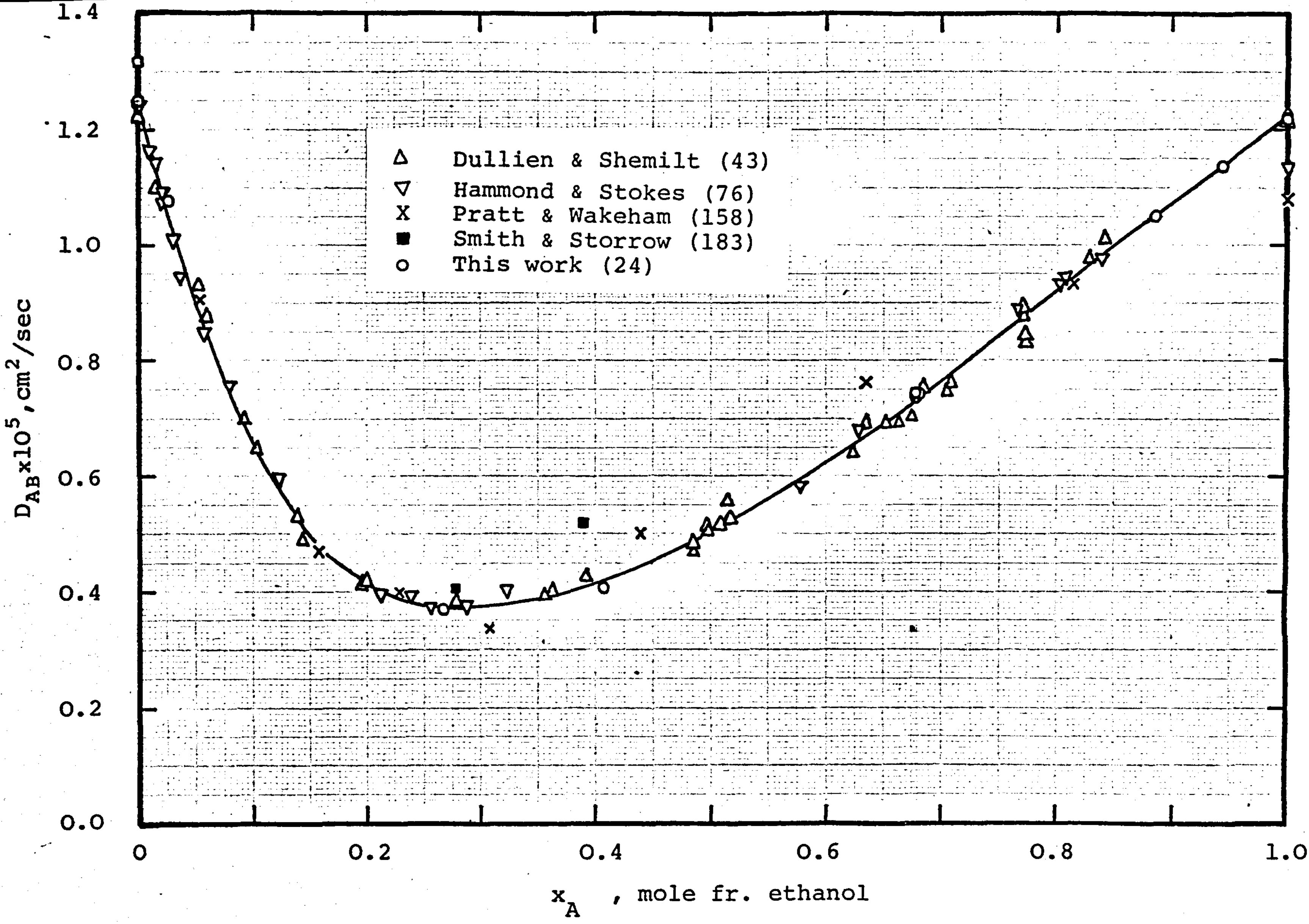


Figure 7-1.1 Differential diffusion coefficients of various authors for ethanol-water mixtures at 25°C

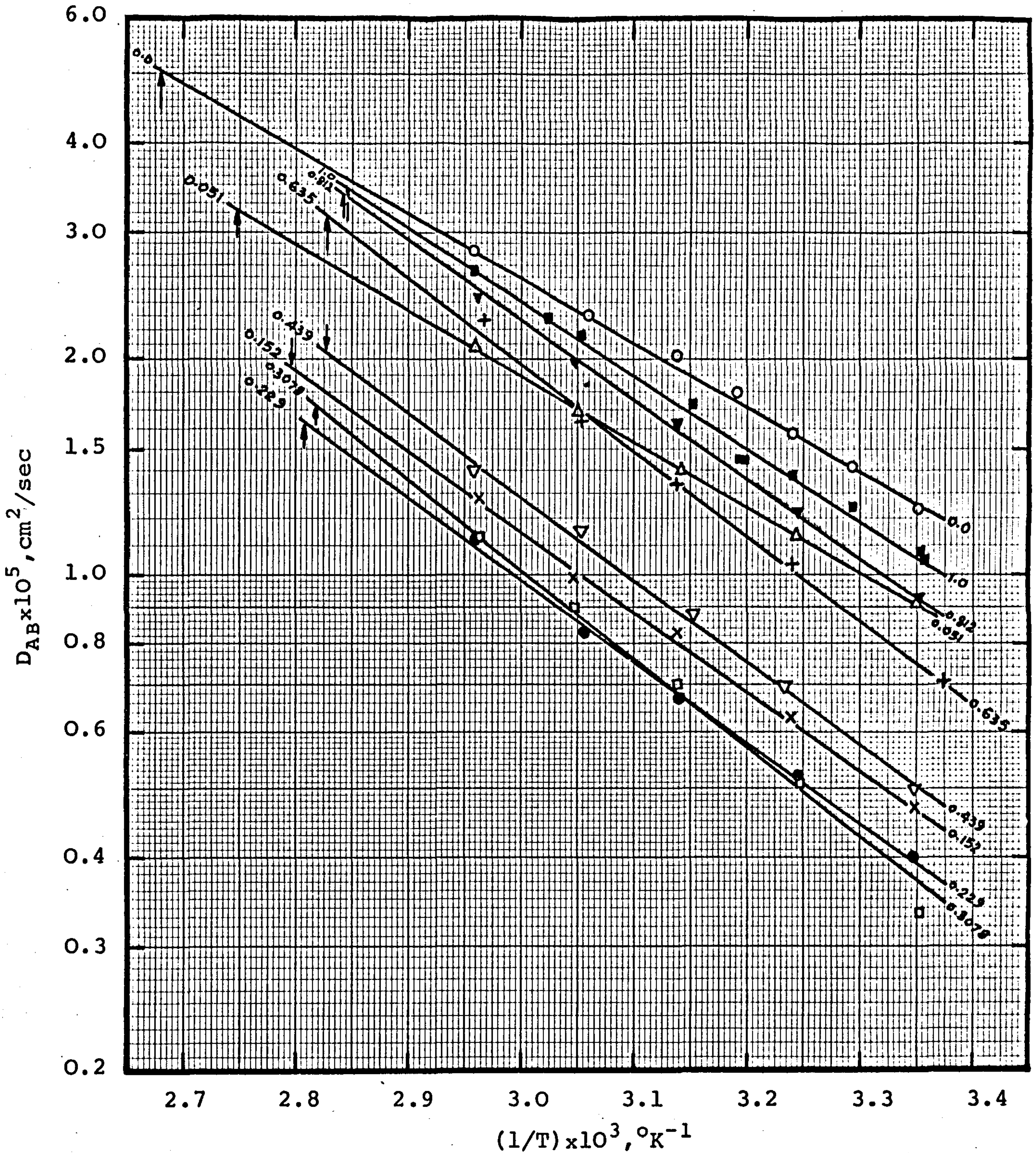


Figure 7-1.2 Variation of ln D_{AB} with (1/T) for ethanol-water mixtures (data of Pratt and Wakeham, ref.158)

↓ ↑ indicate boiling point

Numbers on lines indicate concentration of ethanol in mole fr.

papers (183, 158) are assembled in Table 7-1.1b. The percentage average deviation of the other two sets of data from the data of this work was employed in comparing them. Generally the data of Pratt and Wakeham (158) are considerably more consistent with the data of this work than those of Smith and Storrow (183). The latter data deviate up to 100% at high alcohol concentrations range. The experimental coefficients of Pratt and Wakeham (158) exhibit a convexity around the concentration of 0.6 mole fraction at all temperatures. This is illustrated in Fig. 7-1.3 which is taken from Pratt and Wakeham paper (158).

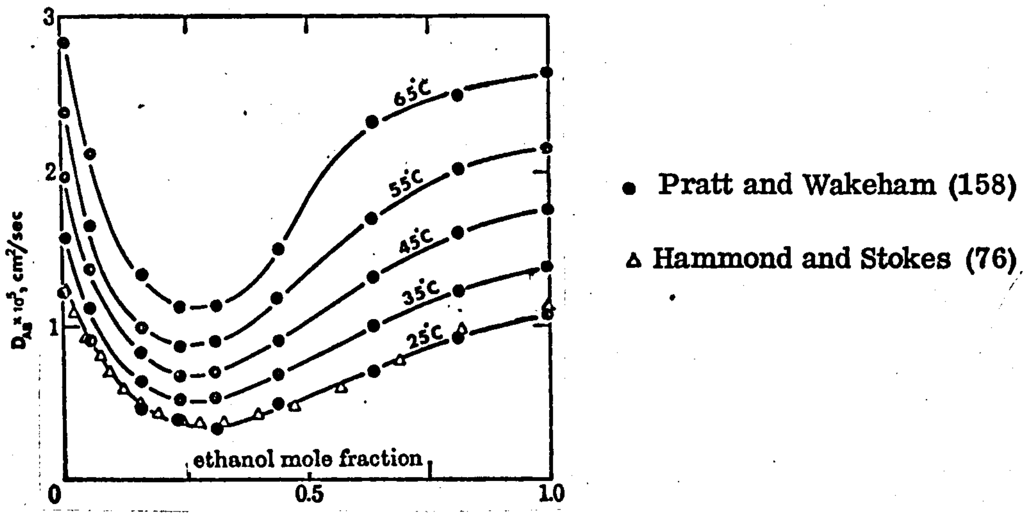


Fig. 7-1.3 Diffusion coefficient of ethanol-water mixtures (from reference 158)

This descrepancy increases with temperature, being 12% at 25°C and 36% at 73°C. It should be noticed that none of the authors (24, 43, 76) who contributed data at 25°C reported a convexity, as may be seen in Fig. 7-1.1. In view of the lack of agreement with the other data shown by the data of Pratt and Wakeham (158) and of Smith and Storrow (183) an experimental determination of the diffusion coefficients at 73°C was repeated for the concentrations 0.59 and 0.79 mole fractions (run R75 and H53 in Table 6-2.1) the results confirmed all the earlier ones. Diffusion coefficients at boiling points obtained in this work are compared with those of Pratt and Wakeham (158) and of Smith and Storrow (183) in Fig. 6-1.4 and Table 7-1.1c. All these results were obtained by extrapolation or interpolation from experimental data at temperatures close to boiling points. They exhibit the same type of deviation as the results at all other temperatures.

7-1.2 Acetone-water system

A comparison of the data of this work with that of Anderson et al 6 for the acetone-water system at 25°C is given in Table 7-1.2 and Fig. 6-2.2. It can be observed that the agreement is very good. No literature data are available for this system at higher temperatures and therefore no comparison is possible.

7-1.3 Acetone-chloroform system

Data of Anderson et al (6) for this system at 25°C and 40°C are compared with that of the author in Table 7-1.3 and Fig. 6-3.2. The agreement is very good.

The experimental data of Anderson et al (6) were obtained by the Mach-Zehnder type diffusiometer (23) regarded as the most accurate measuring technique. The small deviations between the Anderson et al (6) data and the data of this work constitute a good verification of the accuracy of the three-compartment cell used in this work.

7-2 The effect of concentration on the activation energies and on the group $(D_{AB}\mu_{AB}/\alpha_A)$

Leffler and Cullinan (111),in deriving their correlation for the concentration dependence of diffusion coefficient,assumed that the difference in the free energies of activation for viscosity and diffusivity is constant i.e. $\left(\Delta \bar{E}_{\mu,AB} - \Delta \bar{E}_{D,AB}\right)$ = constant. In this work this correlation was modified on the assumption that the difference between the free energies of activation for viscosity and diffusivity is not constant. This can be proved by using the result of Anderson et al (6). They deduced from the Eyring theory that the free energy of activation can be calculated from the following equations

$$\Delta \bar{E}_{\mu,AB} = R \frac{d(\ln \mu_{AB})}{d\left(\frac{1}{T}\right)} \qquad (7\text{-}2.1)$$

and $$\Delta \bar{E}_{D,AB} = -R \frac{d\left(\ln D_{AB}\right)}{d\left(\frac{1}{T}\right)} \qquad (7\text{-}2.2)$$

The experimental data of viscosity and diffusivity for ethanol-water acetone-water and acetone-chloroform systems will be used to verify assumptions made in this work. By plotting ln μ_{AB} against $\frac{1}{T}$ in Figures 7-2.1 (a, b and c) free energy of activation for viscosity is obtained from the slopes of the lines. Similarly from the plot of $\ln D_{AB}$ against $\frac{1}{T}$ in Figures 6-1.3, 6-2.3 and 6-3.3 free energy of activation for diffusivity is obtained. When the values of free energies of activation are plotted against mole fraction concentration in Figures 7-2.2 (a, b and c) it becomes quite obvious that $(\Delta \bar{E}_{\mu,AB} - \Delta \bar{E}_{D,AB})$ varies with concentration. The values of the free energies of activation are also recorded in Table 7-2.1.

Anderson et al (6) ascribed to Eyring et al (155) the statement that $(D_{AB}\,\mu_{AB}/\alpha_A)$ varies linearly with concentration. The plot of $(D_{AB}\,\mu_{AB}/\alpha_A)$ against mole fraction concentration in Figures 7-2.3 (a, b and c) again does not confirm this statement.

Table 7-1.1a Differential diffusion coefficients of various authors for the ethanol-water system at 25°C, (D_{AB} x 10^5, cm^2/sec.)

Mole fr. x_A	Differential diffusion coefficient, D_{AB}										D_{AB} from Fig. (7-1-1)
	T-W	%dev.	D-S	%dev.	H-S	%dev.	P-W	%dev.	S-S	%dev.	
0.000	1.250	+1.08	1.220	-1.35	1.240	+0.27	1.240	+0.270	1.313	+5.0	1.237
0.014	-	-	1.096	-3.01	-		-		-		1.130
0.020	-		-		1.080	0.00	-		-		1.080
0.026	1.076	+2.97	-		-		-		-		1.045
0.050	-		-		-		0.900	-0.55	-		0.905
0.152	-		-		-		0.460	-6.12	-		0.490
0.229							0.390	0.52	-		0.388
0.266	0.368	-1.87	-		-		-		-		0.375
0.276	-		0.377	0.00	0.362	-3.78	-		-		0.377
0.279	-		-		-		-		0.403	+8.92	0.370
0.308	-		-		-		0.335	-10.67	-		0.375
0.390	-								0.520	+27.45	0.408
0.394	-		0.423	+3.17	0.407	-0.73					0.410
0.408	0.405	-3.57	-		-		-		-		0.420
0.439	-		-		-		0.500	+12.36	-		0.445
0.635	-		-		-		0.755	+12.69	-		0.670
0.680	0.745	+1.36	0.747	+1.63	0.766	+4.22	-		-		0.735
0.680	0.743	+1.09	-		-		-		-		0.735
0.680	0.743	+1.09	-	-	-		-		-		0.735
0.742	-		-		-		-		1.480	+78.30	0.830
0.812	-		-		-		0.930	-1.06	-		0.940
0.842	-		1.01	+2.54	-		-		-		0.985
0.844	-		-		0.981	-0.71	-		-		0.988
0.880	1.047	0.00	-		-		-		-		1.047
0.944	1.131	0.00	-		-		-		-		1.131
0.948	-								2.150	+88.6	1.140
1.00	1.220	0.00	1.220	0.00	1.132	-7.21	1.08	-11.50	2.360	+93.4	1.220
Avg. % dev.		1.18		1.46		2.46		6.20		50.28	

T-W	This work
D-S	Dullien and Shemilt (43)
H-S	Hammond and Stokes (76)
P-W	Pratt and Wakeham (158)
S-S	Smith and Storrow (183)

Table 7-1·1 b : A comparison of the differential diffusion coefficients of various authors for the ethanol-water system, (D_{AB} x 10^5 cm^2 /sec.)

Mole fr. of ethanol x_A	D_{AB} at 25°C					D_{AB} at 40°C				
	T-W	P-W	% dev.	S-S	% dev.	T-W	P-W	%dev.	S-S	% dev.
0.000	1.25	1.24	-0.8	1.313	5.0	1.70	1.72	+1.2	1.880	10.6
0.050	0.91	0.90	-1.1	-	-	1.32	1.26	-4.5	-	-
0.152	0.49	0.46	-5.7	-	-	0.78	0.70	-10.3	-	-
0.229	0.38	0.39	+2.6	-	-	0.65	0.60	-7.6	-	-
0.245	-	-	-	-	-	-	-	-	-	-
0.269	-	-	-	-	-	-	-	-	-	-
0.279	0.365	-	-	0.403	10.4	-	-	-	-	-
0.291	-	-	-	-	-	0.61	-	-	0.594	-2.6
0.308	0.37	0.37	0.0	-	-	0.610	0.59	-3.3	-	-
0.390	0.41	-	-	0.52	26.8	-	-	-	-	-
0.439	0.43	0.50	16.3	-	-	0.67	0.78	16.1	-	-
0.450	-	-	-	-	-	-	-	-	-	-
0.472	-	-	-	-	-	-	-	-	-	-
0.488	-	-	-	-	-	0.71	-	-	0.815	
0.635	0.66	0.74	12.1	-	-	0.93	1.15	23.7	-	-
0.718	-	-	-	-	-	-	-	-	-	-
0.742	0.81	-	-	1.48	82.7	-	-	-	-	-
0.766	-	-	-	-	-	-	-	-	-	-
0.770	-	-	-	-	-	1.21	-	-	1.81	14.8
0.812	0.94	0.93	-1.1	-	-	1.30	1.39	6.9	-	-
0.948	1.14	-	-	2.15	88.6	-	-	-	-	-
0.955	-	-	-	-	-	-	-	-	-	-
0.956	-	-	-	-	-	-	-	-	-	-
0.959	-	-	-	-	-	1.56	-	-	2.91	86.5
1.000	1.22	1.08	-11.5	2.36	93.4	1.64	1.54	-6.1	3.20	107.8
Avg. % deviation			5·7		51.2			8.9		44.46

Table 7–1·1 b : A comparison of the differential diffusion coefficients of various authors for the ethanol-water system, (D_{AB} x 10^5 cm^2/sec.)

Mole fr. of ethanol x_A	D_{AB} at 58°C					D_{AB} at 73°C				
	T-W	P-W	% dev.	S-S	% dev.	T-W	P-W	% dev.	S-S	% dev.
0.000	2.40	2.40	0.0	2.63	9.6	2.82	3.26	15.6	3.16	12.0
0.050	1.90	1.82	-4.2	-	-	2.30	2.40	4.3	-	-
0.152	1.18	1.09	-7.6	-	-	1.58	1.54	-2.5	-	-
0.229	0.965	0.942	-2.4	-	-	1.38	1.33	-3.6	-	-
0.245	-	-	-	-	-	1.37	-	-	1.69	23.4
0.269	0.925	-	-	0.882	-4.6	-	-	-	-	-
0.279	-	-	-	-	-	-	-	-	-	-
0.291	-	-	-	-	-	-	-	-	-	-
0.308	0.93	0.97	4.3	-	-	1.34	1.41	5.2	-	-
0.390	-	-	-	-	-	-	-	-	-	-
0.439	1.08	1.22	13.0	-	-	1.48	1.74	17.6	-	-
0.450	1.10	-	-	0.912	17.1	-	-	-	-	-
0.472	-	-	-	-	-	1.55	-	-	1.41	-9.0
0.488	-	-	-	-	-	-	-	-	-	-
0.635	1.454	1.870	28.6	-	-	1.97	2.68	36.0	-	-
0.718	1.64	-	-	1.99	21.3	-	-	-	-	-
0.742	-	-	-	-	-	-	-	-	-	-
0.766	-	-	-	-	-	2.38	-	-	2.70	13.4
0.770	-	-	-	-	-	-	-	-	-	-
0.812	1.84	2.18	18.5	-	-	2.53	3.02	19.4	-	-
0.948	-	-	-	-	-	-	-	-	-	-
0.955	2.23	-	-	3.91	75.3	-	-	-	-	-
0.956	-	-	-	-	-	2.97	-	-	4.80	61.6
0.959	-	-	-	-	-	-	-	-	-	-
1.000	2.36	2.21	-6.4	4.40	86.4	3.10	3.11	0.3	5.40	74.2
Avg. % deviation			9.4		35.7			17.4		32.3

Table 7-1·1 b (continued)

T-W = This work

S-S = Smith and Storrow (183);

P-W = Pratt and Wakeham (from Fig. (7-1·2));

% error = $\left[D_{AB} \text{ (others)} - D_{AB} \text{ (this work)}\right] \times 100/D_{AB}$ (this work)

Table 7-1·1c Comparison of the differential diffusion coefficients (at boiling points) of various authors for the ethanol - water system, ($D_{AB} \times 10^5$, cm^2/sec.)

Mole fr. ethanol x_A	$D_{AB} \times 10^5$, cm^2/sec.				
	T-W	P-W	% dev.	S-S	% dev.
0.0	4.32	5.05	16.90	3.47	-20
0.1	2.50	2.50	0.00	2.87	15
0.2	1.75	1.70	-2.86	1.96	9
0.3	1.61	1.70	5.59	1.61	0
0.4	1.76	1.90	7.95	1.57	-16
0.5	2.05	2.40	17.07	1.26	-39
0.6	2.20	3.05	38.64	2.04	-8
0.7	2.45	3.30	34.69	2.60	6
0.8	2.69	3.40	26.39	3.19	19
0.9	2.97	3.45	16.16	3.63	22
1.0	3.33	3.48	4.50	6.30	89
Avg. % deviation			15.5		22.09

See Fig. 6-1.4

Table 7-1·2 : Comparison of the data of this work with that of Anderson et al (6) for acetone-water system at 25°C (D_{AB} x 10^5, cm^2/sec.)

Mole fr. acetone x_A	D_{AB} x 10^5, cm^2/sec.		
	T-W	A-B*	% dev.
0.0	1.230	1.285	4.47
0.0022	1.280	1.28	0.00
0.0831	0.860	0.854	-0.69
0.2392	0.650	0.635	-2.31
0.4893	0.800	0.819	2.38
0.6653	1.460	1.430	-2.05
0.8036	2.470	2.390	-3.24
0.9265	3.940	3.800	-3.55
0.9696	4.650	4.560	-1.94
1.000	5.200	5.10	-1.92
Avg. % deviation			2.26

* A-B : Anderson et al (6)

Table 7-1·3 : Comparison of the data of this work with that of Anderson et al (6) for acetone-chloroform system at 25°C and 40°C (D_{AB}x10^5, cm^2/sec.)

Mole fr. acetone x_A	D_{AB} at 25°C			D_{AB} at 40°C		
	T-W	A-B	% dev.	T-W	A-B	% dev.
0.0055	2.349	2.35	0.04	2.905	2.89	-0.52
0.2013	-	-	-	3.630	3.58	-1.38
0.2081	2.942	2.97	0.95	-	-	-
0.3903	3.250	3.29	1.23	-	-	-
0.3984	-	-	-	4.055	4.05	-0.12
0.4989	-	-	-	4.160	4.15	-0.24
0.6040	3.45	3.45	0.0	4.215	4.24	0.59
0.7472	3.52	3.52	0.0	-	-	-
0.8592	-	-	-	4.295	4.27	-0.58
0.8641	3.57	3.59	0.56	4.298	4.28	-0.42
0.9948	3.616	3.63	0.39	4.320	4.31	-0.23
0.9953	3.617	3.63	0.36	-	-	-
Avg. % deviation			0.44			0.51

Table 7-2.1 Concentration dependence of experimental activation energies for diffusive flow and viscous flow for binary liquid mixtures.

($\Delta\bar{E}_{D,AB}$ and $\Delta\bar{E}_{\mu,AB}$ in Kcal/gmole)

Mole fr. A	Ethanol (A) and water (B)		Acetone (A) and water (B)		Acetone (A) and chloroform (B)	
	$\Delta\bar{E}^*_{D,AB}$	$\Delta\bar{E}^{**}_{\mu,AB}$	$\Delta\bar{E}^*_{D,AB}$	$\Delta\bar{E}^{**}_{\mu,AB}$	$\Delta\bar{E}^*_{D,AB}$	$\Delta\bar{E}^{**}_{\mu,AB}$
0.0	3.642	3.444	3.168	3.444	2.607	1.696
0.1	4.474	4.860	3.262	4.393	2.544	1.891
0.2	5.102	5.152	3.076	4.319	2.549	1.799
0.3	5.356	5.029	3.123	3.886	2.546	1.827
0.4	5.467	4.841	3.328	3.551	2.482	1.852
0.5	5.452	4.499	4.081	3.109	2.381	1.861
0.6	5.073	4.350	3.500	2.562	2.418	1.836
0.7	4.631	4.006	2.838	2.245	2.360	1.885
0.8	4.179	3.744	2.387	2.090	2.3700	1.868
0.9	4.056	3.600	1.906	1.817	2.357	1.774
1.0	4.000	3.508	1.653	1.692	2.384	1.692

* From Figures (6-1.3), (6-2.3), and (6-3.3) and equation (7-2.2)

** From Figures (7-2.1a), (7-2.1b) and (7-2.1c) and equation (7-2.1)

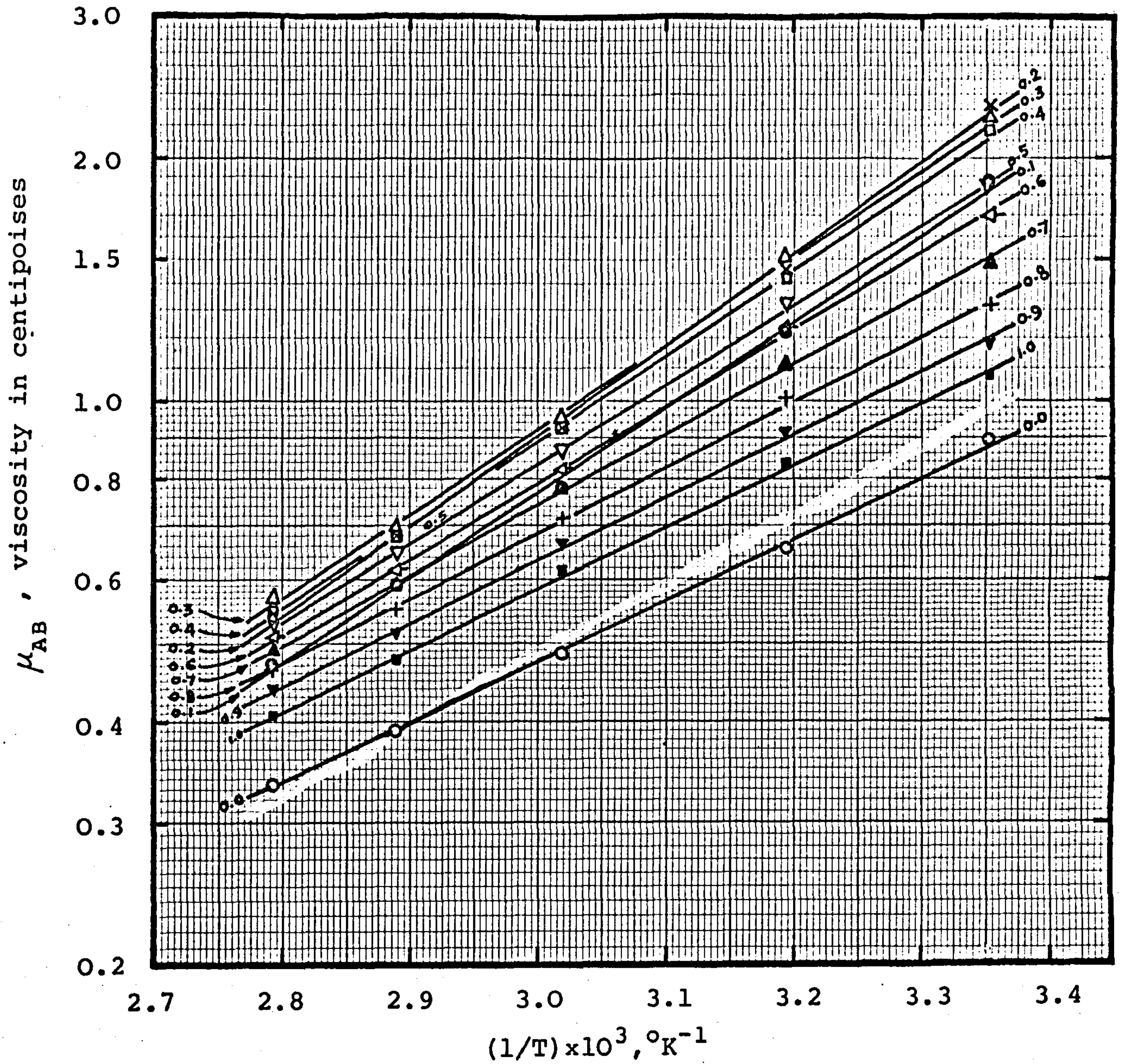


Figure 7-2.1a Variation of ln μ_{AB} with (1/T) for ethanol-water mixtures (from Table 5-3.1a)

Numbers on lines indicate concentration of ethanol in mole fr.

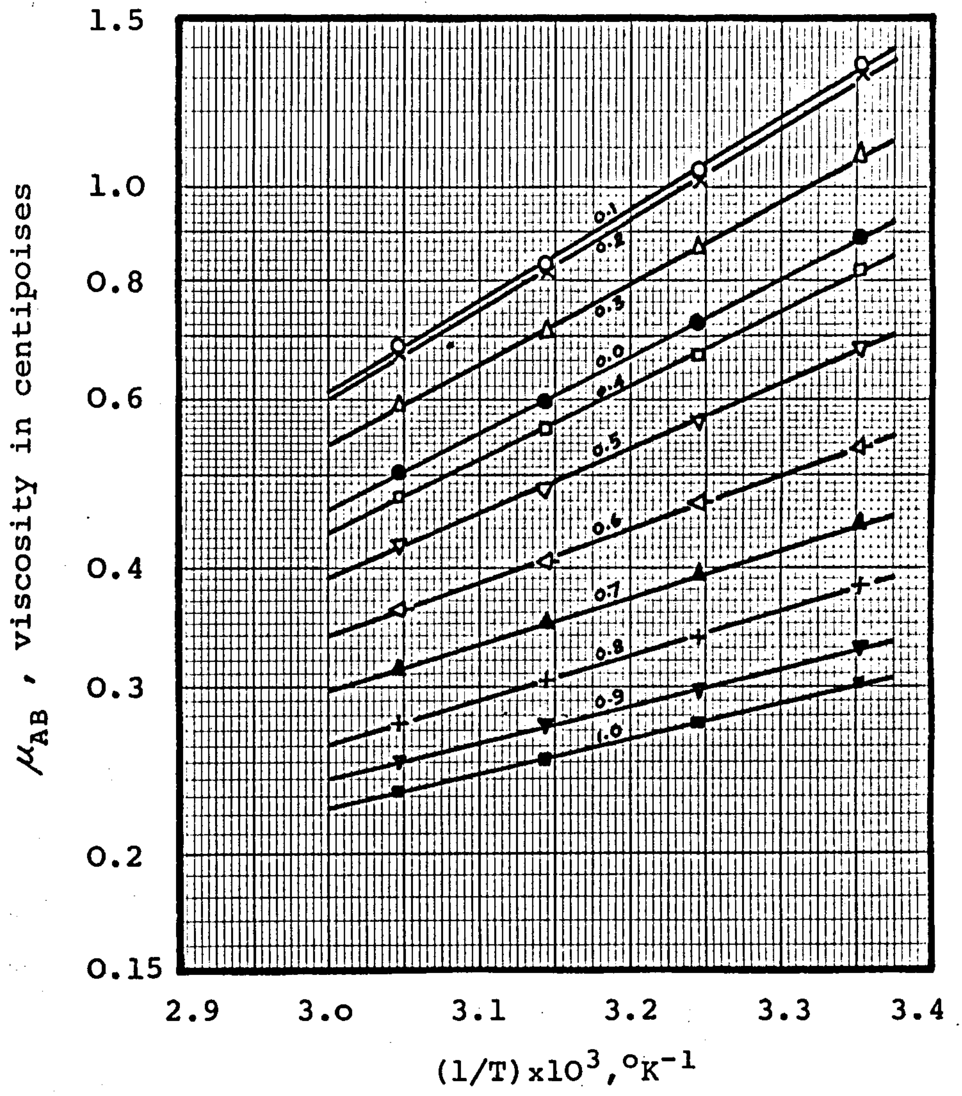


Figure 7-2.1b Variation of $\ln\mu_{AB}$ with (1/T) for acetone-water mixtures (from Table 5-3.2a)

Numbers on lines indicate concentration of acetone in mole fr.

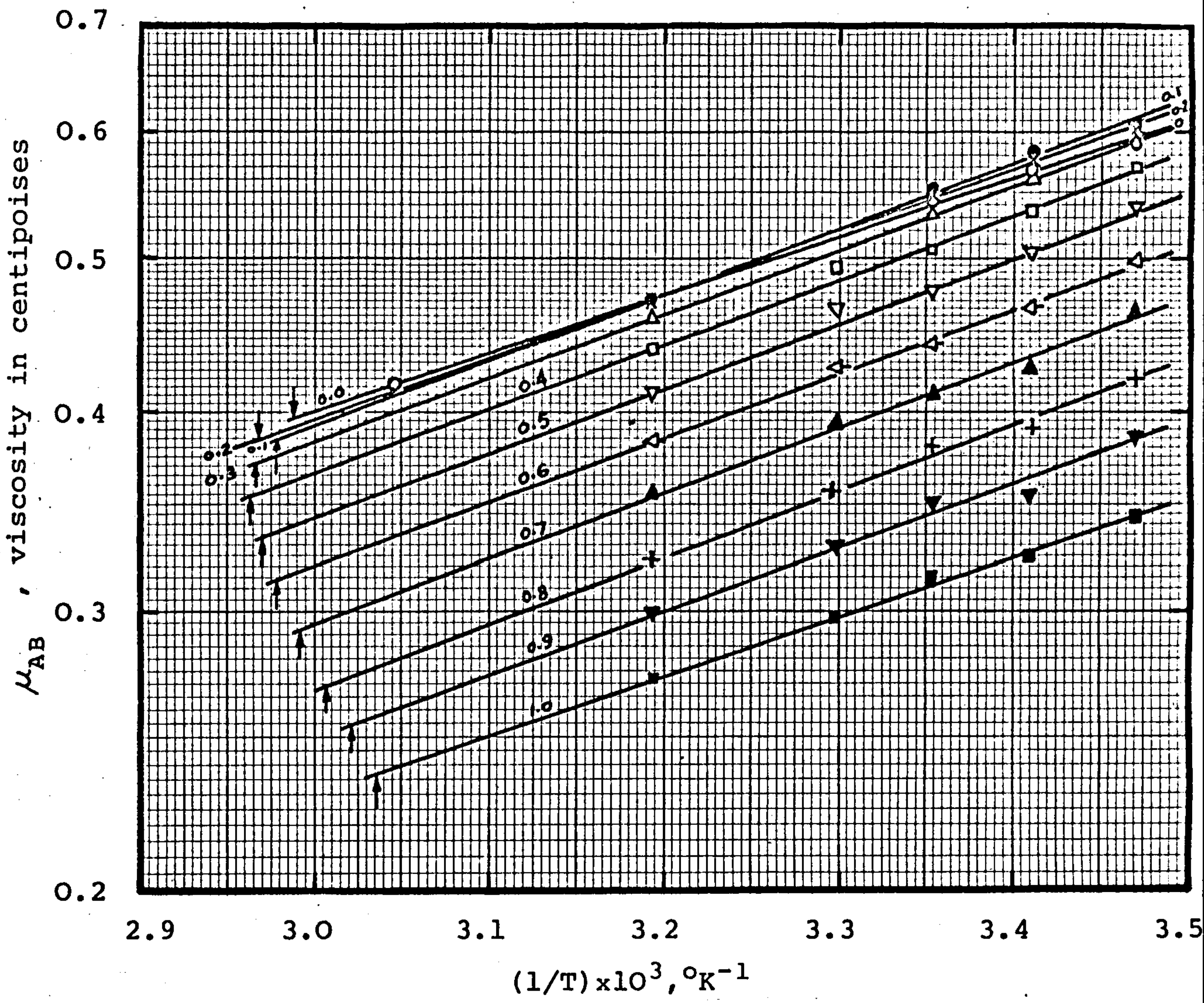


Figure 7-2.1c Variation of $\ln\mu_{AB}$ with (1/T) for acetone-chloroform mixtures (from Table 5-3.3a)

↓ ↑ indicate boiling point

Numbers on lines indicate concentration of acetone in mole fr.

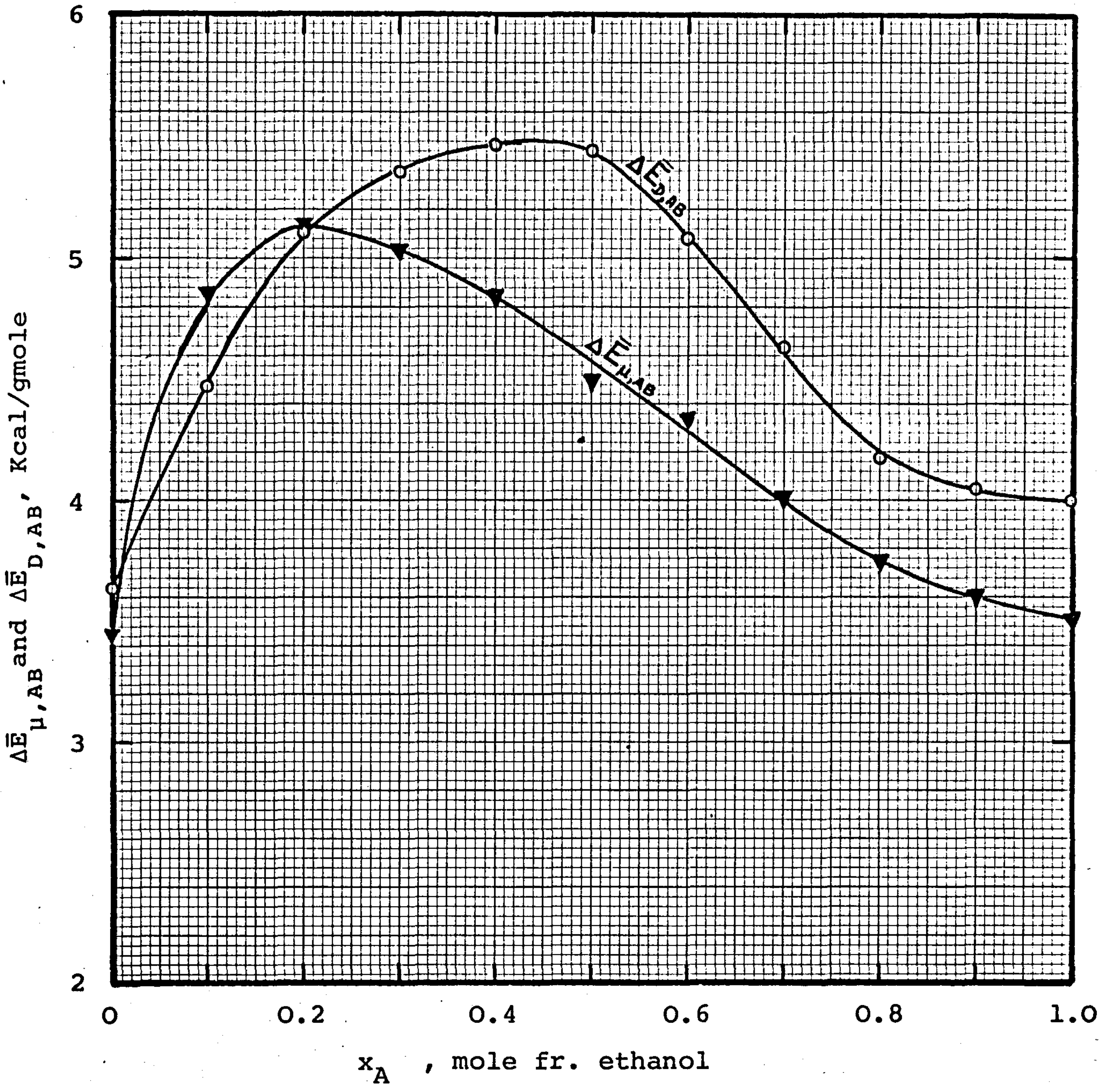


Figure 7-2.2a Experimental activation energies for viscosity and diffusion for ethanol-water mixtures (from Table 7-2.1).

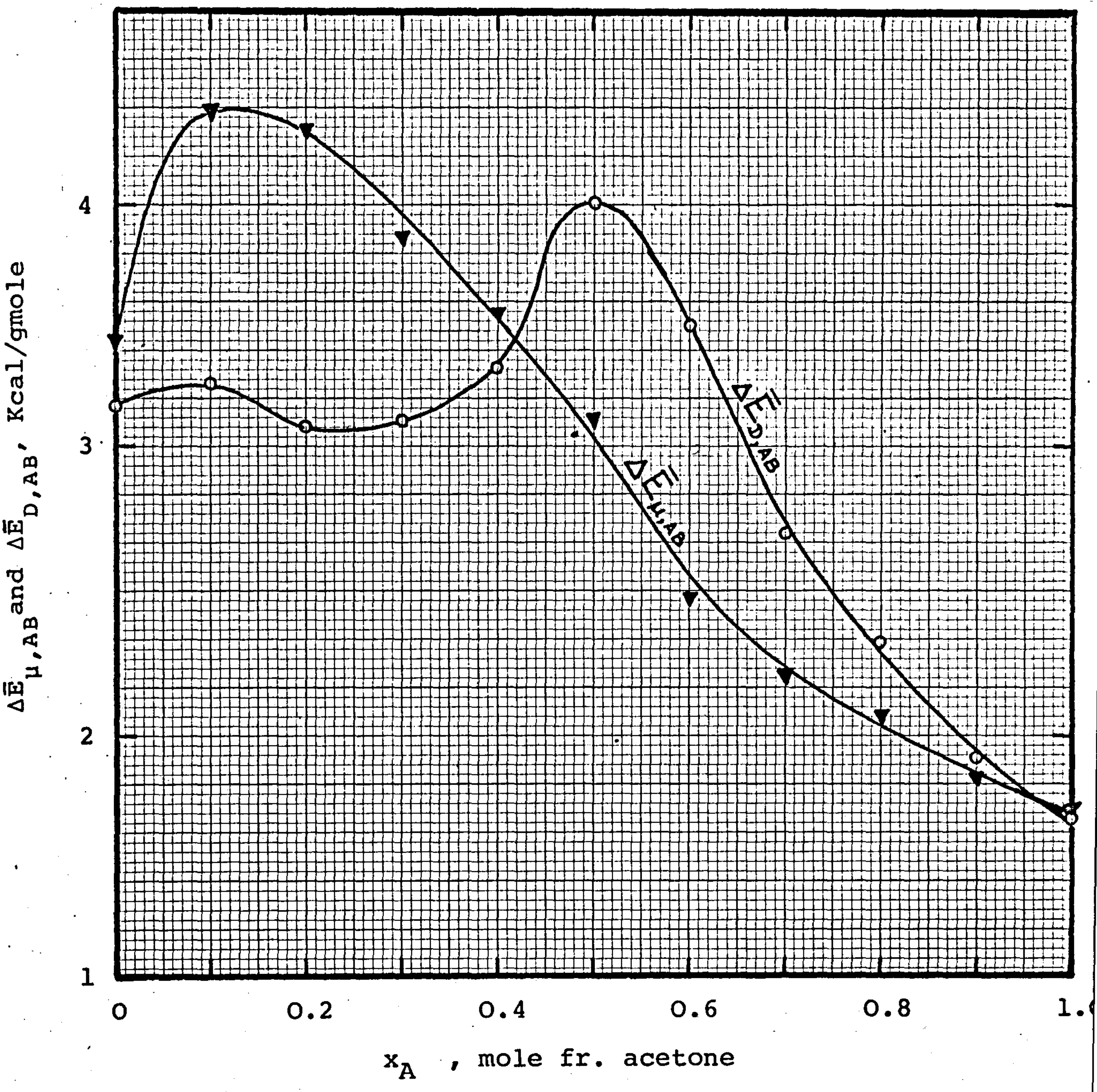


Figure 7-2.2b Experimental activation energies for viscosity and diffusion for acetone-water mixtures (from Table 7-2.1).

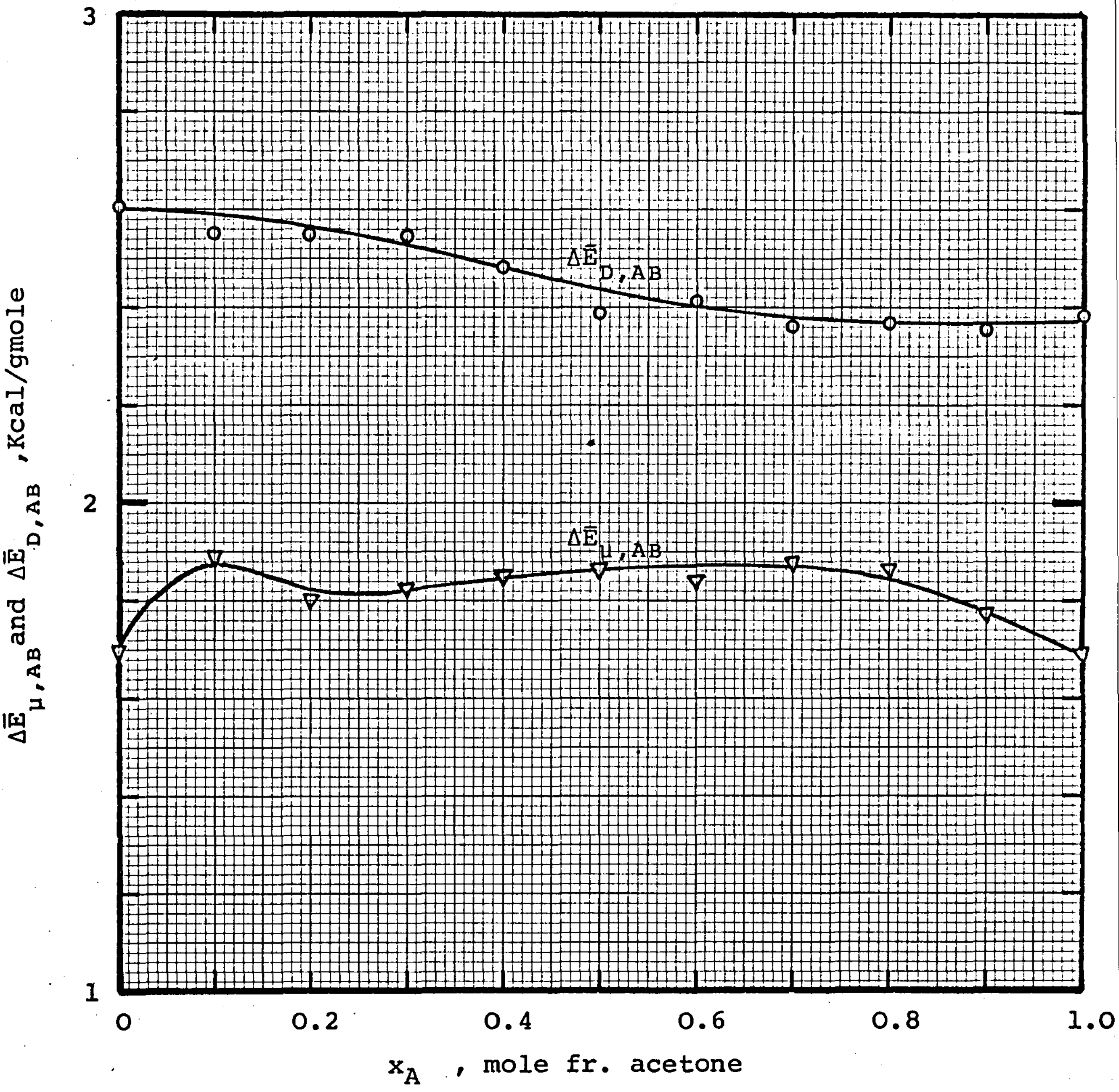


Figure 7-2.2c Experimental activation energies for viscosity and diffusion for acetone-chloroform mixtures (from Table 7-2.1).

Table 7-2.2a Concentration dependence of $(D_{AB}\ \mu_{AB})$ and $(D_{AB}\ \mu_{AB}/\alpha_A)$ for ethanol-water mixtures.

($D_{AB} \times 10^5$ in cm^2/sec ; μ_{AB} in centipoises)

Mole fr. ethanol x_A	25°C		40°C		58°C		73°C	
	$D_{AB}\mu_{AB}$	$\frac{D_{AB}\mu_{AB}}{\alpha_A}$	$D_{AB}\mu_{AB}$	$\frac{D_{AB}\mu_{AB}}{\alpha_A}$	$D_{AB}\mu_{AB}$	$\frac{D_{AB}\mu_{AB}}{\alpha_A}$	$D_{AB}\mu_{AB}$	$\frac{D_{AB}\mu_{AB}}{\alpha_A}$
0.0	1.1098	1.1098	1.1161	1.116	1.1664	1.166	1.1505	1.150
0.1	1.2596	1.657	1.2100	1.613	1.1850	1.662	1.1210	2.411
0.2	0.9471	2.310	0.9901	2.330	0.9445	1.870	0.9656	2.682
0.3	0.8436	2.280	0.9150	2.056	0.8835	2.155	0.9326	2.591
0.4	0.8829	2.487	0.9101	1.750	0.9404	1.862	0.9628	2.348
0.5	0.9163	2.235	0.9563	1.635	1.0321	1.827	1.0465	2.1141
0.6	1.0370	1.957	1.0553	1.702	1.1316	1.802	1.1458	2.028
0.7	1.1175	1.706	1.1745	1.666	1.2243	1.700	1.2716	1.779
0.8	1.1790	1.531	1.2852	1.617	1.2960	1.620	1.3720	1.605
0.9	1.2733	1.392	1.3482	1.457	1.3699	1.548	1.4448	1.557
1.0	1.3176	1.318	1.3710	1.371	1.4514	1.451	1.4849	1.485

Values of D_{AB}, μ_{AB} and α_A are found from Tables 6-2.2, 5-3.1a and 5-3.1b respectively.

Table 7-2.2b Concentration dependence of $(D_{AB}\ \mu_{AB})$ and $(D_{AB}\ \mu_{AB}\ /\ \alpha_A)$ for acetone-water mixtures, $(D_{AB} \times 10^5$, cm^2/sec, μ_{AB} in centipoises)

Mole fr. Acetone x_A	25°C		35°C		45°C		55°C	
	$D_{AB}\mu_{AB}$	$\frac{D_{AB}\mu_{AB}}{\alpha_A}$	$D_{AB}\mu_{AB}$	$\frac{D_{AB}\mu_{AB}}{\alpha_A}$	$D_{AB}\mu_{AB}$	$\frac{D_{AB}\mu_{AB}}{\alpha_A}$	$D_{AB}\mu_{AB}$	$\frac{D_{AB}\mu_{AB}}{\alpha_A}$
0.00	1.1501	1.150	1.1536	1.154	1.0847	1.085	1.0786	1.079
0.10	1.0773	1.691	1.0296	1.674	0.9307	1.616	0.9207	1.689
0.20	0.8010	1.863	0.7964	1.856	0.7426	1.904	0.7169	1.938
0.30	0.7056	2.205	0.6763	2.113	0.6416	2.175	0.6254	2.085
0.40	0.6195	2.065	0.5749	1.825	0.5824	2.044	0.5843	2.291
0.50	0.5950	1.919	0.5843	1.916	0.6244	1.915	0.6372	2.317
0.60	0.6418	1.945	0.6388	1.852	0.6675	1.935	0.7023	2.341
0.70	0.7680	1.873	0.7440	1.730	0.7595	1.707	0.8138	2.035
0.80	0.9635	1.853	0.9153	1.777	0.9120	1.658	0.9735	1.780
0.90	1.2580	1.772	1.1661	1.772	1.1809	1.687	1.2475	1.782
1.00	1.7888	1.789	1.5400	1.540	1.5186	1.519	1.5531	1.553

Values of D_{AB}, μ_{AB} and α_A are found from Tables 6-2.4, 5-3.2a and 5-3.2b respectively.

Table 7-2.2c Concentration dependence of $(D_{AB}\,\mu_{AB})$ and $(D_{AB}\,\mu_{AB}\ /\ \alpha_A)$ for acetone-chloroform mixtures, $(D_{AB} \times 10^5$ in cm^2/sec. μ_{AB} in centipoises$)$

Mole fr. acetone A	25°C		40°C		55°C	
	$D_{AB}\,\mu_{AB}$	$\frac{D_{AB}\mu_{AB}}{\alpha_A}$	$D_{AB}\,\mu_{AB}$	$\frac{D_{AB}\quad{}_{AB}}{\alpha_A}$	$D_{AB}\,\mu_{AB}$	$\frac{D_{AB}\mu_{AB}}{\alpha_A}$
0.0	1.2605	1.261	1.3594	1.359	1.4435	1.444
0.1	1.4929	1.367	1.5609	1.346	1.6277	1.453
0.2	1.6152	1.378	1.6978	1.306	1.7920	1.457
0.3	1.6794	1.155	1.7770	1.269	1.8480	1.422
0.4	1.6822	1.049	1.7823	1.204	1.8212	1.329
0.5	1.6427	1.083	1.7139	1.182	1.7350	1.266
0.6	1.5516	1.128	1.6166	1.198	1.6516	1.270
0.7	1.4420	1.151	1.5088	1.217	1.5369	1.239
0.8	1.3460	1.201	1.3824	1.192	1.4280	1.253
0.9	1.2537	1.183	1.2857	1.169	1.3520	1.313
1.0	1.1403	1.140	1.1750	1.175	1.2667	1.267

Values of D_{AB}, μ_{AB} and α_A are found from Tables 6-2.6, 5-3.3a and 5-3.3b respectively.

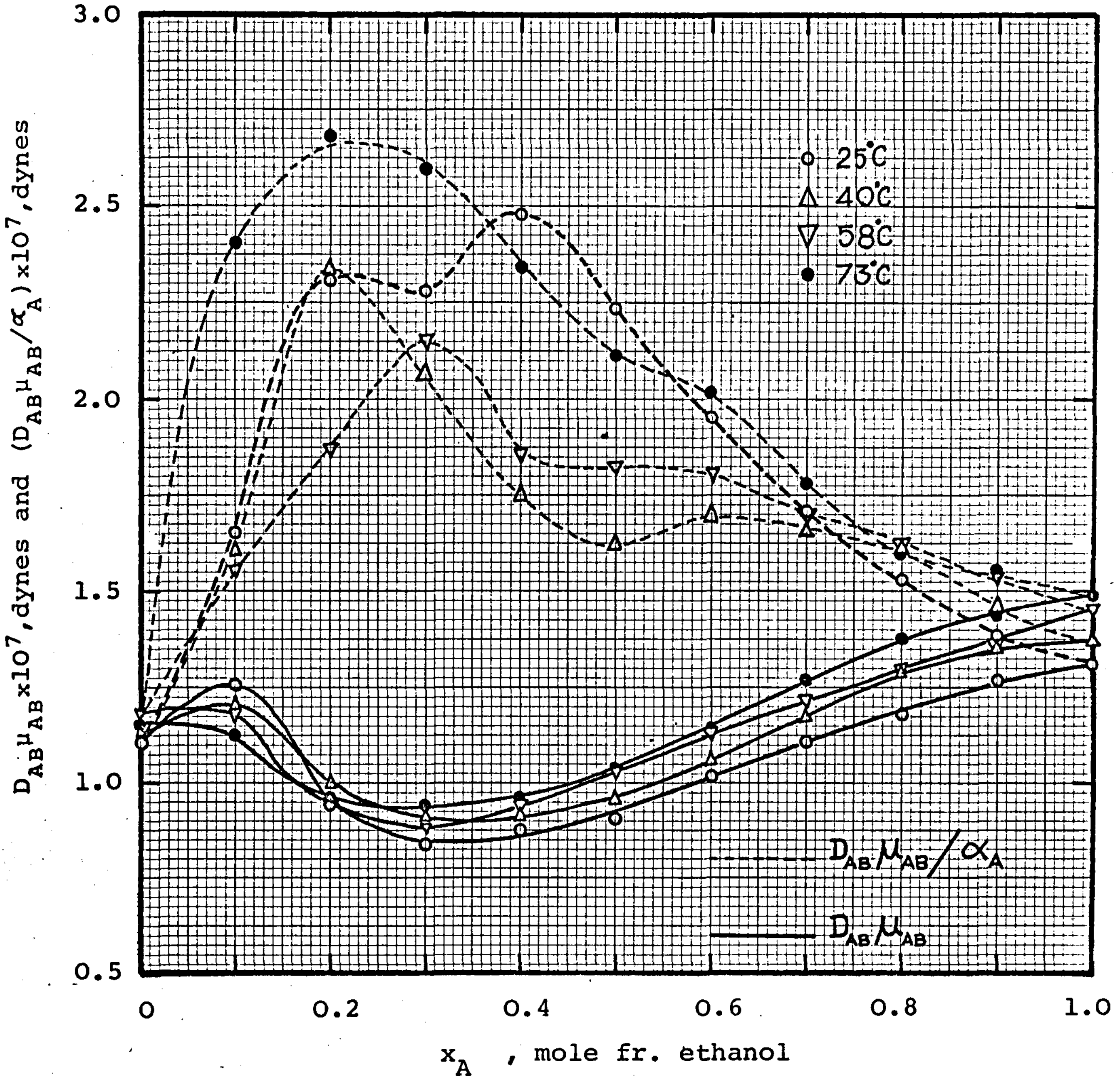


Figure 7-2.3a Concentration dependence of ($D_{AB}\mu_{AB}$) and $(D_{AB}\mu_{AB}/\alpha_A)$ for ethanol-water mixtures.

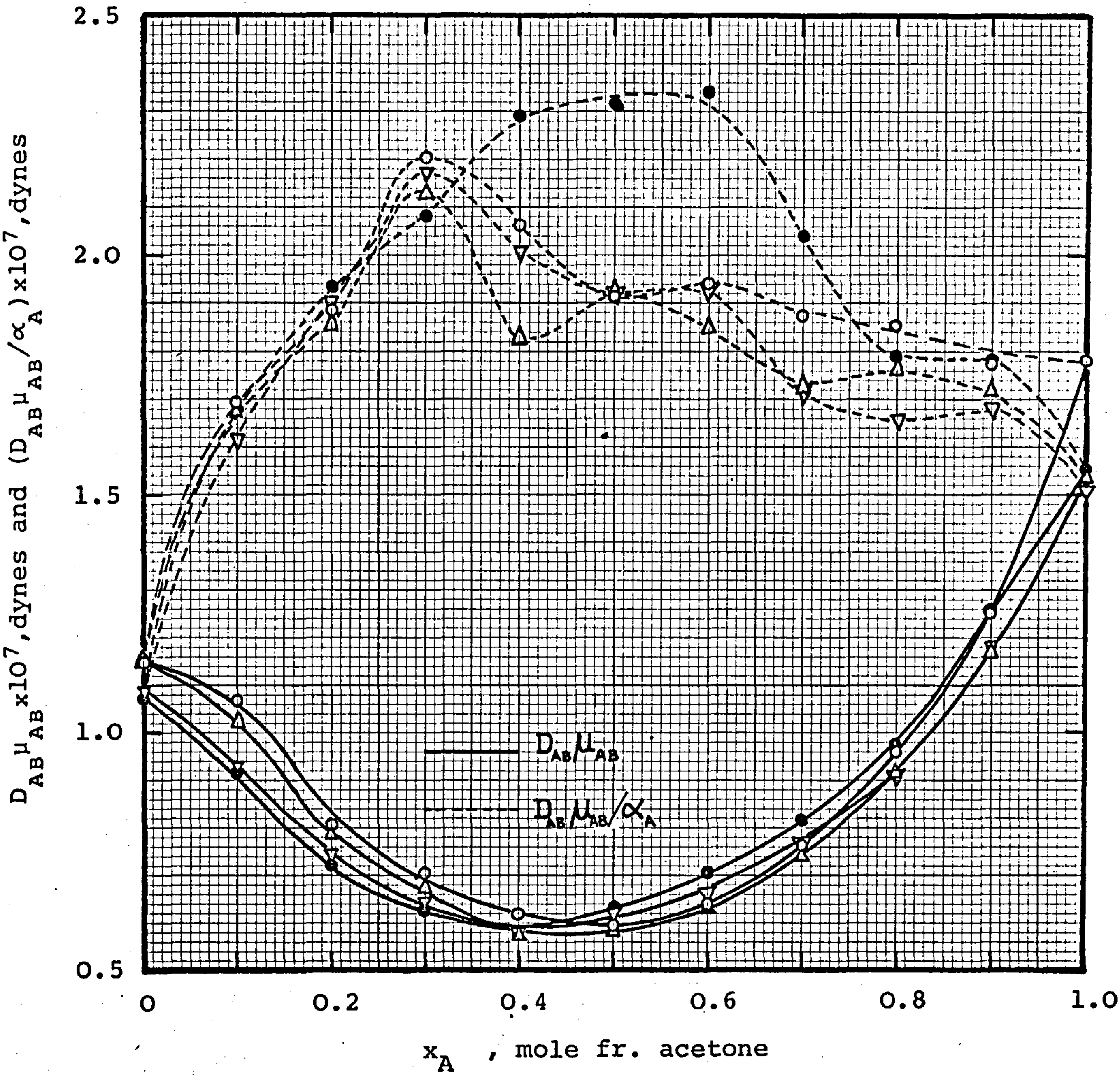


Figure 7-2.3b Concentration dependence of $(D_{AB}\mu_{AB})$ and $(D_{AB}\mu_{AB}/\alpha_A)$ for acetone-water mixtures.

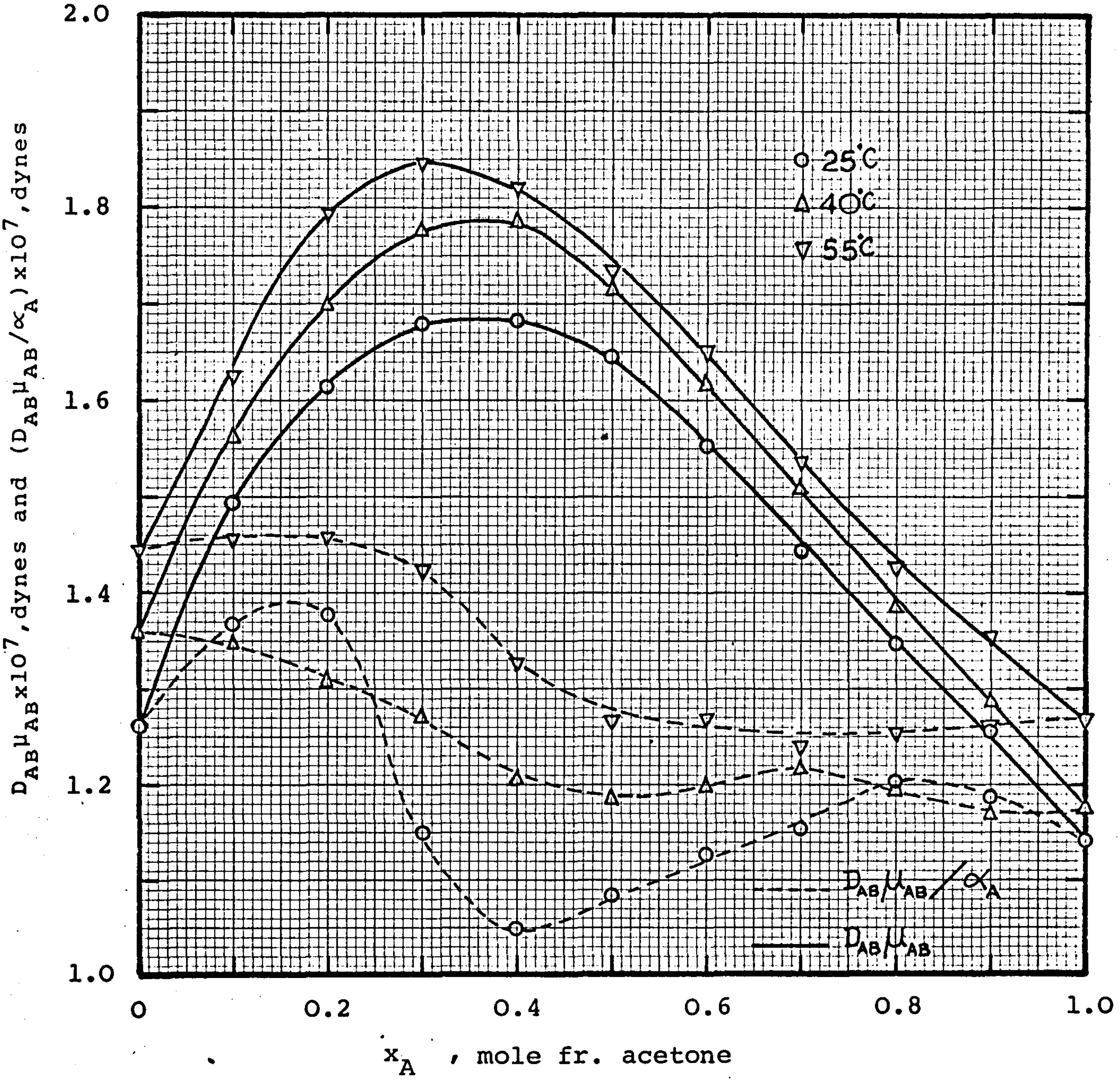


Figure 7-2.3c Concentration dependence of $(D_{AB}\mu_{AB})$ and $(D_{AB}\mu_{AB}/\alpha_A)$ for acetone-chloroform mixtures.

7-3 Testing the correlations with experimental data

7-3.1 Correlations for diffusion coefficients in concentrated solutions

The correlation developed in this work i.e. eq. (3-1.21) as well as the correlation of Leffler and Cullinan i.e. eq. (2-4.16) and that of Vignes i.e. eq. (2-4.12) were tested with the experimental data of this work for ethanol-water, acetone-water and acetone-chloroform mixtures at all temperatures studied. The necessary physical properties required for these calculations are given in section 5. The comparisons of the predicted values, by means of these equations, with the experimental data are given in Tables 7-3.1 (a, b and c) and in Figures 7-3.1 (a, b and c).

For ethanol-water the Leffler and Cullinan equation (2-4.16) consistently underpredicts for all temperatures giving an average deviation of -30%, the Vignes equation (2-4.12) overpredicts at temperatures of 25°C, 40°C and 58°C with an average deviation of +14% while it gives a negative deviation of -12% at 73°C, and equation (3-1.21) gives an average deviation of 9% for all the results and has a tendency to underpredict.

For the acetone-water the Leffler and Cullinan equation (2-4.16) consistantly underpredicts with an average deviation of about 29%, the Vignes equation (2-4.12) mainly underpredicts with an average deviation of about 14% and equation (3-1.21) mainly underpredicts with an average deviation of 10%.

For acetone-chloroform the Leffler and Cullinan equation (2-4.16) gives slightly better predictions than the other two equations, the average deviation being 4.6%, the Vignes equation (2-4.12) and equation (3-1.21) give an average deviation of 13.4% and 8.3% respectively.

It emerges from this comparison of the experimental data with the predicted diffusion coefficients that eq. (3-1.21) gives better predictions than the other two equations in the case of systems when both components, or one of them, have the property of association. The Leffler and Cullinan eq. (2-4.16), on the other hand, predicts best in the case of binary systems in which both components are non-associating.

7-3.2 Correlations for diffusion coefficients at infinite dilution

Equation (3-2.4) developed in section 3-2 for the prediction of diffusion coefficients at infinite dilution was tested, together with the equations of Wilke and Chang, eq. (2-3.16), Sitaraman et al, eq (2-3.27) and King et al (2-3.29), with the experimental data of this work for ethanol-water, acetone-water and acetone-chloroform mixtures. The necessary physical properties for these calculations are given in Appendices 3-2.1 and 3-2.2. The equations are tested for all temperatures up to the normal boiling points of the test solvents. The predicted values are compared with the experimental values in Tables 7-3.2 (a, b and c). Inspection of these tables shows that eq. (3-2.4) compares quite favourably with the other equations.

7-3.3 Correlation for temperature dependence of diffusion coefficients at infinite dilution

In section 3-4.2, a correlation was presented for predicting the diffusion coefficients of dilute binary mixtures at various temperatures from a single value of a diffusion coefficient at one temperature. To test eq. (3-4.7) diffusion coefficients at infinite dilution for the systems, ethanol-water, acetone-water and acetone-chloroform, at $25^{o}C$ were treated as reference coefficients. The critical temperatures for the solvents involved were taken from reference (168). The values of the predicted coefficients are recorded in Table 7-3.3 (a, b and c) and compared with the corresponding experimental values. In the same Table diffusion coefficients predicted by the Stokes-Einstein eq. (2-5.1) are also given and compared with the experimental ones. The deviations of the predicted coefficients from the experimental coefficients for both equations are comparable. It is to be noted that the values of the coefficients at temperatures close to boiling points were not taken into account when calculating the average deviations.

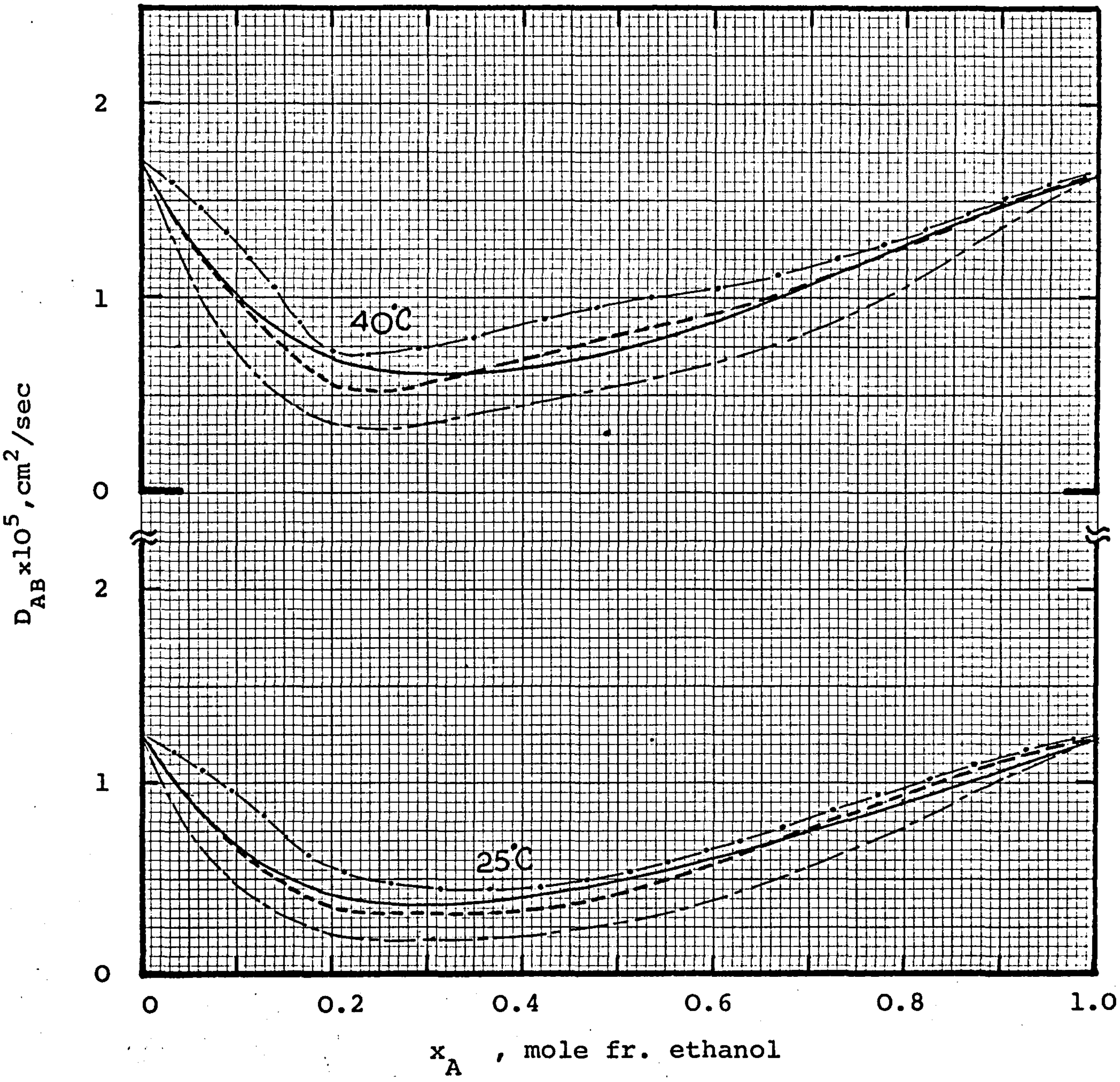


Figure 7-3.1a Comparison of the experimental diffusion coefficients with the predicted coefficients for ethanol-water system.

—·—·—·— Vignes eq.(2-4.12)
— — — — Leffler & Cullinan eq.(2-4.16)
- - - - - - This work, eq.(3-1.21)
———— Experimental, from Table (6-2.2)

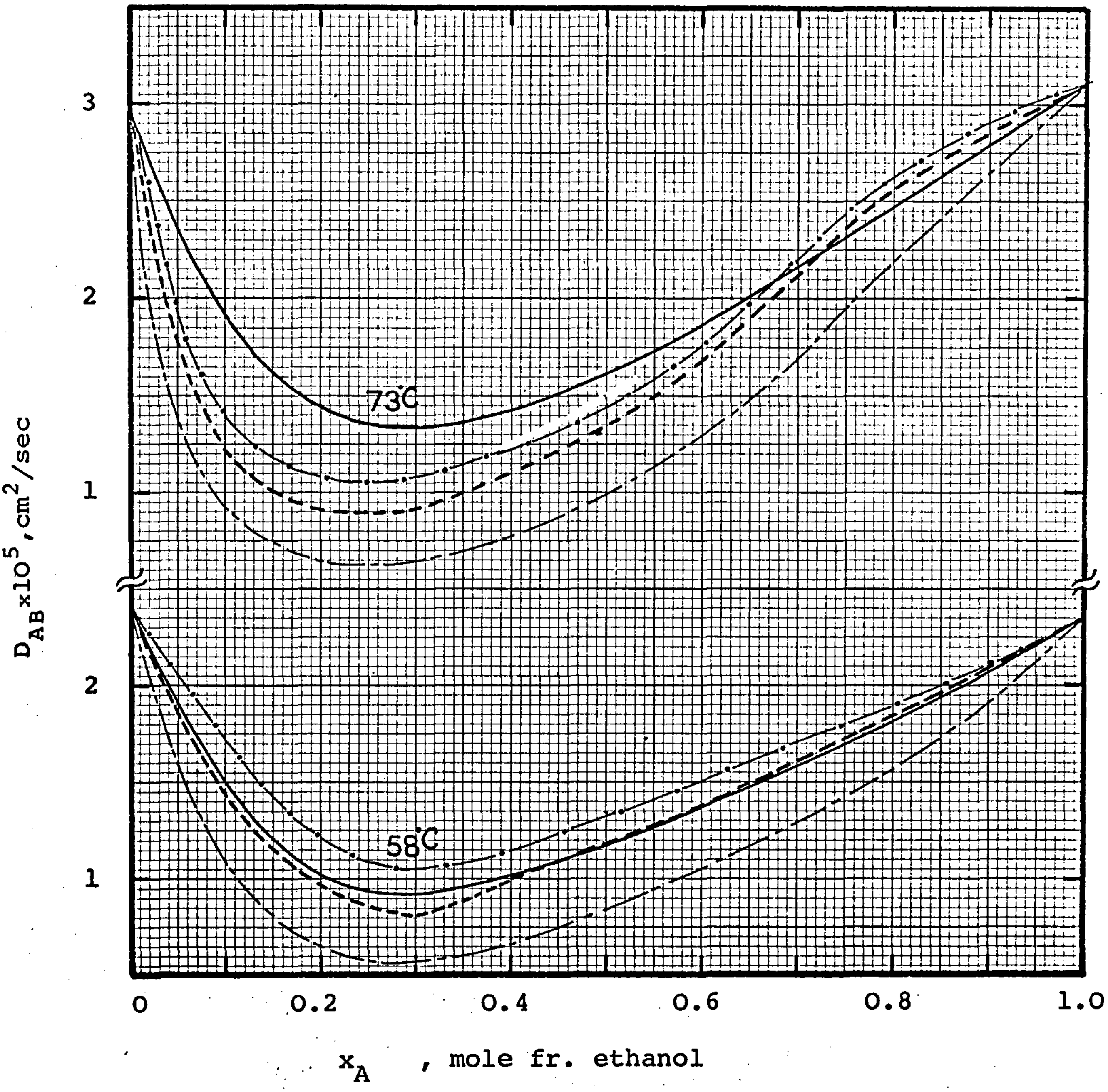


Figure 7-3.1a (continued)

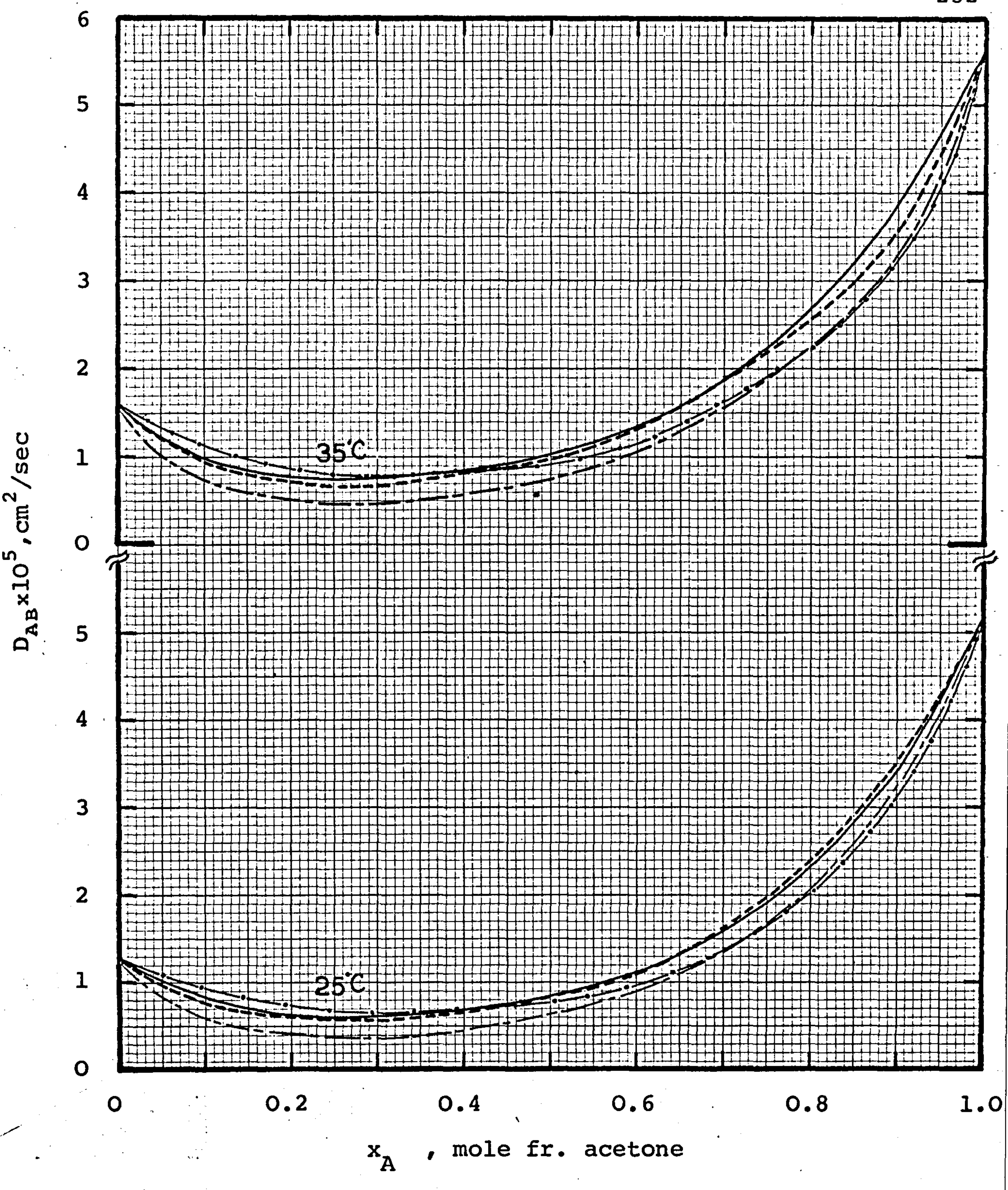


Figure 7-3.1b Comparison of the experimental diffusion coefficients with the predicted coefficients for acetone-water system.

—•—•—•— Vignes eq.(2-4.12)
—-—-—-— Leffler & Cullinan eq.(2-4.16)
- - - - - - - This work, eq.(3.1.21)
———— Experimental, from Table 6-2.4

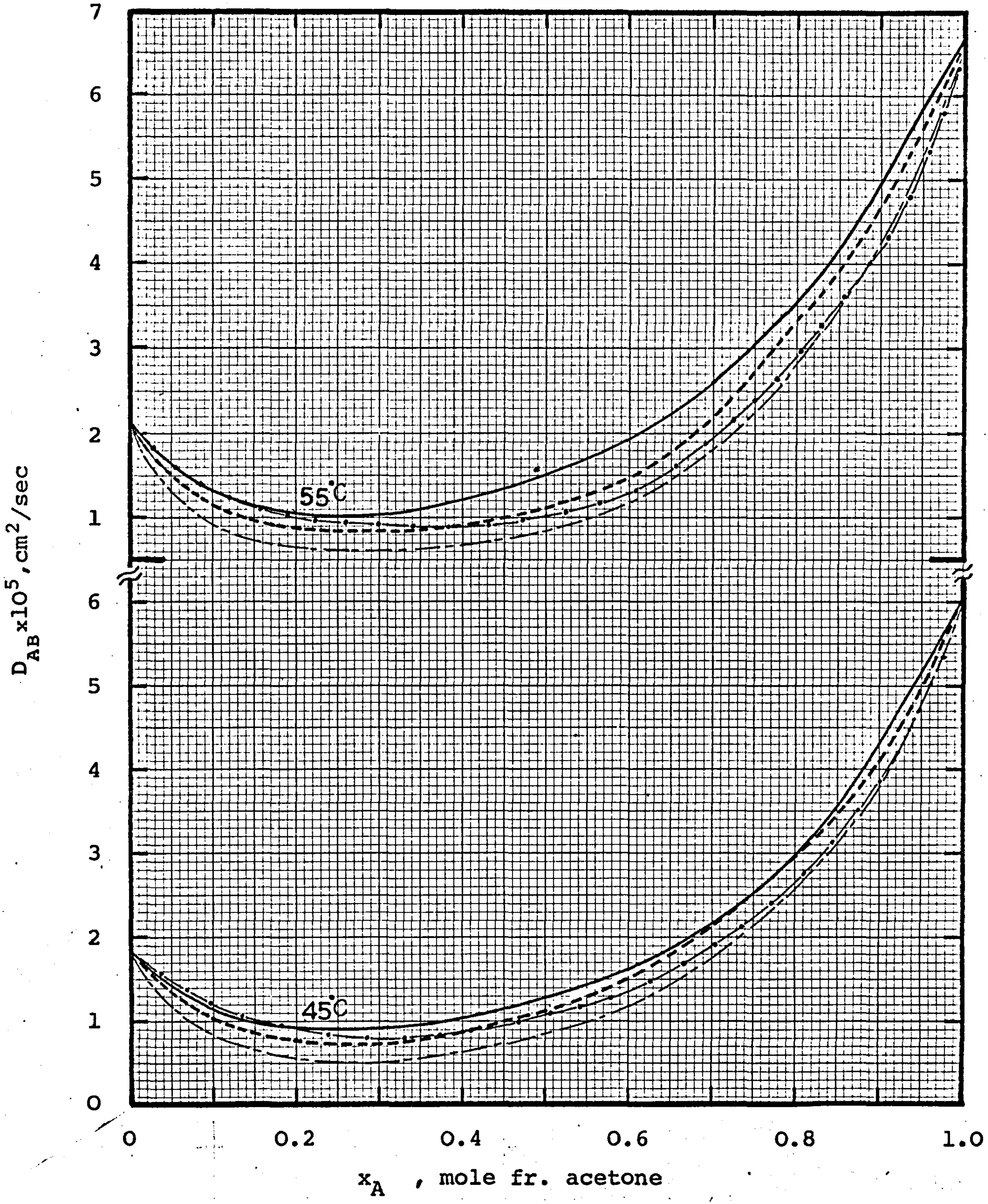


Figure 7-3.1b (continued)

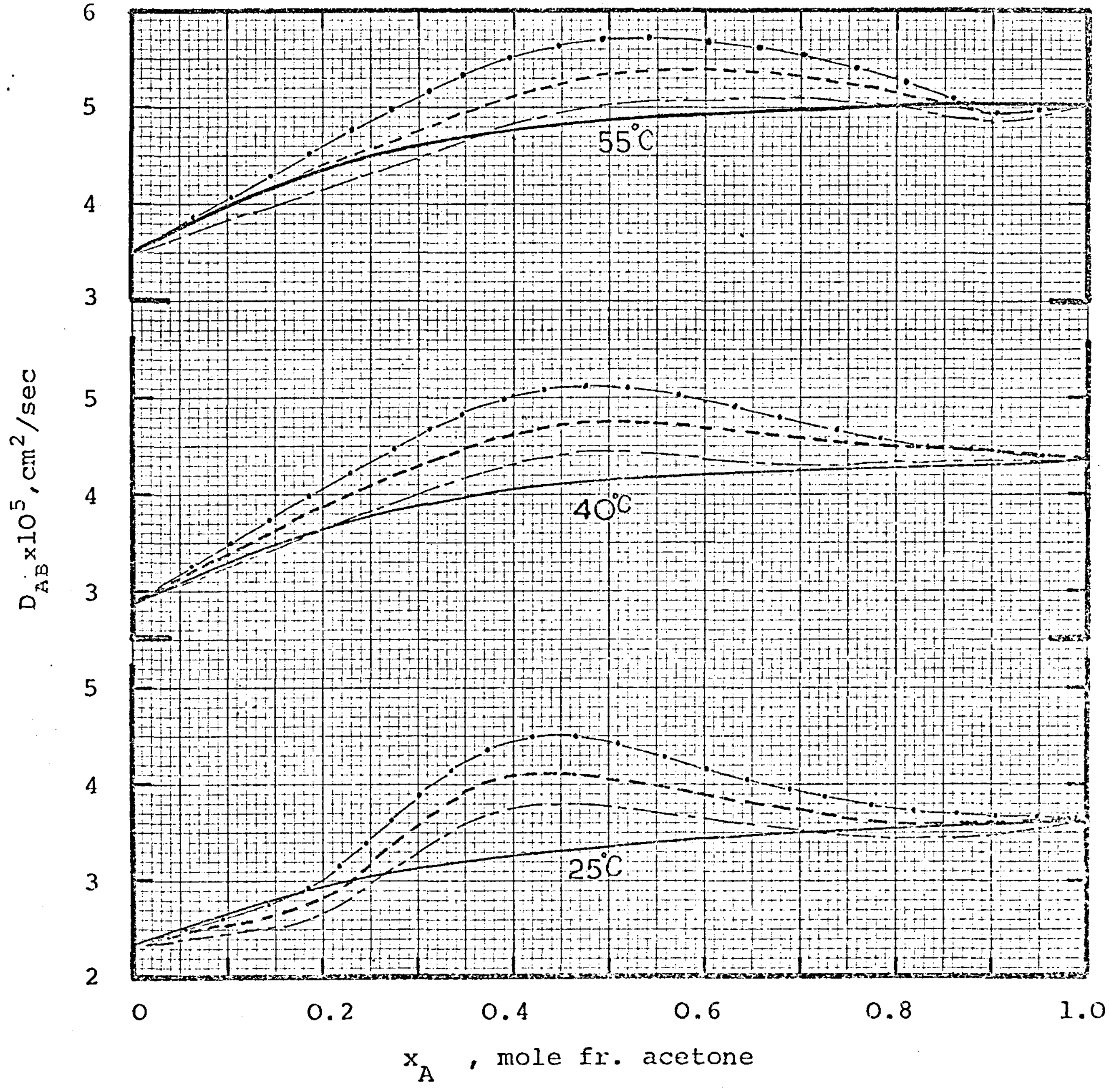


Figure 7-3.1c Comparison of the experimental diffusion coefficients with the predicted coefficients for acetone-chloroform system

—·—·—·— Vignes eq. (2-4.12)

— — — — — Leffler & Cullinan eq. (2-4.16)

- - - - - - - - - This work, eq. (3-1.21)

————— Experimental, from Table 6-2.6

Table 7-3.1a Comparison of the experimental differential diffusion coefficients with the predicted coefficients for ethanol-water system, ($D_{AB} \times 10^5$, cm^2/sec.)

conc. of ethanol x_A	Exper. D_{AB} from Fig. (6-1.2)	This work, calculated from eq. (3-1.21)		Calculated from Leffler-Cullinan eq. (2-4.16)		Calculated from Vignes eq. (2-4.12)	
		D_{AB}	% error	D_{AB}	% error	D_{AB}	% error
	Temperature = 25°C						
0.0	1.240	1.240	-	1.240	-	1.240	-
0.1	0.670	0.678	1.3	0.457	-31.0	0.942	40.6
0.2	0.410	0.348	-15.0	0.205	-50.0	0.508	23.9
0.3	0.370	0.326	-11.0	0.191	-48.0	0.459	24.1
0.4	0.405	0.334	-17.6	0.202	-50.0	0.440	8.6
0.5	0.490	0.414	-15.4	0.267	-45.0	0.508	3.7
0.6	0.610	0.564	-7.5	0.387	-36.0	0.657	7.7
0.7	0.750	0.741	-1.0	0.556	-26.0	0.812	8.3
0.8	0.900	0.916	1.8	0.758	-15.5	0.955	6.1
0.9	1.070	1.117	4.4	1.011	-5.6	1.135	6.1
1.0	1.220	1.220	-	1.220	-	1.220	-
% average deviation			8.3		34.0		14.3
	Temperature = 40°C						
0.0	1.700	1.700	0.00	1.700	0.00	1.700	0.0
0.1	1.000	0.986	-1.37	0.706	-29.40	1.270	27.0
0.2	0.680	0.530	-22.04	0.339	-50.1	0.717	5.5
0.3	0.610	0.564	-7.6	0.352	-42.3	0.748	22.7
0.4	0.640	0.692	8.0	0.443	-30.8	0.871	36.2
0.5	0.730	0.820	12.3	0.551	-24.6	0.977	33.8

Table 7-3.1a (continued)

conc. of ethanol x_A	Exper. D_{AB} from Fig. (6-1.2)	This work, calculated from eq. (3-1.21)		Calculated from Leffler-Cullinan eq. (2-4.16)		Calculated from Vignes eq. (2-4.12)	
		D_{AB}	% error	D_{AB}	% error	D_{AB} ?	% error
	Temperature = 40°C (continued)						
0.6	0.865	0.905	4.6	0.642	-25.8	1.032	19.3
0.7	1.060	1.074	1.4	0.820	-22.6	1.169	10.3
0.8	1.275	1.253	-1.7	1.038	-18.6	1.313	3.0
0.9	1.475	1.497	1.4	1.359	-7.9	1.522	3.2
1.0	1.640	1.640	-0.00	1.640	0.00	1.640	0.0
% average deviation			6.7		28.0		17.9
	Temperature = 58°C						
0.0	2.400	2.400	0.00	2.400	0.00	2.400	0.0
0.1	1.500	1.409	-6.1	1.076	-28.3	1.708	13.9
0.2	1.020	0.959	-6.00	0.665	-34.9	1.208	18.4
0.3	0.930	0.793	-14.8	0.538	-42.20	0.979	5.3
0.4	1.020	1.014	-0.6	0.697	-31.6	1.204	18.0
0.5	1.185	1.183	-0.1	0.844	-28.8	1.345	13.5
0.6	1.380	1.363	-1.2	1.018	-26.20	1.492	8.1
0.7	1.590	1.608	1.2	1.271	-20.1	1.708	7.4
0.8	1.810	1.833	1.3	1.552	-14.2	1.894	4.7
0.9	2.060	2.064	0.20	1.890	-8.36	2.092	1.6
1.0	2.360	2.360	0.00	2.360	0.00	2.360	0.0
% average deviation			3.6		26.1		10.1

Table 7-3.1a (continued)

conc. of ethanol x_A	Exper. D_{AB} from Fig. (6-1.2)	This work, calculated from eq. (3-1.21)		Calculated from Leffler-Cullinan eq. (2-4.16)		Calculated from Vignes eq. (2-4.12)	
		D_{AB}	% error	D_{AB}	% error	D_{AB}	% error
Temperature = 73°C							
0.0	2.950	2.950	-0.00	2.950	0.00	2.950	0.0
0.1	1.900	1.178	-38.0	0.930	-51.0	1.379	-27.4
0.2	1.420	0.889	-37.4	0.641	-54.9	1.073	-24.5
0.3	1.340	0.911	-32.00	0.642	-52.1	1.078	-19.6
0.4	1.420	1.081	-23.9	0.770	-45.7	1.234	-13.1
0.5	1.610	1.359	-15.6	0.995	-38.2	1.497	-7.0
0.6	1.860	1.610	-13.5	1.230	-33.9	1.717	-7.7
0.7	2.170	2.093	-3.6	1.678	-22.7	2.184	0.6
0.8	2.490	2.565	3.0	2.190	-12.1	2.624	5.4
0.9	2.800	2.835	1.3	2.603	-7.0	2.863	2.2
1.0	3.100	3.100	0.00	3.100	0.00	3.100	0.0
% average deviation			18.7		35.3		11.9

Table 7-3.1b Comparison of the experimental differential diffusion coefficients with the predicted coefficients for acetone-water system, (D_{AB} x 10^5, cm^2/sec.)

Conc. of acetone x_A	Exper. D_{AB} from Fig. (6-2.2)	This work, calculated from eq. (3-1.21)		Calculated from Leffler-Cullinan eq. (2-4.16)		Calculated from Vignes eq. (2-4.12)	
		D_{AB}	% error	D_{AB}	% error	D_{AB}	% error
	Temperature = 25°C						
0.0	1.295	1.285	-0.0	1.285	0.0	1.285	0.0
0.1	0.810	0.771	-4.8	0.575	-29.1	0.940	16.0
0.2	0.620	0.604	-2.5	0.416	-32.8	0.728	17.4
0.3	0.630	0.550	-12.8	0.373	-40.8	0.622	-1.3
0.4	0.700	0.654	-6.6	0.462	-34.1	0.669	-4.4
0.5	0.850	0.848	-0.2	0.629	-26.0	0.794	-6.6
0.6	1.120	1.099	-1.9	0.853	-23.8	0.970	-13.4
0.7	1.600	1.614	0.9	1.320	-17.5	1.383	-13.6
0.8	2.350	2.345	-0.2	2.045	-13.0	2.013	-14.3
0.9	3.400	3.482	2.4	3.227	-5.1	3.155	-7.2
1.0	5.200	5.200	0.0	5.200	0.0	5.200	0.0
% average deviation			3.6		24.7		10.5
	Temperature = 35°C						
0.0	1.600	1.600	0.00	1.600	0.00	1.600	0.0
0.1	0.990	0.928	-6.3	0.702	-29.1	1.115	12.7
0.2	0.780	0.737	-5.6	0.514	-34.2	0.882	13.1
0.3	0.780	0.669	-14.2	0.464	-40.5	0.746	-4.4
0.4	0.858	0.833	-2.9	0.609	-29.0	0.832	-3.0
0.5	1.025	0.963	-6.0	0.713	-30.4	0.913	-10.9

Table 7-3.1b (continued)

Conc. of acetone x_A	Exper. D_{AB} from Fig. (6-2.2)	This work, calculated from Eq. (3-1.21)		Calculated from Leffler-Cullinan eq. (2-4.16)		Calculated from Vignes eq. (2-4.12)	
		D_{AB}	% error	D_{AB}	% error	D_{AB}	% error
	Temperature = 35°C (continued)						
0.6	1.365	1.306	-4.3	1.011	-25.9	1.171	-14.2
0.7	1.898	1.900	0.10	1.549	-18.4	1.654	-12.9
0.8	2.700	2.561	-5.2	2.208	-18.2	2.245	-16.9
0.9	3.900	3.559	-8.7	3.293	-15.6	3.251	-16.6
1.0	5.600	5.600	-0.00	5.600	-0.00	5.600	0.0
% average deviation			5.9		26.8		11.6
	Temperature = 45°C						
0.0	1.820	1.820	-0.0	1.820	0.0	1.820	0.0
0.1	1.120	1.006	-10.2	0.778	-30.6	1.182	5.5
0.2	0.910	0.776	-14.7	0.555	-39.1	0.903	-0.8
0.3	0.910	0.709	-22.1	0.502	-44.8	0.770	-15.4
0.4	1.040	0.854	-17.8	0.632	-39.3	0.839	-19.4
0.5	1.290	1.157	-10.3	0.864	-33.0	1.082	-16.1
0.6	1.640	1.449	-11.7	1.125	-31.4	1.291	-21.3
0.7	2.170	2.150	-0.9	1.745	-19.6	1.878	-13.5
0.8	2.990	2.978	-0.4	2.560	-14.4	2.617	-12.5
0.9	4.310	4.082	-5.3	3.751	-13.0	3.756	-12.9
1.0	6.050	6.050	-0.00	6.050	-0.00	6.050	0.0
% average deviation			10.4		29.5		13.0

Table 7-3.1b (continued)

Conc. of acetone x_A	Exper. D_{AB} from Fig. (6-2.2)	This work, calculated from Eq. (3-1.21)		Calculated from Leffler-Cullinan eq. (2-4.16)		Calculated from Vignes eq. (2-4.12)	
		D_{AB}	% error	D_{AB}	% error	D_{AB}	% error
Temperature = 55°C							
0.0	2.140	2.140	0.0	2.140	0.0	2.140	0.0
0.1	1.350	1.133	-16.0	0.894	-33.8	1.307	-3.2
0.2	1.070	0.874	-18.3	0.641	-40.1	0.995	-7.0
0.3	1.060	0.845	-20.3	0.612	-42.3	0.904	-14.7
0.4	1.230	0.888	-27.8	0.670	-45.5	0.861	-30.0
0.5	1.510	1.116	-26.1	0.843	-44.2	1.041	-31.0
0.6	1.940	1.424	-26.6	1.112	-42.7	1.273	-34.4
0.7	2.600	2.175	-16.3	1.779	-31.6	1.903	-26.8
0.8	3.540	3.316	-6.3	2.872	-18.9	2.917	-17.6
0.9	4.990	4.544	-8.9	4.193	-16.0	4.184	-16.1
1.0	6.700	6.700	0.0	6.700	0.0	6.700	0.0
% average deviation			18.5		35.0		20.1

Table 7-3.1c Comparison of the experimental differential diffusion coefficients with the predicted diffusion coefficients for acetone-chloroform system, (D_{AB} x 10^5, $cm^2/sec.$)

Conc. of acetone x_A	Exper. D_{AB} from Fig. (6-3.2)	This work, calculated from eq. (3-1.21)		Calculated from Leffler-Cullinan eq. (2-4.16)		Calculated from Vignes eq. (2-4.12)	
		D_{AB}	% error	D_{AB}	% error	D_{AB}	% error
	Temperature = 25°C						
0.0	2.330	2.330	0.0	2.330	0.0	2.330	0.0
0.1	2.685	2.555	-4.9	2.451	-8.7	2.659	-1.0
0.2	2.926	2.800	-4.3	2.623	-10.3	2.982	1.9
0.3	3.110	3.574	14.9	3.294	5.9	3.867	24.3
0.4	3.260	4.101	25.8	3.762	15.4	4.455	36.7
0.5	3.380	4.068	20.4	3.742	10.7	4.406	30.3
0.6	3.448	3.900	13.1	3.629	5.3	4.176	21.1
0.7	3.500	3.774	7.8	3.574	2.1	3.974	13.5
0.8	3.542	3.575	0.9	3.432	-3.1	3.716	4.9
0.9	3.582	3.581	0.0	3.488	-2.6	3.672	2.5
1.0	3.620	3.620	0.0	3.620	0.0	3.620	0.0
	% average deviation		10.2		7.1		15.1
	Temperature = 40°C						
0.0	2.880	2.880	0.0	2.880	0.0	2.880	0.0
0.1	3.300	3.384	2.5	3.286	-0.4	3.479	5.4
0.2	3.620	3.860	6.6	3.660	1.1	4.060	12.2
0.3	3.880	4.264	9.9	3.978	2.5	4.554	17.4
0.4	4.060	4.665	14.9	4.323	6.5	5.013	23.5
0.5	4.160	4.780	14.9	4.448	6.9	5.115	22.9

Table 7-3.1c (continued)

Conc. of acetone x_A	Exper. D_{AB} from Fig. (6-3.2)	This work, calculated from eq. (3-1.21)		Calculated from Leffler-Cullinan eq. (2-4.16)		Calculated from Vignes eq. (2-4.12)	
		D_{AB}	% error	D_{AB}	% error	D_{AB}	% error
	Temperature = 40°C (continued)						
0.6	4.210	4.670	10.9	4.379	4.0	4.959	17.8
0.7	4.250	4.518	6.3	4.288	0.9	4.743	11.6
0.8	4.280	4.487	4.8	4.345	1.5	4.621	8.0
0.9	4.300	4.477	4.1	4.386	2.0	4.563	6.1
1.0	4.320	4.320	0.0	4.320	0.0	4.320	0.0
	% average deviation		8.1		2.9		13.7
	Temperature = 55°C						
0.0	3.470	3.470	0.0	3.470	0.0	3.470	0.0
0.1	3.970	3.975	0.1	3.892	-2.0	4.055	2.1
0.2	4.360	4.427	1.5	4.209	-3.5	4.645	6.5
0.3	4.620	4.815	4.2	4.511	-2.4	5.122	10.9
0.4	4.780	5.277	10.4	4.926	3.1	5.632	17.8
0.5	4.860	5.532	13.8	5.189	6.8	5.875	20.9
0.6	4.930	5.499	11.5	5.179	5.1	5.816	18.0
0.7	4.990	5.549	11.2	5.304	6.3	5.788	16.0
0.8	5.010	5.428	6.4	5.294	3.8	5.551	8.8
0.9	5.020	5.161	-0.7	5.084	-2.2	5.233	0.6
1.0	5.030	5.030	0.0	5.030	0.0	5.030	0.0
	% average deviation		6.7		3.9		11.3

Table 7-3.2a Comparison of the predicted coefficients with the experimental coefficients for dilute solution of ethanol-water mixtures, ($D^o_{AB} \times 10^5$, cm^2/sec.)

T °C	$D^o_{AB} \times 10^5$ exper. $(x_A \to 0)$	This work Eq. (3-2.4)		W & C Eq. (2-3.16)		King et al Eq. (2-3.29)		Sitar. et al Eq. (2-3.27)	
		D^o_{AB}	% error	D^o_{AB}	% error	D^o_{AB}	% error	D^o_{AB}	% error
25	1.25	1.28	2.4	1.49	19.2	1.23	-1.6	1.08	-13.6
40	1.70	1.85	8.8	2.13	25.3	1.76	3.5	1.50	-11.8
58	2.40	2.67	11.3	3.07	27.9	2.54	5.8	2.11	-12.1
73	2.95	3.47	20.1	3.99	35.3	3.30	11.9	2.69	- 8.8
85	3.503	4.17	19.0	4.79	36.7	3.96	13.1	3.19	- 8.9
100*	4.32	5.0	15.7	5.78	33.8	4.79	10.9	3.80	-12.0
% average error			12.9		29.7		7.8		11.2

T °C	$D^o_{BA} \times 10^5$ Exper. $x_A \to 1$	This work Eq. (3-2.4)		W & C Eq. (2-3.16)		King et al Eq. (2-3.29)		Sitar. et al Eq. (2-3.27)	
		D^o_{BA}	% error	D^o_{BA}	% error	D^o_{BA}	% error	D^o_{BA}	% error
25	1.22	1.29	5.7	1.35	10.7	1.45	18.9	1.37	12.3
40	1.64	1.77	7.9	1.85	12.2	1.99	21.3	1.83	11.6
58	2.36	2.53	7.2	2.64	11.9	2.84	20.3	2.56	8.5
73	3.10	3.37	8.7	3.52	13.5	3.78	21.9	3.34	7.7
78.5*	3.33	3.76	12.9	3.91	17.4	4.21	26.4	3.69	10.8
% average error			8.5		13.1		21.8		10.2

* boiling point temperature

Table 7-3.2b Comparison of the predicted coefficients with the experimental coefficients for dilute solution of acetone-water mixtures ($D^{o}_{AB} \times 10^{5}$, cm^{2}/sec.)

T °C	$D^{o}_{AB} \times 10^{5}$ Exper. $x_A = 0$	This work Eq. (3-2.4)		W & C Eq. (2-3.16)		King et al Eq. (2-3.29)		Sitar. et al Eq. (2-3.27)	
		D^{o}_{AB}	% error	D^{o}_{AB}	% error	D^{o}_{AB}	% error	D^{o}_{AB}	% error
25	1.30	1.18	-9.2	1.31	0.8	1.37	5.4	1.13	-13.1
35	1.60	1.50	-6.3	1.67	4.4	1.74	8.8	1.41	-11.9
45	1.82	1.88	3.3	2.09	14.8	2.19	20.3	1.74	- 4.4
55	2.14	2.29	7.0	2.55	19.2	2.67	24.8	2.09	- 2.3
65	2.45	2.73	11.4	3.05	24.5	3.19	30.2	2.47	0.8
75	2.74	3.24	18.2	3.62	32.0	3.78	38.0	2.89	5.5
85	3.25	3.78	16.3	4.22	29.8	4.42	36.0	3.34	2.8
100*	3.86	4.56	18.1	5.09	31.9	5.32	37.8	3.98	3.1
% average error			11.2		19.7		25.2		5.5

T °C	$D^{o}_{BA} \times 10^{5}$ Exper. $x_A = 1$	This work Eq. (3-2.4)		W & C Eq. (2-3.16)		King et al Eq. (2-3.29)		Sitar. et al Eq. (2-3.27)	
		D^{o}_{BA}	% error	D^{o}_{BA}	% error	D^{o}_{BA}	% error	D^{o}_{BA}	% error
25	5.22	4.83	-7.5	4.32	-17.2	4.57	-12.5	4.17	-20.1
35	5.60	5.50	-1.8	4.90	-12.5	5.19	- 7.3	4.70	-16.1
45	6.05	6.09	0.7	5.44	-10.1	5.75	- 5.0	5.17	-14.5
55	6.70	6.66	-0.6	5.96	-11.0	6.29	- 6.1	5.62	-16.1
56.2*	6.79	6.71	-1.2	6.00	-11.5	6.34	- 6.6	5.66	-16.6
% average error			2.4		12.5		7.5		16.7

Tabl-e 7-3.2c Comparison of the predicted coefficients with the experimental coefficients for dilute solution of acetone-chloroform mixtures (D^{o}_{AB} x 10^{5}, cm^{2}/sec.)

T °C	$D^{o}_{AB} \times 10^{5}$ Exper. $x_A = 0$	This work Eq. (3-2.4)		W & C Eq. (2-3.16)		King et al Eq. (2-3.29)		Sitar. et al Eq. (2-3.27)	
		D^{o}_{AB}	% error	D^{o}_{AB}	% error	D^{o}_{AB}	% error	D^{o}_{AB}	% error
25	2.33	2.49	6.9	3.28	40.8	2.45	5.2	2.16	-7.3
40	2.88	2.99	3.8	3.94	36.8	2.93	1.7	2.56	-11.1
55	3.47	3.57	2.9	4.69	35.2	3.58	3.2	3.01	-13.3
61.5*	3.75	3.83	2.1	5.02	33.9	3.83	0.0	3.21	-14.4
% average error			3.9		36.7		2.5		11.5

T °C	$D^{o}_{BA} \times 10^{5}$ Exper. $x_A = 1$	This work Eq. (3-2.4)		W & C Eq. (2-3.16)		King et al Eq. (2-3.29)		Sitar. et al Eq. (2-3.27)	
		D^{o}_{BA}	% error	D^{o}_{BA}	% error	D^{o}_{BA}	% error	D^{o}_{BA}	% error
25	3.62	3.85	6.4	3.84	5.9	4.27	17.7	3.90	7.3
40	4.32	4.69	8.6	4.52	4.6	5.03	16.4	4.54	5.1
55	5.03	5.59	11.1	5.39	7.2	6.00	19.3	5.35	6.4
56.2*	5.16	5.68	10.1	5.48	6.2	6.10	18.2	5.43	5.2
% average error			9.0		6.0		17.9		6.0

Table 7-3.3a Comparison of the coefficients predicted from Equations (3-4.7) and (2-5.1) with the experimental coefficients at infinite dilution for ethanol-water mixtures, (D^o_{AB} x 10^5, cm^2/sec)

T °C	D^o_{AB}x10^5 exper. x_A=0	Eq. (3-4.7) with n = 6		Eq. (2-5.1)	
		D^o_{AB}	% error	D^o_{AB}	% error
25	1.25	-	-	-	-
40	1.70	1.63	-4.1	1.79	5.3
58	2.40	2.27	-5.4	2.56	6.7
73	2.95	3.04	3.1	3.33	12.9
85	3.50	3.88	10.9	4.01	14.6
100*	4.32*	5.34*	23.6*	4.93*	14.12*
% average error			5.9		9.9

T °C	D^o_{BA}x10^5 exper. x_A = 1	Eq. (3-4.7) with n=4		Eq. (2-5.1)	
		D^o_{BA}	% error	D^o_{BA}	% error
25	1.22	-	-	-	-
40	1.64	1.62	-1.2	1.66	1.2
58	2.36	2.35	-0.4	2.38	0.8
73	3.10	3.29	6.1	3.19	-3.0
78.5*	3.33*	3.76*	12.9*	3.40*	2.1*
% average error			2.6		1.7

* Values not used in the computation of the average deviation because of nearness to boiling point temperature.

x_A mole fr. of ethanol.

Table 7-3.3b Comparison of the coefficients predicted from equations (3-4.7) and (2-5.1) with the experimental coefficients at infinite dilution for acetone-water mixtures. (D^o_{AB} x 10^5, cm^2 /sec.)

T ^oC	D^o_{AB}x10^5 exper. x_a = 0	Eq. (3-4.7) with n = 6		Eq.(2-5.1)		T ^oC	D^o_{BA}x10^5 exper. x_A = 1	Eq.(3-4.7) with n = 3		Eq.(2-5.1)	
		D^o_{AB}	% error.	D^o_{AB}	% error			D^o_{BA}	% error	D^o_{BA}	% error
25	1.30	-	-	-	-	25	5.22	-	-	-	-
35	1.60	1.55	-3.1	1.67	4.4	35	5.60	6.04	7.8	5.91	5.5
45	1.82	1.85	+1.6	2.08	14.3	45	6.05	7.04	16.4	6.68	10.4
55	2.14	2.23	4.2	2.54	18.7	55*	6.70*	8.27*	23.4*	7.47*	11.5*
65	2.45	2.70	10.2	3.03	23.7	56.2*	6.79*	8.44*	24.3*	7.52*	10.8*
75	2.74	3.29	20.1	3.59	31.0						
85	3.25	4.03	24.0	4.20	29.23						
100*	3.86*	5.57*	44.3*	5.06*	31.1*						
% average error			10.5		20.2	% average error			12.1		8.0

x_A = mole fr. of acetone.

Table 7-3.3c Comparison of the coefficients predicted from equations (3-4.7) and (2-5.1) with the experimental coefficients at infinite dilution for acetone-chloroform ($D^o_{AB} \times 10^5$, $cm^2/sec.$)

T °C	$D^o_{AB} \times 10^5$ exper. $x_A = 0$	Eq. (3-4.7) with n = 3		Eq. (2-5.1)		T °C	$D^o_{BA} \times 10^5$ exper. $x_A = 1$	Eq. (3-4.7) with n = 3		Eq. (2-5.1)	
		D^o_{AB}	% error	D^o_{AB}	% error			D^o_{BA}	% error	D^o_{BA}	% error
25	2.33	-		-		25	3.62	-		-	
40	2.88	2.83	-1.7	2.80	-2.8	40	4.32	4.52	4.6	4.40	1.9
55	3.47	3.49	0.6	3.33	-4.0	55	5.03	5.74	14.1	5.25	4.4
61.5*	3.75*	3.84*	2.4*	3.57*	-4.8*	56.2*	5.16*	5.85*	11.8*	5.45*	5.3*
% average error			1.2		3.4	% average error			9.4		3.2

x_A = mole fr. of acetone.

PART 8 CONCLUSIONS

8 CONCLUSIONS

(1) The three-compartment diaphragm cell developed and the experimental procedure described in this work were successfully employed in the determination of diffusion coefficients for three binary mixtures (i.e. ethanol-water, acetone-water and acetone-chloroform). The full concentration range was investigated in each case at temperatures up to the neighbourhood of the normal boiling points.

(2) The values of diffusion coefficients for these systems at their normal boiling points were found by extrapolation or interpolation from the respective plots of ln D_{AB} vs $\frac{1}{T}$. The values of D^{o}_{AB} for these systems, at all temperatures studied, were also found by extrapolation from the plots of D_{AB} vs x_A.

(3) The following correlation for the estimation of concentration and temperature dependence of D_{AB} was developed

$$\frac{D_{AB}\,\mu_{AB}}{\alpha_A} = \left(D^*_A\,\mu_A\right)^{x_A} \left(D^*_B\,\mu_B\right)^{x_B} \exp\left[\frac{\Delta G_{\mu,AB} - \Delta G_{D,AB}}{RT}\right] \qquad (2\text{-}1.21)$$

It was tested with the experimental data of this work. The overall average accuracies obtained are ± 9.6% for ethanol-water system, ± 9.3% for acetone-water system and ± 8.3% for acetone-chloroform system. These accuracies compare well with those of the correlations of Vignes eq. (2-4.12) and of Leffler-Cullinan eq. (2-4.16).

(4) A correlation was developed for the prediction of diffusion coefficients at infinite dilution

$$\frac{D^o_{AB}\,\mu_B}{T} = 8.93 \times 10^{-8} \; \frac{V_A^{1/6}}{V_B^{1/3}} \left[\frac{[P_B]}{[P_A]}\right]^{0.6} \qquad (3\text{-}2.4)$$

It gives better predictions than most of the existing literature correlations. The use of parachors in eq. (3-2.4), it is believed, gives good accuracy because parachors account better for the effect of the intermolecular forces on the diffusion process.

(5) The following correlation was developed for the prediction of the self-diffusion coefficient

$$[M] = \bar{V} \left[\frac{T}{D^*}\right]^{0.13} \qquad (3\text{-}3.4)$$

This equation employs an additive type of constant [M] . The bond and structural contributions, to the constant [M] , of a number of atoms and groups of atoms, were calculated on the basis of 46 liquids for which experimental self-diffusion coefficients were available. Despite the small number of experimental data for the calculation of these contributions, eq. (3-3.4) gives an accuracy only slightly lower than the equation of Stokes and Einstein (2-2.2). More experimental data is required to define more accurately the various bond contributions to the value of the constant [M] .

(6) Dullien's equation (2-2.26) for prediction of self-diffusion coefficient was modified by replacing the critical molal volume by the molal volume at boiling point. This modification makes the equation more convenient to use because molal volumes at boiling points are easier to obtain. The equation has the form

$$\frac{D^*\,\mu\,\bar{V}}{T} = 0.229 \times 10^{-8} \; V_b^{0.636} \qquad (3\text{-}3.6)$$

and predicts self-diffusion coefficients with the same accuracy as eq.(2-2.26).

(7) The following equations were developed for estimating diffusion coefficients at other temperatures from a known value at a single temperature

$$\frac{D^*_2}{D^*_1} = \left(\frac{T_c - T_1}{T_c - T_2}\right)^n \qquad (3\text{-}4.6)$$

$$\frac{\left(D^o_{AB}\right)_2}{\left(D^o_{AB}\right)_1} = \left(\frac{T_c - T_1}{T_c - T_2}\right)^n_B \qquad (3\text{-}4.7)$$

Each of these equations may be used as an alternative to the Stokes-Einstein eq. (2-5.1) when no reliable values of viscosity are available. Equations (3-4.6) and (3-4.7) were tested with the limited amount of available data give an accuracy about the same as equation (2-5.1) (Stokes and Einstein). These equations are recommended only for the temperature range from 10°C above the melting point to 10°C below the boiling point.

8-1 SUGGESTIONS FOR FURTHER WORK

(1) It is desirable to incorporate in the design of this cell an "in situ" method of measuring concentrations of the test solutions. This would speed up considerably the experimental work. The "in situ" method used by Sanni and Hutchison (175) is recommended.

(2) More experimental data should be obtained for such non-ideal and associated systems as methanol-benzene, ethanol-benzene, methanol-water, propanol-water, butanol-water etc. These data are needed to test the correlations developed in this work.

PART 9 APPENDICES

Appendix 3-2.1 Physical Properties of Organic Compounds

Name	Formulae	Mol. wt.	V_b		[P]		ΔH_b	
			$\frac{cm^3}{g\ mole}$	Ref.	$\frac{g^{\frac{1}{4}} cm^3}{mole\ sec^{\frac{1}{2}}}$	Ref.	$\frac{cal.}{g\ mole}$	Ref.
Acetal	$C_6H_{14}O_2$	118.17	160.4	L	306.9	161	7829.8	153
Acetal Salicylic Acid	$C_9H_8O_4$	180.17	-		-		-	
Acetamide	C_2H_5NO	59.07	70.6	L	148	161	12239	GL
Acetanilide	C_8H_9NO	135.16	154.5	L	321.8	161	16043	GL
Acetic Acid	$C_2H_4O_2$	60.05	64.1	168	131.4	161	9529	168
Acetone	C_3H_6O	58.08	77.5	168	161.7	161	6952	168
Acetoin	$C_4H_8O_2$	88.12	103.6	L	213.4	S	12086	GL
Acetonitrile	CH_3CN	41.05	57.4	168	121.2	161	7500	168
Acetyldiphenyl-amine	$C_{14}H_{13}NO$	211.27	243.2	L	496.6	S	-	Sub.
Acetylene	C_2H_2	26.04	42.0	168	90.4	42	4007.6	G
Aconitine	$C_{34}H_{47}NO_{11}$	645.76	-		-		-	
Adipic Acod	$C_6H_{10}O_4$	146.14	173.8	L	308.2	S	17106	GLA
α-Alanine	$C_3H_7NO_2$	89.09	104.8	L	200.8	S	12560	GLA@
Alloxan	$C_4H_2N_2O_4$	142.07	123.6	L	257.3	S	-	Sub.
Allyl Alcohol	C_3H_6O	58.08	74.0	L	154.2	161	9490.8	153
α-Amino Acetic Acid (Glycine)	$C_2H_5NO_2$	75.07	78.0	L	161.8	S	-	
α-AminoButyricAcid	$C_4H_9NO_2$	103.12	122.4	L	239.8	S	-	Sub.
α-AminoCaporicAcid (Caprine)	$C_6H_{13}NO_2$	131.18	166.8	L	317.8	S	-	Sub.
α-AminoValaricAcid (n-Varline)	$C_5H_{11}NO_2$	117.15	144.6	L	278.8	S	-	Sub.
Ammonia	NH_3	17.0	25.0	14	63.8	42	5581	168
Amyl Alcohol	$C_5H_{12}O$	88.15	125.8	L	244.2	161	10030	G
Aniline	C_6H_7N	93.12	109.1	59	235.7	161	10360	214
Anisole	C_7H_8O	108.13	128.1	L	265.5	161	8808.3	214
Anthranilic Acid	$C_7H_7NO_2$	137.13	149.0	L	296.2	S	-	Sub.
Anthracene	$C_{14}H_{10}$	178.24	195.3	L	399.6	S	13499.5	GL
(Argon)	Ar	39.94	28.5	14	54.3	42	1590	153
Azobenzene	$C_{12}H_{10}N_2$	182.22	215.8	L	429.5	161	14399	GL
Benzaldehyde	C_6H_5CHO	106.12	118.2	L	256.2	161	9181.3	214
Benzene	C_6H_6	78.11	96.5	168	207.4	161	7353	168
Benzoic Acid	$C_7H_6O_2$	122.12	134.8	L	266.1	S	12888	GL
Benzyl Alcohol	C_7H_8O	108.13	125.6	L	259.6	161	12140	153
Benzyl Ether	$C_{14}H_{14}O$	198.27	229.0	L	478.0	S	13230	GL
Biphenyl	$C_{12}H_{10}$	154.20	184.6	L	380.0	S	11519	G

Appendix 3-2.1 (continued)

Name	Formulae	Mol. wt.	V_b		[P]		ΔH_b	
			$\frac{cm^3}{g\ mole}$	Ref.	$\frac{g^{\frac{1}{4}}\ cm^3}{mole\ sec^{\frac{1}{2}}}$	Ref.	$\frac{cal.}{g\ mole}$	Ref.
Bromine	Br_2	159.83	53.2	219	130.1	42	7420.0	153
Biphenylmethane	$C_{13}H_{12}$	168.24	206.8	L	416.0	42	12050.8	G
Bromoaniline	C_6H_6NBr	172.03	133.5	L	287.6	S	7563.2	GL
Bromobenzene	C_6H_5Br	157.02	120.0	168	257.0	S	8966.0	168
Bromoform	$CHBr_3$	252.77	99.5	L	227.3	161	9077.4	GL
Bromonaphthalene	$C_{10}H_7Br$	207.07	170.9	L	362.0	161	12705.0	GL
Bromonitrobenzene	$BrC_6H_4NO_2$	202.01	138.7	L	313.5	161	12555.0	GL
2-Bromo-2-Chloro, 1,1,1,Trichloro ethane.	C_2HBrCL_4	246.74	158.7	L	311.9	S	-	
Bromophenol	BrC_6H_4OH	173.02	126.7	L	272.2	S	12232.5	GL
Bromopropionic Acid	$C_3H_5BrO_2$	152.98	113.9	L	222.1	S	11753.0	GL
3-Bromopropylene	C_3H_5Br	120.98	89.9	L	191.1	S	7417.0	GL
m-Bromotoluene	C_7H_7Br	171.04	141.5	L	296.0	161	9703.0	G
Brucine	$C_{23}H_{26}N_2O_4$	394.44	-		-		-	
i-Butanol	$C_4H_{10}O$	74.12	103.6	L	201.9	161	10470.0	168
n-Butanol	$C_4H_{10}O$	74.12	103.6	L	202.6	161	10470.0	168
1-Butene	C_4H_8	56.12	89.5	85	179.2	S	5237.0	152
nButyl Acetate	$C_6H_{12}O_2$	116.16	155.2	L	296.0	161	8730.0	G
Butyramide	C_4H_9NO	87.12	115.5	L	228.8	S	11535.0	GL
Butyric Acid	$C_4H_8O_2$	88.10	107.8	168	209.0		10620.0	168
Caffeine	$C_8H_{10}O_2N_4$	194.21	206.1	L	406.8	S	-	Sub.
Camphor	$C_{10}H_{16}O$	152.23	197.6	L	388.0	S	10812.3	GL
Caproic Acid	$C_6H_{12}O_2$	116.16	152.5	L	287.2	161	13311.0	GL
(Carbon Dioxide)	CO_2	44.01	34.7	L	80.6	216	6030.0	168
Carbon Disulphide	CS_2	76.13	60.4	14	144.7	161	6295.0	153
Carbontetrachloride	CCL_4	153.84	102.0	168	220.5	161	7154.0	168
Carbontetraflouride	CF_4	88.01	57.4	59	113.4	161	3110.0	153
Chlorine	CL_2	70.91	45.5	14	108.6	42	4878.0	G
ChloroaceticAcid	$C_2H_3CLO_2$	94.50	89.3	L	168.3	161	11410.0	GL
Chloral	CCL_3CHO	147.40	114.5	L	232.8	S	7958.0	153
Chloral Hydrate	$C_2H_3CL_3O_2$	165.42	129.3	L	252.2	S	21814.0	153
Chloroaniline	CLC_6H_6N	127.57	131.1	L	273.9	S	11005.0	GL
Chlorobenzene	C_6H_5CL	112.56	115.0	168	244.5	161	8423.0	168
ChlorobenzoicAcid	$C_7H_5O_2CL$	156.57	155.7	L	303.3	S	-	Sub.

Appendix 3-2.1 (continued)

Name	Formulae	Mol. wt.	V_b		[P]		ΔH_b	
			$\frac{cm^3}{g\ mole}$	Ref.	$\frac{g^{\frac{1}{4}}\ cm^3}{mole\ sec^{\frac{1}{2}}}$	Ref.	$\frac{cal}{gmole}$	Ref.
Chlorobromo-methane	CH_2CLBr	129.39	73.8	L	161.3	S	7395.0	GL
Chlorobromo-benzene	C_6H_4BrCL	191.46	140.2	L	295.2	S	10128.0	GL
Chloroform	$CHCL_3$	119.39	84.8	168	183.4	S	6841.0	168
α-Chloro-naphthalene	$C_{10}H_7CL$	162.61	168.5	L	348.4	161	11546.0	GL
Chloronitro-benzene	$C_6H_4CLNO_2$	157.56	140.3	L	300.0	161	12031.0	GL
Chlorophenol	C_6H_4CLOH	128.56	124.3	L	258.0	42	10729.0	GL
Chrysene	$C_{18}H_{12}$	228.28	250.8	L	500.4	S	14415.0	GL
Cinnamic Acid	$C_9H_8O_2$	148.15	167.2	L	333.1	S	13526.0	GL
Cyclohexane	C_6H_{12}	84.16	117.0	168	241.7	161	7895.0	168
Cyclohexanone	$C_6H_{10}O$	98.14	120.7	L	251.4	161	9465.0	GL
Cyclohexanol	$C_6H_{12}O$	100.16	125.6	L	254.3	S	10917.0	GL
Cyclopentane	C_5H_{10}	70.13	99.5	L	205.0	161	6529.0	168
m-Cymene	$C_{10}H_{14}$	134.22	184.8	L	356.9	161	9524.0	G
Decaline	$C_{10}H_{18}$	138.25	184.6	L	371.7	161	9641.0	G
TransDecaline	$C_{10}H_{18}$	138.25	184.6	L	370.1	161	9360.0	G
n-Decane	$C_{10}H_{22}$	142.28	229.4	L	431.0	161	9390.0	168
Dibenzylamine	$C_{14}H_{15}N$	197.27	244.2	L	485.6	161	14154.0	GLA
p-Dibromobenzene	$C_6H_4Br_2$	235.92	142.6	L	305.2	42	10746.0	GL
Dibromonaphtha-lene	$C_{10}H_6Br_2$	285.99	194.2	L	402.7	S	–	
Dichloroacetic Acid	$C_2H_2CL_2O_2$	128.94	104.2	L	206.6	S	11440.0	GL
p-Dichloro-benzene	$C_6H_4CL_2$	147.01	137.8	L	280.0	161	9366.0	G
Dichloronaphtha-lene	$C_{10}H_6CL_2$	197.06	189.4	L	375.2	S	12361.0	GLA
Diethylamine	$C_4H_{11}N$	73.14	109.0	168	220.4	161	6975.0	168
Diiodomethane	CH_2I_2	267.84	96.2	L	225.8	42	9231.0	GL
Dimethyl-acetamide	C_4H_9NO	87.12	116.5	L	228.8	S	9658.6	GL
2-2-Dimethyl-butane	C_6H_{14}	86.17	141.0	L	266.4	161	6355.0	153
Dimethyl-propionamide	$C_5H_{11}NO$	101.15	134.0	L	267.8	S	–	
1,3-Dimethylurea	$C_3H_8N_2O$	88.12	105.4	L	219.4	S	13415.0	GL
m-Dinitrobenzene	$C_6H_4N_2O_4$	168.11	145.8	L	301.1	S	14391.0	GL
Dinitronaphth-alene	$C_{10}H_6N_2O_4$	218.16	197.4	L	398.0	S	–	Sub.

Appendix 3-2.1 (continued)

Name	Formulae	Mol. wt.	V_b		[P]		ΔH_b	
			$\frac{cm^3}{g\ mole}$	Ref.	$\frac{g^{\frac{1}{4}}\ cm^3}{mole\ sec^{\frac{1}{2}}}$	Ref.	$\frac{cal}{gmole}$	Ref.
2,3-Dinitrophenol	$C_6H_4N_2O_5$	184.11	153.2	L	338.5	S	-	Sub.
Dioxane	$C_4H_8O_2$	88.10	93.6	L	202.0	161	8087.0	G
Diphenylamine	$C_{12}H_{11}N$	169.23	198.8	L	409.6	S	13288.0	GL
Docosane	$C_{22}H_{46}$	310.61	495.8	L	892.2	S	16327.0	GL
Dodecane	$C_{12}H_{26}$	170.33	273.8	L	510.0	161	10440.0	214
Dotriacotane	$C_{32}H_{66}$	450.89	717.8	L	1282.2	S	14912.0	GL
Eicosane	$C_{20}H_{42}$	282.56	451.4	L	814.2	S	13800.0	214
Erythritol	$C_4H_{10}O_4$	122.12	125.8	L	247.0	S	24986.0	GL
Ethanol	C_2H_5OH	46.07	62.5	168	128.8	161	9220.0	168
Ethyl Acetate	$C_4H_8O_2$	88.10	106.0	168	216.5	161	7744.0	168
Ethyl Benzene	C_8H_{10}	106.17	140.4	L	284.4	161	8599.0	168
Ethyl Benzoate	$C_9H_{10}O_2$	150.17	175.0	L	350.0	161	9686.0	153
Ethyl Bromide	C_2H_5Br	108.98	75.1	L	165.4	S	6345.0	168
Ethylene Bromide	$C_2H_4Br_2$	187.88	98.4	L	215.2	161	8574.0	G
Ethylene Chloride	$C_2H_4CL_2$	98.96	93.6	L	188.7	161	7728.0	G
Ethylene glycol	$C_2H_6O_2$	62.07	66.6	L	148.9	161	11863.0	153
Ethyl ether	$C_4H_{10}O$	74.12	106.0	L	212.3	161	6442.0	G
Ethyl iodide	C_2H_5I	155.98	85.1	L	187.8	161	7114.3	153
Ethylene iodide	$C_2H_4I_2$	281.86	118.4	L	260.0	S	9695.6	GL
Ethyl nitrate	$C_2H_5NO_3$	91.07	88.6	L	189.5	161	8407.0	GL
Formamide	CH_3ON	45.04	45.5	L	107.3	161	11171.0	GL
Formic acid	HCOOH	46.03	46.2	L	94.0	161	5520.4	153
Furfural	$C_5H_4O_2$	96.08	92.1	L	209.4	161	10329.6	153
Glycerol	$C_3H_8O_3$	92.11	286.9	-	211.3	-	17000.0	-
Glycolamide	$C_2H_5NO_2$	75.07	80.6	L	144,0	S	-	
(Helium)	He	4.00	31.9	14	-		36.9	GL
Hendecane	$C_{11}H_{24}$	156.32	251.6	L	463.2	S	10575.0	GL
Heptane	C_7H_{16}	100.20	162.0	168	311.0	161	7575.0	168
1-Heptanol	$C_7H_{15}OH$	116.20	170.2	L	314.5	161	12187.1	153
n-Heptyl bromide	$C_7H_{15}Br$	179.11	186.1	L	362.8	161	10037.0	GL
Hexachlorobenzene	C_6CL_6	284.79	203.4	L	430.3	S	13457.0	GL@
Hexachloroethane	C_2CL_6	236.74	177.2	L	335.4	S	9343.0	GL
Hexachloro-cyclohexane	$C_6H_6CL_6$	290.83	225.6	L	463.3	S	12942.0	GL

Appendix 3-2.1 (continued)

Name	Formulae	Mol. wt.	V_b		[P]		ΔH_b	
			$\frac{cm^3}{g\ mole}$	Ref.	$\frac{g^{\frac{1}{4}}\ cm^3}{mole\ sec^{\frac{1}{2}}}$	Ref.	$\frac{cal}{g\ mole}$	Ref.
Hexadecane	$C_{16}H_{34}$	226.43	362.6	L	671.8	161	13412.0	G
Hexadecanol	$C_{16}H_{33}OH$	242.45	370.0	L	672.4	S	17202.6	GL
n-Hexane	C_6H_{14}	86.17	140.25	14	271.0	161	6896.0	153
n-Hexyl bromide	$C_6H_{13}Br$	165.08	163.9	L	305.4	S	9390.0	GL
n-Hexyl alcohol	$C_6H_{13}OH$	102.18	148.0	L	282.4	S	11014.0	GL
(Hydrogen)	H_2	2.02	28.4	14	35.0	42	216.0	153
Hydrogen chloride	HCL	36.47	30.6	14	59.1	42	3860.0	153
Hydrogen Iodide	HI	127.93	40.7	L	95.8	S	5089.7	GL
Hydrogen sulphide	H_2S	34.08	32.9	L	82.4	S	4463.0	153
Hydroquinone	$C_6H_4(OH)_2$	110.11	110.8	L	235.5	S	15113.0	GL
Iodine	I_2	253.82	71.6	L	182.0	S	10390.0	153
Iodobenzene	C_6H_5I	204.02	129.3	L	279.8	161	9548.0	168
Iodoform	HCI_3	393.78	129.5	L	295.4	161	–	Sub.
Iodopropionic acid	$C_3H_5IO_2$	199.98	123.9	L	245.1	S	15330.0	GLA@
3-Iodopropylene	C_3H_5I	167.98	99.9	L	214.1	S	7982.5	GL
Lactic acid	$C_3H_6O_3$	90.08	102.6	L	185.4	S	13953.0	GLA
Lauric acid	$C_{12}H_{24}O_2$	200.31	290.4	L	522.2	S	15542.0	GLA
Linoleic acid	$C_{18}H_{32}O_2$	280.44	408.8	L	734.2	S	18542.0	GLA
Malic acid	$C_4H_6O_5$	134.09	141.4	L	244.4	S	-	Dec.
Malonic acid	$C_3H_4O_4$	104.06	107.2	L	191.2	S	-	
Manitol	$C_6H_{14}O_6$	182.17	185.0	L	353.4	S	33455.0	GLA
Mesitylene	C_9H_{12}	120.18	162.6	L	322.0	161	9479.2	G
Methane	CH_4	16.04	37.7	168	72.6	161	1955.0	168
Methanol	CH_3OH	32.04	42.5	168	88.7	161	8491.0	168
Methyl acetate	$C_3H_6O_2$	74.08	83.75	14	177.4	161	7266.5	153
Methylcyclohexane	C_7H_{14}	98.18	140.4	14	281.6	161	7580.0	168
Methylcyclopentane	C_6H_{12}	84.16	120.2	14	242.8	161	7002.0	168
Methyl chloride	CH_3CL	50.49	50.6	168	110.4	S	5162.6	168
Methylene chloride	CH_2CL	84.94	85.8	59	147.6	S	6690.0	168
2-Methyl butane	C_5H_{12}	72.15	118.0	L	230.0	161	5842.0	168
Methylethylketone	C_4H_8O	72.10	97.43	59	200.2	161	7635.4	153
Methyl iodide	CH_3I	141.95	62.9	L	146.5	161	6511.2	153
Methylisobutyl-ketone	$C_6H_{12}O$	100.16	143.1	L	276.0	161	8459.0	G
α-Methylnaphthalene	$C_{11}H_{10}$	142.19	169.8	L	339.8	S	10853.0	G

Appendix 3-2.1 (continued)

Name	Formulae	Mol. wt.	V_b		$[P]$		ΔH_b	
			$\frac{cm^3}{g\ mole}$	Ref.	$\frac{g^{\frac{1}{4}}\ cm^3}{mole\ sec^{\frac{1}{2}}}$	Ref.	$\frac{cal}{g\ mole}$	Ref.
2-Methylpropene	$(C_4H_8)_3$	168.30	266.4	L	537.6	S	9311.0	GL
Methylsalicylate	$C_8H_8O_3$	152.14	160.3	L	323.0	161	12888.0	GL
1-Methyl urea	$C_2H_6N_2O$	74.08	83.2	L	180.4	S	–	Dec.
Myristic acid	$C_{14}H_{28}O_2$	228.36	334.8	L	570.2	S	16669.0	GLA
Naphthalene	$C_{10}H_8$	128.16	142.9	57	312.4	161	10240.0	168
Nicotine	$C_{10}H_{14}N_2$	162.23	204.5	L	396.6	S	11587.0	GLA
Nitrobenzene	$C_6H_5NO_2$	123.11	124.5	L	263.9	161	9735.5	153
m-Nitrobenzaldehyde	$C_7H_5NO_3$	151.12	146.7	L	313.7	S	14015.0	GLA
(Nitrogen)	N_2	28.02	34.7	85	59.0	42	1336.0	153
Nitrous oxide	N_2O	44.02	36.0	85	64.6	42	3956.0	153
Nitromethane	CH_3O_2N	61.04	59.4	59	133.1	161	8438.0	G
α-Nitronaphthalene	$C_{10}H_7NO_2$	173.16	171.0	L	363.3	161	13550.0	GL
Nitrophenol	$C_6H_5NO_3$	139.11	131.9	L	284.0	161	12596.0	GL
n-Octane	C_8H_{18}	114.22	186.6	14	351.0	161	8224.0	168
Octadecane	$C_{18}H_{38}$	254.51	407.0	L	752.0	42	14005.0	G
Octacosane	$C_{28}H_{58}$	394.78	629.0	L	1126.2	S	16323.0	GL
n-Octyl alcohol	$C_8H_{18}O$	130.23	192.4	L	360.4	S	12209.0	GL
n-Octyle bromide	$C_8H_{17}Br$	193.13	208.3	L	397.1	S	10683.0	GL
Oleic acid	$C_{18}H_{34}O_2$	282.45	416.2	L	763.7	161	18075.0	GLA
Oxalic acid	$C_2H_2O_4$	90.04	80.4	L	159.0	161	–	Sub.
(Oxygen)	O_2	32.00	27.9	85	53.4	216	1629.0	153
Palmatic acid	$C_{16}H_{32}O_2$	256.42	374.5	L	693.2		18155.0	GLA
Pentaerythritol	$C(CH_2OH)_4$	136.15	148.0	L	286.0	S	27370.0	GLA
Pentanol (see amyl alcohol)					–		–	
Phathalic acid	$C_8H_6O_4$	166.13	173.6	L	325.1	S	–	Sub.
Phenathrene	$C_{14}H_{10}$	178.24	196.7	L	399.6	S	13499.5	GL
Phenetole	$C_8H_{10}O$	122.17	151.4	L	305.1	S	9734.0	GL
Phenol	C_6H_5OH	94.11	101.4	59	222.7	161	10760.0	168
Phenolphthalein	$C_{20}H_{14}O_4$	318.31	320.9	L	662.6	S	–	
Phenyl acetate	$C_8H_8O_2$	136.16	151.2	L	310.9	S	10871.0	GL
Propane	C_3H_8	44.09	74.5	168	151.2	S	4487.0	168
i-Propanol	C_3H_8O	60.09	82.5	168	164.4	161	9729.0	168
n-Propanol	C_3H_8O	60.09	81.8	168	165.3	161	10030.0	168
Propionic acid	$C_3H_6O_2$	74.08	85.3	14	169.5	161	7319.8	153

Appendix 3-2.1 (continued)

Name	Formulae	Mol. wt.	V_b		[P]		ΔH_b	
			$\frac{cm^3}{g\ mole}$	Ref.	$\frac{g^{\frac{1}{4}}\ cm^3}{mole\ sec^{\frac{1}{2}}}$	Ref.	$\frac{cal}{g\ mole}$	Ref
Propionamide	C_3H_7NO	73.10	98.2	L	181.2	S	11453.0	GL
Propyl acetate	$C_5H_{10}O_2$	102.13	128.9	14	255.0	161	8187.0	G
Propylene	C_3H_6	42.08	68.8	59	139.9	161	4472.0	G
Propyleneglycol	$C_3H_8O_2$	76.09	88.8	L	179.6	S	12600.0	121
Pyridine	C_5H_5N	79.10	93.1	L	197.7	S	8492.0	153
Pyrogallol	$C_6H_6O_3$	126.11	118.2	L	249.7	S	17743.0	GL
Quinone	$C_6H_4O_2$	108.09	103.4	L	237.4	161	-	Sub
Resorcinol	$C_6H_6O_2$	110.11	110.8	L	235.5	S	14883.0	GL
Salicylaldehyde	$C_7H_6O_2$	122.12	125.6	L	275.1	S	9132.1	153
Saligenin	$C_7H_8O_2$	124.13	133.0	L	274.5	S	-	Sub
Salol	$C_{13}H_{10}O_3$	214.21	232.4	L	459.0	S	16168.4	GLA
Serine	$C_3H_7NO_3$	105.10	107.6	L	215.0	S	-	
Stearic acid	$C_{18}H_{36}O_2$	284.47	423.6	L	778.9	161	18044.0	GLA
Sulphur dioxide	SO_2	64.06	43.8	85	88.2	42	5955.0	153
Sucrose	$C_{12}H_{22}O_{11}$	342.30	313.9	L	622.0	S	-	
Hexose	$C_6H_{12}O_6$	180.16	177.6	L	319.2	S	-	
Pentose	$C_5H_{10}O_5$	150.13	148.0	L	266.0	S	-	
Tartaric acid	$C_4H_6O_6$	150.09	153.4	L	258.6	S	-	
Tetrabutylalcohol	$C_4H_{10}O$	74.12	108.2	L	201.3	161	8746.9	G
Tetrabromoethane	$C_2H_2Br_4$	345.70	145.0	L	310.0	161	10502.0	GL
Tetrachloroethane	$C_2H_2CL_4$	176.86	135.4	L	259.0	161	9244.0	153
1,2,4,5-Tetrachlorobenzene	$C_6H_2CL_4$	215.90	179.6	L	355.9	S	11595.0	GL
Tetradecane	$C_{14}H_{13}$	198.38	317.2	L	580.2	S	12047.0	G
Tetrahydrofuran	C_4H_8O	72.12	84.7	L	184.5	S	6820.7	GL
Tetralin	$C_{10}H_{12}$	132.20	162.4	L	336.4	161	10128.0	GL
Thiourea	CH_4N_2S	76.12	79.2	L	169.6	S	-	Dec
Threonine	$C_4H_9NO_3$	119.12	129.8	L	254.0	S	-	
Toluene	C_7H_8	92.13	118.3	168	245.5	161	7933.0	168
Tribromoacetic acid	$C_2HO_2Br_3$	296.76	138.3	L	284.9	S	12128.0	GL
2,4,6-Tribromophenol	$C_6H_3OBr_3$	330.82	173.3	L	339.8	S	13076.0	GL
Trichloroacetic acid	$C_2O_2HCL_3$	163.40	131.1	L	241.3	161	11277.0	GL
1,1,1-Trichloroethane	$C_2H_3CL_3$	133.42	114.5	L	224.8	161	7125.0	GL

Appendix 3-2.1 (continued)

Name	Formulae	Mol. wt.	V_b		[P]		ΔH_b	
			$\frac{cm^3}{g\ mole}$	Ref.	$\frac{g^{\frac{1}{4}}\ cm^3}{mole\ sec^{\frac{1}{2}}}$	Ref.	$\frac{cal}{g\ mole}$	Ref.
Trichloroethylene	C_2HCL_3	131.40	107.1	L	209.0	161	7521.3	153
1,2,4-Trichlorobenzene	$C_6H_3CL_3$	181.46	157.7	L	312.5	S	10512.0	G
2,4,6-Trichlorophenol	$C_6H_3Br_3O$	197.46	166.1	L	298.7	S	12570.0	GL
1,2,3-Trichloropropane	$C_3H_5CL_3$	147.43	136.7	L	262.8	S	9140.0	GL
1,2,4-Trichlorotoluene	$C_7H_5CL_3$	195.48	180.9	L	357.7	S	11574.0	G
Triethyleneglycol	$C_6H_{14}O_4$	150.18	170.2	L	350.9	161	17927.0	GL
2,4,6-Trinitrophenol(Picric acid)	$C_6H_3N_3O_7$	229.11	178.1	L	396.9	S	–	Sub
Trinitrotoluene	$C_7H_5N_3O_6$	227.13	203.7	L	413.8	S	16089.0	GL@
Triphenylmethane	$C_{19}H_{16}$	244.32	295.4	L	591.9	S	14534.0	GL
Urea	CH_4N_2O	60.06	61.0	L	141.4	S	–	Dec
Urethane	$C_3H_7NO_2$	89.10	100.6	L	206.6	S	11170.0	GL
Vanillin	$C_8H_8O_3$	152.14	155.2	L	325.9	161	14617.0	GL
Valeric acid	$C_5H_{10}O_2$	102.13	130.0	L	248.2	161	11817.0	G
Water	H_2O	18.02	18.7	168	52.0	42	9717.0	168
m-Xylene	C_8H_{10}	106.16	140.4	L	284.3	161	8705.0	168

L = Values of 'V_b' estimated by LeBas method (168)

S = Values of [P] estimated by Sugden method (188)

G = Values of 'ΔH_b' estimated by Giacalone equation (168) using experimental P_c , T_c and T_b.

GL = Value of 'ΔH_b' estimated by Giacalone equation (168) using estimated vales of P_c and T_c by Lydersen method (168); and experimental T_b.

GLA = Value of 'ΔH_b' estimated by Giacalone equation (168) using estimated values of P_c and T_c by Lydersen method (168) ; and value of T_b obtained from lower pressure data which is corrected to normal pressure using Adam equation (151).

GLA@ and GL@ = Value of 'ΔH_b' estimated from the sublimation temperature or decomposing temperature; hence not reliable.

Appendix 3-2.2 Comparison of correlations for estimating diffusion coefficients in various solvents at infinite dilution, $D^{\circ}_{AB} \times 10^5$ cm^2/sec

Solvent = Water

Solute	T, °C	D°_{AB} (exp.)	Ref	This work Eq.(3-2.4)		Wilke&Chang Eq.(2-3.16)		King et al Eq.(2-3.29)		Sitara. et al Eq.(2-3.27)	
				Calc.	%Error	Calc.	%Error	Calc.	%Error	Calc.	%Error
orine	25.0	1.250	85	1.375	10.0	1.710	36.8	1.787	42.9	1.683	34.7
mine	12.0	0.900	219	0.875	-2.7	1.077	19.7	0.976	8.4	1.239	37.7
ine	25.0	1.250	166	1.087	-13.0	1.304	4.3	1.135	-9.2	1.577	26.1
hane	4.0	0.840	19	0.899	7.0	1.015	20.8	1.544	83.8	0.868	3.3
"	20.0	1.490	19	1.483	-0.5	1.674	12.4	2.546	70.9	1.382	-7.2
"	40.0	2.380	19	2.427	2.0	2.740	15.1	4.167	75.1	2.185	-8.2
"	60.0	3.550	19	3.613	1.8	4.079	14.9	6.203	74.7	3.164	-10.9
ane	4.0	0.890	19	0.744	-16.4	0.808	-9.2	1.080	21.4	0.736	-17.3
"	20.0	1.200	19	1.228	2.3	1.333	11.1	1.782	48.5	1.172	-2.3
"	40.0	1.940	19	2.010	3.6	2.182	12.5	2.916	50.3	1.853	-4.5
"	60.0	2.940	19	2.992	1.8	3.248	10.5	4.341	47.7	2.683	-8.8
pane	4.0	0.550	19	0.650	18.1	0.674	22.6	0.910	65.4	0.665	20.9
"	20.0	0.970	19	1.072	10.5	1.113	14.7	1.500	54.7	1.059	9.2
"	40.0	1.770	19	1.754	-0.9	1.821	2.9	2.455	38.7	1.674	-5.4
"	60.0	2.710	19	2.611	-3.7	2.710	0.0	3.655	34.9	2.424	-10.6
tane	4.0	0.500	19	0.590	17.9	0.579	15.7	0.798	59.6	0.607	21.4
"	20.0	0.890	19	0.973	9.3	0.954	7.2	1.316	47.9	0.967	8.6
"	40.0	1.590	19	1.592	0.1	1.562	-1.8	2.154	35.5	1.529	-3.9
"	60.0	2.510	19	2.369	-5.6	2.325	-7.4	3.207	27.8	2.213	-11.8
entane	4.0	0.460	19	0.542	17.7	0.512	11.2	0.719	56.3	0.564	22.5
"	20.0	0.840	19	0.894	6.4	0.844	0.5	1.186	41.2	0.898	6.9
"	40.0	1.490	19	1.462	-1.9	1.381	-7.3	1.941	30.3	1.419	-4.7
"	60.0	2.240	19	2.177	-2.8	2.056	-8.2	2.889	29.0	2.055	-8.3
ohexane	2.0	0.460	19	0.491	6.7	0.478	4.0	0.620	34.7	0.529	15.0
	10.0	0.570	19	0.646	13.4	0.630	10.5	0.816	43.2	0.683	19.9
	20.0	0.840	19	0.871	3.6	0.849	1.0	1.099	30.9	0.901	7.3
	40.0	1.310	19	1.425	8.8	1.389	6.0	1.799	37.3	1.425	8.8
	60.0	1.930	19	2.121	9.9	2.067	7.1	2.678	38.8	2.063	6.9
lopentane	2.0	0.560	19	0.526	-6.1	0.532	-5.0	0.670	19.6	0.561	0.1
	10.0	0.640	19	0.693	8.2	0.700	9.4	0.882	37.8	0.724	13.2
	20.0	0.930	19	0.933	0.3	0.944	1.5	1.188	27.8	0.955	2.7
	40.0	1.410	19	1.527	8.3	1.544	9.5	1.944	37.9	1.511	7.1
	60.0	2.180	19	2.273	4.3	2.299	5.4	2.895	32.8	2.187	0.3
hylcyclopentane	2.0	0.480	19	0.492	2.4	0.471	-1.9	0.625	30.3	0.526	9.6
	10.0	0.590	19	0.647	9.7	0.620	5.0	0.823	39.5	0.680	15.2
	20.0	0.850	19	0.872	2.6	0.835	-1.8	1.109	30.5	0.897	5.5
	60.0	1.920	19	2.125	10.7	2.034	5.9	2.702	40.7	2.053	6.9
tylene	0.0	1.100	85	0.762	-30.8	0.820	-25.5	0.913	-17.0	0.673	-38.8
	10.0	1.500	85	1.082	-27.9	1.165	-22.4	1.297	-13.6	0.934	-37.8
	30.0	2.190	85	1.891	-13.6	2.036	-7.0	2.266	3.5	1.569	-28.3
pylene	25.0	1.440	108	1.223	-15.1	1.335	-7.3	1.742	21.0	1.230	-14.6
tene*	7.0	5.160	61	0.670	-87.0	0.670	-87.0	0.906	-82.4	0.689	-86.7
	25.0	6.610	61	1.139	-82.8	1.140	-82.8	1.541	-76.7	1.129	-82.9
	40.0	9.490	61	1.630	-82.8	1.631	-82.8	2.204	-76.8	1.575	-83.4
	60.0	12.500	61	2.427	-80.6	2.428	-80.6	3.281	-73.7	2.230	-81.8
zene	25.0	1.090	19	1.057	-3.0	1.089	-0.1	1.284	17.8	1.087	-0.3
	2.0	0.580	19	0.521	-10.2	0.537	-7.4	0.633	9.1	0.563	-2.9
	10.0	0.750	19	0.686	-8.5	0.707	-5.7	0.833	11.1	0.727	-3.0
	80.0	1.020	19	0.924	-9.4	0.953	-6.6	1.123	10.1	0.960	-5.9

Appendix 3-2.2 (continued)

Solvent = Water

Solute	T, ^{o}C	D^{o}_{AB} (Exp.)	Ref	This work Eq.(3-2.4)		Wilke&Chang Eq.(2-3.16)		King et al Eq.(2-3.29)		Sitara. et al Eq.(2-3.27)	
				Calc.	%Error	Calc.	%Error	Calc.	%Error	Calc.	%Error
Benzene	40.0	1.600	19	1.512	-5.5	1.559	-2.6	1.837	14.8	1.517	-5.2
"	60.0	2.550	19	2.251	-11.7	2.321	-9.0	2.735	7.2	2.196	-13.9
Toluene	2.0	0.450	19	0.487	8.3	0.475	5.6	0.589	30.9	0.525	16.7
"	10.0	0.620	19	0.641	3.4	0.626	0.9	0.775	25.1	0.678	9.4
"	20.0	0.850	19	0.864	1.6	0.843	-0.8	1.045	22.9	0.895	5.3
"	40.0	1.340	19	1.414	5.5	1.380	2.9	1.710	27.6	1.415	5.6
"	60.0	2.150	19	2.105	-2.1	2.054	-4.5	2.545	18.4	2.048	-4.7
Ethyl benzene	2.0	0.440	19	0.459	4.3	0.429	-2.5	0.550	25.0	0.493	12.1
"	10.0	0.610	19	0.604	-1.0	0.565	-7.4	0.724	18.7	0.637	4.4
"	20.0	0.810	19	0.814	0.5	0.761	-6.1	0.975	20.4	0.841	3.8
"	40.0	1.300	19	1.332	2.5	1.245	-4.2	1.596	22.8	1.329	2.2
"	60.0	1.950	19	1.983	1.7	1.853	-5.0	2.376	21.8	1.924	-1.3
Methanol	1.0	0.766	96	0.729	-4.9	0.846	10.4	0.653	-14.8	0.598	-22.0
"	4.0	0.800	65	0.813	1.7	0.944	18.1	0.729	-8.9	0.662	-17.2
"	12.5	1.130	65	1.049	-7.2	1.218	7.8	0.939	-16.9	0.839	-25.8
"	15.0	1.260	168	1.162	-7.8	1.350	7.1	1.041	-17.4	0.923	-26.8
"	24.8	1.700	65	1.533	-9.8	1.780	4.7	1.373	-19.2	1.194	-29.8
"	25.0	1.587	96	1.535	-3.3	1.782	12.3	1.375	-13.4	1.195	-24.7
"	37.0	2.270	65	2.054	-9.5	2.385	5.0	1.840	-19.0	1.567	-31.0
Ethanol	4.0	0.670	65	0.694	3.5	0.750	11.9	0.653	-2.5	0.597	-10.8
"	10.0	0.840	168	0.849	1.1	0.918	9.2	0.800	-4.8	0.721	-14.1
"	12.5	0.890	65	0.894	0.5	0.966	8.6	0.842	-5.4	0.757	-15.0
"	15.0	1.000	168	0.991	-0.9	1.071	7.1	0.934	-6.6	0.833	-16.7
"	24.8	1.260	65	1.307	3.7	1.412	12.1	1.231	-2.3	1.077	-14.5
"	25.0	1.240	168	1.308	5.5	1.414	14.0	1.233	-0.6	1.078	-13.1
"	25.0	1.248	24	1.308	4.8	1.414	13.3	1.233	-1.2	1.078	-13.6
"	37.0	1.770	65	1.751	-1.1	1.892	6.9	1.650	-6.8	1.413	-20.1
Allyl alcohol	15.0	0.900	168	0.916	1.7	0.968	7.5	0.895	-0.6	0.814	-9.5
i-amyl alcohol	15.0	0.690	168	0.759	9.9	0.704	2.0	0.797	15.4	0.704	2.0
n-Propanol	4.0	0.570	65	0.624	9.5	0.639	12.1	0.605	6.1	0.558	-2.1
"	12.5	0.760	65	0.805	5.9	0.824	8.4	0.780	2.6	0.707	-7.0
"	15.0	0.870	168	0.892	2.5	0.913	5.0	0.864	-0.7	0.778	-10.6
"	24.8	1.150	65	1.176	2.3	1.204	4.7	1.140	-0.9	1.006	-12.5
"	37.0	1.560	65	1.576	1.0	1.613	3.4	1.527	-2.1	1.321	-15.3
Sec-Propanol	4.0	0.540	65	0.625	15.7	0.637	17.9	0.604	11.9	0.557	3.1
"	12.5	0.730	65	0.805	10.3	0.821	12.4	0.779	6.7	0.705	-3.4
"	24.8	1.070	65	1.177	10.0	1.200	12.2	1.139	6.4	1.004	-6.2
"	37.0	1.520	65	1.577	3.8	1.608	5.8	1.525	0.3	1.317	-13.4
n-Butanol	1.0	0.435	96	0.515	18.4	0.496	13.9	0.505	16.0	0.470	8.0
"	1.0	0.452	96	0.515	13.9	0.496	9.7	0.505	11.7	0.470	3.9
"	4.0	0.510	65	0.575	12.7	0.553	8.5	0.564	10.5	0.521	2.1
"	12.5	0.690	65	0.741	7.4	0.713	3.4	0.727	5.3	0.659	-4.5
"	15.0	0.770	168	0.821	6.7	0.791	2.7	0.805	4.6	0.725	-5.8
"	24.8	1.000	65	1.084	8.3	1.043	4.3	1.062	6.2	0.938	-6.2
"	25.0	0.956	96	1.085	13.5	1.044	9.2	1.063	11.2	0.939	-1.8
"	25.0	0.972	96	1.085	11.6	1.044	7.4	1.063	9.4	0.939	-3.4
"	37.0	1.420	65	1.451	2.2	1.397	-1.6	1.423	0.2	1.232	-13.3
-Butanol	20.0	0.790	168	0.951	20.4	0.913	15.5	0.930	17.7	0.829	4.9
"	20.0	0.840	168	0.951	13.2	0.913	8.7	0.930	10.7	0.829	-1.3

Appendix 3-2.2 (continued)

Solvent = Water

Solute	T, °C	D°_{AB} (exp.)	Ref	This work Eq.(3-2.4)		Wilke-Chang Eq.(2-3.16)		King et al Eq.(2-3.29)		Sitara. et al Eq.(2-3.27)	
				Calc.	%Error	Calc.	%Error	Calc.	%Error	Calc.	%Error
Butanol	18.0	0.850	96	0.899	5.8	0.863	1.5	0.879	3.4	0.787	-7.5
Butanol	4.0	0.390	65	0.352	-9.7	0.338	-13.4	0.357	-8.4	0.336	-13.9
"	12.5	0.600	65	0.743	23.9	0.713	18.9	0.754	25.7	0.673	12.2
"	24.8	0.980	65	1.087	10.9	1.043	6.4	1.103	12.5	0.958	-2.2
"	37.0	1.310	65	1.456	11.1	1.397	6.6	1.478	12.8	1.258	-4.0
nzyl alcohol	20.0	0.820	168	0.844	2.9	0.813	-0.8	0.836	2.0	0.808	-1.4
ycerol	15.0	0.720	168	0.778	8.0	0.879	22.0	0.651	-9.6	0.730	1.5
"	20.0	0.825	168	0.898	8.9	1.014	22.9	0.751	-8.9	0.835	1.2
"	20.0	0.830	60	0.898	8.2	1.014	22.2	0.751	-9.5	0.835	0.6
"	10.0	0.630	166	0.667	5.8	0.753	19.5	0.558	-11.5	0.633	0.4
hylene glycol	20.0	1.040	168	1.060	1.9	1.190	14.4	0.940	-9.6	0.936	-10.3
"	25.0	1.172	21	1.212	3.4	1.361	16.1	1.075	-8.3	1.060	-9.5
"	40.0	1.640	21	1.734	5.8	1.947	18.7	1.539	-6.2	1.479	-9.8
"	55.0	2.280	21	2.354	3.3	2.643	15.9	2.089	-8.4	1.966	-13.8
"	70.0	2.780	21	3.070	10.4	3.447	24.0	2.723	-2.0	2.516	-9.5
2-Propyleneglycol	20.0	0.880	168	0.994	12.9	1.001	13.8	0.859	-2.3	0.846	-3.8
etone	15.0	1.220	168	0.896	-26.6	0.941	-22.9	1.037	-15.0	0.869	-28.7
"	17.0	1.250	100	0.950	-24.0	0.998	-20.2	1.100	-12.0	0.918	-26.5
"	20.0	1.160	168	1.034	-10.8	1.086	-6.3	1.197	3.2	0.994	-14.3
"	25.0	1.280	168	1.183	-7.6	1.243	-2.9	1.370	7.0	1.126	-12.0
rfural	20.0	1.040	168	0.912	-12.3	0.980	-5.8	0.954	-8.2	0.945	-9.2
etic acid	9.7	0.769	17	0.840	9.3	0.901	17.2	0.782	1.6	0.758	-1.4
"	12.5	0.910	166	0.887	-2.5	0.952	4.6	0.825	-9.3	0.798	-12.3
"	14.0	0.900	96	0.954	6.0	1.024	13.7	0.888	-1.4	0.854	-5.1
"	15.0	0.910	100	0.983	8.0	1.055	15.9	0.915	0.5	0.878	-3.5
"	15.0	0.880	96	0.983	11.7	1.055	19.8	0.915	3.9	0.878	-0.2
"	20.0	1.190	168	1.135	-4.6	1.218	2.3	1.056	-11.3	1.003	-15.7
"	25.0	1.250	17	1.298	3.9	1.393	11.4	1.208	-3.4	1.137	-9.1
"	25.0	1.270	17	1.298	2.2	1.393	9.6	1.208	-4.9	1.137	-10.5
"	25.0	1.210	211	1.298	7.3	1.393	15.1	1.208	-0.2	1.137	-6.1
yric acid	20.0	0.824	17	0.934	13.3	0.891	8.2	0.917	11.3	0.851	3.2
"	25.0	0.918	17	1.068	16.3	1.019	11.0	1.049	14.2	0.964	5.0
mic acid	25.0	1.516	17	1.503	-0.9	1.695	11.8	1.675	10.5	1.431	-5.6
pionic acid	25.0	1.009	17	1.169	15.8	1.173	16.3	1.314	30.2	1.136	12.6
"	20.0	0.898	17	1.022	13.8	1.026	14.2	1.148	27.9	1.003	11.6
eric acid	25.0	0.817	17	0.997	22.1	0.911	11.5	0.964	18.0	0.894	9.4
"	20.0	0.767	17	0.872	13.7	0.797	3.9	0.843	9.9	0.789	2.8
yl acetate	30.0	1.750	145	1.187	-32.2	1.168	-33.2	1.397	-20.2	1.193	-31.8
tonitrile	15.0	1.260	168	1.013	-19.6	1.127	-10.6	1.050	-16.7	0.888	-29.5
onia	12.0	1.640	108	1.183	-27.8	1.694	3.3	1.276	-22.2	1.020	-37.8
"	15.0	1.780	20	1.297	-27.2	1.856	4.2	1.398	-21.5	1.110	-37.6
line	20.0	0.920	168	0.873	-5.1	0.885	-3.8	0.927	0.7	0.865	-6.0
thylamine	20.0	0.970	168	0.909	-6.3	0.885	-8.7	1.129	16.4	0.903	-6.9
yl acetate	20.0	1.000	168	0.915	-8.5	0.900	-9.9	1.077	7.7	0.936	-6.4
rogen sulphide	15.5	1.430	95	1.167	-18.4	1.577	10.3	1.496	4.6	1.265	-11.5

Appendix 3-2.2 (continued)

Solvent = Water

Solute	T, °C	D°_{AB} (exp.)	Ref	This work Eq(3-2.4)		Wilke-Chang Eq.(2-3.16)		King et al Eq.(2-3.29)		Sitara. et al Eq.(2-3.27)	
				Calc.	%Error	Calc.	%Error	Calc.	%Error	Calc.	%Error
Hydrogen sulphide	16.0	1.770	3	1.199	-32.3	1.621	-8.4	1.538	-13.1	1.298	-26.7
"	25.0	1.360	85	1.537	13.0	2.078	52.8	1.972	45.0	1.635	20.2
Hydrogen chloride	20.0	2.640	153	1.447	-45.2	1.897	-28.1	1.876	-28.9	1.584	-40.0
Methyl chloride	22.1	1.390	85	1.280	-7.9	1.483	6.7	1.576	13.4	1.332	-4.1
Carbon dioxide	0.0	0.960	85	0.735	-23.4	0.880	-8.3	0.759	-20.9	0.735	-23.4
"	6.5	1.080	85	0.930	-13.9	1.144	3.1	0.960	-11.1	0.915	-15.3
"	10.0	1.170	85	1.045	-10.7	1.251	6.9	1.078	-7.9	1.019	-12.9
"	10.2	1.300	85	1.046	-19.6	1.252	-3.7	1.079	-17.0	1.020	-21.6
"	15.0	1.370	85	1.219	-11.0	1.460	6.5	1.258	-8.2	1.176	-14.1
"	15.0	1.400	85	1.219	-12.9	1.460	4.3	1.258	-10.1	1.176	-16.0
"	15.8	1.490	85	1.255	-15.8	1.502	0.8	1.295	-13.1	1.208	-18.9
"	16.0	1.570	85	1.256	-20.0	1.503	-4.3	1.296	-17.5	1.209	-23.0
"	16.0	1.630	85	1.256	-23.0	1.503	-7.8	1.296	-20.5	1.209	-25.8
"	16.4	1.570	85	1.274	-18.9	1.525	-2.9	1.314	-16.3	1.225	-22.0
"	20.0	1.630	85	1.407	-13.7	1.685	3.4	1.452	-10.9	1.344	-17.5
"	20.4	1.850	85	1.416	-23.4	1.696	-8.3	1.462	-21.0	1.352	-26.9
"	25.0	2.000	85	1.610	-19.5	1.927	-3.6	1.661	-16.9	1.523	-23.8
"	30.0	2.060	85	1.826	-11.4	2.186	6.1	1.884	-8.5	1.713	-16.9
"	30.0	2.250	85	1.826	-18.8	2.186	-2.8	1.884	-16.2	1.713	-23.9
"	35.0	2.260	85	2.058	-8.9	2.464	9.0	2.124	-6.0	1.914	-15.3
"	35.0	2.180	85	2.058	-5.6	2.464	13.0	2.124	-2.6	1.914	-12.2
"	52.0	3.610	85	2.952	-18.2	3.534	-2.1	3.046	-15.6	2.677	-25.8
"	65.0	4.300	85	3.746	-12.9	4.485	4.3	3.866	-10.1	3.341	-22.3
Nitrogen	15.0	1.940	85	1.435	-26.0	1.524	-21.4	2.705	39.4	1.633	-15.8
"	21.7	2.000	85	1.748	-12.6	1.857	-7.2	3.295	64.8	1.962	-1.9
"	25.0	2.250	85	1.895	-15.8	2.012	-10.6	3.572	58.7	2.115	-6.0
"	37.0	2.700	85	2.536	-6.1	2.693	-0.3	4.780	77.0	2.773	2.7
Nitrous oxide	15.0	1.620	85	1.368	-15.6	1.491	-8.0	1.562	-3.6	1.345	-17.0
"	16.2	1.560	85	1.428	-8.5	1.556	-0.2	1.631	4.6	1.400	-10.3
"	20.0	2.110	85	1.579	-25.2	1.721	-18.4	1.804	-14.5	1.537	-27.1
"	25.0	2.570	85	1.952	-24.0	1.948	-24.2	2.057	-20.0	1.728	-32.8
Oxygen	15.0	1.670	85	1.469	-12.0	1.737	4.0	2.541	52.1	1.775	6.3
"	16.0	1.870	85	1.513	-19.1	1.789	-4.3	2.617	39.9	1.824	-2.4
"	18.2	1.990	85	1.606	-19.3	1.899	-4.6	2.777	39.5	1.928	-3.1
"	20.0	2.010	85	1.696	-15.6	2.006	-0.2	2.933	45.9	2.028	0.9
"	22.0	2.250	85	1.792	-20.4	2.119	-5.8	3.098	37.7	2.134	-5.1
"	22.0	2.220	85	1.792	-19.3	2.119	-4.6	3.098	39.6	2.134	-3.9
"	25.0	2.600	85	1.940	-25.4	2.294	-11.8	3.354	29.0	2.298	-11.6
"	25.0	2.600	85	1.940	-25.4	2.294	-11.8	3.354	29.0	2.298	-11.6
"	25.0	2.420	85	1.940	-19.8	2.294	-5.2	3.354	38.6	2.298	-5.0
"	37.0	3.000	85	2.596	-13.5	3.070	2.3	4.489	49.6	3.013	0.4
Sulphur dioxide	20.0	1.400	85	1.353	-3.3	1.530	9.3	1.423	1.6	1.390	-0.7
"	20.0	1.460	85	1.353	-7.3	1.530	4.8	1.423	-2.5	1.390	-4.8
"	20.0	1.660	85	1.353	-18.5	1.530	-7.8	1.423	-14.3	1.390	-16.2
"	20.0	1.620	85	1.352	-16.6	1.536	-5.2	1.425	-12.1	1.395	-13.9
"	25.0	2.040	85	1.548	-24.1	1.750	-14.2	1.627	-20.2	1.575	-22.8
"	25.0	1.830	85	1.548	-15.4	1.750	-4.4	1.627	-11.1	1.575	-13.9
"	30.0	2.080	85	1.756	-15.6	1.985	-4.6	1.846	-11.2	1.771	-14.8
"	35.0	2.330	85	1.978	-15.1	2.237	-4.0	2.080	-10.7	1.979	-15.0
"	40.0	2.590	85	2.214	-14.5	2.504	-3.3	2.329	-10.1	2.198	-15.1

Appendix 3-2.2 (continued)

Solvent = Water

Solute	T, °C	$\dot{D}_{AB}$ (exp.)	Ref	This work Eq.(3-2.4)		Wilke-Chang Eq.(2-3.16)		King et al Eq.(2-3.29)		Sitara. et al Eq.(2-3.27)	
				Calc.	%Error	Calc.	%Error	Calc.	%Error	Calc.	%Error
Manitol	10.0	0.400	168	0.551	37.7	0.478	19.6	0.350	-12.4	0.446	11.5
"	20.0	0.560	168	0.742	32.5	0.645	15.1	0.472	-15.7	0.588	5.1
"	30.0	0.720	168	0.963	33.7	0.836	16.2	0.613	-14.9	0.750	4.1
"	40.0	0.900	168	1.214	34.9	1.055	17.2	0.773	-14.1	0.930	3.4
"	50.0	1.100	168	1.496	36.0	1.300	18.2	0.952	-13.4	1.130	2.7
"	60.0	1.320	168	1.808	37.0	1.570	19.0	1.150	-12.9	1.347	2.0
"	70.0	1.560	168	2.150	37.8	1.867	19.7	1.368	-12.3	1.582	1.4
"	20.0	0.673	168	0.742	10.3	0.645	-4.2	0.472	-29.8	0.588	-12.6
Resorcinol	20.0	0.770	168	0.869	12.9	0.877	13.9	0.771	0.1	0.813	5.6
Pentaerythritol	20.0	0.690	168	0.812	17.7	0.737	6.8	0.542	-21.5	0.636	-7.8
Pyrogallol	15.0	0.560	168	0.735	31.2	0.731	30.5	0.605	8.1	0.683	22.0
Triethyleneglycol	30.0	0.875	131	0.954	9.0	0.879	0.5	0.849	-3.0	0.879	0.4
Glycine	1.0	0.515	118	0.557	8.2	0.588	14.1				
"	25.0	1.055	168	1.174	11.3	1.238	17.3				
Erythritol	25.0	0.805	168	0.987	22.6	0.929	15.4	0.666	-17.2	0.774	-3.9
Aminobutyric acid	1.0	0.389	118	0.475	22.0	0.448	15.3				
"	25.0	0.829	118	1.000	20.6	0.945	13.9				
Benzoic acid	25.0	1.210	168	0.955	-21.1	0.891	-26.3	0.917	-24.2	0.901	-25.5
Caprine	1.0	0.333	118	0.422	26.7	0.372	11.8				
"	25.0	0.725	118	0.889	22.6	0.785	8.2				
Caproic acid	25.0	0.784	17	0.931	18.7	0.828	5.6	0.884	12.8	0.832	6.1
Oxalic acid	20.0	1.530	168	1.043	-31.8	1.063	-30.5				
Alanine	1.0	0.432	118	0.511	18.2	0.506	17.0	0.463	7.3	0.477	10.5
"	25.0	0.910	118	1.076	18.2	1.065	17.0	0.976	7.3	0.954	4.9
"	5.0	0.500	118	0.591	18.1	0.585	16.9	0.536	7.2	0.546	9.3
"	15.0	0.688	118	0.815	18.4	0.807	17.3	0.739	7.5	0.737	7.1
"	35.0	1.164	118	1.375	18.1	1.362	17.0	1.248	7.2	1.199	3.0
Propionic acid	25.0	1.009	17	1.159	14.9	1.173	16.3	1.314	30.2	1.136	12.6
Propionic acid	20.0	0.898	17	1.014	12.9	1.026	14.2	1.148	27.9	1.003	11.6
Tartaric acid	15.0	0.610	168	0.789	29.3	0.625	2.4				
Valeric acid	25.0	0.817	17	0.989	21.1	0.911	11.5	0.964	18.0	0.894	9.4
"	20.0	0.767	17	0.865	12.8	0.797	3.9	0.843	9.9	0.789	2.8
-Varline	25.0	0.768	118	0.939	22.3	0.855	11.3				
erine	1.0	0.420	118	0.496	18.2	0.484	15.5				
"	25.0	0.880	118	1.045	18.7	1.021	15.9				
hreonine	25.0	0.798	118	0.975	22.2	0.912	14.3				
lloxan	20.0	0.670	20	0.839	25.3	0.821	22.5				
cetamide	4.0	0.610	65	0.639	4.7	0.725	18.9	0.562	-7.9	0.577	-5.4
"	12.5	0.830	65	0.823	-0.8	0.935	12.7	0.724	-12.7	0.731	-12.0
"	15.0	0.960	65	0.913	-4.9	1.036	8.0	0.803	-16.4	0.804	-16.3
"	20.0	1.050	65	1.054	0.3	1.196	13.9	0.927	-11.7	0.919	-12.5
"	24.8	1.320	65	1.204	-8.8	1.367	3.6	1.059	-19.8	1.040	-21.2
"	25.0	1.252	65	1.205	-3.8	1.368	9.3	1.060	-15.3	1.041	-16.9
"	37.0	1.750	65	1.613	-7.9	1.831	4.6	1.419	-18.9	1.365	-22.0
utyramide	4.0	0.450	65	0.540	20.0	0.518	15.2	0.527	17.2	0.504	12.0
"	12.5	0.650	65	0.696	7.1	0.668	2.8	0.680	4.6	0.638	-1.8
"	24.8	1.070	65	1.017	-4.9	0.977	-8.7	0.994	-7.1	0.908	-15.1
"	37.0	1.450	65	1.363	-6.0	1.309	-9.7	1.331	-8.2	1.192	-17.8
affine	10.0	0.420	168	0.515	22.7	0.448	6.8				

Appendix 3-2.2 (continued)

Solvent = Water

Solute	T, °C	D°_{AB} (exp.)	Ref	This work Eq.(3-2.4) Calc.	This work Eq.(3-2.4) %Error	Wilke-Chang Eq.(2-3.16) Calc.	Wilke-Chang Eq.(2-3.16) %Error	King et al Eq.(2-3.29) Calc.	King et al Eq.(2-3.29) %Error	Sitara. et al Eq.(2-3.27) Calc.	Sitara. et al Eq.(2-3.27) %Error
Formamide	4.0	0.850	65	0.724	-14.8	0.928	9.1	0.630	-25.9	0.664	-21.9
"	12.5	1.170	65	0.933	-20.2	1.196	2.2	0.812	-30.6	0.841	-28.1
"	24.8	1.720	65	1.364	-20.7	1.748	1.6	1.187	-31.0	1.197	-30.4
"	37.0	2.200	65	1.828	-16.9	2.342	6.4	1.590	-27.7	1.571	-28.6
"	25.0	1.608	168	1.366	-15.1	1.750	8.8	1.188	-26.1	1.198	-25.5
Glycoamide	25.0	1.142	118	1.266	10.9	1.214	6.3				
"	5.0	0.637	96	0.695	9.1	0.666	4.6				
"	15.0	0.869	96	0.959	10.4	0.919	5.8				
"	25.0	1.140	96	1.266	11.1	1.214	6.5				
"	35.0	1.451	96	1.619	11.6	1.552	6.9				
"	45.0	1.794	96	2.017	12.4	1.933	7.7				
Nicotine	10.0	0.490	168	0.523	6.7	0.451	-8.0	0.586	19.5	0.554	13.1
"	20.0	0.530	20	0.704	32.9	0.607	14.5	0.789	48.9	0.731	37.9
Propionamide	4.0	0.500	65	0.604	20.9	0.571	14.3	0.544	8.7	0.518	3.7
"	12.5	0.730	65	0.779	6.7	0.737	0.9	0.701	-4.0	0.657	-10.1
"	24.8	1.200	65	1.139	-5.1	1.077	-10.3	1.025	-14.6	0.935	-22.1
"	25.0	1.093	168	1.140	4.3	1.078	-1.4	1.026	-6.2	0.935	-14.4
"	37.0	1.600	65	1.526	-4.6	1.443	-9.8	1.373	-14.2	1.227	-23.3
yridine	15.0	0.580	168	0.807	39.2	0.843	45.4	0.910	56.9	0.823	41.9
rea	25.0	1.382	118	1.222	-11.6	1.435	3.8				
"	5.0	0.790	96	0.671	-15.1	0.788	-0.3				
"	15.0	1.063	96	0.926	-12.9	1.087	2.2				
"	25.0	1.377	96	1.222	-11.2	1.435	4.2				
"	35.0	1.731	96	1.563	-9.7	1.834	5.9				
"	12.0	0.990	168	0.845	-14.6	0.992	0.2				
"	20.0	1.200	168	1.069	-10.9	1.254	4.5				
"	25.0	1.378	168	1.222	-11.3	1.435	4.1				
rethane	15.0	0.800	168	0.801	0.2	0.805	0.6	0.783	-2.1	0.760	-5.0
"	15.0	0.870	20	0.801	-7.9	0.805	-7.5	0.783	-9.9	0.760	-12.6
entoses	20.0	0.700	118	0.848	21.1	0.737	5.3				
"	25.0	0.760	118	0.970	27.6	0.843	10.9				
exoses	1.0	0.320	118	0.425	32.9	0.359	12.1				
"	15.0	0.520	118	0.679	30.5	0.572	10.0				
"	25.0	0.680	118	0.896	31.8	0.756	11.1				
saccharides	1.0	0.242	118	0.313	29.5	0.255	5.3				
"	12.0	0.360	118	0.457	26.8	0.371	3.1				
"	25.0	0.523	118	0.660	26.2	0.537	2.6				
iourea	25.0	1.331	118	1.145	-14.0	1.227	-7.8				
thyl urea	25.0	1.168	118	1.112	-4.8	1.191	2.0				
3-Dimethylurea	25.0	0.998	118	1.029	3.1	1.033	3.5	0.937	-6.1	0.912	-8.6
riethyleneglycol	45.0	1.310	135	1.339	2.2	1.234	-5.8	1.191	-9.1	1.205	-8.0
"	65.0	2.180	135	1.956	-10.3	1.804	-17.3	1.741	-20.1	1.714	-21.4

* All four equations give consistently very high deviations for 1-butene. Unfortunately no other set of experimental coefficients for 1-butene was found to verify the coefficients used in this table. The deviations for 1-butene were not taken into account in computing the mean deviation.

Appendix 3-2.2 (continued)

Solvent = Methanol

Solute	T, °C	D°_{AB} (exp.)	Ref	This work Eq.(3-2.4)		Wilke-Chang Eq.(2-3.16)		King et al Eq.(2-3.29)		Sitara. et al Eq.(2-3.27)	
				Calc.	%Error	Calc.	%Error	Calc.	%Error	Calc.	%Error
Benzene	27.0	2.760	123	2.715	-1.6	2.081	-24.6	2.306	-16.5	1.842	-33.3
Toluene	25.0	2.560	123	2.448	-4.4	1.776	-30.6	2.070	-19.2	1.661	-35.1
Biphenyl	25.0	1.890	123	2.029	7.4	1.360	-28.0	1.595	-15.6	1.405	-25.6
Methanol(self)	5.0	1.550	43	1.781	14.9	2.267	46.3	1.639	5.7	1.385	-10.6
"	15.0	1.910	43	2.160	13.1	2.750	44.0	1.938	4.1	1.657	-13.2
"	25.0	2.320	43	2.578	11.1	3.282	41.5	2.373	2.3	1.954	-15.8
"	25.0	2.270	152	2.578	13.6	3.282	44.6	2.373	4.5	1.954	-13.9
"	35.0	2.710	43	3.057	12.8	3.892	43.6	2.813	3.8	2.290	-15.5
"	35.0	2.740	150	3.057	11.6	3.892	42.1	2.813	2.7	2.290	-16.4
"	40.0	2.890	43	3.284	13.6	4.181	44.7	3.022	4.6	2.447	-15.3
"	45.0	3.370	43	3.554	5.5	4.526	34.3	3.271	-2.9	2.634	-21.8
"	55.0	3.880	43	4.151	7.0	5.285	36.2	3.820	-1.5	3.043	-21.6
Allyl alcohol	15.0	1.800	168	1.701	-5.5	1.971	9.5	1.714	-4.8	1.466	-18.6
iso-Amyl alcohol	15.0	1.340	168	1.409	5.2	1.434	7.0	1.526	13.9	1.267	-5.5
i-Propanol	30.0	1.970	123	2.158	9.6	2.393	21.5	2.154	9.4	1.778	-9.8
i-Butanol	30.0	1.840	123	1.984	7.8	2.088	13.5	1.999	8.7	1.661	-9.7
Phenol	15.0	1.400	168	1.437	2.6	1.632	16.6	1.527	9.1	1.399	-0.1
Ethylene glycol	25.0	1.640	123	2.036	24.2	2.507	52.9	1.863	13.6	1.737	5.9
Propylene glycol	15.0	1.240	168	1.599	29.0	1.767	42.5	1.426	15.0	1.333	7.5
Glycerol	15.0	1.150	168	1.445	25.7	1.790	55.7	1.247	8.4	1.315	14.3
Acetone	18.8	2.220	182	1.791	-19.3	2.062	-7.1	2.137	-3.7	1.674	-24.6
"	15.0	2.500	100	1.665	-33.4	1.918	-23.3	1.987	-20.5	1.565	-37.4
Methylethylketone	30.0	1.870	4	1.975	5.6	2.191	17.2	2.379	27.2	1.870	-0.0
Furfural	15.0	1.700	168	1.467	-13.7	1.729	1.7	1.584	-6.8	1.488	-12.5
Benzaldehyde	15.0	1.660	100	1.355	-18.4	1.489	-10.3	1.612	-2.9	1.408	-15.2
Acetic acid	15.0	1.540	96	1.827	18.6	2.149	39.5	1.752	13.8	1.580	2.6
Butyric acid	30.0	1.810	4	1.963	8.4	2.038	12.6	1.921	6.1	1.678	-7.3
Propionic acid	15.0	1.620	100	1.633	0.8	1.810	11.7	1.624	0.2	1.444	-10.9
Ethyl acetate	17.8	1.720	182	1.667	-3.1	1.799	4.6	2.023	17.6	1.655	-3.8
Ethyl benzoate	16.0	1.280	182	1.223	-4.4	1.199	-6.3	1.498	17.1	1.296	1.3
Aniline	15.0	1.490	182	1.406	-5.6	1.562	4.8	1.534	3.0	1.360	-8.7
Acetonitrile	15.0	2.640	182	1.881	-28.8	2.296	-13.0	2.012	-23.8	1.599	-39.4
Nitromethane	16.0	2.230	182	1.796	-19.4	2.257	1.2	1.892	-15.2	1.706	-23.5
Nitrobenzene	16.8	1.480	182	1.391	-6.0	1.494	0.9	1.607	8.6	1.455	-1.7
"	15.0	1.560	168	1.343	-13.9	1.443	-7.5	1.552	-0.5	1.409	-9.7
Pyridine	15.0	1.580	100	1.512	-4.3	1.718	8.7	1.744	10.4	1.481	-6.3
Carbon tetra-	15.0	1.700	182	1.447	-14.9	1.626	-4.3	1.871	10.1	1.793	5.4
" chloride	25.0	2.250	123	1.727	-23.2	1.941	-13.7	2.234	-0.7	2.114	-6.1
"	25.0	2.300	123	1.727	-24.9	1.941	-15.6	2.234	-2.9	2.114	-8.1
Chloroform	15.0	2.070	182	1.567	-24.3	1.817	-12.2	1.974	-4.7	1.843	-11.0
Ethyl bromide	15.0	2.400	182	1.640	-31.7	1.927	-19.7	2.082	-13.2	1.920	-20.0
Ethyl iodide	15.0	2.160	168	1.546	-28.4	1.813	-16.1	1.934	-10.5	1.961	-9.2
Ethylene iodide	15.0	1.950	168	1.460	-25.2	1.662	-14.8	1.720	-11.8	1.832	-6.0
Bromobenzene	15.0	1.750	100	1.356	-22.5	1.475	-15.7	1.627	-7.0	1.570	-10.3
Iodobenzene	15.0	1.650	168	1.305	-20.9	1.410	-14.5	1.557	-5.6	1.603	-2.9
p-di bromobenzene	15.0	1.550	168	1.244	-19.8	1.355	-12.6	1.451	-6.4	1.565	1.0
p-dichlorobenzene	25.0	2.350	168	1.576	-32.9	1.600	-31.9	1.850	-21.3	1.666	-29.1
Chloral hydrate	15.0	1.160	168	1.389	19.7	1.410	21.6	1.030	-11.2	1.200	3.5
Water	15.0	1.780	112	1.906	7.1	1.950	9.9	2.130	19.7	1.991	11.9

Appendix 3-2.2 (continued)

Solvent = Methanol

Solute	T, °C	D°_{AB} (exp)	Ref	This work Eq.(3-2.4)		Wilke-Chang Eq.(2-3.16)		King et al Eq.(2-3.29)		Sitara. et al Eq.(2-3.27)	
				Calc.	%Error	Calc.	%Error	Calc.	%Error	Calc.	%Error
Triphenylmethane	25.0	1.160	123	1.140	-1.7	1.026	-11.6	1.313	13.2	1.203	3.7
Erythritol	25.0	1.150	123	1.671	45.3	1.712	48.8	1.154	0.4	1.268	10.3
Salol	15.0	1.290	168	1.069	-17.1	0.992	-23.1	1.085	-15.9	1.068	-17.2
Phenetol	15.0	1.850	20	1.272	-31.3	1.283	-30.6	1.502	-18.8	1.284	-30.6
Adipic acid	30.0	1.382	4	1.683	21.8	1.536	11.2	1.440	4.2	1.381	-0.1
Anthranilic acid	30.0	1.380	108	1.680	21.7	1.685	22.1				
Bromopropionicacid	15.0	1.350	20	1.467	8.7	1.522	12.7	1.433	6.2	1.480	9.7
Chloroacetic acid	15.0	1.520	168	1.664	9.5	1.761	15.9	1.515	-0.3	1.461	-3.9
Chloroacetic acid	15.0	1.360	20	1.510	11.0	1.605	18.1	1.475	8.4	1.482	9.0
Chlorobenzoic acid	15.0	1.290	20	1.282	-0.6	1.262	-2.2				
Cinnamic acid	30.0	2.520	4	1.596	-36.7	1.573	-37.6	1.630	-35.3	1.507	-40.2
Iodopropionic acid	15.0	1.360	20	1.403	3.2	1.446	6.3	1.237	-9.0	1.424	4.7
Lactic acid	15.0	1.360	20	1.607	18.2	1.620	19.2	1.339	-1.6	1.278	-6.0
Lauric acid	30.0	1.420	108	1.336	-5.9	1.129	-20.5	1.387	-2.3	1.220	-14.1
Linoleic acid	30.0	0.848	108	1.153	35.9	0.920	8.5	1.200	41.5	1.088	28.3
Malic acid	30.0	1.712	20	1.869	9.1	1.739	1.6				
Malonic acid	30.0	1.870	108	2.067	10.6	2.053	9.8				
Myristic acid	30.0	1.070	108	1.251	16.9	1.037	-3.1	1.308	22.3	1.162	8.6
Oleic acid	30.0	0.902	20	1.129	25.2	0.910	0.9	1.211	34.3	1.089	20.7
Phthalic acid	15.0	1.300	168	1.253	-3.7	1.182	-9.1				
Tartaric acid	30.0	1.652	4	1.751	6.0	1.656	0.2				
Chloroacetic acid	30.0	1.860	4	1.859	-0.0	1.820	-2.2	1.859	-0.0	1.825	-1.9
"	15.0	1.450	20	1.429	-1.4	1.399	-3.5	1.429	-1.4	1.429	-1.5
Bromoacetic acid	15.0	1.230	20	1.305	6.1	1.355	10.1	1.366	11.1	1.613	31.1
Phenyl acetate	15.0	1.620	168	1.257	-22.4	1.284	-20.7	1.422	-12.2	1.284	-20.8
Chloroaniline	15.0	1.370	168	1.353	-1.3	1.399	2.1	1.447	5.6	1.343	-2.0
"	15.0	1.340	20	1.353	1.0	1.399	4.4	1.447	8.0	1.343	0.2
Bromoaniline	15.0	1.410	20	1.290	-8.5	1.384	-1.9	1.740	23.4	1.607	14.0
mDinitrobenzene	15.0	1.560	168	1.274	-18.3	1.312	-15.9	1.243	-20.3	1.281	-17.9
Bromonitrobenzene	15.0	1.430	20	1.233	-13.8	1.352	-5.4	1.342	-6.1	1.433	0.2
Chloronitrobenzene	15.0	1.680	20	1.269	-24.5	1.343	-20.1	1.368	-18.5	1.346	-19.9
tyldiphenylamine	25.0	0.980	20	1.227	25.2	1.152	17.6				
Dibenzylamine	15.0	0.860	168	1.116	29.7	1.089	26.6	1.228	42.8	1.122	30.4
itronaphthalene	15.0	1.320	168	1.133	-14.1	1.094	-17.1	1.418	7.4	1.324	0.3
mNitrobenzaldehyde	15.0	1.240	168	1.244	0.3	1.308	5.5	1.258	1.5	1.249	0.7
Nitrophenol	15.0	1.380	168	1.284	-7.0	1.449	5.0	1.366	-1.0	1.361	-1.4
2,4-Dinitrophenol	15.0	1.400	20	1.308	-6.5	1.274	-9.0				
2,4,6,Trinitrophenol	15.0	1.410	20	1.116	-20.9	1.164	-17.5				
Hydroquinone	15.0	1.250	20	1.411	12.9	1.546	23.7	1.270	1.6	1.274	1.9
Iodoform	15.0	1.330	168	1.265	-4.9	1.409	6.0				
DiIodomethane	15.0	1.680	168	1.413	-15.9	1.684	0.3	1.664	-1.0	2.003	19.2
Ethylene iodide	15.0	1.560	168	1.344	-13.9	1.487	-4.7	1.568	0.5	1.819	16.6
Acetanilide	15.0	1.500	168	1.236	-17.6	1.267	-15.5	1.166	-22.3	1.138	-24.2
lorobromomethane	15.0	2.500	168	1.288	-48.5	1.344	-46.3	1.492	-40.3	1.492	-40.3
Dichloronaphthalene	15.0	1.520	20	1.166	-23.3	1.122	-26.2	1.284	-15.5	1.237	-18.6
Dibromonaphthalene	15.0	1.330	168	1.122	-15.6	1.105	-16.9				
2,4,6-tribromophenol	15.0	1.120	168	1.219	8.9	1.183	5.6	1.267	13.1	1.466	30.9
2,4,6,Trichlorophenol	15.0	1.210	168	1.308	8.1	1.214	0.3	1.302	7.6	1.309	8.2
Bromophenol	15.0	1.340	168	1.339	-0.1	1.428	6.6	1.380	3.0	1.442	7.6
Chlorophenol	15.0	1.320	168	1.361	3.1	1.444	9.4	1.479	12.0	1.389	5.2
Bromopropylene	15.0	2.220	20	1.544	-30.4	1.754	-21.0	1.877	-15.5	1.760	-20.7
Iodopropylene	15.0	1.720	20	1.468	-14.6	1.647	-4.3	1.778	3.4	1.799	4.6
rathane	15.0	1.410	168	1.501	6.5	1.640	16.3	1.501	6.5	1.368	-3.0
anillin	15.0	1.000	168	1.228	22.8	1.264	26.4	1.221	22.1	1.204	20.4
Ethyl nitrate	15.0	2.200	168	1.548	-29.6	1.770	-19.6	1.767	-19.7	1.581	-28.2

Appendix 3-2.2 (continued)

Solvent = Ethanol

Solute	T, °C	D°_{AB} (exp.)	Ref	This work Eq(3-2.4)		Wilke-Chang Eq.(2-3.16)		King et al Eq.(2-3.29)		Sitara. et al Eq.(2-3.27)	
				Calc.	%Error	Calc.	%Error	Calc.	%Error	Calc.	%Error
xygen	29.6	2.640	3	2.003	-24.1	2.515	-4.7	3.608	36.7	2.378	-9.9
odine	25.0	1.320	168	1.019	-22.8	1.296	-1.8	1.108	-16.1	1.489	12.8
"	40.0	1.772	219	1.406	-20.6	1.790	1.0	1.529	-13.7	2.010	13.5
"	8.0	0.900	20	0.699	-22.4	0.889	-1.2	0.760	-15.6	1.049	16.5
enzene	25.0	1.810	3	1.760	-2.5	1.084	-40.1	1.253	-30.8	1.028	-43.2
oluene	15.0	1.600	3	1.480	-7.5	0.777	-51.5	0.944	-41.0	0.788	-50.8
thanol (self-)	7.0	0.618	43	0.818	32.4	0.939	52.0	0.803	30.0	0.700	13.3
"	15.0	0.770	43	0.992	28.9	1.139	47.9	0.974	26.5	0.838	8.8
"	25.0	1.010	43	1.225	21.3	1.407	39.3	1.203	19.1	1.019	0.9
"	35.0	1.300	43	1.518	16.8	1.743	34.1	1.490	14.6	1.244	-4.3
"	45.0	1.660	43	1.875	12.9	2.152	29.6	1.840	10.8	1.513	-8.8
"	55.0	2.060	43	2.281	10.7	2.618	27.1	2.239	8.7	1.816	-11.8
"	65.0	2.610	43	2.767	6.0	3.176	21.7	2.715	4.0	2.173	-16.7
llyl alcohol	20.0	0.980	168	1.015	3.5	1.139	16.2	1.033	5.4	0.900	-8.1
"	20.0	0.960	123	1.015	5.7	1.139	18.6	1.033	7.6	0.900	-6.2
-amyl alcohol	20.0	0.810	168	0.842	4.0	0.828	2.3	0.920	13.5	0.778	-3.9
"	20.0	0.780	219	0.842	8.0	0.828	6.2	0.920	17.9	0.778	-0.2
"	20.0	0.760	20	0.842	10.8	0.828	9.0	0.920	21.0	0.778	2.4
henol	20.0	0.800	20	0.857	7.1	0.943	17.9	0.920	15.0	0.859	7.4
lycerol	20.0	0.530	168	0.862	62.7	1.034	95.1	0.751	41.7	0.807	52.3
cetic acid	15.3	0.640	96	0.730	14.4	1.124	75.6	0.956	49.3	0.885	38.2
Cl_4	25.0	1.500	3	1.710	14.4	1.048	-30.1	1.258	-16.1	1.219	-18.7
odobenzene	20.0	1.000	168	0.778	-22.2	0.815	-18.5	0.938	-6.2	0.984	-1.6
"	20.0	0.970	3	0.778	-19.8	0.815	-16.0	0.938	-3.3	0.984	1.5
hloroform	20.0	1.250	20	0.935	-25.2	1.050	-16.0	1.189	-4.9	1.132	-9.4
iline	18.5	2.700	219	0.815	-69.8	0.877	-67.5	0.901	-66.6	0.815	-69.8
ridine	20.0	1.110	168	0.908	-18.2	0.992	-10.6	1.051	-5.3	0.910	-18.0
"	20.0	1.120	219	0.908	-19.0	0.992	-11.4	1.051	-6.2	0.910	-18.8
rbon dioxide	17.0	3.200	168	1.255	-60.8	1.615	-49.5	1.366	-57.3	1.228	-61.6
ter	18.0	1.100	182	1.100	0.0	1.080	1.5	1.231	11.9	1.176	6.9
"	25.0	1.220	45	1.280	5.0	1.260	3.4	1.432	17.4	1.354	11.0
"	25.0	1.132	168	1.280	13.1	1.260	11.3	1.432	26.5	1.354	19.7
etal	20.0	1.130	20	0.763	-32.5	0.716	-36.6	1.000	-11.5	0.808	-28.5
loral	20.0	0.614	20	0.852	38.7	0.877	42.8	1.049	70.8	1.001	63.0
iphenyl methane	25.0	0.718	3	0.636	-11.5	0.554	-22.9	0.739	3.0	0.694	-3.3
sorcinol	20.0	0.451	20	0.841	86.5	0.894	98.2	0.771	71.0	0.787	74.4
omoform	20.0	0.970	168	0.844	-13.0	0.952	-1.9	1.005	3.6	1.195	23.2
omonaphthalene	20.0	0.760	219	0.699	-8.1	0.689	-9.3	0.776	2.2	0.802	5.5
"	20.0	0.740	20	0.699	-5.6	0.689	-6.9	0.776	4.9	0.802	8.3
ea	12.0	0.540	168	0.866	60.3	1.071	98.3				
obenzene	20.0	0.740	168	0.655	-11.4	0.599	-19.0	0.703	-5.0	0.671	-9.3
etamide	20.0	0.670	20	1.020	52.2	1.220	82.1	0.927	38.4	0.889	32.6
droquinone	20.0	0.488	20	0.841	72.4	0.894	83.2	0.765	56.8	0.783	60.5
mphor	20.0	0.700	168	0.687	-1.9	0.632	-9.7	0.822	17.4	0.719	2.8
phenyl	25.0	1.160	3	1.367	17.8	0.734	-36.7	0.898	-22.6	0.811	-30.1
etoin	20.0	0.556	20	0.882	58.7	0.931	67.4	0.865	55.6	0.808	45.4
aric acid	20.0	0.590	20	0.513	-13.0	0.400	-32.2	0.560	-5.1	0.521	-11.7
igenin	20.0	0.608	20	0.791	30.1	0.801	31.8				

Appendix 3-2.2 (continued)

Solvent = Carbontetrachloride

Solute	T, °C	D°_{AB} (exp.)	Ref	This work Eq.(3-2.4)		Wilke-Chang Eq.(2-3.16)		King et al Eq.(2-3.29)		Sitara. et al Eq.(2-3.27)	
				Calc.	%Error	Calc.	%Error	Calc.	%Error	Calc.	%Error
Methane	25.0	2.890	81	2.249	-22.2	3.430	18.7	3.277	13.4	1.965	-32.0
Methanol	25.0	2.610	81	2.034	-22.1	3.192	22.3	1.547	-40.7	1.499	-42.6
CF$_4$	25.0	2.040	81	1.846	-9.5	2.665	30.7	2.423	18.8	2.283	11.9
Ethanol	25.0	1.950	81	1.734	-11.1	2.533	29.9	1.387	-28.9	1.353	-30.6
Acetone	20.0	1.860	168	1.434	-22.9	2.036	9.4	1.409	-24.2	1.300	-30.1
"	20.0	1.890	166	1.434	-24.1	2.036	7.7	1.409	-25.4	1.300	-31.2
"	25.0	1.700	81	1.568	-7.7	2.226	30.9	1.541	-9.3	1.413	-16.9
ulphurhexaflouride	25.0	1.710	81	1.358	-20.6	2.221	29.9	1.716	0.4	1.937	13.3
Benzene	25.0	1.540	81	1.401	-9.0	1.952	26.7	1.445	-6.2	1.364	-11.4
CCL$_4$ (self-)	15.0	1.092	150	1.147	5.1	1.589	45.5	1.222	11.9	1.379	26.3
"	20.0	1.180	43	1.246	5.6	1.726	46.3	1.327	12.5	1.489	26.2
"	25.0	1.320	43	1.363	3.3	1.888	43.0	1.451	10.0	1.618	22.6
"	25.0	1.410	129	1.363	-3.3	1.888	33.9	1.451	2.9	1.618	14.8
"	25.0	1.296	150	1.363	5.2	1.888	45.7	1.451	12.0	1.618	24.9
"	30.0	1.428	31	1.483	3.8	2.053	43.8	1.579	10.6	1.750	22.6
"	35.0	1.750	129	1.604	-8.3	2.221	26.9	1.708	-2.4	1.883	7.6
"	40.0	1.780	150	1.739	-2.3	2.409	35.3	1.852	4.1	2.030	14.1
"	40.0	1.683	31	1.739	3.4	2.409	43.1	1.852	10.1	2.030	20.6
"	45.0	2.000	43	1.878	-6.1	2.601	30.1	2.000	0.0	2.181	9.0
"	45.0	1.990	129	1.878	-5.6	2.601	30.7	2.000	0.5	2.181	9.6
"	50.0	2.000	43	2.023	1.2	2.802	40.1	2.155	7.7	2.337	16.8
"	50.0	1.937	31	2.023	4.5	2.802	44.7	2.155	11.2	2.337	20.6
"	60.0	2.440	43	2.330	-4.5	3.226	32.2	2.481	1.7	2.664	9.2
Phenol	25.0	1.370	81	1.354	-1.2	1.895	38.3	1.185	-13.5	1.263	-7.8
niline	25.0	1.580	81	1.324	-16.2	1.813	14.8	1.193	-24.5	1.230	-22.2
Pentane	25.0	1.570	81	1.355	-13.7	1.729	10.1	1.526	-2.8	1.276	-18.7
-Methyl butane	25.0	1.490	81	1.362	-8.6	1.730	16.1	1.568	5.2	1.296	-13.1
oluene	25.0	1.400	81	1.310	-6.4	1.727	23.4	1.345	-4.0	1.272	-9.1
yclohexane	25.0	1.270	81	1.320	3.9	1.739	36.9	1.415	11.4	1.281	0.9
enzyl alcohol	25.0	1.280	81	1.279	-0.0	1.666	30.2	1.076	-15.9	1.149	-10.2
Hexane	25.0	1.500	81	1.270	-15.3	1.559	4.0	1.402	-6.5	1.199	-20.0
"	25.0	1.470	16	1.270	-13.6	1.559	6.1	1.402	-4.6	1.199	-18.4
,2-Dimethylbutane	25.0	1.250	81	1.284	2.7	1.554	24.4	1.459	16.7	1.224	-2.1
aphthalene	25.0	1.200	81	1.178	-1.8	1.503	25.2	1.139	-5.1	1.166	-2.8
eptane	25.0	1.340	81	1.198	-10.6	1.430	6.7	1.306	-2.5	1.140	-15.0
esitylene	25.0	1.190	81	1.175	-1.3	1.422	19.5	1.165	-2.1	1.121	-5.8
ctane	25.0	1.260	81	1.140	-9.5	1.314	4.3	1.224	-2.8	1.082	-14.1
soOctane	25.0	1.130	81	1.153	2.0	1.321	16.9	1.291	14.3	1.118	-1.0
iphenyl	25.0	1.070	81	1.085	1.4	1.322	23.6	1.036	-3.2	1.076	0.6
exadecane	25.0	0.780	81	0.863	10.6	0.882	13.1	0.858	10.0	0.839	7.5
"	25.0	0.765	16	0.863	12.8	0.882	15.3	0.858	12.2	0.839	9.6
cetic acid	6.5	1.151	219	0.893	-22.4	1.748	51.9	0.952	-17.3	1.025	-11.0
"	14.8	1.267	219	1.060	-16.4	2.074	63.7	1.130	-10.8	1.201	-5.2
"	25.0	1.420	168	1.275	-10.2	2.495	75.7	1.359	-4.3	1.426	0.4
"	25.0	1.490	219	1.275	-14.5	2.495	67.4	1.359	-8.8	1.426	-4.3
"	40.0	1.780	219	1.626	-8.6	3.183	78.8	1.734	-2.6	1.789	0.5
ormic acid	8.5	1.612	219	1.171	-27.4	2.410	49.5	1.496	-7.2	1.448	-10.2
"	25.0	1.888	219	1.475	-21.9	3.036	60.8	1.885	-0.2	1.795	-4.9
"	15.0	1.673	219	1.242	-25.8	2.556	52.8	1.587	-5.2	1.530	-8.6

Appendix 3-2.2 (continued)

Solvent = Carbontetrachloride

Solute	T, °C	D°_{AB} (exp.)	Ref.	This work Eq.(3-2.4)		Wilke-Chang Eq.(2-3.16)		King et al Eq.(2-3.29)		Sitara. et al Eq.(2-3.27)	
				Calc.	%Error	Calc.	%Error	Calc.	%Error	Calc.	%Error
Tetrahydrofuran	25.0	1.470	81	1.471	0.0	2.110	43.6	1.533	4.3	1.447	-1.5
Dimethylacetamide	25.0	1.230	81	1.363	10.8	1.743	41.7	1.222	-0.7	1.194	-2.9
Hexachloroethane	25.0	1.010	81	1.162	15.0	1.355	34.2	1.158	14.7	1.310	29.7
Tetraline	25.0	1.100	81	1.143	3.9	1.428	29.8	1.129	2.6	1.134	3.1
Phenathrene	25.0	1.030	81	1.065	3.4	1.272	23.5	0.947	-8.1	1.040	1.0
Anthracene	25.0	1.030	81	1.065	3.4	1.272	23.5	0.947	-8.1	1.040	1.0
Hexachlorobenzene	25.0	0.922	81	1.024	11.1	1.249	35.5	0.944	2.3	1.170	26.9
Biphenylmethane	25.0	0.985	81	1.048	6.4	1.235	25.3	0.994	0.9	1.032	4.8
chlorocyclohexane	25.0	0.843	81	0.997	18.2	1.172	39.1	0.945	12.1	1.133	34.4
Benzoic acid	25.0	0.882	81	0.945	7.1	1.597	81.1	1.032	17.0	1.131	28.2
2-Methyl propane	25.0	0.884	81	0.937	6.0	1.061	20.0	1.084	22.6	0.987	11.6
Dodecane	25.0	0.954	81	0.972	1.9	1.043	9.4	1.019	6.8	0.946	-0.8
"	25.0	0.964	16	0.972	0.8	1.043	8.2	1.019	5.7	0.946	-1.8
Triphenylmethane	25.0	0.694	81	0.900	29.7	0.997	43.7	0.853	22.9	0.921	32.8
Hexadecanol	25.0	0.741	81	0.865	16.8	0.871	17.6	0.755	1.9	0.790	6.6
Octadecane	25.0	0.690	81	0.822	19.2	0.823	19.3	0.824	19.4	0.811	17.6
Eicosane	25.0	0.664	81	0.798	20.1	0.774	16.5	0.816	22.8	0.800	20.4
Docosane	25.0	0.620	81	0.767	23.7	0.731	17.9	0.738	19.1	0.750	20.9
Octacosane	25.0	0.528	81	0.694	31.4	0.634	20.0	0.710	34.4	0.718	35.9
Dotriacontane	25.0	0.479	81	0.656	37.0	0.585	22.2	0.726	51.6	0.718	49.9
Iodine	20.0	1.360	20	1.318	-3.1	2.136	57.1	1.169	-14.1	1.820	33.8
"	25.0	1.500	219	1.441	-3.9	2.336	55.8	1.278	-14.8	1.978	31.9
Benzene	10.0	1.084	96	1.060	-2.2	1.476	36.2	1.093	0.8	1.052	-2.9
"	25.0	1.419	96	1.401	-1.3	1.952	37.5	1.445	1.8	1.364	-3.9
"	40.0	1.775	96	1.788	0.7	2.491	40.3	1.844	3.9	1.711	-3.6
"	20.0	1.250	96	1.281	2.5	1.785	42.8	1.321	5.7	1.255	0.4
Cyclohexane	25.0	1.275	176	1.320	3.5	1.739	36.4	1.415	11.0	1.281	0.5
"	55.0	1.979	176	2.111	6.7	2.781	40.5	2.264	14.4	1.983	0.2
"	40.0	1.611	176	1.684	4.5	2.219	37.7	1.806	12.1	1.608	-0.2

Appendix 3-2.2 (continued)

Solvent = Benzene

Solute	T, ^{o}C	D°_{AB} (exp.)	Ref	This work Eq.(3-2.4)		Wilke-Chang Eq.(2-3.16)		King et al Eq.(2-3.29)		Sitara. et al Eq.(2-3.27)	
				Calc.	%Error	Calc.	%Error	Calc.	%Error	Calc.	%Error
Bromine	12.0	2.000	168	1.937	-3.2	2.335	16.8	1.874	-6.3	2.311	15.6
"	25.0	2.700	153	2.472	-8.5	2.980	10.4	2.392	-11.4	2.900	7.4
Iodine	20.0	1.950	168	1.954	0.2	2.285	17.2	1.763	-9.6	2.412	23.7
"	25.0	1.980	27	2.132	7.7	2.494	25.9	1.924	-2.8	2.616	32.1
n-Heptane	25.0	2.100	25	1.765	-16.0	1.522	-27.5	1.964	-6.5	1.504	-28.4
"	45.0	2.750	25	2.453	-10.8	2.115	-23.1	2.730	-0.7	2.042	-25.7
"	65.0	3.650	25	3.262	-10.6	2.813	-22.9	3.631	-0.5	2.662	-27.1
"	75.0	4.070	25	3.655	-10.2	3.152	-22.5	4.068	-0.0	2.959	-27.3
"	80.1	4.250	25	3.868	-9.0	3.336	-21.5	4.305	1.3	3.119	-26.6
"	85.0	4.600	25	4.020	-12.6	3.467	-24.6	4.475	-2.7	3.233	-29.7
"	25.0	1.785	176	1.765	-1.1	1.522	-14.7	1.964	10.1	1.504	-15.8
"	40.0	2.279	176	2.277	-0.1	1.963	-13.8	2.534	11.2	1.905	-16.4
"	55.0	2.795	176	2.850	2.0	2.458	-12.1	3.172	13.5	2.348	-16.0
n-Hexane	15.0	1.780	96	1.565	-12.1	1.395	-21.6	1.768	-0.7	1.345	-24.4
Cyclohexane	25.0	2.090	176	1.943	-7.0	1.857	-11.1	2.131	2.0	1.695	-18.9
"	25.0	2.101	101	1.943	-7.5	1.857	-11.6	2.131	1.4	1.695	-19.3
"	40.0	2.650	176	2.506	-5.4	2.396	-9.6	2.749	3.7	2.148	-18.9
"	60.0	3.445	176	3.356	-2.6	3.209	-6.9	3.681	6.9	2.819	-18.2
Benzene(self-)	10.0	1.650	150	1.556	-5.7	1.573	-4.7	1.642	-0.5	1.389	-15.8
"	15.0	1.870	43	1.727	-7.7	1.746	-6.7	1.822	-2.6	1.530	-18.2
"	20.0	1.910	150	1.890	-1.1	1.910	0.0	1.994	4.4	1.664	-12.9
"	25.0	2.140	129	2.062	-3.6	2.085	-2.6	2.176	1.7	1.805	-15.7
"	25.0	2.220	43	2.062	-7.1	2.085	-6.1	2.176	-2.0	1.805	-18.7
"	35.0	2.590	43	2.448	-5.5	2.475	-4.4	2.583	-0.3	2.117	-18.3
"	40.0	2.580	150	2.660	3.1	2.689	4.2	2.807	8.8	2.287	-11.4
"	45.0	3.040	43	2.866	-5.7	2.897	-4.7	3.024	-0.5	2.451	-19.4
"	55.0	3.500	43	3.330	-4.9	3.366	-3.8	3.514	0.4	2.818	-19.5
"	60.0	3.400	150	3.563	4.8	3.602	5.9	3.759	10.6	3.001	-11.7
"	65.0	4.030	43	3.812	-5.4	3.853	-4.4	4.022	-0.2	3.195	-20.7
"	80.0	4.370	150	4.518	3.4	4.567	4.5	4.767	9.1	3.743	-14.4
Toluene	25.0	1.847	176	1.928	4.4	1.845	-0.1	2.025	9.6	1.683	-8.9
"	40.0	2.385	176	2.487	4.3	2.379	-0.2	2.612	9.5	2.132	-10.6
Naphthalene	7.5	1.190	168	1.229	3.3	1.147	-3.6	1.220	2.5	1.127	-5.3
Methanol	11.0	2.875	96	2.296	-20.1	2.615	-9.1	1.786	-37.9	1.550	-46.1
"	15.0	2.500	96	2.507	0.3	2.855	14.2	1.951	-22.0	1.682	-32.7
"	25.0	3.820	168	2.995	-21.6	3.410	-10.7	2.330	-39.0	1.984	-48.1
"	40.0	4.670	6	3.863	-17.3	4.398	-5.8	3.005	-35.6	2.514	-46.2
Ethanol	15.0	2.400	96	2.138	-10.9	2.265	-5.6	1.749	-27.1	1.517	-36.8
"	25.2	3.020	6	2.559	-15.3	2.712	-10.2	2.094	-30.7	1.793	-40.6
"	25.0	3.300	96	2.553	-22.6	2.706	-18.0	2.089	-36.7	1.790	-45.8
"	40.0	3.740	6	3.293	-11.9	3.490	-6.7	2.695	-28.0	2.268	-39.4
n-Propanol	15.0	1.600	168	1.925	20.3	1.928	20.5	1.618	1.1	1.415	-11.5
i-Propanol	15.0	1.800	100	1.934	7.4	1.918	6.5	1.626	-9.7	1.415	-21.4
i-Amyl alcohol	15.0	1.480	168	1.630	10.1	1.487	0.5	1.492	0.8	1.282	-13.4
Phenol	5.0	1.270	100	1.336	5.2	1.357	6.9	1.196	-5.8	1.152	-9.3
"	25.0	1.680	153	1.992	18.6	2.024	20.5	1.784	6.2	1.671	-0.5
Ethyl ether	15.0	2.210	168	1.731	-21.7	1.650	-25.3	1.916	-13.3	1.498	-32.2
"	25.0	2.730	153	2.067	-24.3	1.971	-27.8	2.289	-16.2	1.767	-35.3
Acetone	40.0	3.250	55	2.978	-8.4	3.067	-5.6	2.994	-7.9	2.368	-27.1
"	54.5	3.740	55	3.686	-1.4	3.797	1.5	3.706	-0.9	2.888	-22.8
Methylethylketone	30.0	2.086	4	2.289	9.8	2.250	7.8	2.314	10.9	1.876	-10.1
Benzaldehyde	15.0	1.730	168	1.574	-9.0	1.546	-10.7	1.576	-8.9	1.426	-17.6

Appendix 3-2.2 (continued)

Solvent = Benzene

Solute	T, °C	D°_{AB} (exp.)	Ref	This work Eq.(3-2.4)		Wilke-Chang Eq.(2-3.16)		King et al Eq.(2-3.29)		Sitara. et al Eq.(2-3.27)	
				Calc.	%Error	Calc.	%Error	Calc.	%Error	Calc.	%Error
Salicylaldehyde	15.0	1.780	168	1.523	-14.4	1.490	-16.3	1.565	-12.1	1.443	-18.9
Acetic acid	5.9	1.580	27	1.296	-17.9	1.841	16.5	1.414	-10.5	1.338	-15.3
"	15.0	1.920	168	1.571	-18.2	2.231	16.2	1.713	-10.8	1.600	-16.7
"	25.0	2.090	168	1.626	-22.2	2.309	10.5	1.773	-15.2	1.651	-21.0
"	25.0	2.110	27	1.626	-22.9	2.309	9.4	1.773	-16.0	1.651	-21.7
Formic acid	6.2	1.990	27	1.506	-24.3	2.248	13.0	1.968	-1.1	1.690	-15.1
"	13.9	2.310	27	1.771	-23.3	2.645	14.5	2.315	0.2	1.965	-14.9
Nitrobenzene	15.0	1.840	168	1.548	-15.8	1.536	-16.5	1.528	-16.9	1.455	-20.9
Bromobenzene	7.5	1.480	168	1.335	-9.8	1.299	-12.3	1.349	-8.8	1.363	-7.9
"	15.0	1.860	168	1.575	-15.3	1.532	-17.7	1.591	-14.5	1.590	-14.5
"	25.0	2.300	153	1.880	-18.2	1.829	-20.5	1.900	-17.4	1.875	-18.5
"	7.3	1.410	219	1.333	-5.4	1.297	-8.0	1.347	-4.4	1.362	-3.4
Chlorobenzene	15.0	1.420	168	1.616	13.8	1.571	10.7	1.653	16.4	1.503	5.9
"	25.0	2.660	153	1.930	-27.4	1.877	-29.5	1.974	-25.8	1.773	-33.3
p-Dibromobenzene	15.0	1.370	20	1.444	5.4	1.407	2.7	1.419	3.6	1.585	15.7
p-Dichlorobenzene	15.0	1.900	20	1.537	-19.1	1.392	-26.8	1.516	-20.2	1.431	-24.7
,3Trichlorobenzene	7.5	1.340	20	1.227	-8.5	1.155	-13.8	1.206	-10.0	1.240	-7.5
Iodobenzene	7.3	1.350	20	1.284	-4.9	1.237	-8.4	1.288	-4.6	1.387	2.8
CCL$_4$	7.3	1.120	219	1.423	27.0	1.430	27.7	1.550	38.4	1.555	38.9
"	20.0	1.760	168	1.839	4.5	1.848	5.0	2.003	13.8	1.974	12.2
"	25.0	1.920	90	2.006	4.5	2.017	5.0	2.186	13.8	2.141	11.5
"	25.0	2.000	168	2.006	0.3	2.017	0.8	2.186	9.3	2.141	7.1
Chloroform	15.0	2.110	168	1.819	-13.8	1.886	-10.6	1.930	-8.5	1.866	-11.6
"	25.0	2.500	153	2.173	-13.1	2.253	-9.9	2.305	-7.8	2.201	-11.9
Ethylene bromide	15.0	1.970	168	1.700	-13.7	1.725	-12.4	1.682	-14.6	1.856	-5.8
Methyl iodide	7.5	2.060	168	1.679	-18.5	1.913	-7.1	1.763	-14.4	1.957	-5.0
,4Trichlorobenzene	7.6	1.340	168	1.173	-12.4	1.016	-24.2	1.110	-17.2	1.116	-16.7
Bromophenol	15.0	1.340	168	1.536	14.6	1.483	10.6	1.350	0.7	1.460	9.0
Chlorophenol	15.0	1.420	168	1.580	11.3	1.500	5.6	1.446	1.8	1.406	-1.0
Quinone	15.0	1.680	168	1.612	-4.1	1.675	-0.3				
Methylsalicylate	15.0	1.560	168	1.441	-7.7	1.287	-17.5	1.265	-18.9	1.245	-20.2
Benzoic acid	15.0	1.170	27	1.164	0.6	1.428	22.1	1.302	11.2	1.269	8.4
"	15.0	1.360	168	1.164	-14.4	1.428	5.0	1.302	-4.3	1.269	-6.7
"	25.0	1.380	168	1.391	0.8	1.706	23.6	1.554	12.6	1.496	8.4
"	40.0	1.760	27	1.772	0.7	2.174	23.5	1.981	12.6	1.875	6.5
Cinnamic acid	25.0	1.210	27	1.265	4.5	1.477	22.1	1.458	20.5	1.394	15.2
"	25.0	1.120	168	1.265	12.9	1.477	31.9	1.458	30.2	1.394	24.4
hloracetic acid	15.0	1.480	168	1.431	- 3.3	1.829	23.6	1.482	0.1	1.480	-0.0
hthalic acid	15.0	1.370	168	0.994	-27.5	1.227	-10.4				
-Dinitrobenzene	15.0	1.540	168	1.479	-4.0	1.363	-11.5	1.216	-21.1	1.297	-15.8
hloronitrobenzene	15.0	1.700	20	1.473	-13.4	1.395	-18.0	1.338	-21.3	1.363	-19.8
romonitrobenzene	15.0	1.330	20	1.432	7.6	1.404	5.6	1.313	-1.3	1.451	9.1
-Nitronaphthalene	15.0	1.390	168	1.357	-2.4	1.238	-10.9	1.220	-12.2	1.236	-11.1
initronaphthalene	15.0	1.230	168	1.316	7.0	1.136	-7.6				
etyldiphenylamine	15.0	0.900	168	1.193	32.5	1.003	11.4				

Appendix 3-2.2 (continued)

Solvent = Benzene

Solute	T, °C	D°_{AB} (exp.)	Ref	This work Eq.(3-2.4)		Wilke-Chang Eq.(2-3.16)		King et al Eq.(2-3.29)		Sitara. et al Eq.(2-3.27)	
				Calc.	% Error	Calc.	% Error	Calc.	% Error	Calc.	% Error
Ethylene chloride	7.5	1.770	168	1.543	-12.8	1.508	-14.8	1.595	-9.9	1.444	-18.4
Bromoaniline	15.0	1.410	168	1.498	6.3	1.437	1.9	1.702	20.7	1.627	15.4
Chloroaniline	15.0	1.560	168	1.541	-1.2	1.452	-6.9	1.415	-9.3	1.360	-12.8
Trinitrotoluene	15.0	1.390	168	1.292	-7.0	1.115	-19.8	1.087	-21.8	1.170	-15.8
Tetrachlorobenzene	7.6	1.240	20	1.176	-5.2	1.021	-17.7	1.110	-10.5	1.151	-7.2
Iodoform	15.0	1.380	168	1.468	6.4	1.463	6.0				
α-Bromonaphthalene	7.3	1.040	219	1.153	10.9	1.050	1.0	1.068	2.7	1.134	9.0
"	15.0	1.300	168	1.360	4.6	1.239	-4.7	1.260	-3.1	1.322	1.7
Dibromonaphthalene	15.0	1.250	168	1.303	4.2	1.147	-8.2				
Chloronaphthalene	15.0	1.200	168	1.388	15.7	1.249	4.1	1.325	10.4	1.277	6.4
iChloronaphthalene	15.0	1.400	168	1.354	-3.3	1.165	-16.8	1.256	-10.3	1.252	-10.5
Ethylene iodide	15.0	1.400	168	1.560	11.4	1.544	10.3	1.533	9.5	1.842	31.6
3Trichloropropane	15.0	1.720	168	1.588	-7.7	1.416	-17.6	1.542	-10.3	1.462	-15.0

Avg. % error 10.1 12.2 10.8 17.8

Total number of systems = 59,(53); Total number of data points = 110, (108).

Appendix 3-2.2 (continued)

Solvent = n-Hexane

Solute	T, °C	D°_{AB} (exp.)	Ref	This work Eq.(3-2.4)		Wilke-Chang Eq.(2-3.16)		King et al Eq.(2-3.29)		Sitara. et al Eq.(2-3.27)	
				Calc.	%Error	Calc.	%Error	Calc.	%Error	Calc.	%Error
soOctane	25.0	3.380	81	3.612	6.9	3.042	-10.0	4.115	21.8	2.875	-14.9
thane	25.0	5.790	81	5.832	0.7	6.292	8.7	7.310	26.2	4.284	-26.0
ctone	25.0	5.260	81	4.913	-6.6	5.128	-2.5	4.912	-6.6	3.632	-31.0
enzene	15.0	3.700	219	3.697	-0.1	3.787	2.3	3.878	4.8	2.990	-19.2
"	25.0	4.640	81	4.389	-5.4	4.496	-3.1	4.605	-0.8	3.507	-24.4
Cl_4	25.0	3.860	81	4.270	10.6	4.349	12.7	4.625	19.8	4.161	7.8
"	25.0	3.700	168	4.270	15.4	4.349	17.5	4.625	25.0	4.161	12.5
entane	25.0	4.590	81	4.244	-7.5	3.983	-13.2	4.864	6.0	3.281	-28.5
-Methylbutane	25.0	4.400	81	4.265	-3.1	3.985	-9.4	4.995	13.5	3.331	-24.3
yclohexane	25.0	3.770	81	4.134	9.7	4.005	6.2	4.509	19.6	3.295	-12.6
-Hexane (self-)	0.0	3.000	150	2.810	-6.3	2.537	-15.4	3.155	5.2	2.232	-25.6
"	25.0	4.120	150	3.978	-3.4	3.592	-12.8	4.467	8.4	3.084	-25.1
"	25.0	4.210	43	3.978	-5.5	3.592	-14.7	4.467	6.1	3.084	-26.7
"	20.0	3.850	150	3.613	-6.2	3.262	-15.3	4.057	5.4	2.819	-26.8
"	40.0	4.820	150	4.684	-2.8	4.230	-12.3	5.260	9.1	3.590	-25.5
"	40.0	4.860	150	4.684	-3.6	4.230	-13.0	5.260	8.2	3.590	-26.1
"	60.0	6.000	150	5.908	-1.5	5.334	-11.1	6.634	10.6	4.454	-25.8
"	80.0	7.300	150	6.955	-4.7	6.280	-14.0	7.809	7.0	5.184	-29.0
2dimethylbutane	25.0	3.630	81	4.023	10.8	3.581	-1.4	4.650	28.1	3.147	-13.3
eptane	25.0	3.780	81	3.756	-0.6	3.282	-13.2	4.157	10.0	2.922	-22.7
ctane	25.0	3.470	81	3.572	3.0	3.027	-12.8	3.901	12.4	2.782	-19.8
ecane	25.0	3.020	81	3.269	8.2	2.674	-11.5	3.527	16.8	2.589	-14.3
odecane	25.0	2.740	81	3.044	11.1	2.404	-12.3	3.247	18.5	2.433	-11.2
exadecane	25.0	2.210	81	2.703	22.3	2.030	-8.1	2.734	23.7	2.155	-2.5
romobenzene	7.3	2.600	166	3.088	18.8	3.044	17.1	3.103	19.3	2.863	10.1
odine	25.0	4.050	219	4.515	11.5	5.382	32.9	4.072	0.5	5.086	25.6
"	25.0	4.240	219	4.515	6.5	5.382	26.9	4.072	-4.0	5.086	20.0
oluene	25.0	4.210	219	4.103	-2.5	3.979	-5.5	4.285	1.8	3.270	-22.3
ethylethylketone	30.0	3.740	108	4.823	29.0	4.802	28.4	4.846	29.6	3.612	-3.4
etraline	25.0	3.270	81	3.568	9.1	3.290	0.6	3.597	10.0	2.916	-10.8
henanthrene	25.0	3.080	81	3.335	8.3	2.930	-4.9	3.017	-2.0	2.674	-13.2
-Methyl propene@	25.0	2.680	81	2.935	9.5	2.447	-8.7	3.456	28.9	2.539	-5.3
tadecane	25.0	2.010	81	2.576	28.1	1.896	-5.7	2.625	30.6	2.086	3.8
-Hexylbromide	7.6	2.310	219	2.936	27.1	2.527	9.4	2.882	24.8	2.482	7.4
thane	25.0	8.640	81	7.044	-18.5	7.901	-8.5	10.444	20.9	5.052	-41.5
	Avg. % error				9.3		11.5		13.9		18.8

Total number of systems = 25; Total number of data points = 35

@ 2-Methyl propene in 'trimeric' form

Appendix 3-2.2 (continued)

Solvent = Toluene

Solute	T, °C	D°_{AB} (exp.)	Ref	This work Eq.(3-2.4)		Wilke-Chang Eq.(2-3.16)		King et al Eq.(2-3.29)		Sitara. et al Eq.(2-3.27)	
				Calc.	%Error	Calc.	%Error	Calc.	%Error	Calc.	%Error
Acetic acid	15.0	1.905	219	1.817	-4.6	2.712	42.3	2.061	8.2	1.866	-2.1
"	6.8	1.661	219	1.571	-5.4	2.344	41.1	1.781	7.2	1.629	-1.9
"	20.0	2.000	168	1.965	-1.7	2.933	46.7	2.229	11.4	2.007	0.4
"	25.0	2.265	219	2.126	-6.1	3.173	40.1	2.411	6.5	2.159	-4.7
Formic acid	6.2	2.285	219	1.802	-21.1	2.827	23.7	2.448	7.1	2.033	-11.0
"	14.1	2.463	219	2.071	-15.9	3.248	31.9	2.813	14.2	2.314	-6.1
"	25.0	2.646	219	2.462	-6.9	3.862	45.9	3.344	26.4	2.718	2.7
CCl_4	25.0	2.190	219	2.274	3.8	2.401	9.6	2.575	17.6	2.450	11.9
Methyl iodide	7.4	2.230	219	2.010	-9.8	2.407	7.9	2.194	-1.6	2.357	5.7
Chlorobenzene	20.0	2.060	168	2.022	-1.8	2.065	0.3	2.150	4.4	1.886	-8.4
"	25.0	2.210	4	2.188	-1.0	2.234	1.1	2.326	5.3	2.029	-8.2
Diethylamine	20.0	2.360	168	2.262	-4.2	2.269	-3.9	2.536	7.5	1.914	-18.9
Acetone	20.0	2.930	168	2.419	-17.4	2.617	-10.7	2.528	-13.7	1.988	-32.2
Ethanol	15.0	3.000	168	2.473	-17.6	2.753	-8.2	2.103	-29.9	1.769	-41.0
Methylethylketone	30.0	2.210	4	2.577	16.6	2.660	20.4	2.706	22.5	2.133	-3.5
Bromobenzene	7.0	1.590	20	1.583	-0.5	1.617	1.7	1.662	4.5	1.626	2.3
"	25.0	2.270	20	2.131	-6.1	2.178	-4.1	2.239	-1.4	2.145	-5.5
Iodine	8.7	1.660	219	1.853	11.6	2.287	37.8	1.746	5.2	2.348	41.4
"	19.9	1.959	219	2.212	12.9	2.730	39.3	2.084	6.4	2.768	41.3
"	20.0	1.950	20	2.224	14.0	2.745	40.8	2.095	7.4	2.782	42.7
"	25.0	2.160	219	2.406	11.4	2.969	37.5	2.266	4.9	2.993	38.6
"	25.0	2.130	186	2.406	12.9	2.969	39.4	2.266	6.4	2.993	40.5
Benzene	25.0	2.545	176	2.338	-8.1	2.482	-2.5	2.563	0.7	2.065	-18.9
"	40.0	3.240	176	2.910	-10.2	3.090	-4.6	3.191	-1.5	2.532	-21.9
Cyclohexane	25.0	2.420	176	2.202	-9.0	2.211	-8.6	2.510	3.7	1.940	-19.8
"	40.0	3.060	176	2.742	-10.4	2.753	-10.0	3.125	2.1	2.378	-22.3
"	55.0	3.800	176	3.341	-12.1	3.355	-11.7	3.809	0.2	2.858	-24.8
Methylcyclohexane	25.0	2.210	75	2.071	-6.3	1.982	-10.3	2.372	7.3	1.833	-17.0
"	45.0	3.090	75	2.763	-10.6	2.644	-14.4	3.164	2.4	2.396	-22.4
"	60.0	3.660	75	3.358	-8.2	3.214	-12.2	3.846	5.1	2.874	-21.5
niline	25.0	2.100	75	2.210	5.2	2.306	9.8	2.116	0.8	1.862	-11.4
"	45.0	2.780	75	2.947	6.0	3.076	10.6	2.822	1.5	2.434	-12.5
"	60.0	3.600	75	3.583	-0.5	3.739	3.9	3.431	-4.7	2.918	-18.9
-Propanol	25.0	3.560	180	2.606	-26.8	2.741	-23.0	2.256	-36.6	1.901	-46.6
ethanol	25.0	3.620	179	3.394	-6.2	4.060	12.2	2.745	-24.2	2.270	-37.3
oluene (self-)	10.0	2.080	150	1.709	-17.8	1.718	-17.4	1.865	-10.3	1.532	-26.4
"	20.0	2.320	150	2.020	-12.9	2.031	-12.5	2.205	-4.9	1.790	-22.8
"	40.0	2.950	150	2.721	-7.8	2.735	-7.3	2.970	0.7	2.361	-20.0
"	60.0	3.660	150	3.544	-3.2	3.562	-2.7	3.868	5.7	3.019	-17.5
"	80.0	4.560	150	4.534	-0.6	4.558	-0.1	4.949	8.5	3.796	-16.8
"	100.0	5.600	150	5.614	0.2	5.642	0.8	6.127	9.4	4.630	-17.3
"	110.0	6.250	150	6.179	-1.1	6.211	-0.6	6.744	7.9	5.062	-19.0
enzoic acid	16.0	1.289	219	1.367	6.1	1.762	36.7	1.588	23.2	1.500	16.4
"	20.0	1.740	168	1.457	-16.3	1.878	7.9	1.693	-2.7	1.592	-8.5
"	25.0	1.493	219	1.576	5.6	2.031	36.1	1.831	22.7	1.712	14.7
"	40.0	1.851	219	1.963	6.0	2.529	36.6	2.280	23.2	2.099	13.4
innamic acid	25.0	1.180	219	1.478	21.0	1.785	51.3	1.725	46.2	1.613	36.7
enzotrichloride	7.6	1.320	219	1.489	12.8	1.388	5.1	1.483	12.3	1.441	9.2
Bromonaphthalene	7.5	1.240	219	1.381	11.4	1.322	6.6	1.330	7.3	1.366	10.1
Bromotoluene	7.4	1.520	219	1.510	-0.7	1.480	-2.6	1.570	3.3	1.523	0.2
Avg. % error					8.9		17.1		10.0		17.5

Total number of systems = 23; Total number of data points = 50

Appendix 3-2.2 (continued)

Solute	T, °C	D°_{AB} (exp.)	Ref	This work Eq.(3-2.4)		Wilke-Chang Eq.(2-3.16)		King et al Eq.(2-3.29)		Sitara. et al Eq.(2-3.27)	
				Calc.	%Error	Calc.	%Error	Calc.	%Error	Calc.	%Error
Solvent = Acetone											
cetic acid	15.0	2.916	219	2.977	2.1	3.939	35.1	3.289	12.8	2.924	0.3
"	25.0	3.309	219	3.390	2.4	4.491	35.7	3.750	13.3	3.304	-0.2
"	40.0	4.044	219	4.045	0.1	5.350	32.3	4.467	10.5	3.888	-3.9
ormic acid	6.5	3.132	219	3.074	-1.9	4.275	36.5	4.068	29.9	3.309	5.6
"	25.0	3.768	168	3.924	4.1	5.467	45.1	5.202	38.0	4.159	10.4
thyl benzoate	20.0	2.470	219	2.821	14.2	2.302	-6.8	2.945	19.2	2.504	1.4
itrobenzene	20.0	2.940	219	3.135	6.6	2.895	-1.5	3.131	6.5	2.826	-3.9
enzene	40.0	4.560	55	4.449	-2.4	4.186	-8.2	4.750	4.2	3.718	-18.5
"	54.5	5.070	55	5.116	0.9	4.813	-5.1	5.461	7.7	4.233	-16.5
hloroform	25.2	3.630	6	3.983	9.7	3.843	5.9	4.274	17.7	3.897	7.3
cetone (self-)	25.0	4.500	106	4.181	-7.1	4.008	-10.9	4.253	-5.5	3.272	-27.3
"	25.0	4.835	43	4.181	-13.5	4.008	-17.1	4.253	-12.0	3.272	-32.3
enzoic acid	25.0	2.662	168	2.519	-5.4	2.875	8.0	2.848	7.0	2.620	-1.6
"	13.2	2.368	219	2.157	-8.9	2.462	4.0	2.439	3.0	2.268	-4.2
"	40.0	3.054	219	3.000	-1.8	3.425	12.2	3.393	11.1	3.083	0.9
romoform	20.0	2.740	219	3.327	21.4	3.230	17.9	3.342	22.0	3.833	39.9
"	25.0	3.240	163	3.553	9.7	3.450	6.5	3.570	10.2	4.076	25.8
nnamic acid	25.0	2.410	219	2.282	-5.3	2.527	4.8	2.682	11.3	2.468	2.4
ter	25.0	4.560	145	4.766	4.7	4.720	3.6	4.746	4.1	4.657	2.1
	Avg. % error				6.4		11.9		12.9		10.8
tal number of system = 11 ; Total number of data point = 19											
Solvent = n-Octane											
thylcyclohexane	25.0	2.302	169	2.386	3.6	2.388	3.7	2.819	22.5	2.062	-10.4
dine	15.0	2.430	219	2.351	-3.2	3.035	24.9	2.286	-5.9	2.890	18.9
"	25.0	2.760	219	2.771	0.4	3.577	29.6	2.694	-2.4	3.367	22.0
"	40.0	3.220	219	3.393	5.4	4.380	36.0	3.299	2.4	4.065	26.2
Octane (self-)	0.0	1.470	150	1.438	-2.2	1.321	-10.2	1.693	15.2	1.245	-15.3
"	0.0	1.560	150	1.438	-7.8	1.321	-15.3	1.693	8.5	1.245	-20.2
"	20.0	1.950	150	2.010	3.1	1.846	-5.3	2.367	21.4	1.700	-12.8
"	20.0	2.100	150	2.010	-4.3	1.846	-12.1	2.367	12.7	1.700	-19.1
"	25.0	2.368	208	2.193	-7.4	2.015	-14.9	2.583	9.1	1.843	-22.2
"	25.0	2.250	43	2.193	-2.5	2.015	-10.5	2.583	14.8	1.843	-18.1
"	25.0	2.000	41	2.193	9.7	2.015	0.7	2.583	29.1	1.843	-7.8
"	25.0	2.348	208	2.193	-6.6	2.015	-14.2	2.583	10.0	1.843	-21.5
"	40.0	2.550	150	2.684	5.3	2.465	-3.3	3.161	24.0	2.224	-12.8
"	40.0	2.730	150	2.684	-1.7	2.465	-9.7	3.161	15.8	2.224	-18.5
"	60.0	3.300	150	3.478	5.4	3.194	-3.2	4.095	24.1	2.830	-14.2
"	60.0	3.535	208	3.478	-1.6	3.194	-9.6	4.095	15.8	2.830	-19.9
"	60.0	3.410	150	3.478	2.0	3.194	-6.3	4.095	20.1	2.830	-17.0
"	60.0	3.570	208	3.478	-2.6	3.194	-10.5	4.095	14.7	2.830	-20.7
"	70.0	3.800	150	3.934	3.5	3.613	-4.9	4.632	21.9	3.174	-16.5
"	80.0	4.150	150	4.474	7.8	4.109	-1.0	5.268	26.9	3.577	-13.8
"	100.0	5.200	150	5.468	5.2	5.023	-3.4	6.440	23.8	4.311	-17.1
ctyl bromide	7.5	1.460	219	1.550	6.2	1.409	-3.5	1.662	13.9	1.438	-1.5
xadecane	25.0	1.719	39	1.660	-3.5	1.352	-21.3	1.811	5.3	1.429	-16.9
"	60.0	2.724	39	2.631	-3.4	2.144	-21.3	2.871	5.4	2.194	-19.4
	Avg. % error				4.4		11.5		15.2		16.8
	Total number of systems = 5 ; Total number of data points = 24										

Appendix 3-2.2 (continued)

Solute	T, °C	D°_{AB} (exp.)	Ref	This work Eq.(3-2.4)		Wilke-Chang Eq.(2-3.16)		King et al Eq.(2-3.29)		Sitara. et a Eq.(2-3.27)	
				Calc.	%Error	Calc.	%Error	Calc.	%Error	Calc.	%Erro
Solvent	= n-Propanol										
n-Propanol	25.0	0.646	96	0.659	2.0	0.769	19.0	0.676	4.7	0.592	-8.4
Methylethylketone	30.0	0.552	4	0.693	25.5	0.793	43.6	0.855	54.9	0.700	26.8
Water	15.0	0.610	96	0.568	-6.9	0.603	-1.2	0.647	6.1	0.640	5.0
Triphenylmethane	25.0	0.394	123	0.380	-3.6	0.356	-9.7	0.450	14.1	0.432	9.7
Benzene	25.0	1.280	123	1.220	-4.7	0.696	-45.6	0.762	-40.5	0.640	-50.0
Toluene	25.0	1.350	123	1.140	-15.0	0.616	-54.4	0.709	-47.5	0.597	-55.8
Biphenyl	25.0	0.727	123	0.940	29.0	0.472	-35.1	0.546	-24.9	0.505	-30.5
p-Dichlorobenzene	25.0	1.050	123	1.080	3.0	0.555	-47.2	0.634	-39.7	0.599	-43.0
n-Propanol	15.0	0.504	43	0.490	-2.8	0.571	13.4	0.503	-0.2	0.449	-10.8
Methanol	30.0	0.804	181	0.983	22.3	1.304	62.2	0.934	16.2	0.798	-0.7
Isobutanol	30.0	0.584	181	0.695	19.1	0.764	30.8	0.722	23.7	0.627	7.4
	Avg. % error				12.2		32.9		24.8		22.6
	Total number of systems = 10 ; Total number of data points = 11										
Solvent	= iso-Propanol										
Trichloroacetic	30.0	0.574	108	0.468	-18.5	0.648	12.9	0.650	13.3	0.669	16.6
Oleic acid	30.0	0.297	108	0.284	-4.2	0.324	9.0	0.423	42.6	0.399	34.4
Tartaric acid	30.0	0.440	108	0.441	0.3	0.589	33.9	0.672	52.8	0.628	42.6
Adipic acid	30.0	0.417	108	0.424	1.6	0.547	31.0	0.503	20.7	0.506	21.3
Cinnamic acid	30.0	0.410	108	0.402	-1.9	0.559	36.4	0.570	39.0	0.552	34.7
	Avg. % error				5.3		24.6		36.7		29.9
	Total number of systems = 5 ; Total number of data points = 5										
Solvent =	Aniline										
Toluene	25.0	0.478	75	0.325	-32.0	0.327	-31.5	0.399	-16.6	0.355	-25.7
"	45.0	0.880	75	0.627	-28.7	0.632	-28.2	0.770	-12.5	0.655	-25.6
"	60.0	1.270	75	0.892	-29.8	0.899	-29.2	1.095	-13.8	0.908	-28.5
Methylcyclohexane	60.0	0.865	75	0.845	-2.3	0.811	-6.2	1.088	25.8	0.865	-0.1
Benzene	25.0	0.540	162	0.347	-35.7	0.370	-31.5	0.428	-20.7	0.381	-29.5
Cl$_4$	25.0	0.520	162	0.338	-35.0	0.358	-31.2	0.430	-17.2	0.452	-13.1
ater	20.0	0.700	168	0.498	-28.8	0.821	17.3	0.406	-42.0	0.421	-39.8
	Avg. % error				27.5		25.0		21.2		23.2
	Total number of systems = 5; Total number of data points = 7										

Appendix 3-2.2 (continued)

Solute	T, °C	D°_{AB} (exp.)	Ref	This work Eq.(3-2.4)		Wilke-Chang Eq.(2-3.16)		King et al Eq.(2-3.29)		Sitara. et a Eq.(2-3.27)	
				Calc.	%Error	Calc.	%Error	Calc.	%Error	Calc.	%Error
Solvent = n-Butanol											
Butyric acid	30.0	0.512	4	0.543	6.1	0.628	22.7	0.563	9.9	0.515	0.7
ethylethylketone	30.0	0.580	4	0.548	-5.5	0.668	15.1	0.695	19.8	0.569	-1.9
Benzene	25.0	0.988	123	1.074	8.7	0.608	-38.4	0.642	-35.0	0.539	-45.4
Biphenyl	25.0	0.627	123	0.832	32.0	0.412	-34.3	0.461	-26.5	0.425	-32.2
-Dichlorobenzene	25.0	0.817	123	0.956	17.0	0.485	-40.7	0.821	0.5	0.641	-21.6
-Butanol(self-)	25.0	0.504	152	0.498	-1.1	0.583	15.6	0.532	5.6	0.466	-7.6
"	35.0	0.649	152	0.635	-2.1	0.743	14.4	0.678	4.5	0.583	-10.1
"	45.0	0.822	152	0.830	1.0	0.971	18.1	0.886	7.8	0.748	-9.0
Adipic acid	30.0	0.399	4	0.466	16.8	0.472	18.2	0.422	5.6	0.423	6.0
Cinnamic acid	30.0	0.446	4	0.442	-1.0	0.483	8.2	0.477	6.9	0.462	3.5
alic acid	30.0	0.446	4	0.518	16.0	0.534	19.7	-			-
leic acid	30.0	0.251	4	0.313	24.4	0.279	11.2	0.355	41.1	0.334	32.7
artaric acid	30.0	0.405	4	0.459	13.4	0.508	25.5	-		-	
	Avg. % error				11.2		21.7		14.8		15.5
	Total number of systems = 11,(9); Total number of data points = 13,(11)										
Solvent = Iso-Butanol											
ethylethylketone	30.0	0.596	4	0.429	-28.1	0.523	-12.3	0.544	-8.7	0.454	-23.9
cetone	20.0	0.740	113	0.333	-55.0	0.426	-42.5	0.421	-43.2	0.355	-52.1
cetic acid	20.0	0.340	113	0.365	7.5	0.477	40.4	0.371	9.1	0.358	5.3
"	20.0	0.300	166	0.365	21.8	0.477	59.1	0.371	23.6	0.358	19.3
imethylamine	20.0	0.340	113	0.293	-13.9	0.347	2.1	0.397	16.7	0.322	-5.2
ater	20.0	0.360	113	0.381	5.8	0.435	20.8	0.451	25.3	0.451	25.3
-Propanol	30.0	0.398	181	0.467	17.4	0.581	45.9	0.493	23.9	0.436	9.4
ethanol	30.0	0.587	181	0.608	3.6	0.860	46.5	0.595	1.3	0.518	-11.8
	Avg. % error				19.1		33.7		19.0		19.0
	Total number of systems = 7; Total number of data points = 8										
Solvent = Ethyl acetate											
thyl benzoate	20.0	1.850	219	2.161	16.8	2.023	9.4	2.337	26.3	2.018	9.1
itrobenzene	20.0	2.250	219	2.402	6.7	2.545	13.1	2.485	10.4	2.277	1.2
cetone	20.0	3.180	113	2.998	-5.7	3.298	3.7	3.160	-0.6	2.480	-22.0
cetic acid	20.0	2.180	113	2.430	11.8	3.696	69.5	2.786	27.8	2.504	14.9
ater	20.0	3.200	113	3.430	7.3	3.360	5.2	3.387	5.9	3.157	-1.4
"	30.0	3.600	145	3.970	10.3	3.890	8.1	3.917	8.8	3.613	0.4
ethylethylketone	30.0	2.932	4	3.168	8.1	3.325	13.4	3.356	14.5	2.641	-9.9
odine	20.0	2.150	20	2.756	28.2	3.458	60.9	2.619	21.8	3.471	61.5
loroform	25.0	2.530	163	3.070	21.4	3.400	34.4	3.414	34.9	3.159	24.9
	Avg. % error				12.9		24.2		16.4		16.4
	Total number of systems = 8; Total number of data points = 9										

Appendix 3-2.2 (continued)

Solute	T, °C	D°_{AB} (exp.)	Ref	This work Eq.(3-2.4)		Wilke-Chang Eq.(2-3.16)		King et al Eq.(2-3.29)		Sitara. et al Eq.(2-3.27)	
				Calc.	%Error	Calc.	%Error	Calc.	%Error	Calc.	%Error
Solvent = n-Heptane											
Cl	25.0	3.170	219	3.357	5.9	3.569	12.6	3.783	19.3	3.402	7.3
odine	20.0	2.670	20	3.278	22.8	4.074	52.6	3.074	15.1	3.858	44.5
"	25.0	3.420	219	3.551	3.8	4.413	29.0	3.330	-2.6	4.156	21.5
oluene	6.9	2.950	219	2.457	-16.7	2.486	-15.7	2.669	-9.5	2.075	-29.6
"	25.0	3.720	219	3.226	-13.3	3.265	-12.2	3.505	-5.8	2.674	-28.1
"	40.0	4.330	219	3.903	-9.9	3.951	-8.8	4.240	-2.1	3.192	-26.3
enzene	25.0	3.915	176	3.451	-11.9	3.690	-5.8	3.766	-3.8	2.867	-26.8
"	40.0	4.744	176	4.175	-12.0	4.464	-5.9	4.557	-4.0	3.423	-27.8
"	55.0	5.616	176	5.071	-9.7	5.422	-3.4	5.535	-1.4	4.102	-27.0
"	25.0	3.400	25	3.451	1.5	3.690	8.5	3.766	10.8	2.867	-15.7
"	45.0	4.400	25	4.440	0.9	4.748	7.9	4.846	10.1	3.625	-17.6
"	65.0	6.050	25	5.677	-13.3	6.071	-7.3	6.197	-5.4	4.556	-30.4
"	85.0	7.300	25	7.173	-1.7	7.670	5.1	7.828	7.2	5.663	-22.4
"	98.4	8.400	25	7.902	-5.9	8.449	0.6	8.624	2.7	6.196	-26.2
exadecane	25.0	1.775	15	2.125	19.7	1.667	-6.1	2.236	26.0	1.763	-0.7
-Heptane (self-)	0.0	2.080	43	1.989	-4.4	1.814	-12.8	2.290	10.1	1.654	-20.5
"	20.0	2.800	150	2.740	-2.2	2.499	-10.7	3.154	12.7	2.228	-20.4
"	20.0	3.000	150	2.740	-8.7	2.499	-16.7	3.154	5.1	2.228	-25.7
"	25.0	3.120	43	2.953	-5.4	2.694	-13.7	3.400	9.0	2.389	-23.4
"	35.5	3.220	43	3.277	1.8	2.989	-7.2	3.773	17.2	2.632	-18.3
"	40.0	3.600	150	3.573	-0.8	3.259	-9.5	4.114	14.3	2.852	-20.8
"	40.0	3.750	150	3.573	-4.7	3.259	-13.1	4.114	9.7	2.852	-24.0
"	56.5	4.210	43	4.468	6.1	4.076	-3.2	5.144	22.2	3.511	-16.6
"	60.0	4.500	150	4.548	1.1	4.149	-7.8	5.236	16.4	3.569	-20.7
"	60.0	4.550	150	4.548	-0.1	4.149	-8.8	5.236	15.1	3.569	-21.6
"	80.0	5.600	150	5.894	5.3	5.377	-4.0	6.786	21.2	4.543	-18.9
"	80.0	5.400	150	5.894	9.2	5.377	-0.4	6.786	25.7	4.543	-15.9
"	80.2	5.760	43	5.897	2.4	5.380	-6.6	6.790	17.9	4.545	-21.1
"	90.0	5.850	150	6.196	5.9	5.653	-3.4	7.134	22.0	4.759	-18.7
"	95.8	6.560	43	6.652	1.4	6.068	-7.5	7.658	16.7	5.083	-22.5
"	100.0	6.800	150	6.791	-0.1	6.195	-8.9	7.819	15.0	5.183	-23.8
-Heptyl bromide	7.4	1.520	219	2.117	39.3	1.915	26.0	2.223	46.2	1.914	25.9
	Avg. % error				7.7		10.7		13.2		22.2

Total number of system = 7; Total number of data points = 32

Solute	T, °C	D°_{AB} (exp.)	Ref	This work Calc.	%Error	Wilke-Chang Calc.	%Error	King et al Calc.	%Error	Sitara. et al Calc.	%Error
Solvent = Ethyl ether											
romobenzene	7.3	3.500	219	4.032	15.2	3.887	11.1	3.941	12.6	3.687	5.3
hloroform	25.0	4.475	176	5.801	29.6	5.961	33.2	5.953	33.0	5.308	18.6
"	25.0	4.510	5	5.801	28.6	5.961	32.2	5.953	32.0	5.308	17.7
itrobenzene	8.0	3.240	20	4.018	24.0	3.827	18.1	3.783	16.8	3.329	2.8
henol	19.0	3.600	20	4.924	36.8	4.958	37.7	4.265	18.5	3.750	4.2
romoform	17.0	3.300	20	4.717	43.0	4.866	47.5	4.527	37.2	5.084	54.1
	Avg. % error				29.5		30.0		25.0		17.1

Total number of systems = 5; Total number of data points = 6

Appendix 3-2.2 (continued)

Solute	T, °C	D°_{AB} (exp.)	Ref	This work Eq.(3-2.4)		Wilke-Chang Eq.(2-3.16)		King et al Eq.(2-3.29)		Sitara. et al Eq.(2-3.27)	
				Calc.	%Error	Calc.	%Error	Calc.	%Error	Calc.	%Error
Solvent = Chloroform											
enzene	15.0	2.510	168	1.956	-22.1	2.520	0.4	2.009	-20.0	1.846	-26.5
cetone	15.0	2.360	168	2.189	-7.2	2.875	21.8	2.143	-9.2	1.912	-19.0
"	25.1	2.350	6	2.501	6.4	3.284	39.7	2.448	4.2	2.163	-7.9
"	40.0	2.900	6	2.997	3.4	3.936	35.7	2.933	1.2	2.560	-11.7
thanol	15.0	2.200	168	2.421	10.0	3.271	48.7	1.928	-12.3	1.830	-16.8
thyl ether	15.0	2.070	168	1.960	-5.3	2.382	15.1	2.113	2.1	1.807	-12.7
"	25.0	2.150	5	2.239	4.1	2.720	26.5	2.412	12.2	2.044	-4.9
ethylethylketone	25.0	2.130	163	2.285	7.3	2.862	34.4	2.247	5.5	2.012	-5.5
thyl acetate	25.0	2.020	163	2.211	9.4	2.720	34.7	2.200	8.9	2.038	0.9
-Butyl acetate	25.0	1.710	163	1.942	13.6	2.209	29.2	1.956	14.4	1.812	5.9
odine	10.0	1.930	20	1.867	-3.2	2.800	45.1	1.649	-14.6	2.498	29.4
henol	10.0	1.600	20	1.754	9.6	2.271	41.9	1.528	-4.5	1.594	-0.4
hloroform	25.0	2.580	43	2.353	-8.8	3.110	20.6	2.430	-5.8	2.547	-1.3
"	27.0	3.300	147	2.414	-26.9	3.190	-3.3	2.492	-24.5	2.608	-21.0
ethylisobutylketone	25.0	1.890	163	2.009	6.3	2.273	20.3	1.992	5.4	1.788	-5.4
	Avg. % error				9.6		27.8		9.7		11.3
	Total number of systems = 11; Total number of data points = 15										
Solvent = Bromoform											
etone	25.0	0.784	163	0.770	-1.8	1.365	74.1	0.827	5.5	0.827	5.5
yl alcohol	20.0	0.516	20	0.607	17.6	0.948	83.8	0.590	14.4	0.626	21.4
hanol	20.0	0.976	20	0.791	-18.9	1.443	47.8	0.692	-29.1	0.740	-24.2
opanol	20.0	0.770	20	0.713	-7.4	1.228	59.4	0.640	-16.9	0.690	-10.4
	Avg. % error				11.4		66.3		16.5		15.4
	Total number of systems = 4; Total number of data points = 4										
Solvent = Hexadecane											
Heptane	25.0	0.750	16	0.457	-39.0	0.516	-31.3	0.658	-12.3	0.476	-36.5
Hexane	25.0	0.850	16	0.485	-43.0	0.562	-33.8	0.707	-16.9	0.501	-41.1
xadecane	25.0	0.320	16	0.329	2.8	0.319	-0.3	0.433	35.3	0.351	9.8
decane	25.0	0.490	16	0.371	-24.4	0.378	-22.9	0.514	4.9	0.396	-19.1
	Avg. % error				27.3		22.1		17.4		26.6
	Total number of systems = 4; Total number of data points = 4										
Solvent = Dodecane											
Hexane	25.0	1.440	17	1.010	-29.8	1.093	-24.1	1.333	-7.4	0.939	-34.8
luene	25.0	1.380	219	1.041	-24.5	1.214	-12.0	1.280	-7.3	0.998	-27.7
Octane	25.0	1.142	208	0.907	-20.6	0.923	-19.2	1.165	2.0	0.849	-25.7
ecane	25.0	0.813	208	0.772	-5.0	0.734	-9.8	0.970	19.3	0.743	-8.6
xadecane	25.0	0.670	206	0.688	2.6	0.621	-7.2	0.818	22.1	0.660	-1.5
	Avg. % error				16.5		14.5		11.6		19.7
	Total number of systems = 5; Total number of data points = 5										
Solvent = Cyclohexanone											
Heptanol	25.0	0.576	169	0.555	-3.7	0.501	-13.0	0.546	-5.2	0.494	-14.2
"	55.0	1.050	169	1.0622	1.2	0.960	-8.5	1.046	-0.4	0.904	-13.9
"	90.0	1.918	169	2.016	5.1	1.822	-5.0	1.985	3.5	1.641	-14.4
ctane	25.0	0.741	169	0.527	-28.8	0.474	-36.0	0.655	-11.7	0.526	-29.0
	Avg. % error				9.7		15.6		5.2		17.8
	Total number of systems = 2 ; Total number of data points = 4										

Appendix 3-2.2 (continued)

Solute	T, °C	D°_{AB} (exp.)	Ref	This work Eq.(3-2.4)		Wilke-Chang Eq.(2-3.16)		King et al Eq.(2-3.29)		Sitara. et al Eq.(2-3.27)	
				Calc.	%Error	Calc.	%Error	Calc.	%Error	Calc.	%Error
Solvent = Methylcyclohexane											
-Octane	25.0	1.611	169	1.578	-2.0	1.396	-13.4	1.767	9.7	1.339	-16.9
odine	30.0	2.300	219	2.159	-6.2	2.685	16.7	1.996	-13.2	2.634	14.5
"	40.0	2.710	219	2.595	-4.2	3.228	19.1	2.399	-11.5	3.127	15.4
oluene	25.0	1.650	75	1.813	9.9	1.834	11.2	1.941	17.6	1.574	-4.6
"	45.0	2.180	75	2.579	18.3	2.610	19.7	2.761	26.7	2.185	0.2
"	60.0	2.730	75	3.280	20.1	3.318	21.5	3.511	28.6	2.732	0.1
niline	60.0	2.690	75	3.316	23.3	3.483	29.5	3.114	15.8	2.641	-1.8
ethylcyclohexane	10.0	1.400	150	1.321	-5.7	1.272	-9.1	1.483	6.0	1.174	-16.2
"	20.0	1.700	159	1.574	-7.4	1.516	-10.8	1.767	4.0	1.381	-18.8
"	40.0	2.420	150	2.235	-7.6	2.153	-11.0	2.510	3.7	1.914	-20.9
"	60.0	3.280	150	3.108	-5.2	2.994	-8.7	3.491	6.4	2.601	-20.7
	Avg. % error				10.0		15.5		13.0		11.8
	Total number of systems = 5; Total number of data points = 11										
Solvent = Cyclohexane											
Cl_4	25.0	1.490	168	1.382	-7.3	1.402	-5.9	1.495	0.4	1.482	-0.5
"	40.0	1.915	176	1.840	-3.9	1.867	-2.5	1.991	4.0	1.934	1.0
"	55.0	2.415	176	2.376	-1.6	2.412	-0.1	2.572	6.5	2.454	1.6
romobenzene	7.3	0.900	219	0.853	-5.2	0.838	-6.9	0.856	-4.8	0.880	-2.2
odine	15.0	1.540	219	1.204	-21.8	1.430	-7.2	1.084	-29.6	1.513	-1.8
"	30.0	1.920	219	1.631	-15.1	1.937	0.9	1.469	-23.5	2.006	4.5
"	40.0	2.300	219	1.946	-15.4	2.311	0.5	1.753	-23.8	2.364	2.8
nzene	25.0	1.896	176	1.420	-25.1	1.450	-23.5	1.489	-21.5	1.249	-34.1
"	25.0	1.880	101	1.420	-24.4	1.450	-22.9	1.489	-20.8	1.249	-33.5
"	40.0	2.450	176	1.891	-22.8	1.930	-21.2	1.982	-19.1	1.630	-33.5
"	60.0	3.285	176	2.675	-18.6	2.730	-16.9	2.803	-14.7	2.251	-31.5
luene	25.0	1.569	176	1.328	-15.4	1.283	-18.2	1.385	-11.7	1.165	-25.7
"	40.0	1.913	176	1.768	-7.6	1.708	-10.7	1.844	-3.6	1.520	-20.5
"	55.0	2.409	176	2.284	-5.2	2.207	-8.4	2.382	-1.1	1.929	-19.9
clohexane	10.0	1.050	150	0.953	-9.2	0.920	-12.4	1.038	-1.1	0.856	-18.5
"	20.0	1.230	150	1.208	-1.8	1.166	-5.2	1.316	7.0	1.067	-13.2
"	25.0	1.380	43	1.338	-3.0	1.292	-6.4	1.458	5.6	1.174	-15.0
"	25.0	1.475	150	1.338	-9.3	1.292	-12.4	1.458	-1.2	1.174	-20.4
"	25.0	1.433	159	1.338	-6.6	1.292	-9.9	1.458	1.7	1.174	-18.1
"	25.0	1.420	150	1.338	-5.8	1.292	-9.0	1.458	2.7	1.174	-17.4
"	25.0	1.410	150	1.338	-5.1	1.292	-8.4	1.458	3.4	1.174	-16.8
nzene	25.0	1.883	174	1.420	-24.6	1.450	-23.0	1.489	-20.9	1.249	-33.7
"	35.0	2.207	174	1.762	-20.2	1.798	-18.5	1.846	-16.3	1.526	-30.8
clohexane	40.0	1.750	150	1.782	1.8	1.720	-1.7	1.941	10.9	1.532	-12.5
"	60.0	2.340	150	2.520	7.7	2.432	3.9	2.745	17.3	2.114	-9.6
"	80.0	3.140	150	3.471	10.5	3.350	6.7	3.781	20.4	2.848	-9.3
"	100.0	4.110	150	4.710	14.6	4.546	10.6	5.132	24.9	3.783	-8.0
romonaphthalene	7.3	0.850	219	0.732	-13.9	0.678	-20.2	0.678	-20.2	0.732	-13.9
	Avg. % error				11.6		10.5		12.1		16.1
	Total number of systems = 7; Total number of data points = 28										

Appendix 3-2.2 (continued)

Solute	T, °C	D°_{AB} (exp.)	Ref	This work Eq.(3-2.4)		Wilke-Chang Eq.(2-3.16)		King et al Eq.(2-3.29)		Sitara. et al Eq.(2-3.27)	
				Calc.	%Error	Calc.	%Error	Calc.	%Error	Calc.	%error
Solvent = Bromobenzene											
odine	30.0	1.390	27	1.397	0.5	2.203	58.5	1.372	-1.3	1.996	43.6
enzene	7.5	1.020	219	0.897	-12.0	1.216	19.2	1.025	0.5	0.936	-8.2
hlorobenzene	10.0	1.007	169	0.882	-12.4	1.150	14.2	0.977	-3.0	0.963	-4.4
"	20.0	1.180	169	1.054	-10.7	1.374	16.4	1.168	-1.0	1.137	-3.7
"	26.8	1.342	169	1.195	-10.9	1.558	16.1	1.342	-1.3	1.278	-4.8
"	40.0	1.584	169	1.454	-8.2	1.895	19.7	1.611	1.7	1.533	-3.2
"	25.0	1.260	100	1.161	-7.8	1.514	20.1	1.286	2.1	1.244	-1.3
oluene	25.0	1.410	100	1.160	-17.7	1.488	5.5	1.319	-6.5	1.180	-16.3
	Avg. % error				10.0		21.2		2.2		10.7
	Total number of systems = 4; Total number of data points = 8										
Solvent = Chlorobenzene											
romobenzene	25.0	1.640	100	1.552	-5.3	1.747	6.5	1.666	1.6	1.673	2.0
luene	25.0	1.690	100	1.592	-5.8	1.762	4.3	1.775	5.0	1.502	-11.1
nzene	20.0	1.250	168	1.588	27.1	1.857	48.6	1.779	42.3	1.509	20.8
luene	10.0	1.345	96	1.286	-4.4	1.423	5.8	1.434	6.6	1.231	-8.5
"	20.0	1.560	96	1.485	-4.8	1.643	5.3	1.656	6.1	1.407	-9.8
"	27.0	1.756	96	1.655	-5.8	1.831	4.3	1.845	5.1	1.557	-11.4
"	40.0	2.113	96	2.009	-4.9	2.222	5.2	2.240	6.0	1.864	-11.8
	Avg. % error				8.3		11.4		10.4		10.8
	Total number of systems = 3 ; Total number of data points = 7										
Solvent = Butyl acetate											
etone	20.0	2.660	182	1.976	-25.7	2.349	-11.7	2.217	-16.6	1.723	-35.2
etic acid	20.0	1.640	182	1.600	-2.0	2.632	60.5	1.955	19.2	1.740	6.1
thylethylketone	30.0	1.852	4	2.136	15.3	2.422	30.8	2.409	30.1	1.874	1.2
loroform	25.0	1.960	163	2.027	3.4	2.426	23.8	2.400	22.5	2.199	12.2
	Avg. % error				11.6		31.7		22.1		13.7
	Total number of systems = 4 ; Total number of data points = 4										
Solvent = Nitrobenzene											
hylbenzoate	20.0	0.600	219	0.520	-13.3	0.539	-10.1	0.607	1.3	0.571	-4.8
etone	17.8	0.790	22	0.695	-12.1	0.846	7.1	0.790	0.0	0.678	-14.2
hyl acetate	16.8	0.640	182	0.603	-5.8	0.688	7.6	0.697	9.0	0.627	-2.0
tromethane	18.6	0.810	182	0.758	-6.4	1.008	24.5	0.761	-6.0	0.747	-7.8
	Avg. % error				9.4		12.3		4.1		7.2
	Total number of systems = 4 ; Total number of data points = 4										
Solvent = Ethyl benzoate											
trobenzene	20.0	0.730	219	0.554	-24.1	0.679	-6.9	0.618	-15.4	0.606	-17.0
etone	17.0	0.830	182	0.652	-21.4	0.830	0.0	0.740	-10.8	0.624	-24.8
hyl acetate	15.7	0.680	182	0.565	-16.9	0.674	-1.0	0.652	-4.1	0.577	-15.1
tromethane	14.9	0.730	182	0.674	-7.6	0.936	28.2	0.676	-7.5	0.655	-10.3
	Avg. error				17.5		9.0		9.5		16.8
	Total number of systems = 4 ; Total number of data points = 4										

Appendix 3-2.2 (continued)

Solute	T, °C	D°_{AB} (exp.)	Ref	This work Eq.(3-2.4)		Wilke-Chang Eq.(2-3.16)		King et al Eq.(2-3.29)		Sitara. et a Eq.(2-3.27)	
				Calc.	%Error	Calc.	%Error	Calc.	%Error	Calc.	%Error
Solvent = n-Decane											
luene	25.0	2.090	216	1.584	-24.2	1.760	-15.8	1.869	-10.6	1.443	-31.0
-Decane (self-)	25.0	1.310	43	1.262	-3.7	1.183	-9.7	1.538	17.4	1.142	-12.8
"	20.0	1.290	150	1.150	-10.8	1.079	-16.4	1.402	8.7	1.048	-18.7
	Avg.% error				12.9		13.9		12.2		20.8
	Total number of systems = 2 ; Total number of data points = 3										
Solvent = m-Xylene											
omobenzene	7.3	1.520	108	1.562	2.8	1.662	9.3	1.715	12.8	1.643	8.1
dine	20.0	1.680	20	2.164	28.8	2.780	65.5	2.131	26.8	2.773	65.0
"	25.0	1.890	180	2.353	24.5	3.022	59.9	2.317	22.6	2.997	58.6
	Avg. % error				18.7		44.9		20.7		43.9
	Total number of systems = 2 ; Total number of data points = 3										
Solvent = n-Heptanol											
thylcyclohexane	25.0	0.470	169	0.550	18.0	0.256	-45.6	0.293	-37.7	0.240	-48.9
nzene	25.0	0.640	123	0.620	-1.9	0.320	-50.0	0.316	-50.6	0.271	-57.7
Dichlorobenzene	25.0	0.475	123	0.550	17.0	0.255	-46.3	0.263	-44.6	0.253	-46.7
	Avg. % error				12.3		47.3		44.3		51.1
	Total number of systems = 3 ; Total number of data points = 3										
Solvent = Dioxane											
dine	25.0	1.070	219	1.046	-2.2	1.313	22.7	0.995	-7.0	1.430	33.6
L_4	25.0	1.020	219	0.989	-3.0	1.062	4.1	1.131	10.9	1.170	14.7
	Avg. % error				2.6		13.4		9.0		24.2
	Total number of systems = 2 ; Total number of data points = 2										
Solvent = Isopropyl acetate											
thylethylketone	30.0	2.210	108	2.659	20.3	2.907	31.5	2.895	31.0	2.265	2.5
Solvent = Methyl acetate											
hylethylketone	30.0	3.150	108	3.610	14.6	3.620	14.9	3.771	17.8	2.957	-6.1
Solvent = Iso-Amyl alcohol											
nol	19.0	0.200	20	0.270	35.0	0.354	77.2	0.293	46.6	0.290	45.2
Solvent = Methylethylketone											
oroform	25.0	2.860	163	3.247	13.5	3.314	15.9	3.602	26.0	3.269	14.3
Solvent = m-Cymene											
mobenzene	7.3	1.340	219	1.033	-22.9	1.181	-11.9	1.187	-11.4	1.143	-14.7
Solvent = Tetradecane											
uene	25.0	1.020	219	0.702	-31.1	0.859	-15.8	0.923	- 9.5	0.772	-29.3
ine	25.0	0.960	219	0.773	-19.5	1.161	20.9	0.877	- 8.6	1.122	16.8
	Avg. % error				25.3		18.4		9.1		23.1
	Total number of systems = 2; Total number of data points = 2										

Appendix 3-2.2 (continued)

Solute	T, °C	$D^\bullet_{AB}$ (exp.)	Ref	This work Eq.(3-2.4)		Wilke-Chang Eq.(2-3.16)		King et al Eq.(2-3.29)		Sitara. et al Eq.(2-3.27)	
				Calc.	%Error	Calc.	%Error	Calc.	%Error	Calc.	%Error
Solvent = Methylene chloride											
ethyl Iodide	7.5	2.060	219	2.476	20.2	3.262	58.4	2.615	26.9	3.042	47.6
Solvent = Ethylene chloride											
thylene bromide	7.3	1.110	219	1.130	1.8	1.356	22.2	1.198	7.9	1.400	26.1
Solvent = Ethyl benzene											
romobenzene	7.3	1.440	219	1.456	1.1	1.555	8.0	1.592	10.5	1.536	6.7
Solvent = Mesitylene											
romobenzene	7.3	1.310	219	1.395	6.5	1.539	17.5	1.597	21.9	1.512	15.4
Solvent = Transdecalin											
Bromonaphthalene	7.3	0.340	219	0.387	13.9	0.410	20.7	0.400	17.6	0.431	26.7
Cl_4	25.0	0.776	20	0.627	-19.2	0.733	-5.5	0.762	-1.8	0.762	-1.8
romobenzene	7.3	0.470	20	0.448	-4.6	0.507	8.0	0.506	7.6	0.518	10.3
	Avg. % error				12.6		11.4		9.0		12.9
	Total number of systems = 3; Total number of data points = 3										
Solvent = α-Methyl naphthalene											
romonaphthalene	7.5	0.226	219	0.199	-11.8	0.220	-2.6	0.221	-2.2	0.248	9.8
Solvent = Methyl isobutyl ketone											
loroform	25.0	2.100	163	2.593	23.5	2.925	39.3	3.043	44.9	2.722	29.6
Solvent = Carbondisulphide											
omine	16.0	3.600	20	3.581	-0.5	4.528	25.8	3.150	-12.5	4.109	14.2
enol	19.0	3.400	20	2.996	-11.9	3.191	-6.1	2.438	-28.3	2.451	-27.9
	Avg. % error				6.2		16.0		20.4		21.0
	Total number of systems = 2; Total number of data points = 2										
Solvent = Tetralin											
omobenzene	7.0	0.480	20	0.495	3.1	0.557	16.1	0.581	20.9	0.589	22.8
romonaphthalene	7.0	0.360	20	0.427	18.7	0.451	25.2	0.459	27.5	0.490	36.0
	Avg. % error				10.9		20.7		24.2		29.2
	Total number of systems = 2; Total number of data points = 2										
Solvent = Tetrachloroethane											
trabromoethane	50.0	0.940	20	1.052	11.9	1.422	51.3	1.177	25.2	1.509	60.6
Solvent = Anisole											
dine	20.0	1.130	20	1.006	-11.0	1.318	16.6	0.991	-12.3	1.382	22.3
Solvent = Acetic acid											
dine	20.0	1.030	20	1.364	32.4	1.063	3.2	0.995	-3.4	1.392	35.2

Appendix 3-2.2 (continued)

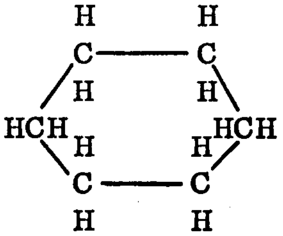
Solute	T°C	D^{o}_{AB} (Exp.)	Ref.	This work Eq.(3-2.4)		Wilke-Chang Eq.(2-3.16)		King et al Eq.(2-3.29)		Sitara. et al Eq.(2-3.27)	
				Calc.	%Error	Calc.	%Error	Calc.	%Error	Calc.	%Error
Solvent = n-Pentanol											
enzene	25	0.985	123	0.873	-11.4	0.467	-52.6	0.458	-53.5	0.395	-59.9
iphenyl	25	0.571	123	0.676	18.4	0.317	-44.5	0.328	-42.5	0.311	-45.5
-Dichlorobenzene	25	0.733	123	0.771	5.2	0.377	-48.6	0.382	-47.9	0.373	-49.2
	Avg. % error				11.7		48.6		48.0		51.5
	Total number of systems = 3; Total number of data points = 3										
Solvent = Ethyleneglycol											
thyleneglycol(self)	25	0.096	135	0.078	-19.0	0.082	-14.3	0.077	-19.7	0.088	-8.2
'	30	0.114	135	0.095	-16.6	0.100	-11.8	0.094	-17.3	0.106	-6.7
'	40	0.151	135	0.148	-2.0	0.156	3.7	0.147	-2.8	0.160	6.2
'	50	0.207	135	0.217	5.1	0.230	11.2	0.215	4.2	0.229	10.9
yclohexanol	26.6	0.061	135	0.067	10.2	0.060	-1.1	0.077	27.2	0.082	34.4
'	30	0.064	135	0.076	20.1	0.069	7.7	0.088	38.5	0.092	45.1
'	39.9	0.107	135	0.119	11.1	0.107	-0.3	0.137	28.2	0.140	30.2
	Avg. % error				12.2		8.7		19.5		20.8
	Total number of systems = 2; Total number of data points = 7										
Solvent = Diethyleneglycol											
thyleneglycol	25	0.056	135	0.049	-11.3	0.061	9.3	0.054	-2.4	0.061	9.4
'	30	0.065	135	0.062	-5.2	0.076	16.9	0.068	4.4	0.075	15.2
'	40	0.100	135	0.097	-2.2	0.120	20.6	0.107	7.7	0.115	15.2
yclohexanol	26.6	0.046	135	0.041	-9.8	0.043	-5.7	0.053	15.5	0.055	19.9
'	30	0.050	135	0.050	0.1	0.052	4.7	0.064	28.3	0.065	31.5
'	39.9	0.083	135	0.079	-5.0	0.082	-0.7	0.101	21.6	0.100	20.7
	Avg. % error				5.6		9.7		13.3		18.7
	Total number of systems = 2; Total number of data points = 6										
Solvent = Propyleneglycol											
hyleneglycol	25	0.048	135	0.031	-35.1	0.036	-25.2	0.033	-31.6	0.039	-18.8
'	30	0.053	135	0.045	-15.2	0.052	-2.2	0.048	-10.5	0.055	3.5
'	40	0.092	135	0.078	-15.1	0.090	-2.2	0.083	-10.4	0.092	-0.3
'	50	0.126	135	0.129	2.5	0.149	18.1	0.136	8.1	0.146	16.2
clohexanol	26.6	0.026	135	0.026	0.0	0.025	-2.1	0.032	23.0	0.035	35.2
	30	0.031	135	0.036	17.4	0.036	14.7	0.045	44.0	0.048	54.7
	39.9	0.057	135	0.063	10.6	0.062	8.0	0.078	35.7	0.080	40.2
	Avg. % error				13.7		10.3		23.3		24.1
	Total number of systems = 2; Total number of data points = 7										

Appendix 3-3.1a Sample calculation for estimating D* from additive method

Example(1):

Cyclohexane at T=333.2°K

Structural formulae :



$[M] = 12\,(C\text{-}H) + 6\,(C-C) +$ ⬡

From Table 3-3.2 $(C\text{-}H) = 14$

$(C\text{-}C) = 7$

⬡ $= 7$

$[M] = 12\,(14) + 6\,(7) + 7 = 217.0$

$\bar{V}$ at 333.2°K = 113.64 cm^3/gmole

From eq. (3-3.4)

$$D^*_{cal} = T\left(\frac{\bar{V}}{[M]}\right)^{7.7}$$

$$= 333.2\left(\frac{113.64}{217.0}\right)^{7.7} = 2.30\ cm^2/sec.$$

Experimental $D^*_{exp} = 2.34\ cm^2/sec.$

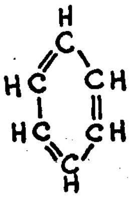
$$\%\ error = \frac{D^*_{cal.} - D^*_{exp}}{D^*_{exp}} \times 100$$

$$= \left(\frac{2.30 - 2.34}{2.34}\right) \times 100 = -1.7\%$$

Example(2):

Benzene at T = 328.2°K

Structural formulae



$[M] = 6\,(C\text{-}H) + 3\,(C\text{-}C) + 3\,(C{=}C) +$ ⬡

Appendix 3-2.1a (continued)

From Table 3-3.2 (C-H) = 14

(C-C) = 7

(C=C) = 19

 = 7

$[M] = 6\ (14) + 3\ (7) + 3\ (19) + 7 = 169$

$\bar{V}$ at T = 92.87 cm^3/gmole

From eq. (3-3.4)

$$D^*_{cal.} = T \left(\frac{\bar{V}}{[M]}\right)^{7.7}$$

$$= 328.2 \left(\frac{92.87}{169}\right)^{7.7} = 3.28 \times 10^{-5}\ cm^2/sec.$$

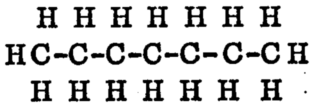
Experimental $D^*_{exp} = 3.50 \times 10^{-5}\ cm^2/sec.$

$$\%\ error = \left(\frac{3.28 - 3.5}{3.5}\right) \times 100 = -6.2\%.$$

Example (3):

n Heptane at T=313.2°K

Structural formulae :



$$\begin{array}{c} H\ H\ H\ H\ H\ H\ H \\ HC-C-C-C-C-C-CH \\ H\ H\ H\ H\ H\ H\ H \end{array}$$

$[M] = 16\ (C-H) + 6\ (c-c)$

From Table (c-H) = 14

(c-c) = 7

$[M] = 16\ (14) + 6\ (7) = 266$

$\bar{V}$ at 313.2°K = 150.34

From eq. (3-3.4)

$$D^*_{cal} = T\left(\frac{\bar{V}}{[M]}\right)^{7.7}$$

$$= 313.2 \left(\frac{150.36}{266}\right)^{7.7} = 3.89 \times 10^{-5}\ cm^2/sec.$$

Experimental $D^*_{exp.} = 3.75 \times 10^{-5}\ cm^2/sec.$

$$\%\ error = \left(\frac{3.89 \times 3.75}{3.75}\right) \times 100 = 3.7\%$$

Appendix 3.3.1b Comparisons of predicted values of self-diffusion coefficients from the additive method with the experimental values, ($D^* \times 10^5$, cm^2/sec)

Liquid	T ^oK	Exper. D*		Exper. $\bar{V}$		D*, calculated @	
		cm^2/sec.	Ref.	cm^3/gmole	Ref.	cm^2/sec.	% error
Paraffins -							
Methane	90.7	2.60	43	35.24	43	2.57	-1.0
	95.2	3.05	43	35.74	43	3.01	-1.4
	100.0	3.70	43	36.29	43	3.55	-3.9
	106.1	4.45	43	37.06	43	4.43	-0.4
	110.5	5.45	43	37.65	43	5.21	-4.4
	111.11	5.23	48	37.74	48	5.28	1.8
							2.2
Ethane	103.2	0.87	150	47.73	62	0.72	-17.0
	123.2	1.35	150	48.89	62	1.04	-23.3
	143.2	2.32	150	50.53	62	1.55	-33.1
	163.2	3.66	150	52.38	62	2.33	-36.3
	183.2	5.05	150	54.57	62	3.59	-29.0
							27.7
n-Pentane	194.7	1.38	43	100.84	43	0.98	-29.0
	250.3	2.97	43	108.29	43	2.22	-25.2
	273.2	4.14	43	111.81	43	3.13	-24.4
	298.2	5.535	43	116.18	43	4.64	-16.3
	298.2	5.450	41	116.18	196	4.64	-14.9
	303.2	5.650	150	117.03	196	4.99	-11.7
	308.7	6.290	43	118.22	43	5.51	-12.4
							19.1
Iso-pentane	273.2	3.83	56	112.86	196	3.37	-12.0
	283.2	4.26	56	114.61	196	3.95	-7.3
	298.2	4.85	56	115.48	196	4.42	- 8.9
	298.2	4.81	204	115.48	196	4.42	-8.1
							9.1
2 - Methyl butane	298.2	5.3	43	117.31	43	5.01	-5.5
n-Hexane	233.2	1.63	150	121.03	196	1.62	-0.6
	253.2	2.25	150	124.16	196	2.13	-5.1
	293.2	3.85	150	130.66	196	3.66	-4.9
	298.2	4.12	43	131.56	196.	3.92	-4.7
	298.2	4.21	150	131.56	196	3.92	-6.9
	313.2	4.80	150	134.39	196	4.86	1.3
	313.2	4.86	150	134.39	196	4.86	0.0
	333.2	6.00	150	138.51	196	6.52	8.6
	353.2	7.30	150	143.09	196	8.87	21.5
							6.0

Appendix 3-3.1b (contd.)

Liquids	T °K	Exper. D*		Exper. $\bar{V}$		Calculated D* @	
		cm^2/sec.	Ref.	cm^3/gmole	Ref.	cm^2/sec.	% error
2-Methyl pentane	273.2	2.97	150	128.38	196	2.98	0.3
	283.2	3.36	150	130.07	196	3.41	1.6
	293.2	3.75	150	131.72	196	3.89	3.9
	298.2	3.98	43	132.57	43	4.16	4.6
	303.2	4.18	150	133.49	196	4.46	6.8
	313.2	4.62	150	135.27	196	5.10	10.5
							4.6
3-Methyl pentane	273.2	2.67	150	126.37	196	2.64	-1.2
	283.2	3.02	150	128.02	196	3.02	0.0
	293.2	3.42	150	129.78	196	3.47	1.6
	298.2	3.61	43	130.61	43	3.71	2.8
	303.2	3.81	150	131.56	196	3.99	4.7
	313.2	4.23	150	132.29	196	4.30	1.7
							2.0
2,2-dimethyl butane	298.2	3.41	43	133.65	43	4.43	29.9
2,3-dimethyl butane	273.2	2.55	150	126.82	196	2.71	6.3
	283.2	2.91	150	128.48	196	3.10	6.7
	293.2	3.27	150	130.22	196	3.56	9.1
	298.2	3.50	43	131.14	43	3.83	9.4
	303.2	3.65	150	132.06	196	4.11	12.6
	313.2	4.07	150	133.97	196	4.74	16.5
							10.1
n Heptane	233.2	1.12	150	136.14	196	1.35	20.5
	250.3	1.52	43	139.26	196	1.72	13.4
	273.2	2.25	150	143.06	196	2.31	2.9
	273.2	2.08	43	143.06	196	2.31	12.7
	293.2	3.00	150	146.57	196	2.99	0.2
	293.2	2.80	150	146.52	196	2.99	6.8
	298.2	3.12	43	147.46	43	3.19	2.2
	305.7	3.22	43	148.89	43	3.52	9.4
	313.2	3.60	150	150.34	196	3.89	8.0
	313.2	3.75	150	150.34	196	3.89	3.7
	329.7	4.21	43	153.75	43	4.86	15.5
	333.2	4.55	150	154.37	196	5.07	11.4
	353.2	5.60	150	158.77	196	6.67	19.1
	353.4	5.76	43	158.80	43	6.68	16.0
	369.0	6.56	43	162.48	43	8.30	26.9
							10.0

Appendix 3-3.1b (contd.)

Liquid	T ^{o}K	Exper. D*		Exper. $\bar{V}$		Calculated D* @	
		cm^2/sec.	Ref.	cm^3/gmole	Ref.	cm^2/sec.	% error
n-Octane	273.2	1.47	150	158.95	196	1.60	14.5
	273.2	1.56	150	158.95	196	1.60	2.6
	293.2	1.95	150	162.63	196	2.05	5.2
	293.2	2.10	150	162.63	196	2.05	-2.4
	298.2	2.25	43	163.61	43	2.19	-2.9
	298.2	2.00	150	163.61	196	2.19	9.5
	298.2	2.37	150	163.61	196	2.19	-9.6
	298.2	2.35	150	163.61	196	2.19	-6.8
	313.2	2.55	150	166.47	196	2.62	2.8
	313.2	2.73	150	166.47	196	2.62	-4.0
	333.2	3.30	150	170.60	196	3.37	2.2
	333.2	3.41	150	170.60	196	3.37	-1.2
	333.2	3.55	150	170.60	196	3.37	-5.1
	343.2	3.80	150	172.74	196	3.82	0.5
	353.2	4.15	150	175.02	196	4.35	4.8
	373.2	5.20	150	179.81	196	5.65	8.7
	393.2	6.40	150	185.51	196	7.57	18.3
							6.0
n-Nonane	273.2	1.10	150	174.97	196	1.44	31.0
	293.2	1.63	150	178.70	196	1.82	11.6
	293.2	1.61	150	178.70	196	1.82	13.0
	298.2	1.70	43	179.67	43	1.93	13.4
	313.2	2.20	150	182.69	196	2.30	4.7
	313.2	2.17	150	182.69	196	2.30	6.0
	333.2	2.87	150	186.68	196	2.89	0.8
	333.2	3.00	150	186.68	196	2.89	3.7
	353.2	3.65	150	190.85	196	3.63	-0.4
	353.2	3.81	150	190.85	196	3.63	-4.2
	373.2	4.50	150	196.34	196	4.78	6.1
							8.6
n-Decane	273.2	0.76	150	191.04	196	1.32	74
	293.2	1.29	150	194.94	196	1.66	28.6
	298.2	1.31	43	195.89	43	1.75	33.7
							45.4
n-Dodecane	298.2	1.719	150	228.58	196	1.52	-11.5
n-Octadecane	323.2	0.46	43	334.87	43	0.465	1.1

Appendix 3-3.1b (contd.)

Liquids	T °K	Exper. D*		Exper. $\bar{V}$		Calculated D* @	
		cm^2/sec.	Ref.	cm^3/gmole	Ref.	cm^2/sec.	% error
<u>Cycloparaffins</u>							
Cyclopentane	273.2	2.00	56	91.68	196	2.07	0.0
	298.2	2.88	56	94.72	196	2.90	0.6
	313.2	3.41	56	96.60	196	3.54	3.8
							1.5
Cyclohexane	293.2	1.23	150	108.10	196	1.38	12.0
	298.2	1.39	43	108.76	43	1.47	5.6
	313.2	1.75	150	110.81	196	1.78	1.8
	333.2	2.34	150	113.64	196	2.30	-1.7
	353.2	3.14	150	116.89	196	3.03	-3.5
							5.0
Methylcyclohexane	273.2	1.13	150	124.83	196	1.23	8.8
	283.2	1.40	150	126.20	196	1.39	-1.0
	293.2	1.70	150	127.62	196	1.56	-8.0
	313.2	2.42	150	130.645	196	2.00	-17.0
	333.2	3.28	150	133.76	196	2.55	-22.2
	353.2	4.35	150	137.01	196	3.25	-25.2
	373.2	5.60	150	140.61	196	4.20	-25.0
							15.3
<u>Aromatics</u>							
Benzene	283.2	1.65	150	87.81	196	1.84	11.4
	288.2	1.87	43	88.34	43	1.96	4.8
	288.2	1.88	129	88.34	43	1.96	4.3
	298.2	2.22	43	89.40	43	2.22	0.0
	298.2	2.15	129	89.40	43	2.22	3.3
	308.2	2.59	43	90.51	43	2.53	-2.4
	308.2	2.40	129	90.51	43	2.53	5.4
	313.2	2.58	150	91.08	196	2.69	4.5
	318.2	3.01	31	91.66	43	2.88	-4.4
	318.2	3.04	43	91.66	43	2.88	-5.3
	318.2	2.67	129	91.66	43	2.88	7.9
	328.2	3.50	43	92.87	43	3.28	-6.2
	338.2	4.03	43	94.12	43	3.75	-7.0
	353.2	4.37	150	95.90	196	4.51	3.2
	373.2	6.15	43	98.50	43	5.87	-4.6
							4.98
Toluene	283.2	2.08	150	105.11	196	1.73	-17.1
	293.2	2.32	150	106.28	196	1.94	-16.4
	313.2	2.95	150	108.63	196	2.46	-16.7
	333.2	3.66	150	111.11	196	3.11	-15.0
	353.2	4.56	150	113.72	196	3.94	-13.5
	373.2	5.60	150	116.67	196	5.07	-9.4
							14.7

Appendix 3-3.1b (contd.)

Liquid	T ^oK	Exper. D*		Exper. $\bar{V}$		Calculated D* @	
		cm^2/sec.	Ref.	cm^3/gmole	Ref.	cm^2/sec.	% error
Alcohols							
Methanol	278.2	1.55	43	39.56	43	2.03	30.9
	288.2	1.91	43	40.25	43	2.40	25.7
	298.2	2.32	43	40.74	43	2.72	17.6
	308.2	2.71	43	41.17	43	3.06	12.8
	308.2	2.74	150	41.17	43	3.06	11.7
	313.2	2.89	43	41.45	43	3.09	7.1
	318.2	3.37	43	41.64	43	3.44	2.1
	328.2	3.88	43	42.15	43	3.90	0.5
	298.2	2.36	96	40.74	43	2.72	15.3
							13.7
Ethanol	280.0	0.618	43	57.33	43	0.95	54.3
	288.2	0.770	43	58.05	43	1.08	40.4
	298.2	1.010	43	58.68	43	1.22	20.3
	298.2	1.020	96	58.68	43	1.22	19.6
	298.2	1.05	72	58.68	43	1.22	16.2
	296.5	1.37	106	58.50	196	1.18	-13.9
	295.9	1.26	106	58.40	196	1.16	-7.8
	308.2	1.30	43	59.32	43	1.365	5.0
	318.2	1.66	43	60.02	43	1.54	-7.1
	328.2	2.06	43	60.73	43	1.74	-15.5
	333.2	2.60	106	61.00	196	1.83	-29.6
	338.2	2.61	43	61.53	43	1.98	-24.0
							21.1
n-propanol	288.2	0.504	43	74.42	43	0.63	25.1
	298.2	0.646	152	75.14	196	0.702	8.7
	308.2	0.814	152	75.895	196	0.784	-3.7
	318.2	1.017	152	76.743	196	0.882	-13.3
							12.7
i-propanol	288.2	0.474	43	74.985	43	0.668	41.0
	298.2	0.649	152	76.956	196	0.844	30.1
	308.2	0.867	152	77.867	196	0.955	11.3
	318.2	1.145	152	78.817	196	1.083	-5.4
							22.0
n-Butanol	298.2	0.504	152	91.998	196	0.52	3.5
	308.2	0.649	152	92.88	196	0.58	-10.6
	318.2	0.822	152	93.66	196	0.64	-22.3
							12.1

Appendix 3-3.1b (contd.)

Liquid	T °K	Exper. D*		Exper. $\bar{V}$		Calculated D* @	
		cm^2/sec.	Ref.	cm^3/gmole	Ref.	cm^2/sec.	% error
t-Butanol	308.2	0.497	152	96.15	196	0.75	52.0
	318.2	0.744	152	97.53	196	0.87	17.2
	328.2	1.070	152	98.98	196	1.01	-5.8
							25.0
Organic halids							
Methyl iodide	294.2	2.50	106	62.35	196	2.32	-7.1
	270.2	1.86	106	60.57	196	1.71	-8.2
							7.6
Chloroform	200	0.50	43	71.84	196	0.43	-13.4
	298.2	2.58	43	80.69	43	1.58	-38.7
	298.2	2.44	43	80.69	43	1.58	-35.2
							29.1
Carbon-tetra-chloride	293.2	1.18	43	96.51	43	1.36	15.3
	298.2	1.32	43	97.12	43	1.455	10.3
	298.2	1.41	129	97.12	43	1.455	6.3
	308.2	1.75	129	98.31	196	1.65	-5.6
	313.2	1.78	150	98.93	43	1.76	-1.0
	313.2	1.82	43	98.93	43	1.76	-3.3
	318.2	1.99	129	99.49	196	1.87	-6.0
	303.2	1.428	31	97.69	196	1.548	8.4
	313.2	1.683	31	98.93	43	1.76	4.6
	323.2	2.00	43	100.16	43	2.00	0.0
	323.2	1.937	31	100.16	43	2.00	3.2
	333.2	2.44	43	101.41	43	2.28	-7.0
							5.9
Ethylbromide	295.7	3.80	72	74.83	196	3.16	-16.8
	288.2	3.60	72	74.10	196	2.86	-20.6
	303.2	3.96	72	75.67	196	3.53	-10.8
							16.0
Ethyl iodide	292.5	2.212	43	80.688	43	2.13	-3.6
Butyl iodide	292.5	1.347	26	113.81	196	1.656	22.9
Chlorobenzene	298.0	1.80	147	102.25	196	1.47	-18.4
Bromobenzene	298.2	1.12	43	105.02	43	1.29	15.6

Appendix 3-3.1b (contd.)

Liquids	T ^{o}K	Exper. D*		Exper. $\bar{V}$		Calculated D* @	
		cm^2/sec.	Ref.	cm^3/gmole	Ref.	cm^2/sec.	% error
<u>Ketones</u>							
Acetone	298.2	4.835	43	74.0	43	4.97	2.8
	298.2	4.30	106	74.0	43	4.97	15.6
	333.2	7.00	106	78.0	196	8.33	18.9
							12.4
<u>Ethers</u>							
Diethyl ether	287.4	6.30	106	102.88	196	5.27	-16.3
	266.9	5.20	106	99.78	196	3.87	-25.5
	239.7	3.3	106	95.78	196	2.54	-23.0
							21.6
p-dioxan	307.2	1.49	43	86.37	43	1.60	7.8
1,1,Diethoxy-methane	294.7	3.20	106	125.8	196	4.0	25.0
	261.0	2.10	106	120.6	196	2.56	21.9
	333.2	5.3	106	132.17	196	6.60	24.8
1,2,Dimethoxy-ethane	292.9	3.0	106	104.40	216	3.58	19.2
<u>Acids</u>							
Acetic acid	290.2	0.89	106	57.07	196	0.98	10.7
	303.2	1.27	106	67.78	196	1.13	-10.8
	323.2	1.83	106	59.02	196	1.42	-22.3
	357.2	3.00	106	61.35	196	2.12	-29.3
							18.3
<u>Miscellaneous</u>							
Tetrahydro-furan	293.2	3.0	106	81.22	216	2.62	-12.8
			% Average deviation			=	11.8%

@ Calculated from eq. (3-3.4) by using the values of [M] from Table 3-3.2

Appendix 3-3.2 Sample calculation for D* from eq. (3-3.6)

Benzene at T = 328.2°K

$V_b = 96.5 \text{ cm}^3/\text{gmole}$ (Appendix 3-2.1)

$\bar{V}(\text{at } T) = 92.87 \text{ cm}^3/\text{gmole}$ (Ref. 43)

$\mu(\text{at } T) = 0.415 \times 10^{-2}$ poises (Ref. 43)

From Eq. (3-3.6)

$$D^* = 0.229 \times 10^{-8} \left(V_b\right)^{0.636} \left(\frac{T}{\mu \bar{V}}\right)$$

$$= 0.229 \times 10^{-8} \frac{(96.5)^{0.636} \quad 328.2}{0.415 \times 10^{-2} \times 92.87}$$

$$= \frac{0.229 \times 18.288 \times 328.2}{0.415 \times 92.87} \times 10^{-6}$$

$$= 3.566 \times 10^{-5} \text{ cm}^2/\text{sec.}$$

Experimental $D^* = 3.50 \times 10^{-5} \text{ cm}^2/\text{sec.}$ (ref. 43)

$$\% \text{ error} = \left[\frac{D^*_{\text{cal.}} - D^*_{\text{exp.}}}{D^*_{\text{exp.}}}\right] \times 100$$

$$= \left[\frac{3.566 - 3.50}{3.50}\right] \times 100$$

$$= 1.9\%$$

Appendix 3–4.1 Sample calculation for estimating the temperature dependence of D* from eq. (3–4.6)

Benzene :

From Appendix 3-2.1b at $T_1 = 298.2^{\circ}K$;

$$D_1^* = 2.22 \times 10^{-5} \ cm^2/sec$$

From Ref. (168) $T_c = 562.1^{\circ}K$

To estimate D_2^* at $T_2 = 328.2^{\circ}K$

From eq. (3–4.6) $D^*_2 = D_1^* \left[\frac{T_c - T_1}{T_c - T_2}\right]_B^{\,n}$

For benzene $n = 4$ (from Table 3–4.5)

$$D_2^* = 2.22 \times 10^{-5} \left[\frac{562.1 - 298.2}{562.1 - 328.2}\right]^4$$

$$= 2.22 \times 10^{-5}\left[\frac{263.9}{233.9}\right]^4$$

$$= 3.597 \times 10^{-5} \ cm^2/sec.$$

Experimental D^*_2 $= 3.50 \times 10^{-5} \ cm^2/sec.$ (ref. 43)

% error $= \left[\frac{D^*_{2,cal} - D^*_{2,\,exp.}}{D^*_{2,\,exp.}}\right] \times 100$

$$= \left[\frac{3.597 - 3.50}{3.50}\right] \times 100$$

$$= 2.78\%$$

Appendix 4-3.1 Sample calculation for β

For the run RC4 :

$$\left.\begin{aligned} C_1 &= 0.101541 \\ C_2 &= 0.00000 \\ C_3 &= 0.071583 \\ C_4 &= 0.029963 \end{aligned}\right\} \quad \text{concentrations are in} \left(\frac{\text{gm mole}}{\text{litre}}\right) \text{ at } 25^{\circ}\text{C}$$

$$\bar{C}_B = \frac{C_1 + C_3}{2} = 0.086562 \quad \text{g mole/litre}$$

$$\bar{C}_T = \frac{C_2 + C_4}{2} = 0.0149815 \quad \text{g mole/litre}$$

$$\bar{D}^{o}_{B} \text{ at } \bar{C}_B = 1.8789 \times 10^{-5} \text{ cm}^2/\text{sec} \quad \text{from Fig. 4-3.2}$$

$$\bar{D}^{o}_{T} \text{ at } \bar{C}_T = 1.92950 \times 10^{-5} \text{ cm}^2/\text{sec} \quad \text{from Fig. 4-3.2}$$

From eq. (4-3.3)

$$\bar{D}_{AB} = \frac{\bar{C}_B \bar{D}^{o}_{B} - \bar{C}_T \bar{D}^{o}_{T}}{\bar{C}_B - \bar{C}_T}$$

$$= \frac{(0.086562 \times 1.8789) - (0.0149815 \times 1.9295)}{0.086562 - 0.0149815} \times 10^{-5} \quad \text{cm}^2/\text{sec}$$

$$= 1.86835 \times 10^{-5} \quad \text{cm}^2/\text{sec.}$$

From eq. (4-3.1)

$$\beta = \frac{1}{\bar{D}_{AB}\, t} \log_{10}\left(\frac{C_1 - C_2}{C_3 - C_4}\right)$$

$$= \frac{1}{(1.86835 \times 10^{-5})(24 \times 3600)} \log_{10}\left(\frac{0.101541 - 0.0000}{0.071583 - 0.029963}\right)$$

$$= 0.2388 \quad \text{cm}^{-2}$$

Appendix 4-3.2 Sample calculation for $\bar{D}_{AB}$ for acetone-water at 55°C

Run No. H30

$$\beta = 0.3106 \text{ cm}^{-2} \quad \text{(from Fig. 4-3.4)}$$

$$V = V_1 \approx V_2 \approx V_3 \approx V_4 = 41.8 \text{ cm}^3 \text{ at } 55^{\circ}\text{C}$$

$$\lambda = \frac{V_D}{V} = \frac{0.850}{41.8} = 0.02033 \quad \text{(from Table 4-1.1)}$$

Concentrations C_1, C_2 and C_4 are derived by an analysis of test solution (density measurement)

$$\left.\begin{aligned} C_1 &= 57.450 \\ C_2 &= 66.700 \\ C_4 &= 64.000 \end{aligned}\right\} \quad \text{in (gm acetone/100 cm}^3 \text{ at } 55^{\circ}\text{C)}$$

Concentration C_3 is obtained by material balance:

From eq. (4-3.7)

$$C_3 = \frac{C_1 + C_2 (1+\lambda)}{1 + 0.5\lambda} - C_4$$

$$= \frac{(57.450) + (66.700 \times 1.02033)}{1 + (0.5 \times 0.02033)} - 64.00$$

$$= 60.2437 \text{ gm acetone /100 cm}^3 \text{ at } 55^{\circ}\text{C}$$

From eq. (4-3.1)

$$\bar{D}_{AB} = \frac{1}{\beta t} \log\left[\frac{C_1 - C_2}{C_3 - C_4}\right]$$

$$= \frac{1}{0.3106 \times (24 \times 3600)} \log\left(\frac{57.45 - 66.70}{60.244 - 64.00}\right)$$

$$= 1.5332 \times 10^{-5} \text{ cm}^2/\text{sec.}$$

Appendix 4-4.1

Sample calculation for possible error in cell constant β

For the run RC4 :

$$\left.\begin{aligned} C_1 &= 0.101541 \\ C_2 &= 0.00000 \\ C_3 &= 0.071583 \\ C_4 &= 0.029963 \end{aligned}\right\}$$

Concentrations are in $\frac{\text{gm mole}}{\text{litre}}$ at 25°C

$$\Delta C_1 = \Delta C_2 = \Delta C_3 = \Delta C_4 \approx 0.0002$$

$$\delta\Delta C_i = \delta\Delta C_f = \left[(2 \times 10^{-4})^2 + (2 \times 10^{-4})^2\right]^{\frac{1}{2}} = 2.828 \times 10^{-4}$$

$$\Delta C_i = C_1 - C_2 = 0.101541$$

$$\Delta C_f = C_3 - C_4 = 0.041620$$

From eq. (4-4.2)

$$\therefore \quad \delta\beta = \frac{\beta}{\log_{10}\left(\frac{\Delta C_i}{\Delta C_f}\right)}\left[\left(\frac{\delta\Delta C_i}{\Delta C_i}\right)^2 + \left(\frac{\delta\Delta C_f}{\Delta C_f}\right)^2\right]^{\frac{1}{2}}$$

$$= \frac{0.23887}{0.387339}\left[775.7 + 4618.3\right]^{\frac{1}{2}} \times 10^{-4}$$

$$= 0.453 \times 10^{-2}$$

$$\therefore \quad \%\ \text{error} = \frac{0.453}{0.23887} = 1.896\%$$

Appendix 4-4.2

Sample calculation for possible error in $\bar{D}_{AB}$ from the determination of concentration by density measurement.

For the run R15 :

$$\left.\begin{aligned} C_1 &= 67.89549 \\ C_2 &= 72.33529 \\ C_3 &= 68.53367 \\ C_4 &= 71.64577 \end{aligned}\right\}$$

Concentrations are in gm/100cm^3 at 25°C

$$\Delta C_1 = \Delta C_2 = \Delta C_3 = \Delta C_4 = \Delta C \approx 0.005$$

$$\delta\Delta C_i = \delta\Delta C_f = \left[(\Delta C)^2 + (\Delta C)^2\right]^{\frac{1}{2}} = \left[(5\text{x}10^{-3})^2 + (5\text{x}10^{-3})^2\right]^{\frac{1}{2}}$$

$$= 0.707 \text{ x } 10^{-2}$$

$$\Delta C_i = C_2 - C_1 = 4.4398$$

$$\Delta C_f = C_3 - C_4 = 3.1210$$

From eq. (4-4.1)

$$\therefore \ \delta D_{AB} = \frac{D_{AB}}{\log_{10}\left(\frac{\Delta C_i}{\Delta C_f}\right)} \left[\left(\frac{\delta\Delta C_i}{\Delta C_i}\right)^2 + \left(\frac{\delta\Delta C_f}{\Delta C_f}\right)^2\right]^{\frac{1}{2}}$$

$$= \frac{0.7433}{0.15308} \left[0.02535 + 0.05131\right]^{\frac{1}{2}} \text{ x } 10^{-2}$$

$$= 1.3437 \text{ x } 10^{-2}$$

$$\therefore \ \% \text{ error} = \frac{1.3437}{0.7433} = 1.80775 \ \%$$

Appendix 4-4.3 Sample calculation of $\bar{D}_{AB}$ for ethanol-water system at 85°C

Run No. R5

$\beta = 0.2340 \ \ cm^{-2}$ (from Fig. 4-3.3)

$V = V_1 \approx V_2 \approx V_3 \approx V_4 = 46.2 \ cm^3$ at 85°C

$\lambda = \frac{V_D}{V} = \frac{1.10}{46.2} = 0.0238$ (from Table 4-1.1)

(1) Concentrations C_1, C_2 , C_3, C_4 are derived by an analysis of test solution (density measurement).

$$\left.\begin{aligned} C_1 &= 0.000 \\ C_2 &= 11.850 \\ C_3 &= 4.640 \\ C_4 &= 7.300 \end{aligned}\right\} \text{ in (gm ethanol/100cm}^3\text{ at } 85^{\circ}\text{C)}$$

From eq. (4-3.1)

$$(\bar{D}_{AB})_1 = \frac{1}{\beta t} \quad \log_{10}\left(\frac{C1 - C_2}{C_3 - C_4}\right)$$

$$= \frac{1}{0.234 \times (24 \times 3600)} \quad \log_{10}\left(\frac{0.000 - 11.850}{4.64 - 7.300}\right)$$

$$= 3.2093 \times 10^{-5} \quad cm^2/sec.$$

(2) Concentration C_3 is derived by a material balance.

From eq. (4-3.7)

$$C_3^* = \frac{C_1 + C_2 \ (1+\lambda)}{1 + 0.5\lambda} - C_4$$

$$= \frac{0.00 + (11.85 \times 1.0238)}{1 + (0.5 \times 0.0238)} - 7.30$$

$$= 4.68935 \quad \text{gm ethanol/100 cm}^3 \text{ at } 85^{\circ}\text{C}$$

The same value of C_1, C_2 and C_4 are used as given above

Then
$$(\bar{D}_{AB})_2 = \frac{1}{\beta t} \log_{10}\left(\frac{C_1 - C_2}{C_3^* - C_4}\right)$$

$$= \frac{1}{0.234 \times (24 \times 3600)} \log_{10}\left(\frac{0.000 - 11.85}{4.689 - 7.300}\right)$$

$$= 3.24959 \times 10^{-5} \text{ cm}^2 \text{/sec.}$$

$$\%\text{error} = \frac{(\bar{D}_{AB})_1 - (\bar{D}_{AB})_2}{(\bar{D}_{AB})_2} \times 100$$

$$= \frac{3.2093 - 3.2496}{3.2496} \times 100$$

$$= -1.24\%$$

Appendix 7-3.1 Sample calculation of D_{AB} using eq. (3-1.21).

For ethanol water system for the concentration of 0.1 mole fr. at 25°C

Values of pure component properties at 25°C

Component	$D^* \times 10^5$ cm^2/sec	$D^o_{ij} \times 10^5$ cm^2/sec	$\bar{V}_i$ cm^3/gmole	$\Delta\bar{H}i$ cal/gmole	$\Delta\bar{H}i$-x cal/gmole	$\mu_i \times 10^2$ poises
Ethanol A	1.050	1.220	58.68	10010.0	5500	1.080
Water B	2.236	1.240	18.054	10484.5	5250	0.895

From eq. (3-1.28)

$$\Delta G_{\mu,A} = \frac{\Delta\bar{H}_A - RT}{2.45} = \frac{10010-(1.9872\text{x}298.2)}{2.45} = 3844 \text{ cal/gmole}$$

From eq. (3-1.29)

$$\Delta G_{\mu,B} = \frac{\Delta\bar{H}_B - RT}{2.45} = \frac{10484.5-(1.9872\text{x}298.2)}{2.45} = 4038 \text{ cal/gmole}$$

At $x_A = 0.1$, $\mu_{AB} = 1.88 \times 10^{-2}$ poises

From eq. (3-1.30)

$$\Delta G_m = RT\,[\ln \mu_{AB} - (x_A \ln \mu_A + x_B \ln \mu_B)]$$

$$= (1.9872\text{x}298.2)\quad [\ln (0.0188)-(0.1 \ln(0.0108)-0.9\ln(0.00895))]$$

$$= 428.623 \frac{\text{cal}}{\text{gmole}}$$

From eq. (3-1.27)

$$\Delta G_{\mu,AB} = x_A\,\Delta G_{\mu,A} + x_B\,\Delta G_{\mu,B} + \Delta G_m$$

$$= (0.1)\ (3844) + (0.9)\ (4038) + 428.623$$

$$= 4447.22 \frac{\text{cal}}{\text{gmole}}$$

From eq. (3-1.41)

$$\Delta G^{j}_{D^*,A} = \tfrac{1}{2}\Delta G_{\mu,A} = 1922 \ \frac{\text{cal}}{\text{gmole}}$$

and
$$\Delta G^{j}_{D^*,B} = \tfrac{1}{2}\Delta G_{\mu,B} = 2019 \ \frac{\text{cal}}{\text{gmole}}$$

From eq. (3-1.43)

$$\Delta G_{\mu,A\text{-}H} = \left(\frac{\Delta \bar{H}_{A\text{-}H}}{\Delta \bar{H}_{A}}\right)\Delta G_{\mu,A}$$

$$= \frac{5500}{10010} \times 3844 = 2110.4 \ \frac{\text{cal}}{\text{gmole}}$$

and
$$\Delta G_{\mu,B\text{-}H} = \left(\frac{\Delta \bar{H}_{B\text{-}H}}{\Delta \bar{H}_{B}}\right)\Delta G_{\mu,B}$$

$$= \frac{5250}{10484.5} \times 4038 = 2019 \ \frac{\text{cal}}{\text{gmole}}$$

From eq. (3-1.42)

$$\Delta G^{j}_{D^*,A\text{-}H} = \tfrac{1}{2}\ \Delta G_{\mu,A\text{-}H} = 1055.2 \ \frac{\text{gal}}{\text{gmole}}$$

and
$$\Delta G^{j}_{D^*,B\text{-}H} = \tfrac{1}{2}\Delta G_{\mu,B\text{-}H} = 1009.5 \ \frac{\text{cal}}{\text{gmole}}$$

From eq. (3-1.39)

$$\Delta G^{j}_{D^*,A\text{-}I} = \Delta G^{j}_{D^*,A} - \Delta G^{j}_{D^*,A\text{-}H}$$

$$= 1922 - 1055.2 = 866.8 \ \frac{\text{cal}}{\text{gmole}}$$

and
$$\Delta G^{j}_{D^*,B\text{-}I} = \Delta G^{j}_{D^*,B} - \Delta G^{j}_{D^*,B\text{-}H}$$

$$= 2019 - 1009.5 = 1009.5 \ \frac{\text{cal}}{\text{gmole}}$$

From equations (3-1.37), (3-1.35) and (3-1.36)

$$\delta_A = \frac{2\ \bar{V}_A^{\frac{1}{3}}}{\bar{V}_A^{\frac{1}{3}} + \bar{V}_B^{\frac{1}{3}}} = \frac{2(58.68)^{\frac{1}{3}}}{(58.68)^{\frac{1}{3}} + (18.054)^{\frac{1}{3}}} = 1.194$$

and $$\delta_B = \frac{2\bar{V}_B^{\frac{1}{3}}}{\bar{V}_A^{\frac{1}{3}} + \bar{V}_B^{\frac{1}{3}}} = \frac{2\ (18.054)^{\frac{1}{3}}}{(58.68)^{\frac{1}{3}} + (18.054)^{\frac{1}{3}}} = 0.805$$

From eq. (3-1.34)

$$\Delta G^j_{D,AB-H} = \left[x_A \sqrt{\delta_A\ \Delta G^j_{D^*,A-H}} + x_B\sqrt{\delta_B \Delta G^j_{D^*,B-H}}\right]^2$$

$$= \left[0.1\sqrt{(1.194 \times 1055.2)} + 0.9\sqrt{(0.805 \times 1009.5)}\right]^2$$

$$= 853.3\ \frac{\text{cal}}{\text{gmole}}$$

From eq. (3-1.38)

$$\Delta G^j_{D,AB-I} = \left[x_A \sqrt{\left(\frac{1}{\delta_A}\right)^2 \Delta G^j_{D^*,A-I}} + x_B\sqrt{\left(\frac{1}{\delta_B}\right)^2 \Delta G^j_{D^*,B-I}}\right]^2$$

$$= \left[0.1\sqrt{\left(\frac{1}{1.194}\right)^2 \times 866.8} + 0.9\sqrt{\left(\frac{1}{0.805}\right)^2 \times 1009.5}\right]^2$$

$$= 1443.97\ \frac{\text{cal}}{\text{gmole}}$$

From eq. (3-1.31)

$$\Delta G^j_{D,AB} = \Delta G^j_{D,AB-H} + \Delta G^j_{D,AB-I}$$

$$= 853.3 + 1443.97$$

$$= 2297.27\ \frac{\text{cal}}{\text{gmole}}$$

From eq. (3-1.47a)

$$\Delta G^j_{D^o,BA} = \delta_A\ \Delta G^j_{D^*,A-H} + \left(\frac{1}{\delta_A}\right)^2\ \Delta G^j_{D^*,A-I}$$

$$= (1.194 \times 1022.5) + \left(\frac{1}{1.194}\right)^2 \times 866.8$$

$$= 1828.87\ \frac{\text{cal}}{\text{gmole}}$$

From eq. (3-1.46a)

$$f_A = \frac{1}{\Delta G^j_{D^o,BA}}\left[\frac{1}{2}\ \Delta G_{\mu,A} - RT \ln\left(\frac{D^o_{BA}}{D^*_A}\right)\right]$$

$$= \frac{1}{1828.87}\left[1922 - 1.9872\text{x}298.2\ \ln\left(\frac{1.22}{1.05}\right)\right]$$

$$= 1.0023$$

From eq. (3-1.47b)

$$\Delta G^{j}_{D^{o},AB} = \delta_B\ \Delta G^{j}_{D^*,B-H} + \left(\frac{1}{\delta_B}\right)^2 \Delta G^{j}_{D^*,B-I}$$

$$= (0.805 \text{ x } 1009.5) + \left(\frac{1}{0.805}\right)^2 \text{ x } 1009.5$$

$$= 2370.46\ \frac{\text{cal}}{\text{gmole}}$$

From eq. (3-1.46b)

$$f_B = \frac{1}{\Delta G^{j}_{D^{o},AB}}\left[\tfrac{1}{2}\ G_{\mu,B} - RT\ \ln\left(\frac{D^{o}_{AB}}{D^*_B}\right)\right]$$

$$= \frac{1}{2370.46}\left[2019 - 1.9872 \text{ x } 298.2\ \ln\left(\frac{1.24}{2.236}\right)\right]$$

$$= 0.99911$$

From eq. (3-1.44) for $x_A = 0.1$

$$f_{AB} = \left(f_A\right)^{x_A}\ \left(f_B\right)^{x_B}$$

$$= (1.0023)^{0.1}\ (0.99911)^{0.9}$$

$$= 0.99943$$

From eq. (3-1.26a)

$$\Delta G_{\mu,AB} - \Delta G_{D,AB} = \tfrac{1}{2}\ \Delta G_{\mu,AB} - f_{AB}\ \Delta G^{j}_{D,AB}$$

$$= (\tfrac{1}{2} \text{ x } 4447.22) - (0.99943 \text{ x } 2297.27)$$

$$= -72.35$$

From eq. (3-1.21)

$$D_{AB} = \left(D^*_A\ \mu_A\right)^{x_A}\ \left(D^*_B\ \mu_B\right)^{x_B}\ \frac{\alpha_A}{\mu_{AB}}\ \exp\left(\frac{\Delta G_{\mu,AB} - \Delta G_{D,AB}}{RT}\right)$$

$$= (1.08 \text{ x } 0.0108)^{0.1}(2.236\text{x}0.00895)^{0.9}\left(\frac{0.76}{0.0188}\right)\exp\left(\frac{-72.35}{1.9872\text{x}298.2}\right)$$

$$= 0.6784 \text{ x } 10^{-5}\ \text{cm}^2/\text{sec.}$$

Experimental $D_{AB} = 0.67 \times 10^{-5}$ cm^2/sec.

$$\% \text{ error} = \frac{D_{AB,cal} - D_{AB,exp.}}{D_{AB,exp}} \times 100$$

$$= \frac{0.678 - 0.67}{0.67} \times 100$$

$$= 1.3\%$$

Appendix 7-3.2 Sample calculation of D^o_{AB} using eq. (3-2.4)

For ethanol (A) - water (B) system at 100°C

$$\left.\begin{aligned} V_A &= 62.5 \text{ cm}^3/\text{gmole} \\ V_B &= 18.7 \text{ cm}^3/\text{gmole} \\ [P_A] &= 128.8 \\ [P_B] &= 52.0 \end{aligned}\right\} \text{from Appendix (3-2.1)}$$

$\mu_B = 0.288$ centipoises

$T = 373.2^oK$

From eq. (3-2.4)

$$D^o_{AB} = 8.93 \times 10^{-8} \frac{V_A^{1/6}}{V_B^{1/3}} \left[\frac{[P_B]}{[P_A]}\right]^{0.6} \frac{T}{\mu_B}$$

$$= 8.93 \times 10^{-8} \frac{(62.5)^{\frac{1}{6}}}{(18.7)^{\frac{1}{3}}} \left(\frac{52}{128.8}\right)^{0.6} \times \frac{373.2}{0.288}$$

$$= \frac{8.93 \times 1.992 \times 0.58029 \times 373.2}{2.65425 \times 0.288} \times 10^{-8}$$

$$= 5.00 \times 10^{-5} \text{ cm}^2/\text{sec.}$$

Experimental $D^o_{AB} = 4.32 \times 10^{-5}$ cm^2/sec.

$$\% \text{ error} = \left[\frac{D^o_{AB,cal} - D^o_{AB,exp.}}{D_{AB,\ exp}}\right] \times 100$$

$$= \frac{5.00 - 4.32}{4.32} \times 100$$

$$= +15.7\%$$

Appendix 7-3.3 Sample calculation for estimating the temperature dependence of D^{o}_{AB} using eq. (3-4.7)

Ethanol (A) - Water (B) system :

At $T_1 = 298.2^{o}K$ (from Table 6-2.2)

$$D^{o}_{AB} = 1.25 \times 10^{-5} \ cm^2/sec$$

from ref. (168) T_c (of water) = $647^{o}K$

To estimate D^{o}_{AB} at $T_2 = 346.2^{o}K$

From eq. (3-4.7)

$$(D^{o}_{AB})_2 = (D^{o}_{AB})_1 \left[\frac{T_c - T_1}{T_c - T_2}\right]^{n}_{B}$$

For solvent water, n = 6 (from Table 3-4.2)

$$D^{o}_{AB\ 2} = 1.25 \times 10^{-15} \left(\frac{647 - 298.2}{647 -. 346.2}\right)^{6}$$

$$= 3.04 \times 10^{-5} \ cm^2/sec.$$

Experimental D^{o}_{AB} at $346.2^{o}K = 2.95 \times 10^{-5}$ $cm^2/sec.$

$$\% \text{ error} = \frac{3.04 - 2.95}{2.95} \times 100$$

$$= +3.1\%$$

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A = surface area defined in eq. (3-1.2) or effective mass transfer area of the diaphragm in eq. (4-3.2), cm^2.

C_1, C_3 = initial and final concentrations of bottom compartment respectively, $gm/100cm^3$ at $T^{o}C$ (or gmole/liter at $25^{o}C$ for KCl - H_2O solution).

C_2, C_4 = initial and final concentrations of top compartment respectively, $gm/100cm^3$ at $T^{o}C$ (or gmole/liter at $25^{o}C$ for KCl-H_2O solution).

C_A = concentration of solute A, gm solute/$100cm^3$ at $T^{o}C$.

C_B, C_T = concentrations of the bottom and the top compartments, respectively, in eq. (4-3.3).

C^{o}_{D}, C_D = initial and final concentrations of liquid in the diaphragm as defined in Fig. 4-3.13.

C^{1} = $(C_2 + C_4)/2$.

C^{11} = $(C_1 + C_3)/2$.

D^*, D^*_A, D^*_B = self-diffusion coefficients of pure components, cm^2/sec.

D_{AB} = differential diffusion coefficient, cm^2/sec.

$\bar{D}_{AB}$ = integral diffusion coefficient, cm^2/sec.

$\bar{D}_{CB}$ = integral diffusion coefficient of a run of vanishingly short duration with initial concentrations C_B and zero on the two sides of the diaphragm, cm^2/sec.

$\bar{D}_{CT}$ = integral diffusion coefficient of a run of vanishingly short duration with initial concentrations C_T and zero on the two sides of the diaphragm, cm^2/sec.

D^{o}_{AB}, D^{o}_{BA} = limiting diffusion coefficients when $x_A \rightarrow 0$ and $x_B \rightarrow 0$ respectively, cm^2/sec.

ΔE, ΔE_A, ΔE_B = energy of vaporisation for pure components, cal/gmole.

NOMENCLATURE (contd.)

ΔE_D, $\Delta E_{D,A}$, $\Delta E_{D,B}$ = activation energy of diffusional flow for pure components at 0°K, cal/gmole.

$\Delta E_{D,AB}$ = activation energy of diffusional flow for binary mixture at 0°K.

ΔE_{μ}, $\Delta E_{\mu,A}$, $\Delta E_{\mu,B}$ = activation energy of viscous flow for pure components at 0°K.

$\Delta \bar{E}_{\mu,AB}$, $\Delta \bar{E}_{D,AB}$ = activation energy of viscous and diffusional flows as defined in equations (7-2.1) and (7-2.2) respectively, cal/gmole.

F_x = force in x- direction in eq. (3-1.3).

f = viscous resistance per molecule or frictional coefficient.

f_A, f_B = bond breaking factors for pure components.

f_{AB} = bond breaking factor for binary mixture.

f_x = shear stress in the x-direction in eq. (3-1.4).

ΔG_D, $\Delta G_{D,A}$, $\Delta G_{D,B}$ = free energy of activation for pure components, cal/gmole.

$\Delta G_{D,AB}$ = free energy of activation for diffusional flow, cal/gmole.

$\Delta G_D^o{}_{,AB}$, $\Delta G_D^o{}_{,BA}$ = free energy of activation for diffusional flows for $x_A \longrightarrow 0$ and $x_B \longrightarrow 0$, respectively, cal/gmole.

$\Delta G^h_{D,AB}$, $\Delta G^j_{D,AB}$ = contribution of free energy of activation for hole forming stage and for jumping stage in diffusional flow respectively, cal /gmole.

$\Delta G^j_{D,AB-H}$, $\Delta G^j_{D,AB-I}$ = contribution of free energy of activation for jumping in diffusional flow due to hydrogen bonding and to dispersion forces respectively, cal/gmole.

$\Delta G^j_{D^*,X}$ = contribution of free energy of activation for jumping in diffusional flow for pure component, cal/gmole.

$\Delta G^j_{D^*,X-H}$, $\Delta G^j_{D^*,X-I}$ = contribution of free energy for activation for jumping in diffusional flow due to hydrogen bonding and to dispersion forces respectively for pure component, cal/gmole.

NOMENCLATURE (Contd.)

ΔG_m = excess free energy of mixing, cal/gmole.

$\left.\begin{array}{l}\Delta G_{\mu,A}\\ \Delta G_{\mu,B}\end{array}\right\}$ = free energy of activation for viscous flow for pure components, cal/gmole.

$\Delta G_{\mu,X}$ = free energy of activation for viscous flow for pure components, cal/gmole.

$\Delta G_{\mu,AB}$ = free energy of activation for viscous flow in binary mixtures, cal/gmole.

$\left.\begin{array}{l}\Delta G^{+}_{\mu,AB}\\ \Delta G^{-}_{\mu,AB}\end{array}\right\}$ = free energy of activation for forward and backward flow in viscous process, cal/gmole.

$\left.\begin{array}{l}\Delta G^{h}_{\mu,AB},\\ \Delta G^{j}_{\mu,AB}\end{array}\right\}$ = contribution of free energy of activation for hole forming and for jumping, respectively, in viscous flow, cal/gmole.

$\Delta G^{j}_{\mu,X}$ = contribution of free energy of activation for jumping in viscous flow for pure component, cal/gmole.

$\left.\begin{array}{l}\Delta G^{j}_{\mu,X-H},\\ \Delta G^{j}_{\mu,X-I}\end{array}\right\}$ = contribution of free energy of activation for jumping in viscous flow due to hydrogen bonding and to dispersion forces respectively, cal/gmole.

$\Delta\bar{H}_A, \Delta\bar{H}_B$ = heats of vaporisation for pure components at T^oK, cal/gmole.

$\Delta H_A, \Delta H_B$ = heats of vaporisation for pure components at normal boiling points, cal/gmole.

$\Delta\bar{H}_x$ = heat of vaporisation of pure components at T^oK, cal/gmole.

$\Delta\bar{H}_{X-H}$ = heat of vaporisation of pure components due to hydrogen bonding at T^oK, cal/mole.

h = Plank's constant, 6.624×10^{-27} erg. sec.

J = mass flux in eq. (4-3.5) $gm/cm^2 sec$.

K = constant in eq. (3-2.3).

NOMENCLATURE (Contd.)

k = Boltzman's constant, $\frac{R}{N} = 1.3805 \times 10^{16}$ erg/molecule ^{o}K.

l = effective length of the diaphragm in eq. (4-3.2), cm.

$\Delta L_A, \Delta L_B$ = heats of vaporisation of pure components at normal boiling points, cal/gm.

L_A, L_B = test liquids in compartment A and B respectively.

M, M_A, M_B = molecular weight of pure components.

$[M]$ = constant in eq. (3-3.4).

N = Avogadro's number, 6.023×10^{23} molecules/mole.

n = association factor in eq. (3-2.5).

$[P]$, $[P_A]$, $[P_B]$ = parachors of pure components, $gm^{\frac{1}{4}}$ cm^3/gmole $sec^{\frac{1}{2}}$.

P = pressure.

P_c = critial pressure.

R = gas law constant, 1.9872 cal/gmole ^{o}K.

$[Rh]$ = rheochor.

r, r_A, r_B = molecular radii of pure components.

T = temperature in ^{o}K.

T_c = critical temperature, ^{o}K.

T_r = reduced temperature (T/Tc).

t = time.

$\bar{V}, \bar{V}_A, \bar{V}_B$ = molecular volumes of pure components at $T^{o}K$, cm^3/gmole.

V_1, V_2, V_D = volumes of liquid in lower compartment, upper compartment and diaphragm pores respectively in section 4.

V_b, V_A, V_B = molecular volumes of pure components at normal boiling points, cm^3/gmole.

V_c, V_{Ac}, V_{Bc} = critical volume of pure components, cm^3/gmole.

V_f = free volume, cm^3/gmole.
x_A, x_B = mole fraction of A and B respectively.
Z = number of all nearest neighbours.
W_A = weight fraction of A

Greek Letters

α_A = $1 + \left(\frac{d \ln \gamma_A}{d \ln x_A}\right)$ = thermodynamic factor
β = cell constant, cm^{-2}
δ = distance of momentum transfer.
δ_A, δ_B = dimension-less intermolecular distances defined by equations (3-1.35) and (3-1.36).
ρ = density, gm/cm^3.
μ, μ_A, μ_B = viscosity of pure components, poises;(centipoises in eq.3-2.4)
μ_{AB} = viscosity of binary mixture, poises.
ξ, ξ_A, ξ_B = number of nearest neighbours in one plane
$\lambda = \left(\frac{V_D}{V_1}\right)$ = ratio of volume of diaphragm pores to one of the compartments of diaphragm cell (of section 4).
$\lambda_1, \lambda_2, \lambda_3$ = distances between liquid molecules.
λ_D, λ_μ = distances between successive equilibrium positions for diffusional flow and for viscous flow respectively.
γ = activity coefficient.
σ_A, σ_A = friction coefficients in eq. (2-4.5).
σ = surface tension at T^{o}K, dymes/cm.
ν^+, ν^- = frequencies of forward and backward motion of a molecule.
$\left(\frac{\lambda_1}{\xi \lambda_2 \lambda_3}\right)$ = length parameter.
ϵ , δ = Lennard-Jones Parameters, erg/molecule and A^o, respectively in eq. (3-2.1).

NOMENCLATURE (Contd.)

Superscripts

o = infinite dilution of one compartment in mixture.

$*$ = self-diffusion.

h = hole forming.

j = jumping.

$+$ = forward.

$-$ = backward.

Subscripts

A = pure component A.

B = pure component B.

b = normal boiling point.

AB = binary mixture of A and B.

c = critical.

D = diffusion.

H = hydrogen bonding.

I = dispersion.

l = liquid.

m = melting point.

X = general statement indicating either A or B.

v = vapour.

μ = viscosity.

1, 2 = indicate temperature level in equations (2-5.1), and (3-4.6), and (3-4.7).

1, 2, 3 = three dimensional indicators in λ_1, λ_2 and λ_3.

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