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HUGH DAVID ELLERTON.

INTERACTIONS IN LIQUID SYSTEMS
OF
TWO AND THREE COMPONENTS
BY
DIFFUSION AND VAPOUR PRESSURE MEASUREMENTS.

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26th June, 1966

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SUMMARY.

This thesis deals with an investigation of the behaviour of aqueous solutions containing either one or two non-electrolytes using the techniques of vapour pressure, diffusion, density and viscosity measurements. It is believed to be the first time that all these techniques have been studied together in the same laboratory for a ternary system containing two non-electrolytes.

Isopiestic vapour pressure measurements are reported for the systems water-urea and water-urea-sucrose at 25°. Osmotic and activity coefficients are calculated for the water-urea system and the deviations from ideality are discussed in terms of the association of urea. Activity coefficients are calculated for the system water-urea-sucrose. The results are discussed in terms of the association of urea and the hydration of sucrose. A theory, following the approach of Robinson and Stokes, is derived for obtaining the molal activity coefficients of the solutions in a ternary system by utilising experimental information from both the binary and ternary systems.

Isothermal ternary diffusion may be described by flow equations containing four diffusion coefficients.

Results are presented in this thesis for the diffusion coefficients of the system water-urea-sucrose at one ternary point. The diffusion data are combined with thermodynamic data from isopiestic vapour pressure measurements to compute frictional coefficients, which are independent of the frame of reference used. The Onsager Reciprocal Relation has also been tested for the one ternary point. Diffusion measurements in the binary systems water-urea and water-sucrose agree quite satisfactorily with previously reported values in the literature.

Thermodynamic measurements have been reported in the literature for the ternary system water-sucrose-mannitol, and the behaviour of the system was discussed in relation to hydration of both sucrose and mannitol. Interactions in this system are reported at four ternary points by isothermal diffusion. The concentration dependence of the diffusion coefficients has been measured, frictional coefficients are calculated and the Onsager Reciprocal Relation has been tested for the four ternary points. Binary diffusion measurements in the water-mannitol system were found to agree quite well with the values reported in the literature.

Density and relative viscosity measurements

are reported for both the water-urea-sucrose and the water-sucrose-mannitol systems, and also for the system water-thiourea. An attempt to measure solvent activities of aqueous thiourea solutions is reported.

This thesis contains no material previously submitted for a degree or diploma in any University, or any material previously written by any other person, except when due reference is made in the text.

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H.D.E.

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CHAPTER 1.

INTRODUCTION.

One of the earliest recorded observations of molecular interactions in solution has been attributed to Brown, who observed random movement in particles of microscopic size. This motion, due to thermal agitation of the particles, is the phenomenon now known as Brownian movement. Einstein showed later that diffusion in liquids was the direct consequence of Brownian movement of particles. This diffusion differs from isothermal free diffusion which is to be discussed in more detail in this thesis, in that there is no preferred direction of movement.

In the last few decades, a variety of methods has been used to study the interaction of molecules in solution. For example, measurements of the conductivity of solutions and the E.M.F.'s of electrochemical cells have revealed valuable information on the behaviour of electrolytes. However, the techniques of vapour pressure measurements, density, viscosity and diffusion may be applied to the study of both electbolytes and non-electrolytes. This thesis deals with an investigation of the behaviour of aqueous solutions containing either one or two non-electrolytes using these techniques.

The process of diffusion, from a macroscopic point of view, as against the random movement from the microscopic point of view, is brought about by some force applied to the molecules in a system. In the case of thermal diffusion, the motion is brought about by a temperature gradient in the system; for isothermal diffusion, it occurs because of a chemical potential gradient. A discussion of diffusion usually stabts with the work of Adolf Fick[1] and the phenemenological laws which now bear his name, and with the experimental work of Thomas Graham,[2] who was responsible for separating solutes by dialysis. Interacting flows brought about by gradients of chemical potential are of wide interest in the study of biological systems. Although much work in this field remains to be done in order to gain a more complete understanding of the subject, it has already been established that transport processes through cell walls and within the cell itself are dependent on the flow of potassium and sodium ions and if the flow of these ions is restricted, the functioning of the cell is severely impaired. Diffusion measurements are of biological interest also in connection with the use of the ultracentrifuge,[3] since information from diffusion measurements may be combined with sedimentation data to provide valuable information about molecular weights of proteins and other macro-molecules.

In a binary solution containing one solute component, the single diffusion coefficient provides useful information about the mobility of the solute. However, when two or more solutes are present, we no longer have a single diffusion coefficient, and the flows depend on the concentration gradients of *all* the solute components present. In ternary isothermal diffusion, for example, we measure four diffusion coefficients, two *main* diffusion coefficients analogous to the single diffusion coefficient of a binary solution, and two *cross-term* coefficients which describe the flows due to the interaction between solutes. It is these latter diffusion coefficients which are of particular interest since their magnitude may possibly give valuable information as to the nature of the intermolecular forces acting in the solution.

Diffusion in multi-component systems has become increasingly important in recent years since many systems being studied, particularly biological ones, are complex in nature and need a more refined theoretical treatment. Several years ago Fujita and Gosting[4,5] presented mathematical treatments of ternary diffusion from experiments using the Gouy diffusiometer, and more recently, Sundelöf, and also Sundelöf and Södervi have presented[6,7] general discussions of diffusion in multi-component systems. In 1963, Albright presented[8] a theory for the experimental study of ternary diffusion in liquid systems involving chemical reactions. The gravitational stability of three-component systems during free diffusion has been discussed[9] by Wendt, who has also, more recently, presented[10] equations for estimating phenomenological coefficients and diffusion coefficients for ternary systems of strong and weak electrolytes. Relations between mutual and tracer diffusion coefficients associated with a ternary system have been discussed recently by Dunlop.[11] It is interesting to note that in the last few years Kirkaldy and co-workers[12,13] have presented several discussions of a number of general theoretical problems pertaining to multicomponent diffusion in metals. Also, Lane and Kirkaldy have presented a discussion of a quasi-crystalline model of diffusion in ternary liquid systems[14] as well as a previous discussion of diffusion in multi-component substitutional alloys.[15]

The theoretical treatment of multi-component diffusion describes the solute flows in terms of the more fundamental force, the gradient of chemical potential. Thus, as will be shown in more detail in a later chapter, it is possible to write a set of phenomenological equations in which the flows of solutes in the system relative to the solvent are described in terms of gradients of chemical potentials of the solutes,[16,17] and Onsager[18,19] showed that the phenomenological coefficients, L_{ij}, of the linear relationships, for a particular frame of reference, and for $i \neq j$, were equal. This equality is known as the Onsager Reciprocal Relation (ORR).

Although the ORR is quite general, and may be applied to flows of electricity or heat, as well as flows of matter, it was not until the late 1950's that the relation was first tested[17,20-22] for ternary isothermal diffusion in liquid systems, using diffusion data previously published. A more definitive test has since been made[23] for one system, also using data published previously. In recent years several other workers have studied ternary isothermal diffusion in systems containing either two electrolytes[24-25] or an electrolyte and a non-electrolyte[26] as solute components and have tested the ORR for those systems.

The testing of the ORR for ternary systems also involves the computation of the gradients of chemical potentials. It will be shown in a later chapter that these gradients may be determined from measurements of the activity of the solvent in a ternary system. The computation of the gradients also requires a knowledge of the partial molar volumes of the components of a system; these may be determined from measurements of the densities of solutions used in diffusion measurements.

Multi-component diffusion may also be discussed in terms of a set of frictional coefficients. The advantage of this approach is that the frictional coefficients are <u>independent</u> of the frame of reference, since they depend on the <u>difference</u> of diffusion velocities. This approach has been discussed by Onsager,[27] Lamm,[28] Laity,[29] Bearman[30] and, most recently, by Dunlop,[31] the latter author having developed the necessary theory to enable the frictional coefficients to be calculated using experimental diffusion measurements and corresponding thermodynamic data.

In the last decade, isothermal diffusion measurements have been made in several three-component systems, and the diffusing species have consisted mainly of either two electrolytes or an electrolyte and a non-electrolyte as solutes. The only aqueous systems containing two non-electrolytes for which ternary diffusion experiments have been reported are the water-raffinose-urea[32] and water-sucrose-glycine[33] systems. Because there is no thermodynamic data yet available to determine accurately the chemical potential derivatives of these non-electrolyte mixtures, it has not yet been possible to make accurate calculations to test the ORR, although an estimate of the chemical potential derivatives has been made[21] for the system water-raffinose-urea using available data from the binary systems. It was found to be possible to verify the ORR for the water-raffinose-urea system within the limits of the estimated error.

The purpose of the work reported in this thesis is to present accurate diffusion data, together with the necessary density and activity data so that phenomenological coefficients may be calculated and the ORR tested for the system water-urea-sucrose. Also, diffusion and density measurements for the system water-sucrose-mannitol are presented, and the results are combined with activity data already available[34] in order that tests of the ORR may also be made for this system. Frictional coefficients have also been calculated for both three-component systems.

New activity data for the binary system water-urea is reported in this thesis. A description is also given of an attempt to measure solvent activities in the system water-thiourea, from absolute vapour pressure measurements, in the hope that a comparison could be made between thiourea and urea. Careful density and relative viscosity measurements have also been reported for the water-thiourea system. Relative viscosity measurements for both ternary systems have also been reported.

The thesis is presented so that all the non-diffusion material is discussed first, and this is followed by the diffusion work. Chapter 2 presents the activity measurements from isopiestic vapour pressure studies, whilst Chapter 3 describes the activity measurements attempted using an absolute vapour pressure apparatus. Chapter 4 presents the density and relative viscosity measurements. Chapter 5 reviews the theoretical background to the diffusion measurements, the calculation of frictional coefficients, and tests for the ORR. The experimental results of this diffusion work are presented finally in Chapters 6 and 7.

References to Chapter 1.

1. A Fick, Pogg. Ann., 94, 59 (1855).
2. T. Graham, Phil. Trans. Roy. Soc., 140, 1 (1850); 151, 183 (1861).
3. T. Svedberg and K. O. Pedersen, Eds., "The Ultracentrifuge," Oxford University Press, 1940.
4. H. Fujita and L. J. Gosting, J. Amer. Chem. Soc., 78, 1099 (1956).
5. H. Fujita and L. J. Gosting, J. Phys. Chem., 64, 1256 (1960).
6. L - O. Sundelöf, Arkiv Kemi, 20, 369 (1963).
7. L - O. Sundelöf and I. Södervi, ibid., 21, 143 (1963).
8. J. G. Albright, J. Phys. Chem., 67, 2628 (1963).
9. R. P. Wendt, ibid., 66, 1740 (1962).
10. R. P. Wendt, ibid., 69, 1227 (1965).
11. P. J. Dunlop, ibid., 69, 1693 (1965).
12. J. S. Kirkaldy, Canad. J. Phys., 35, 435 (1957), ibid., 36, 899, 907, 917 (1958), ibid., 37, 30 (1959).
13. J. S. Kirkaldy and G. R. Purdy, ibid., 40, 208 (1962).
14. J. E. Lane and J. S. Kirkaldy, Canad. J. Chem., 43, 1812 (1965).
15. J. E. Lane and J. S. Kirkaldy, Canad. J. Phys., 42, 1643 (1964).
16. J. G. Kirkwood, R. L. Baldwin, P. J. Dunlop, L. J. Gosting and G. Kegeles, J. Chem. Phys., 33, 1505 (1960).
17. P. J. Dunlop andL. J. Gosting, J. Phys. Chem., 63, 86 (1959).

18. L. Onsager, Phys. Rev., 37, 405 (1931).

19. L. Onsager, ibid., 38, 2265 (1931).

20. D. G. Miller, J. Phys. Chem., 62, 767 (1958).

21. D. G. Miller, ibid., 63, 570 (1959).

22. D. G. Miller, Chem. Revs., 60, 15 (1960).

23. D. G. Miller, J. Phys. Chem., 69, 3374 (1965).

24. P. J. Dunlop, ibid., 63, 612 (1959).

25. R. P. Wendt, ibid., 66, 1279 (1962).

26. L. A. Woolf, D. G. Miller and L. J. Gosting, J. Am. Chem. Soc., 84, 317 (1962).

27. L. Onsager, Ann. N.Y. Acad. Sci., 46, 241 (1945).

28. O. Lamm, Acta Chem. Scand., 11, 362 (1957).

29. R. W. Laity, J. Phys. Chem., 63, 80 (1959).

30. R. J. Bearman, ibid., 65, 1961 (1961).

31. P. J. Dunlop, ibid., 68, 26 (1964).

32. P. J. Dunlop, ibid., 61, 1619 (1957).

33. P. J. Dunlop and L. J. Gosting, ibid., 68, 3874 (1964).

34. R. A. Robinson and R. H. Stokes, ibid., 65, 1954 (1961).

CHAPTER 2.

ACTIVITY COEFFICIENTS FOR THE SYSTEMS UREA-WATER AND UREA-SUCROSE-WATER AT 25° FROM ISOPIESTIC MEASUREMENTS.

2.1. Introduction.

The measurement of vapour pressures and chemical activities of substances in solution is a topic that has been studied for many years, and the methods available for their estimation are numerous and quite diversified in their approach. The vapour pressure of a component is a particularly convenient measure of its activity, and the vapour pressure of water in equilibrium with an aqueous solution can be determined directly by either static or dynamic methods. One such static method will be described in the next chapter.

Once the vapour pressure as a function of molality has been determined accurately for one solution, it is not necessary to repeat absolute measurements of the activity of water for other solutions. The "isopiestic method"[1a] as introduced by Bousfield[2] and Sinclair[3] is a simple, convenient method for comparing the vapour pressures of two solutions, and is one which yields accurate results. The experimental arrangement consists of a glass desiccator containing a silver-plated copper block in good thermal contact with several dishes, as shown in the photograph, plate 2.1. The desiccator is maintained in a thermostat and rocked to agitate the solutions. When equilibrium has been reached after several days, all the solutions must have the same vapour pressure. From analyses of the solutions, including a reference solution for which the vapour pressure is accurately known as a function of molality, one then has the partial pressure of water in equilibrium with the solution being studied. Using the Gibbs-Duhem equation, one can obtain the activity coefficient of the solute as a function of molality from the determination of the vapour pressure, and therefore the activity, of the solvent in the solution. The main limitation of the isopiestic method is, of course, that it is a relative method, so that accurate information for one solute has to be obtained from an absolute method before it becomes applicable. Also, it cannot be used for solute concentrations below approximately 0.1 molal.

The isopiestic measurements made on systems in recent years have been quite diversified in the nature and field of interest. In binary systems of non-electrolytes, studies have been made in aqueous

Plate 2.1. Desiccator and silver dishes used for isopiestic vapour pressure measurements.

solutions of glycolamide,[4] urea,[5,6] sorbitol,[7] sucrose,[8] mannitol[8] and several amino acids.[9,10] The results for many electrolyte solutions have been tabulated,[1b] and an extensive range of data is now available. Considerable interest has been shown recently in tetraalkyl ammonium halides, and activity data has been obtained from E.M.F. measurements[11] and also isopiestic measurements.[12,13] The influence of the structure of electrolytes on activity coefficients has recently been discussed.[14] Also, measurements of activity coefficients have been made on methane- and ethane-sulphonic acids and their quaternary ammonium salts,[15] on several sulphonates and their derivatives[16,17] and on some polysulphonates.[18] It is interesting to note that in recent years the isopiestic technique has been extended to include aqueous salt solutions at elevated temperatures.[19]

The isopiestic vapour pressure method has been used in this work to measure solute activity coefficients in a ternary system as well as a binary system, since this information forms part of the experimental data necessary to test current theories of ternary diffusion. This technique has also been used elsewhere to study several aqueous ternary systems containing two electrolytes,[20-28] to others containing an electrolyte and a non-electrolyte,[29-34] and also to study one system containing two non-electrolytes.[35]

In this work, isopiestic vapour pressure measurements are reported for the systems urea-water and urea-sucrose-water at 25°C. Osmotic and activity coefficients have been calculated for the system urea-water, and the deviations from ideality have been discussed in terms of association of urea. In the system urea-sucrose-water, it has been found that, up to 7 molal urea and 4.3 molal sucrose, each solute component is "salted in" by the other. It is interesting to compare this with the results for the system sucrose-mannitol-water,[35] where Robinson and Stokes reported that each solute was "salted out" by the other, whereas in the system urea-NaCl-water, Bower and Robinson[33] showed that at moderate solute concentrations a very small "salting out" effect was observed, although at lower and higher concentrations the effect was one of "salting in". Also, the deviations from ideality in the sucrose-mannitol-water system were discussed[35] in terms of hydration of both solutes, whereas in the system urea-sucrose-water the behaviour will be discussed in terms of hydration of the sucrose and association of the urea. A theory will be derived for obtaining the solvent activity in a ternary system and hence the molal activity coefficients of the solutes by utilising the experimental information from both binary and ternary systems. The author acknowledges with gratitude the assistance of Dr. P. J. Dunlop in the preparation of this theory section.

2.2 Theory

Notation.

γ_1, γ_2 = molal activity coefficients of solutes 1 and 2 in a ternary solution containing components 1 and 2 with molalities m_1 and m_2, respectively.

ϕ_1, γ_1^o = molal osmotic coefficient and activity coefficient, respectively, of a binary solution containing only solute 1 at molality m_1.

ϕ_2, γ_2^o = molal osmotic coefficient and activity coefficient, respectively, of a binary solution containing only solute 2 at molality m_2.

m_R, ϕ_R = molality and molal osmotic coefficient, respectively, of the reference solution.

a_0 = activity of the solvent.

M_0 = molecular weight of solvent.

We assume that the activity coefficients of two non-electrolytes in a ternary solution may be represented by the Taylor series

$$\ln \gamma_1 = \sum_{i=0}^{\infty} \sum_{j=0}^{\infty} A_{ij}\, m_1{}^i m_2{}^j \qquad (A_{00} = 0) \qquad (2.1)$$

and

$$\ln \gamma_2 = \sum_{i=0}^{\infty} \sum_{j=0}^{\infty} B_{ij}\, m_1{}^i m_2{}^j \qquad (B_{00} = 0) \qquad (2.2)$$

where the A_{ij} and B_{ij} are not independent and are functions of the derivatives of $\ln \gamma_1$ and $\ln \gamma_2$, respectively, at $m_1 = m_2 = 0$. Our aim is to find a method for evaluating the A_{ij} and the B_{ij} from isopiestic vapour pressure measurements of ternary systems. One method has already been reported by Robinson and Stokes,[35] but their derivation is somewhat different from that given here.

We first expand equation 2.1 to include all terms of fourth order

$$\begin{aligned}\ln \gamma_1 = {} & A_{10}m_1 + A_{01}m_2 + A_{20}m_1^2 + A_{11}m_1m_2 + A_{02}m_2^2 \\ & + A_{30}m_1^3 + A_{21}m_1^2m_2 + A_{12}m_1m_2^2 + A_{03}m_2^3 \\ & + A_{40}m_1^4 + A_{31}m_1^3m_2 + A_{22}m_1^2m_2^2 + A_{13}m_1m_2^3 \\ & + A_{04}m_2^4 \end{aligned} \qquad (2.3)$$

For ternary systems it is found that further terms are generally not required to represent the experimental data. The coefficients of those terms in equation 2.3 which contain only powers of m_1 can be obtained from isopiestic measurements for the two-component system.[10] Thus the coefficients in the expression

$$\ln \gamma_1^{\circ} = A_{10}m_1 + A_{20}m_1^2 + A_{30}m_1^3 + A_{40}m_1^4 \qquad (2.4)$$

may be derived from the osmotic coefficients, ϕ_1. With the aid of equation 2.4, equation 2.3 becomes

$$\begin{aligned}\ln \gamma_1 = \ln \gamma_1^{\circ} &+ A_{01}m_2 + A_{11}m_1m_2 + A_{02}m_2^2 \\ &+ A_{03}m_2^3 + A_{21}m_1^2m_2 + A_{12}m_1m_2^2 \\ &+ A_{31}m_1^3m_2 + A_{22}m_1^2m_2^2 + A_{13}m_1m_2^3 \\ &+ A_{04}m_2^4 \end{aligned} \tag{2.5}$$

The relations between the A_{ij} and the B_{ij} may be obtained by differentiating equation 2.5 with respect to m_2 and using the cross-differentiation relation

$$\left[\frac{\partial \ln\gamma_1}{\partial m_2}\right]_{m_1} = \left[\frac{\partial \ln\gamma_2}{\partial m_1}\right]_{m_2} \tag{2.6}$$

to give, after integration,

$$\begin{aligned}\ln \gamma_2 = \ln \gamma_2^{\circ} &+ A_{01}m_1 + (A_{11}/2)m_1^2 + 2A_{02}m_1m_2 \\ &+ (A_{21}/3)m_1^3 + A_{12}m_1^2m_2 + 3A_{03}m_1m_2^2 \\ &+ (A_{31}/4)m_1^4 + (2A_{22}/3)m_1^3m_2 + (3A_{13}/2)m_1^2m_2^2 \\ &+ 4A_{04}m_1m_2^3 \end{aligned} \tag{2.7}$$

Explicit relations between the A_{ij} and the B_{ij} may be obtained by equating the corresponding coefficients in equation 2.2 when it is expanded to include terms of fourth order.

For use later in the derivation, we next write the Gibbs-Duhem relation for ternary systems in the form

$$(1000/M_0)\ d\ln a_0 + m_1 d\ln(m_1\gamma_1) + m_2 d\ln(m_2\gamma_2) = 0 \tag{2.8}$$

and recall that for a non-electrolyte in a binary solution with a volatile solvent the osmotic coefficient is defined by

$$\phi_i = -(1000/M_0 m_i)\ln a_0 \qquad (i = 1,2) \qquad (2.9)$$

Then utilising the Gibbs-Duhem relation for two-component systems and equation 2.9 we obtain

$$d(m_i\phi_i) = m_i \, d\ln(m_i\gamma_i{}^{0}) = -(1000/M_0)d\ln a_0 \qquad (2.10)$$

$$(i = 1,2)$$

Now ternary isopiestic measurements are usually performed by equilibrating a binary solution of a reference solute, R, with various solutions of a given ternary system. For the reference solution in equilibrium with a given ternary solution we may write (see equation 2.10)

$$d(\nu_R m_R \phi_R) = -(1000/M_0)d\ln a_0 \qquad (2.11)$$

and, as we shall see later, it is convenient to define

$$\Delta = [(-1000/M_0)\ \ln a_0 - m_1\phi_1 - m_2\phi_2] \qquad (2.12a)$$

or $\Delta = (\nu_R m_R \phi_R - m_1\phi_1 - m_2\phi_2)$ (2.12b)

where ν_R is the number of species given in solution by one molecule of the reference solute.

As a first step in relating Δ to the A_{ij} of equations 2.5 and 2.7 we combine the differentials of these two relations with equations 2.8, 2.10 and 2.11 and use the relation

$$d(\Delta) = d(\nu_R m_R \phi_R - m_1\phi_1 - m_2\phi_2) \qquad (2.13)$$

to give

$$\begin{aligned} d(\Delta) = d[m_1 m_2(A_{01} &+ A_{11}m_1 + 2A_{02}m_2 + 3A_{03}m_2{}^2 \\ &+ A_{21}m_1{}^2 + A_{31}m_1{}^3 + 4A_{04}m_2{}^3)] \\ &+ \tfrac{3}{2}\, d[m_1m_2(A_{12}m_1m_2)] \\ &+ \tfrac{4}{3}\, d[m_1m_2(A_{22}m_1{}^2m_2)] + 2d[m_1m_2(A_{13}m_1m_2{}^2)] \end{aligned}$$

Integration of this expression then yields

$$\begin{aligned} [\Delta/(m_1m_2)] = A_{01} &+ A_{11}m_1 + 2A_{02}m_2 \\ &+ A_{21}m_1{}^2 + (3/2)A_{12}m_1m_2 + 3A_{03}m_2{}^2 \\ &+ A_{31}m_1{}^3 + (4/3)A_{22}m_1{}^2m_2 + 2A_{13}m_1m_2{}^2 \\ &+ 4A_{04}m_2{}^3 \qquad (2.14) \end{aligned}$$

If we now compare this relation with the series expansion for $(\partial \ln\gamma_1/\partial m_2)_{m_1}$ which may be derived from equation 2.5 we obtain

$$\begin{aligned} \left[\frac{\partial \ln\gamma_1}{\partial m_2}\right]_{m_1} = \left[\frac{\partial \ln\gamma_2}{\partial m_1}\right]_{m_2} &= \frac{\Delta}{m_1m_2} + \frac{1}{2}A_{12}m_1m_2 + \frac{2}{3}A_{22}m_1{}^2m_2 \\ &\quad + A_{13}m_1m_2^2 \qquad (2.15) \end{aligned}$$

and for the special case that $A_{12} = A_{22} = A_{13} = 0$

equation 2.15 is identical with the relation derived previously by Robinson and Stokes[35]

$$\left[\frac{\partial \ln \gamma_1}{\partial m_2}\right]_{m_1} = \left[\frac{\partial \ln \quad {}_2}{\partial m_1}\right]_{m_2} = \frac{\Delta}{m_1 m_2} \qquad (2.16)$$

Now an inspection of equations 2.12 and 2.14 will show that the $[\Delta/(m_1 m_2)]$ values can be measured directly by the isopiestic method and the coefficients A_{ij} can be found by the method of least squares. Thus the concentration dependencies of γ_1 and γ_2 for ternary systems (see equations 2.5 and 2.7) can be obtained if γ_1° and γ_2° have also been measured as functions of m_1 and m_2 , respectively.

2.3 Experimental.

A. Materials.

Urea was obtained from British Drug Houses, and the Analar grade material was once recrystallised from doubly-distilled water. Samples which had been once and twice recrystallised were shown by the isopiestic method[1a] to be identical.

Sucrose was B.D.H. micro-analytical grade and was used without further purification.

Sodium chloride (reference solute) was from the same sample as described previously.[10] This had been recrystallised once from water, dried in a vacuum, and fused in a platinum crucible. Samples once, twice and three times recrystallised had been shown to be isopiestically identical.

The solutions were prepared gravimetrically, and the weights corrected to vacuum[36] assuming the density of the stainless steel weights to be 7.76 gm/c.c. The density of air at the time of weighing, which is also required in order to correct the weights to vacuum, was calculated by the method described in the "Handbook of Chemistry and Physics." Doubly-distilled demineralised water was used as solvent. The densities of solid sodium chloride, urea and sucrose for vacuum corrections were taken as 2.165, 1.335 and 1.588 gm/c.c., respectively, whilst the corresponding molecular weights used were 58.443, 60.056, and 343.303, respectively.[38]

B. Apparatus.

The apparatus used was the same as that which has been described previously.[10] The dishes used for containing the solutions were made of silver, the bases of which had been ground and polished to a high degree of flatness. About 5 mls. of the solution whose solvent activity we wished to determine were added by means of a pipette to each of 3 or 4 of the cylindrical silver dishes. Each dish was approximately 3.5 cm. in diameter and 2 cm. in height, and each had a lid which had been ground so as to fit perfectly. A similar quantity of the reference solution was placed in another set of silver dishes. The dishes, with lids removed, were placed on a flat, silver-plated copper block contained in a vacuum desiccator and evacuated to a pressure of approximately 25 mm. of mercury, using a Metrovac vacuum pump. The evacuation process was generally carried out in stages for as long as 24 hours for newly prepared solutions to avoid splattering, although shorter periods were used for solutions that were being evacuated for the second or third time. The solutions were then allowed to equilibrate under vacuum for five or six days in a large thermostat bath at 25°, controlled to approximately ± 0.002°,[39] before being reweighed. Each dish contained three stainless steel ball bearings to assist equilibration while the desiccator was being rocked in the thermostat bath. The actual temperature shown by the thermometer was adjusted from day to day according to the barometric pressure, as it was found from measurements in a pressure chamber that the thermometer reading increased 0.003°C for every centrimetre increase in atmospheric pressure.

Generally, several solute compositions, containing urea and sucrose in varying proportions, were equilibrated with the same reference solution. Samples of each solution were present in triplicate dishes, and the sodium chloride reference solute was present either in triplicate or quadruplicate. A set of dishes containing urea only accompanied most runs. Thus, a total of 21 or 22 dishes were usually equilibrated together at the one time. The concentrations of unknown and reference solutions were prepared initially so as to be fairly close to the anticipated equilibrium value.

For ternary solutions containing a total solute concentration of approximately 1 molal or less, some difficulty was experienced in attaining equilibrium, due to bacterial activity. To overcome this problem, extra precautions were taken in cleaning and sterilising the apparatus, and the water used as solvent for the solutions was distilled once more.

The solutions were accepted as being at equilibrium if the molalities of a particular set differed by not more than 0.1%, but as an additional precaution, the desiccator containing the solutions was re-evacuated and the solutions were allowed to equilibrate for a further 3 days and were then reweighed. In some cases, the solutions were concentrated further by pumping under vacuum for a prolonged period of time. They were then allowed to re-equilibrate for six days, after which the solutions were re-weighed. A further check weighing was made after another three days' equilibration.

2.4 Results.

A. The system Urea-water.

Isopiestic data for the system urea-water have been previously reported by Scatchard, Hamer and Wood.[5] It was decided, however, to make a completely new set of measurements concurrently with the work on the three-component system. All experiments were performed either in triplicate or quadruplicate, and the technique of prolonged pumping to concentrate the solutions as described above was found particularly useful at the higher urea concentrations. The molality of a saturated urea solution was found to be 20.027, which may be compared with a value of 20.007 obtained by Scatchard et al.[5] Table 2.1 gives the molalities of urea solutions in isopiestic equilibrium with sodium chloride solutions. In this work, 0, 1 and 2 are used to designate water, urea and sucrose, respectively.

The osmotic coefficients of urea solutions up to 7 molal (the region covered by the three-component work) can be represented by the equation[40]

$$\phi_1 = 1 - 0.043702m_1 + 0.006348m_1^2 - 0.000695m_1^3 + 0.000034m_1^4 \quad (m_1 \leq 7) \quad (2.17)$$

with an average deviation of ± 0.047%. The osmotic coefficients over the complete concentration range are

TABLE 2.1

ISOPIESTIC SOLUTIONS OF UREA AND SODIUM CHLORIDE AT 25°

m_1	ϕ_1	m_R
0.2054	0.9909	0.1093
0.2101	0.9895	0.1117
0.4071	0.9835	0.2168
0.4137	0.9838	0.2204
0.6100	0.9765	0.3234
0.6192	0.9763	0.3282
0.8094	0.9682	0.4258
0.8365	0.9658	0.4397
1.0280	0.9613	0.5361
1.0372	0.9607	0.5405
1.4238	0.9493	0.7294
1.4374	0.9486	0.7357
1.9905	0.9333	0.9932
2.0015	0.9345	0.9997
2.4309	0.9228	1.1901
2.4509	0.9220	1.1984
2.4848	0.9206	1.2125
2.5035	0.9202	1.2207
2.9434	0.9105	1.4081
2.9922	0.9099	1.4290
3.8354	0.8937	1.7660
3.8590	0.8931	1.7748
4.9354	0.8757	2.1754
4.9638	0.8757	2.1865
5.3814	0.8691	2.3322
5.4766	0.8676	2.3648
5.8135	0.8634	2.4805
5.8638	0.8627	2.4973
6.0428	0.8601	2.5564
6.0930	0.8596	2.5737
6.3962	0.8557	2.6725
6.4421	0.8555	2.6883
6.8203	0.8505	2.8086
6.8760	0.8502	2.8272
7.1813	0.8469	2.9233
7.2449	0.8460	2.9426
7.9257	0.8387	3.1496
8.0696	0.8374	3.1930
9.8320	0.8236	3.7008
9.9048	0.8235	3.7223
12.0781	0.8093	4.2955
12.1676	0.8088	4.3181
14.0050	0.7991	4.7678
14.1703	0.7981	4.8061
15.6122	0.7905	5.1340
16.0436	0.7886	5.2299
18.1145	0.7819	5.6852
18.3441	0.7802	5.7288
19.8828	0.7753	6.0482
20.0270	0.7750	6.0783

best represented by the extended equation

$$\phi_1 = 1 - 0.043384m_1 + 0.006122m_1^2 - 0.000703m_1^3 + 0.000052m_1^4 - 0.0000020m_1^5 \quad (m_1 < 20) \qquad (2.18)$$

with an average deviation of ± 0.054% .

The corresponding activity coefficients of urea may be obtained[10] from the relation

$$\ln \gamma_1^{\circ} = \sum_{i=1}^{5} \frac{(i+1)}{i} E_i m_1^{i} \qquad (2.19)$$

where the E_i are the coefficients of the m_1^{i} terms in equation 2.18, and hence

$$\ln \gamma_1^{\circ} = - 0.086768m_1 + 0.009183m_1^2 - 0.000937m_1^3 + 0.000065m_1^4 - 0.0000024m_1^5 \qquad (2.20)$$

Since this work was commenced, Bower and Robinson[6] have published a limited amount of data for the urea-water system. Their results are substantially in agreement with this work, particularly at lower concentrations, although at higher concentrations their osmotic coefficients for some points show a scatter of as much as ± 0.6% from the data presented here. For example, at $m_1 = 10.427$, Bower and Robinson's experimental data gave $\phi_1 = 0.8141$, whereas from this work, a value of $\phi_1 = 0.8188$ was obtained. Likewise, at $m_1 = 18.041$, Bower and Robinson obtained $\phi_1 = 0.784_7$ whereas $\phi_1 = 0.779_3$ from this work.

B. The System Sucrose-water.

Accurate isopiestic data for the sucrose-water system have been published recently by Robinson and Stokes,[35] and their equation 2.5 for the relationship of osmotic coefficient to molality was used throughout this work,

$$\phi_2 = 1 + 0.07028m_2 + 0.01847m_2^2$$
$$- 0.004045m_2^3 + 0.000228m_2^4 \quad (m_2 < 5.8) \quad (2.21)$$

C. The System Urea-Sucrose-water.

The equilibrium molalities of urea and sucrose mixtures and the reference sodium chloride solution are given in Table 2.2 . Also given in this table are values of the experimental quantity $[\Delta/(m_1m_2)]$, which is derived from equation 2.12 . Values of ϕ_R were interpolated from data already published,[1c] whilst ϕ_1 and ϕ_2 were obtained from equations 2.18 and 2.20, respectively. Column 4 of Table 2.2 gives the values of $[\Delta/(m_1m_2)]$ calculated from the least square equation 2.24 . The last column gives the percentage error in the molality of the reference solution which would account for the difference between the experimental and computed values of $[\Delta/(m_1m_2)]$. This percentage error is defined[29] by

TABLE 2.2
THE SYSTEM: UREA-SUCROSE-WATER.

m_1	m_2	$\frac{\Delta}{m_1 m_2}^{\dagger}$ (Expt)	$\frac{\Delta}{m_1 m_2}^{\dagger}$ (Calc)	m_R	%
.1635	.3500	-.11737	-.11740	.2793	.00
.1663	.3561	-.11629	-.11726	.2843	-.01
.2711	.2493	-.11266	-.11755	.2790	-.06
.2749	.2528	-.11523	-.11744	.2828	-.02
.3747	.1459	-.12288	-.11785	.2764	.05
.3807	.1483	-.11725	-.11772	.2810	.00
.4573	.0631	-.11656	-.11812	.2759	.00
.4650	.0642	-.11299	-.11799	.2806	-.02
.1456	.8355	-.10884	-.10991	.5558	-.01
.3386	.6791	-.11058	-.10955	.5558	.02
.1443	.8277	-.11464	-.11005	.5501	.05
.3354	.6728	-.11531	-.10969	.5501	.12
.5482	.4976	-.11296	-.10947	.5544	.09
.7473	.2925	-.10819	-.11008	.5429	-.04
.9224	.1227	-.11420	-.11058	.5429	.04
.7552	.2956	-.10567	-.10992	.5486	-.09
.9320	.1240	-.10772	-.11042	.5486	-.03
.2500	1.4587	-.10566	-.09977	.9931	.11
.6092	1.2075	-.09669	-.09813	.9931	-.05
1.0149	.9011	-.09552	-.09700	.9931	-.07
1.7810	.2214	-.09911	-.09774	.9931	.02
.2515	1.4671	-.10304	-.09965	.9997	.06
.6134	1.2159	-.09763	-.09796	.9997	-.01
1.0231	.9084	-.09776	-.09678	.9997	.04
1.4745	.5257	-.09546	-.09670	.9997	-.05
1.7927	.2229	-.09611	-.09758	.9997	-.03
.2960	1.7270	-.09499	-.09586	1.1900	-.01
.7292	1.4452	-.09185	-.09344	1.1900	-.07
1.2291	1.0913	-.09254	-.09158	1.1900	.05
1.7873	.6372	-.09155	-.09112	1.1900	.02
2.1783	.2708	-.09402	-.09214	1.1900	.04
.2982	1.7395	-.09812	-.09569	1.1984	.05
.7348	1.4565	-.09345	-.09322	1.1984	.01
1.2392	1.1003	-.09356	-.09132	1.1984	.13
1.8022	.6425	-.09225	-.09086	1.1984	.07
2.1961	.2730	-.09479	-.09190	1.1984	.07
.4552	1.9574	-.08877	-.09112	1.4080	-.07
.9598	1.6455	-.08607	-.08801	1.4080	-.11
1.9423	.9443	-.08410	-.08485	1.4080	-.05
1.2840	1.4307	-.08535	-.08648	1.4080	-.07
2.5049	.4571	-.08667	-.08546	1.4080	.05
.4621	1.9872	-.09207	-.09070	1.4289	.04
.9746	1.6710	-.08643	-.08752	1.4289	-.06
1.3028	1.4517	-.08359	-.08599	1.4289	-.16
1.9727	.9591	-.08239	-.08429	1.4289	-.13
2.5464	.4647	-.08501	-.08488	1.4289	.00
.4116	2.4013	-.08800	-.08727	1.6887	.02

TABLE 2.2 (CONT.)

m_1	m_2	$\frac{\Delta}{m_1 m_2}^{\dagger}$ (Expt)	$\frac{\Delta}{m_1 m_2}^{\dagger}$ (Calc)	m_R	%
1.0345	2.0505	-.08128	-.08264	1.6887	-.08
1.7838	1.5838	-.07818	-.07863	1.6887	-.03
2.6527	.9458	-.07595	-.07682	1.6887	-.06
3.2611	.4055	-.07847	-.07815	1.6887	.01
.4159	2.4264	-.08775	-.08699	1.7074	.02
1.0463	2.0738	-.08133	-.08226	1.7074	-.06
1.8054	1.6030	-.07792	-.07816	1.7074	-.02
2.6880	.9584	-.07605	-.07627	1.7074	-.01
3.3045	.4109	-.07798	-.07763	1.7074	.02
.6069	2.4073	-.08169	-.08466	1.7660	-.12
1.3371	1.9962	-.07894	-.07947	1.7660	-.04
2.1204	1.4915	-.07421	-.07584	1.7660	-.15
2.7396	1.0366	-.07326	-.07469	1.7660	-.11
3.1214	.7179	-.07317	-.07503	1.7660	-.12
3.4380	.4246	-.07424	-.07609	1.7660	-.07
3.5872	.2790	-.07894	-.07683	1.7660	.06
3.7205	.1370	-.08454	-.07776	1.7660	.10
.6099	2.4194	-.08229	-.08452	1.7747	-.09
1.3439	2.0064	-.07877	-.07928	1.7747	-.03
2.1322	1.4999	-.07415	-.07561	1.7747	-.13
2.7560	1.0428	-.07334	-.07444	1.7747	-.09
3.1411	.7225	-.07362	-.07476	1.7747	-.07
3.4592	.4273	-.07461	-.07584	1.7747	-.05
3.6071	.2806	-.07753	-.07661	1.7747	.02
3.7417	.1378	-.08301	-.07754	1.7747	.08
.6117	3.0066	-.07857	-.07985	2.1753	-.05
2.4134	2.0333	-.06581	-.06691	2.1753	-.12
4.0646	.8637	-.06266	-.06409	2.1753	-.11
.6147	3.0214	-.07842	-.07971	2.1864	-.05
1.4691	2.5875	-.07059	-.07254	2.1864	-.16
2.4286	2.0461	-.06622	-.06662	2.1864	-.04
3.2774	1.4897	-.06243	-.06379	2.1864	-.15
4.0885	.8688	-.06206	-.06381	2.1864	-.14
4.5572	.4456	-.06474	-.06559	2.1864	-.03
.6539	3.2141	-.07625	-.07799	2.3321	-.07
2.6051	2.1948	-.06329	-.06343	2.3321	-.01
3.5329	1.6059	-.05976	-.06014	2.3321	-.04
4.4253	.9403	-.05968	-.06003	2.3321	-.03
4.9365	.4827	-.06169	-.06201	2.3321	-.01
.6630	3.2589	-.07690	-.07761	2.3647	-.03
1.5932	2.8060	-.06902	-.06948	2.3647	-.04
2.6498	2.2324	-.06411	-.06265	2.3647	.18
3.5971	1.6351	-.06051	-.05924	2.3647	.15
4.5031	.9569	-.05939	-.05919	2.3647	.01
.6947	3.4149	-.07671	-.07635	2.4805	.01
1.6728	2.9461	-.06697	-.06763	2.4805	-.06
2.7900	2.3506	-.06139	-.06026	2.4805	.14

TABLE 2.2 (CONT.)

m_1	m_2	$\frac{\Delta}{m_1 m_2}^{\dagger}$ (Expt)	$\frac{\Delta}{m_1 m_2}^{\dagger}$ (Calc)	m_R	%
3.8001	1.7273	-.05764	-.05650	2.4805	.15
4.7783	1.0153	-.05754	-.05629	2.4805	.12
.6993	3.4374	-.07663	-.07618	2.4972	.02
1.6845	2.9669	-.06683	-.06737	2.4972	-.05
2.8110	2.3683	-.06121	-.05990	2.4972	.17
3.8311	1.7415	-.05753	-.05609	2.4972	.19
4.8197	1.0241	-.05751	-.05587	2.4972	.16
.6400	3.5475	-.07516	-.07636	2.5564	-.05
2.9908	2.3638	-.05870	-.05820	2.5564	.06
4.4204	1.4567	-.05517	-.05409	2.5564	.13
5.4515	.6247	-.05643	-.05630	2.5564	.00
.6443	3.5712	-.07542	-.07619	2.5736	-.03
1.7163	3.0673	-.06494	-.06639	2.5736	-.14
3.0144	2.3824	-.05875	-.05782	2.5736	.12
4.4574	1.4689	-.05504	-.05366	2.5736	.17
5.4960	.6298	-.05566	-.05592	2.5736	-.01
.6689	3.7076	-.07587	-.07528	2.6724	.02
3.1427	2.4838	-.05690	-.05583	2.6724	.15
4.6648	1.5373	-.05305	-.05134	2.6724	.22
5.7678	.6609	-.05406	-.05370	2.6724	.02
.6723	3.7263	-.07397	-.07516	2.6882	-.05
3.1641	2.5007	-.05686	-.05551	2.6882	.19
4.6994	1.5487	-.05299	-.05096	2.6882	.26
5.8093	.6657	-.05340	-.05337	2.6882	.00
.7020	3.8907	-.07341	-.07418	2.8086	-.03
1.8794	3.3590	-.06221	-.06303	2.8086	-.08
6.1464	.7043	-.05178	-.05079	2.8086	.07
.7066	3.9164	-.07335	-.07403	2.8272	-.03
1.8923	3.3820	-.06196	-.06278	2.8272	-.08
6.1951	.7099	-.05074	-.05044	2.8272	.02
.7297	4.0448	-.07055	-.07335	2.9233	-.13
1.9588	3.5008	-.06046	-.06154	2.9233	-.12
6.4667	.7410	-.04891	-.04852	2.9233	.03
.7350	4.0737	-.07182	-.07320	2.9426	-.06
1.9740	3.5280	-.06108	-.06126	2.9426	-.01
6.5251	.7477	-.04912	-.04812	2.9426	.08
.2083	3.1172	-.08338	-.08431	2.1197	-.01
4.6045	.2007	-.06716	-.06880	2.1197	-.03
.2100	3.1431	-.08878	-.08412	2.1370	.07
4.6496	.2027	-.06569	-.06840	2.1370	-.06
.2410	3.6067	-.08323	-.08110	2.4757	.03
5.5874	.2435	-.05920	-.06064	2.4757	-.03
.2430	3.6375	-.08669	-.08092	2.4967	.10
5.6473	.2461	-.05871	-.06019	2.4967	-.04
.2843	4.2556	-.08068	-.07823	2.9416	.04
6.9685	.3037	-.04840	-.05156	2.9416	-.10
.2869	4.2933	-.08005	-.07811	2.9686	.03
7.0566	.3076	-.04957	-.05108	2.9686	-.05

† The fourth and fifth decimals were retained to minimise ‘rounding off’ errors in the least squaring of the data.

$$\text{Diff. \%} = 100 \quad \frac{[m_{R(\text{calc.})} - m_{R(\text{expt.})}]}{m_{R(\text{expt.})}} \qquad (2.22)$$

where

$$m_{R(\text{calc.})} = [(m_1\phi_1 + m_2\phi_2 + \Delta_{\text{calc.}}) / (\nu_R\phi_R)] \qquad (2.23)$$

$\Delta_{\text{calc.}}$ can be derived from column 4. ϕ_R is assumed to remain constant for small changes in m_R, and when sodium chloride solutions are used as reference solute, $\nu_R = 2$.

Now, in order to evaluate the cross-differential (equation 2.15), it is necessary to fit the values of $[\Delta/(m_1m_2)]$, derived experimentally from equation 2.12, to a power series in m_1 and m_2 with the form of equation 2.14. Four different polynomials were tried, involving terms up to either squares or cubes in m_1 and m_2, both with and without cross-terms present.[41] The series that best represented the data was

$$\frac{\Delta}{m_1m_2} = -0.12597 + 0.015004m_1 + 0.018236m_2$$
$$- 0.000710m_1^2 - 0.000500m_1m_2 - 0.001848m_2^2$$
$$(m_1<7.0,\ m_2<4.3) \qquad (2.24)$$

with an average deviation of ± 0.0015. Surprisingly, the cubic series with cross-terms gave the greatest average deviation, while the two series without cross-terms had average deviations between these two. The other three series, and their average deviations, are as follows:

$$\frac{\Delta}{m_1m_2} = -0.1346_6 + 0.025808m_1 + 0.021479m_2 - 0.004691m_1^2 + 0.000682m_1m_2 - 0.001052m_2^2 + 0.000436m_1^3 - 0.000695m_1^2m_2 + 0.000158m_1m_2^2 - 0.000499m_2^3 \qquad (2.24a)$$

Average deviation = ± 0.0035

$$\frac{\Delta}{m_1m_2} = -0.1244_6 + 0.014061m_1 + 0.016749m_2 - 0.000622m_1^2 - 0.001615m_2^2 \qquad (2.24b)$$

Average deviation = ± 0.0016

$$\frac{\Delta}{m_1m_2} = -0.1253_2 + 0.016341m_1 + 0.016357m_2 - 0.001536m_1^2 - 0.001434m_2^2 + 0.000093m_1^3 - 0.000025m_2^3 \qquad (2.24c)$$

Average deviation = ± 0.0016

An equation involving the first powers only in m_1 and m_2 [42] was also found to represent the data quite well. Computer programme listings may be found in the appendix for the calculation of Δ/m_1m_2 from equation 2.12, for the calculation of percentage differences from equations 2.22 and 2.23, and for the least-squared equations of Δ/m_1m_2 versus m_1 and m_2 (equations 2.24

and 2.24a). The variations of Δ/m_1m_2 with m_1 and m_2 are illustrated by the three-dimensional diagram, Figure 2.1 .

Activity coefficients for the ternary system may be determined from a knowledge of the values of the coefficients of equation 2.24 . Thus from equations 2.5, 2.14 and 2.24, we obtain

$$\begin{aligned} \ln \gamma_1 \;=\; & \ln \gamma_1{}^{o} - 0.12597m_2 + 0.015004m_1m_2 \\ & + 0.009118m_2{}^2 - 0.000616m_2{}^3 \\ & - 0.000710m_1{}^2m_2 - 0.000333m_1m_2{}^2 \qquad (2.25) \end{aligned}$$

and from equations 2.7, 2.14 and 2.24,

$$\begin{aligned} \ln \gamma_2 \;=\; & \ln \gamma_2{}^{o} - 0.12597m_1 + 0.007502m_1{}^2 \\ & + 0.018236m_1m_2 - 0.001848m_1m_2{}^2 \\ & - 0.000237m_1{}^3 - 0.000333m_1{}^2m_2 \qquad (2.26) \end{aligned}$$

2.5 Discussion.

A. The System Urea-water.

The deviations from ideality of the water activity of urea solutions have been discussed previously by Schellman[43] . The negative heat of dilution of the polar urea molecule was attributed to intermolecular hydrogen bonding between CO and NH groups. Using the activity data of Scatchard *et al*.[5] and the heat of

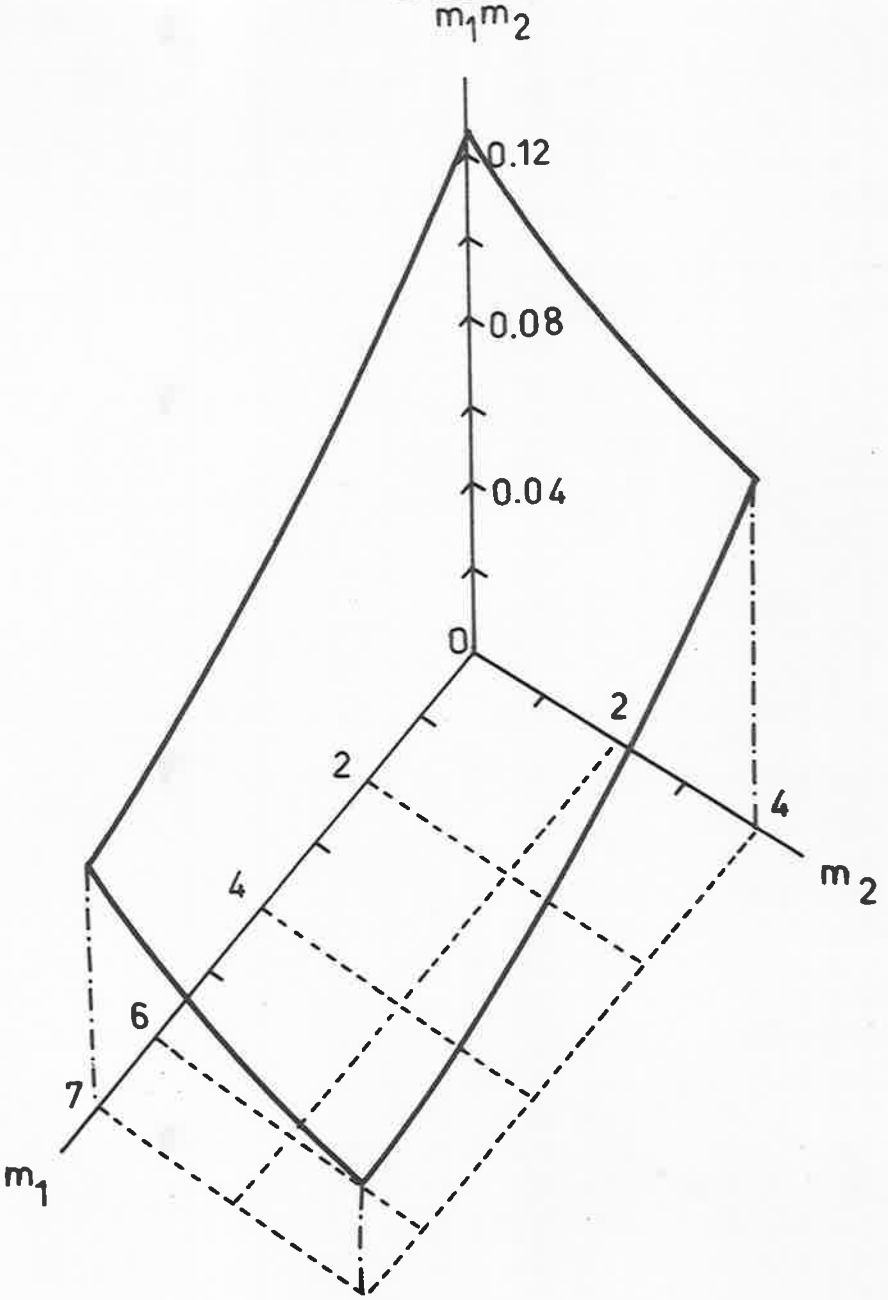

Figure 2.1. Variation of the term Δ/m_1m_2 with m_1 and m_2 for the system water-urea-sucrose.

dilution of Gucker and Pickard[44], Schellman obtained the enthalpy of formation of an amide hydrogen bond in water,[43] and later extended the work to discuss the stability of hydrogen bonding in peptides.[45]

Kresheck and Scheraga,[46] in an extension of Schellman's work, have discussed the temperature dependence of the enthalpy of formation of the amide hydrogen bond, and have pointed out that it may be possible to account for the non-ideal behaviour of aqueous urea solutions by mechanisms other than dimerisation, trimerisation, etc. Nevertheless, T'so, Melvin and Olson,[47] in a binary study of aqueous purine and nucleoside solutions, consider that it is reasonable to assume that the large lowering of osmotic and activity coefficients in those systems may be ascribed to association.

If it is assumed that urea forms a series of dimers, trimers, etc. in water, we may write

$$\begin{aligned} &U + U \rightarrow U_2 \\ &U_2 + U \rightarrow U_3 \qquad\qquad (2.27) \\ &\cdots\cdots\cdots\cdots \end{aligned}$$

so that m_U, m_{U_2},.... etc. are equilibrium concentrations of monomer, dimer, etc. If we further assume, as our data suggest, that at low concentrations dimerisation is the important step, then the equilibrium constant, K, may be written

$$K = \frac{m_{U_2}}{(m_U)^2} \qquad (2.28)$$

Hence the total molality, $(m_1)_T$, of urea (monomer and dimer) in a solution at equilibrium is

$$\begin{aligned} (m_1)_T &= m_U + m_{U_2} \\ &= m_U + K(m_U)^2 \qquad (2.29) \end{aligned}$$

A value for $(m_1)_T$ may be obtained from the known stoichiometric molality, m_1, of the solution, since

$$m_1 = m_U + 2K(m_U)^2 \qquad (2.30)$$

and hence, using equations 2.29 and 2.30,

$$(m_1)_T = \frac{4Km_1 - 1 + \sqrt{1 + 8Km_1}}{8K} \qquad (2.31)$$

Now, if dimerisation is regarded as the cause for departure from ideality of aqueous urea solutions, then the corresponding water activities are given by

$$a_0 = [1 + 0.001M_0(m_1)_T]^{-1} \qquad (2.32)$$

and hence equation 2.9 becomes

$$\phi_1 = [1000/(M_0 m_1)] \ln [1 + 0.001M_0(m_1)_T] \qquad (2.33)$$

Values of ϕ_1 were computed for various values of K over a range of m_1 values, using equations 2.31 and 2.33 . A listing of the computer programme used may be found in the appendix. It was found that, up to approximately 2 molal, a value of K = 0.032 gave agreement with experimental results to 0.1% or better. At higher urea concentrations, the values of ϕ_1 corresponding to K = 0.032 deviate from the experimental values increasingly with increase of m_1, which suggests that the formation of trimer, etc., is becoming more important. Nevertheless, the results show that at low concentrations, the deviations from ideality of aqueous urea solutions can be adequately described in terms of a single equilibrium constant of dimerisation, and even at 4 molal the calculated osmotic coefficient differs from the observed value by only 0.7%. Our value of K = 0.032 may be compared with K = 0.041 obtained by Schellman.[43] The reasons for the difference in these values are probably twofold. Firstly, Schellman used the activity data of Scatchard et al.,[5] whose points, at low concentrations, show some scatter, and secondly, Schellman's calculations are based on the assumption that equilibrium constants for the formation of dimer, trimer, etc. are identical.

B. The System Urea-Sucrose-Water.

The deviations from ideality of the water activity of sucrose-water solutions have been discussed previously by Scatchard,[48] and more recently by Robinson and Stokes[35] in terms of a hydration number, h, the number of moles of water bound to one mole of component 2 (sucrose). Thus, if we have a solute of stoichiometric molality m_2 in which h moles of water are bound to each mole of component 2, we may write the activity of water in the binary solution as

$$a_0 = \frac{\dfrac{1000}{M_0} - hm_2}{\dfrac{1000}{M_0} - hm_2 + m_2} \qquad (2.34)$$

and hence

$$-(1000/M_0)\ln a_0 = -\frac{1000}{M_0}\ln\left[\frac{1 - 0.001M_0hm_2}{1 - 0.001M_0m_2(h-1)}\right] \qquad (2.35)$$

so that, using equation 2.9, this becomes

$$\phi_2 = -\frac{1000}{M_0m_2}\ln\left[\frac{1 - 0.001\ M_0hm_2}{1 - 0.001\ M_0m_2\ (h-1)}\right] \qquad (2.36)$$

Robinson and Stokes[35] expanded the logarithmic term to give

$$\phi_2 = 1 + 0.018(h - \tfrac{1}{2})m_2 + (0.018)^2(h^2 - h + \tfrac{1}{3})m_2{}^2 \qquad (2.37)$$

The coefficient of the term containing the first power in m_2 in equation 2.37 was then related to the corresponding experimentally determined coefficient (equation 2.21) to solve for h, and a value of h = 4.61 was obtained.

In the course of describing the results for the urea-sucrose-water system, we tried fitting the sucrose-water data of Robinson and Stokes[35] to equation 2.36 to obtain h for known values of m_2 and ϕ_2. The purpose here was to avoid having to neglect terms containing higher powers in m_2, as was the case in the method discussed by Robinson and Stokes.[35] An average value of h = 4.86, with variation of ± 0.05 up to approximately two molal was obtained, but at higher concentrations the value of h became gradually lower, although even for a near-saturated 6 molal solution the water activity could still, according to equation 2.21, be ascribed a hydration number of 3.6, if one assumes that even at higher concentrations the main deviation from ideality is still due to hydration.

Now, if association of urea and hydration of sucrose can be used to describe the deviations from ideality of the activity of water in the two-component systems, it might be expected that a simple combination of these phenomena would describe the solvent activities of solutions in a ternary system. We therefore next derive an expression for the solvent activity for a ternary system in which one solute is hydrated and the other associates to give dimers. If m_1 and m_2 are the stoichiometric molalities of the two components, and if we assume that component 2 is hydrated, then the new molalities of the two components are given by

$$m_1' = m_1(1 - 0.001\ hm_2M_0)^{-1} \qquad (2.38)$$

and

$$m_2' = m_2(1 - 0.001\ hm_2M_0)^{-1} \qquad (2.39)$$

Now, if we also assume that component 1 (urea) associates to form dimers then the new <u>total</u> molality of component 1, $(m_1')_T$, is given by the relation (see equation 2.31)

$$(m_1')_T = \frac{4Km_1' - 1 + \sqrt{1 + Km_1'}}{8K} \qquad (2.40)$$

Thus, for the ternary system,

$$a_0 = [1 + 0.001\ M_0\ [(m_1')_T + m_2']]^{-1} \qquad (2.41)$$

Hence the activity of water in the ternary system may be evaluated using equation 2.41 for any given values of K and h. $(m_1')_T$ and m_2' may be determined from equations 2.38 to 2.40 .

The aim of the next part of this work was to calculate the values of K and h which best represented the experimental water activities in the ternary solutions and which were also consistent with the values of K and h in the binary systems. Equation 2.24 was used to obtain values of A and hence, using equation 2.12a, the experimental solvent activities, a_0, for various values of m_1 and m_2. The osmotic coefficients, ϕ_1 and ϕ_2, which are needed in equation 2.12a, were obtained from equations 2.33 and 2.36 . Corresponding theoretical values for a_0 were calculated by equation 2.41 . A large range of values of K and h were selected in order to determine, if possible, solvent activities which best agreed with the experimental data. Using these values of K and h, experimental and theoretical values for a_0 were calculated for twenty-five compositions of the system with $m_1 < 2$ and $m_2 < 2$. An I.B.M. 1620 computer was used for all calculations; a programme listing may be found in the appendix.

It was not possible to obtain agreement between the experimental values of a_0 and those calculated by using the binary values for K and h in equation 2.41 . It was also impossible to obtain agreement either by holding K constant and varying h or by holding h constant and varying K.

Table 2.3 illustrates the type of computation made, when K was kept constant at 0.032, and h was varied from 0 to 4.86. If we select values of solvent

TABLE 2.3
EXAMPLES OF THE VARIATION OF SOLVENT ACTIVITY WITH K AND H FOR THE SYSTEM UREA-SUCROSE-WATER

m_1	m_2	a_0(expt)	a_0(calc)	a_0(diff)	
K= .032	H= .00				
.25000	.25000	.99112	.99110	-.00002	
.50000	.25000	.98693	.98680	-.00012	
1.00000	.25000	.97879	.97846	-.00032	
1.50000	.25000	.97094	.97046	-.00047	
2.00000	.25000	.96334	.96276	-.00057	
.25000	.50000	.98652	.98670	.00017	
.50000	.50000	.98246	.98243	-.00003	
1.00000	.50000	.97456	.97417	-.00039	
1.50000	.50000	.96692	.96624	-.00068	
2.00000	.50000	.95950	.95860	-.00089	
.25000	1.00000	.97675	.97801	.00126	
.50000	1.00000	.97292	.97381	.00089	
1.00000	1.00000	.96545	.96570	.00024	
1.50000	1.00000	.95819	.95790	-.00028	
2.00000	1.00000	.95108	.95039	-.00068	
.25000	1.50000	.96614	.96947	.00332	
.50000	1.50000	.96253	.96534	.00281	
1.00000	1.50000	.95544	.95737	.00192	
1.50000	1.50000	.94850	.94971	.00121	
2.00000	1.50000	.94166	.94233	.00066	
.25000	2.00000	.95472	.96107	.00635	
.50000	2.00000	.95130	.95702	.00572	
1.00000	2.00000	.94455	.94918	.00463	
1.50000	2.00000	.93789	.94165	.00375	AV DIF
2.00000	2.00000	.93130	.93440	.00309	= 0.00162
K= .032	H= 1.00				
.25000	.25000	.99112	.99106	-.00006	
.50000	.25000	.98693	.98674	-.00018	
1.00000	.25000	.97879	.97837	-.00041	
1.50000	.25000	.97094	.97034	-.00060	
2.00000	.25000	.96334	.96260	-.00073	
.25000	.50000	.98652	.98658	.00005	
.50000	.50000	.98246	.98227	-.00018	
1.00000	.50000	.97456	.97395	-.00061	
1.50000	.50000	.96692	.96595	-.00097	
2.00000	.50000	.95950	.95825	-.00124	
.25000	1.00000	.97675	.97761	.00086	
.50000	1.00000	.97292	.97335	.00042	
1.00000	1.00000	.96545	.96510	-.00035	
1.50000	1.00000	.95819	.95718	-.00100	
2.00000	1.00000	.95108	.94956	-.00152	
.25000	1.50000	.96614	.96864	.00250	
.50000	1.50000	.96253	.96442	.00189	
1.00000	1.50000	.95544	.95625	.00080	
1.50000	1.50000	.94850	.94841	-.00008	
2.00000	1.50000	.94166	.94086	-.00080	
.25000	2.00000	.95472	.95968	.00496	
.50000	2.00000	.95130	.95549	.00419	
1.00000	2.00000	.94455	.94740	.00285	
1.50000	2.00000	.93789	.93964	.00174	AV DIF
2.00000	2.00000	.93130	.93216	.00085	= 0.00119

TABLE 2.3 (CONT.)

m_1	m_2	a_0(expt)	a_0(calc)	a_0(diff)
K= .032	H= 2.00			
.25000	.25000	.99112	.99102	-.00010
.50000	.25000	.98693	.98668	-.00024
1.00000	.25000	.97879	.97828	-.00051
1.50000	.25000	.97094	.97021	-.00072
2.00000	.25000	.96334	.96244	-.00089
.25000	.50000	.98652	.98646	-.00006
.50000	.50000	.98246	.98212	-.00034
1.00000	.50000	.97456	.97372	-.00084
1.50000	.50000	.96692	.96566	-.00126
2.00000	.50000	.95950	.95790	-.00159
.25000	1.00000	.97675	.97720	.00045
.50000	1.00000	.97292	.97286	-.00005
1.00000	1.00000	.96545	.96448	-.00097
1.50000	1.00000	.95819	.95643	-.00175
2.00000	1.00000	.95108	.94869	-.00239
.25000	1.50000	.96614	.96778	.00164
.50000	1.50000	.96253	.96344	.00091
1.00000	1.50000	.95544	.95507	-.00037
1.50000	1.50000	.94850	.94704	-.00145
2.00000	1.50000	.94166	.93931	-.00235
.25000	2.00000	.95472	.95818	.00346
.50000	2.00000	.95130	.95385	.00255
1.00000	2.00000	.94455	.94549	.00093
1.50000	2.00000	.93789	.93747	-.00042
2.00000	2.00000	.93130	.92977	-.00153
AV DIF =	.00111			
K= .032	H= 3.00			
.25000	.25000	.99112	.99098	-.00014
.50000	.25000	.98693	.98662	-.00030
1.00000	.25000	.97879	.97818	-.00060
1.50000	.25000	.97094	.97008	-.00085
2.00000	.25000	.96334	.96229	-.00105
.25000	.50000	.98652	.98633	-.00019
.50000	.50000	.98246	.98195	-.00050
1.00000	.50000	.97456	.97348	-.00107
1.50000	.50000	.96692	.96536	-.00156
2.00000	.50000	.95950	.95754	-.00195
.25000	1.00000	.97675	.97678	.00003
.50000	1.00000	.97292	.97236	-.00055
1.00000	1.00000	.96545	.96383	-.00162
1.50000	1.00000	.95819	.95566	-.00253
2.00000	1.00000	.95108	.94779	-.00329
.25000	1.50000	.96614	.96686	.00072
.50000	1.50000	.96253	.96241	-.00011
1.00000	1.50000	.95544	.95382	-.00161
1.50000	1.50000	.94850	.94559	-.00290
2.00000	1.50000	.94166	.93768	-.00398
.25000	2.00000	.95472	.95656	.00184
.50000	2.00000	.95130	.95208	.00078
1.00000	2.00000	.94455	.94343	-.00112
1.50000	2.00000	.93789	.93515	-.00274
2.00000	2.00000	.93130	.92720	-.00410
AV DIF =	.00144			

TABLE 2.3 (CONT.)

m_1	m_2	a_0(expt)	a_0(calc)	a_0(diff)
K= .032	H= 4.00			
.25000	.25000	.99112	.99094	-.00018
.50000	.25000	.98693	.98656	-.00036
1.00000	.25000	.97879	.97808	-.00070
1.50000	.25000	.97094	.96995	-.00098
2.00000	.25000	.96334	.96213	-.00121
.25000	.50000	.98652	.98621	-.00031
.50000	.50000	.98246	.98179	-.00067
1.00000	.50000	.97456	.97325	-.00131
1.50000	.50000	.96692	.96506	-.00186
2.00000	.50000	.95950	.95717	-.00232
.25000	1.00000	.97675	.97634	-.00040
.50000	1.00000	.97292	.97185	-.00107
1.00000	1.00000	.96545	.96317	-.00228
1.50000	1.00000	.95819	.95485	-.00333
2.00000	1.00000	.95108	.94686	-.00422
.25000	1.50000	.96614	.96590	-.00024
.50000	1.50000	.96253	.96132	-.00120
1.00000	1.50000	.95544	.95250	-.00293
1.50000	1.50000	.94850	.94407	-.00443
2.00000	1.50000	.94166	.93596	-.00570
.25000	2.00000	.95472	.95482	.00010
.50000	2.00000	.95130	.95017	-.00112
1.00000	2.00000	.94455	.94121	-.00334
1.50000	2.00000	.93789	.93265	-.00524
2.00000	2.00000	.93130	.92443	-.00686
AV DIF =	.00209			
K= .032	H= 4.86			
.25000	.25000	.99112	.99091	-.00021
.50000	.25000	.98693	.98651	-.00041
1.00000	.25000	.97879	.97800	-.00078
1.50000	.25000	.97094	.96984	-.00109
2.00000	.25000	.96334	.96199	-.00134
.25000	.50000	.98652	.98610	-.00042
.50000	.50000	.98246	.98165	-.00081
1.00000	.50000	.97456	.97304	-.00152
1.50000	.50000	.96692	.96479	-.00213
2.00000	.50000	.95950	.95685	-.00264
.25000	1.00000	.97675	.97595	-.00079
.50000	1.00000	.97292	.97138	-.00153
1.00000	1.00000	.96545	.96257	-.00288
1.50000	1.00000	.95819	.95414	-.00404
2.00000	1.00000	.95108	.94603	-.00504
.25000	1.50000	.96614	.96502	-.00112
.50000	1.50000	.96253	.96033	-.00219
1.00000	1.50000	.95544	.95131	-.00413
1.50000	1.50000	.94850	.94268	-.00581
2.00000	1.50000	.94166	.93441	-.00725
.25000	2.00000	.95472	.95320	-.00151
.50000	2.00000	.95130	.94840	-.00289
1.00000	2.00000	.94455	.93916	-.00539
1.50000	2.00000	.93789	.93033	-.00755
2.00000	2.00000	.93130	.92188	-.00942
AV DIF =	.00292			

activity from Table 2.3 which agree with experimental values, it was found to be possible to represent most of the solvent activities for $(m_1/m_2) < 1$; for values of $(m_1/m_2) > 1$, negative values of h were required. This may be best understood by studying the data in Table 2.4, in which the hydration numbers have been selected by interpolation of the data from Table 2.3 so as to give best agreement between experimental and calculated solvent activities for K = 0.032 .

TABLE 2.4

Calculated Values of Hydration Number, h, of Sucrose for Association Constant of Urea, K=0.032, in the System Urea-Sucrose-Water.

m_2 m_1	0.25	0.5	1.0	1.5	2.0
0.25	-0.3	1.5	3.0	3.8	4.0
0.5	-2.0	-0.2	1.9	2.9	3.4
1.0	-3.0	-2.0	0.5	1.6	2.4
1.5	-3.0	-2.0	-0.3	0.9	1.8
2.0	-3.5	-2.6	-0.7	0.4	1.3

By using h = 4.86 and varying K, positive values of K always gave values of the calculated water activity which were too low.

Solvent activities were therefore computed so that the K values varied linearly with the sucrose concentration, such that $(\partial K/\partial m_2)_{m_1} = 0.064$, and $(\partial K/\partial m_1)_{m_2} = 0$. This choice, although arbitrary, was made so that all values of h in the concentration ranges studied became either positive or zero. Some support for this assumption is given by the fact that the dielectric increment for binary sucrose solutions[49] is -7.5 (the value for urea is +2.7) and thus one would expect the association constant for urea to increase with increasing sucrose concentration. With this assumption it was possible to obtain excellent agreement between the experimental values of a_0 and those calculated by equation 2.41 . In addition, the values of K and h were consistent with the requirements that $K \rightarrow 0.32$ as $m_2 \rightarrow 0$ and $h \rightarrow 4.86$ as $m_1 \rightarrow 0$. The results may be best understood by studying the data in Table 2.5. The manner in which K and h vary is also illustrated in the three-dimensional diagram, figure 2.2.

It should be noted, however, that although, from an experimental point of view, the molality scale is extremely useful to use, it is not strictly rigorous to calculate association constants, K, in both two and three-component solutions, using molalities. The solvent

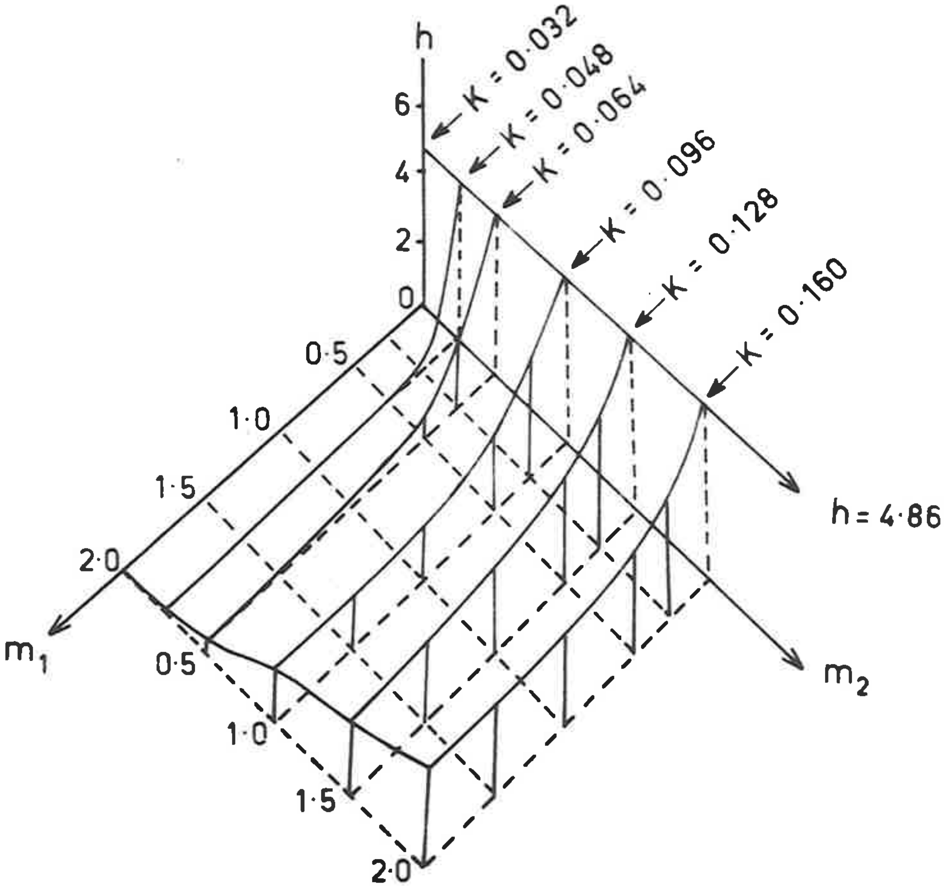

Figure 2.2. Proposed variation of association constant, K, of urea, and hydration number, h, of sucrose calculated from solvent activities in the three-component system water-urea-sucrose.

TABLE 2.5

Values of the Association Constant, K, of Urea and Hydration Number, h, of Sucrose, which can Represent the Solvent Activity in the System Urea-Sucrose-Water.

K	0.048	0.064	0.096	0.128	0.160
m_2 / m_1	0.25	0.5	1.0	1.5	2.0
			h		
0.25	0	1.6	3.2	3.8	4.2
0.5	0	0.5	2.4	3.2	3.6
1.0	0	0	1.7	2.6	3.0
1.5	0	0	1.7	2.4	2.9
2.0	0	0.5	1.8	2.3	2.8

activities (equations 2.32 and 2.34) are determined on the basis of mole fractions, so,that the association constants should also be calculated on the same scale. To test whether values of the hydration number in the ternary system obtained by calculating solvent activities on the mole fraction scale would be compatible with those reported in Table 2.5, a new set of equations were derived, which were similar to, but more complicated than, the relations described above. It was found that the new relations required the K values to be 55.5 times larger than those on the molality scale, and the hydration numbers computed, using correspondingly larger K values, resulted in a variation of h which was almost identical with the data presented in Table 2.5 .

The effect of urea on the structure of water has been discussed in considerable detail recently by Abu-Hamdiyyah,[50] who has suggested that urea takes an active part in the formation of an open structure in solution. This structure would be similar in nature to that proposed for water,[1d,52] and the urea would contribute to the open structure by the same mechanism as water molecules. The overall result would be that, on addition of urea to water, there is little or no change in the structure of the system, except that urea molecules have replaced some of the water molecules. Abu-Hamdiyyah suggests that the relatively low association constant of urea in water supports this view.

It has also been proposed[50] that this explanation for the effect of urea on the structure of water could account for the increased solubility of non-polar substances in urea solution. If non-polar substances occupy interstitial positions in aqueous solution, then increased solubility in urea solution can be accounted for if it is considered that the number of interstitial cavities is increased. Evidence supporting this theory comes from the fact that the solubility of hydrocarbons increases almost linearly with increasing urea concentration. Analogously, therefore, it seems reasonable to expect that a large, polar molecule might also have increased solubility because of the increase in interstitial cavities. The "salting in" effect observed from the study of the urea-sucrose-water system presented here gives support to this possibility.

In conclusion, it can be seen that in a system such as urea-sucrose-water, where it is possible to have competing effects such as association and hydration of solutes, it is necessary to consider the relative extent to which each effect is significant when attempting to describe the experimental results. The resulting picture of describing the solvent activity behaviour of the system requires a variation of both parameters K and h, but by varying these in the way proposed, a reasonable explanation may be obtained, particularly as both K and h values were selected so as to approach the values for binary solutions in the limiting cases.

Additional note.

Calculations recently performed in this laboratory have pointed to another, perhaps equally valid, description of the behaviour of the urea-sucrose-water system.

It is first assumed that urea is associated and has an equilibrium constant, $K_1 = 0.032$, and that sucrose is hydrated and has a hydration number, h=4.86. Then consider that in the three-component system, a further association takes place, between an unassociated molecule of the urea and a molecule of the hydrated sucrose.

Calculations have shown that it is possible to reproduce the solvent activity of the water to ±0.00005 in three-component solutions up to 1 molal in both urea and sucrose, by assuming the equilibrium constant between the urea and the sucrose is 0.23 (using the molality scale for calculations). It has been shown that an experimental error of 0.1% in both the molality and osmotic coefficient of the reference electrolyte used for the isopiestic experiments will give an average error of ±0.00004 in the solvent activity over the same concentration range. It seems likely, therefore, that up to 1 molal at least, it is possible to describe the behaviour of the solvent activity of the system by introducing this additional association constant.

The author wishes to thank Dr. P. J. Dunlop for suggesting this new approach, and for making these preliminary calculations.

References to Chapter 2.

1. R. A. Robinson and R. H. Stokes, "Electrolyte Solutions", Butterworth's Scientific Publications, London, 1959, (a) pp. 177 - 181, (b) Appendicies 8.3 - 8.10, (c) Appendix 8.3, p.476 (d) Chapter 1.

2. W. R. Bousfield, Trans. Faraday Soc., 13, 401 (1918).

3. D. A. Sinclair, J. Phys. Chem., 37, 495 (1933).

4. R. H. Stokes, Trans. Faraday Soc., 50., 565 (1954).

5. G. Scatchard, W. J. Hamer, S. E. Wood, J. Amer. Chem. Soc., 60, 3061 (1938).

6. V. E. Bower and R. A. Robinson, J. Phys. Chem., 67, 1524 (1963).

7. V. E. Bower & R. A. Robinson, ibid., 67, 1540 (1963).

8. R. A. Robinson and R. H. Stokes, ibid., 65, 1954 (1961).

9. R. A. Robinson, J. Biol. Chem., 199, 71 (1952).

10. H. D. Ellerton, G. Reinfelds, D. E. Mulcahy and P. J. Dunlop, J. Phys. Chem., 68, 398 (1964).

11. M. A. V. Devanathan and M. J. Fernando, Trans. Faraday Soc., 58, 784 (1962).

12. V. E. Bower and R. A. Robinson, ibid., 59, 1717 (1963).

13. S. Lindenbaum and G. E. Boyd, J. Phys. Chem., 68, 911 (1964).

14. H. S. Frank, Z. Physik. Chem., 228, 364 (1965).

15. H. P. Greger, M. Rothenberg and N. Fine, J. Phys. Chem., 67, 1110 (1963).

16. O. D. Bonner and W. C. Rampey, ibid., 65, 1602 (1961) and references cited therein.

17. C. H. Brubaker, Jr., and P. G. Rasmussen, ibid., 67, 330 (1963).

18. O. D. Bonner and J. R. Overton, ibid., 67, 1035 (1963).

19. B. A. Soldano and M. Meek, J. Chem. Soc., 4424 (1963) and references cited therein.

20. R. A. Robinson, J. Amer. Chem. Soc., 74, 6035 (1952).

21. R. A. Robinson and C. K. Lim, Trans. Faraday Soc., 49, 1144, 1147 (1953).

22. W. H. McCoy and W. E. Wallace, J. Am. Chem. Soc., 78, 1830 (1956).

23. R. A. Robinson, J. Phys. Chem., 65, 662 (1961).

24. R. A. Robinson and V. E. Bower, J. Res. Natl. Bur. Std., 69A, 19, 365 (1965).

25. M. S. Stakhanova, V. A. Vasilev and Y. A. Epikhin, Russ. J. Phys. Chem., 37, 182 (1963).

26. M. M. Shul'ts, L. L. Makarov, A. N. Merimichev and S. Yu-Zhen', ibid., 37, 652 (1963).

27. A. N. Kirgintsev and A. V. Luk'yanov, ibid., 37, 1501 (1963); ibid., 38, 702, 867 (1964).

28. L. L. Makarov, Yu. G. Vlasov and R. Kopunets, ibid., 37, 1495 (1963); ibid., 38, 1055, 1297 (1964).

29. F. J. Kelly, R. A. Robinson and R. H. Stokes, J. Phys. Chem., 65, 1958 (1961).

30. R. A. Robinson and R. H. Stokes, ibid., 66, 506 (1962).

31. M. Sarnowski and B. Baranowski, in "Electrolytes", B. Peace, Ed., Permagon Press Ltd., London, 1962., p. 187.

32. M. Sarnowski and B. Baranowski, Bull. Acad. Polon. Sci. Ser. Sci. Chim., 10, 101 (1962).

33. V. E. Bower and R. A. Robinson, J. Phys. Chem., 67, 1524 (1963).

34. V. E. Bower and R. A. Robinson, ibid., 67, 1540 (1963); J. Res. Natl. Bur. Std., 69A, 131 (1965).

35. R. A. Robinson and R. H. Stokes, J. Phys. Chem., 65, 1954 (1961).

36. For the method of applying vacuum corrections, see Mettler News (1 - 22)E, p. 81 (1961). This publication is available from Mettler agents.

37. Handbook of Chemistry and Physics", Chemical Rubber Co., Cleveland, U.S.A., 45th Edition 1964-5, pages F6, E21, E22, D92 and E27.

38. Using atomic weights compiled in International Union of Pure and Applied Chemistry, Information Bulletin No. 14b (1961).

39. Thermometers were calibrated by National Standards Laboratory, Commonwealth Scientific & Industrial Research Organisation, Sydney, N.S.W., Australia.

40. An I.B.M. 1620 computer was used to least square the data.

41. This was determined by the method of least squares using a CDC 3600 computer belonging to Commonwealth Scientific and Industrial Research Organisation, Canberra. Double Precision was used to minimise errors due to "rounding off".

42. We are indebted to Dr. R. A. Robinson of the National Bureau of Standards, Washington, D.C., U.S.A., for arranging for this computation to be made, and also for a trial computation of a second order polynomial.

43. J. A. Schellman, Compt. Rend. trav. lab., Carlsberg, Ser. Chim., 29, 223 (1955).

44. F. Gucker and W. Pickard, J. Am. Chem. Soc., 26, 1464 (1940).

45. J. A. Schellman, Compt. Rend. trav. lab. Carlsberg, Ser. Chim., 29, 230 (1955).

46. G. C. Kresheck and H. A. Scheraga, J. Phys. Chem., 69, 1704 (1965).

47. P.O.P.Ts'O, I. S. Melvin and A. C. Olson, J. Am. Chem. Soc., 85, 1289 (1963).

48. G. Scatchard, ibid., 43, 2406 (1921).

49. E. J. Cohn and J. T. Edsall, "Proteins, Amino Acids and Peptides", Reinhold Publishing Corporation, New York, 1943, p. 144.

50. M. Abu-Hamdiyyah, J. Phys. Chem., 69, 2720 (1965).

51. H. S. Frank and W. Y. Wen, Disc. Faraday Soc., 24, 133 (1957).

CHAPTER 3.

THE MEASUREMENT OF VAPOUR PRESSURES BY THE DIRECT STATIC METHOD.

3.1. Introduction.

It was pointed out in Chapter 2 that the isopiestic method for measuring vapour pressures has the disadvantage of being a comparative method - the vapour pressure of the unknown solution must be equilibrated against a solution of known vapour pressure.

The behaviour of urea in both binary and ternary aqueous solutions by isopiestic vapour pressure measurements has been described in the previous chapter. In view of the evidence which suggested association of urea, as observed in both binary and ternary systems, and considering the hydrogen-bond breaking capabilities of urea, it was decided that it would be both interesting and pertinent to measure the vapour pressures of a compound with a structure closely similar to urea.

The compound chosen for study was thiourea, $NH_2.CS.NH_2$. The choice of this compound was particularly significant since it can be appreciated that any differences in activities observed as compared to urea, $NH_2.CO.NH_2$, must be due to the replacement of the oxygen atom by a sulphur atom. In addition, as both of these atoms are members of the same group in the periodic table, the effect of the replacement of the oxygen by sulphur becomes doubly interesting. One could speculate beforehand, perhaps, that because of the lower electronegativity of the sulphur compared to the oxygen, then hydrogen-bonding would be present in aqueous thiourea solutions to a considerably weaker extent than in corresponding aqueous urea solutions. That the sulphur atom does exert a considerable influence on the behaviour of thiourea can, perhaps, be best illustrated by the fact that although urea is soluble in water at up to 20 molal (25°C), thiourea is only soluble up to approximately 1.7 molal.

An isopiestic vapour pressure experiment was commenced, but after approximately 24 hours equilibration, extensive blackening was noted of the silver dishes containing the thiourea, which had apparently been brought about because of the reduction of silver to silver sulphide by the thiourea.

The stock of isopiestic dishes available contained several which were made of copper and had been electroplated with gold. These dishes had been shown previously to give identical isopiestic results compared to the silver dishes.[1] A solution of thiourea was placed in one of the gold-plated dishes, to test whether it was resistant to attack from thiourea. After a few days, it was found that the thiourea had stripped off the gold plating, leaving the copper beneath readily exposed for reduction by the thiourea. After conferring with an Adelaide electroplating firm, one of the dishes was gold-electroplated by using a type of new gold-plating solution which, according to the manufacturers, resulted in a gold-plating which was extremely resistant to chemical reaction. Subsequent testing of the newly gold-plated dish with the thiourea solution showed that the gold-plating was again attacked, and that no advantage could be gained from using the new gold-plating solution. It became apparent that to obtain satisfactory results by the isopiestic method it would be necessary to use either platinum or "palau" (a paladium-gold alloy) dishes, but the cost of either of these materials made a purchase impracticable at the time. As an apparatus had been designed at about that time for making absolute vapour pressure measurements, and a start had been made on its construction, it was decided to attempt vapour pressure measurements on thiourea solutions using this apparatus.

3.2. Selection of suitable apparatus design: a review of some forms of apparatus used by other workers.

Differential static methods for measuring vapour pressure depend either on the use of a manometer containing a non-volatile oil or mercury, or on the bending of a spring loaded diaphragm. Calibration of the former class of pressure measuring device requires only a knowledge of the density of the manometric fluid at the working temperature, whereas the latter class requires calibration over the pressure range used against some primary standard.

Although the principle involved in making static vapour pressure measurements is extremely simple, involving only the measurement of the displacement of manometer fluid by the pressure of vapour, the apparatus used for the determinations can vary from relatively simple to extremely complex. The systems studied vary too, from those of purely academic interest to those of commercial importance. Bottomley and Seiflow[2] have measured the vapour pressures of halothane as a function of temperature. Halothane is used as an inhalant anaesthetic and, as such, accurate vapour pressure and vapour density information was required to give correct dosage. The vapour pressures were determined by a static isoteniscope method, in which the vapour pressure of a sample is balanced by an externally applied and measured air pressure. Mercury manometers were used. Dunning, Evans and Taylor have described[3] an apparatus used for determining the vapour pressures of sucrose solutions at relatively high temperatures. An external barometer was connected to one arm of a manometer, the other being connected to the solution whose vapour pressure was being measured. The pressure in the barometer was then adjusted to be equal to the vapour pressure of the solution by varying the pressure so that the mercury level was the same in both arms of the manometer. Sucrose solutions in the concentration range 45 to 90 gm/100 gm. solution over the temperature range 60 - 90°C were studied by this method.

Some interesting applications of vapour pressure measurements have been made in the thermodynamic investigation of certain organic systems.

Baxendale, Enüstün and Stern[4] have made precise measurements of the vapour pressures of pure benzene and benzene in solutions of diphenyl in benzene in the temperature range 30 - 80°C. Their method was to de-gas a sample of benzene in a flask external to the main thermostatically-controlled part of the apparatus, to dry the sample by repeated distillations from one flask to another and back, through a phosphorus pentoxide column, and finally distillation of the dry degassed benzene into a flask in a thermostated bath ready for the vapour pressure measurement at the desired temperature. A mercury manometer made from precision bore tubing of 22 m.m. diameter was used to measure the vapour pressures. In the case of the benzene-diphenyl measurements, a known weight of diphenyl was first introduced into the flask in the thermostat, and then known weights of benzene were introduced by distillation and the vapour pressure measurements made at various tempteratures. A little more benzene was then introduced, enabling measurements to be made over the whole concentration range. Allen, Everett and Penney[5] have also described an apparatus for making accurate determinations of vapour pressures of liquids in the temperature range 0 to 80°C and pressure range 5 to

760 m.m. mercury. Their apparatus differed from the others so far described notably because of the insertion of a bellows-type differential manometer in the thermostat bath, between the vapour and mercury manometer. A measured air pressure was applied to the mercury manometer so that the null reading manometer indicated a pressure equal to that of the vapour in the cell.

Two other forms of apparatus have recently been described for vapour pressure measurements using the null manometer technique. The apparatus described by Scatchard, Wilson & Satkiewicz[6] can be used from -10 to 120°C at pressures not greater than 1 atmosphere, and has been used for vapour pressure measurements on the system ethanol-cyclohexane[7] from 5 to 65°C, and the system water-butyl glycol[8] from 5 to 85°C. On the other hand, de Nordwall and Jones' apparatus[9] has been specifically designed for use in the temperature range 100 to 250°C. The principle used is to translate wet steam pressure into dry gas pressure for solution and solvent separately using the movement of a diaphragm as a null detection device. The two gas pressures are then compared away from the hot zone of the apparatus using a mercury manometer.

For vapour pressure measurements of aqueous solutions over a moderate range of temperatures, several workers have reported that the most satisfactory form of apparatus is the one based on the design of Gibson and Adams.[10] A diagrammatic sketch of their apparatus is shown in Figure 3.1. The apparatus consisted essentially of two flasks, one containing solvent and the other containing the solution whose vapour pressure was required, and these were connected by three-way taps to either the vacuum line or the manometer. In this way it was possible, by suitable manipulation of the taps, to measure either the vapour pressure of the solvent or the solution separately, and also the difference in vapour pressures of the two. Freshly distilled n-butyl phthalate was used as manometer liquid. Further success was claimed with a similar type of apparatus by Shankman and Gordon,[11] with measurements on aqueous solutions of sulphuric acid, and by Olynyk and Gordon[12] with measurements on aqueous sodium chloride solutions at 20, 25 and 30° for concentrations from 2 molal to saturation. Cenco Hyvac pump oil was used as manometer liquid. Vlasov, in thermodynamic studies of alkali metal-halide systems[13] has used an apparatus of similar design to determine activity coefficients of aqueous

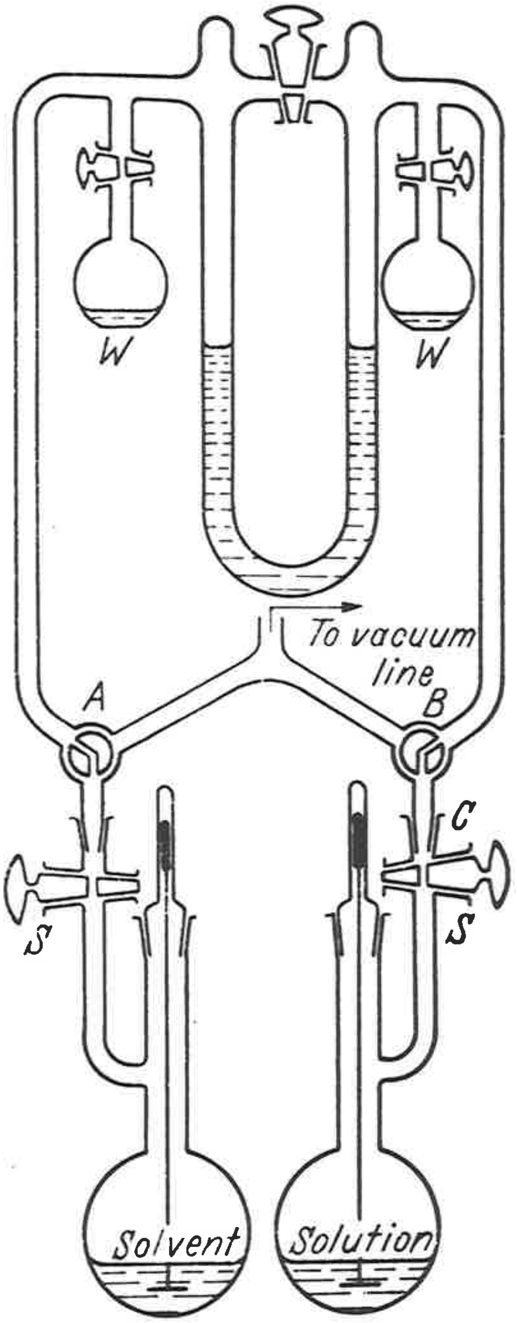

Figure 3.1. Diagrammatic arrangement of Gibson and Adams' apparatus for making absolute vapour pressure measurements.

sodium chloride solutions at 45°. The vapour pressure of the ternary system calcium oxide-phosphoric oxide-water at 25°C has been studied[14] using a Gibson and Adams type of apparatus, with a manometer liquid of dioctyl sabacate. This system was studied because of a wide interest in the properties of phosphoric acid and calcium phosphate solutions in industrial, agronomic and biochemical fields.

Gibson and Adams[10] stated that their apparatus was "designed for accuracy and convenience," and this claim was later substantiated by Shankman and Gordon. These recommendations, together with an investigation of the advantages and disadvantages of other forms of apparatus, led us to the conclusion that the most suitable form of apparatus for our work should be based on the design of Gibson and Adams.

3.3 Experimental.

A. The apparatus.

The actual arrangement of the apparatus is shown in Figure 3.2.* Instead of using three-way taps as in the Gibson and Adams apparatus,[10] a rectangular glass manifold C was constructed and the flasks and manometer were connected at appropriate points. The flasks A were of 100 ml. capacity and were used to

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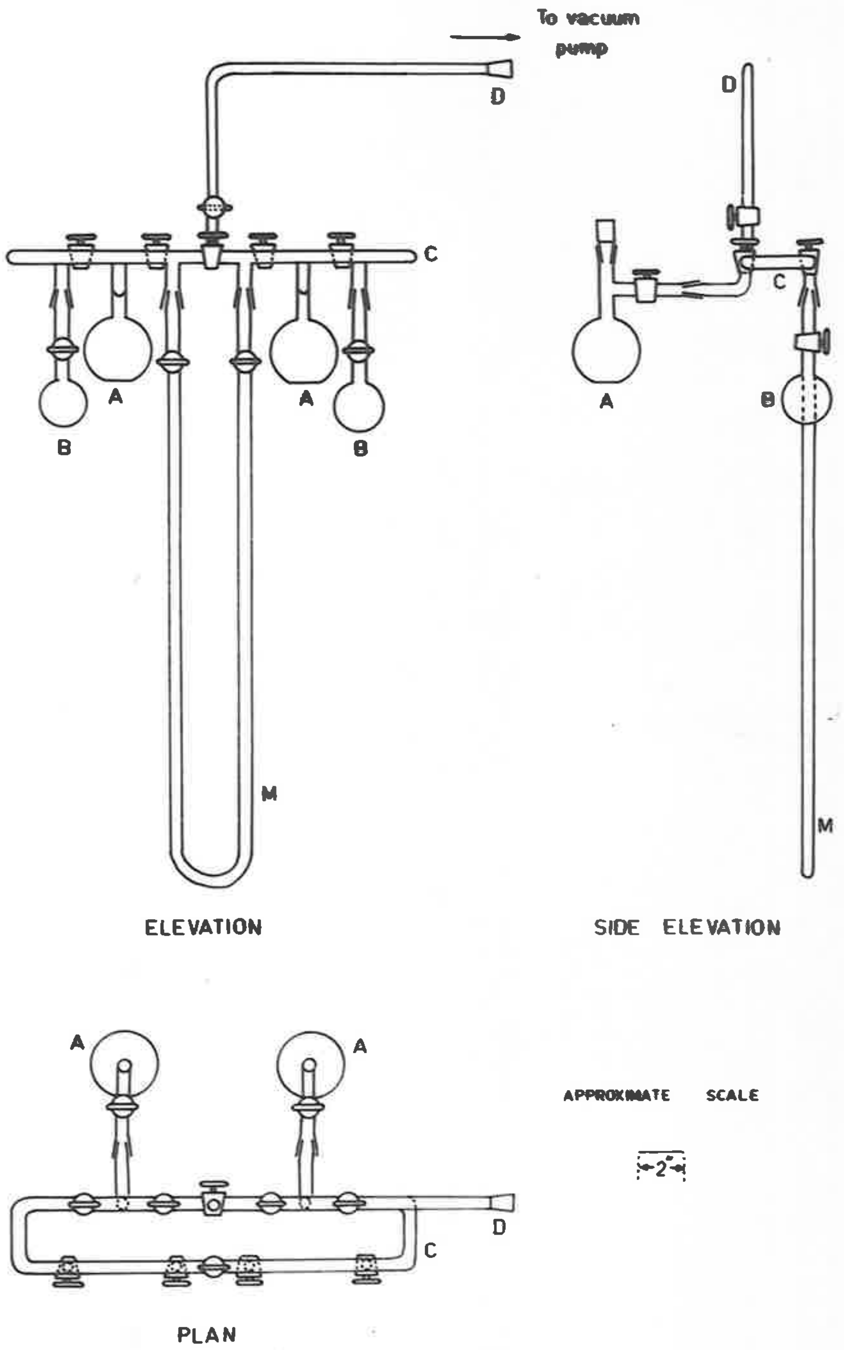
*See also Plate 3.1.



ELEVATION

SIDE ELEVATION

PLAN

<u>Figure 3.2</u>. Diagrammatic arrangement of the absolute vapour pressure apparatus described in this work.

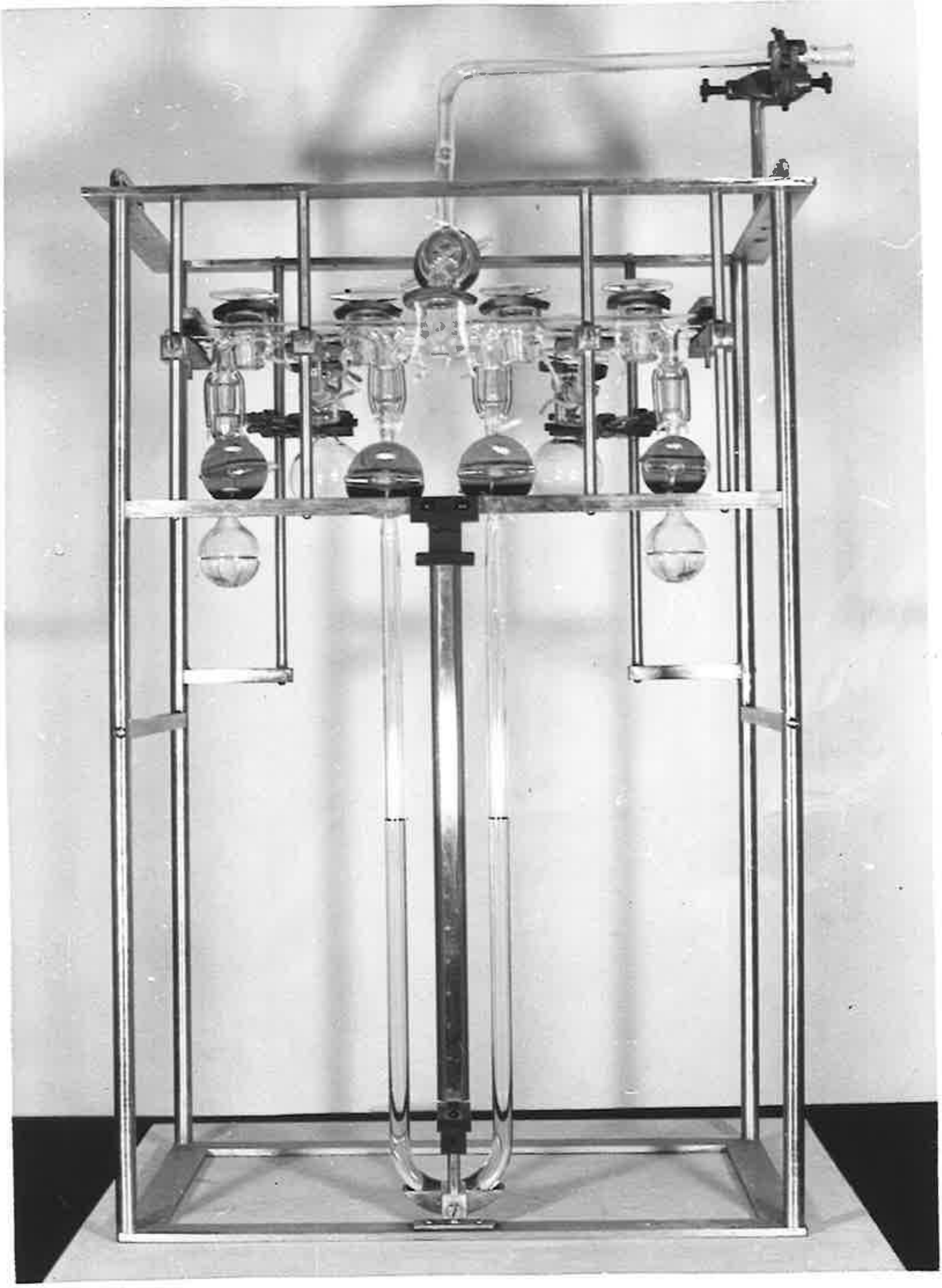


Plate 3.1. The absolute vapour pressure apparatus described in this work.

contain the solutions of unknown vapour pressure, and had the bottoms slightly flattened to enable magnetic stirrers to be used during the de-gassing process. The flasks B were of 50 ml. capacity and were filled with about 25 ml. of solvent. Manometer tubes of 15 mm. diameter were chosen to eliminate errors due to capillarity, and were of sufficient length so that, using n-butyl phthalate as manometer liquid, the vapour pressure of water could be measured. The density of freshly distilled n-butyl phthalate at 25° was measured in duplicate in pycnometers of approximately 25 c.c. capacity, and was found to be 1.04221 ± 0.00001 gm/c.c., which agrees satisfactorily with Gibson and Adams' value [10] of 1.0418. The advantages of using n-butyl phthalate instead of mercury as manometer liquid were that the vapour pressure of n-butyl phthalate at 25° is much lower (7.8×10^{-5} m.m.) than mercury (2.3×10^{-3} m.m.) and the lower density of n-butyl phthalate compared to mercury means that an error in measurement of 0.01 m.m. n-butyl phthalate would correspond to less than 0.001 m.m. mercury.

All glass connections were made with B14 "Quickfit" cones and sockets, and "Apiezon grade N" grease was used for vacuum taps and joints. The whole of the apparatus shown in Figure 2.2 was then mounted in a rectangular chromium-plated brass frame which gave rigid support to the glassware and enabled levelling adjustments to be made. An "invar" bar, graduated in divisions of approximately 5m.m. was mounted on the frame, between the two arms of the manometer. This bar was calibrated in the Metrology Laboratory of the South Australian Railways, with an accuracy of ±0.0001 c.m.

The apparatus was connected at point D by a short rubber vacuum hose to a vacuum manifold which was connected to a "Speedivac" high vacuum pump, (model 2SC20A) which was backed by a single-stage mercury diffusion pump. A liquid air trap was placed between the manifold and vacuum pump to prevent contamination of vacuum pump oil with water vapour which had been lost during de-gassing of solutions. Connections on the manifold allowed an Edwards "vacustat" type McLeod gauge (range 1 to 0.001 m.m. mercury) and a Pirani vacuum gauge (manufactured by W. Edwards & Co. (London) Ltd.) to be connected to the system. The purpose of the flexible rubber connection was to enable the apparatus to be readily moved in and out of the thermostatted water bath, and to enable a connection to be made for de-gassing purposes before immersing in the water bath. The vacuum manifold was mounted on a metal framework on a 2 ft. x 2 ft. table, and the vacuum pump was mounted on a platform below. The glass-fronted thermostatted water bath of approximately 90 gallon capacity was regulated at 25°C to better than ±0.002°C by means of a mercury-toluene regulator immersed in the bath and connected to a "thyratron" regulated heater.

B. Materials.

Sodium chloride was from the same sample as described in Chapter 2.

Thiourea was Grade A material obtained from Calbiochem., U.S.A., and was once recrystallised from doubly-distilled water.

The solutions were prepared gravimetrically. Doubly-distilled demineralised water was used as solvent, and a 20 litre flask was set aside especially for this work, to ensure consistency of the solvent used. The density of thiourea was taken as 1.405 gm./c.c., whilst the corresponding molecular weight was taken as 76.120.

n-butyl phthalate, used as manometer liquid, was purchased from Townson and Mercer (S.A) Pty. Ltd., Adelaide, and was vacuum-distilled as required. The freshly distilled material was quickly transferred to the manometer and the system evacuated

C. Operation of Apparatus.

Shankman and Gordon[11] have pointed out that "the most serious experimental difficulty in static vapour pressure measurement is the removal of the residual air from the liquid." This claim has been fully substantiated by this work. The de-gassing was effected by freezing the solutions and solvent, using liquid air, while they were boiling under vacuum, until the residual pressure was approximately 0.001 m.m., as determined on the McLeod gauge. Care had to be exercised to avoid splashing caused by "bumping" during de-gassing of solutions for the first or second time, but subsequent de-gassings became less vigorous. Gibson and Adams[10] claimed that at least three de-gassings were necessary, and Shankman and Gordon[11] used 5 or 6. In this work, 6 de-gassings were first tried, and later 10, but both were found to be insufficient to give satisfactory values for the vapour pressure of water, giving values approximately 0.09 and 0.06 m.m. higher than the value reported by Robinson and Stokes.[15] However, after 20 de-gassings, an average value of 23.755 m.m. of mercury was obtained, and compares favourably with the value 23.753 given by Robinson and Stokes. All solutions were subsequently de-gassed 20 times before measuring the vapour pressures.

When de-gassing had been completed, the apparatus was immersed in the thermostat water bath, a vacuum was re-established across the rubber connection, and the solutions were allowed to equilibrate, generally overnight. In the meantime, the level of the apparatus was adjusted so that the "invar" bar was vertical, as shown by a plumbob line. Then the legs of the cathetometer stand were adjusted so that identical readings were obtained from both limbs of the manometer. Next day, the vapour pressure in one flask of solvent was measured, then the vapour pressure of one solution, and finally, as a check, the difference in vapour pressure between the two. The procedure was then repeated for the other flasks of solvent and solution. The solutions were allowed to re-equilibrate for 30 - 40 min. before a reading was taken with the cathetometer.

The level of the menisci of the n-butyl phthalate manometer liquid was read by means of a 1 meter cathetometer supplied by the Precision Tool and Instrument Co. Ltd., Surrey, England. The telescope supplied with this instrument was replaced by one purchased from the Gaertner Scientific Corporation, Chicago, U.S.A., which gave a clearer, larger image than the original instrument. The meniscus was illuminated by lowering a 15 watt pilot lamp into a 2" diameter glass tubing, sealed at one end, and immersed in the water bath. The differences of pressure were obtained by measuring the position of the meniscus with respect to the nearest calibration point on the "invar" bar. No diminution in clarity of meniscus with time was detected with the n-butyl phthalate, as reported by previous workers.[10,11] The observed pressures were converted to millimetres of mercury at 0° assuming a mercury density of 13.5951 gm./c.c.[16]

It was pointed out earlier that the main interest here in static vapour pressure measurements was to obtain data for the system thiourea-water, for comparison with the urea-water data reported in Chapter 2. However, in order to ascertain the accuracy of the results obtainable from the apparatus, it was decided to measure the vapour pressure of a sodium chloride solution, as well as the thiourea solution. Accordingly, approximately 1 molal solutions of sodium chloride and thiourea were prepared, and 50 - 75 c.c. samples of each were de-gassed 20 times and the vapour pressure measured. The thiourea solution was analysed afterwards by duplicate density measurements of the solution used, using 25 c.c. pycnometers as described in Chapter 4. The molality of the sodium chloride solutions was determined by adding weighed 5 c.c. samples to isopiestic silver dishes (described in Chapter 2) and evaporating to dryness, firstly by heating in an oven at 90 - 95°C until most of the water had been evaporated, and then finally overnight at 160° to remove any residual water.

3.4 Results.

After 20 de-gassings, the following results were obtained for the vapour pressure of water (in m.m. of mercury) from two separate samples:

Flask 1:	23.762 m.m.	Flask 2:	23.753 m.m.
	23.756 "		23.752 "
	23.753 "		23.752 "

Average: 23.755 m.m.

The molal osmotic coefficient, ϕ_1, of a solute is related to the vapour pressure of a solution by the equation

$$\nu_1 m_1 \phi_1 = \frac{-1000}{M_0} \ln a_0$$

so that $$\nu_1 m_1 \phi_1 = \frac{-1000}{M_0} \ln p/p_0 \qquad (3.1)$$

where p is the vapour pressure of the solution, whose solvent activity is a_0, p_0 is the vapour pressure of the pure solvent at the same temperature, M_0 the molecular weight of the solvent, m_1 the molality of the solute and ν_1 the number of ions formed by one mole of solute.

Now p = dgh, and for a particular manometer liquid, d, the density is constant, and g is the gravitational constant, so that

$$\frac{p}{p_0} = \frac{h}{h_0} \qquad (3.2)$$

where h and h_0 are the measured heights (in m.m. of n-butyl phthalate) of solution and solvent respectively.

Table 3.1 summarises the results for approximately 1 molal solutions of sodium chloride and thiourea, respectively.

TABLE 3.1

Static vapour pressure measurements on sodium chloride and thiourea solutions of approximately 1 molal concentration.

	Sodium Chloride	Thiourea
Observed height (m.m. of n-butyl phthalate).	299.754 m.m.	304.854 m.m.
$a_0 = p/p_0$	0.9673_9	0.9837_2
$\nu_1 m_1 \phi_1$	1.8403_{00}	0.9111_{30}
m_1	1.003_{39} [a]	1.039_{50} [b]
ϕ_1	0.917_0	0.876_5

Notes:

(a) The molality of the sodium chloride solution was the average of two determinations: 1.003_{82} and 1.002_{96}.

(b) The molality of the thiourea solution was obtained from a duplicate density determination of the solution used for the vapour pressure measurements. The average density was then interpolated to get the molality using the known relation of density versus molality given by equation 4.16 in Chapter 4.

The measured densities were 1.01778_9 and 1.01779_5 giving an average value of 1.01779_2.

3.5 Discussion.

(a) Sodium chloride solution.

The value of the osmotic coefficient of sodium chloride obtained from a large scale graphical interpolation of the data given by Robinson and Stokes[15b] for a molality $m_1 = 1.003_{39}$ is $\phi_1 = 0.935_6$ which represents a difference of 1.9% from this work. If allowance is made of 0.1% error in the determination of molalities, then 1.8% of the error still has to be accounted for by the vapour pressure measurements.

It can be seen from equation 3.1 that an error in concentration measurement is directly reflected in ϕ_1. However, the effect of an error in p/p_0 is very much more drastic. A 1% error in p/p_0 for a one molal solution, for which p/p_0 is approximately 0.97, leads to an error in ϕ_1 of approximately 30%. As the measurement of the vapour pressure of pure water, reported above, was in excellent agreement with the value reported in the literature,[15a] it was concluded that the error lies in the measurement of vapour pressure of the solution. Therefore, if the error in ϕ_1 is 1.8%, then the error is 0.06% in p/p_0, which corresponds to 0.2 m.m. of n-butyl phthalate in the manometer, or 0.02 m.m. of mercury. It can be appreciated that this is an extremely small experimental tolerance, and is presumably accounted for by either, or both, of the following reasons:

(1) The necessity for complete de-gassing of solutions. This has already been emphasised, but it can only be concluded that the 20 freezings were still insufficient to completely lose all residual gas. It may be, perhaps, that the presence of solute molecules causes some residual air to be held more tenaciously than in pure water, and this effect may be further increased by the larger bulk of the solution used (~50 - 75 c.c.) compared with the amount of solvent (~ 25 c.c.).

(2) The likelihood of slight leaks occurring in the greased vacuum taps. This problem was aggravated by the fact that, uncommon with many workers using high vacuum techniques, it was necessary for the apparatus to be taken from room temperature (approximately 19 - 20°C), to water bath temperature (25°C), and then, a day or two later, back to room temperature again. It was found that

the viscosity of the Apiezon grease was considerably temperature dependent, even over this relatively small temperature range, and in fact it was found that after removing the apparatus from the thermostat bath at 25°, the taps had to be left untouched to equilibrate for 24 hours if they were to be of any further use without re-greasing. The safest way was to completely clean and re-grease all parts that were immersed in the bath at 25°, every time it was used for a new measurement. A device, consisting of a $\frac{1}{4}$ inch thick "slice" of a $1\frac{1}{2}$" diameter rubber bung, held in position around the key of the tap with pipe-cleaners, was used to minimise the possibility of the taps "lifting" slightly whilst in use. It may be concluded that a more satisfactory result could probably be obtained using greaseless metal taps, but if this were done, extreme care would have to be exercised in the use of the apparatus in order to avoid contaminating the taps with corrosive materials.

It is worth noting, however, that the osmotic coefficients of sodium chloride reported by Robinson and Stokes are averaged values taken from the results of several workers. When plotted graphically,[15c] these show a scatter of approximately 0.8% in ϕ. This is still, however, less than half the estimated error from this work.

(b) Thiourea, and its effect on the structure of water.

For the thiourea solution, it can be concluded that, without further experimentation, the same error of approximately 1.8% in ϕ_1, as for sodium chloride, must also apply for thiourea. Thus for $m_1 = 1.039_{50}$, $\phi_1 = 0.87_{65} \pm 0.015$.

Nevertheless, it can be seen that, even considering the broad limits of error in the thiourea, the osmotic coefficient is considerably lower for thiourea than a corresponding 1 molal urea solution which has an osmotic coefficient of 0.962_1. If again, we consider that the deviations from ideality are caused by association, we can calculate an approximate association constant for thiourea at 1 molal, using equations 2.31 and 2.33. This gives a value of $K = 0.19 \pm 0.04$ which is some 5 or 6 times greater than the value of $K = 0.032$ for urea at the same concentration.

The urea-water system has been considered in considerable detail in Chapter 2, and particular reference was made to the recent contribution by

Abu-Hamdiyyah[17] on the effect of urea on the structure of water. In a portion of that paper, Abu-Hamdiyyah speculated on the behaviour of alkyl-substituted ureas in water, compared to urea itself. It was pointed out firstly that an alkyl-urea would have a decreased ability to hydrogen bond with water compared to unsubstituted urea, and secondly that the alkyl substituent groups themselves, when they are introduced into the solution, can only accommodate themselves in cavities in the aqueous solution. Both of these effects would result in the alkyl-substituted urea being less capable of participating in cluster formation with water, as has been suggested for urea.

It is, therefore, pertinent to consider the effect of thiourea on the structure of water, where here we have a sulphur atom replacing the oxygen atom on the carbonyl group of the urea. Due to the lower electronegativity of sulphur compared to oxygen, one might expect that thiourea in solution is less capable of hydrogen bond formation. Furthermore, since for thiourea, *one* atom has been *replaced* by another, whereas for alkyl-substituted ureas a *group of atoms* has replaced one atom, it may be assumed that any change in the properties of aqueous thiourea solutions compared to aqueous urea solutions must be due only to this weakening of the hydrogen-bonded structure, caused by the replacement of a nitrogen by a sulphur atom.

In considering the effect of thiourea on the structure of water, and comparing this with the effect of urea on the structure of water, three points need to be considered.

(1) The vapour pressure measurement, which suggests a considerably higher degree of association in thiourea ($K = 0.19$) compared with urea ($K = 0.032$).

(2) The relative viscosity data, the values of which are lower for thiourea than for urea at similar concentrations (e.g. at 1M, $\eta_r = 1.023$ for thiourea and $\eta_r = 1.041$ for urea).

(3) The remarkably lower solubility of thiourea (~ 1.7 m) compared with urea (20 m).

In his recent paper,[17] Abu-Hamdiyyah has discussed the effect of various types of solutes on the structure of water. If the solute consists of structure forming ions, these ions destroy the hydrogen-bonded structure by orientating the water around themselves (the ions). On the other hand, non-polar solutes, it was postulated, fill in the intersticies in the open water structure. With urea as solute, however, Abu-Hamdiyyah suggested that the urea actually takes an active part in the formation of the open structure of the solution, i.e. urea contributes to the open structure in the solution by the same mechanism as water molecules.

Now, considering the effect of thiourea as solute, it may first be noted that thiourea has an even weaker structure forming tendency than urea. This conclusion arises from an inspection of the relative viscosity data, where we have a small value for the coefficient F_1 of equation 4.31. This term is approximately equivalent to the "B-coefficient" of the Dole-Jones viscosity equation[18], where a large positive B-coefficient indicates a strong structure forming tendency, and a negative coefficient indicates disordering of the water structure.

If we conclude from the viscosity data that the structure of the thiourea-water system is changed very little, we have to next consider whether the thiourea takes part in the "open" water structure, as has been postulated for urea,[17] or whether the thiourea fits into the interstitial spaces, in the manner suggested for a non-polar solute. The higher association constant of thiourea suggests that the thiourea may be filling in the interstitial spaces in the water structure, and because of the limited space available in the structure, the solute molecules are forced closer together. This view could also be supported by the solubility data, where the solubility limit of 1.7 molal may represent the limit to which thiourea can be accommodated in the interstitial spaces available. On the other hand, however, the lower solubility of thiourea may be a reflection of the weaker ability of the sulphur atom to form hydrogen bonds compared with the oxygen atoms of urea. This could mean that thiourea is able to participate in a structure of a type similar to that postulated for urea in water,[17] but that this can only maintain stability if proportionally fewer thiourea molecules participate.

From the evidence presented here, it is not possible to conclude which of the two structures is the more likely for the thiourea-water system. It is worth noting, however, that it has been shown[19] that thiourea is effective in the denaturation of proteins, as also is urea. Further, it has been shown[19] that either alkyl substitution or increasing the alkyl chain length of thiourea decreased or abolished its denaturing effectiveness. It would seem, therefore, that the behaviour of thiourea in solution is somewhat similar to that of urea.

References to Chapter 3.

1. H. D. Ellerton, G. Reinfelds, D. E. Mulcahy, and P. J. Dunlop, J. Phys. Chem., 68, 398 (1964).
2. G. A. Bottomley and G. H. F. Seiflow, J. Appl. Chem., 13, 399 (1963).
3. W. J. Dunning, H. C. Evans and M. Taylor, J. Chem. Soc., (1951) 2363.
4. J. H. Baxendale, B. V. Enüstün and J. Stern, Phil. Trans., A, 243, 169 (1951).
5. P. W. Allen, D. H. Everett and M. F. Penney, Proc. Royal Soc., A, 212, 149 (1952).
6. G. Scatchard, G. M. Wilson and F. G. Satkiewicz, J. Am. Chem. Soc., 86, 125 (1964).
7. G. Scatchard and F. G. Satkiewcz, ibid., 86, 130 (1964).
8. G. Scatchard and G. M. Wilson, ibid., 86, 133 (1964).
9. H. J. de Nordwall and P. J. Jones, AERE Report No. R3565.
10. R. E. Gibson and L. H. Adams, J. Am. Chem. Soc., 55, 2679 (1933).
11. S. Shankman and A. R. Gordon, ibid., 61, 2370 (1939).
12. P. Olynyk and A. R. Gorden, ibid., 65, 224 (1943).
13. Yu. G. Vlasov, Russ. J. Phys. Chem., 37, 1399 (1963).
14. E. O. Huffman, J. D. Fleming and A. J. Smith, Chem. and Eng. Data Series, 3, 17 (1958).
15. R. A. Robinson and R. H. Stokes, "electrolyte Solutions", Butterworth's Scientific Publications, London, 1959. (a) p. 457, (b) p. 476, (c) p. 215.

16. A. Weissberger, "Techniques of Organic Chemistry", Vol. I, part I, page 415.

17. M. Abu-Hamdiyyah, J. Phys. Chem., 69, 2720 (1965).

18. R. W. Gurney, "Ionic Processes in Solution", McGraw-Hill Book Co., Inc., N.Y., Chapter 9.

19. J. A. Gorden and W. P. Jencks, Biochem., 2, 47 (1963).

CHAPTER 4.

DENSITY AND VISCOSITY MEASUREMENTS.

A. DENSITY MEASUREMENTS.

4.1. Introduction.

Density measurements afford a simple, convenient and accurate method of characterisation of substances in either solid, liquid or gaseous phases. Measurements with an accuracy of 0.1% can be made extremely easily, and with more care, measurements of 1 part in 100,000, and even 1 part in 1,000,000, or more, may be made.

Density measurements of solutions are of both practical and theoretical interest. On the one hand, measurements in the system calcium phosphate-phosphoric acid-water have been made[1] for agronomical purposes, whereas other density and molal volume measurements on both electrolytes[2-6] and non-electrolytes[7,8] have been made because the results furnish some interesting information regarding molecular state and structure. Partial specific volumes of proteins, which can be determined from density measurements, have become extremely important in the last decade or two, with the development of the ultracentrifuge. This requires extremely accurate data, since it has been shown[9] that an error of 1% in the determination of the partial molar volume results in an error of 3% in the molecular weight of the protein. Using the magnetic float method,[10] accurate partial specific volumes have been measured[9] for gelatin, edestin, ovalbumin and serum albumins. However, systems encountered in the study of materials of biological interest almost always contain three components. Aqueous protein solutions, for example, are frequently buffered, or may contain an added salt, so it is important to formulate a convention so that no ambiguity results. Casassa and Eisenberg[11] have shown how an unambiguous molecular weight for a polymeric species can be obtained from density and sedimentation equilibrium measurements without explicitly evaluating the interaction of the species with the supporting electrolyte. Density data from aqueous solutions of "association colloidal electrolytes" has also been analysed and methods have been suggested for deriving the partial specific volume and density of micelles.[12]

Most of the density measurements reported here have been used in the study of interacting flows in ternary isothermal systems undergoing diffusion. Current theories of ternary diffusion require accurate density information, and it is the purpose of this section to describe how these results were obtained.

4.2. Definitions and Methods.

Density, d, is defined by the equation

$$d = \frac{\text{mass}}{\text{volume}} = \frac{m}{V}$$

It may be noted, in passing, that in this work all densities will be expressed in the units grams per cubic centimetre, instead of grams per millilitre, as is commonly reported in the literature. The millilitre is defined as 1/1000 part of the volume of one kilogram of pure, ordinary water at its temperature of maximum density (3.98°C). However in later chapters of this work we will be concerned with the rates of flow of substances (in cm./sec.) through a system of certain cross-sectional area (expressed in square cms.), so that it becomes desirable, from the outset, to express densities as grams/c.c. Nevertheless, the two units are very close to being equal, since 1 c.c. = 0.999972 ml., so that[13]

$$d(\text{gm/c.c.}) = d(\text{gm/ml})/1.000028$$

but the difference is significant when, as in this work, fifth and sixth decimal place accuracy is required.

Two of the most convenient methods for

measuring the density of a solution are the magnetic float method and the pycnometric method. In the magnetic float method, the upward buoyant force on a magnetically controlled float which is immersed in the liquid whose density we wish to measure is just balanced by passing a current through an adjacent solenoid.[10,14] The greater the current required to obtain equilibrium, the greater is the density of the liquid. An accuracy of 1 part in 1,000,000 has been claimed for this type of apparatus, and work done in this laboratory has confirmed this claim.[15] The main disadvantage of the magnetic float method is the relatively large quantity of sample required (100-300 c.c.).

Numerous types of pycnometers have been used by various workers, and a selection of these have been described elsewhere.[16] The density measurements reported in this work were made with pycnometers which had a glass bulb of approximately 25 c.c. capacity, and a stem made of precision bore capillary of 1.2 mm. diameter. At the end of the capillary there was a B10 Quickfit cone, which could be fitted with a stopper made of a Quickfit socket. A fine scratch mark on the capillary marked the point to which the volume is accurately known. The pycnometers are shown in the photograph, Plate 4.1. It will be noted from the photograph that a sealed "tare"

Plate 4.1. The four pycnometers and tare used for density measurements in this work.

was also used, the purpose of which is to avoid the necessity of making corrections due to the buoyancy of air. The tare was constructed so as to be almost identical in weight, shape and volume to the pycnometer filled to the mark with water. The pycnometers containing the solution of unknown density were then compared in weight with the tare. A detailed discussion of the theory of the "tare" follows in the next section. It is of interest to note that Washburn and Smith[17] used a similar technique over 30 years ago in an effort to detect differences in isotopic composition of water from different natural sources by density measurements. These workers cited several advantages to their method, and the following points are also relevant to this discussion.

1. The dry weights of the pycnometers are not required.
2. The pycnometers and tare are so closely alike that effects due to varying humidity are balanced.
3. The small effect of dissolved air is balanced, and it is not necessary to prepare air-free water.
4. The correction for air buoyancy affects only the difference of differences. Washburn and Smith's "difference" related to volumes, but in the theory described in the following section the "difference" applies to weights. It is the difference in weight

of (a) the tare and the pycnometer filled with solution of unknown density, from (b) the tare and pycnometer filled with water.

4.3. Theory of sealed tare.

Let m_T = mass of sealed tare in vacuum (glass + water)

m_P = mass of dry pycnometer in vacuum.

m_{H_2O} = mass of water to mark in vacuum.

m_S = mass of solution to mark in vacuum.

m_{W1} = extra mass required to balance tare against pycnometer containing water.

m_{W2} = extra mass required to balance tare against pycnometer containing the solution whose density we wish to measure.

Firstly, let us balance a pycnometer filled to the mark with water against the tare, by adding extra weights, W_1, to the tare, in air:

$$(m_P + m_{H_2O}) - U(P + H_2O) = m_T - U_T + m_{W1} - U_{W1} \qquad (4.1)$$

$U(P + H_2O)$ = upthrust on pycnometer containing water,

U_T = upthrust on sealed tare,

and U_{W1} = upthrust on extra weight added to tare.

Next, let us balance a pycnometer filled to the mark with solution against the tare, by adding extra weights, W_2, to the tare, in air:

$$(m_P + m_S) - U(P+S) = m_T - U_T + m_{W2} - U_{W2}. \qquad (4.2)$$

where $U(P+S)$ = upthrust on pycnometer containing solution,

U_{W2} = upthrust on extra weight added to tare.

Now since the pycnometers are made so as to be of almost equal weight and volume, we can make the approximations that

$$U(P + H_2O) = U_T \qquad (4.3)$$

and

$$U(P + S) = U_T \qquad (4.4)$$

Hence

$$m_{H_2O} = m_T - m_P + m_{W1} - U_{W1} \qquad (4.5)$$

and

$$m_S = m_T - m_P + m_{W2} - U_{W2} \qquad (4.6)$$

Now the density of the solution and water respectively are given by

$$d_S = \frac{m_S}{V} \quad \text{and} \quad d_{H_2O} = \frac{m_{H_2O}}{V} \qquad (4.7)$$

where V is the volume of the pycnometer to the mark. Thus, we can write

$$d_S = \frac{m_S\, d_{H_2O}}{m_{H_2O}} \qquad (4.8)$$

$$= \frac{d_{H_2O}}{m_{H_2O}}\left[m_{H_2O} - (m_{W1} - U_{W1}) + (m_{W2} - U_{W2})\right] \qquad (4.9)$$

$$= d_{H_2O}\,\frac{\left[(m_{W2} - U_{W2}) - (m_{W1} - U_{W1})\right]}{V} \qquad (4.10)$$

$$= d_{H_2O}\left[\frac{m'_{W2} - m'_{W1}}{V}\right]$$

$$d_S = d_{H_2O} + \frac{\Delta m_{12}}{V} \qquad (4.11)$$

where Δm_{12} represents the difference between firstly the tare and pycnometer containing solution (m'_{W2}) and secondly, the tare and pycnometer containing pure solvent, (m'_{W1}) <u>as measured in air.</u>

Because of the upthrust of the air on the weights used, it is necessary to correct the difference in weights for the buoyancy of the air. Since the difference is measured by stainless steel weights on a Mettler balance, allowance can be made as follows, assuming that the density of stainless steel is 7.76 gm/c.c. Thus,

$$d_S = d_{H_2O} + \frac{\Delta m_{12}}{V}\left(1 - \frac{d_a}{7.76}\right) \qquad (4.12)$$

where d_a is the density of air. As this buoyancy correction only applies to a <u>difference</u> in weights, we may assume that d_a is approximately constant, so that

$$d_a = 1.2 \times 10^{-3} \text{ gm/c.c.}$$

Hence the corrected equation for determining the density of a solution, d_S becomes

$$d_S = d_{H_2O} + \frac{\Delta m_{12}}{V} (0.999845) \qquad (4.13)$$

4.4. Experimental.

The solutions were prepared gravimetrically and the weights corrected to vacuum using the same methods as described in other chapters of this thesis. Measurements were usually made in quadruplicate using four single stem pycnometers of the type described in section 4.2.

The pycnometers and caps were prepared for use by thoroughly cleaning with chromic acid, followed by rinsing with distilled water for several minutes. The rinsing was effected by inverting the pycnometer over stainless steel capillaries which, in turn, were connected to a supply of distilled water. The surplus water was then removed from the pycnometers by connecting the stainless steel capillaries to a Buchner pump for several minutes. The pycnometers were then rinsed three times with 2 - 3 c.c. of the solution to be used, and then finally completely filled with a syringe to somewhere close to the scratch mark on the capillary. Any surplus droplets of solution were removed with thin strips of No. 50 wet strength filter paper.

The pycnometers with caps replaced were transferred to a stand mounted in a thermostat bath which was controlled by a mercury-toluene regulator[18] to 25.000 ± 0.002°C. Experience had shown that if the pycnometers were filled directly with solution which had been prepared at a temperature a few degrees below 25°, then invariably a number of air bubbles would form on the inside of the pycnometer bulbs, which were very difficult to remove even by gentle tapping of the pycnometers. This problem was overcome by pre-heating the stock solution in a stoppered "quickfit" flask sealed with "Parafilm" in an oven at approximately 27 - 28° first before use.

The level of the meniscus in each of the pycnometers was adjusted by means of a syringe to be within about 0.5 m.m. of the scratch mark, so that the correction to the mark would be small. The meniscus was measured using a cathetometer supplied by the Precision Tool and Instrument Co. Ltd., Surrey, England, which was fitted with a telescope purchased from the Gaertner Scientific Corporation, Chicago, U.S.A. Knowing the cross-sectional area of the capillary, (0.01110 sq. cm.) it was possible to calculate the weight of the pycnometer + solution as if filled exactly to the mark.

Finally, the pycnometers were removed from the thermostat bath, the exterior surfaces were washed with distilled water and dried by wiping carefully with chamois leather, then allowed to stand for about 1½ hours and weighed full. The sealed "tare" was also rinsed, dried and allowed to stand in the same way, so that any surface moisture effects should be balanced by having treated both the pycnometers and tare in the same manner.

The volumes of the pycnometers were accurately determined to the mark by using doubly-distilled water, assuming the density of water[19] at 25° is 0.997048 gm/c.c. Simultaneously with the volume measurements, the quantity m'_{W_1} was determined, which is the difference in weight in air, between the tare and the pycnometer filled with water to the mark. Values for the volumes, and weight differences for each of the pycnometers, designated α, β, γ and δ are given in Tables 4.1 and 4.2 respectively.

TABLE 4.1.

Pycnometer Calibrations - Volumes of Pycnometers.

Pycnometer	α	β	γ	δ
Volume	25.2162	25.2185	25.2117	25.2236
	25.2165	25.2185	25.2115	25.2237
	25.2165	25.2183	25.2115	25.2233
	25.2164	25.2176	25.2117	25.2234
	25.2164	25.2177	25.2114	25.2239
	25.2166	25.2183	-	25.2235
	25.2164	25.2184	25.2115	25.2233
Average	25.2164	25.2182	25.2116	25.2235

TABLE 4.2.

Pycnometer Calibrations - Values of the Term m'_{W_1}.

Pycnometer	α	β	γ	δ
m'_{W_1}	0.00462	0.00675	0.00025	0.01169
	.00461	.00664	.00017	.01155
	.00484	.00676	.00022	.01158
	.00476	.00671	.00047	.01168
	.00462	.00649	.00007	-
	.00471	.00660	-	.01159
	.00475	.00691	.00052	.01164
Average	0.0047_0	0.0066_9	0.0002_8	0.0116_2

4.5 Results and Discussion.

The precision which is attainable using a set of pycnometers with a tare is illustrated by the set of results, obtained for a thiourea solution, which are summarised in Table 4.3.

The density results for the ternary systems water-urea-sucrose and water-sucrose-mannitol are summarised in Tables 4.4 and 4.5. The values at each ternary point were fitted, using an I.B.M. 1620 computer, to a Taylor series of the form

$$d = d(\overline{C}_1,\overline{C}_2) + H_1(C_1 - \overline{C}_1) + H_2(C_2 - \overline{C}_2) \qquad (4.14)$$

where $d(\overline{C}_1,\overline{C}_2)$ is the density of the solution whose concentrations are exactly $\overline{C}_1$ and $\overline{C}_2$. The numerical values of these equations are given in the Tables after each set of data. The unit of concentration is moles/1000 c.c.

The densities of aqueous thiourea solutions, as a function of both molarity and molality are given in Table 4.6. This data was least squared, using an I.B.M. 1620 computer, to give the relations of the form

$$d = d_0 + \sum_{i=1}^{2} A_i C^i \qquad (4.15)$$

TABLE 4.3

A Set of Densities Obtained in Quadruplicate Using Four Pycnometers and a "Tare".

System: 0.67201 Molar Thiourea in Water.

	α	β	γ	δ
Weight tare	58.4935_7	58.4935_7	58.4935_7	58.4935_7
Difference in length between meniscus and scratch mark (cm.)	0.0290	0.0255	0.0254	0.0222
Volume difference (c.c.)	0.00032	0.00028	0.00028	0.00025
Weight pycnometer	58.8579_3	58.8599_7	58.8535_0	58.8649_6
$m'W_2$	0.36404	0.36612	0.35965	0.37114
$m'W_1$	0.00470	0.00669	0.00028	0.01162
Δm_{12}	0.35934	0.35943	0.35937	0.35952
Δd	0.01424_8	0.01425_1	0.01425_2	0.01425_1
Average Δd =	0.01425_1			
Average d =	1.01129_9			

TABLE 4.4

DENSITIES OF WATER - UREA - SUCROSE SOLUTIONS AT 25°

$\overline{C}_1 = 0.50$ $\overline{C}_2 = 0.50$

d	C_1	C_2
1.068782	0.41527	0.49950
1.071369	0.58368	0.49948
1.068752	0.43254	0.49710
1.071592	0.56776	0.50292
1.068311	0.48169	0.48776
1.072033	0.51795	0.51222
1.067959	0.49722	0.48340
1.072249	0.49740	0.51647

$$d = 1.07016_3 + 0.01540_0(C_1 - 0.50) + 0.1296_4(C_2 - 0.50)$$

AVERAGE DEVIATION = ± 0.000011

$\overline{V}_0 = 18.058$ $\overline{V}_1 = 44.7_6$ $\overline{V}_2 = 213.1_7$

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TABLE 4.5

DENSITIES OF WATER - SUCROSE - MANNITOL SOLUTIONS AT 25°

$\bar{C}_1=0.25$ $\bar{C}_2=0.25$

d	C_1	C_2
1.042975	0.24997	0.21049
1.047891	0.24997	0.28948
1.042591	0.22822	0.25002
1.048269	0.27172	0.25000
1.042912	0.24580	0.21836
1.047957	0.25419	0.28175
1.042693	0.23284	0.24194
1.048177	0.26716	0.25814

$$d = 1.04543_4 + 0.1305_1(C_1-0.25) + 0.06226\,(C_2-0.25)$$

AVERAGE DEVIATION = ± 0.000002

$\bar{V}_0=18.064$ $\bar{V}_1=212.3_8$ $\bar{V}_2=120.2_5$

$\bar{C}_1=0.25$ $\bar{C}_2=0.50$

d	C_1	C_2
1.058442	0.24993	0.45922
1.063464	0.24993	0.54064
1.058116	0.22814	0.49990
1.063767	0.27170	0.49989
1.058368	0.24567	0.46749
1.063524	0.25421	0.53267
1.056870	0.23237	0.47132
1.063690	0.26733	0.50821

$$d = 1.06095_1 + 0.1297_8(C_1-0.25) + 0.06191\,(C_2-0.50)$$

AVERAGE DEVIATION = ± 0.000012

$\bar{V}_0=18.059$ $\bar{V}_1=213.0_4$ $\bar{V}_2=120.5_6$

TABLE 4.5 (CONT.)

DENSITIES OF WATER - SUCROSE - MANNITOL SOLUTIONS AT 25°

$\bar{C}_1 = 0.50$ $\bar{C}_2 = 0.25$

d	C_1	C_2
1.075442	0.49991	0.21031
1.080319	0.49986	0.28952
1.074974	0.47746	0.24989
1.080775	0.52230	0.24989
1.075368	0.49575	0.21810
1.080395	0.50422	0.28190
1.075097	0.48240	0.24172
1.080669	0.51755	0.25826

$$d = 1.07789_2 + 0.1294_2(C_1 - 0.50) + 0.06164\,(C_2 - 0.25)$$

AVERAGE DEVIATION = ± 0.000007

$\bar{V}_0 = 18.055$ $\bar{V}_1 = 213.3_6$ $\bar{V}_2 = 120.8_0$

$\bar{C}_1 = 0.50$ $\bar{C}_2 = 0.50$

d	C_1	C_2
1.090652	0.49875	0.45862
1.095627	0.49935	0.54010
1.090331	0.47733	0.49992
1.096102	0.52218	0.49977
1.090670	0.49567	0.46673
1.095876	0.50433	0.53328
1.090467	0.48230	0.49155
1.096062	0.51761	0.50856

$$d = 1.09327_4 + 0.1291_2(C_1 - 0.50) + 0.06064\,(C_2 - 0.50)$$

AVERAGE DEVIATION = ± 0.000019

$\bar{V}_0 = 18.044$ $\bar{V}_1 = 213.5_2$ $\bar{V}_2 = 121.7_3$

TABLE 4.6

DENSITIES AND RELATIVE VISCOSITIES OF AQUEOUS THIOUREA SOLUTIONS AT 25°.

C	m	d	η_r
0.098895	0.099731	0.999145	1.0016
0.29413	0.29986	1.003302	1.0052
0.48519	0.49998	1.007354	1.0091
0.67201	0.69990	1.011299	1.0133
0.94500	0.99989	1.017031	1.0221
1.20943	1.29974	1.022577	1.0297
1.46580	1.59963	1.027912	1.0393

$d = 0.997048 + 0.021311\,C - 0.000171\,C^2 \qquad C<1.5$

$d = 0.997048 + 0.021192\,m - 0.001190\,m^2 \qquad m \leqslant 1.6$

$\Phi = 54.971 + 0.1715\,C \qquad C<1.5$

$\eta_r = 1 + 0.01510\,C + 0.00799\,C^2 \qquad C<1.5$

and

$$d = d_0 + \sum_{i=1}^{2} B_i m^i \qquad (4.16)$$

with average deviations of ± 0.000005 and ± 0.000007 respectively.

The densities of aqueous sucrose solutions, given in Table 4.7, can be represented by the equation

$$d = 0.997048 + 0.13153\ C - 0.001570\ C^2 \qquad (4.15a)$$

with an average deviation of ± 0.000007.

Apparent molar volumes of thiourea Φ_1, are given by the relation

$$\Phi_1 = \frac{1000}{C}\left[\frac{d_0 - d}{d_0}\right] + (M/d_0) \qquad (4.17)$$

where M is the molecular weight of the thiourea. By combining equations 4.15 and 4.17, the apparent molar volumes may be expressed by an equation of the form

$$\Phi_1 = \Phi_1^{\,o} + EC \qquad (4.18)$$

where

$$\Phi_1^{\,o} = (M - 1000A_1)/d_0 \qquad (4.18a)$$

and

$$E = -(1000A_2)/d_0 \qquad (4.18b)$$

The numerical solutions to equations 4.15, 4.16 and 4.18 may be found at the foot of Table 4.6.

The density results for thiourea may be compared with those of Indelli.[7] On converting Indelli's data from moles per 1000ml. to moles per 1000c.c., the value obtained at 1 molar is 1.01813_7, which may be compared with 1.01818_8 obtained from this work. At 0.5 molar, the densities are 1.00762_7 and 1.00766_0 , respectively. Indelli obtained the apparent molar volume as a function of the square root of concentration, and derived $\Phi_1^{\circ} = 54.79_3$, whereas from this work the value of $\Phi_1^{\circ} = 54.97_1$ was calculated.

B. VISCOSITY MEASUREMENTS.

4.6 Introduction.

The measurement of viscosity forms an important part of many processes and studies. In industry, the maintenance of machinery depends on the fluidity of the oils and greases used, and in the scientific laboratory, the rate of transport of a particular species in solution, or the nature of a particular polymer, depends on its viscosity.

Viscosity measurements, in common with density measurements, provide useful information regarding molecular state and structure, and electrolytes have been studied in aqueous solution,[20,21] and mixed electrolytes,[22] and non-electrolytes[8] have also been studied in aqueous solution. Viscosity determinations are of considerable importance in studies of high polymers[23] and also proteins.[24]

In the work presented here, relative viscosity measurements are reported for two ternary systems, and for the binary system water-thiourea. The computation of the relative viscosities of the solutions also involved the incorporation of the density data discussed above.

4.7 Theory.

The first hypothesis concerning the magnitude of the force required to overcome viscous resistance was postulated by Isaac Newton:[25]

> "The resistance which arises from the lack of slipperiness originating in a fluid - other things being equal - is proportional to the velocity by which parts of the fluid are being separated from each other."

This tells us that, if we consider two parallel planes in a liquid, each of area A, seperated by a distance x and moving at velocities v_1 and v_2 in the direction of either of the planes, then the force required to maintain this difference of velocity is proportional to the gradient of velocity,

$$\text{i.e.} \quad F \propto \frac{A.(v_1 - v_2)}{x} \tag{4.19}$$

but as the velocity of the liquid is changing continuously,

$$F \propto A.\frac{dv}{dx} = \eta\, A.\frac{dv}{dx} \tag{4.20}$$

The constant of proportionality, η, is termed the "coefficient of viscosity" of the liquid.

However, one of the earliest expressions related to viscosity was derived empirically by Poiseuille:

$$Q = K \cdot \frac{PD^4}{L} \qquad (4.21)$$

where Q is the quantity discharged in unit time, L the tube length, D its diameter, P the pressure difference between the ends of the capillary, and K is a constant characteristic of the liquid. Soon afterwards, Wiedemann, and later Hagenbach, deduced a theoretical formula for the volume discharged in unit time, which is the more familiar form of the Poiseuille equation

$$Q = \frac{\pi P r^4}{8L} \qquad (4.22)$$

where r is the radius of the tube. However, in this equation, we have assumed that all the potential energy is used to overcome viscous resistance, whereas actually a portion is used to impart velocity, i.e. kinetic energy, to a liquid. Thus the equation

$$Q = \frac{\pi P r^4}{8\eta L} \qquad (4.23)$$

when corrected for kinetic energy becomes

$$\eta = \frac{\pi P r^4}{8QL} - \frac{mQd}{8\pi L} \qquad (4.24)$$

where m is a small constant, usually about 1.12, and d is the density of the solution.

Couette suggested a second correction to allow for the non-laminar flow at the ends of the capillary.

This takes the form of a "fictitious lengthening" of the capillary whereby equation 4.24 becomes

$$\eta = \frac{\pi P r^4}{8V(L+\lambda)} \cdot t - \frac{mVd}{8\pi(L+\lambda)t} \qquad (4.25)$$

where V is the volume of liquid passing through the capillary in time t, and λ is a small end correction of magnitude several diameters of the capillary. This may be written in the form

$$\eta = A\,dt - Bd/t \qquad (4.26)$$

or

$$\frac{\eta}{dt} = A - \frac{B}{t^2} \qquad (4.27)$$

Neglecting second order correction terms, the corrected relative viscosity is given by

$$\eta_r = \frac{\eta}{\eta_0} = \frac{dt}{d_0 t_0}\left[1 + K\left[\frac{1}{t_0{}^2} - \frac{1}{t^2}\right]\right] \qquad (4.28)$$

where

$$K = \frac{B}{A} = \frac{mV^2}{\pi^2 hgr^4} \qquad (4.29)$$

and h is the difference of the distance from the mean position between the two observation marks on the viscometer and the bottom of the capillary.

4.8 Experimental.

The Ubbelohde type viscometer used in this work required about 32 c.c. of solution, and is shown in the photograph, Plate 4.2. It was cleaned before use with chromic acid, washed with doubly-distilled water, rinsed with 20 c.c. acetone and dried for 20 to 30 minutes by connecting to a vacuum pump. To prevent dust particles from entering the capillary and causing blockages or restrictions, the solutions used were poured into the viscometer through a sintered glass funnel.

The viscometer was placed in a glass-fronted water bath controlled to 25.000 ± 0.002° with a mercury-toluene regulator,[18] and allowed to equilibrate, and the alignment checked with a plumbob. The time for the solution to flow between two marks was observed with an electronic decade counter and results were recorded to the nearest 1/100 second. Four or five flow times were recorded for each solution, and the greatest difference between any two readings of a series was always less than 0.05%.

4.9 Results.

A. Kinetic Energy Correction.

Values of (η/dt) against $(1/t^2)$ were plotted for water at 20°, 25° and 30°, and for 20% and 30% sucrose at 25°. For 20% sucrose, a value of

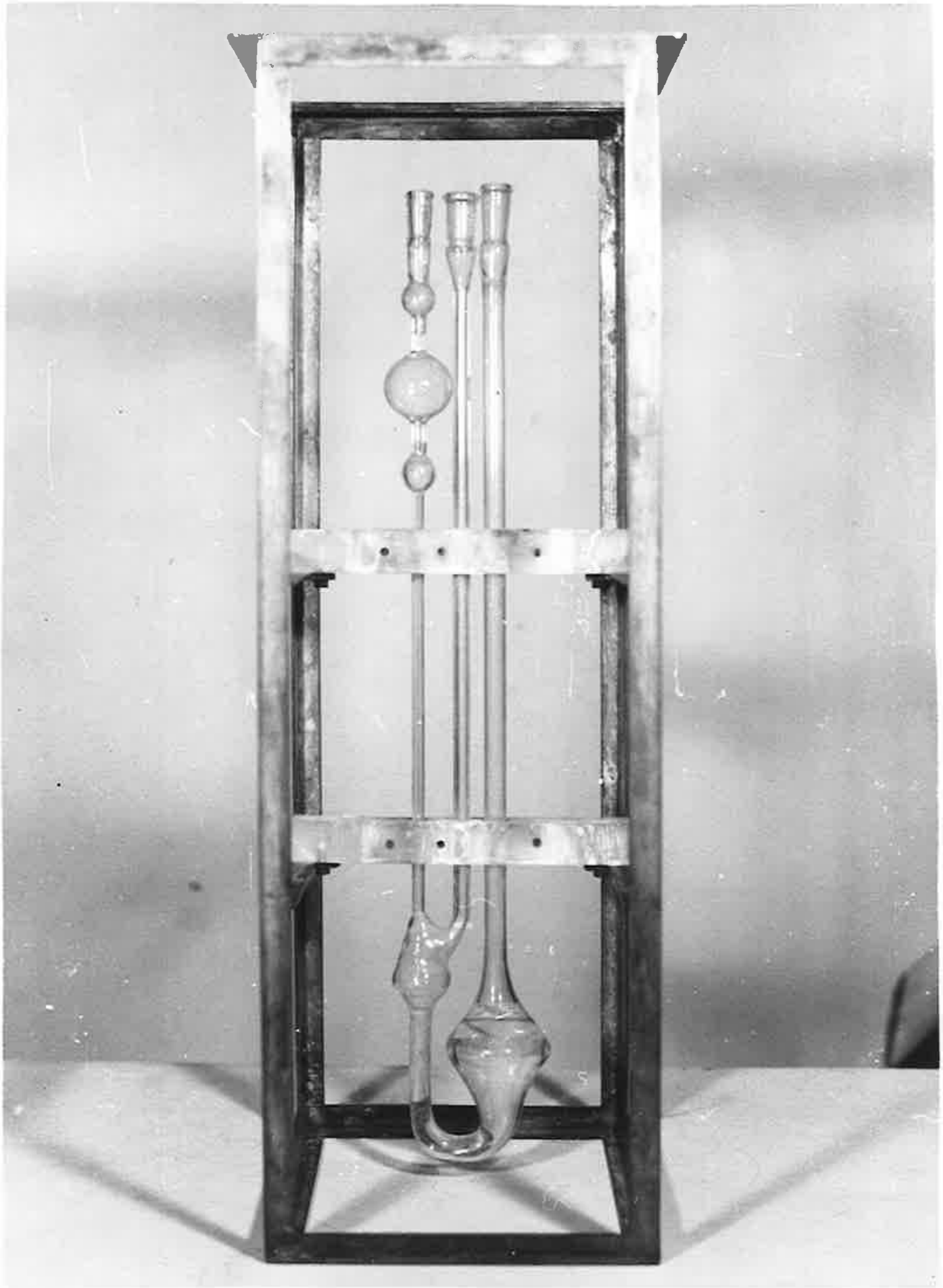

Plate 4.2. The Ubbelohde viscometer.

$\eta = 1.701$ was used, and for 30% sucrose, a value of $\eta = 2.735$ was assumed.[26] The results are given in Table 4.7 and plotted in Figure 4.1. Since these calibration points were obtained over a period of about 2¼ years from April 1962 to July 1964, the water flow times at 25°, which were always measured at the same time as those for the other solutions tested in Table 4.7, as a standard of reference, varied by about 0.45 sec. over this time, mainly due to "settling down" after repairs were made on the viscometer at the beginning of this period. Consequehtly, all flow times listed in the Table have been adjusted relative to a constant flow time of 288.54 seconds for water at 25°. It is worth noting however, that for measurements on binary and ternary systems described in the following sections of this chapter, (except for early measurements in the water-sucrose system), the flow time for water at 25° remained essentially unchanged, the values between February 1964 and September 1965 fluctuating only between 288.50 and 288.61 seconds.

The values of (η/dt) versus $(1/t^2)$ fitted to a straight line to within 0.1%, as shown in Figure 4.1. From this line, the slope and intercept were obtained, according to equations 4.27 and 4.29, to give a value for the kinetic energy correction $K = 290$.

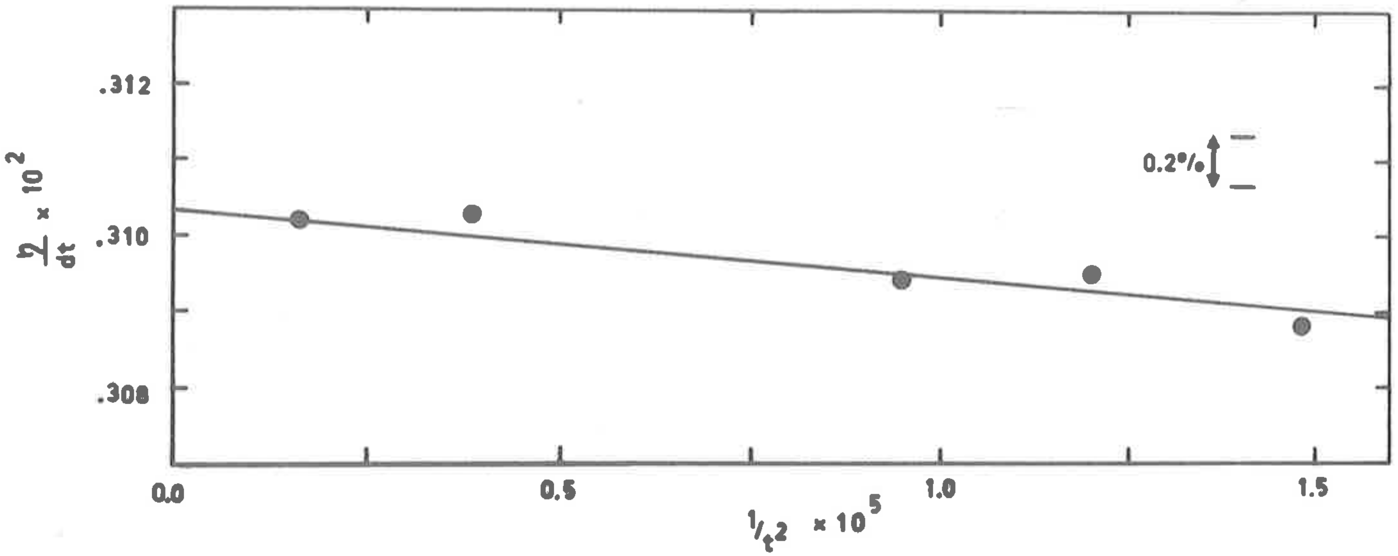

Figure 4.1. Plot of η/dt versus $1/t^2$ to determine the kinetic energy correction of the Ubbelohde viscometer.

TABLE 4.7

Estimation of Kinetic Energy Correction for Ubbelohde Viscometer.

Liquid	T°C	Adjusted flow time of solution.	$\frac{\eta}{dt} \times 10^2$	$\frac{1}{t^2} \times 10^5$
Water	25°	288.54	0.3095	1.2011
Water	20°	324.39	0.3094	0.9503
Water	29.945°	259.67	0.3088	1.4831
20% Sucrose	25°	507.88	0.3103	0.3877
30% Sucrose	25°	783.41	0.3102	0.1629

It is worth noting that a viscometer has been described recently[27] which has a long-flared capillary. By incorporating such a capillary into an otherwise conventional viscometer, it is claimed to be possible to produce an instrument in which no significant kinetic energy correction occurs.

B. Relative Viscosities of the System Water-Sucrose and the Ternary Systems.

The densities and relative viscosities (where determined) of several sucrose solutions at 25° are given in Table 4.8, and can be represented by the equation

$$\eta_r = 1 + 0.8505_5C + 0.7357_3C^2 - 0.0653_8C^3 + 0.6148_4C^4 \qquad (4.30)$$

with an average deviation of ± 0.0004.

The viscosity results for the ternary systems water-urea-sucrose and water-sucrose-mannitol are summarised in Tables 4.9 and 4.10 respectively. The values at each ternary point were fitted, using an I.B.M. 1620 computer, to a Taylor series of the form

$$\eta_r = \eta(\bar{C}_1, \bar{C}_2) + a_1(C_1 - \bar{C}_1) + a_2(C_2 - \bar{C}_2) \qquad (4.31)$$

The numerical values of these equations are given in the Tables after each set of data.

TABLE 4.8

Densities and Relative Viscosities of Sucrose Solutions at 25°.

C	Weight %	d	Flow time of soln.	Flow time of water.	η_r
0.13123_2	4.4288_4	1.01428_5[a]	318.97	288.76	1.124_4
0.30288_4	10.0002_6	1.03674_5[a]	368.20	288.67	1.328_1
0.48350_5	15.6092_8	1.06029_5	436.37	288.70	1.610_5
0.51654_7	16.6090_1	1.06457_3	450.58	288.70	1.669_8
0.63066_2	20.0002_4	1.07937_1[b]	508.03	288.67	1.909_7
0.98621_5	30.0003_2	1.12523_7[c]	783.41	288.54	3.073_4
0.04100_4	1.40018_3	1.00242_3	-	-	-
0.10659_1	3.60876	1.01104_6[a]	-	-	-
0.22830_2	7.60947_8	1.02698_9	-	-	-
0.27179_9	9.00929_9	1.03268_5	-	-	-
0.75947_7	23.71921	1.09603_4[a]	-	-	-
0.90284_4	27.72962	1.11449_6[a]	-	-	-

a. Densities measured by Dr. P. J. Dunlop.

b. Density quoted by B.J.Steel, Ph.D., thesis, University of New England, Armidale, N.S.W., Australia, 1960.

c. Density and relative viscosity measured by Mr. D. E. Mulcahy.

TABLE 4.9

RELATIVE VISCOSITIES OF WATER - UREA - SUCROSE SOLUTIONS AT 25°.

$\bar{C}_1=0.5$ $\bar{C}_2=0.5$

η_r	C_1	C_2
1.6737	0.43254	0.49710
1.6981	0.56776	0.50292
1.6599	0.48169	0.48776
1.7113	0.51795	0.51222
1.6536	0.49722	0.48340
1.7178	0.49740	0.51647

$$\eta_r = 1.685_9 + 0.09712(C_1-0.50) + 1.945_0(C_2-0.50)$$

AVERAGE DEVIATION = ± 0.00017

TABLE 4.10

RELATIVE VISCOSITIES OF WATER - SUCROSE - MANNITOL SOLUTIONS AT 25°.

$\bar{C}_1 = 0.25$ $\bar{C}_2 = 0.25$

η_r	C_1	C_2
1.4157	0.24997	0.21049
1.4821	0.24997	0.28948
1.4152	0.22822	0.25002
1.4813	0.27172	0.25000
1.4160	0.24580	0.21836
1.4823	0.25419	0.28175
1.4159	0.23284	0.24194
1.4887	0.26716	0.25814

$$\eta_r = 1.450_0 + 1.589_2(C_1 - 0.25) + 0.8633(C_2 - 0.25)$$

AVERAGE DEVIATION = ± 0.0013

$\bar{C}_1 = 0.25$ $\bar{C}_2 = 0.5$

η_r	C_1	C_2
1.6401	0.24993	0.45922
1.7266	0.24993	0.54064
1.6471	0.22814	0.49990
1.7229	0.27170	0.49989
1.6401	0.24567	0.46749
1.7240	0.25421	0.53267
1.6205	0.23237	0.47132
1.7232	0.26733	0.50821

$$\eta_r = 1.683_5 + 1.766_9(C_1 - 0.25) + 1.066_7(C_2 - 0.50)$$

AVERAGE DEVIATION = ± 0.0011

TABLE 4.10 (CONT.)

RELATIVE VISCOSITIES OF WATER - SUCROSE - MANNITOL SOLUTIONS AT 25 °.

$\overline{C}_1 = 0.5$ $\overline{C}_2 = 0.25$

η_r	C_1	C_2
1.8703	0.49991	0.21031
1.9699	0.49986	0.28952
1.8690	0.47746	0.24989
1.9733	0.52230	0.24989
1.8716	0.49575	0.21810
1.9715	0.50422	0.28190
1.8685	0.48240	0.24172
1.9724	0.51755	0.25826

$$\eta_r = 1.921_0 + 2.340_1(C_1 - 0.50) + 1.259_0(C_2 - 0.25)$$

AVERAGE DEVIATION = ± 0.0005

$\overline{C}_1 = 0.5$ $\overline{C}_2 = 0.5$

η_r	C_1	C_2
2.2074	0.49875	0.45862
2.3349	0.49935	0.54010
2.2079	0.47733	0.49992
2.3279	0.52218	0.49977
2.2085	0.49567	0.46673
2.3496	0.50433	0.53328
2.2090	0.48230	0.49155
2.3393	0.51761	0.50856

$$\eta_r = 2.274_0 + 2.782_8(C_1 - 0.50) + 1.648_7(C_2 - 0.50)$$

AVERAGE DEVIATION = ± 0.0039

C. Relative Viscosities for the System Water-Thiourea.

The relative viscosities of aqueous thiourea solutions are given in Table 4.6. This data was least squared as a function of molarity, using an I.B.M. 1620 computer, to give a relation of the form

$$\eta_r = 1 + \sum_{i=1}^{2} F_i C^i \qquad (4.32)$$

The numerical solution to this equation is given at the foot of Table 4.6, and the data has an average deviation of ± 0.0002 from the equation.

The viscosity data are plotted graphically in Figure 4.2, and it can be seen that the values are considerably lower than for urea solutions at corresponding concentrations. The relative viscosities of urea solutions were derived from the equation

$$\eta_r = 1 + 0.0370\ C + 0.00434\ C^2 \qquad (4.33)$$

which had been obtained by Amsley and Gosting[28] from data available in the literature.

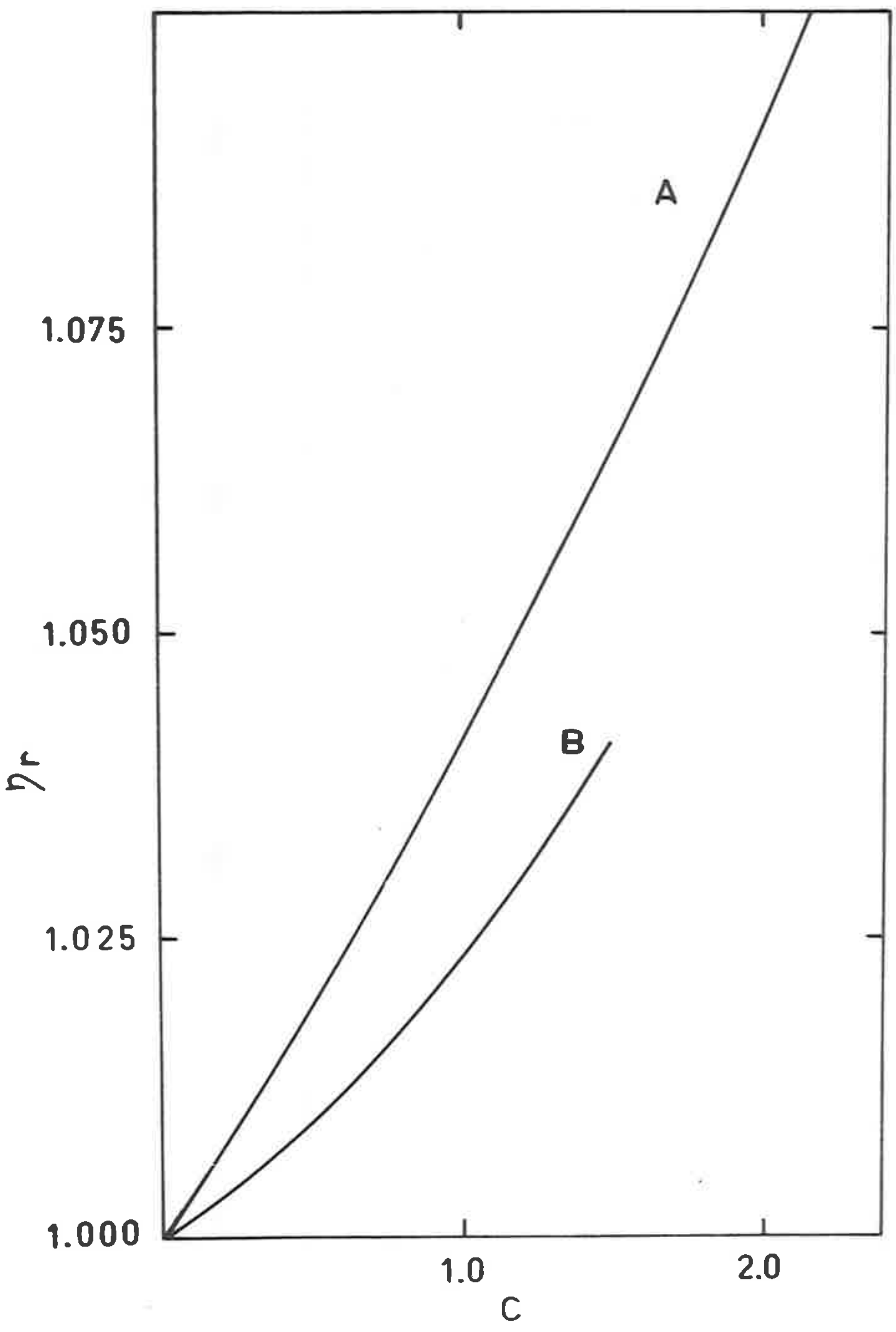

Figure 4.2. The concentration dependence of relative viscosity.

A, Urea; B, Thiourea.

References to Chapter 4.

1. A. J. Smith and E. O. Huffan, Chem. Eng. Data Series, 1, 99 (1956).
2. O. Redlich and D. M. Meyer, Chem. Revs., 64, 221 (1964).
3. O. Redlich, J. Phys. Chem., 67, 496 (1963).
4. J. Padova, J. Chem. Phys., 39, 2599 (1963).
5. W. Y. Wen and S. Saito, J. Phys. Chem., 68, 2639 (1964).
6. B. J. LeVien, Aust. J. Chem., 18, 1161 (1965).
7. A. Indelli, Ann. di Chim., 53, 605 (1963).
8. H. D. Ellerton, G. Reinfelds, D. E. Mulcahy and P. J. Dunlop, J. Phys. Chem., 68, 398 (1964).
9. P. A. Charlwood, J. Am. Chem. Soc., 79, 776 (1957).
10. D. A. MacInnes, D. O. Dayhoff and B. R. Ray, Rev. Sci. Instr., 22, 642 (1951).
11. E. F. Casassa and H. Eisenberg, J. Phys. Chem., 65, 427 (1961).
12. P. Mukerjee, ibid., 66, 1733 (1962).
13. P. H. Bigg, J. Roy. Inst. Chem., 408 (1963).
14. A. B. Lamb and R. E. Lee, J. Am. Chem. Soc., 35, 1668 (1913).
15. D. E. Mulcahy and B. J. Steel, unpublished results.
16. N. Bauer and S. Z. Lewin, in A. Weissberger ed., "Physical Methods of Organic Chemistry", Vol. I, pt. 1, pages 148-162, Interscience, New York, 1959.
17. E. W. Washburn and E. R. Smith, J. Res. Natl. Bur. Std., 12, 305 (1934).
18. R. H. Stokes, N.Z. Journal of Science and Technology, 27, 75 (1945).

19. B. B. Owen, J. R. White and J. S. Smith, J. Am. Chem. Soc., 78, 3561 (1956). These authors quote the density of water at 25° as 0.997075 gm/ml.

20. E. R. Nightingale, Jr., J. Phys. Chem., 63, 742 (1959); 66, 894 (1962).

21. E. R. Nightingale, Jr., and J. F. Kuecker, ibid., 69, 2197 (1965).

22. J. Padova, J. Chem. Phys., 38, 2635 (1963).

23. O. E. Ohrn, Arkiv. für. Kemi, 12, 397 (1958).

24. P. A. Charlwood, Canad. J. Chem., 33, 1043 (1955).

25. Isaac S. Newton, "Philosophiae Naturalis Principia Mathematica", 1st. Edition, 1687, Book 2 Section IX.

26. J. F. Swindells, C. F. Snyder, R. C. Hardy and P. E. Golden, Supp. to N.B.S. Circular 440, July 31, 1958.

27. W. A. Caw and R. G. Wylie, British J. Appl. Phys., 12, 94 (1961).

28. D. F. Akeley and L. J. Gosting, J. Am. Chem. Soc., 74, 2058 (1952).

CHAPTER 5.

ISOTHERMAL DIFFUSION MEASUREMENTS USING THE GOUY DIFFUSIOMETER: THEORY AND EXPERIMENTAL.

5.1 Introduction.

A variety of methods has been developed in recent decades for the measurement of the rate of diffusion of substances in solution. A technique which is of considerable interest involves the use of the diaphragm-cell. This apparatus, in which two solutions of different concentrations are separated by a sintered glass diaphragm, so that the diffusion process takes place through the capillary pores, has been developed in recent years, particularly with adaptations by Stokes[1], and is now used extensively in diffusion studies in various laboratories. After diffusion has taken place, the solutions may be analysed by chemical, optical or conductance methods. An adaption of the diaphragm-cell method has been made with the study of tracer diffusion, and Mills[2,3] has studied several systems using a similar experimental technique, except that the radio-active species is measured using radio-counting apparatus. Further details of other types of apparatus applicable to the study of diffusion may be found elsewhere, and the reader is directed, in particular, to a review by Gosting[4], and to the monograph by Robinson and Stokes.[5]

Considerable success has also been obtained, however, by using optical methods. One such optical system, which utilises Gouy interference optics, was used in the measurements reported in this work. The experimental method will be discussed more fully in a later section. The Gouy optics, first reported in 1880 by Gouy,[6] were left largely unused until interest was revived in 1945 by Longsworth.[7] A theory for interpreting the non-equal fringe spacings was derived by Kegeles and Gosting,[8] and almost simultaneously by Coulson _et al_.[9] The latter authors sacrificed accuracy for ability to make rapid determinations with small samples of solutions, whereas Gosting and co-workers have concentrated on achieving the maximum possible accuracy, so that isothermal diffusion coefficients may be obtained for a binary system with an accuracy of 0.1%.

The work described in this thesis uses a Gouy diffusiometer of a similar type to Gosting and co-workers.

It is intended that this chapter should provide most of the theoretical and experimental information necessary to describe the results which follow in the two succeeding chapters. Of necessity, therefore, much of the theory described will be a review of material already published, but it is considered that this is necessary, and justified, in order to make the experimental application complete.

5.2 Theory of Diffusion.

A. Fick's Laws.

Fick's first law,[10] which defines the diffusion coefficient, D, is the simplest of all experimental flow equations. For diffusion at constant temperature and pressure in a binary system, Fick's first law for one dimensional transport of solute is

$$J_i = - D \left[\frac{\partial C_i}{\partial x}\right]_t \qquad (i = 0,1) \qquad (5.1)$$

i.e. At any time, t, and position x, the flow J_i of solute relative to the cell is directly proportional to the concentration gradient.

By substitution of the first law into the equation of continuity we obtain directly Fick's second law,

$$\left[\frac{\partial C_i}{\partial t}\right]_x = D \left[\frac{\partial^2 C_i}{\partial x^2}\right]_t \qquad (i = 0,1) \qquad (5.2)$$

In deriving this equation we have assumed that D is independent of concentration. Experimentally, it is arranged so that the difference in concentration between two diffusing solutions is small, in order that this requirement may be satisfied.

B. Measurement of D by the Gouy Interference Method.

When a horizontal beam of light is passed through a cell in which diffusion is taking place in a vertical direction across a concentration gradient, and if the light beam is focussed on to a vertical plane by means of a lens, a set of interference fringes are obtained, as shown in Plate 5.1. These fringes, first observed by Gouy, arise from the fact that parallel light rays are passing through conjugate regions of equal refractive index gradient. The optical arrangement is shown in Figure 5.1. It can be seen that light rays passing through upper and lower parts of the cell, C, where there is no refractive index gradient, suffer no deflection, whereas those passing through the centre of the cell, where the refractive index gradient is a maximum, suffer maximum deflection.

If the refractive index of a three-component system is a linear function of each solute concentration

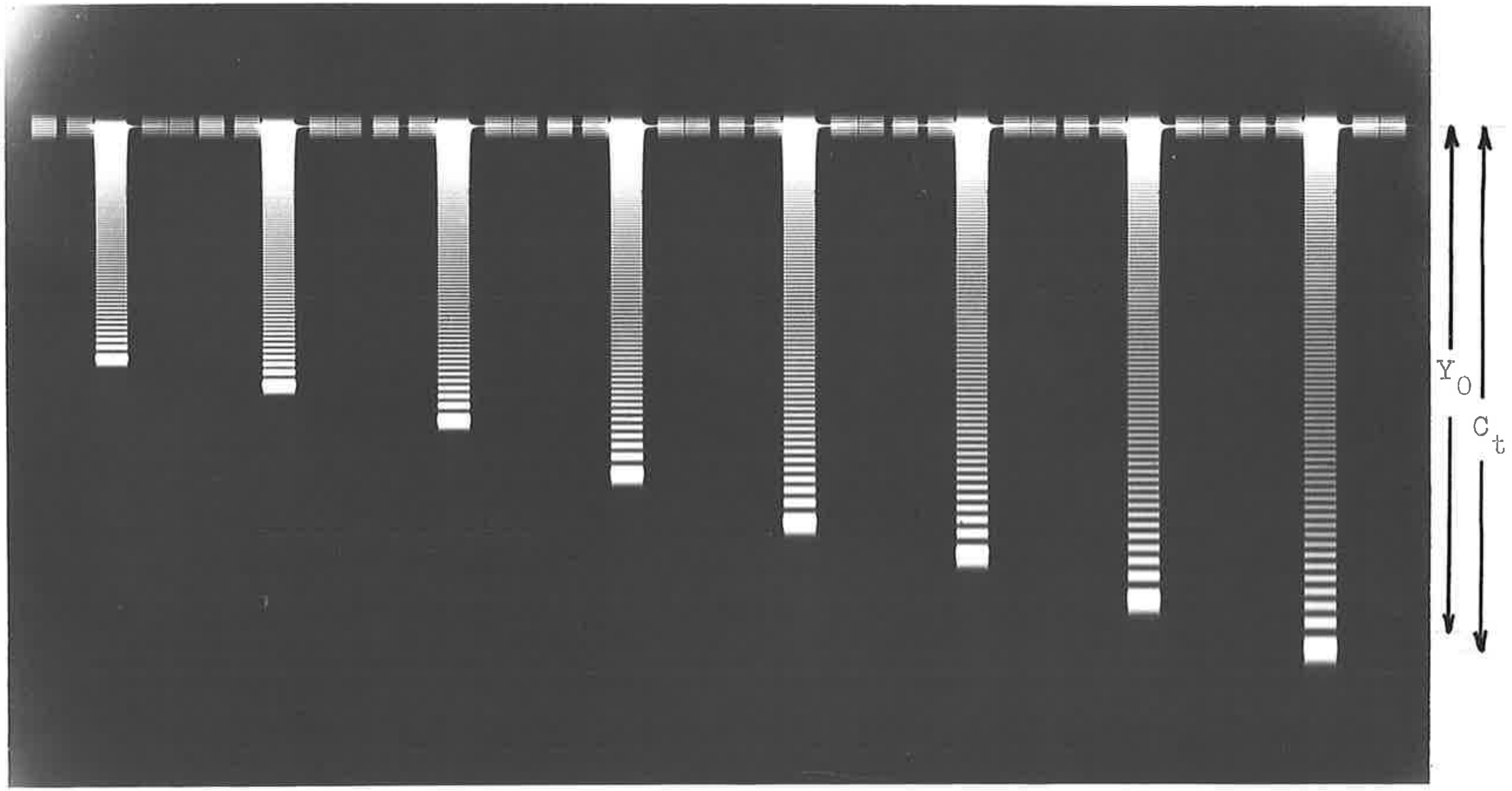

Plate 5.1. Typical set of Gouy interference fringe photographs, taken during an experiment, showing the variation in pattern size with time.

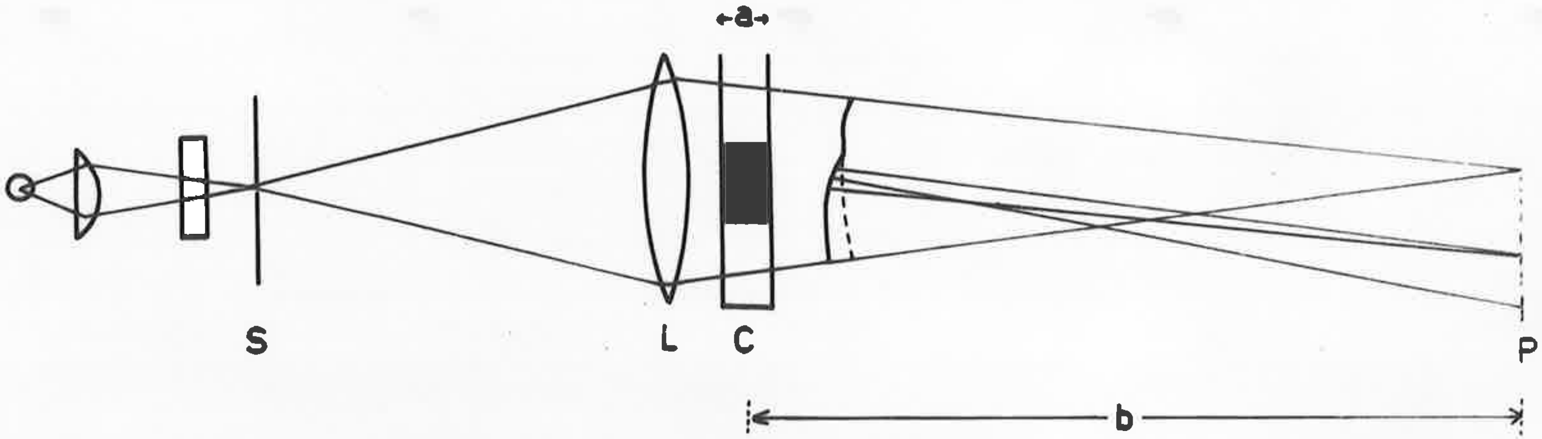

Figure 5.1. Diagrammatic arrangement of apparatus for measuring diffusion by the Gouy interference method.

over the relatively small concentration range encounntered in the diffusion cell, we may write

$$n = n(\bar{C}_1,\bar{C}_2) + \sum_{i=1}^{2} R_i(C_i - \bar{C}_i) \qquad (5.3)$$

where $n(\bar{C}_1,\bar{C}_2)$ is the refractive index at solute concentrations $\bar{C}_1$ and $\bar{C}_2$, and the constants R_i, the differential refractive increments, are the changes of refractive index corresponding to unit change in solute concentration. The refractive index distribution for free diffusion, for the case of D_i independent of the C_i, becomes

$$\frac{\partial n}{\partial x} = \sum_{i=1}^{2} \frac{\alpha_i}{2} \frac{\Delta n}{\sqrt{\pi D_i t}} \cdot \exp\left[\frac{-x^2}{4D_i t}\right] \qquad (5.4)$$

where the α_i are the solute fractions on the basis of refractive index, and are defined by

$$\alpha_i = \frac{R_i \; \Delta C_i}{\Delta n} \qquad (i = 1,2) \qquad (5.5)$$

It is convenient to define here the "reduced height-area ratio", which is given by

$$\mathscr{D}_A = \frac{(\Delta n)^2}{4\pi t \left[\frac{\partial n}{\partial x}\right]^2_{\max.}} \qquad (5.6)$$

For the special case of binary systems only in which D is independent of C and n is linear in C, it may be shown by substitution of equation 5.4 into equation 5.5 that

$$\mathcal{D}_A = D \tag{5.7}$$

A set of interference fringes obtained using the Gouy optical system is shown in the photograph, Plate 5.1. The displacements, Y_j, of the fringe minima, formed by the angular deflection of the light due to the concentration gradient present in the solution undergoing free diffusion, are shown in the photograph, and are numbered j = 0, 1, 2 etc., starting with the fringe which has undergone most deflection. The total number of fringes, J, is given by

$$J = \frac{a\Delta n}{\lambda} \tag{5.7a}$$

where a is the internal thickness of the cell along the light path, Δn is the refractive index difference across the initial boundary, and λ is the wavelength of the monochromatic light used.

The reduced height-area ratio becomes

$$\mathcal{D}'_A = \frac{(J\lambda b)^2}{4\pi t' C_t^2} \tag{5.8}$$

where t' is the time at which the photograph is taken after forming an initial sharp boundary, C_t is the greatest downward deflection of light at the photographic plate that is predicted by ray optics, and b is the optical distance, from the centre of the cell to the emulsion of the photographic plate, given[11] by $\sum_i l_i/n_i$, where l_i is the distance along the optic axis in medium i of refractive index n_i .

As C_t cannot be measured directly from the photographs, calculations of values of C_t are made from the measured distance Y_j between the normal slit image and minima in the interference pattern using the equation

$$C_t = Y_j / e^{-\zeta_j^2} \tag{5.9}$$

where $e^{-\zeta_j^2}$ is read from tables of the function

$$f(\zeta_j) = \frac{2}{\pi}\left[\int_0^{\zeta_j} e^{-\beta^2} d\beta \quad - \quad \zeta_j e^{-\zeta_j^2}\right] \tag{5.10}$$

which is in turn obtained from the interference condition

$$f(\zeta_j) = \frac{(j + \frac{3}{4} + \ldots\ldots)}{J} = \frac{Z_j}{J} \qquad (0<f(\zeta_j)<1) \tag{5.11}$$

where the approximation Z_j to the series $(j + \frac{3}{4} + \ldots\ldots)$ has been tabulated.[12] For a binary system, where the refractive index gradient curve is Gaussian, values of $Y_j / e^{-\zeta_j^2}$ are constant, and C_t is determined from the average of values obtained from several of the lower fringe minima. For a ternary system, however, $Y_j / e^{-\zeta_j^2}$ varies with j, so that values of the ratio are plotted against $Z_j^{2/3}$, and a value of C_t is obtained from the extrapolation of $Z_j^{2/3} = 0$.

It is necessary to make a small correction, Δt, to the observed times t', since the initial boundary formed will always be slightly blurred, so that the true value of $\mathcal{D}_A$ is related to $\mathcal{D}'_A$ by the expression

$$\mathcal{D}'_A = \mathcal{D}_A \left[1 + \frac{\Delta t}{t} \right] \tag{5.12}$$

$\mathcal{D}_A$ and Δt may be readily obtained from a plot of $\mathcal{D}'_A$ versus $1/t'$.

C. Three-Component Systmms, and Frames of Reference.

In a binary system, the procedure outlined above may be used to determine the diffusion constant directly from the reduced height-area ratio. In a ternary system, however, we have to consider the flows caused by the diffusion of two solute species. By generalising Fick's first law, the following experimental flow equations may be written[13,14]

$$(J_1)_V = -(D_{11})_V \left[\frac{\partial \hat{C}_1}{\partial x}\right]_{T,P,t} - (D_{12})_V \left[\frac{\partial \hat{C}_2}{\partial x}\right]_{T,P,t} \qquad (5.13)$$

$$(J_2)_V = -(D_{21})_V \left[\frac{\partial \hat{C}_1}{\partial x}\right]_{T,P,t} - (D_{22})_V \left[\frac{\partial \hat{C}_2}{\partial x}\right]_{T,P,t} \qquad (5.14)$$

Thus for a system containing two solutes, (designated here as 1 and 2) we now have to determine 4 diffusion coefficients. $(D_{11})_V$ and $(D_{22})_V$ are the main diffusion coefficients, and $(D_{12})_V$ and $(D_{21})_V$ are termed the cross-term diffusion coefficients, which are due to interactions between solutes. Clearly, in the limiting case where the concentration of either 1 or 2 approaches zero, the resulting flow equation is reduced to the simple statement of Fick's law (see equation 5.1). The subscript V denotes the volume-fixed frame of reference, which moves such that no net volume change occurs relative to this frame at the time and level in question; i.e.

$$\sum_{i=0}^{2} \bar{V}_i (J_i)_V = 0 \qquad (5.15)$$

where $\bar{V}_i$ is the partial molar volume of component i, in c.c./mole. The concentrations, $\hat{C}_i$, in equations 5.13 and 5.14 are expressed in moles per c.c., and the $(D_{ij})_V$ have the units cm.^{2}/sec. The volume-fixed reference frame is almost identical with the cell or apparatus reference frame, the condition for equality being the partial molar volumes are independent of concentration. Under the experimental conditions used, this condition is generally fulfilled.

The procedure used to determine $\mathscr{D}_A$ for a ternary system is similar to that for a binary, except that C_t values are obtained by extrapolation, as described in the previous section. The diffusion coefficients, $(D_{ij})_V$, may not be directly determined from $\mathscr{D}_A$, but can be obtained by a somewhat lengthy calculation, which will be described in the experimental section of this chapter.

The theoretical treatment of multicomponent diffusion derives a set of phenomenological equations in which the flows of solute relative to the solvent are described in terms of linear functions of chemical potential gradients of the solutes[15,16] (see equations 5.29 and 5.30), and Onsager[17,18] showed that the phenomenological coefficients, L_{ij}, of the linear equations, for $i \neq j$, were equal (see equation 5.31). This equality is known as the Onsager Reciprocal Relation (ORR).

One method of testing the Onsager Reciprocal Relation necessitates the conversion of the volume-fixed diffusion coefficients to diffusion coefficients on the solvent-fixed scale, where this scale is defined[14,15] so that the net flow of solvent relative to it is zero, i.e.

$$(J_0)_0 = 0 \qquad (5.16)$$

A detailed discussion of frames of reference is beyond the scope of this discussion, and although further mention will be made in the next section, the reader is referred to the paper by Kirkwood et al[15] for further information.

The flow of components 1 and 2 with respect to the solvent frame of reference $(J_1)_0$ and $(J_2)_0$, may also be written in terms of products of concentration gradients and diffusion coefficients, $(D_{ij})_0$, to give equations similar to 5.12 and 5.14. The diffusion coefficients $(D_{ij})_0$ may be obtained[16] from the relation

$$(D_{ij})_0 = (D_{ij})_V + \frac{C_i}{C_0\overline{V}_0} \sum_{k=1}^{2} \overline{V}_k \, (D_{kj})_V \qquad \begin{matrix}(i = 1,2)\\(j = 1,2)\end{matrix}$$

(5.17)

where $\overline{V}_k$ denotes the partial molar volume of component k. Values of $\overline{V}_k$, in c.c./mole, may be obtained from the relation[16]

$$\bar{V}_k = \frac{M_k - 1000\, H_k}{d - \sum_{j=1}^{2} H_j C_j} \qquad (k = 1,2) \qquad (5.18)$$

where M_k is the molecular weight of component k, and

$$H_k = \left[\frac{\partial d}{\partial C_k}\right]_{T,P,C_{i \neq k}} \qquad (5.19)$$

The concentration of solvent, C_0, may be obtained from

$$\sum_{i=0}^{2} M_i C_i = 1000\, d \qquad (5.20)$$

so that $\bar{V}_0$ can be determined from

$$\sum_{i=0}^{2} C_i \bar{V}_i = 1000 \qquad (5.21)$$

Concentrations, C_i are in moles/1000c.c.

5.3 Tests of the Onsager Reciprocal Relation.

A. Thermodynamic Description.

The "entropy production", or "dissipation", $T\sigma$, may be calculated[19] for a system of (q + 1) non-reacting components (0,1 .... q, where 0 denotes solvent) from the relation

$$T\sigma = \sum_{i=0}^{q} J_i X_i \qquad (5.22)$$

where T is the absolute temperature, σ the local entropy production per unit volume, and, for isothermal diffusion, J_i is the flow of component i (moles/cm^{2}sec.) and the X_i are the generalised forces of component i. For one-dimensional diffusion along a direction x, we can write

$$X_i = - \partial(\mu_i)_{T,P} / \partial x \qquad (5.23)$$

where μ_i is the chemical potential of component i.
From the Gibbs-Duhem equation

$$\sum_{i=0}^{q} C_i X_i = 0 \qquad (5.24)$$

We may eliminate X_0 from equation 5.22, so that, using the equations 5.15 and 5.16, one obtains[14]

$$T\sigma = \sum_{i=1}^{q} (J_i)_0 X_i \qquad (5.25)$$

$$T\sigma = \sum_{i=1}^{q} (J_i)_V \, Y_i \qquad (5.26)$$

for the solvent-fixed and volume-fixed reference frames respectively, where[14]

$$Y_i = \sum_{j=1}^{q} \alpha_{ij} X_j \qquad (5.27)$$

and

$$\alpha_{ij} = \delta_{ij} + \left[(C_j\bar{V}_i)/(C_0\bar{V}_0)\right] \qquad (i,k = 1,2) \qquad (5.28)$$

δ_{ij} being the Kronecker delta.

For isothermal diffusion in a ternary solution, the flow $(J_i)_0$ of solute relative to the solvent, (component 0) may be expressed in terms of linear functions of chemical potential gradients, $(\partial\mu_i/\partial x)$, of the two solutes[15,16]

$$(J_1)_0 = -(L_{11})_0 \frac{\partial\mu_1}{\partial x} - (L_{12})_0 \frac{\partial\mu_2}{\partial x} \qquad (5.29)$$

$$(J_2)_0 = -(L_{21})_0 \frac{\partial\mu_1}{\partial x} - (L_{22})_0 \frac{\partial\mu_2}{\partial x} \qquad (5.30)$$

A similar set of equations may be written for the volume-fixed frame of reference. Using the principle of "microscopic reversibility", namely,

> "under equilibrium conditions, any molecular process, and the reverse process, will be taking place on the average at the same rate",

Onsager showed[17,18] using fluctuation theory, that[20]

> "Provided the J_i and X_i are chosen from the expression for $T\sigma$ and are independent, the phenomenological coefficients L_{ij} of the linear laws satisfy the symmetry relation

$$L_{ij} = L_{ji} \qquad (5.31)$$

for all i and j" (provided $i \neq j$).

For isothermal ternary diffusion, we can write either

$$(L_{ij})_0 = (L_{ji})_0 \qquad (5.32a)$$

or

$$(L_{ij})_V = (L_{ji})_V \qquad (5.32b)$$

but in general, $(L_{ij})_0 \neq (L_{ij})_V$ except when all solute concentrations approach zero. The coefficients $(L_{ij})_0$ may be expressed as products of diffusion coefficients and the gradients of chemical potentials, so that[15,16]

$$(L_{11})_0 = \left[(D_{11})_0\,\mu_{22} - (D_{12})_0\,\mu_{21}\right]/1000S \qquad (5.33a)$$

$$(L_{12})_0 = \left[(D_{12})_0\,\mu_{12} - (D_{11})_0\,\mu_{12}\right]/1000S \qquad (5.33b)$$

$$(L_{21})_0 = \left[(D_{21})_0\,\mu_{22} - (D_{22})_0\,\mu_{21}\right]/1000S \qquad (5.33c)$$

$$(L_{22})_0 = \left[(D_{22})_0\,\mu_{11} - (D_{21})_0\,\mu_{12}\right]/1000S \qquad (5.33d)$$

where

$$S = \mu_{11}\mu_{22} - \mu_{12}\mu_{21} \qquad (5.34)$$

and

$$\mu_{ij} = (\partial\mu_i/\partial C_j)_{T,P,C_{k\neq j}} \qquad (5.35)$$

where T, P and $C_{k\neq j}$ indicate that temperature, pressure and concentration of the other solute are held constant during the differentiation. The factor of 1000 is introduced into equations 5.33 because concentrations are expressed as moles per 1000 c.c., whereas when considering flows the units should be moles per c.c.

The phenomenological coefficients on the volume-fixed reference frame, $(L_{ij})_V$, are given by

$$(L_{11})_V = \left[a_{22}(D_{11})_V - a_{12}(D_{12})_V\right]/1000\phi \qquad (5.36a)$$

$$(L_{12})_V = \left[a_{11}(D_{12})_V - a_{21}(D_{11})_V\right]/1000\phi \qquad (5.36b)$$

$$(L_{21})_V = \left[a_{22}(D_{21})_V - a_{12}(D_{22})_V\right]/1000\phi \qquad (5.36c)$$

$$(L_{22})_V = \left[a_{11}(D_{22})_V - a_{21}(D_{21})_V\right]/1000\phi \qquad (5.36d)$$

where

$$\phi = a_{11}a_{22} - a_{12}a_{21} \qquad (5.37)$$

such that

$$a_{jl} = \sum_{k=1}^{2} \alpha_{lk}\mu_{kj} \qquad (5.38)$$

and the α_{lk} are defined by equation 5.28.

B. Derivatives of the Solute Chemical Potentials.

In order to evaluate the phenomenological coefficients $(L_{ij})_0$, in equations 5.33 it is necessary to first determine values for the derivatives of the solute chemical potentials.

The chemical potential derivatives, μ_{ij}, as defined by equation 5.35, may be written[16,21] as

$$\mu_{ij} = \sum_{k=1}^{2} A_{ik}B_{kj} \tag{5.39}$$

where

$$A_{ik} = (\partial\mu_i/\partial m_k)_{T,P,m_{l\neq k}} \tag{5.40}$$

$$= RT\nu_i\left[\,(\delta_{ik}/m_k) + \Gamma_{ik}\right] \tag{5.40a}$$

and

$$B_{kj} \times 10^{-3} = (\partial m_k/\partial C_j)_{T,P,C_{l\neq 0,j}} \tag{5.41}$$

$$= \frac{m_k}{C_k}\left[\delta_{kj} + \frac{C_k\overline{V}_k}{C_0\overline{V}_0}\right] \quad (k=1,2) \tag{5.41a}$$

Equation 5.40a is obtained from the expression for chemical potential

$$\mu_i = \mu_i^{\circ} + \nu_i RT \ln m_i\gamma_i \tag{5.42}$$

where the μ_i° are standard chemical potentials, R is the gas constant, ν_i is the number of ions produced by the dissociation of 1 mole of component i, the γ_i are the molal activity coefficients which are functions of both m_1 and m_2, and the molalities m_i, may be derived from

$$m_i = 1000\, C_i/(1000d - C_1M_1 - C_2M_2) \qquad (5.43)$$

Also, we can write

$$\Gamma_{ik} = (\partial \ln \gamma_i/\partial m_k)_{T,P,m_{l\neq k}} \qquad (5.44)$$

and

$$\nu_i\Gamma_{ik} = \nu_k\Gamma_{ki} \qquad (5.44a)$$

Values for the derivatives Γ_{ik} may be obtained directly from equations derived in Chapter 2. Differentiation of equations 2.5 and 2.7 and the use of equations 2.4, 2.14 and 2.15, with substitution of the appropriate numerical values of the constants, produces the desired relations to evaluate the derivatives.

5.4 The Frictional Coefficient Approach.

Multicomponent diffusion coefficients may also be used to derive a set of generalised flow equations from which a set of frictional coefficients may be obtained. Such coefficients have been suggested in slightly differing forms, by several authors[22-26] to whom the reader is referred for further details.

It will be shown that an advantage of using this notation is that frictional coefficients depend on the difference in diffusion velocities, and consequently are independent of the frame of reference. A brief summary only of the equations used will be given here, using the approach outlined by Dunlop.[21,26]

It is assumed that the forces causing relative motion of the components are the gradients X_i, of chemical potentials μ_i (see equation 5.23) so that we define

$$X_i = \sum_{k=0}^{2} R_{ik}\,\hat{C}_k \left[(v_i)_V - (v_k)_V \right] \qquad (5.45)$$

and

$$R_{ik} = R_{ki} \qquad (5.45a)$$

where the diffusion velocities, $(v_i)_V$, for the volume frame of reference are given by

$$(J_i)_V = \hat{C}_i (v_i)_V \qquad (5.46)$$

The R_{ik} may be expressed in terms of the measured diffusion coefficients $(D_{ij})_V$ by the relations[21,26]

$$R_{10} = \frac{\hat{C}_1(\hat{C}_1 P_{11} + \hat{C}_2 P_{12})}{\hat{C}_0(\hat{C}_1 e_{11} + \hat{C}_2 e_{12})} \qquad (5.47a)$$

$$R_{12} = \frac{\hat{C}_1(e_{12}P_{11} - e_{11}P_{12})}{(\hat{C}_1 e_{11} + \hat{C}_2 e_{12})} \qquad (5.47b)$$

$$R_{21} = \frac{\hat{C}_2(e_{21}P_{22} - e_{22}P_{21})}{(\hat{C}_1 e_{21} + \hat{C}_2 e_{22})} \qquad (5.47c)$$

$$R_{20} = \frac{\hat{C}_2(\hat{C}_1 P_{21} + \hat{C}_2 P_{22})}{\hat{C}_0(\hat{C}_1 e_{21} + \hat{C}_2 e_{22})} \qquad (5.47d)$$

where

$$e_{ik} = \delta_{ik} + (\hat{C}_i \bar{V}_k / \hat{C}_0 \bar{V}_0) \qquad (i,k = 1,2) \qquad (5.48)$$

$$P_{11} = -(N_{22}/K); \quad P_{12} = (N_{12}/K) \qquad (5.49)$$

$$P_{21} = (N_{21}/K); \quad P_{22} = -(N_{11}/K)$$

$$K = |N_{ij}| = (N_{11}N_{22} - N_{12}N_{21}) \qquad (5.49a)$$

and

$$N_{11} = -\left[(D_{11})_V\mu_{22} - (D_{12})_V\mu_{21}\right]/S \qquad (5.50a)$$

$$N_{12} = \left[(D_{11})_V\mu_{12} - (D_{12})_V\mu_{11}\right]/S \qquad (5.50b)$$

$$N_{21} = \left[(D_{22})_V\mu_{21} - (D_{21})_V\mu_{22}\right]/S \qquad (5.50c)$$

$$R_{22} = -\left[(D_{22})_V\mu_{11} - (D_{21})_V\mu_{12}\right]/S \qquad (5.50d)$$

where S is defined by equation 5.34.

It has been pointed out[26] that the validity of the ORR would be shown by the equality of the frictional coefficients R_{12} and R_{21} for a particular ternary composition. This equality has been tested in a recent paper,[21] and will also be computed here for the water-urea-sucrose and water-sucrose-mannitol systems.

5.5 Experimental.

A. Materials.

The urea and sucrose samples used in the diffusion studies were the same as those used for the activity measurements described in Chapter 2. The mannitol was B.D.H. micro-analytical grade. The molecular weights of urea, sucrose and mannitol used were 60.056, 342.303 and 182.175 respectively, and the corresponding densities of the solid reagents, used for calculating vacuum corrections, were 1.335, 1.588 and 1.489, respectively.

B. Solutions.

All solutions were prepared using doubly-distilled demineralised water. The weights were corrected to vacuum by the same procedure as described in Chapter 2.

For binary isothermal diffusion experiments in the systems water-urea, water-sucrose and water-mannitol, two solutions, of concentration $(C_i)_A$ and $(C_i)_B$ were prepared, whose mean concentration was $\bar{C}_i$, where

$$\bar{C}_i = [(C_i)_A + (C_i)_B]/2 \qquad (i = 1,2) \qquad (5.51)$$

Values of $\bar{C}_i$ were chosen for comparison later with the ternary systems. Values of ΔC_i, where

$$\Delta C_i = (C_i)_B - (C_i)_A \qquad (i = 1,2) \qquad (5.52)$$

were chosen so as to obtain approximately 80 to 100 interference fringes, and were estimated from data already published.[27,12,21]

For ternary systems, it is necessary to perform at least two and preferably three or four, diffusion experiments at each ternary point. To prepare solutions of the desired concentrations, the weight of water required for a solution of known volume, V, was computed from the relation,

$$V = n_0\bar{V}_0^0 + n_1\phi_1 + n_2\phi_2 \qquad (5.53)$$

where n_0, n_1 and n_2 are the number of moles of water and solute components 1 and 2 respectively, and $\bar{V}_0^0$ is the volume of a mole of water at 25°. The apparent molar volumes were determined from the following relations:

Urea:[28] $\Phi = 44.218 + 0.13999C - 0.002601C^2$ (5.54)

Sucrose: $\Phi = 211.402 + 1.5746C$ (5.55)

Mannitol:[21] $\Phi = 119.418 + 0.75623C$ (5.56)

Two preliminary diffusion experiments were performed so that in each case there was a gradient of only one of the two solutes. The other component was present in both upper and lower solutions at the same concentration. Thus the refractive fractions, α_1, for these solution pairs were close to 0 and 1, respectively, (i.e. $\Delta C_1 = 0$ and $\Delta C_2 = 0$, respectively) where

$$\alpha_1 = \frac{R_1 \Delta C_1}{R_1 \Delta C_1 + R_2 \Delta C_2} \tag{5.57}$$

and R_1 and R_2 are the differential refractive increments, defined by equation 5.3. Hence values of R_1 and R_2 could be determined from the relation[29]

$$\left[\frac{\lambda}{a}\right] \frac{J}{\Delta C_1 + \Delta C_2} = \frac{\Delta C_1}{\Delta C_1 + \Delta C_2}(R_1 - R_2) + R_2 \tag{5.58}$$

Two further diffusion experiments for each ternary point were performed at $\alpha_1 = 0.2$ and 0.8 respectively, in order to provide internal checks on the data. The required values of ΔC_1 and ΔC_2 were determined from equation 5.57 using the preliminary data from the first two experiments and the values of R_1 and R_2 determined from equation 5.58. An arbitrarily selected value of $(\Delta C_1 + \Delta C_2)$ was used according to the number of Gouy fringes required (approximately 65 for the water-urea-sucrose system, and 95 for the water-sucrose-mannitol system).

The densities of the required solutions were determined by fitting the preliminary density data to the truncated Taylor series

$$d = d(\overline{C}_1, \overline{C}_2) + H_1(C_1 - \overline{C}_1) + H_2(C_2 - \overline{C}_2) \qquad (5.59)$$

All density measurements were performed in quadruplicate using single stem pycnometers.

C. Apparatus and Experimental Procedure.

The Gouy diffusiometer is illustrated in the photograph, Plate 5.2, and diagrammatically in Figure 5.1. Light from a mercury lamp passes through a condenser lens and filter (Wratten 77A for mercury green line (λ = 5460.7 Å) and illuminates a horizontal slit, S. An image of the slit is focussed through the cell, by means of a long focal length lens, L, on to a photographic plate, P. Light rays passing through the region of refractive index gradient in the cell are deflected downwards below the position of the normal slit image, and if the source slit is made quite

Plate 5.2. The Gouy diffusiometer.

narrow, the band is resolved into the Gouy interference fringes. The optical distance, b, from the centre of the diffusion cell to the photographic plate[11] was measured[30] and found to be 305.18 cm.

The diffusion experiments reported here were carried out in a quartz Tiselius type cell (designated in this laboratory as "Cell no. 2") in which the perpendicular distance a, between windows was 2.504_3 cm. Each experiment was performed so that diffusion took place from an upper solution A into a more concentrated lower solution, B. A boundary between these was sharpened by withdrawing 45 - 55 c.c. of solution at the rate of approximately 1 to 2 c.c. per minute from the cell with a stainless steel capillary adjusted to the level of the optic axis. After sharpening, the time was noted at the instant the siphon was turned off, and then the siphon was slowly withdrawn from the solution and the cell was closed off.

Diffusion reference corrections, δ, and refractometer corrections, δ', were obtained by[31] averaging 6 sets of photographs. The former were obtained with the cell closed, and the latter with the cell open and the siphon lowered in place so that its tip was in line with the optic axis. Values of the fractional part of J were obtained by taking photographs when the boundary had been sharpened, and just before the siphon was turned off. Kodak OTC Pan plates were used for all of these photographs, developed in D19 developer. Ten Gouy fringe photographs were taken over a period of approximately 6 hours after the formation of the boundary. The faster Ilford HP3 plates were used for these fringes. Since convergence of the Gouy fringes makes measurement of the integral number of fringes difficult, a photograph using Rayleigh optics was taken. A small reference correction was also made by taking a similar Rayleigh photograph before the boundary was sharpened.

The photographs were measured with a Gaertner toolmaker's microscope fitted with a projection screen. The positions of the interference fringe minima were determined visually for most experiments, but for several a newly installed photoelectric null-indicator[32] was used. The minima could be measured to within approximately ± 5 microns for the widely spaced fringes and ± 2 microns for the closer fringes when measured visually, but this uncertainty was reduced by a half or more when the photoelectric null-indicator was used.

D. Calculation of Diffusion Coefficients.

Values of the reduced height-area ratio, $\mathscr{D}_A$, were computed from fringe measurements using equations discussed in section 5.2B. The calculation was made using a two-part programme for an I.B.M. 1620 computer, a listing of which may be found in the Appendix. Values of $\mathscr{D}_A'$ versus $1/t'$ were least-squared to determine $\mathscr{D}_A$. Using a series form

$$(\mathscr{D}_A)_{25^o} = (\mathscr{D}_A)_{T^o} \left[1 + 0.0264\,(25 - T) + \ldots\right] \quad (5.60)$$

of the Stokes - Einstein relation, the $(\mathscr{D}_A)_T$ values were corrected to 25° from the temperature of measurement, which never differed by more than 0.005° and were constant to ± 0.002° during each experiment. The refractive increments, $\Delta n/\Delta C$, for two-component solutions were calculated by using the equation

$$\Delta n/\Delta C = \lambda J/(a\Delta C) \quad (5.61)$$

The relative fringe deviations[33] Ω_j, given by

$$\Omega_j = e^{-\zeta_j^2} - Y_j/C_t \quad (5.62)$$

determine the deviation of the refractive index gradient curve from Gaussian shape. A value of Ω_j, averaged from the value obtained from each of the 10 photographs taken, was plotted against $f(\zeta_j)$, the reduced fringe number. The area of each graph, Q, where

$$Q = \int_0^1 \Omega \, df(\zeta) \tag{5.63}$$

was measured by applying Simpson's one-third rule to a smoothed curve of average Ω values, with readings taken every 0.05 along the $f(\zeta)$ axis.

The procedure used to calculate the four diffusion coefficients, $(D_{ij})_V$, for isothermal ternary diffusion was the method, developed by Fujita and Gosting,[34] which has been used in the study of several ternary systems in recent years.[14,35-40] The method, which involved the use of the area, Q, under the fringe deviation graph, is an improvement on an earlier procedure[41] which only used one value of Ω from each fringe deviation graph.

On completion of a set of 3 or 4 diffusion experiments at a particular ternary concentration, the initial data was analysed using the procedure described in sections 5.3B and 5.3C, and then the values of the four $(D_{ij})_V$ were computed. Fujita and Gosting have given the theoretical basis in the original article,[34] so the discussion here will be limited to the equations actually used. The calculations were made using a programme written for an I.B.M. 1620 computer, and a listing of this programme may be found in the appendix.

The reduced height-area ratio, $\mathscr{D}_A$, may be written as a function of the refractive fraction, α_1, according to

$$1/\sqrt{\mathscr{D}_A} = I_A + S_A\alpha_1 \qquad (5.64)$$

so that the values of I_A and S_A may be determined by the method of least squares. Using these values of I_A and S_A, a calculated value of $\mathscr{D}_A$ may be obtained, using equation 5.64 for particular values of α_1, and using the calculated $\mathscr{D}_A$ value it is possible to compute values of the constants E_0, E_1 and E_2, where

$$Q/\sqrt{\mathscr{D}_A} = E = E_0 + E_1\alpha_1 - E_2\alpha_1^2 \qquad (5.65)$$

However, since the coefficients I_A, S_A, E_0, E_1 and E_2 are not independent, it is not permissible to calculate E_0, E_1 and E_2 directly by the method of least squares. A method of successive approximations is used, by writing

$$\hat{E} = (E/E_2 + \alpha_1^2) = (E_0/E_2) + (E_1/E_2)\alpha_1 \qquad (5.66)$$

Assuming a starting value of E_2, values of E may be computed, and from the linear dependence of this quantity on α_1, values of (E_0/E_2) and (E_1/E_2) could be obtained. Values of the $(D_{ij})_V$ could then be determined if, following the notation of Fujita and Gosting,[34] we write

$$u = S_A/I_A \tag{5.67}$$

$$v = -(E_0/E_2)u \tag{5.68}$$

$$w = (E_1/E_2)u \tag{5.69}$$

so that

$$(D_{11})_V = \frac{1 + v(2 - u + w)}{A\, I_A^2} \tag{5.70}$$

$$(D_{12})_V = \frac{v\,(2 + w)\,R_2}{A\, I_A^2 R_1} \tag{5.71}$$

$$(D_{21})_V = \frac{(w - u - v)(2 + w)\,R_1}{A\, I_A^2 R_2} \tag{5.72}$$

$$(D_{22})_V = \frac{(1 + w)^2 - v(2 + u + w)}{A\, I_A^2} \tag{5.73}$$

where $$A = (1 + w + uv)^2 \tag{5.74}$$

and R_1 and R_2 are the differential refractive increments (see equation 5.3). A second approximation for E_2 was made using the calculated $(D_{ij})_V$ values, and from this a new set of $(D_{ij})_V$ were computed. This iteration process was repeated until successive values of the $(D_{ij})_V$ agreed to within 0.000001×10^{-5}.

Thus, in the theoretical section of this chapter, it has been shown how theoretical flow equations may be related to experimentally determined quantities. The method for determining experimental diffusion coefficients has been described in the experimental section above, and methods for determining densities and activity data have been described in preceding chapters. It is the purpose of the next two chapters to present the experimental diffusion data for both two- and three-component systems, and to use the latter to test the Onsager Reciprocal Relation.

References to Chapter 5.

1. R. H. Stokes, J. Am. Chem. Soc., 72, 763 (1950).

2. R. Mills, J. Phys. Chem., 67, 600 (1963); ibid, 69, 3116 (1965).

3. J. G. Albright and R. Mills, ibid., 69, 3120 (1965).

4. L. J. Gosting, Advances in Protein Chemistry, 11, 429 (1956).

5. R. A. Robinson and R. H. Stokes, "electrolyte Solutions", Butterworth's Scientific Publications, London, 1959, Chapter 10.

6. G. L. Gouy, Compt. rend., 90, 307 (1880).

7. L. G. Longsworth, Ann. N.Y. Acad. Sci., 46, 211 (1945).

8. G. Kegeles and L. J. Gosting, J. Am. Chem. Soc., 69, 2516 (1947).

9. C. A. Coulson, J. T. Cox, A. G. Ogston and J. St L. Philpot, Proc. Roy. Soc., 192A, 382 (1948).

10. A. Fick, Pogg. Ann., 94, 59 (1855).

11. J. G. Albright and L. J. Gosting, J. Phys. Chem., 64, 1537 (1960).

12. L. J. Gosting and M. S. Morris, J. Am. Chem. Soc., 71, 1998 (1949).

13. D. G. Miller, ibid., 63, 570 (1959).

14. L. A. Woolf, D. G. Miller and L. J. Gosting, J. Am. Chem. Soc., 84, 317 (1962).

15. J. G. Kirkwood, R. L. Baldwin, P. J. Dunlop, L. J. Gosting and G. Kegeles, J. Chem. Phys., 33, 1505 (1960).

16. P. J. Dunlop and L. J. Gosting, J. Phys. Chem., 63, 86 (1959).

17. L. Onsager, Phys. Rev., 37, 405 (1931).

18. L. Onsager, ibid., 38, 2265 (1931).

19. S. R. de Groot, "Thermodynamics of Irreversible Processes", Interscience Publishers, Inc., New York, 1951.

20. D. G. Miller, Chem. Revs. 60, 15 (1960).

21. P. J. Dunlop, J. Phys. Chem., 69, 4276 (1965).

22. L. Onsager, Ann. N.Y. Acad. Sci., 46, 241 (1945).

23. O. Lamm, Acta. Chem. Scand., 11, 362 (1957).

24. R. W. Laity, J. Phys. Chem., 63, 80 (1959).

25. R. J. Bearman, ibid., 65, 1961 (1961).

26. P. J. Dunlop, ibid., 68, 26 (1964).

27. L. J. Gosting and D. F. Akeley, J. Am. Chem. Soc., 74, 2058 (1952).

28. F. T. Gucker, F. W. Gage and C. E. Moser, J. Am. Chem. Soc., 60, 2582 (1938).

29. I. J. O'Donnell and L. J. Gosting, in "The Structure of Electrolyte Solutions," W. J. Hamer, ed., John Wiley & Sons, Inc., New York, 1959.

30. This distance was measured by the Metrology Laboratory of the South Australian Railways.

31. L. J. Gosting, J. Am. Chem. Soc., 72, 4418 (1950).

32. J. M. Bennett and W. F. Kohler, J. Opt. Soc. Am., 49, 466 (1959).

33. D. F. Akeley and L. J. Gosting, J. Am. Chem. Soc., 75, 5685 (1953).

34. H. Fujita and L. J. Gosting, J. Phys. Chem., 64, 1256 (1960).

35. R. P. Wedt, J. Phys. Chem., 66, 1279 (1962).

36. L. A. Woolf, ibid., 67, 273 (1963).

37. G. Reinfelds and L. J. Gosting, ibid., 68, 2464 (1964).

38. P. J. Dunlop, ibid., 68, 3062 (1964).

39. P. J. Dunlop,+L. J. Gosting, ibid., 68, 3874 (1964).

40. E. L. Cussler, Jr., and E. N. Lightfoot, ibid., 69, 1135 (1965).

41. H. Fujita and L. J. Gosting, J. Am. Chem. Soc., 78, 1099 (1956).

CHAPTER 6.

DIFFUSION RESULTS AND DISCUSSION FOR THE TWO-COMPONENT SYSTEMS AND THE TERNARY SYSTEM WATER-UREA-SUCROSE.

6.1 The Two Component Systems.

Binary diffusion experiments were performed at all compositions required for comparison with the ternary systems.

The experimental procedure used for preparing the solutions and performing the experiments has been described in Chapter 5, and the results are summarised in Table 6.1. Rows 1 and 2 give the weight percentages of upper and lower solutions, and rows 3 and 4 give the corresponding molar concentrations of these solutions. The other quantities are defined in Chapter 5, except that "av. dev. %" is the percentage average deviation of the $\mathscr{D}'_A$ values from the least-squared straight line of $\mathscr{D}'_A$ versus $1/t'$.

A. The System: Water-Urea.

The experiment at 0.5M urea was found to be in good agreement with data previously published,[1] the diffusion coefficients agreeing to 0.15%, and the refractive index increments to 0.1%. The reason for

TABLE 6.1

INITIAL DIFFUSION DATA FOR THE TWO - COMPONENT SYSTEMS *

	WATER - SUCROSE			WATER - MANNITOL		WATER - UREA
EXP. NO.	S/8	S/7	S/6	M/2	M/1	U/1
$(W_1)_A$	–	7.609478	15.609279	3.797959	8.157888	2.287693
$(W_1)_B$	1.400183	9.009299	16.609008	5.196265	9.556773	3.688304
$(C_1)_A$	–	0.228302	0.483505	0.210627	0.459404	0.382123
$(C_1)_B$	0.041004	0.271799	0.516547	0.289587	0.540850	0.618370
C_1	0.020502	0.250051	0.500026	0.250107	0.500127	0.500247
ΔC_1	0.041004	0.043497	0.033042	0.078960	0.081446	0.236247
d_A	–	1.026989	1.060300	1.010307	1.025901	1.003140
d_B	1.002423	1.032685	1.064577	1.015260	1.030989	1.006881
δ	-0.022	-0.024	-0.023	-0.024	-0.019	-0.018
δ'	-0.020	-0.023	-0.019	-0.020	-0.006	-0.007
J	92.10	97.48	73.94	93.74	96.19	92.93
$D \times 10^5$	0.51804	0.45879	0.40073	0.61457	0.56684	1.3413
Av.dev.%	0.034	0.032	0.039	0.044	0.019	0.075
Δt	13.9	13.9	29.2	20.0	10.5	130.7
$(\Delta n/\Delta C) \times 10^3$	48.979	48.867	48.797	25.887	25.770	8.577

* EXPERIMENTS NUMBERED CHRONOLOGICALLY.
UNITS. CONCENTRATIONS C_i, MOLES/1000 CC, DENSITIES d GM/CC, DIFFUSION COEFFICIENTS D, CM^2/SEC.

† MORE THAN THE MINIMUM NUMBER OF SIGNIFICANT DIGITS WERE RETAINED IN THESE VALUES TO MINIMISE ACCUMULATION OF ERRORS IN CALCULATION.

the rather high time correction is not understood, but it is believed that it is due either to an incorrect starting time being recorded during the experiment, or to some disturbance of the boundary when initially formed, possibly when the siphon was removed.

B. The System: Water-Sucrose.

As well as the experiments at 0.25 and 0.5M, another experiment was performed at a lower concentration. The purpose of this experiment was firstly to compare the results with data already published,[2,3] and secondly, to compare the results with those obtained by other workers[4] in the same laboratory using different samples. Table 6.2 summarises the results.

It can be seen that the value of the diffusion coefficient obtained from this work is slightly greater than the values previously reported,[2,3] but lies between the results obtained by other workers in this laboratory.[4] The refractive index increment obtained from this work is slightly higher than all the others, although in no case is this difference greater than 0.1%.

Diffusion measurements on sucrose solutions have been reported at very low concentrations by Chatterjee,[5] using a microdiffusion cell and Jamin interference optics. The results are in good agreement with all the data reported in Table 6.2.

Table 6.2.

COMPARISON OF DIFFUSION AND REFRACTIVE INDEX DATA AT 25° FOR ONE COMPOSITION OF THE SYSTEM WATER-SUCROSE.

	Gosting and Morris[2]	Akeley and Gosting[3]	Dunlop[4]	Gassler[4]	Ellerton
Sample[a]	Merk reagent	N.B.S.	B.D.H. Analar	C.S.R. reagent	B.D.H., M.A.R.
ΔC[b]	0.043861	0.043832	0.040056	0.040780	0.041004
$\bar{C}$	0.021930	0.021916	0.020028	0.020390	0.020502
J	97.74	-	89.96	91.52	92.10
$D \times 10^5$	0.5176[c]	0.5170	0.5194	0.5176	0.5180
$\Delta n/\Delta C \times 10^3$	48.960	48.942	48.970	48.954	48.979

Notes: a Abbreviations: N.B.S., National Bureau of Standards, Washington, D.C.; B.D.H., British Drug Houses; M.A.R., Microanalytical reagent grade; C.S.R., Colonial Sugar Refining Co. of Australia.

b Concentrations expressed as moles/1000c.c.

c D value corrected to 25° using equation 5.60.

At higher sucrose concentrations, results have been reported by Irani and Adamson,[6] and also Henrion,[7] using the diaphragm-cell technique. The former authors' results seem to decrease too quickly with increasing concentration so that at 0.25 M and 0.5 M their results are approximately 4% and 8%, respectively lower than this work. Conversely, Henrion's results are approximately 2½% higher than the data reported here. However, the results of Gosting and Morris[2] are in excellent agreement with the data reported here.

C. The System: Water-Mannitol.

The results may be compared with some comprehensive data recently published[8] for this system. The diffusion coefficients differ by 0.2% at 0.25M and 0.3% at 0.5M, but the refractive index increments agree to better than 0.1% at both concentrations.

6.2 The Ternary System: Water-Urea-Sucrose.

Diffusion experiments in this ternary system were made according to the procedure outlined in Chapter 5. The measured fringe minima from the Gouy photographs were then used to compute the Θ_A value for each experiment using a two-part I.B.M. 1620 computer programme. Examples of the output from each part are given in Tables 6.3 and 6.4, and programme listings are given in the appendix. It may be noted that this two-part programme was also used for computing the binary diffusion coefficients described in section 6.2, and "average C_t values" from the first part of the programme may be used to calculate the diffusion coefficients in the second part. For ternary diffusion, however, graphically extrapolated C_t values are required to calculate the reduced height-area ratio, $\mathscr{D}_A$.

The initial diffusion data for the system water-urea-sucrose is summarised in Table 6.5. The first eight rows of data give the concentrations of the solutions used, A(upper) and B(lower), firstly as weight percentages, and then as mplarities. The arithmetic averages, $\bar{C}_i$, and then the differences, ΔC_i , of each component between upper and lower solutions is given in rows 9 to 12, followed by the densities of upper and lower solutions in rows 13 and 14. Values of the small corrections δ and δ' are then listed, followed by the total number of fringes, J_{exp}, used for each experiment, and values of J_{cal}, which were calculated using equation 5.58. The reduced height-area ratios, $\mathscr{D}_A$, are given in line 19, followed by the average percentage deviation of the $\mathscr{D}_A$ values from the least-squared straight line of $\mathscr{D}_A$ versus $1/t'$, and the small time

TABLE 6.3

EXAMPLE OF OUTPUT FROM DIFFUSION PROGRAMME PART 1 (EXPT. SU/4)

```
    Y VALUES
2.0702 1.8099 1.6165 1.4235 1.3299 1.2481 1.1605 1.1243 1.0495 1.0403
1.9694 1.7216 1.5372 1.3536 1.2646 1.1867 1.1035 1.0690  .9978  .9887
1.8856 1.6492 1.4729 1.2967 1.2114 1.1368 1.0570 1.0239  .9561  .9471
1.8117 1.5843 1.4151 1.2457 1.1634 1.0917 1.0152  .9836  .9181  .9098
1.7433 1.5248 1.3618 1.1988 1.1198 1.0508  .9772  .9467  .8838  .8760
1.6816 1.4703 1.3124 1.1556 1.0794 1.0132  .9423  .9128  .8524  .8449
1.6239 1.4200 1.2677 1.1163 1.0429  .9787  .9102  .8817  .8229  .8156
1.4215 1.2426 1.1096  .9771  .9127  .8569  .7965  .7718  .7204  .7140
1.2079 1.0563  .9434  .8305  .7759  .7284  .6770  .6562  .6123  .6068
1.0230  .8949  .7989  .7034  .6574  .6173  .5734  .5559  .5189  .5141
 .7110  .6220  .5550  .4888  .4565  .4288  .3983  .3862  .3604  .3571
 .4532  .3967  .3535  .3115  .2909  .2733  .2537  .2460  .2291  .2273
 .2387  .2089  .1861  .1634  .1526  .1439  .1333  .1294  .1203  .1192
 .0644  .0569  .0498  .0435  .0411  .0394  .0355  .0348  .0319  .0311
    CT VALUES
2.2057 1.9284 1.7223 1.5167 1.4170 1.3298 1.2365 1.1979 1.1182 1.1084
2.2055 1.9280 1.7215 1.5159 1.4162 1.3289 1.2358 1.1971 1.1174 1.1072
2.2027 1.9265 1.7206 1.5148 1.4151 1.3280 1.2347 1.1961 1.1169 1.1063
2.1997 1.9236 1.7182 1.5125 1.4126 1.3255 1.2326 1.1942 1.1147 1.1046
2.1949 1.9198 1.7146 1.5094 1.4099 1.3230 1.2303 1.1919 1.1127 1.1029
2.1924 1.9169 1.7110 1.5066 1.4073 1.3209 1.2285 1.1900 1.1113 1.1015
2.1898 1.9148 1.7095 1.5053 1.4063 1.3197 1.2274 1.1889 1.1096 1.0998
2.1819 1.9073 1.7031 1.4998 1.4009 1.3153 1.2226 1.1846 1.1057 1.0959
2.1716 1.8991 1.6961 1.4931 1.3949 1.3095 1.2171 1.1797 1.1008 1.0909
2.1621 1.8914 1.6885 1.4866 1.3894 1.3046 1.2119 1.1749 1.0967 1.0865
2.1449 1.8764 1.6743 1.4745 1.3771 1.2935 1.2015 1.1650 1.0872 1.0772
2.1274 1.8622 1.6594 1.4623 1.3655 1.2829 1.1909 1.1548 1.0754 1.0670
2.1153 1.8512 1.6492 1.4480 1.3523 1.2752 1.1813 1.1467 1.0661 1.0563
2.1282 1.8803 1.6457 1.4375 1.3582 1.3020 1.1731 1.1500 1.0541 1.0277
    AVERAGE CT VALUES
 2.1987   1.9226   1.7168   1.5116   1.4120
 1.3251   1.2323   1.1937   1.1144   1.1044
```

TABLE 6.4

EXAMPLE OF OUTPUT FROM DIFFUSION PROGRAMME PART 2 (EXPT. SU/4)

```
   D VALUES
 .766142   .764319   .763840   .763209   .764748
 .763589   .763708   .763172   .762838   .763474
   D         CONST       DELTM
 .762386 80.789610E-05   10.596
   DA        DD        1/T
 .762934  -.000547  3.96825
 .761873   .000513  3.03030
 .761890   .000496  2.41545
 .761697   .000689  1.87265
 .763426  -.001039  1.63398
 .762428  -.000041  1.43678
 .762702  -.000315  1.24378
 .762230   .000156  1.16550
 .762017   .000368  1.01626
 .762668  -.000281   .99800
  DEVAV   DEVPC
 .000445   .058
   FRINGE DEVIATIONS                                   AVERAGE
 39.4   46.2   45.6   48.4   37.5   36.9   42.2   37.9   43.1   36.8     41.4
 38.5   45.9   47.8   50.9   40.5   40.8   45.1   41.7   47.3   44.5     44.3
 47.7   50.3   50.2   55.0   45.4   45.4   50.4   47.5   49.4   49.2     49.0
 56.9   60.8   59.8   65.1   58.3   58.8   62.5   58.2   63.2   60.0     60.4
 72.1   74.2   74.1   79.1   71.2   71.6   74.8   71.3   75.0   70.1     73.4
 78.4   83.3   87.3   90.3   83.0   81.0   83.6   81.0   82.3   77.4     82.7
 84.5   88.4   91.2   93.6   85.1   85.0   87.6   85.2   90.5   86.3     87.7
 97.4  103.0  103.8  105.9   99.5   96.5  102.2   98.1  102.1   98.5    100.7
109.0  111.6  111.4  114.7  108.3  106.3  111.6  106.4  111.6  109.1    110.0
113.0  113.7  115.6  117.7  110.6  107.7  115.0  109.6  112.3  111.5    112.7
105.0  105.3  108.1  108.7  106.1  103.0  108.1  103.9  106.6  105.7    106.0
 84.2   83.2   87.7   87.0   85.4   83.1   87.6   84.9   90.8   87.6     86.2
 50.7   50.4   53.1   56.6   55.7   50.5   55.2   52.5   57.5   57.2     54.0
 11.8    8.9   14.8   17.2   13.7    7.4   16.7   13.2   18.6   23.1     14.6
```

TABLE 6.5

INITIAL DIFFUSION DATA FOR THE SYSTEM *
WATER - UREA - SUCROSE

$\bar{C}_1 = 0.5$ $\bar{C}_2 = 0.5$

EXP. NO.	SU/6	SU/5	SU/4	SU/2
$(W_1)_A$ †	2.796084	2.707848	2.430528	2.333465
$(W_2)_A$	15.493984	15.628451	15.921200	15.997567
$(W_1)_B$	2.785878	2.901602	3.181963	3.271860
$(W_2)_B$	16.487815	16.355144	16.064825	15.958395
$(C_1)_A$	0.497220	0.481688	0.432535	0.415273
$(C_2)_A$	0.483400	0.487756	0.497098	0.499496
$(C_1)_B$	0.497395	0.517954	0.567764	0.583683
$(C_2)_B$	0.516474	0.512217	0.502915	0.499479
C_1	0.497308	0.499821	0.500150	0.499478
C_2	0.499937	0.499986	0.500006	0.499488
ΔC_1	0.000175	0.036266	0.135229	0.168410
ΔC_2	0.033074	0.024461	0.005817	-0.000017
d_A	1.067959	1.068311	1.068752	1.068782
d_B	1.072249	1.072038	1.071592	1.071369
δ	-0.027	-0.020	-0.018	-0.019
δ'	-0.026	-0.017	-0.009	-0.007
J(exp)	73.68	68.48	65.47	65.46
J(cal)	73.67	68.52	65.47	65.38
$\mathcal{D}_A \times 10^5$	0.39685	0.45852	0.76239	0.93413
Av.dev.%	0.047	.039	0.058	0.038
Δt	31.0	18.6	10.6	10.6
$Q(\mathrm{exp}) \times 10^4$	7.96	74.48	76.96	-16.71
$Q(\mathrm{cal}) \times 10^4$	9.88	72.23	75.18	-14.48
α_1	0.0009	0.2056	0.8023	1.0006
I_A		502.53		
S_A		-175.08		
E_0		0.47959		
E_1		17.9618		
E_2		18.9035		
$R_1 \times 10^3$		8.470		
$R_2 \times 10^3$		48.527		

* EXPERIMENTS NUMBERED CHRONOLOGICALLY.
UNITS. CONCENTRATIONS C_i, MOLES/1000 CC, DENSITIES d GM/CC, REDUCED HEIGHT-AREA RATIOS CM^2/SEC

† MORE THAN THE MINIMUM NUMBER OF SIGNIFICANT DIGITS WERE RETAINED IN THESE VALUES TO MINIMISE ACCUMULATION OF ERRORS IN CALCULATION.

corrections Δt (see equation 5.12). Lines 22 and 23 give experimental and computed areas of the fringe deviation graphs for each experiment. The refractive fractions, α_i, in line 24 were computed from concentration differences, ΔC_i, and the refractive index derivatives, R_i, are listed in lines 30 and 31. Lines 25 to 29 list other data necessary for the computation of D_{ij} values, to which reference was made in the experimental section of Chapter 5.

Computation of the four $(D_{ij})_V$ values for the three-component system, using the relevant data from Table 6.5, required another computer programme, and an example of the output is given in Table 6.6. A programme listing may be found in the Appendix. Values of the $(D_{ij})_V$ are given in Table 6.7. The errors of each $(D_{ij})_V$ were estimated firstly by assuming an error of ±0.12% in each $\mathscr{D}_A$ value (the average error of the $\mathscr{D}_A$ for this ternary point) and an error of $\pm 2\times10^{-4}$ in each Q value.[8] The latter error was found to produce a much greater error (by nearly four times) in the $(D_{ij})_V$ values than the former, so that later computations for estimating errors in the $(D_{ij})_V$ values, used in connection with tests of the ORR, were based on the errors in the Q values rather than in the $\mathscr{D}_A$ values.

TABLE 6.6

EXAMPLE OF OUTPUT FROM 3 COMPONENT DIFFUSION PROGRAMME.
SYSTEM WATER - UREA - SUCROSE

```
   R1              R2
.8470213E-02  .4852706E-01

 DC1        DC2       J OBS     J CAL     J DIF     A1
.000175   .033074   73.683    73.673    -.009     .00092
.036266   .024461   68.481    68.524     .043     .20558
.135229   .005817   65.466    65.474     .008     .80228
.168410  -.000017   65.463    65.380    -.082    1.00057

   I          S
502.5349 -175.0781

  A1       D OBS            D CAL          D DIF
 .00092   .396840E-05    .396229E-05   -.6105E-08
 .20558   .458520E-05    .459429E-05    .9090E-08
 .80228   .762390E-05    .762795E-05    .4053E-08
1.00057   .934150E-05    .933170E-05   -.9800E-08

  D11              D12              D21              D22
 .908955E-05      .754735E-06      .221568E-07      .389221E-05

  SIG+             SIG-             PS               PL
 .257135E+06      .109977E+06      .653989E+00      .312722E+00

  E0                E1                E2
 .4795868E+00      .1796180E+02      .1890351E+02

   7.9633     9.8836     1.9203
  74.4833    72.2321    -2.2511
  76.9567    75.1761    -1.7805
 -16.7133   -14.4755     2.2377

 .10000E-10    .26960E-11
```

6.3 Computation of the L_{ij}, R_{ik} and Test of the ORR.

As a first step in determining the phenomenological coefficients, the experimental diffusion coefficients, $(D_{ij})_V$, were converted to diffusion coefficients on the solvent-fixed scale, $(D_{ij})_O$, using equation 5.17, together with the necessary partial molar volume data (see Chapter 4). $(L_{ij})_O$, $(L_{ij})_V$ and R_{ik} values were computed from equations 5.33, 5.36 and 5.47, respectively, and the necessary diffusion data. The chemical potential derivatives, μ_{ij}, which are also required in the computation of these quantities, were determined using equations 5.39 to 5.41. The terms Γ_{ik} (equation 5.44), were determined, for the water-urea-sucrose system, from activity data presented in Chapter 2. Equations for Γ_{11} and Γ_{22} were obtained by differentiation of equations 2.5 and 2.7, whilst Γ_{12} $(= \Gamma_{21})$ could be determined directly using equations 2.14 and 2.15. The required molalities were calculated using equation 5.43. The $(D_{ij})_O$, $(L_{ij})_O$, $(L_{ij})_V$ and R_{ik} were all calculated using a computer programme[9] (listed in the Appendix), and the results are summarised in Table 6.7. The quantities A_{ik} and B_{kj} (see equations 5.40 and 5.41) are listed in Table 6.8 together with the partial differentials of the chemical potentials with respect to

Table 6.7.

DIFFUSION, PHENOMENOLOGICAL AND FRICTIONAL COEFFICIENTS FOR THE SYSTEM WATER-UREA-SUCROSE.

C_1	0.5	$(L_{11})_V \times 10^{19}$	1.81_{89}
C_2	0.5	$(L_{12})_V \times 10^{19}$	0.00_{40}
$(D_{11})_V \times 10^5$	0.909_0 $\pm 0.003_3$	$(L_{21})_V \times 10^{19}$	-0.04_{11}
$(D_{12})_V \times 10^5$	0.075_5 $\pm 0.016_1$	$(L_{22})_V \times 10^{19}$	0.56_{92}
$(D_{21})_V \times 10^5$	0.002_2 $\mp 0.000_3$	$R_{10} \times 10^{-17}$	0.44_{54}
$(D_{22})_V \times 10^5$	0.389_2 $\mp 0.001_4$	$(\delta R_{10})_1 \times 10^{-17}$	$\mp 0.02_{17}$
$(D_{11})_0 \times 10^5$	0.932_6	$(\delta R_{10})_2 \times 10^{-17}$	$\pm 0.00_{24}$
$(D_{12})_0 \times 10^5$	0.125_0	$R_{12} \times 10^{-17}$	9.57_{07}
$(D_{21})_0 \times 10^5$	0.025_8	$(\delta R_{12})_1 \times 10^{-17}$	$\pm 1.94_{53}$
$(D_{22})_0 \times 10^5$	0.446_1	$(\delta R_{12})_2 \times 10^{-17}$	$\pm 0.14_{37}$
$(L_{11})_0 \times 10^{20}$	1.91_{75}	$R_{21} \times 10^{-17}$	5.77_{41}
$(L_{12})_0 \times 10^{20}$	0.13_{06}	$(\delta R_{21})_1 \times 10^{-17}$	$\mp 0.04_{56}$
$(L_{21})_0 \times 10^{20}$	0.07_{92}	$(\delta R_{21})_2 \times 10^{-17}$	$\pm 0.06_{66}$
$(L_{22})_0 \times 10^{20}$	0.72_{92}	$R_{20} \times 10^{-17}$	1.39_{63}
		$(\delta R_{20})_1 \times 10^{-17}$	$\pm 0.00_{66}$
		$(\delta R_{20})_2 \times 10^{-17}$	$\pm 0.00_{17}$
		Δ%(exp)	−49.4%
		Δ%(calc)	±28.6%
			(±33.3%)

Table 6.8.[a,b]

COMPUTATION OF THE CHEMICAL POTENTIAL DERIVATIVES, μ_{ij}, FOR THE SYSTEM WATER-UREA-SUCROSE.

C_1	0.5
C_2	0.5
m_1	0.5753_8
m_2	0.5753_8
Γ_{11}	-0.0690_3
$\Gamma_{12} = \Gamma_{21}$	-0.1079_1
Γ_{22}	0.1764_5
$A_{11} \times 10^{-10}$	4.1373_3
$(A_{12} = A_{21}) \times 10^{-10}$	-0.2675_2
$A_{22} \times 10^{-10}$	4.7459_0
$B_{11} \times 10^{-3}$	1.1803_4
$B_{12} \times 10^{-3}$	0.1408_1
$B_{21} \times 10^{-3}$	0.2957_1
$B_{22} \times 10^{-3}$	1.2915_8
$\mu_{11} \times 10^{-13}$	4.8755
$\mu_{12} \times 10^{-13}$	0.2370
$\mu_{21} \times 10^{-13}$	-0.1754
$\mu_{22} \times 10^{-13}$	6.0920

[a] More than the minimum number of significant digits have been retained in the quantities listed in the Table to minimise the accumulation of errors in the L_{ij} and R_{ik}.

[b] The μ_{ij} have units c.c. erg mole^{-2}.

concentration, μ_{ij} (equation 5.39). The values of the gas constant, R, and the absolute temperature, T, were taken to be 8.3144×10^7 erg.deg.$^{-1}$mole^{-1} and -273.16°, respectively.

It has been pointed out[8,10] that the equality of the frictional coefficients R_{12} and R_{21}, would be a measure of the validity of the ORR for a particular system and that the difference between the R_{12} and the R_{21} would be a measure of the accuracy of the test. It is, therefore, convenient to follow the method of Dunlop,[8] and define

$$\Delta\%(\mathrm{exp}) = 100(R_{12} - R_{21})/\bar{R} \qquad (6.1)$$

where

$$\bar{R} = (|R_{12}| + |R_{21}|)/2 \qquad (6.2)$$

The value of $\Delta\%$(exp) for the water-urea-sucrose system is given in Table 6.7. The quantity $\Delta\%$(calc), in the same Table, was computed by the same procedure as described by Dunlop,[8] who assumed that the main errors in the R_{ik} were due to the errors in the $(D_{ij})_V$ (in Table 6.7) and in the Γ_{ik}. Errors in concentrations and partial molar volumes are considered to be negligible compared with these quantities. Thus, errors due to the $(D_{ij})_V$ are designated $(\delta R_{ik})_1$, and those due to the Γ_{ik} are designated $(\delta R_{ik})_2$. The average deviation of the experimental isopiestic activity data given in Chapter 2 (equation 2.24) was ± 0.0015, so that it was considered reasonable to assume an error in Γ_{12} and Γ_{21} of ±0.002. An error of ±0.003 was assumed in the determination of Γ_{11} and Γ_{22}, since these required an integration followed by a differentiation. The total calculated error, Δ%(calc), was then given[8] by the relation

$$\Delta\%(\text{calc}) = \frac{100}{\bar{R}} \sum_{\substack{i,k,l=1 \\ (i\neq k)}}^{2} \left|(\delta R_{ik})_l\right| \qquad (6.3)$$

Inspection of Table 6.7 shows that, contrary to expectations, the experimental error is greater than the calculated error, so that within the scope of the test applied, the ORR cannot be confirmed for this ternary point in the system. To try to obtain a satisfactory test, several modifications to the error calculation procedures were made. Firstly, the experiment with the greatest uncertainty was discarded from the set, so that the $(D_{ij})_V$, and hence the R_{ik}, were recalculated, in the hope that better agreement might be obtained; no significant improvement resulted.

Next, the possibility was considered that the calculated error in the $(D_{ij})_V$ may be actually underestimated, due to some cancellation of positive and negative errors, so variations were made to the calculation procedure, in order to increase the estimated error. The most successful procedure was to add two units to a positive area, Q, under a fringe deviation graph, and to subtract two units from the experiment which had a negative area. This procedure, which is quite valid, since the choice of addition of units[8,11] of Q is quite arbitrary, resulted in an increase in Δ%(calc) to 33.3%. Although this is still well below the estimated experimental error, it may be noted that an inspection of the relative magnitudes of δR_{12} and δR_{21} shows that of the 33% error, approximately 30% is contributed by the error in the $(D_{ij})_V$ values. Consequently, if we increase the estimated error in the fringe deviation graphs from $\pm 2 \times 10^{-4}$ to $\pm 3 \times 10^{-4}$ units of Q, then the calculated error will agree closely with the experimental value, and the ORR for the ternary point of this system may then be considered as tested. This procedure does not seem unreasonable when an inspection of the differences between experimental and calculated Q values in Table 6.5 shows that for 2 experiments the differences are slightly greater than $\pm 2 \times 10^{-4}$ units.

References to Chapter 6.

1. L. J. Gosting and D. F. Akeley, J. Am. Chem. Soc., 74, 2058 (1952).

2. L. J. Gosting and M. S. Morris, ibid., 71, 1998 (1949).

3. D. F. Akeley and L. J. Gosting, ibid., 75, 5685 (1953).

4. P. J. Dunlop and E. L. Cussler, Jr., unpublished results.

5. A. Chatterjee, J. Am. Chem. Soc., 86, 793 (1964).

6. R. R. Irani and A. W. Adamson, J. Phys. Chem., 62, 1517 (1958).

7. P. N. Henrion, Trans. Faraday Soc., 60, 72 (1964).

8. P. J. Dunlop, J. Phys. Chem., 69, 4276 (1965).

9. The portion of this programme which computed frictional coefficients was written by Dr. P. J. Dunlop.

10. P. J. Dunlop, J. Phys. Chem., 68, 26 (1964).

11. R. P. Wendt, ibid., 66, 1279 (1962).

CHAPTER 7.

DIFFUSION RESULTS AND DISCUSSION FOR THE TERNARY SYSTEM WATER-SUCROSE-MANNITOL.

7.1 Diffusion Measurements.

The diffusion experiments on this system were performed using the procedure discussed in Chapter 5, and the photographs were measured, and the results were calculated using the same computer programmes, as discussed in Chapter 6. The initial diffusion data for the system are summarised in Table 7.1. The various quantities listed have the same significance as those described for Table 6.5 in Chapter 6.

The reduced height-area ratios and other relevant data from each experiment were then used to compute the $(D_{ij})_V$ values for each ternary composition. The results are summarised in Table 7.2, together with the estimated error, calculated by assuming an error[1] of $\pm 2 \times 10^{-4}$ in each Q value.

7.2 Concentration dependence of the $(D_{ij})_V$, $\bar{V}_i$ and R_i.

The concentration dependence of the diffusion coefficients, $(D_{ij})_V$, has been discussed elsewhere for a three-component system containing two electrolytes,[2] and for a system containing an electrolyte and a non-electrolyte,[3] so that it is pertinent to discuss the

TABLE 7.1

INITIAL DIFFUSION DATA FOR THE SYSTEM * WATER - SUCROSE - MANNITOL

$\overline{C}_1 = 0.25$ $\overline{C}_2 = 0.25$

EXP. NO.	SM/9	SM/16	SM/17	SM/13
$(W_1)_A$ †	8.204087	8.067656	7.643872	7.492979
$(W_2)_A$	3.676660	3.814327	4.227038	4.368586
$(W_1)_B$	8.165485	8.302861	8.724760	8.872827
$(W_2)_B$	5.032574	4.897898	4.486583	4.344661
$(C_1)_A$	0.249973	0.245801	0.232841	0.228222
$(C_2)_A$	0.210493	0.218362	0.241938	0.250015
$(C_1)_B$	0.249970	0.254191	0.267164	0.271722
$(C_2)_B$	0.289479	0.281750	0.258144	0.250000
C_1	0.249986	0.249996	0.250003	0.249972
C_2	0.249972	0.250056	0.250041	0.250007
C_1	-0.000003	0.008390	0.034323	0.043500
C_2	0.078986	0.063388	0.016206	-0.000015
d_A	1.042975	1.042912	1.042693	1.042591
d_B	1.047891	1.047957	1.048177	1.048269
δ	-0.019	-0.027	-0.024	-0.025
δ'	-0.014	-0.021	-0.024	-0.023
J(exp)	93.34	93.68	95.93	97.30
J(cal)	93.33	93.68	95.94	97.30
$\mathcal{D}_A \times 10^5$	0.55039	0.52141	0.44294	0.42091
Av.dev.%	0.033	0.059	0.049	0.025
Δt	13.3	15.3	6.7	15.8
$Q(\mathrm{exp}) \times 10^4$	-19.57	-4.43	9.88	9.22
$Q(\mathrm{cal}) \times 10^4$	-19.10	-5.24	10.76	8.67
α_1	-0.0001	0.2004	0.8004	1.0002
I_A		425.98		
S_A		61.38		
E_0		-0.81384		
E_1		3.3363		
E_2		2.0996		
$R_1 \times 10^3$		48.781		
$R_2 \times 10^3$		25.768		

* EXPERIMENTS NUMBERED CHRONOLOGICALLY.
UNITS. CONCENTRATIONS C_i, MOLES/1000 CC, DENSITIES d GM/CC, REDUCED HEIGHT-AREA RATIOS CM^2/SEC

† MORE THAN THE MINIMUM NUMBER OF SIGNIFICANT DIGITS WERE RETAINED IN THESE VALUES TO MINIMISE ACCUMULATION OF ERRORS IN CALCULATION.

TABLE 7.1 (CONT.)

INITIAL DIFFUSION DATA FOR THE SYSTEM *
WATER - SUCROSE - MANNITOL

$\overline{C}_1 = 0.25$ $\overline{C}_2 = 0.50$

EXP. NO.	SM/5	SM/11	SM/12	SM/6
$(W_1)_A$ †	8.082746	7.945583	7.526196	7.380488
$(W_2)_A$	7.903941	8.046786	8.124154	8.606775
$(W_1)_B$	8.044789	8.181807	8.603008	8.742806
$(W_2)_B$	9.261394	9.124286	8.703974	8.560803
$(C_1)_A$	0.249928	0.245670	0.232373	0.228143
$(C_2)_A$	0.459221	0.467488	0.471315	0.499902
$(C_1)_B$	0.249935	0.254206	0.267334	0.271698
$(C_2)_B$	0.540643	0.532669	0.508211	0.499887
C_1	0.249932	0.249938	0.249854	0.249921
C_2	0.499932	0.500078	0.489763	0.499895
ΔC_1	0.000007	0.008536	0.034961	0.043555
ΔC_2	0.081422	0.065181	0.036896	-0.000015
d_A	1.058442	1.058368	1.056870	1.058116
d_B	1.063464	1.063524	1.063690	1.063767
δ	-0.020	-0.029	-0.027	-0.021
δ'	-0.017	-0.027	-0.024	-0.014
J(exp)	95.82	95.86	121.31	97.05
J(cal)	95.89	95.77	121.35	97.04
$\mathcal{D}_A \times 10^5$	0.50959	0.48073	0.42547	0.38421
Av.dev.%	0.035	0.032	0.032	0.046
Δt	1.8	13.9	14.1	26.8
$Q(\text{exp}) \times 10^4$	-19.61	-2.79	15.94	15.16
$Q(\text{cal}) \times 10^4$	-19.10	-3.17	15.46	15.52
α_1	0.0002	0.1986	0.6420	1.0002
I_A		442.73		
S_A		66.89		
E_0		-0.84685		
E_1		4.0062		
E_2		2.3673		
$R_1 \times 10^3$		48.592		
$R_2 \times 10^3$		25.675		

TABLE 7.1 (CONT.)

INITIAL DIFFUSION DATA FOR THE SYSTEM WATER - SUCROSE - MANNITOL *

$\overline{C}_1=0.50$ $\overline{C}_2=0.25$

EXP. NO.	SM/7	SM/14	SM/15
$(W_1)_A$ †	15.911731	15.780171	15.359117
$(W_2)_A$	3.562514	3.694821	4.095923
$(W_1)_B$	15.838209	15.975172	16.393566
$(W_2)_B$	4.882105	4.753401	4.353722
$(C_1)_A$	0.499912	0.495745	0.482395
$(C_2)_A$	0.210308	0.218103	0.241719
$(C_1)_B$	0.499859	0.504217	0.517554
$(C_2)_B$	0.289517	0.281902	0.258264
C_1	0.499886	0.499981	0.499974
C_2	0.249913	0.250003	0.249992
ΔC_1	-0.000053	0.008472	0.035159
ΔC_2	0.079209	0.063799	0.016545
d_A	1.075442	1.075368	1.075097
d_B	1.080319	1.080395	1.080669
δ	-0.021	-0.026	-0.028
δ'	-0.015	-0.027	-0.025
J(exp)	92.93	93.74	97.81
J(cal)	92.88	93.79	97.80
$\mathcal{D}_A \times 10^5$	0.49574	0.46502	0.38822
Av.dev.%	0.035	0.036	0.028
Δt	321.7	16.3	43.3
$Q(\text{exp}) \times 10^4$	-44.98	-15.75	6.94
$Q(\text{cal}) \times 10^4$	-41.28	-20.54	8.05
α_1	-0.0013	0.2013	0.8014
I_A		449.16	
S_A		72.813	
E_0		-1.8479	
E_1		4.9947	
E_2		2.7191	
$R_1 \times 10^3$		48.606	
$R_2 \times 10^3$		25.602	

TABLE 7.1 (CONT.)

INITIAL DIFFUSION DATA FOR THE SYSTEM *
WATER - SUCROSE - MANNITOL

$\bar{C}_1=0.50$ $\bar{C}_2=0.50$

EXP. NO.	SM/1	SM/3	SM/4	SM/2
$(W_1)_A$ †	15.653327	15.556561	15.139540	14.985363
$(W_2)_A$	7.660549	7.795754	8.211898	8.352793
$(W_1)_B$	15.600884	15.752908	16.164959	16.307217
$(W_2)_B$	8.980443	8.865117	8.452670	8.306244
$(C_1)_A$	0.498749	0.495674	0.482297	0.477326
$(C_2)_A$	0.458624	.466726	0.491550	0.499921
$(C_1)_B$	0.499345	0.504326	0.517606	0.522180
$(C_2)_B$	0.540097	0.533282	0.508558	0.499766
C_1	0.499047	0.500000	0.499952	0.499753
C_2	0.499360	0.500004	0.500054	0.499843
ΔC_1	0.000596	0.008652	0.035309	0.044854
ΔC_2	0.081473	0.066556	0.017008	-0.000155
d_A	1.090652	1.090670	1.090467	1.090331
d_B	1.095627	1.095876	1.096062	1.096102
δ	-0.018	-0.018	-0.020	-0.017
δ'	-0.016	-0.018	-0.020	-0.019
J(exp)	95.12	97.20	98.50	99.48
J(cal)	95.25	97.12	98.41	99.54
$\mathscr{D}_A \times 10^5$	0.45622	0.42798	0.35499	0.33325
Av.dev.%	0.051	0.070	0.048	0.029
Δt	8.4	23.6	42.4	5.0
$Q(\text{exp}) \times 10^4$	-47.50	-20.66	21.15	23.50
$Q(\text{cal}) \times 10^4$	-46.96	-21.14	20.54	24.06
α	-0.0009	0.1981	0.7978	1.0018
I_A^1		467.95		
S_A		79.291		
E_0		-2.1924		
E_1		6.5021		
E_2		2.9928		
$R_1 \times 10^3$		48.480		
$R_2 \times 10^3$		25.516		

concentration dependence of the diffusion coefficients in a ternary system containing two non-electrolytes. The behaviour of the system is shown in the three-dimensional diagrams, Figure 7.1. The $(D_{11})_V$ values for the ternary points have been connected by lines and extended to the $(D_{11})_V$ - C_1 plane, where the $(D_{11})_V$ values may be identified with the mutual diffusion coefficients in the binary system water-sucrose. Likewise, the values of $(D_{22})_V$ have been connected in the $(D_{22})_V$ - C_2 plane with the mutual diffusion coefficients of the system water-mannitol. The data for the binary experiments were reported in Chapter 6. It may be noted that the $(D_{11})_V$ values vary almost linearly with change in C_2, and that the $(D_{22})_V$ values similarly are nearly linear with change in C_1. If tracer diffusion data were available, we would also be able to observe the variation of $(D_{11})_V$ with C_1 as $C_1 \rightarrow 0$ and C_2 is constant, and likewise the variation of $(D_{22})_V$ with C_2 for $C_2 \rightarrow 0$ and C_1 constant. The values of the $(D_{12})_V$ have been plotted, and extrapolated to zero at constant C_2, since[2,3] $(D_{12})_V \rightarrow 0$ as $C_1 \rightarrow 0$. Similarly the $(D_{21})_V$ have been extrapolated to zero at constant C_1.

It is interesting to note the overall similarity in shape between the diagrams of the concentration dependence of the $(D_{ij})_V$ reported here and those

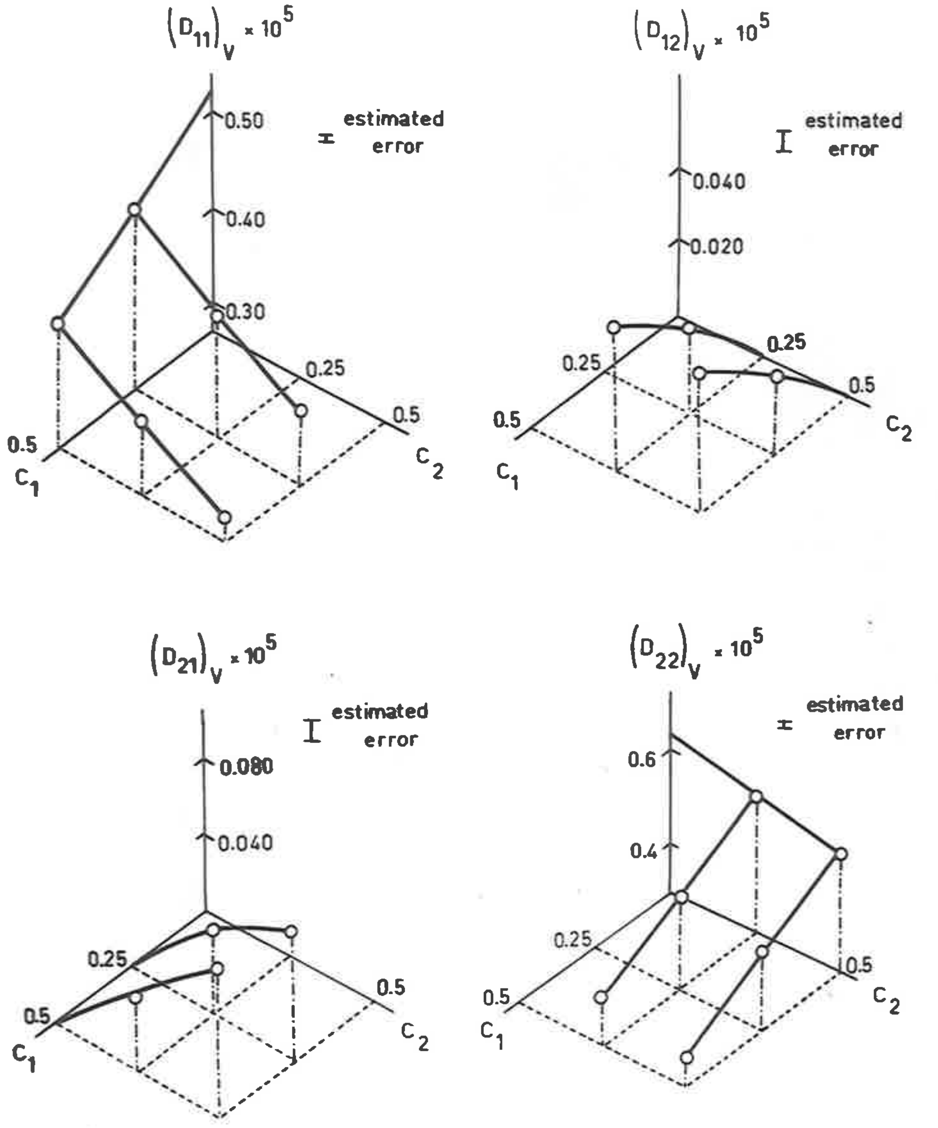

Figure 7.1. The dependence on solute concentrations of the volume fixed diffusion coefficients, $(D_{ij})_V$, for the system water-sucrose-mannitol at 25°.

reported[3] for the system water-glycine-KCl over the same concentration range. The main difference is that both the $(D_{12})_V$ and the $(D_{21})_V$ values are all negative for the latter system, whereas those reported here for the water-sucrose-mannitol system are all positive. The fact that the diffusion coefficients for the ternary system containing an electrolyte and a non-electrolyte behave in a qualitatively similar manner to a ternary system containing two non-electrolytes is perhaps not completely surprising when one is reminded[3] that the condition of zero electric current requires that K^+ and Cl^- ions in the system water-glycine-KCl move with the same velocity, so that the system becomes somewhat comparable with a solution of two non-electrolytes. This condition distinguishes both the water-sucrose-mannitol and the water-glycine-KCl systems from the water-NaCl-KCl, and water-sodium sulphate-sulphuric acid systems,[2,4] (for which similar diffusion data is available), since the presence of a common ion no longer requires the other ions to move with the same velocity.

The variations in the partial molar volumes, $\bar{V}_i$, are illustrated in Figure 7.2a. As with the $(D_{ij})_V$ values, the ternary data have been connected to the binary data in the $\bar{V}_1 - C_1$ plane and in the $\bar{V}_2 - C_2$ plane. If tracer partial molar volumes were available,

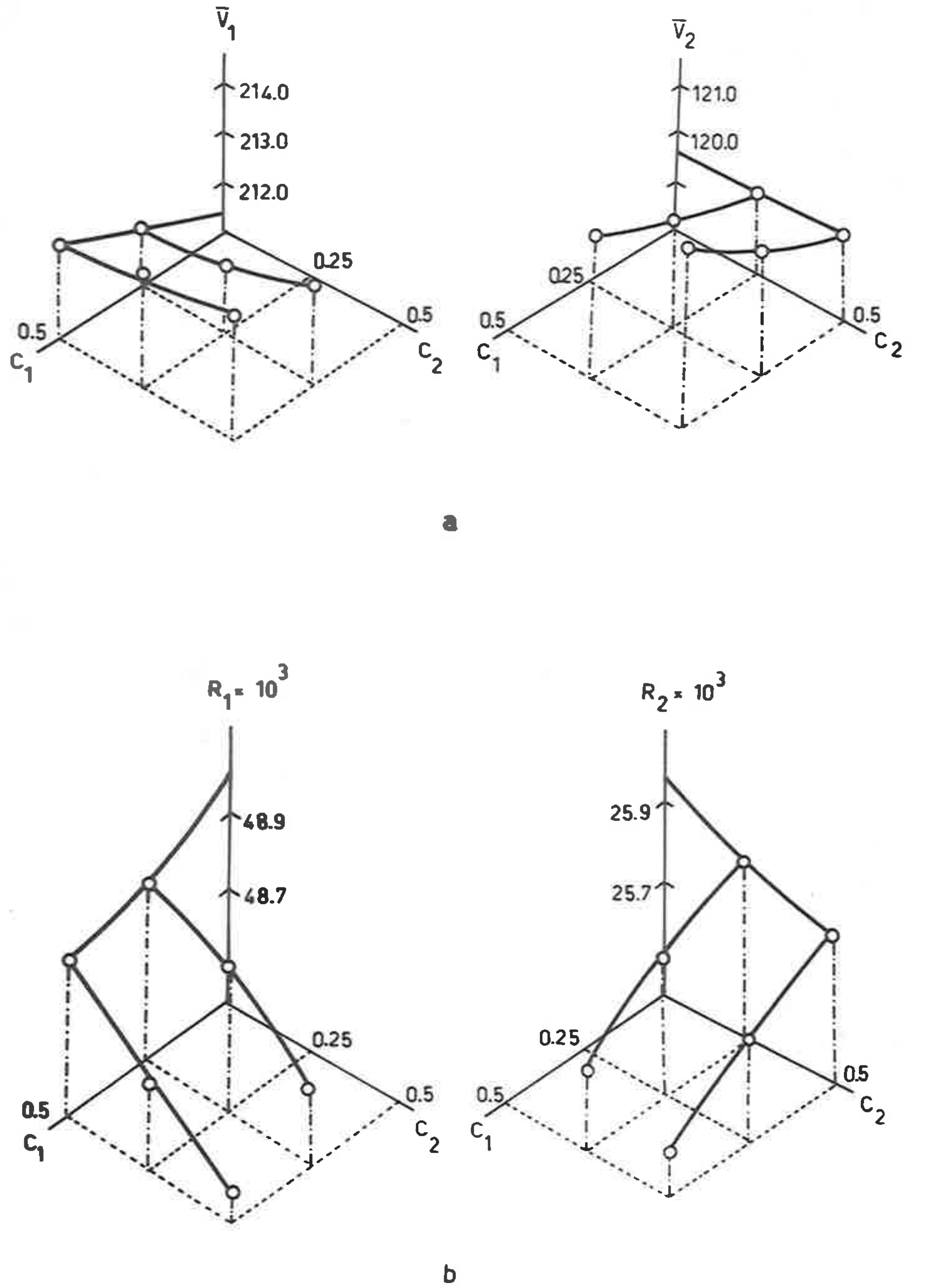

Figure 7.2. The solute concentration dependence of (a) Partial molar volumes, $\overline{V}_i$, and (b) Refractive index derivatives, R_i, in the ternary system water-sucrose-mannitol at 25°.

it would also be possible to link the ternary points to the $\bar{V}_1 - C_2$ plane and to the $\bar{V}_2 - C_1$ plane, and thereby define all points in the system.

The concentration dependence of the refractive index derivatives, R_i, is illustrated in Figure 7.2b. It may be noted that the R_1 and R_2 values decrease with increasing C_1 and C_2, which might be expected since the $\bar{V}_i$ increase with increasing C_1 and C_2. A similar concentration dependence has also been reported for the water-glycine-KCl and water-NaCl-KCl systems[3,2,5] but not for the water-sodium sulphate-sulphuric acid system.[4]

7.3 Computation of the L_{ij}, R_{ik} and Tests of the ORR.

The phenomenological and frictional coefficients may be calculated from the $(D_{ij})_V$ values, the partial molar volumes and chemical potential derivatives. The partial molar volumes, calculated from experimental density data using equation 5.18, were first used to compute diffusion coefficients on the solvent-fixed scale, $(D_{ij})_0$(see equation 5.17). The appropriate diffusion and chemical potential data were then combined to determine the $(L_{ij})_0$ (equations 5.33), the $(L_{ij})_V$ (equations 5.36) and the R_{ik} (equations 5.47). The chemical potential derivatives, μ_{ij}, were again determined using equations 5.39 to 5.41, and the Γ_{ik} terms (equation 5.44) were determined, as for the previous chapter, by differentiation of equation 2.5 and equation 2.7 for Γ_{11} and Γ_{22}, and from equations 2.14 and 2.15 directly for Γ_{12} (and Γ_{21}). The numerical values of the constants required in these relations were determined from isopiestic activity data of Robinson and Stokes.[6] Use of the constants of equations 5 and 1, respectively, of Robinson and Stokes[6] enable Γ_{11} and Γ_{22} to be determined, whilst Γ_{12} (and Γ_{21}) may be obtained directly from their equation 23. The diffusion, phenomenological and frictional coefficients are summarised in Table 7.2, whilst the chemical potential derivatives and other related data are given in Table 7.3.

To determine the accuracy with which the tests of the ORR have been made, it was necessary, as with the water-urea-sucrose system, to make an estimate of the errors involved in determining the frictional coefficients. Again the method of Dunlop,[1] described in Chapter 6, was used. Errors in the frictional coefficients due to errors in the $(D_{ij})_V$ which in turn were caused by an inaccuracy of $\pm 2 \times 10^{-4}$ in the area under the fringe deviation graphs, were designated $(\delta R_{ik})_1$, and errors due to the Γ_{ik} were designated $(\delta R_{ik})_2$.

Table 7.2.

DIFFUSION, PHENOMENOLOGICAL AND FRICTIONAL COEFFICIENTS FOR THE SYSTEM WATER-SUCROSE-MANNITOL.

	I	II	III	IV
C_1	0.25	0.25	0.50	0.50
C_2	0.25	0.50	0.25	0.50
$(D_{11})_V \times 10^5$	0.402_1 $\mp 0.004^{1}_{4}$	0.355_7 $\mp 0.003^{7}_{8}$	0.353_8 $\mp 0.003^{8}_{3}$	0.301_2 $\mp 0.002^{2}_{7}$
$(D_{12})_V \times 10^5$	0.023_7 $\mp 0.002^{7}_{5}$	0.020_6 $\mp 0.002^{6}_{2}$	0.038_2 $\mp 0.001^{2}_{8}$	0.036_6 $\mp 0.001^{6}_{5}$
$(D_{21})_V \times 10^5$	0.044_1 $\pm 0.010^{1}_{3}$	0.068_9 $\pm 0.009^{9}_{0}$	0.031_9 $\pm 0.007^{9}_{8}$	0.079_4 $\pm 0.006^{4}_{7}$
$(D_{22})_V \times 10^5$	0.496_2 $\pm 0.005^{2}_{7}$	0.462_1 $\pm 0.005^{1}_{0}$	0.404_7 $\pm 0.004^{7}_{4}$	0.368_4 $\pm 0.003^{4}_{7}$
$(D_{11})_0 \times 10^5$	0.426_8	0.379_4	0.399_7	0.345_7
$(D_{12})_0 \times 10^5$	0.041_3	0.037_5	0.071_2	0.068_2
$(D_{21})_0 \times 10^5$	0.068_8	0.116_4	0.054_8	0.123_8
$(D_{22})_0 \times 10^5$	0.513_2	0.494_9	0.420_2	0.398_0
$(L_{11})_0 \times 10^{20}$	3.87_{56}	3.40_{74}	6.45_{44}	5.44_{75}
$(L_{12})_0 \times 10^{20}$	0.18_{22}	0.30_{44}	0.27_{16}	0.53_{43}
$(L_{21})_0 \times 10^{20}$	0.25_{31}	0.32_{80}	0.28_{17}	0.84_{51}
$(L_{22})_0 \times 10^{20}$	4.97_{55}	9.22_{26}	4.04_{45}	7.24_{57}
$(L_{11})_V \times 10^{20}$	3.46_{71}	3.04_{45}	5.13_{58}	4.29_{87}
$(L_{12})_V \times 10^{20}$	-0.17_{23}	-0.33_{35}	-0.30_{88}	-0.48_{22}
$(L_{21})_V \times 10^{20}$	-0.10_{77}	-0.31_{40}	-0.30_{14}	-0.22_{85}
$(L_{22})_V \times 10^{20}$	4.67_{49}	8.13_{77}	3.80_{31}	6.34_{85}

Table 7.2. (Continued)

	I	II	III	IV
$R_{10}\times10^{-18}$	0.12_{27}	0.14_{01}	0.15_{71}	0.18_{65}
$(\delta R_{10})_1\times10^{-18}$	$\pm0.00_{19}$	$\pm0.00_{25}$	$\pm0.00_{17}$	$\pm0.00_{22}$
$(\delta R_{10})_2\times10^{-18}$	$\pm0.00_{02}$	$\pm0.00_{02}$	$\pm0.00_{03}$	$\pm0.00_{04}$
$R_{12}\times10^{-18}$	0.94_{61}	0.96_{96}	1.04_{09}	1.36_{20}
$(\delta R_{12})_1\times10^{-18}$	$\mp0.11_{07}$	$\mp0.11_{32}$	$\mp0.05_{22}$	$\mp0.05_{51}$
$(\delta R_{12})_2\times10^{-18}$	$\mp0.00_{98}$	$\mp0.01_{10}$	$\mp0.01_{16}$	$\mp0.01_{31}$
$R_{21}\times10^{-18}$	1.31_{21}	1.03_{97}	1.07_{38}	2.13_{89}
$(\delta R_{21})_1\times10^{-18}$	$\pm0.46_{88}$	$\pm0.24_{15}$	$\pm0.47_{43}$	$\pm0.25_{72}$
$(\delta R_{21})_2\times10^{-18}$	$\mp0.01_{20}$	$\mp0.01_{30}$	$\mp0.01_{48}$	$\mp0.01_{37}$
$R_{20}\times10^{-18}$	0.09_{27}	0.10_{52}	0.11_{81}	0.12_{73}
$(\delta R_{20})_1\times10^{-18}$	$\mp0.00_{33}$	$\mp0.00_{23}$	$\mp0.00_{59}$	$\mp0.00_{38}$
$(\delta R_{20})_2\times10^{-18}$	$\pm0.00_{01}$	$\pm0.00_{02}$	$\pm0.00_{03}$	$\pm0.00_{04}$
Δ%(exp)	-32.4%	- 7.0%	- 3.1%	-44.4%
Δ%(calc)	±53.3% (±71.0%)	±37.7% (±55.3%)	±52.3% (±83.8%)	±19.4% (±29.6%)

Table 7.3 [a,b]

COMPUTATION OF THE CHEMICAL POTENTIAL DERIVATIVES, μ_{ij}, FOR THE SYSTEM WATER-SUCROSE-MANNITOL.

	I	II	III	IV
C_1	0.25	0.25	0.50	0.50
C_2	0.25	0.50	0.25	0.50
m_1	0.2734_3	0.2827_1	0.5805_9	0.6016_6
m_2	0.2734_3	0.5654_3	0.2902_9	0.6016_6
Γ_{11}	0.1636_6	0.1737_2	0.1749_3	0.1833_9
$\Gamma_{12}= \Gamma_{21}$	0.0867_8	0.0902_2	0.0960_2	0.0998_8
Γ_{22}	0.0131_7	0.0133_9	0.0203_3	0.0208_2
$A_{11}\times10^{-10}$	9.4721_5	9.1993_4	4.7035_1	4.5749_4
$(A_{12}=A_{21})\times10^{-10}$	0.2151_4	0.2236_5	0.2380_3	0.2476_1
$A_{22}\times10^{-10}$	9.0990_7	4.4175_3	8.5900_9	4.1719_2
$B_{11}\times10^{-3}$	1.1570_5	1.1988_0	1.3046_9	1.3576_6
$B_{12}\times10^{-3}$	0.0358_6	0.0384_5	0.0812_6	0.0879_9
$B_{21}\times10^{-3}$	0.0633_4	0.1358_9	0.0717_6	0.1543_4
$B_{22}\times10^{-3}$	1.1295_8	1.2077_5	1.2018_0	1.2913_1
$\mu_{11}\times10^{-13}$	10.9734	11.0585	6.1537	6.2494
$\mu_{12}\times10^{-13}$	0.5827	0.6238	0.6683	0.7223
$\mu_{21}\times10^{-13}$	0.8252	0.8684	0.9270	0.9801
$\mu_{22}\times10^{-13}$	10.2858	5.3439	10.3430	5.4090

[a] More than the minimum number of significant digits have been retained in the quantities listed in the Table to minimise the accumulation of errors in the L_{ij} and R_{ik}.

[b] The μ_{ij} have units c.c. erg mole^{-2}.

It was assumed that the activity data of Robinson and Stokes[6] would have approximately the same average error as the activity data described in this work (Chapter 2), so that an error of ±0.002 was assumed for Γ_{12} and Γ_{21}, and ±0.003 for Γ_{11} and Γ_{22} (see Chapter 6). The calculated errors in the frictional coefficients are listed in Table 7.2. From this data, the total calculated error, Δ%(calc), which defines the limits for which R_{12} and R_{21} may differ and yet the ORR may still be valid, can be calculated (see equation 6.3). This value may then be compared with the experimental error, Δ%(exp) (equation 6.1). If the experimental error is less than the calculated limit, then the ORR is considered to be valid for the ternary point under consideration.

Inspection of the errors listed in Table 7.2 shows that the test of the ORR is satisfactory for three of the points in the ternary system, but not for the point at $C_1 = C_2 = 0.5$. At first, it seemed surprising that disagreement was present at the ternary point where Q values were the largest of the four points considered, since it has been pointed out[4] that the largest errors in the $(D_{ij})_V$ occur for experiments with the smallest values of Q. This fact is illustrated by the observation that the calculated error is smallest for $C_1 = C_2 = 0.5$, and largest for $C_1 = C_2 = 0.25$.

In an endeavour to obtain a satisfactory test of the ORR for the ternary point where $C_1 = C_2 = 0.5$, several calculations were tried, similar to those outlined for the water-urea-sucrose system in Chapter 6. The addition of 2×10^{-4} units to the area of positive fringe deviation graphs, and the subtraction of 2×10^{-4} units to the area of negative fringe deviation graphs, instead of the customary[1,4] (and entirely arbitrary) addition of Q units to all areas, when estimating errors, resulted in the calculated error increasing from 19.4% to 29.6%. This new error still falls considerably short of the experimental error of 44.4%, but an inspection of the data shows that the errors in the $(D_{ij})_V$ contribute the greater portion of the error in the R_{ik}. Therefore if the error in the values of Q is increased to $\pm 3 \times 10^{-4}$ units, then the calculated error would increase sufficiently for agreement with the experimental error to be obtained, and the ORR would then be verified. It may, perhaps, be considered somewhat inconsistent to suggest that a larger error in the Q values can be applied to a ternary point where all the experimental and calculated Q values agree to within $\pm 1 \times 10^{-4}$. Nevertheless, the resulting increase in the estimated error is not nearly so drastic as would be obtained for a ternary point which had somewhat smaller values of Q (at $C_1 = C_2 = 0.25$, for example). Furthermore, experience in this laboratory has shown that it it possible to get a difference in Q of ±2 to 3 × 10^{-4} with experiments whose areas are approximately 40 × 10^{-4}, by comparing values obtained for the same experiments before and after installation of the photoelectric null indicator.

References to Chapter 7.

1. P. J. Dunlop, J. Phys. Chem., 69, 4276 (1965).
2. I. J. O'Donnell and L. J. Gosting, in "The Structure of Electrolyte Solutions," W. J. Hamer, ed., John Wiley and Sons, Inc., New York, 1959.
3. L. A. Woolf, D. G. Miller and L. J. Gosting, J. Am. Chem. Soc., 84, 317 (1962).
4. R. P. Wendt, J. Phys. Chem., 66, 1279 (1962).
5. P. J. Dunlop and L. J. Gosting, ibid., 63, 86 (1959).
6. R. A. Robinson and R. H. Stokes, ibid., 65, 1954 (1961).

GENERAL CONCLUSIONS.

Interactions in liquid systems of two and three components have been studied by vapour pressure, diffusion, density and relative viscosity measurements. The vapour pressure, diffusion and density data have been combined for two aqueous ternary systems and tests of the validity of the Onsager Reciprocal Relation have been made for five ternary points. Of these, three agreed very satisfactorily, and the other two points would also agree if a slightly larger error than usual in the measurements is accepted.

APPENDIX A.

COMPUTER PROGRAMME LISTINGS.

(The author is indebted to Dr. N. Capon of the Department of Computing Science of the University of Adelaide for supplying the subroutine "solve" which is incorporated into the least squares programmes.)

```
C     1005 ELLERTON 3 COMPONENT ACTIVITY DATA
      DIMENSIONC1(20),C2(20)
    2 FORMAT(/)
    7 READ,M
      IF(M)11,13,14
   11 PUNCH12
   12 FORMAT(10H MORE DATA)
   14 PUNCH3
    3 FORMAT(35H ELLERTON 3 COMPONENT ACTIVITY DATA)
      PUNCH2
      PUNCH4
    4 FORMAT(4X 2HM1 7X 2HM2 7X1HM 8X3H1/M 6X 4HM1/M 5X 1HD 7X 6HD/M1M2)
      READ,N
      READ,A1,A2,A3,A4,A5,A6
      READ,B1,B2,B3,B4,B5,B6
      DO10J=1,N
      READ,K,REFM,REFC,CA,CT1,CB,CT2
      DO6I=1,K
    6 READ,C1(I),C2(I)
      DO8I=1,K
      CO1=1.+A1*C1(I)+A2*C1(I)*C1(I)+A3*C1(I)**3+A4*C1(I)**4+A5*C1(I)**5
      CO11=A6*C1(I)**6
      COT1=CO1+CO11
      CO2=1.+B1*C2(I)+B2*C2(I)*C2(I)+B3*C2(I)**3+B4*C2(I)**4+B5*C2(I)**5
      CO22=B6*C2(I)**6
      COT2=CO2+CO22
      C=C1(I)+C2(I)
      RC=1.0/C
      XC=C1(I)/C
      DEL=2.0*REFM*REFC-C1(I)*COT1-C2(I)*COT2
```

```
      DELMM=DEL/(C1(I)*C2(I))
    8 PUNCH9,C1(I),C2(I),C,RC,XC,DEL,DELMM
    9 FORMAT(7F9.5)
      CAR=1.0/CA
      CBR=1.0/CB
      PUNCH15,REFM,REFC,CA,CT1,CAR,CB,CT2,CBR
   15 FORMAT(2F11.5/3F11.5/3F11.5)
   10 PUNCH2
      GOTO7
   13 STOP
      END
```

```
C     1005 ELLERTON - 3 COMPONENT ACTIVITY DEVIATIONS
   11 READ,N,M
      IF(N)4,4,3
    3 PUNCH5
    5 FORMAT(43H ELLERTON - 3 COMPONENT ACTIVITY DEVIATIONS/)
      IF(M)17,16,16
   16 PUNCH6
    6 FORMAT(/4X 2HM1 7X 2HM2 5X 34HDMM EXP   DMM CAL     M REF    OS REF/)
      GOTO15
   17 PUNCH18
   18 FORMAT(/4X 2HM1 7X 2HM2 5X 34HDMM EXP   DMM CAL     M REF   PC DIF /)
   15 READ,A1,A2,A3,A4,A5,A6
      READ,B1,B2,B3,B4,B5,B6
      DO7I=1,N
      READ,RM,RC,C1,C2,DME,DMC
      D=DMC*C1*C2
      CO1=1.+A1*C1+A2*C1*C1+A3*C1**3+A4*C1**4+A5*C1**5+A6*C1**6
      CO2=1.+B1*C2+B2*C2*C2+B3*C2**3+B4*C2**4+B5*C2**5+B6*C2**6
      RMC=(D+C1*CO1+C2*CO2)/(2.0*RC)
      DIF=RMC-RM
      DPC=DIF*100.0/RM
      IF(M)12,13,14
   13 PUNCH9,C1,C2,DME,DMC,RM,RC,DPC
    9 FORMAT(2F9.4,2F9.5,2F9.4,F7.2)
      GOTO7
   12 PUNCH10,C1,C2,DME,DMC,RM,DPC
   10 FORMAT(2F9.4,2F9.5,F9.4,F7.2)
      GOTO7
   14 PUNCH8,C1,C2,DME,DMC,RM,RC,RMC,DIF,DPC
    8 FORMAT(2F9.4,2F9.5,4F9.4,F7.2)
    7 CONTINUE
      GOTO11
    4 STOP
      END
```

```
C     ELLERTON - LEAST SQUARE TWO VARIABLES - TYPE 1  CDC
      DIMENSIONA(6,7),X(200),Y(200),Z(200)
      TYPE DOUBLE A,X,Y,Z
      DIMENSION TITLE(12)
   99 READ (60,20) TITLE
   20 FORMAT(12A6)
      WRITE (61,21) TITLE
   21 FORMAT(1H1/1X,12A6/1H0)
      DO22I=1,6
      DO22J=1,7
   22 A(I,J)=0.0
      DELL=0.0
    2 READ (60,3) N
    3 FORMAT(I3)
      READ (60,4) (Z(I),X(I),Y(I),I=1,N)
    4 FORMAT(6F10.0)
      DO10 I=1,N
      A(1,1)=A(1,1)+1.0
      A(2,2)=A(2,2)+X(I)**2
      A(3,3)=A(3,3)+Y(I)**2
      A(4,4)=A(4,4)+X(I)**4
      A(5,5)=A(5,5)+X(I)**2*Y(I)**2
      A(6,6)=A(6,6)+Y(I)**4
      A(1,2)=A(1,2)+X(I)
      A(1,3)=A(1,3)+Y(I)
      A(1,5)=A(1,5)+X(I)*Y(I)
      A(2,4)=X(I)**3+A(2,4)
      A(2,5)=X(I)**2*Y(I)+A(2,5)
      A(2,6)=X(I)*Y(I)**2+A(2,6)
      A(3,6)=A(3,6)+Y(I)**3
      A(4,5)=A(4,5)+X(I)**3*Y(I)
      A(5,6)=A(5,6)+X(I)*Y(I)**3
      A(1,7)=A(1,7)+Z(I)
      A(2,7)=A(2,7)+Z(I)*X(I)
      A(3,7)=A(3,7)+Z(I)*Y(I)
      A(4,7)=A(4,7)+Z(I)*X(I)**2
      A(5,7)=A(5,7)+Z(I)*X(I)*Y(I)
   10 A(6,7)=A(6,7)+Z(I)*Y(I)**2
      A(1,4)=A(2,2)
      A(4,1)=A(2,2)
      A(1,6)=A(3,3)
      A(6,1)=A(3,3)
      A(2,1)=A(1,2)
      A(3,1)=A(1,3)
      A(5,1)=A(1,5)
      A(2,3)=A(1,5)
      A(3,2)=A(1,5)
      A(4,2)=A(2,4)
      A(5,2)=A(2,5)
      A(3,4)=A(2,5)
```

```
      A(4,3)=A(2,5)
      A(6,2)=A(2,6)
      A(3,5)=A(2,6)
      A(5,3)=A(2,6)
      A(5,4)=A(4,5)
      A(4,6)=A(5,5)
      A(6,4)=A(5,5)
      A(6,5)=A(5,6)
      A(6,3)=A(3,6)
      CALLSOLVE(A,6)
      WRITE (61,35)
   35 FORMAT(27H COEFFICIENTS OF POLYNOMIAL/1H )
      WRITE (61,36)
   36 FORMAT(6X 4HX0Y0 12X 4HX1Y0 12X 4HX0Y1)
      WRITE (61,12) A(1,7),A(2,7),A(3,7)
   12 FORMAT(3(1XE15.8)/1H )
      WRITE (61,37)
   37 FORMAT(6X 4HX2Y0 12X 4HX1Y1 12X 4HX0Y2)
      WRITE (61,12) A(4,7),A(5,7),A(6,7)
      WRITE (61,38)
   38 FORMAT(5X 1HX 13X 1HY 13X 1HZ 12X 6HZ CALC 8X 3HDIF)
      DO14I=1,N
      ZCALC=A(1,7)+A(2,7)*X(I)+A(3,7)*Y(I)+A(4,7)*X(I)**2
     1+A(5,7)*X(I)*Y(I)+A(6,7)*Y(I)**2
      DEL=(ZCALC-Z(I))
      DELL=DELL+ABSF(DEL)
   14 WRITE (61,13) X(I),Y(I),Z(I),ZCALC,DEL
   13 FORMAT(5(1XE13.6))
      WRITE (61,39)
   39 FORMAT(1H /1H ,4X,5HAVDEV)
      AVDEV=DELL/FLOATF(N)
      WRITE (61,15) AVDEV
   15 FORMAT(1XE15.8/1H )
      GO TO 99
      END
      SUBROUTINESOLVE(A,N)
C     SOLVES SET OF LINEAR EQNS. MATRIX A HAS N ROWS,N+1 COLUMNS.
C     THE(N+1) COLUMN CONSISTS OF RHS OF EQNS.
C     THE SOLUTION REPLACES THIS COLUMN.
      DIMENSIONA(6,7)
      TYPE DOUBLE A
      NI=N+1
      ND=N-1
      DO6J=1,ND
      JR=J
      SL=A(J,J)
      K=J+1
      DO2I=K,N
      IF(ABSF(SL)-ABSF(A(I,J)))3,2,2
    3 SL=A(I,J)
      JR=I
```

```
  2 CONTINUE
    IF(SL)15,10,15
 10 WRITE (61,14)
 14 FORMAT(9H DET ZERO)
    WRITE (61,300) A(N,N),J
300 FORMAT(E14.8,I3)
    STOP
 15 IF(JR-J)7,7,8
  8 DO5L=J,NI
    TEMP=A(J,L)
    A(J,L)=A(JR,L)
  5 A(JR,L)=TEMP
  7 DO6I=K,N
    AM=A(I,J)/A(J,J)
    DO6L=J,NI
  6 A(I,L)=A(I,L)-AM*A(J,L)
    IF(A(N,N))9,10,9
  9 A(N,NI)=A(N,NI)/A(N,N)
    DO30K=2,N
    S=0
    I=N-K+1
    L=I+1
    DO31M=L,N
 31 S=S+A(I,M)*A(M,NI)
 30 A(I,NI)=(A(I,NI)-S)/A(I,I)
    RETURN
    END
```

```
C     ELLERTON - LEAST SQUARE TWO VARIABLES - TYPE 2  CDC
      DIMENSIONA(10,11),X(200),Y(200),Z(200)
      TYPE DOUBLE A,X,Y,Z
      DIMENSION TITLE(12)
   99 READ (60,20) TITLE
   20 FORMAT(12A6)
      WRITE (61,21) TITLE
   21 FORMAT(1H1/1X,12A6/1H0)
      DO22I=1,10
      DO22J=1,11
   22 A(I,J)=0.0
      DELL=0.0
    2 READ (60,3) N
    3 FORMAT(I3)
      READ (60,4) (Z(I),X(I),Y(I),I=1,N)
    4 FORMAT(6F10.0)
      DO10 I=1,N
      A(1,1)=A(1,1)+1.0
      A(2,2)=A(2,2)+X(I)**2
      A(3,3)=A(3,3)+Y(I)**2
      A(4,4)=A(4,4)+X(I)**4
      A(5,5)=A(5,5)+X(I)**2*Y(I)**2
      A(6,6)=A(6,6)+Y(I)**4
      A(7,7)=A(7,7)+X(I)**6
      A(8,8)=A(8,8)+X(I)**4*Y(I)**2
      A(9,9)=A(9,9)+X(I)**2*Y(I)**4
      A(10,10)=A(10,10)+Y(I)**6
      A(1,2)=A(1,2)+X(I)
      A(1,3)=A(1,3)+Y(I)
      A(1,5)=A(1,5)+X(I)*Y(I)
      A(1,7)=A(1,7)+X(I)**3
      A(1,8)=A(1,8)+X(I)**2*Y(I)
      A(1,9)=A(1,9)+X(I)*Y(I)**2
      A(1,10)=A(1,10)+Y(I)**3
      A(2,8)=A(2,8)+X(I)**3*Y(I)
      A(2,10)=A(2,10)+X(I)*Y(I)**3
      A(4,7)=A(4,7)+X(I)**5
      A(4,8)=A(4,8)+X(I)**4*Y(I)
      A(4,9)=A(4,9)+X(I)**3*Y(I)**2
      A(4,10)=A(4,10)+X(I)**2+Y(I)**3
      A(5,10)=A(5,10)+X(I)*Y(I)**4
      A(6,10)=A(6,10)+Y(I)**5
      A(7,8)=A(7,8)+X(I)**5*Y(I)
      A(7,10)=A(7,10)+X(I)**3*Y(I)**3
      A(9,10)=A(9,10)+X(I)*Y(I)**5
      A(1,11)=A(1,11)+Z(I)
      A(2,11)=A(2,11)+Z(I)*X(I)
      A(3,11)=A(3,11)+Z(I)*Y(I)
      A(4,11)=A(4,11)+Z(I)*X(I)**2
      A(5,11)=A(5,11)+Z(I)*X(I)*Y(I)
```

```
      A(6,11)=A(6,11)+Z(I)*Y(I)**2
      A(7,11)=A(7,11)+Z(I)*X(I)**3
      A(8,11)=A(8,11)+Z(I)*X(I)**2*Y(I)
      A(9,11)=A(9,11)+Z(I)*X(I)*Y(I)**2
   10 A(10,11)=A(10,11)+Z(I)*Y(I)**3
      A(1,4)=A(2,2)
      A(1,6)=A(3,3)
      A(2,1)=A(1,2)
      A(2,3)=A(1,5)
      A(2,4)=A(1,7)
      A(2,5)=A(1,8)
      A(2,6)=A(1,9)
      A(2,7)=A(4,4)
      A(2,9)=A(5,5)
      A(3,1)=A(1,3)
      A(3,2)=A(1,5)
      A(3,4)=A(1,8)
      A(3,5)=A(1,9)
      A(3,6)=A(1,10)
      A(3,7)=A(2,8)
      A(3,8)=A(5,5)
      A(3,9)=A(2,10)
      A(3,10)=A(6,6)
      A(4,1)=A(2,2)
      A(4,2)=A(1,7)
      A(4,3)=A(1,8)
      A(4,5)=A(2,8)
      A(4,6)=A(5,5)
      A(5,1)=A(1,5)
      A(5,2)=A(1,8)
      A(5,3)=A(1,9)
      A(5,4)=A(2,8)
      A(5,6)=A(2,10)
      A(5,7)=A(4,8)
      A(5,8)=A(4,9)
      A(5,9)=A(4,10)
      A(6,1)=A(3,3)
      A(6,2)=A(1,9)
      A(6,3)=A(1,10)
      A(6,4)=A(5,5)
      A(6,5)=A(2,10)
      A(6,7)=A(4,9)
      A(6,8)=A(4,10)
      A(6,9)=A(5,10)
      A(7,1)=A(1,7)
      A(7,2)=A(4,4)
      A(7,3)=A(2,8)
      A(7,4)=A(4,7)
      A(7,5)=A(4,8)
      A(7,6)=A(4,9)
```

```
      A(7,9)=A(8,8)
      A(8,1)=A(1,8)
      A(8,2)=A(2,8)
      A(8,3)=A(5,5)
      A(8,4)=A(4,8)
      A(8,5)=A(4,9)
      A(8,6)=A(4,10)
      A(8,7)=A(7,8)
      A(8,9)=A(7,10)
      A(8,10)=A(9,9)
      A(9,1)=A(1,9)
      A(9,2)=A(5,5)
      A(9,3)=A(2,10)
      A(9,4)=A(4,9)
      A(9,5)=A(4,10)
      A(9,6)=A(5,10)
      A(9,7)=A(8,8)
      A(9,8)=A(7,10)
      A(10,1)=A(1,10)
      A(10,2)=A(2,10)
      A(10,3)=A(6,6)
      A(10,4)=A(4,10)
      A(10,5)=A(5,10)
      A(10,6)=A(6,10)
      A(10,7)=A(7,10)
      A(10,8)=A(9,9)
      A(10,9)=A(9,10)
      CALLSOLVE(A,10)
      WRITE (61,35)
   35 FORMAT(27H COEFFICIENTS OF POLYNOMIAL/1H )
      WRITE (61,36)
   36 FORMAT(6X 4HX0Y0 12X 4HX1Y0 12X 4HX0Y1 12X 4HX2Y0 12X 4HX1Y1)
      WRITE (61,12) A(1,11),A(2,11),A(3,11),A(4,11),A(5,11)
   12 FORMAT(5(1XE15.8)/1H )
      WRITE (61,37)
   37 FORMAT(6X4HX0Y2 12X 4HX3Y0 12X 4HX2Y1 12X 4HX1Y2 12X 4HX0Y3)
      WRITE (61,12) A(6,11),A(7,11),A(8,11),A(9,11),A(10,11)
      WRITE (61,38)
   38 FORMAT(5X 1HX 13X 1HY 13X 1HZ 12X 6HZ CALC 8X 3HDIF)
      DO14I=1,N
      ZCALC=A(1,11)+A(2,11)*X(I)+A(3,11)*Y(I)+A(4,11)*X(I)**2
     1+A(5,11)*X(I)*Y(I)+A(6,11)*Y(I)**2+A(7,11)*X(I)**3
     2+A(8,11)*X(I)**2*Y(I)+A(9,11)*X(I)*Y(I)**2+A(10,11)*Y(I)**3
      DEL=(ZCALC-Z(I))
      DELL=DELL+ABSF(DEL)
   14 WRITE (61,13) X(I),Y(I),Z(I),ZCALC,DEL
   13 FORMAT(5(1XE13.6))
      WRITE (61,39)
   39 FORMAT(1H /1H ,4X,5HAVDEV)
      AVDEV=DELL/FLOATF(N)
```

```
      WRITE (61,15) AVDEV
   15 FORMAT(1XE15.8/1H )
      GO TO 99
      END
      SUBROUTINESOLVE(A,N)
C     SOLVES SET OF LINEAR EQNS. MATRIX A HAS N ROWS,N+1 COLUMNS.
C     THE(N+1) COLUMN CONSISTS OF RHS OF EQNS.
C     THE SOLUTION REPLACES THIS COLUMN.
      DIMENSIONA(10,11)
      TYPE DOUBLE A
      NI=N+1
      ND=N-1
      DO6J=1,ND
      JR=J
      SL=A(J,J)
      K=J+1
      DO2I=K,N
      IF(ABSF(SL)-ABSF(A(I,J)))3,2,2
    3 SL=A(I,J)
      JR=I
    2 CONTINUE
      IF(SL)15,10,15
   10 WRITE (61,14)
   14 FORMAT(9H DET ZERO)
      WRITE (61,300) A(N,N),J
  300 FORMAT(E14.8,I3)
      STOP
   15 IF(JR-J)7,7,8
    8 DO5L=J,NI
      TEMP=A(J,L)
      A(J,L)=A(JR,L)
    5 A(JR,L)=TEMP
    7 DO6I=K,N
      AM=A(I,J)/A(J,J)
      DO6L=J,NI
    6 A(I,L)=A(I,L)-AM*A(J,L)
      IF(A(N,N))9,10,9
    9 A(N,NI)=A(N,NI)/A(N,N)
      DO30K=2,N
      S=0
      I=N-K+1
      L=I+1
      DO31M=L,N
   31 S=S+A(I,M)*A(M,NI)
   30 A(I,NI)=(A(I,NI)-S)/A(I,I)
      RETURN
      END
```

```
C     1005 ELLERTON - ASSOCIATION OF SOLUTE
      DIMENSION XA(50)
    1 READ,N,WM
      FN=N
      IF(N)15,15,11
   11 PUNCH2
    2 FORMAT(33H ELLERTON - ASSOCIATION OF SOLUTE/)
      READ,R1,R2,R3,R4,R5,R6
      DO4I=1,N
    4 READ,XA(I)
      PUNCH3,WM,R1,R2,R3,R4,R5,R6
    3 FORMAT(F8.3/1XE13.7,1XE13.7,1XE13.7/1XE13.7,1XE13.7,1XE13.7)
      READ,C1,CX,C2,D1,DX,D2
      PUNCH5
    5 FORMAT(/42H    MA       M      OS CAL  OS EXP  OS DIF)
      D=D1
   12 C=C1
   10 PUNCH6,C,D
    6 FORMAT(/4H K1=F10.6,8H     K2=F10.6)
      YT=0.0
      DO7I=1,N
      X=XA(I)+C*XA(I)*XA(I)+C*D*XA(I)**3
      XB=XA(I)+2.0*C*XA(I)*XA(I)+3.0*C*D*XA(I)**3
      YA=(1000.0/(XB*WM))*LOGF(1.0+0.001*WM*X)
      YB=1.0+R1*XB+R2*XB*XB+R3*XB**3+R4*XB**4+R5*XB**5+R6*XB**6
      YD=YA-YB
      YT=YT+ABSF(YD)
    7 PUNCH8,XA(I),XB,YA,YB,YD
    8 FORMAT(2F9.5,3F8.4)
      YT=YT/FN
      PUNCH9,YT
    9 FORMAT(7H AVDEV=F8.4)
      C=C+CX
      IF(C-C2)10,10,17
   17 D=D+DX
      IF(D-D2)12,12,1
   15 PRINT14
   14 FORMAT(18H PROGRAM COMPLETED)
      STOP
      END
```

```
C     ELLERTON - ASSOCIATION AND HYDRATION
      DIMENSIONC1(6),C2(6),CP1(6),CP2(6),ACT(6,6)
      PUNCH3
    3 FORMAT(37H ELLERTON - ASSOCIATION AND HYDRATION/)
   19 READ,N,M
      IF(N)99,99,20
   20 READ,G1,GX,G2,H1,HX,H2
      READ,A1,A2,A3,A4,A5
      READ,B1,B2,B3,B4
      READ,D1,D2,D3,D4,D5,D6
      DO9I=1,N
    9 READ,C1(I)
      DO4I=1,N
      CO1=1.+A1*C1(I)+A2*C1(I)**2+A3*C1(I)**3+A4*C1(I)**4+A5*C1(I)**5
    4 CP1(I)=CO1*C1(I)
      DO10J=1,M
   10 READ,C2(J)
      DO5J=1,M
      CO2=1.+B1*C2(J)+B2*C2(J)**2+B3*C2(J)**3+B4*C2(J)**4
    5 CP2(J)=CO2*C2(J)
      PUNCH11
   11 FORMAT(6H    M17X2HM27X3HDMM6X3HDEL5X4HLN A)
      DO6J=1,M
      DO6I=1,N
      DMM=D1+D2*C1(I)+D3*C2(J)+D4*C1(I)**2+D5*C1(I)*C2(J)+D6*C2(J)**2
      DEL=DMM*C1(I)*C2(J)
      ATL=(DEL+CP1(I)+CP2(J))/(-55.509)
      ACT(I,J)=EXPF(ATL)
    6 PUNCH7,C1(I),C2(J),DMM,DEL,ATL
    7 FORMAT(5F9.5)
```

```
      L=M*N
      FL=L
      PUNCH12
   12 FORMAT(/45H    M1       M2       A EXP    A CAL    A DIF)
      H=H1
   18 G=G1
   16 PUNCH13,G,H
   13 FORMAT(/4H  K=F5.3,7H     H=F5.2)
      DT=0.0
      DO14J=1,M
      DO14I=1,N
      C11=C1(I)/(1.-0.018015*H*C2(J))
      T=SQRTF(1.+(8.*G*C11))
      C1T=(2.*C11)/(1.+T)+G*((2.*C11)/(1.+T))**2
      C22=C2(J)/(1.-0.018015*H*C2(J))
      ACS=55.5093/(55.5093+C1T+C22)
      DF=ACS-ACT(I,J)
      DT=DT+ABSF(DF)
   14 PUNCH7,C1(I),C2(J),ACT(I,J),ACS,DF
      DT=DT/FL
      PUNCH15,DT
   15 FORMAT(9H AV DIF =F9.5)
      G=G+GX
      IF(G-G2)16,16,17
   17 H=H+HX
      IF(H-H2)18,18,19
   99 STOP
      END
```

```
C     1005 UNIVERSITY ADELAIDE ELLERTON DIFFUSION EXPT PT 1
      DIMENSIONR(10),Y(20,10),EZS(20),C(20,10),AV(10)
      PUNCH3
    3 FORMAT(/)
   15 READ5,N
    5 FORMAT(I3)
      IF(N)44,44,10
   10 PUNCH2
    2 FORMAT(39H ELLERTON DIFFUSION EXPERIMENT PART ONE)
      PUNCH3
      PUNCH4
    4 FORMAT(13H      Y VALUES)
      READ6,R(1),R(2),R(3),R(4),R(5)
      READ6,R(6),R(7),R(8),R(9),R(10)
    6 FORMAT(5F8.4)
      DO41J=1,N
   41 READ42,EZS(J)
   42 FORMAT(F8.5)
      DO9J=1,N
      READ11,A,B,E,F,G,H,P,Q,S,T
   11 FORMAT(10F7.4)
      Y(J,1)=A
      Y(J,2)=B
      Y(J,3)=E
      Y(J,4)=F
      Y(J,5)=G
      Y(J,6)=H
      Y(J,7)=P
      Y(J,8)=Q
      Y(J,9)=S
    9 Y(J,10)=T
      DO12J=1,N
      DO13K=1,10
   13 Y(J,K)=R(K)-Y(J,K)
      A=Y(J,1)
      B=Y(J,2)
      E=Y(J,3)
      F=Y(J,4)
      G=Y(J,5)
      H=Y(J,6)
      P=Y(J,7)
      Q=Y(J,8)
      S=Y(J,9)
      T=Y(J,10)
   12 PUNCH11,A,B,E,F,G,H,P,Q,S,T
      PUNCH3
      PUNCH14
   14 FORMAT(14H      CT VALUES)
      DO16J=1,N
      DO8K=1,10
```

```
  8 C(J,K)=Y(J,K)/EZS(J)
    BA=C(J,1)
    BB=C(J,2)
    BC=C(J,3)
    BD=C(J,4)
    BE=C(J,5)
    BF=C(J,6)
    BG=C(J,7)
    BH=C(J,8)
    BP=C(J,9)
    BQ=C(J,10)
 16 PUNCH11,BA,BB,BC,BD,BE,BF,BG,BH,BP,BQ
    PUNCH3
    PUNCH17
 17 FORMAT(22H     AVERAGE CT VALUES)
    DO20K=1,10
    AV(K)=0.0
    DO19J=1,7
 19 AV(K)=AV(K)+C(J,K)
 20 AV(K)=AV(K)/7.0
 18 FORMAT(5F8.4)
    PUNCH18,AV(1),AV(2),AV(3),AV(4),AV(5)
    PUNCH18,AV(6),AV(7),AV(8),AV(9),AV(10)
    PUNCH3
    GOTO15
 44 STOP
    END
```

```
C      1005 UNIVERSITY ADELAIDE ELLERTON DIFFUSION EXPT PT 2
       DIMENSIONY(10),C(10),D(10),TM(10),DA(10),DD(10),X(10)
       DIMENSION TR(10)
       PUNCH3
     3 FORMAT(/)
    15 READ5,N
     5 FORMAT(I3)
       IF(N)44,44,45
    45 READ46,M,Z,CON,FN
    46 FORMAT(I3,F5.1,F9.5,F9.3)
       PUNCH43
    43 FORMAT(39H ELLERTON DIFFUSION EXPERIMENT PART TWO)
       READ7,TM(1),TM(2),TM(3),TM(4),TM(5)
       READ7,TM(6),TM(7),TM(8),TM(9),TM(10)
     7 FORMAT(5F9.1)
       READ18,C(1),C(2),C(3),C(4),C(5)
       READ18,C(6),C(7),C(8),C(9),C(10)
    18 FORMAT(5F8.4)
       PUNCH3
       PUNCH21
    21 FORMAT(13H     D VALUES)
       DO23K=1,10
    23 D(K)=(CON*FN*FN)/(C(K)*C(K)*TM(K))
       PUNCH24,D(1),D(2),D(3),D(4),D(5)
       PUNCH24,D(6),D(7),D(8),D(9),D(10)
    24 FORMAT(5F10.6)
       PUNCH3
       PUNCH25
    25 FORMAT(32H     D          CONST          DELTM)
       SIGA=0.0
       SIGB=0.0
       SIGC=0.0
       SIGD=0.0
       DO26K=1,M
       SIGA=SIGA+D(K)
       SIGB=SIGB+10000.0/TM(K)
       SIGC=SIGC+(10000.0/TM(K))*D(K)
    26 SIGD=SIGD+(10000.0/TM(K))*(10000.0/TM(K))
       AB=(Z*SIGC-SIGB*SIGA)/(Z*SIGD-(SIGB*SIGB))
       AA=(SIGA*SIGD-SIGB*SIGC)/(Z*SIGD-(SIGB*SIGB))
       AC=AB*10000.0/AA
       PUNCH27,AA,AB,AC
    27 FORMAT(F10.6,E14.6,F9.3)
       PUNCH3
       PUNCH28
    28 FORMAT(28H     DA         DD          1/T)
       DEVT=0.0
       DO29K=1,M
       DA(K)=D(K)/(1.0+(10000.0*AB)/(AA*TM(K)))
       DD(K)=AA-DA(K)
       TR(K)=10000.0/TM(K)
```

```
   PUNCH30,DA(K),DD(K),TR(K)
30 FORMAT(2F10.6,F9.5)
29 DEVT=DEVT+ABSF(DD(K))
   PUNCH3
   PUNCH31
31 FORMAT(17H    DEVAV   DEVPC)
   DEVAV=DEVT/Z
   DEVPC=DEVAV*100.0/AA
   PUNCH32,DEVAV,DEVPC
32 FORMAT(F10.6,F7.3)
   PUNCH3
   PUNCH33
33 FORMAT(22H     FRINGE DEVIATIONS)
   DO34J=1,N
   READ42,EZS
42 FORMAT(F8.5)
   READ10,Y(1),Y(2),Y(3),Y(4),Y(5),Y(6),Y(7),Y(8),Y(9),Y(10)
10 FORMAT(10F7.4)
   DO39K=1,10
39 X(K)=(EZS-Y(K)/C(K))*10000.0
   XA=0.0
   DO37K=1,M
37 XA=XA+X(K)
   XA=XA/Z
34 PUNCH35,X(1),X(2),X(3),X(4),X(5),X(6),X(7),X(8),X(9),X(10),XA
35 FORMAT(10F7.1,F9.1)
   PUNCH3
   GOTO15
44 STOP
   END
```

```
C     ELLERTON - 3 COMPONENT DIFFUSION PROGRAMME
      DIMENSIONFJ(6),C1(6),C2(6),D(6),Q(6),DA(6),E(6),Y(6),X(6)
      DIMENSIONA(6),EX(6)
      PUNCH2
    2 FORMAT(33H ELLERTON - 3 COMPONENT DIFFUSION)
   31 READ,N,AD,E2
      IF(N)32,32,33
   33 WL=0.54607E-04
      FN=N
      DO3I=1,N
      READ,FJ(I),C1(I),C2(I),D(I),Q(I)
      DA(I)=1.0/(SQRTF(D(I)))
      E(I)=Q(I)/(SQRTF(D(I)))
      Y(I)=(WL*FJ(I))/(AD*(C1(I)+C2(I)))
    3 X(I)=C1(I)/(C1(I)+C2(I))
      RA=0.0
      RB=0.0
      RC=0.0
      RD=0.0
      DO9I=1,N
      RA=RA+Y(I)
      RB=RB+X(I)
      RC=RC+Y(I)*X(I)
    9 RD=RD+X(I)*X(I)
      R2=(RA*RD-RB*RC)/(FN*RD-(RB*RB))
      R1=R2+(FN*RC-RB*RA)/(FN*RD-(RB*RB))
      PUNCH10
   10 FORMAT(/21H     R1            R2)
      PUNCH11,R1,R2
   11 FORMAT(1XE13.7,1XE13.7)
      PUNCH12
   12 FORMAT(/48H   DC1      DC2      J OBS    J CAL    J DIF     A1)
      DO13I=1,N
      FK=(AD*(C1(I)+C2(I)))*(X(I)*(R1-R2)+R2)/WL
      A(I)=R1*C1(I)/(R1*C1(I)+R2*C2(I))
      FJJ=FK-FJ(I)
   13 PUNCH14,C1(I),C2(I),FJ(I),FK,FJJ,A(I)
   14 FORMAT(2F9.6,2F8.3,F7.3,F9.5)
      PUNCH4
    4 FORMAT(/15H     I        S)
      SA=0.0
      SB=0.0
      SC=0.0
      SD=0.0
      DO5I=1,N
      SA=SA+DA(I)
      SB=SB+A(I)
      SC=SC+DA(I)*A(I)
    5 SD=SD+A(I)*A(I)
      AA=(SA*SD-SB*SC)/(FN*SD-(SB*SB))
```

```
      AB=(FN*SC-SB*SA)/(FN*SD-(SB*SB))
      U=AB/AA
      PUNCH15,AA,AB
   15 FORMAT(2F10.4)
      PUNCH16
   16 FORMAT(/46H    A1      D OBS          D CAL         D DIF)
      DO6I=1,N
      DB=AA+AB*A(I)
      DC=1.0/(DB*DB)
      DD=DC-D(I)
    6 PUNCH7,A(I),D(I),DC,DD
    7 FORMAT(F9.5,2XE12.6,2XE12.6,2XE10.4)
      DX=0.1E-10
      DD11=0.0
   19 TA=0.0
      TB=0.0
      TC=0.0
      TD=0.0
      DO8I=1,N
      EX(I)=E(I)/E2+A(I)*A(I)
      TA=TA+EX(I)
      TB=TB+A(I)
      TC=TC+EX(I)*A(I)
    8 TD=TD+A(I)*A(I)
      BA=(TA*TD-TB*TC)/(FN*TD-(TB*TB))
      BB=(FN*TC-TB*TA)/(FN*TD-(TB*TB))
      V=-BA*U
      W=BB*U
      W1=(1.0+W+U*V)**2
      W2=W1*AA*AA
      D11=(1.0+V*(2.0-U+W))/W2
      D12=(V*(2.0+W)*R2)/(W2*R1)
      D21=((W-U-V)*(2.0+W)*R1)/(W2*R2)
      D22=((1.0+W)**2-V*(2.0+U+W))/W2
      IF(DD11)17,18,17
   17 DF11=D11-DD11
      DF12=D12-DD12
      DF21=D21-DD21
      DF22=D22-DD22
      DS=ABSF(DF11+DF12+DF21+DF22)
      IF(DS-DX)20,18,18
   18 TE=SQRTF((D22-D11)**2+4.0*D12*D21)
      SIG1=((D22+D11)+TE)/(2.0*(D11*D22-D12*D21))
      SIG2=((D22+D11)-TE)/(2.0*(D11*D22-D12*D21))
      PA=SQRTF(SIG2/SIG1)
      DD11=D11
      DD12=D12
      DD21=D21
      DD22=D22
      CN=2.0
```

```
   CN=SQRTF(CN)
   PC=1.0+PA-((2.0*CN*PA)/(SQRTF(1.0+PA*PA)))
   PD=2.0*CN*(1.0-PA)*(1.0-PA)
   PB=PC/PD
   E2=((PC/PD)*AB*AB)/(SQRTF(SIG1))
   GOTO19
20 PUNCH21
21 FORMAT(/49H   D11          D12          D21          D22)
   PUNCH22,D11,D12,D21,D22
22 FORMAT(2XE12.6,2XE12.6,2XE12.6,2XE12.6)
   PUNCH23
23 FORMAT(/48H   SIG+         SIG-         PS           PL)
   PUNCH22,SIG1,SIG2,PA,PB
   PUNCH24
24 FORMAT(/36H    E0             E1             E2)
   E0=BA*E2
   E1=BB*E2
   PUNCH25,E0,E1,E2
25 FORMAT(2XE13.7,2XE13.7,2XE13.7)
   PUNCH1
 1 FORMAT( )
   DO27I=1,N
   QA=(SQRTF(D(I))*(E0+E1*A(I)-E2*A(I)*A(I))*10.0**4)
   Q(I)=(Q(I)*10.0**4)
   QD=QA-Q(I)
27 PUNCH28,Q(I),QA,QD
28 FORMAT(3F10.4)
   PUNCH1
   PUNCH30,DX,DS
30 FORMAT(2XE11.5,2XE11.5/)
   GOTO31
32 STOP
   END
```

```
C     ELLERTON-FRIC. COEFFS. AND TEST OF O.R.R.
    4 READ,R,T,CN1,CN2
      IF(R)5,6,5
    5 READ,W0,W1,W2
      READ,C1,C2,DE,H1,H2
      AB=DE-H1*C1-H2*C2
      V1=(W1-1000.*H1)/AB
      V2=(W2-1000.*H2)/AB
      C0=(1000.*DE-W1*C1-W2*C2)/W0
      V0=(1000.-C1*V1-C2*V2)/C0
      PUNCH7
    7 FORMAT(/32H      C0          C1          C2)
      PUNCH8,C0,C1,C2
    8 FORMAT(3F12.6)
      PUNCH9
    9 FORMAT(/32H      V0          V1          V2)
      PUNCH8,V0,V1,V2
      READ,D11,D12,D21,D22
      DA11=D11+(C1/(C0*V0))*(V1*D11+V2*D21)
      DA12=D12+(C1/(C0*V0))*(V1*D12+V2*D22)
      DA21=D21+(C2/(C0*V0))*(V1*D11+V2*D21)
      DA22=D22+(C2/(C0*V0))*(V2*D12+V2*D22)
      PUNCH10
   10 FORMAT(/50H     D11           D12           D21           D22)
      PUNCH11,D11,D12,D21,D22
   11 FORMAT(/1XE14.8,1XE14.8,1XE14.8,1XE14.8)
      PUNCH12
   12 FORMAT(/50H    DA11          DA12          DA21          DA22)
      PUNCH11,DA11,DA12,DA21,DA22
      TH=(1000.*DE-C1*W1-C2*W2)/1000.
      CA1=C1/TH
      CA2=C2/TH
      READ,FA1,FA2,FA3,FA4,FA5
      READ,FB1,FB2,FB3,FB4,FB5
      READ,F00,F10,F01,F20,F11,F02,F30,F21,F12,F03
```

```
      G11=FA1+2.*FA2*CA1+3.*FA3*CA1*CA1+4.*FA4*CA1*CA1*CA1+F10*CA2
      G11=G11+2.*F20*CA1*CA2+2.*F11*CA2*CA2/3.+3.*F30*CA1*CA1*CA2
      G11=G11+3.*F21*CA1*CA2*CA2/2.+F12*CA2*CA2*CA2/2.
      G11=G11+5.*FA5*CA1*CA1*CA1*CA1
      G22=FB1+2.*FB2*CA1+3.*FB3*CA1*CA1+4.*FB4*CA1*CA1*CA1+F01*CA1
      G22=G22+2.*F11*CA1*CA1/3.+2.*F02*CA1*CA2+F21*CA1*CA1*CA1/2.
      G22=G22+3.*F12*CA1*CA1*CA2/2.+3.*F03*CA1*CA2*CA2
      G22=G22+5.*FB5*CA2*CA2*CA2*CA2
      G12=F00+F10*CA1+F01*CA2+F20*CA1*CA1+4.*F11*CA1*CA2/3.+F02*CA2*CA2
      G12=G12+F30*CA1*CA1*CA1+1.5*F21*CA1*CA1*CA2+1.5*F12*CA1*CA2*CA2
      G12=G12+F03*CA2 *CA2*CA2
      G21=CN1*G12/CN2
      PUNCH13
   13 FORMAT(/20H      M1          M2)
      PUNCH8,CA1,CA2
      PUNCH14
   14 FORMAT(/50H     G11           G12           G21           G22)
      PUNCH11,G11,G12,G21,G22
      A11=R*T*CN1*((1.0/CA1)+G11)
      A12=R*T*CN1*G12
      A21=R*T*CN2*G21
      A22=R*T*CN2*((1.0/CA2)+G22)
      E1=(CA1/C1)
      E2=(CA2/C2)
      B11=E1*(1.0+(C1*V1)/(C0*V0))
      B12=E1*(C1*V2)/(C0*V0)
      B21=E2*(C2*V1)/(C0*V0)
      B22=E2*(1.0+(C2*V2)/(C0*V0))
      U11=A11*B11+A12*B21
      U12=A11*B12+A12*B22
      U21=A21*B11+A22*B21
      U22=A21*B12+A22*B22
      PUNCH11,A11,A12,A21,A22
      PUNCH11,B11,B12,B21,B22
      PUNCH11,U11,U12,U21,U22
      TT=U11*U22-U12*U21
```

```
      PW11=(DA11*U22-DA12*U21)/TT
      PW12=(DA12*U11-DA11*U12)/TT
      PW21=(DA21*U22-DA22*U21)/TT
      PW22=(DA22*U11-DA21*U12)/TT
      PUNCH18
   18 FORMAT(/50H    LA11          LA12          LA21          LA22)
      PUNCH11,PW11,PW12,PW21,PW22
      AL11=(1.+((C1*V1)/(C0*V0)))
      AL12=(C2*V1)/(C0*V0)
      AL21=(C1*V2)/(C0*V0)
      AL22=(1.+((C2*V2)/(C0*V0)))
      AU11=AL11*U11+AL12*U21
      AU12=AL21*U11+AL22*U21
      AU21=AL11*U12+AL12*U22
      AU22=AL21*U12+AL22*U22
      T2=AU11*AU22-AU12*AU21
      PUNCH11,AU11,AU12,AU21,AU22
      PV11=(AU22*D11-AU12*D12)/T2
      PV12=(AU11*D12-AU21*D11)/T2
      PV21=(AU22*D21-AU12*D22)/T2
      PV22=(AU11*D22-AU21*D21)/T2
      PUNCH20
   20 FORMAT(/50H     L11           L12           L21           L22)
      PUNCH11,PV11,PV12,PV21,PV22
      AA11=(D12*U21-D11*U22)/TT
      AA12=(D11*U12-D12*U11)/TT
      AA21=(D22*U21-D21*U22)/TT
      AA22=(D21*U12-D22*U11)/TT
      Q=AA11*AA22-AA12*AA21
      P11=-(AA22/Q)
      P12=(AA12/Q)
      P21=(AA21/Q)
      P22=-(AA11/Q)
      R10=V0*(C1*P11+C2*P12)
      R12=(C1*V2*P11-(C0*V0+C1*V1)*P12)
```

```
      R21=(C2*V1*P22-(C0*V0+C2*V2)*P21)
      R20=V0*(C1*P21+C2*P22)
      PUNCH21
   21 FORMAT(50H     R10           R12           R21           R20)
      PUNCH11,R10,R12,R21,R20
      GOTO4
    6 STOP
      END
```

APPENDIX B.

PUBLICATIONS.

1. "Activity, Density and Relative Viscosity Data for Several Amino Acids, Lactamide, and Raffinose in Aqueous Solution at 25°".

2. "The Mutual Frictional Coefficients of Several Amino Acids in Aqueous Solution at 25°".

   by H. David Ellerton, Gundega Reinfelds, Dennis E. Mulcahy and Peter J. Dunlop,
   J. Phys. Chem., 68, 398 and 403 (1964).

Although a portion of the work presented in these papers has been reported previously, (H. D. Ellerton, Honours Report, 1961), the work was extended and completed whilst this author was a candidate for the degree of Doctor of Philosophy.

Ellerton, H. D., Reinfelds, G., Mulcahy, D. E. & Dunlop, P. J. (1964). Activity, density, and relative viscosity data for several amino acids, lactamide, and raffinose in aqueous solution at 25°. *Journal of Physical Chemistry, 68*(2), 398-402.

NOTE:
This publication is included in the print copy
of the thesis held in the University of Adelaide Library.

It is also available online to authorised users at:
https://doi.org/10.1021/j100784a034

Ellerton, H. D., Reinfelds, G., Mulcahy, D. E. & Dunlop, P. J. (1964). The mutual frictional coefficients of several amino acids in aqueous solution at 25°. *Journal of Physical Chemistry, 68*(2), 403-408.

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