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Isothermal Diffusion Measurements on the System H_2O–Glycine–KCl at 25°; Tests of the Onsager Reciprocal Relation[1]

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Diffusion coefficients, partial molal volumes and refractive index derivatives are reported for six compositions of this ternary system; some new data are presented for diffusion coefficients and refractive index derivatives of the systems H_2O–glycine and H_2O–KCl. The Onsager reciprocal relation connecting the four diffusion coefficients at each composition of the ternary system is tested by using data from the diffusion experiments reported in this paper and existing activity coefficient data for the systems H_2O–glycine, H_2O–KCl and H_2O–glycine–KCl; the relation is satisfied within the estimated experimental error. Equations connecting Onsager phenomenological coefficients for the solvent- and volume-fixed frames of reference are derived and discussed.

Introduction

Previous tests[3–7] of the Onsager reciprocal relation[8,9] (ORR) for ternary isothermal diffusion have, except for one case, been subject to the limitation that experimental data for the diffusion coefficients and activity coefficients had not been determined in the same range of composition. Only for the system H_2O–NaCl–KCl with both solutes 1.5 molar[6,7] were all the necessary data available at the same composition. For that case (perhaps because measured values of the diffusion coefficients may be less accurate with solute concentrations that high) the confirmation of the ORR was not quite as good as in some of the other tests at lower concentrations. For the other tests activity coefficients were available only in concentration ranges different from those required or they had never been determined; therefore various procedures were used to approximate the activity coefficients in the range of concentration where diffusion had been studied. The best approximations for activity coefficients could be made for systems in which both solutes were electrolytes, and these systems gave the best confirmation of the ORR. For the other two classes of ternary systems investigated, namely, those containing as solutes either one electrolyte and one non-electrolyte or two non-electrolytes, the activity coefficient approximations were rather more uncertain. Therefore it seems desirable to make additional tests of the ORR by measuring diffusion in systems, from these two classes, for which activity coefficients have been determined. For the present study we chose the system H_2O–glycine–KCl (components 0, 1 and 2, respectively) because activity coefficients have been determined in a suitable concentration range[10] and because these solid solutes are easily handled in preparing solutions of accurately known concentrations. More-

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(3) D. G. Miller, *J. Phys. Chem.*, **62**, 767 (1958); see also corrections, *ibid.*, **63**, 2089 (1959).

(4) P. J. Dunlop and L. J. Gosting, *ibid.*, **63**, 86 (1959).

(5) D. G. Miller, *ibid.*, **63**, 570 (1959).

(6) P. J. Dunlop, *ibid.*, **63**, 612 (1959); see also corrections, *ibid.*, **63**, 2089 (1959).

(7) H. Fujita and L. J. Gosting, *ibid.*, **64**, 1256 (1960).

(8) L. Onsager, *Phys. Rev.*, **37**, 405 (1931); **38**, 2265 (1931); L. Onsager and R. M. Fuoss, *J. Phys. Chem.*, **36**, 2689 (1932), especially pp. 2759–2761.

(9) S. R. de Groot, "Thermodynamics of Irreversible Processes," Interscience Publishers, Inc., New York, N. Y., 1951.

(10) R. M. Roberts and J. G. Kirkwood, *J. Am. Chem. Soc.*, **63**, 1373 (1941).

over we wished to learn whether there is sufficient interaction between the ions and the dipolar glycine to give large values of the cross-term diffusion coefficients. Although it was found that the cross-term coefficients are not unusually large in the concentration range studied, some features of their magnitude and concentration dependence are of interest as will be seen later in this paper.

Theory and Definitions

Previous tests of the Onsager Reciprocal Relation for isothermal ternary diffusion differed in that they used two different sets of phenomenological coefficients L_{ij}, which are the coefficients of forces in the linear laws expressing flows in terms of forces. One set[4,6,7] was based on the solvent-fixed frame of reference and the other[3,5] was based on the volume-fixed frame.[11] The values of the coefficients in these two sets may differ considerably at higher concentrations; in this section we derive equations for computing one set from the other. This derivation helps emphasize the importance, which is often overlooked, of specifying the frame of reference. Some other equations and definitions required subsequently in this paper will also be presented.

The Thermodynamic Description and Frames of Reference.—Here we consider isothermal diffusion in a system of $q + 1$ non-reacting components $(0, 1, \ldots, q$, where 0 denotes the solvent) and begin with the following equation for the entropy production[9]

$$T\sigma = \sum_{i=0}^{q} J_i X_i \qquad (1)$$

Here T is the absolute temperature, σ is the local entropy production per unit volume per sec., J_i is the flow[14] of component i in mole/(cm.^{2} sec.) and X_i is the corresponding thermodynamic force. Throughout this paper we consider only one-dimensional diffusion along a coördinate x, with the gravitational field negligible. Then

$$X_i = -\partial\mu_{iTP}/\partial x \qquad (2)$$

where μ_{iTP} is the chemical potential of component i per mole at constant T and pressure P.

It is customary to use the flows and forces appearing in a suitable form of the equation for entropy production as the forces and flows in the linear laws (such as equations 11 and 12) which define the phenomenological coefficients, L_{ij}.

To *insure* that these linear laws will be valid and that the L_{ij} will be subject to the ORR, the entropy production equation should first be arranged so that all flows and all forces in it are independent.[9,16,17] Because the forces in equation 1 are related by the Gibbs–Duhem equation

$$\sum_{i=0}^{q} c_i X_i = 0 \qquad (3)$$

where c_i is the concentration of component i in moles per liter, we may use this relation to eliminate X_0 from equation 1. This yields

$$T\sigma = \sum_{i=1}^{q} [J_i - (c_i/c_0)J_0]X_i \qquad (4)$$

in which all the X_i are now independent and the flows J_i may still be referred to an arbitrary frame of reference.[19]

The linear relation[9,12,18] among the J_i (for a reference frame of class S, which is suitable for writing each J_i as a simple linear function of the forces)[17] may be used to eliminate J_0 from equation 4 so that the remaining J_i will be independent. Here we consider only the solvent-fixed and volume-fixed[20] frames of reference which may be defined, respectively, by

$$(J_0)_0 = 0 \qquad (5)$$

$$\sum_{i=0}^{q} \bar{V}_i(J_i)_V = 0 \qquad (6)$$

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(11) Actually in ref. 3 and 5 a cell- or apparatus-fixed reference frame was employed, although this was not stated explicitly there. However, the cell-fixed and volume-fixed frames coincide if there is no volume flow (see footnote 20, and equation 7 of ref. 5), *i.e.*, if the partial molal volumes are independent of concentration[12] or if the concentration differences within the diffusion cell are sufficiently small.[13] Since the experiments used to test the ORR should meet the latter condition, the equations from 7 on in ref. 5 which depend on choice of a reference frame should refer equally to volume-fixed and cell-fixed reference frames. However, if a volume flow exists these equations in ref. 5 would be valid only for the volume-fixed frame.

(12) G. J. Hooyman, H. Holtan, Jr., P. Mazur and S. R. de Groot, *Physica*, **19**, 1095 (1953).

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

(14) Because the system is at constant temperature and at mechanical equilibrium, equation 1 is valid regardless of the frame of reference chosen for the J_i.[9,15]

(15) I. Prigogine, "Etude Thermodynamique des Phénomènes Irréversibles," (Thesis, Brussels) Editions Desoer, Liège, 1947.

(16) G. J. Hooyman and S. R. de Groot, *Physica*, **21**, 73 (1955).

(17) Valid linear laws for the J_i may be written if the frame of reference for these flows is a member of the class for which the J_i for all components are linearly related[9,16,18]; this class of reference frames, which we denote by S in this paper, includes the volume-fixed frame, the solvent-fixed frame, the mass-fixed frame, etc. It is possible to write valid linear laws without the L_{ij} necessarily being subject to the ORR[16]: *e.g.*, ORR do not necessarily exist if the J_i for each component relative to the volume-fixed frame is written in terms of every X_i. Reference frames which are not members of class S may not be suitable for writing the usual linear laws. For example, equation 1 is valid if a frame of reference fixed on the diffusion cell is chosen for the flows $(J_i)_C$, where the subscript C denotes the cell-fixed frame. In general, however, the expressions

$$(J_i)_C = -\sum_{j=0}^{q} (L_{ij})_C(\partial\mu_{jTP}/\partial x) \quad (i = 0, 1, \ldots, q)$$

are not valid linear laws unless another term is added to each to describe any bulk flow. This may be seen by considering a homogeneous region in the liquid where all chemical potential gradients are zero and by supposing that the fluid in the cell is being moved by a piston, a process for which $T\sigma = 0$. Because the $(J_i)_C$ are not zero, but all $\partial\mu_{jTP}/\partial x = 0$, it is evident that the above expressions do not correctly describe $(J_i)_C$.

(18) G. J. Hooyman, *Physica*, **22**, 751 (1956).

(19) Note that the conjugate flow for force X_i in equation 4 is *not* J_i but is the composite flow $\bar{J}_i = [J_i - (c_i/c_0)J_0]$; therefore the linear laws corresponding to this entropy production equation are written

$$\bar{J}_i = \sum_{j=1}^{q} \bar{L}_{ij}X_j$$

By using equation 5 and the relation between flows of a component for two frames of reference (equation 1 of ref. 13) it may be shown that $\bar{J}_i = (J_i)_0$.

(20) The velocity of a volume-fixed frame of reference relative to the cell may be written $u_{VC} = r\sum_{i=0}^{q}\bar{V}_i(J_i)_C$, where subscript C denotes the cell- or apparatus-fixed frame of reference, $\bar{V}_i$ is the partial molal volume of component i in ml./mole, and $r = 1.000027$ is the number of cc. in a ml. Because the condition of no volume flow relative to the cell is $u_{VC} = 0$, it is evident from the relation $(J_i)_C = (J_i)_V + (c_i/1000\,r)u_{VC}$ that under this condition $(J_i)_C = (J_i)_V$.

in which $\bar{V}_i$ is the partial molal volume of component i in ml./mole, and the subscripts 0 and V outside the parentheses indicate the reference frame. If equations 5 and 6 are substituted into equation 4 one obtains, respectively

$$T\sigma = \sum_{i=1}^{q} (J_i)_0 X_i \qquad (7)$$

$$T\sigma = \sum_{i=1}^{q} (J_i)_V Y_i \qquad (8)$$

where[21]

$$Y_i = \sum_{j=1}^{q} \alpha_{ij} X_j \qquad (9)$$

$$\alpha_{ij} = \delta_{ij} + [(c_j \bar{V}_i)/(c_0 \bar{V}_0)] \qquad (10)$$

δ_{ij} being the Kronecker delta.

Relations Connecting the Solvent- and Volume-Fixed Phenomenological Coefficients $(L_{ij})_0$ and $(L_{ij})_V$.—Because the flows and forces in equations 7 and 8 are in the proper independent form, the linear laws may be written

$$(J_i)_0 = \sum_{j=1}^{q} (L_{ij})_0 X_j \quad (i = 1, \ldots, q) \qquad (11)$$

$$(J_i)_V = \sum_{j=1}^{q} (L_{ij})_V Y_j \quad (i = 1, \ldots, q) \qquad (12)$$

and for these different descriptions of isothermal diffusion the ORR (for the non-trivial cases $i \neq j$) have the forms,[22] respectively

$$(L_{ij})_0 = (L_{ji})_0 \qquad (13)$$

$$(L_{ij})_V = (L_{ji})_V \qquad (14)$$

Either description is equally valid (as are many others based on other frames of reference) but in general $(L_{ij})_0 \neq (L_{ij})_V$ (see Table VIII); they become the same only as all solute concentrations approach zero.

The $(L_{ij})_0$ and $(L_{ij})_V$ may now be related as follows: by substituting equations 11 and 12 into 7 and 8, respectively, and by using equation 9, one gets after trivial subscript changes

$$T\sigma = \sum_{i=1}^{q} \sum_{j=1}^{q} (L_{ij})_0 X_i X_j \qquad (15)$$

$$T\sigma = \sum_{k=1}^{q} \sum_{l=1}^{q} (L_{kl})_V Y_k Y_l = \sum_{i=1}^{q} \sum_{j=1}^{q} \sum_{k=1}^{q} \sum_{l=1}^{q} \alpha_{ki}\alpha_{lj}(L_{kl})_V X_i X_j \qquad (16)$$

Because the X_i are independent, the coefficients of $X_i X_j$ in equations 15 and 16 can be identified term by term, giving the desired relation[23]

$$(L_{ij})_0 = \sum_{k=1}^{q} \sum_{l=1}^{q} \alpha_{ki}\alpha_{lj}(L_{kl})_V \qquad (17)$$

The inverse relation is obtained if equation 17 is multiplied by $\epsilon_{im}\epsilon_{jn}$, summed over $i = 1$ to q and $j = 1$ to q, and then the relation

$$\sum_{i=1}^{q} \alpha_{ki}\epsilon_{im} = \sum_{i=1}^{q} \alpha_{ik}\epsilon_{mi} = \delta_{km} \qquad (18)$$

is applied (equation 18 is a consequence of equation 47 written for $q + 1$ components); this gives

$$(L_{ij})_V = \sum_{k=1}^{q} \sum_{l=1}^{q} \epsilon_{ki}\epsilon_{lj}(L_{kl})_0 \qquad (19)$$

where

$$\epsilon_{ki} = \delta_{ki} - (c_i \bar{V}_k/1000) \qquad (19a)$$

Fick's First Law and the $(L_{ij})_V$.—The diffusion coefficients $(D_{ij})_V$ reported in this paper are those defined by the following generalization[18,24] of Fick's first law

$$(J_i)_V = -\sum_{j=1}^{q} (D_{ij})_V \frac{\partial n_j}{\partial x} \quad (i = 1, \ldots, q) \qquad (20)$$

Here n_j is the concentration of component j in mole/cc. and the $(D_{ij})_V$ are diffusion coefficients in cm.^{2}/sec. corresponding to the volume-fixed frame of reference. Diffusion coefficients $(D_{ij})_0$ for the solvent-fixed reference frame are defined by[18]

$$(J_i)_0 = -\sum_{j=1}^{q} (D_{ij})_0 \frac{\partial n_j}{\partial x} \quad (i = 1, \ldots, q) \qquad (21)$$

where[4,13,18]

$$(D_{ij})_0 = \sum_{k=1}^{q} \alpha_{ki}(D_{kj})_V \qquad (22)$$

When calculating the coefficients $(L_{ij})_V$ in a later section it is convenient to express concentrations as molarities in derivatives of chemical potentials with respect to concentrations; to simplify some equations we define diffusion coefficients corresponding to molarity gradients by

$$(J_i)_V = -\sum_{j=1}^{q} (\hat{D}_{ij})_V \frac{\partial c_j}{\partial x} \quad (i = 1, \ldots, q) \qquad (23)$$

Here $(\hat{D}_{ij})_V$ has the units l./(cm. sec.) and c_j is in moles/l. By using the conversion factor between l. and cc., it is seen that

$$(\hat{D}_{ij})_V = (D_{ij})_V/1000.027 \qquad (24)$$

To express the $(L_{ij})_V$ in terms of the $(\hat{D}_{ij})_V$ equation 12 is rewritten in terms of molarity gradients[25]

$$(J_i)_V = -\sum_{j=1}^{q} \sum_{l=1}^{q} a_{jl}(L_{il})_V \frac{\partial c_j}{\partial x} \qquad (25)$$

$$a_{jl} = \sum_{k=1}^{q} \alpha_{lk}\mu_{kj} \qquad (26)$$

$$\mu_{kj} = (\partial \mu_k/\partial c_j)_{c_{l \neq 0,j}} \qquad (27)$$

Comparison of equations 23 and 25 term by term and solution of the resulting equations gives each $(L_{ij})_V$ in terms of the $(\hat{D}_{ij})_V$. For ternary systems

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[21] The α_{11}, α_{12}, α_{21} and α_{22} are the α, β, γ and δ of ref. 5.

[22] We emphasize that for the volume-fixed reference frame the existence of ORR (equation 14) between the phenomenological coefficients depends on the proper choice of the forces Y_j (ref. 5). If the volume-fixed flows $(J_i)_V$ had been written in terms of the forces X_j ($j = 1, \ldots, q$), there would be no corresponding ORR.

[23] Compare with G. J. Hooyman, S. R. de Groot and P. Mazur, *Physica*, **21**, 360 (1955). Their relations, which are in matrix notation, were not specialized to particular cases.

[24] R. L. Baldwin, P. J. Dunlop and L. J. Gosting, *J. Am. Chem. Soc.*, **77**, 5235 (1955).

[25] The details of this derivation are given in ref. 5. It should be noted that equation 5 and hence equations 13, 14, 15 and the L_{ij} in Table III of that paper have the wrong sign. However, no change of absolute numerical values or conclusions there is involved.

($q = 2$) one obtains[26]

$$\begin{aligned} (L_{11})_V &= [a_{22}(\hat{D}_{11})_V - a_{12}(\hat{D}_{12})_V]/A \\ (L_{12})_V &= [a_{11}(\hat{D}_{12})_V - a_{21}(\hat{D}_{11})_V]/A \\ (L_{21})_V &= [a_{22}(\hat{D}_{21})_V - a_{12}(\hat{D}_{22})_V]/A \\ (L_{22})_V &= [a_{11}(\hat{D}_{22})_V - a_{21}(\hat{D}_{21})_V]/A \end{aligned} \quad (28)$$

where

$$A = a_{11}a_{22} - a_{12}a_{21} \quad (28a)$$

The necessary and sufficient condition[3,5] for the validity of the ORR is seen to be

$$a_{11}(\hat{D}_{12})_V + a_{12}(\hat{D}_{22})_V = a_{21}(\hat{D}_{11})_V + a_{22}(\hat{D}_{21})_V \quad (29)$$

when

$$A \neq 0 \quad (29a)$$

Experimental

Materials.—Pfanstiehl C. P. glycine and Merck reagent grade KCl were each recrystallized once from doubly-distilled water by dissolving at 90–95°, filtering and cooling finally to about −5° after removing some of the crystals at a higher temperature. All crystals were centrifugally drained before drying. The glycine crystals were dried *in vacuo* at 85° to constant weight (about 16 hr.). The recrystallized KCl was vacuum dried at room temperature for 10 hr. and then fused in platinum dishes in air.

Molecular Weights.—Throughout this paper we use 18.0160, 75.070 and 74.557 as the molecular weights M_i of H_2O, glycine and KCl, respectively.

Solutions.—All solutions for studies of diffusion were prepared with doubly-distilled water which had been saturated with air. To prepare each solution with predetermined molarities c_i, a preliminary value for the density d of that solution was computed by using the formula[27]

$$d = d_0 + \sum_{i=1}^{2} (c_i/1000)(M_i - d_0\phi_i) \quad (30)$$

The density d_0 of pure water at 25° was taken as 0.997075 g./ml., and for the apparent molal volumes ϕ_i we used the following expressions for binary systems: for H_2O–glycine[28]

$$\phi_1 = 43.199 + 0.8614c_1 \quad (31)$$

and for H_2O–KCl[29]

$$\phi_2 = 26.742 + 2.000\sqrt{c_2} + 0.1110c_2 \quad (32)$$

This procedure is rigorous for binary systems (either $c_1 = 0$ or $c_2 = 0$) but is only approximate for ternary systems. Therefore the density of a solution was measured in which both glycine and KCl were about 0.5 molar; the difference between this density and that predicted by equations 30–32 was used to evaluate the coefficient, $k = 21 \times 10^{-4}$, of a correction term kc_1c_2 which then was subtracted from equation 30. Subsequent measurements of densities of the solutions used in the diffusion experiments showed that the equation obtained by substituting equations 31 and 32 into equation 30 and subtracting $21 \times 10^{-4}\, c_1c_2$ predicts densities of this ternary system within a few parts in 100,000 in the concentration range studied.

Densities estimated in this way were used to calculate the relative weights of the components required to give solutions of the desired composition for each diffusion experiment. All solutions were prepared by weight, and after correcting the weights in air to those in vacuum[30] the molarities were obtained by using densities calculated from equations 30–32 for the binary solutions and measured densities for the ternary solutions.

Density Measurements.—The density of each ternary solution was measured (usually in triplicate and always by weighing against a sealed tare) at 25 ± 0.005° with Pyrex pycnometers which had been calibrated with air-saturated, doubly-distilled water for which the density was taken to be 0.997075 g./ml. Three matched 30 ml. single-neck pycnometers, filled to measured positions in their capillary necks, were used for solutions prepared for the experiments of sets S-1, S-3 and S-6 of Table III. Densities of the solutions for sets S-2, S-4 and S-5 were measured with three matched 40 ml. Pyrex pycnometers of the Ostwald–Sprengel type[31] having two fine capillary arms; the volume of each pycnometer was determined by the tip of one capillary arm and a scribed mark on the other.

***p*H Measurements.**—The *p*H of every solution used in the three-component diffusion experiments was measured at room temperature with a Beckman Model G *p*H meter, which had been standardized with a *p*H 7.00 buffer. All *p*H readings lay in the range 5.98 (solution A of experiment 32) to 6.21 (solutions B of experiments 24 and 25). From values[32] of the dissociation constants for the acidic and basic groups of glycine and the constant for equilibrium between the dipolar ion and the uncharged molecule, it is estimated that in this range of *p*H about 99.95% of the glycine is in the dipolar form.

Apparatus and General Experimental Procedure.—For all experiments reported here free diffusion was studied by using Gouy interference fringes. A general description of this optical method and some references to its development are available elsewhere.[33] The Gouy diffusiometer used has been described in previous publications.[34–36] The three fused quartz diffusion cells which were used had the optical constants listed in Table I.

TABLE I

OPTICAL CONSTANTS OF THE DIFFUSION APPARATUS[a]

Cell	*a*, cm.	*b*, cm.
SD	2.5063	306.84
SE	2.5079	306.90
SF	2.5074	307.06

[a] As in previous publications *b* is the optical lever arm from the center of the cell to the emulsion of the photographic plate (referred to a refractive index of unity for air); *a* denotes the thickness of the cell along the optical path.

In each experiment the sharp initial boundary between the less dense upper solution (denoted by A) and the more dense lower solution (denoted by B) was formed in the diffusion cell by sharpening[37,38] with a single-prong stainless steel capillary. For solute *i* the concentration difference across this initial boundary is

$$\Delta c_i = (c_i)_B - (c_i)_A \quad (i = 1,2) \quad (33)$$

and the mean concentration is

$$c_i = [(c_i)_B + (c_i)_A]/2 \quad (i = 1,2) \quad (34)$$

During free diffusion between solutions A and B, 6 to 10 photographs of the Gouy fringes were taken on Tri-X Panchromatic plates at various times t' after sharpening was stopped. From measurements[29,34,39] on each photograph of the displacements of intensity minima below the position of the undeviated slit image, a value of C_t (the maximum displacement of light at that time according to ray optics) was obtained by the usual extrapolation procedure.[7,40,41]

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[26] The a_{11}, a_{12}, a_{21}, a_{22} are the *a*, *b*, *c*, *d* of ref. 5, respectively.

[27] Equation 30 is readily derived from the relation $1000 = (c_0M_0/d_0) + c_1\phi_1 + c_2\phi_2$ and equation 46.

[28] F. T. Gucker, Jr., W. L. Ford and C. E. Moser, *J. Phys. Chem.*, **43**, 153 (1939).

[29] L. J. Gosting, *J. Am. Chem. Soc.*, **72**, 4418 (1950).

[30] Densities of 1.607 g./ml. for glycine, 1.984 g./ml. for KCl and 0.997075 g./ml. for H_2O were used in these computations.

[31] F. Daniels, J. H. Mathews, J. W. Williams, P. Bender and R. A. Alberty, "Experimental Physical Chemistry," 5th Ed., McGraw-Hill Book Co., Inc., New York, N. Y., 1956, p. 89.

[32] J. T. Edsall and M. H. Blanchard, *J. Am. Chem. Soc.*, **55**, 2337 (1933).

[33] L. J. Gosting, in "Advances in Protein Chemistry," M. L. Anson, K. Bailey and J. T. Edsall, eds., Vol. XI, Academic Press, Inc., New York, N. Y., 1956, pp. 476 ff.

[34] L. J. Gosting, E. M. Hanson, G. Kegeles and M. S. Morris, *Rev. Sci. Instr.*, **20**, 209 (1949).

[35] P. J. Dunlop and L. J. Gosting, *J. Am. Chem. Soc.*, **75**, 5073 (1953).

[36] P. J. Dunlop and L. J. Gosting, *ibid.*, **77**, 5238 (1955).

[37] D. S. Kahn and A. Polson, *J. Phys. and Colloid Chem.*, **51**, 816 (1947).

[38] See ref. 33, Fig. 9.

[39] D. F. Akeley and L. J. Gosting, *J. Am. Chem. Soc.*, **75**, 5685 (1953).

[40] Equation 31 of ref. 39.

[41] L. J. Gosting and H. Fujita, *J. Am. Chem. Soc.*, **79**, 1359 (1957).

For those experiments with the ternary system which gave large fringe deviation graphs the extrapolations to obtain C_t deviated from linearity with increase of the fringe number j. Therefore data for large j were included to help guide each extrapolation to $Z_j^{2/3} = 0$, where $Z_j \simeq j + 3/4$. In most experiments 15 to 20 fringe minima were measured, including all fringes in the range $j = 0$ to $j = 4$ or 6; other fringe minima measured were at approximately equal intervals of j up to within a few fringes of J, the total number of interference fringes. For each photograph a preliminary value $\mathfrak{D}_A'$ of the reduced height-area ratio $\mathfrak{D}_A$ for that experiment was calculated by using the equation

$$\mathfrak{D}_A' = (J\lambda b)^2/(4\pi C_t^2 t') \qquad (35)$$

Then $\mathfrak{D}_A$, corrected[42,43] for imperfections in the initial boundary, was obtained by using the method of least squares to extrapolate the $\mathfrak{D}_A'$ to $1/t' = 0$. The starting time correction Δt obtained from the slope of each extrapolation varied from 7.5 to 32.1 seconds for the several experiments. The integral and fractional parts of J were obtained, respectively, from photographs of Rayleigh integral fringes taken during diffusion and of ordinary Rayleigh fringes taken during the boundary sharpening process.[29,44] These fringes were recorded on Kodaline C.T.C. panchromatic plates, as were the special sets of fringes photographed earlier in each experiment to determine the small corrections[29] δ and δ'. Because of residual imperfections in the optical system these corrections must be applied to positions of the reference fringes associated, respectively, with the Gouy photographs and with the ordinary Rayleigh photographs for determining the fractional part of J. The wave length λ of the essentially monochromatic light used to illuminate the source slit was 5460.7 A. in air.

A fringe deviation graph[39,45] was calculated for each experiment. This graph is independent of time and summarizes all information provided by the Gouy fringes about deviations of the refractive index gradient curve from Gaussian shape. It was made by plotting (for each fringe j that was measured) the average value of Ω_j, the reduced fringe deviation, against $f(\zeta_j)$, the reduced fringe number.[46] The area

$$Q = \int_0^1 \Omega \mathrm{d}f(\zeta) \qquad (36)$$

of each graph (where subscript j is now omitted) was measured by applying Simpson's one-third rule to the values of Ω read, at intervals of 0.05 along the $f(\zeta)$ axis, from a smooth curve through the averaged experimental values of Ω.

The temperature τ of each diffusion experiment was within ±0.006° of 25° and never fluctuated more than ±0.003°; τ was measured during the period of diffusion with a mercury-in-glass thermometer which was calibrated occasionally against a platinum resistance thermometer. Each $\mathfrak{D}_A$ reported in subsequent tables is the value at 25°; it was obtained from the measured value $(\mathfrak{D}_A)_\tau$ by using the expression

$$\mathfrak{D}_A = (\mathfrak{D}_A)_\tau\,[1 + 0.0264(25 - \tau) + \ldots] \qquad (37)$$

Procedure and Data for the Systems H_2O–glycine and H_2O–KCl.—Some experiments were performed on these binary systems to test the purity of the recrystallized solutes, to provide some current tests of the apparatus and to obtain data at the mean concentrations of each solute corresponding to the concentrations used for the ternary system. The results of these experiments are recorded in Table II where they are compared with values interpolated from some data in the literature.[29,39,47–52] In this table the Δc and $\bar{c}$ for the solute of either binary system are defined by equations 33 and 34. Data for the refractive index difference Δn between the two initial solutions for each experiment are reported as $\Delta n/\Delta c$; this ratio was calculated from the total number of interference fringes J and the corresponding Δc by using the equation

$$\Delta n/\Delta c = \lambda J/(a\Delta c) \qquad (38)$$

The values of $\mathfrak{D}_A$ listed[53] as D in Table II have been converted to 25.00$_0$° by using equation 37. Most areas Q of fringe deviation graphs reported in Table II are zero[54] within the expected uncertainty of measurement. This is evident for cell SE and data for some other experiments (not reported here) help support this conclusion for cell SF. However a small positive value of Q seemed to be obtained consistently when cell SD was used; therefore in the next section (for the ternary system) all values of Q obtained with cell SD have been corrected by subtracting $1._{05} \times 10^{-4}$ from each observed value.

Procedure and Initial Data for the Ternary System H_2O–glycine–KCl.—The procedure for performing the experiments follows closely that described in a report[55] of earlier work on the system H_2O–NaCl–KCl. However, a new method[7] has been used to analyze the initial data and obtain the four diffusion coefficients at each composition. Except for a few special cases this method is applicable regardless of the relative magnitude of the diffusion coefficients. A previous method[56] which was used for the system H_2O–NaCl–KCl is not suitable for the present study because it depends on a series which does not converge well for the system H_2O–glycine-KCl. Furthermore the new method gives somewhat more accurate results for the D_{ij} because, instead of using only one value of Ω from each fringe deviation graph, it uses the area Q of each graph.

Although only two suitable experiments are required to obtain the four diffusion coefficients for each composition, here a set of at least four experiments was performed for each composition to provide checks among the data and to increase accuracy. To prepare the two initial solutions for each experiment it was necessary to specify the desired values of $\bar{c}_1$, $\bar{c}_2$, Δc_1 and Δc_2. For all experiments of a given set $\bar{c}_1$ and $\bar{c}_2$ were numerically equal to, respectively, the two solute molarities for the composition being studied. The relative values of Δc_1 and Δc_2 for different experiments in a set were varied subject to the restriction $\Delta c_1 + \Delta c_2 = 0.15$ molar.[57] The remaining restriction necessary to specify the values of Δc_1 and Δc_2 for each experiment was imposed by choosing a convenient value of α_1, the fraction of the total refractive index increment due to component 1

$$\alpha_1 = R_1\Delta c_1 / \sum_{j=1}^{2} R_j \Delta c_j \qquad (39)$$

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(42) L. G. Longsworth, *J. Am. Chem. Soc.*, **69**, 2510 (1947).

(43) H. Fujita, *J. Phys. Soc. Japan*, **11**, 1018 (1956).

(44) R. P. Wendt and L. J. Gosting, *J. Phys. Chem.*, **63**, 1287 (1959).

(45) See Figs. 19 and 21 of ref. 33.

(46) See equations 8 and 9 of ref. 39, or equations A-5 and A-8 of ref. 7.

(47) H. S. Harned and R. L. Nuttall, *J. Am. Chem. Soc.*, **71**, 1460 (1949).

(48) R. H. Stokes, *ibid.*, **72**, 2243 (1950).

(49) M. S. Lyons and J. V. Thomas, *ibid.*, **72**, 4506 (1950).

(50) L. G. Longsworth, *ibid.*, **75**, 5705 (1953).

(51) P. J. Dunlop, *ibid.*, **77**, 2994 (1955).

(52) In Table II our data for H_2O–glycine are compared only with data from ref. 49 because the values in ref. 50 and 51 are for lower concentrations. Our data and those of ref. 51, which were also obtained using C.P. glycine that had been recrystallized once, may be represented by the following linear equations determined by the method of least squares: $D \times 10^5 = 1.058_9 - 0.179_7 c \pm 0.06\%$ and $(\Delta n/\Delta c) \times 10^3 = 13.60_0 - 0.620_3 c \pm 0.01\%$. If the data in ref. 49 and 50 (obtained using commercially available glycine without further purification) are considered with those from ref. 51 and the present study, the following linear equations may be obtained by least squares as representative of all these data for the system H_2O–glycine at 25°: $D \times 10^5 = 1.061_9 - 0.188_0 c \pm 0.15\%$ and $(\Delta n/\Delta c) \times 10^3 = 13.60_6 - 0.634_9 c \pm 0.04\%$. Before obtaining the last equation it was necessary to convert the data of ref. 49 and 50 to concentrations of mole/l. and to refer the data of ref. 49 to a refractive index of unity for air.

(53) A small value of Δc (usually about 0.15 mole/l.) was used for each experiment to reduce the effects of any concentration dependence of the diffusion coefficient or partial molal volumes and of any non-linear dependence of the refractive index on the solute concentration. As $\Delta c \rightarrow 0$ for experiments with a given mean concentration the values of $\mathfrak{D}_A$ should approach the desired binary diffusion coefficient D at that composition $c = \bar{c}$ (see ref. 41).

(54) For a binary system Q should be zero if the solute is pure, if Δc is sufficiently small and if the optical elements of the diffusiometer are perfect.

(55) I. J. O'Donnell and L. J. Gosting, in "The Structure of Electrolytic Solutions," W. J. Hamer, ed., John Wiley and Sons, Inc., New York, N. Y., 1959, p. 160.

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

(57) This total concentration difference was chosen, instead of the value 0.2 molar used for the system H_2O–NaCl–KCl (ref. 55), to reduce further any effects of concentration dependences of the diffusion coefficients or the partial molal volumes or of a non-linear dependence of refractive index on the solute concentrations.

TABLE II

DATA FOR THE BINARY SYSTEMS AT 25°

Exp. no.[a]	Cell	System	$\bar{c}$, mole/l.	Δc, mole/l.	J	This work[b] $(\Delta n/\Delta c) \times 10^3$ l./mole	Other work[b] $(\Delta n/\Delta c) \times 10^3$ l./mole	This work[c] $D \times 10^5$ cm.²/sec.	Other work $D \times 10^5$ cm.²/sec.	$Q \times 10^4$
4	SD	H_2O–glycine	0.25000	0.14999	92.55_0	13.444	13.451[d]	1.012_8	1.015_4[e]	$+1._0$
5	SE	H_2O–glycine	.49960	.14911	91.01_0	13.290	13.287[d]	0.9696	0.9674[e]	$-2._3$
35	SF	H_2O–KCl	.12500	.15001	69.12_1	10.035	...	1.841_8	1.839[f] 1.846[h] 1.842[g]	$+1._5$
36	SF	H_2O–KCl	.12500	.15002	69.16_4	10.040	...	1.842_0	1.839[f] 1.846[h] 1.842[g]	$+1._0$
37	SD	H_2O–KCl	.12500	.15000	69.11_3	10.039	...	1.843_7	1.839[f] 1.846[h] 1.842[g]	$+1._4$
3	SE	H_2O–KCl	.19999	.19999	91.36_1	9.947	9.942[h] 9.944[i]	1.837_4	1.836[f] 1.839_2[h] 1.834[g] 1.833_9[i]	$0._0$
1	SE	H_2O–KCl	.21525	.23089	105.29	9.929	9.924[h] 9.927[i]	1.839_6	1.837[f] 1.838_6[h] 1.833[g] 1.835_8[i]	$+1._6$
2	SD	H_2O–KCl	.21524	.23086	105.20_4	9.929	9.924[h] 9.927[i]	1.835_2	1.837[f] 1.838_6[h] 1.833[g] 1.835_8[i]	$+1._1$
19	SF	H_2O–KCl	.24999	.15000	68.11_1	9.889	9.886[h]	1.838_8	1.838[f] 1.838_2[h] 1.831[g]	$+1._1$
18	SD	H_2O–KCl	.50002	.15003	66.51_2	9.659	9.658[h]	1.847_1	1.851[f] 1.849_7[h] 1.834[g]	$+1._0$

[a] Experiments are numbered chronologically with those of Table III. [b] Values of Δn correspond to a choice of unity for the refractive index of air. [c] The diffusion coefficients correspond to a volume-fixed frame of reference and are defined by equation 20 with $q = 1$. [d] From the data for $\Delta n/\Delta c$ at 25° in Table I of ref. 49: those data were converted to l./mole and to a refractive index of unity for air and then represented by a linear equation determined by the method of least squares. [e] From the equation for D at 25° in Table III of ref. 49. [f] Smoothed values from ref. 47. [g] Smoothed values from ref 48. [h] Interpolated from the data in ref. 29. [i] Data from ref. 39.

Here the coefficients R_j may be defined[58] by

$$n(c_1,c_2) = n(\bar{c}_1,\bar{c}_2) + R_1(c_1 - \bar{c}_1) + R_2(c_2 - \bar{c}_2) \quad (40)$$

where $n(c_1,c_2)$ denotes the refractive index of this ternary system at solute concentrations c_1 and c_2, provided they are quite close to the chosen reference concentrations $\bar{c}_1$ and $\bar{c}_2$, respectively, and $n(\bar{c}_1, \bar{c}_2)$ is the refractive index of a solution with $c_1 = \bar{c}_1$ and $c_2 = \bar{c}_2$. The first two experiments of each set were performed with $\alpha_1 \simeq 0$ and $\alpha_1 \simeq 1$, respectively (*i.e.*, with $\Delta c_1 \simeq 0$ and $\Delta c_2 \simeq 0$); then preliminary values of R_1 and R_2 were calculated from the Δc_i and J for these experiments by using the relation[59]

$$\frac{\lambda}{a}\left(\frac{J}{\Delta c_1 + \Delta c_2}\right) = \left(\frac{\Delta c_1}{\Delta c_1 + \Delta c_2}\right)(R_1 - R_2) + R_2 \quad (41)$$

Intermediate rounded values of α_1 (usually 0.2 and 0.8) then were chosen for the remaining experiments of the set, and the required values of Δc_1 and Δc_2 corresponding to each α_1 were calculated by substituting the preliminary R_j into equation 39 and applying the chosen restriction $\Delta c_1 + \Delta c_2 = 0.15$.

Initial data for the diffusion experiments on this system are reported in Table III. The solute concentrations c_1 and c_2 corresponding to each composition studied are shown at the top of the table just below the number (S-1, S-2, etc.) assigned to the set of experiments for that composition. Measured densities of initial solutions A and B for each experiment are reported in lines 5 and 8; for these two solutions the solute concentrations $(c_i)_A$ and $(c_i)_B$, which were obtained from the weights of the components (in vacuum) and the measured densities, are shown in lines 3, 4, 6 and 7. In lines 9 and 10 are listed the mean solute concentrations calculated by using equation 34. For each composition the measured values of J (J_{exp} in line 11) and the values of Δc_i, obtained from the $(c_i)_A$ and $(c_i)_B$ by using equation 33, were used to determine the final values of R_1 and R_2 (reported later in Table V); equation 41 and the method of least squares were used for this calculation. From R_1, R_2 and the Δc_i the values of α_1 in line 13 were calculated for each experiment of the set by using equation 39. The reliability of J_{exp}, line 11, is indicated by comparing those data with the values J_{calcd}, line 12, which were calculated from R_1, R_2, Δc_1 and Δc_2 by using equation 41. For each experiment the reduced height-area ratio, which has been converted to 25° by using equation 37, is reported as $(\mathfrak{D}_A)_{exp}$ in line 14. Determination of the area of each fringe deviation graph has been described elsewhere (near equation 36 and at the end of the preceding subsection); the final values are shown as Q_{exp} in line 16.

The theoretical basis of the new method for obtaining values of the four $(D_{ij})_V$ from data for the $\mathfrak{D}_A$ and Q has been described in detail in the original article.[7] Here we give only a brief summary of its application as we have used it, and we refer directly to equations in the original article by adding the letter F to those equation numbers. For each set of experiments the constants I_A and S_A (lines 18 and 19 of Table III) in the linear relation (equation 15F)

$$1/\sqrt{\mathfrak{D}_A} = I_A + S_A\alpha_1 \quad (42)$$

were determined from the experimental values of α_1 and $\mathfrak{D}_A$ (lines 13 and 14) by the method of least squares. Then the area Q (line 16) of each fringe deviation graph was multiplied by the corresponding smoothed value of $1/\sqrt{\mathfrak{D}_A}$ (calculated from equation 42 by using I_A and S_A from lines 18 and 19 and the appropriate α_1 from line 13) to give the ratio (equation 21F)

$$Q/\sqrt{\mathfrak{D}_A} \equiv E = E_0 + E_1\alpha_1 - E_2\alpha_1^2 \quad (43)$$

Here E_0, E_1 and E_2 are functions of the four diffusion coefficients only (equations 17F–19F); however, as I_A and S_A are also functions of those diffusion coefficients (equations 57 and 58 of ref. 56) these five coefficients are not independent. Accordingly, because I_A and S_A have already been determined, it is not now permissible to use the method of least squares to obtain E_0, E_1 and E_2 of equation 43; we have used the method of successive approximations described following equation 22F to determine the ratios E_0/E_2 and E_1/E_2 in the following form of equation 43

$$\hat{E} \equiv [(E/E_2) + \alpha_1^2] = (E_0/E_2) + (E_1/E_2)\alpha_1 \quad (44)$$

The approximate starting value of E_2 required to calculate the first approximations for $\hat{E}$ was determined from the slope of a graph of $(E - E_0)/\alpha_1$ *versus* α_1 (using for E_0 the experimental value of $Q/\sqrt{\mathfrak{D}_A}$ at $\alpha_1 \simeq 0$). First approximations for E_0/E_2 and E_1/E_2 were then determined from the $\hat{E}$ by the method of least squares, and from these values first approximations for the four D_{ij} then were calculated.[60] A second approximation for E_2 was obtained from these D_{ij} by using

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(58) See equation 7 of ref. 24 for a definition of the R_j in terms of derivatives of the refractive index.

(59) See equation 13 of ref. 55.

(60) See footnote 17 of ref. 7.

TABLE III[a]

INITIAL DATA FOR THE SYSTEM H_2O–GLYCINE–KCl AT 25°

1 = glycine; 2 = KCl

		S 1 $c_1 = 0.25$; $c_2 = 0.125$				S-2 $c_1 = 0.25$; $c_2 = 0.25$				S-3 $c_1 = 0.25$; $c_2 = 0.5$				
1	Exp. no.[b]	31	34	33	32	17	21	22	20	11	15	16	13	9
2	Cell	SD	SD	SD	SD	SF	SF	SF	SF	SD	SD	SD	SD	SD
3	$(c_1)_A$	0.24999	0.23832	0.19397	0.17500	0.24991	0.23824	0.19404	0.17501	0.24999	0.23849	0.21849	0.19423	0.17500
4	$(c_2)_A$	0.05002	0.06167	0.10600	0.12501	0.17498	0.18663	0.23094	0.24999	0.42501	0.43649	0.45649	0.48077	0.50000
5	$(d)_A$	1.00734_9	1.00752_3	1.00819_2	1.00848_1	1.01309_4	1.01331_8	1.01397_7	1.01426_9	1.02458_7	1.02474_5	1.02504_4	1.02539_5	1.02569_0
6	$(c_1)_B$	0.24999	0.26168	0.30601	0.32499	0.25000	0.26160	0.30596	0.32501	0.25000	0.26150	0.28149	0.30576	0.32500
7	$(c_2)_B$	0.19998	0.18831	0.14397	0.12502	0.32498	0.31335	0.26905	0.25003	0.57501	0.56350	0.54350	0.51924	0.50000
8	$(d)_B$	1.01428_4	1.01410_6	1.01344_4	1.01316_4	1.01998_1	1.01984_4	1.01919_3	1.01893_5	1.03137_1	1.03120_0	1.03090_7	1.03055_0	1.03027_1
9	$\bar{c}_1$	0.24999	0.25000	0.24999	0.25000	0.24996	0.24992	0.25000	0.25001	0.25000	0.25000	0.24999	0.25000	0.25000
10	$\bar{c}_2$	0.12500	0.12499	0.12498	0.12502	0.24998	0.24999	0.25000	0.25001	0.50001	0.50000	0.50000	0.50000	0.50000
11	J_{exp}	67.83_8	71.64_7	85.85_6	91.96_3	67.08_4	70.79_9	85.21_8	91.47_8	65.48_0	69.30_5	75.94_6	84.00_7	90.41_1
12	J_{calcd}	67.85_5	71.62_4	85.86_8	91.95_8	67.05_3	70.82_8	85.24_2	91.45_5	65.47_7	69.30_5	75.94_9	84.01_2	90.40_7
13	α_1	0.0000	0.2000	0.7999	1.0000	0.0008	0.2010	0.8004	0.9998	0.0001	0.2001	0.5000	0.8001	1.0000
14	$(\mathfrak{D}_A)_{exp} \times 10^5$	1.751_4	1.546_9	1.113_7	1.009_7	1.758_2	1.552_2	1.114_7	1.007_9	1.785_5	1.570_5	1.316_5	1.120_3	1.012_2
15	$(\mathfrak{D}_A)_{calcd.} \times 10^5$	1.750_2	1.547_9	1.114_0	1.009_3	1.758_3	1.552_4	1.113_8	1.008_6	1.784_2	1.571_4	1.317_2	1.119_9	1.012_1
16	$Q_{exp} \times 10^4$	$7._{19}$	4 .	$29._{30}$	$-2._{26}$	$6._{52}$	$40._{78}$	$29._{89}$	$-4._{47}$	$3._{12}$	$38._{14}$	$53._{08}$	$28._{91}$	$-2._{35}$
17	$Q_{calcd} \times 10^4$	$8._{67}$	$40._{45}$	$29._{06}$	$-1._{81}$	$7._{54}$	$40._{07}$	$28._{26}$	$-3._{16}$	$3._{33}$	$38._{37}$	$52._{24}$	$29._{32}$	$-2._{34}$
18	I_A		239.03	Av. dev. from			238.42	Av. dev. from			236.74	Av. dev. from		
19	S_A		75.73	line = ±0.023%			76.49	line = ±0.020%			77.59	line = ±0.022%		
20	E_2[c]		5.46497				5.58070				5.74842			
21	E_0/E_2[c]		0.037910				0.031443				0.013640			
22	E_1/E_2[c]		0.951704				0.950745				0.973549			

		S-4 $c_1 = 0.5$; $c_2 = 0.125$				S-5 $c_1 = 0.5$; $c_2 = 0.25$					S-6 $c_1 = 0.5$; $c_2 = 0.5$				
1	Exp. no.[b]	27	29	30	28	8	23	12	14	10	7	26	24	25	6
2	Cell	SF	SF	SF	SF	SE	SF	SE	SE	SE	SD	SD	SD	SD	SD
3	$(c_1)_A$	0.50001	0.48837	0.44407	0.42493	0.50002	0.49996	0.48840	0.44410	0.42492	0.49999	0.49445	0.48855	0.44430	0.42503
4	$(c_2)_A$	0.05001	0.06161	0.10595	0.12503	0.17502	0.17499	0.18653	0.23081	0.25000	0.42497	0.43057	0.43649	0.48070	0.50004
5	$(d)_A$	1.01514_9	1.01532_5	1.01599_1	1.01628_0	1.02084_4	1.02085_8	1.02103_5	1.02169_6	1.02197_4	1.03219_2	1.03227_7	1.03236_7	1.03300_8	1.03328_6
6	$(c_1)_B$	0.49997	0.51161	0.55590	0.57494	0.49995	0.49997	0.51156	0.55579	0.57505	0.50001	0.50557	0.51146	0.55570	0.57502
7	$(c_2)_B$	0.19998	0.18840	0.14408	0.12501	0.32499	0.32497	0.31355	0.26916	0.24999	0.57499	0.56946	0.56356	0.51930	0.50001
8	$(d)_B$	1.02201_1	1.02185_4	1.02118_2	1.02090_3	1.02766_9	1.02769_2	1.02751_1	1.02685_0	1.02657_2	1.03891_1	1.03883_1	1.03875_4	1.03809_2	1.03780_7
9	$\bar{c}_1$	0.49998	0.49999	0.49998	0.49994	0.49998	0.49996	0.49998	0.49994	0.49998	0.50000	0.50001	0.50000	0.50000	0.50002
10	$\bar{c}_2$	0.12500	0.12500	0.12502	0.12502	0.25000	0.24998	0.25004	0.24998	0.25000	0.49998	0.50002	0.50002	0.50000	0.50002
11	J_{exp}	66.71_7	70.57_1	84.87_0	90.99_2	65.94_0	65.90_0	69.78_2	84.30_9	90.59_8	64.62_2	66.36_0	68.27_7	83.11_7	89.53_6
12	J_{calcd}	66.74_3	70.55_0	84.83_6	91.02_0	65.88_8	65.92_7	69.82_0	84.27_7	90.61_6	64.54_7	66.38_6	68.34_0	83.11_0	89.53_0
13	α_1	−0.0004	0.1999	0.7999	1.0001	−0.0006	0.0001	0.2002	0.8000	1.0000	0.0002	0.1000	0.2001	0.8002	1.0001
14	$(\mathfrak{D}_A)_{exp} \times 10^5$	1.681_0	1.483_5	1.072_4	0.971_7	1.698_4	1.700_3	1.496_2	1.073_6	0.973_6	1.731_5	1.623_5	1.523_9	1.083_6	0.977_4
15	$(\mathfrak{D}_A)_{calcd} \times 10^5$	1.679_0	1.486_0	1.072_0	0.971_8	1.698_5	1.697_7	1.498_9	1.074_7	0.972_7	1.732_3	1.623_3	1.523_9	1.082_9	0.977_9
16	$Q_{exp} \times 10^4$	$14._{29}$	$45._{83}$	$30._{65}$	$-1._{72}$	$8._{41}$	$10._{70}$	$47._{99}$	$29._{70}$	$-3._{74}$	$2._{57}$	$23._{38}$	$37._{99}$	$31._{57}$	$-3._{72}$
17	$Q_{calcd} \times 10^4$	$15._{04}$	$45._{04}$	$30._{24}$	$-1._{26}$	$11._{48}$	$11._{60}$	$43._{40}$	$29._{42}$	$-2._{77}$	$2._{61}$	$23._{46}$	$38._{44}$	$29._{66}$	$-2._{37}$
18	I_A		244.09	Av. dev. from			242.70	Av. dev. from				240.26	Av. dev. from		
19	S_A		76.69	line = ±0.043%			77.94	line = ±0.053%				79.51	line = ±0.019%		
20	E_2[c]		5.51041				5.70148					5.93664			
21	E_0/E_2[c]		0.067024				0.049435					0.010467			
22	E_1/E_2[c]		0.925651				0.934948					0.976822			

[a] Units: concentrations c_i, mole/l.; densities d, g./ml.; reduced height-area ratios $\mathfrak{D}_A$, cm.²/sec. [b] Experiments are numbered chronologically. [c] More than the minimum number of significant digits were retained in these values to minimize accumulation of errors in calculation.

equation 19F, and the process of successive approximations was repeated until the values of D_{ij} [reported later in Table V as $(D_{ij})_V$] were constant (well within 0.0001×10^{-5} in all D_{ij}). The final values for E_2, E_0/E_2 and E_1/E_2 are given in lines 20, 21 and 22 of Table III. As a check on the calculations, and on the consistency of data from the experiments in each set, the four $(D_{ij})_V$ for each composition (Table V) were used to calculate values of $\mathfrak{D}_A$ and Q for each experiment in that set. These values are shown as $(\mathfrak{D}_A)_{\text{calcd.}}$ and $Q_{\text{calcd.}}$ in lines 15 and 17 and are seen to be in reasonable agreement with the measured values.

In previous studies[5,7,55] the validity of equations 41–44 to represent experimental data for a given set of experiments was confirmed over rather limited ranges of α_1 (usually between 0.0 and 0.2 and between 0.8 and 1.0). The experiments of set S-3 of Table III provide data for α_1 equal to 0.5 (experiment 16) in addition to 0.0, 0.2, 0.8 and 1.0. Because $J_{\text{exp.}}$ and $J_{\text{calcd.}}$, $(\mathfrak{D}_A)_{\text{exp.}}$ and $(\mathfrak{D}_A)_{\text{calcd.}}$ and $Q_{\text{exp.}}$ and $Q_{\text{calcd.}}$ agree within experimental error for each of the five experiments of this set, these data provide an improved confirmation of the adequacy of equations 41–44 to describe experiments with α_1 ranging from 0.0 to 1.0.

Experimental Results

In this section we report and discuss our results for the diffusion coefficients, partial molal volumes and refractive index derivatives at six compositions of the ternary system H_2O–glycine–KCl; with these results we include some corresponding data for H_2O-glycine and H_2O–KCl because these binary systems may be considered as limiting cases of the ternary system.

Partial Molal Volumes.—Values of the $\bar{V}_i$ for six compositions of the system were calculated from the measured densities reported in Table III. First, for each set of experiments, the method of least squares was used to determine the three constants in the equation

$$d(c_1,c_2) = d(\bar{c}_1,\bar{c}_2) + H_1(c_1 - \bar{c}_1) + H_2(c_2 - \bar{c}_2) \quad (45)$$

These constants are reported in Table IV. Equation 45 is adequate to express the density $d(c_1, c_2)$ of the system provided c_1 and c_2 are not too far from the chosen reference concentrations $\bar{c}_1$ and $\bar{c}_2$ (which we take as rounded values of $\bar{c}_1$ and $\bar{c}_2$ in Table III). Here $d(\bar{c}_1, \bar{c}_2)$ is the density of the solution when $c_1 = \bar{c}_1$ and $c_2 = \bar{c}_2$, and H_1 and H_2 may be defined as derivatives of the density (see equation 3a of ref. 4). Next the data in Table IV were used with equation 3 of Dunlop and Gosting[4] to calculate the values of $\bar{V}_1$ and $\bar{V}_2$ which are shown in lines 5 and 6, columns H-M, of Table V; each composition is indicated by the solute concentrations in lines 1 and 2. The values shown for $\bar{V}_1$ and $\bar{V}_2$ for the two binary systems at corresponding molarities were taken from experimental results in the literature,[28,61] as was the limiting value of $\bar{V}_1$ as $c_1 \rightarrow 0$ when $c_2 = 0$ and the limiting value of $\bar{V}_2$ as $c_2 \rightarrow 0$ when $c_1 = 0$. All solvent molarities c_0 in line 3 of Table V were calculated[62] by using the equation

$$c_0M_0 + c_1M_1 + c_2M_2 = 1000d \quad (46)$$

TABLE IV

CONSTANTS OF EQUATION 45 FOR THE DENSITIES OF THE SYSTEM H_2O–GLYCINE–KCl AT 25°

1 = glycine; 2 = KCl

Set of exps.	$\bar{c}_1$, mole/l.	$\bar{c}_2$, mole/l.	$d(\bar{c}_1,\bar{c}_2)$, g./ml.	H_1[a]	H_2[a]	Av. dev.,[b] %
S-1	0.25000	0.12500	1.01081_8	0.0312_1	0.0462_4	0.0002
S-2	.25000	.25000	1.01657_8	$.0310_5$	$.0458_4$	.0018
S-3	.25000	.50000	1.02797_6	$.0305_7$	$.0452_5$	.0003
S-4	.50000	.12500	1.01858_7	$.0308_2$	$.0458_0$	.0004
S-5	.50000	.25000	1.02427_1	$.0305_8$	$.0455_0$	.0007
S-6	.50000	.50000	1.03555_2	$.0301_4$	$.0447_9$	.0004

[a] The units of H_i are (g. l.)/(mole ml.). [b] Av. dev. is the average deviation of the experimentally determined densities for each set of experiments recorded in Table III from the plane surface defined by equation 45.

Then the relation

$$c_0\bar{V}_0 + c_1\bar{V}_1 + c_2\bar{V}_2 = 1000 \quad (47)$$

was used to obtain each value of $\bar{V}_0$ in line 4.

Refractive Index Derivatives.—The results for R_1 and R_2, equation 40,[58] are reported in lines 7 and 8 of Table V. For experiments with both glycine and KCl present these R_i were computed from the data for J_{exp} in Table III by using equation 41 as described in an earlier section. For each binary system the R_i shown are values for $\Delta n/\Delta c$ obtained in this study and reported in Table II, except that the two limiting values were taken from the literature[39,52] because no data were obtained at high dilution in this study. The Δc_i were sufficiently small in all experiments that the values for R_i should not differ significantly from those for experiments with infinitely small concentration increments.

Diffusion Coefficients.—In lines 9–12 of Table V are values of the diffusion coefficients $(D_{ij})_V$ corresponding to a volume-fixed frame of reference (equation 20). These values in columns H-M were obtained from the data in Table III by the procedure outlined under "Experimental" in connection with equations 42–44. Also shown are the new values from Table II for the mutual diffusion coefficients for the binary systems H_2O–glycine and H_2O–KCl; values for the two limiting binary diffusion coefficients are from the literature.[52,63,64]

Diffusion coefficients $(D_{ij})_0$ corresponding to the solvent-fixed frame of reference are reported in lines 13–16. Equations 22 and 10 were used to obtain these values from the $(D_{ij})_V$ and other data in Table V; the α_{ki} for this conversion in columns H-M are also used in a later section and are listed in Table VI. Data for the $(D_{ij})_0$ are used in one route[4] of testing the Onsager reciprocal relations, and it is also of interest to compare their values with those for the $(D_{ij})_V$.

Discussion.—To consider the relationships between data for the two binary systems H_2O–glycine and H_2O–KCl and for the six compositions studied for the system H_2O–glycine–KCl, it is helpful to refer to three-dimensional graphs, Figs. 1 and 2. In these figures solid curves are used to represent the data available for the two binary systems; solid curves are also used to connect the binary data with the new data for the ternary system. The absence of solid curves for some limiting cases (*e.g.*, the $\bar{V}_1$—$\sqrt{c_2}$ plane and the D_{22}—c_1 plane) indicates the absence of data in those regions. Because many properties of an electrolyte solute at high dilution vary linearly with the square root rather than the first power of the electrolyte concentration,[65] we have chosen to use $\sqrt{c_2}$ rather than c_2 as one of the coördinates for each graph. This avoids infinite limiting slopes as $c_2 \rightarrow 0$ for the surfaces for $\bar{V}_2$, R_2, D_{22}, *etc.* Although limiting slopes of zero are then obtained as $\sqrt{c_2} \rightarrow 0$ for some properties of the dipolar solute,[66] this seems preferable here to limiting slopes which are infinite.

The surfaces for $\bar{V}_1$ and $\bar{V}_2$ in Fig. 1a appear to be consistent with the above comments concerning limiting slopes as $\sqrt{c_2} \rightarrow 0$; however, data

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[61] D. A. MacInnes and M. O. Dayhoff, *J. Am. Chem. Soc.*, **74**, 1017 (1952).

[62] For columns H-M each value of d used in equation 46 was taken directly from Table IV; for columns A and B each value of d was calculated by using equations 30 and 31; for columns E-G each d was obtained from equation 4 of ref. 61 and equation 30. The value d = 0.997075 g./ml. was used for columns C and D.

[63] H. S. Harned and B. B. Owen, "The Physical Chemistry of Electrolytic Solutions," 3rd Ed., Reinhold Publishing Corp., New York, N. Y., 1958.

[64] R. A. Robinson and R. H. Stokes, "Electrolyte Solutions," 2nd Ed., Academic Press, Inc., New York, N. Y., 1959.

[65] See for example ref. 63, chapters 3, 6 and 8.

[66] The derivative $\partial W_1/\partial\sqrt{c_2} \rightarrow 0$ as $c_2 \rightarrow 0$ for any property W_1 of solute 1 for which the derivative $\partial W_1/\partial c_2$ is not infinite; this may be seen from the relation $\partial W_1/\partial\sqrt{c_2} = 2\sqrt{c_2}(\partial W_1/\partial c_2)$. The activity coefficient term ln γ_1 of glycine is such a property; as the KCl molality m_2 approaches zero, $\partial \ln \gamma_1/\partial m_2$ approaches a non-infinite, non-zero, value (see equation 10 of ref. 10, after converting to our notation). Consequently we may also expect that the derivative $\partial\bar{V}_1/\partial m_2 = \partial(\partial\mu_1/\partial P)/\partial m_2 = \partial(\partial\mu_1/\partial m_2)/\partial P = RT\, \partial(\partial \ln \gamma_1/\partial m_2)/\partial P$ should be non-infinite (here P denotes pressure) and therefore that $\partial V_1/\partial\sqrt{c_2} \rightarrow 0$ as $c_2 \rightarrow 0$.

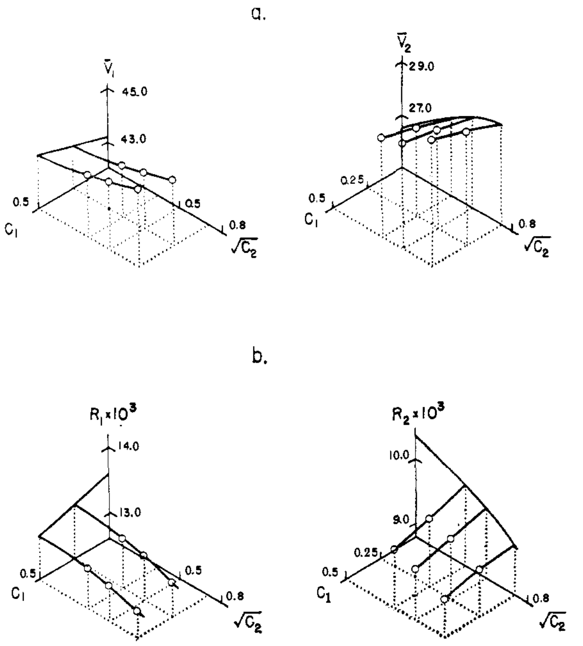

Fig. 1.—Dependence of (a) the partial molal volumes $\bar{V}_i$, and (b) the refractive index derivatives R_i, on solute concentrations for the system H_2O–glycine–KCl at 25°. Circles represent data from the present study of the ternary system; solid curves connect these points and data for the binary systems. Units: $\bar{V}_i$, ml./mole; R_i, l./mole; c_i, mole/l.

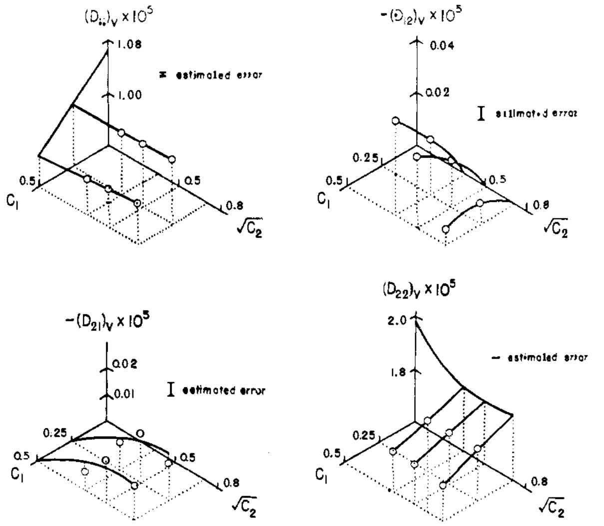

Fig. 2.—Dependence on solute concentrations of the volume-fixed diffusion coefficients $(D_{ij})_V$ defined by equations 48 and 49 for the system H_2O–glycine–KCl at 25°. Circles represent data from the present study of the ternary system; solid curves connect these points and data for the binary systems. Note that for $(D_{12})_V$ and $(D_{21})_V$ the direction of the vertical axes has been reversed and the scale of these axes expanded. The $(D_{ij})_V$ are in cm.²/sec. and for amounts of solutes expressed in moles (not grams).

at lower values of c_2 (and plotted on an expanded scale) are required to provide adequate experimental confirmation. As indicated in Fig. 1a and in Table V, values are not yet available for the tracer partial molal volume of either solute 1 or solute 2: *i.e.*, there are no data for the $\bar{V}_1$—$\sqrt{c_2}$ plane or the $\bar{V}_2$—c_1 plane, respectively. If the appropriate partial molal volumes were obtained at compositions of the ternary system successively nearer these planes, the tracer values in each plane could be obtained by extrapolation. Then, by extrapolating the tracer $\bar{V}_1$ to $\sqrt{c_2} = 0$ in the $\bar{V}_1$—$\sqrt{c_2}$ plane and the tracer $\bar{V}_2$ to $c_1 = 0$ in the $\bar{V}_2$—c_1 plane, the two limiting tracer values could be determined. Because the limiting tracer $\bar{V}_i$ for solute i may be expected to equal the limiting $\bar{V}_i$ for the binary system (*e.g.*, the limit of $\bar{V}_1$ as $c_1 \rightarrow 0$ and then $\sqrt{c_2} \rightarrow 0$ equals the limit of $\bar{V}_1$ as $\sqrt{c_2} \rightarrow 0$ and then $c_1 \rightarrow 0$), we show in parentheses in column D of Table V the same value of $\bar{V}_1$ that is reported in column C; similarly in column C we show in parentheses the same value of $\bar{V}_2$ that is reported in column D.

The graphs for R_1 and R_2 in Fig. 1b may be discussed in essentially the same way as those for $\bar{V}_1$ and $\bar{V}_2$. It is of interest that R_1 and R_2 both decrease with increasing values of c_1 and c_2, as might be anticipated from the fact that both $\bar{V}_1$ and $\bar{V}_2$ increased with increasing values of c_1 and c_2.

Before considering the four diffusion coefficients illustrated by Fig. 2, we should emphasize that it is not entirely rigorous to consider the system H_2O–glycine–KCl as a ternary system. This is because both the glycine and the water ionize to a small extent. The existence of these ionizations does not affect the definition and measurement of certain equilibrium properties of the main components, such as $\bar{V}_1$ and $\bar{V}_2$, but it should be considered if diffusion measurements were made with very high precision or near certain limiting compositions.[67] However it does not significantly affect the available diffusion data for this system because (1) the concentrations of glycine ions were negligible compared to the concentration of dipolar glycine, and (2) all measurements with KCl present were made at salt concentrations much greater than the concentrations of H^+ and OH^- ions. Therefore in the following discussion we neglect the ionization of both the glycine and the water, even as $c_2 \rightarrow 0$. Under these circumstances the condition of zero

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(67) The ionization of water was also neglected in an earlier discussion of data for diffusion coefficients for the system H_2O–NaCl–KCl (see ref. 55). An exact description of that system and of the present system requires the consideration of more than four $(D_{ij})_V$. For a simple illustration of the problem involved, consider diffusion in an aqueous solution of NaCl. If the concentrations of Na^+ and Cl^- are much higher than the concentrations of H^+ and OH^-, very accurate measurements would be required to detect any difference in the velocities of Na^+ and Cl^- ions; therefore for most studies of diffusion, one may assume H_2O–NaCl to be a binary system and describe the measurements accurately by simply reporting data for a mutual diffusion coefficient. However, if the salt is so dilute that the concentrations of Na^+ and Cl^- are comparable to or less than the concentrations of ions from the water, then the velocity of Na^+ will generally be different from the velocity of Cl^- because of the difference in limiting mobilities of these ions; the development of techniques for studying diffusion by using radioactive tracers has made this range of composition experimentally accessible. A rigorous description of diffusion at any composition of NaCl in water could be made in terms of the four diffusion coefficients for the ternary system H_2O–NaOH–HCl. This ternary system is sufficiently general to consider the diffusion of trace amounts of Na^+ and/or Cl^-, and it reduces to the binary system H_2O–NaCl when the concentrations of components NaOH and HCl are equal. In aqueous solutions of a salt of the type M_jX_k (containing j cations M of valence z_+ and k anions X of valence z_- per molecule) diffusion may be described by the four $(D_{ij})_V$ for the system H_2O–$H_{z_-}X$–$M(OH)_{z_+}$ (z_- and z_+ written as absolute values).

Table V[a]

Data for the Four Diffusion Coefficients, Partial Molal Volumes and Refractive Index Derivatives for the System H_2O-Glycine-KCl at 25°

0 = H_2O, 1 = glycine, 2 = KCl; M_0 = 18.0160, M_1 = 75.070, M_2 = 74.557

		H_2O–glycine–KCl												
		H_2O–glycine			H_2O–KCl				S-1, S-2, ..., S-6					
		A	B	C	D	E	F	G	H	I	J	K	L	M
1	c_1	0.5000	0.2500	$c_1 \to 0$	0	0.0000	0.0000	0.0000	0.2500	0.2500	0.2500	0.5000	0.5000	0.5000
2	c_2	0.0000	0.0000	0	$c_2 \to 0$	0.1250	0.2500	0.5000	0.1250	0.2500	0.5000	0.1250	0.2500	0.5000
3	c_0	54.1365	54.7432	55.3439	55.3439	55.1535	54.9584	54.5620	54.5477	54.3501	53.9482	53.9372	53.7354	53.3270
4	$\bar{V}_0$	18.0650	18.0679	18.0688	18.0688	18.0679	18.0664	18.0634	18.0659	18.0638	18.0574	18.0620	18.0593	18.0505
5	$\bar{V}_1$	44.05[b]	43.63[b]	43.20[b]	(43.20)	n.d.	n.d.	n.d.	43.98	44.13	44.60	44.36	44.59	45.02
6	$\bar{V}_2$	n.d.[c]	n.d.	(26.50)[e]	26.50[g]	27.95[g]	28.40[g]	28.85[g]	28.40	28.79	29.37	28.83	29.12	29.82
7	$R_1 \times 10^3$	13.290	13.444	13.606[f]	(13.606)	n.d.	n.d.	n.d.	13.3574	13.2756	13.1319	13.2155	13.1430	13.0073
8	$R_2 \times 10^3$	n.d.	n.d.	(10.370)	10.370[h]	10.038[j]	9.889	9.659	9.8587	9.7254	9.5099	9.6958	9.5723	9.3727
9	$(D_{11})_V \times 10^5$	0.9695	1.0128	1.0619[f]	(1.0619)	n.d.	n.d.	n.d.	1.0145	1.0174	1.0186	0.9754	0.9804	0.9842
10	$(D_{12})_V \times 10^5$	n.d.	n.d.	(0)	0	0	0	0	−0.0212	−0.0177	−0.0077	−0.0360	−0.0269	−0.0057
11	$(D_{21})_V \times 10^5$	0[d]	0	0	(0)	n.d.	n.d.	n.d.	−0.0107	−0.0187	−0.0138	−0.0073	−0.0160	−0.0134
12	$(D_{22})_V \times 10^5$	n.d.	n.d.	(1.994)	1.994[i]	1.8425[j]	1.8388	1.8471	1.7932	1.7955	1.8004	1.7516	1.7534	1.7445
13	$(D_{11})_0 \times 10^5$	0.9913	1.0240	1.0619	(1.0619)	n.d.	n.d.	n.d.	1.0257	1.0287	1.0302	0.9975	1.0027	1.0070
14	$(D_{12})_0 \times 10^5$	n.d.	n.d.	(0)	0	0	0	0	−0.0085	−0.0047	0.0058	−0.0109	−0.0012	0.0212
15	$(D_{21})_0 \times 10^5$	0	0	0	(0)	n.d.	n.d.	n.d.	−0.0051	−0.0074	0.0093	−0.0018	−0.0049	0.0094
16	$(D_{22})_0 \times 10^5$	n.d.	n.d.	(1.994)	1.994	1.8490	1.8520	1.8741	1.7996	1.8085	1.8274	1.7579	1.7662	1.7714

[a] Units: molecular weights M_i, g./mole; concentrations c_i, mole/l.; partial molal volumes $\bar{V}_i$, ml./mole; diffusion coefficients $(D_{ij})_V$ and $(D_{ij})_0$, expressed as cm.²/sec., correspond to the volume-fixed and solvent-fixed frames of reference, respectively, and are reported for flow equations which are written in terms of moles (not grams). [b] From the equation for $\bar{V}_{glycine}$ in Table VI, ref. 28. [c] Wherever "n.d." appears it signifies that no data have yet been obtained nor are any predictions of these values available. [d] All entries 0 (meaning a value of exactly zero) for $(D_{ij})_V$ and $(D_{ij})_0$ were obtained by consideration of flow equations 21, 48 and 49. [e] Entries in parentheses represent limiting cases which have been evaluated by deduction (see under "Discussion" in "Experimental Results"). [f] From the appropriate equation in footnote 52. [g] From the equation for $\bar{V}_{KCl}$ following equation 6 in ref. 61. [h] From equation 48 of ref. 39. [i] From ref. 63, p. 700. [j] Average of the values for experiments 35–37 in Table II.

net electric current requires that the K^+ and Cl^- ions move with the same velocity. Because of these restrictions the system H_2O-glycine-KCl is in some ways comparable to an aqueous system containing two non-electrolytes as solutes; an aqueous solution of two electrolytes with a common ion (such as H_2O-NaCl-KCl, ref. 55) is more complicated, because the condition of zero electric current does not require the ions in such systems to move with the same velocity.

Subject to this assumption (that only K^+ and Cl^- ions are present in the system H_2O-glycine-KCl), we now use Fig. 2 to illustrate for this system the relation between the mutual diffusion coefficients, the tracer diffusion coefficients and the values of the four $(D_{ij})_V$ in columns H-M of Table V. To assist in clarifying this discussion we write here equations 20 for a ternary system

$$(J_1)_V = -(D_{11})_V(\partial n_1/\partial x) - (D_{12})_V(\partial n_2/\partial x) \quad (48)$$

$$(J_2)_V = -(D_{21})_V(\partial n_1/\partial x) - (D_{22})_V(\partial n_2/\partial x) \quad (49)$$

where $n_i = c_i/1000.027$. If $c_2 = 0$ we have only the binary system H_2O-glycine; then the values of $(D_{11})_V$ may be identified with the mutual diffusion coefficient which has been measured at several compositions of this binary system and which is represented by the solid curve in the $(D_{11})_V$—c_1 plane. Similarly the solid curve in the $(D_{22})_V$—$\sqrt{c_2}$ plane represents the mutual diffusion coefficient for the binary system H_2O-KCl. No data are available for the diffusion of trace amounts of glycine in aqueous KCl solutions; when values of this tracer diffusion coefficient are measured, they will determine the intersection of the $(D_{11})_V$ surface with the $(D_{11})_V$—$\sqrt{c_2}$ plane. Similarly, the intersection of the $(D_{22})_V$ surface with the $(D_{22})_V$—c_1 plane would be provided by values of the tracer diffusion coefficient for KCl in aqueous glycine solutions[68] (provided c_2 was kept appreciably greater than the concentrations of ions from the water[67]). Because we assume that only the two ionic species K^+ and Cl^- are present, we may expect that the limiting value of $(D_{22})_V$ when $c_1 \rightarrow 0$ and then $\sqrt{c_2} \rightarrow 0$ is the same as when $\sqrt{c_2} \rightarrow 0$ and then $c_1 \rightarrow 0$. The two corresponding limits for $(D_{11})_V$ should also be identical. Therefore the value of $(D_{11})_V$, line 9, [and of $(D_{11})_0$, line 13] in column D of Table V is shown in parentheses as equal to the value in column C, and the value of $(D_{22})_V$, line 12, [and of $(D_{22})_0$, line 16] in column C is shown in parentheses as equal to the value in column D.

As pointed out earlier,[55] the value of $(D_{12})_V$ should approach zero as $c_1 \rightarrow 0$ because $(J_1)_V \rightarrow 0$ as $c_1 \rightarrow 0$, regardless of the (non-infinite) value of $\partial c_2/\partial x$. Similarly $(D_{21})_V \rightarrow 0$ as $\sqrt{c_2} \rightarrow 0$. This information was used in drawing the solid curves in the graphs of these two cross-term diffusion coefficients in Fig. 2; it also is the source of the values of zero for the cross-term diffusion coefficients in lines 10, 11, 14 and 15 of Table V. An interesting characteristic of this system is that $(D_{12})_V$ appears to become appreciably more negative with decreasing c_2; also $(D_{21})_V$ seems to become slightly more negative with decreasing c_1. It is hoped that procedures eventually will be developed to obtain values of the cross-term diffusion coefficients much closer to the $(D_{12})_V$—c_1 plane and the $(D_{21})_V$—$\sqrt{c_2}$ plane. Presumably for the present system (still assuming that K^+ and Cl^- are the only ions present) the limit of $(D_{12})_V$ [and $(D_{12})_0$] is zero when $\sqrt{c_2} \rightarrow 0$ and then $c_1 \rightarrow 0$, and the limit of $(D_{21})_V$ [and $(D_{21})_0$] is zero when $c_1 \rightarrow 0$ and then $\sqrt{c_2} \rightarrow 0$; therefore for these two limiting cases values of zero are shown in parentheses in columns C and D of Table V.

The graphs in Fig. 2 are seen to be quite different in form from those for the system H_2O-NaCl-KCl,[71] even if c_2 replaced $\sqrt{c_2}$ as a coordinate in Fig. 2. When both solutes are electrolytes the limiting values of each diffusion coefficient at infinite dilution depend on the way in which infinite dilution is approached: *i.e.*, the limiting value for each $(D_{ij})_V$ when first $c_1 \rightarrow 0$ and then $c_2 \rightarrow 0$ is different from its limiting value when first $c_2 \rightarrow 0$ and then $c_1 \rightarrow 0$. At non-zero solute concentrations there are also basic differences between the forms of corresponding graphs of the $(D_{ij})_V$ for these two types of systems. In the system H_2O-NaCl-KCl, because the ions may diffuse with different velocities, the flow of each neutral salt component may be influenced by both the electrophoretic effect and the time-of-relaxation effect. However, in the system H_2O-glycine-KCl, where the K^+ and Cl^- ions are constrained to move with equal velocities, the relaxation effect is absent and the electrophoretic effect will influence only the flow of the KCl. Of course in a three-component system containing only non-electrolytes neither of these effects should be present. However, corresponding graphs of the $(D_{ij})_V$ for these three types of ternary systems have at least one feature in common: the concentration dependence of each $(D_{ij})_V$ is determined in part by the dependence of the activity coefficients on the solute concentrations.

Tests of the Onsager Reciprocal Relation

Values of the diffusion coefficients which were reported for six compositions of this ternary system in columns H-M of Table V will now be used with the other required data to test the Onsager reciprocal relation for each of these compositions. In connection with these tests we obtain and report values of the phenomenological coefficients $(L_{ij})_0$ and $(L_{ij})_V$ defined by equations 11 and 12, and we calculate and compare values of the right- and left-hand sides of equation 29 (which is used in this paper, as it was in ref. 5, as the necessary and sufficient condition for the validity of the ORR). These computations require knowledge of certain derivatives μ_{kj} of the solute chemical potentials; they were obtained by the following procedure from data in the literature for the systems H_2O-glycine, H_2O-KCl and H_2O-glycine-KCl.

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[68] Radioactive tracer measurements with all the K^+ ions, or all the Cl^- ions, tagged would yield these values provided their concentrations were much greater than the concentrations of other ions (from the water and the glycine). A procedure[69,70] for extrapolating suitable data from higher concentrations could also be used to yield these tracer diffusion coefficients.

[69] R. H. Stokes, L. A. Woolf and R. Mills, *J. Phys. Chem.*, **61**, 1634 (1957).

[70] L. A. Woolf, *ibid.*, **64**, 481 (1960).

[71] See ref. 55, Fig. 4(b).

Table VI[a]

Chemical Potential Derivatives and Related Information for Six Compositions of the System H_2O–Glycine–KCl at 25° (1 = glycine; 2 = KCl)

	H	I	J	K	L	M
c_1 (molar)	0.25000	0.25000	0.25000	0.50000	0.50000	0.50000
c_2 (molar)	.12500	.25000	.50000	.12500	.25000	.50000
m_1 (molal)	.25439	.25532	.25722	.51454	.51648	.52043
m_2 (molal)	.12720	.25532	.51444	.12864	.25824	.52043
α_{11}	1.011157	1.011237	1.011446	1.022767	1.022974	1.023385
α_{12}	0.005579	0.011237	0.022891	0.005692	0.011487	0.023385
α_{21}	0.007205	0.007331	0.007537	0.014797	0.015004	0.015490
α_{22}	1.003602	1.007331	1.015074	1.003699	1.007502	1.015490
m_{11}	1.028926	1.032748	1.040657	1.052519	1.056686	1.065207
m_{12}	0.007331	0.007487	0.007755	0.015227	0.015498	0.016123
m_{21}	0.005677	0.011476	0.023553	0.005857	0.011866	0.024341
m_{22}	1.021238	1.028759	1.044390	1.032897	1.040704	1.056989
$d \ln \gamma_2^0/dm_2$	−0.76635	−0.41905	−0.21395	−0.75840	−0.41678	−0.21259
$\partial \ln \gamma_1/\partial m_1$[b]	− .16376	− .15070	− .13242	− .13702	− .12378	− .10527
$\partial \ln \gamma_1/\partial m_2$	− .22064	− .17634	− .13157	− .19018	− .15247	− .11721
$\partial \ln \gamma_2/\partial m_1$	− .11032	− .08817	− .06579	− .09509	− .07624	− .05860
$\partial \ln \gamma_2/\partial m_2$	− .70073	− .38417	− .19601	− .63500	− .35273	− .18075
$\partial \ln y_1/\partial c_1$[c]	− .12512	− .11271	− .09512	− .09980	− .08665	− .06822
$\partial \ln y_1/\partial c_2$	− .19771	− .15322	− .10829	− .16893	− .13059	− .09460
$\partial \ln y_2/\partial c_1$	− .07286	− .05052	− .02730	− .05827	− .03879	− .02005
$\partial \ln y_2/\partial c_2$	− .68760	− .36656	− .17507	− .62775	− .33826	− .16102
μ_{11}/RT	3.87488	3.88729	3.90488	1.90020	1.91335	1.93178
μ_{12}/RT	−0.19771	−0.15322	−0.10829	−0.16893	−0.13059	−0.09460
μ_{21}/RT	−0.14572	−0.10104	−0.05459	−0.11654	−0.07759	−0.04011
μ_{22}/RT	14.62479	7.26689	3.64985	14.74451	7.32348	3.67796

[a] To reduce accumulation of errors more figures than are significant are retained in the activity coefficient derivatives and chemical potential derivatives; estimates of errors for molal activity coefficient derivatives are given in Table VII. [b] Abbreviations for $(\partial \ln \gamma_k/\partial m_l)_{m_{i \neq l}}$. [c] Abbreviations for $(\partial \ln y_k/\partial c_j)_{c_{i \neq 0,j}}$.

Chemical Potential Derivatives.—The μ_{kj} defined by equation 27 may be written for this system as[72]

$$\mu_{kj} = RTr_k \left[\frac{\delta_{kj}}{c_j} + \left(\frac{\partial \ln y_k}{\partial c_j}\right)_{c_{i \neq 0,j}}\right] \qquad (50)$$

where R is the gas constant and y_k is the activity coefficient of solute k corresponding to the molarity (mole/l.) concentration scale; for the dipolar glycine $r_1 = 1$ and for the KCl $r_2 = 2$.

Activity coefficient data for calculation of the μ_{kj} have been reported for the concentration scale of moles of solute i per kg. of H_2O, m_i. Therefore the values of $\partial \ln y_k/\partial c_j$ in equation 50 were obtained from data for the derivatives $\partial \ln \gamma_k/\partial m_l$ of the molal activity coefficients by using the equations[73]

$$\left(\frac{\partial \ln y_k}{\partial c_j}\right)_{c_{i \neq 0,j}} = \frac{\bar{V}_j}{c_0 \bar{V}_0} + \sum_{l=1}^{2} m_{lj} \left(\frac{\partial \ln \gamma_k}{\partial m_l}\right)_{m_{i \neq l}} \qquad (51)$$

$$m_{lj} \equiv \left(\frac{\partial m_l}{\partial c_j}\right)_{c_{j \neq 0,j}} = \left(\frac{1000}{c_0 M_0}\right) \alpha_{jl} \qquad (52)$$

where α_{jl} is defined by equation 10. Required values of the α_{jl} and the m_{lj} (which are the B_{lj} of ref. 4) have been computed from the data in Table V and are reported in Table VI. Also shown in Table VI are values of the solute molalities m_1 and m_2 which were calculated from the densities in Table IV and from the c_i at the top of Table VI by the relation

$$m_i = 1000c_i /(1000d - c_1 M_1 - c_2 M_2) \qquad (53)$$

A. Molal Activity Coefficient Derivatives.—By measuring the electromotive force $\mathcal{E}$ of cells with transference, Roberts and Kirkwood[10] obtained values for the quantity $\ln (\gamma_2/\gamma_2^0)$ over a molality range of m_1 and of m_2 from 0.05 to 0.5[74]; here γ_2 is

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(72) See for example equation 41 of ref. 5.

(73) Equations 49 and 28 of ref. 5.

(74) Roberts and Kirkwood used cells of the type

$$Ag | AgCl_{(s)}, KCl(m_2) \vdots KCl(m_2), \text{glycine}(m_1), AgCl_{(s)} | Ag$$

for which in our notation the expression for $\mathcal{E}$ is[10,75]

$$\mathcal{E} = -\frac{RT}{F} \int_{\alpha}^{\beta} [2t_+ \, d \ln (m_2\gamma_2) + t_1' \, d \ln (m_1\gamma_1)] \qquad (I)$$

Here F is the Faraday, t_+ the cation transference number, t_1' the transference number of the non-electrolyte[75-77] glycine, and α and β denote the two homogeneous solutions separated by the liquid junction. Roberts and Kirkwood simplified both terms on the right-hand side by assuming that the coupled diffusion in this system is sufficiently small that dm_2/dm_1 (our notation), which was initially zero in their experiments, would remain substantially zero (see their equation 3); also from a theoretical estimate of t_1' they decided that the second term could be neglected. With these simplifications they obtained and used a form of equation 1 similar to

$$\ln (\gamma_2/\gamma_2^0) = -(F/2RT) \int_0^{\mathcal{E}} (1/t_+) \, d\mathcal{E} \qquad (II)$$

Their assumption of negligible coupled diffusion is equivalent (if there is no volume change on mixing) to assuming that $(\bar{D}_{21})_0 = 0$ in the flow equations

$$(J_i)_0 = -\sum_{j=1}^{2} (\bar{D}_{ij})_0 (\partial m_j/\partial x) \qquad (III)$$

To test this assumption by using data from Table V we require equations relating $(\bar{D}_{ij})_0$ to $(\hat{D}_{ij})_0$ [$= (D_{ij})_0/1000.027$]. General equations of this type for any reference frame of the class S (see footnote 17) are readily obtained by differentiation with change of variables after first writing equation III for a system of $q + 1$ components and replacing the subscripts denoting the reference frames in equations III and 23 by S. Application of equations 52 and 18 (or 29 of ref. 5) gives

$$(\bar{D}_{ij})_s = (c_0 M_0/1000) \sum_{k=1}^{q} \epsilon_{jk} (\hat{D}_{ik})_S \qquad (1V)$$

the mean ionic activity coefficient (molal scale) of KCl at a given composition of the system, and γ_2^0 is its value for the same m_2 but with $m_1 = 0$. From their data they determined the coefficients in the following polynomial (denoted here by g')

$$\ln(\gamma_2/\gamma_2^0) = g' \equiv A'm_1 + B'm_1m_2^{1/2} + C'm_1^2 + D'm_1m_2 \quad (54)$$

by the method of least squares and obtained $A' = -0.2059$, $B' = 0.2824$, $C' = 0.02474$ and $D' = -0.1446$. Because we must differentiate $\ln(\gamma_2/\gamma_2^0)$, it was thought that more reliable derivatives would be obtained by fitting the results of Roberts and Kirkwood to a higher order polynomial, which we denote by g

$$\ln(\gamma_2/\gamma_2^0) = g \equiv Am_1 + Bm_1m_2^{1/2} + Cm_1^2 + Dm_1m_2 + Em_1^2m_2^{1/2} + Fm_1m_2^{3/2} \quad (55)$$

The values of these coefficients as obtained by least squares are -0.2229_4, 0.3699_8, 0.044091, -0.30956, -0.043175 and 0.1200_2, respectively. For subsequent estimation of the error $\delta(\partial \ln \gamma_k/\partial m_l)$ (see Table VII) in each derivative $(\partial \ln \gamma_k/\partial m_l)_{m_{i \neq l}}$, the error in the contribution from g to each derivative has been taken as the difference in the contributions calculated from equations 54 and 55.

Formal expressions for the four molal activity coefficient derivatives required for equation 51 may now be obtained from equation 55 and the cross-differentiation relation[10,78,79]

$$\left(\frac{\partial \ln \gamma_1}{\partial m_2}\right)_{m_1} = 2\left(\frac{\partial \ln \gamma_2}{\partial m_1}\right)_{m_2} \quad (56)$$

Integration of equation 56 with respect to m_2 from $m_2 = 0$ to m_2 at constant m_1 yields

$$\ln \gamma_1 - \ln \gamma_1^0 = 2\int_0^{m_2}\left(\frac{\partial \ln \gamma_2}{\partial m_1}\right)_{m_2} \mathrm{d}m_2 = 2\int_0^{m_2}\left(\frac{\partial g}{\partial m_1}\right)_{m_2} \mathrm{d}m_2 \ (m_1 \text{ const.}) \quad (57)$$

Here γ_1^0 in the integration constant is the molal activity coefficient of glycine at molality m_1 in the binary system H_2O–glycine. Then from equations 55–57 expressions are obtained for the required activity coefficient derivatives

$$\left(\frac{\partial \ln \gamma_1}{\partial m_1}\right)_{m_2} = \frac{\mathrm{d} \ln \gamma_1^0}{\mathrm{d}m_1} + 2\left(\frac{\partial\left[\int_0^{m_2} (\partial g/\partial m_1)_{m_2}\, \mathrm{d}m_2\right]}{\partial m_1}\right)_{m_2} \quad (58)$$

$$\left(\frac{\partial \ln \gamma_1}{\partial m_2}\right)_{m_1} = 2\left(\frac{\partial \ln \gamma_2}{\partial m_1}\right)_{m_2} = 2\left(\frac{\partial g}{\partial m_1}\right)_{m_2} \quad (59)$$

$$\left(\frac{\partial \ln \gamma_2}{\partial m_2}\right)_{m_1} = \frac{\mathrm{d} \ln \gamma_2^0}{\mathrm{d}m_2} + \left(\frac{\partial g}{\partial m_2}\right)_{m_1} \quad (60)$$

The first terms on the right of equations 58 and 60 are written as total rather than partial derivatives because they refer to the two binary systems; under side-headings 1 and 2 which follow we describe our calculation of these derivatives from data for the binary systems.

1. Activity Coefficient Derivatives for H_2O–glycine.—The activity and osmotic coefficients of glycine in water[80] have been obtained from freezing point measurements[81] (to 2 molal) and two independent isopiestic measurements[82,83] (to about 3 molal) at 25°. Data for the osmotic coefficient ϕ from the two isopiestic determinations agree quite well.[84] However, the values of ϕ at 25° calculated from the freezing point[81] and thermal data depend on whose thermal data are used: the ϕ obtained by using thermal data of Gucker, *et al.*,[84] lie above, and those obtained with thermal data of Zittle and Schmidt[85] generally lie below, the corresponding ϕ from isopiestic measurements. In the concentration range of interest to us the values of ϕ obtained with thermal data from ref. 85 lie closest to the isopiestic ones. Gucker, *et al.*,[84] have presented the equations[80,86] for ϕ

$$\phi_{SS} = 1 - 0.105m_1 + 0.040m_1^2 - 0.0058m_1^3 \quad (61)$$

$$\phi_{SPZS} = 1 - 0.09632m_1 + 0.02313m_1^2 \quad (62)$$

Here ϕ_{SS} denotes the data of Smith and Smith[82,86] and ϕ_{SPZS} denotes those from ref. 81 and 85. Substitution of equation 61 or 62 into the relation[87]

$$\frac{\mathrm{d} \ln \gamma_1^0}{\mathrm{d}m_1} = \frac{\mathrm{d}\phi}{\mathrm{d}m_1} + \frac{\phi - 1}{m_1} \quad (63)$$

gives, respectively, expressions 64 and 65 for the first term on the right of equation 58

$$(\mathrm{d} \ln \gamma_1^0/\mathrm{d}m_1)_{SS} = -0.210 + 0.120m_1 - 0.0232m_1^2 \quad (64)$$

$$(\mathrm{d} \ln \gamma_1^0/\mathrm{d}m_1)_{SPZS} = -0.19264 + 0.06939m_1 \quad (65)$$

For our calculations we have chosen to use equation 64, which represents the isopiestic data obtained at 25°. As an estimate of the error $\delta(\mathrm{d} \ln \gamma_1^0/\mathrm{d}m_1)$ in the value of this derivative at each composition (see Table VII) we have, for lack of a more reliable indication, used half the difference between the value from equation 64 and the corresponding value from equation 65.

2. Activity Coefficient Derivatives for H_2O–KCl.—The smoothed activity coefficient data at 25°

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and

$$(\hat{D}_{1j})_s = (1000/c_0M_0)\sum_{k=1}^{q} \alpha_{jk}\,(\bar{D}_{1k})_S \quad (V)$$

Here α_{jk} and ϵ_{jk} are defined by equations 10 and 19a, respectively. Conversion of the $(D_{ij})_0$ in columns H–M of Table V to $(\hat{D}_{ij})_0$ and application of equation IV shows that for these six compositions $-(\bar{D}_{21})_0$ has a maximum value of $0.03_1 \times 10^{-8}$ [compared to $-(\hat{D}_{21})_V = 0.01_4 \times 10^{-8}$] at $c_1 = 0.25$ and $c_2 = 0.5$, and a minimum value of $0.01_1 \times 10^{-8}$ [compared to $-(\hat{D}_{21})_V = 0.00_7 \times 10^{-8}$] at $c_1 = 0.5$ and $c_2 = 0.125$. Estimation of the effect of these small but non-zero values of $(\bar{D}_{21})_0$ on the data reported by Roberts and Kirkwood for $\ln(\gamma_2/\gamma_2^0)$ would require extensive calculations including evaluation of the derivative $(\mathrm{d}m_2/\mathrm{d}m_1)$. We do not attempt those calculations in this paper.

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(77) A. J. Staverman, *Trans. Faraday Soc.*, **48**, 176 (1952).

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(79) H. A. C. McKay, *Trans. Faraday Soc.*, **49**, 237 (1953).

(80) The activity coefficients are compared by E. J. Cohn, T. L. McMeekin, J. D. Ferry and M. H. Blanchard, *J. Phys. Chem.*, **43**, 169 (1939).

(81) G. Scatchard and S. S. Prentiss, *J. Am. Chem. Soc.*, **56**, 1486 (1934); **56**, 2314 (1934).

(82) E. R. B. Smith and P. K. Smith, *J. Biol. Chem.*, **117**, 209 (1937).

(83) M. M. Richards, *ibid.*, **122**, 727 (1938).

(84) F. T. Gucker, Jr., H. B. Pickard and W. L. Ford, *J. Am. Chem. Soc.*, **62**, 2698 (1940).

(85) C. A. Zittle and C. L. A. Schmidt, *J. Biol. Chem.*, **108**, 161 (1935).

(86) P. K. Smith and E. R. B. Smith, *ibid.*, **121**, 607 (1937).

(87) See, for example, the equation immediately preceding equation 2.27 of ref. 64.

Table VII

Estimated Errors in Activity Coefficient Derivatives Used in Tests of the ORR

	H	I	J	K	L	M
$\delta(\mathrm{d}\ln\gamma_1^0/\mathrm{d}m_1)$	0.003_0	0.003_0	0.002_9	0.001_3	0.001_3	0.001_3
$\delta(\mathrm{d}\ln\gamma_2^0/\mathrm{d}m_2)$	$.006_9$	$.005_2$	$.003_2$	$.006_0$	$.007_2$	$.004_4$
$\delta(\partial\ln\gamma_1/\partial m_1)$	$.005_5$	$.005_7$	$.004_0$	$.004_8$	$.005_0$	$.003_2$
$\delta(\partial\ln\gamma_1/\partial m_2)$	$.001_3$	$.001_4$	$.001_6$	$.005_3$	$.004_1$	$.013_9$
$\delta(\partial\ln\gamma_2/\partial m_1)$	$.000_7$	$.000_7$	$.000_8$	$.002_7$	$.002_1$	$.006_9$
$\delta(\partial\ln\gamma_2/\partial m_2)$	$.007_1$	$.005_2$	$.005_5$	$.007_7$	$.008_6$	$.006_3$

compiled by Robinson and Stokes[88] were employed to obtain values of $\mathrm{d}\ln\gamma_2^0/\mathrm{d}m_2$. At 0.1 and 0.2 molal the derivatives depended markedly on the technique used to get them; at 0.3, 0.4 and 0.5 molal the various methods gave more concordant values. Numerical differentiation methods which were tried included Stirling's, Bessel's and Newton's formulas[89] as well as Lagrange[90,91] formulas (using not less than 5 nor more than 11 points); the scatter in the derivatives obtained by numerical differentiation seems to be the result of some scatter in the smoothed data. Various empirical equations were also fitted to the data and then differentiated; included were an equation based on hydration[92] refitted from $m_2 = 0.1$ to $m_2 = 0.8$, a relation previously employed in diffusion studies,[93] and several multiconstant polynomials of the form

$$\log\gamma_2^0 = b_1m_2^{1/2} + b_2m_2 + b_3m_2^{3/2} + b_4m_2^2 + b_5m_2^{5/2} \quad (66)$$

which used three to five constants and were fitted to the data from 0.1 to 1.0 molal and also from 0.1 to 2.0 molal. Most final values used for $\mathrm{d}\ln\gamma_2^0/\mathrm{d}m_2$ (given in Table VI) were obtained by averaging the four results from Stirling's, Bessel's, or Newton's formulas to third differences, from the equation[93] in ref. 29 and from the two 5-constant forms of equation 66: the first form was fitted from 0.1 to 1.0 molal with $b_1,\ldots,b_5$ as -0.5085 (Debye–Hückel limiting value), 0.65774, -0.74238, 0.53938 and -0.16539, respectively; the second form was fitted from 0.1 to 2.0 molal with $b_1,\ldots,b_5$ equal to -0.5085, 0.61343, -0.55976, 0.30065 and -0.06529, respectively. The error $\delta(\mathrm{d}\ln\gamma_2^0/\mathrm{d}m_2)$ in this derivative has been taken as the maximum deviation from the average and is reported in Table VII.

B. Molar Activity Coefficient Derivatives, and μ_{kj}.—Values of $\partial\ln\gamma_k/\partial m_l$ shown in Table VI were obtained by substituting into equations 58–60 the appropriate data described above. From unrounded values of the $\partial\ln\gamma_k/\partial m_l$ and other required quantities from Tables V and VI the derivatives $\partial\ln y_k/\partial c_j$ were calculated by using equations 51, 52 and 10. Then these derivatives were substituted into equation 50 to obtain the values of μ_{kj} which are reported at the bottom of Table VI.

Values of the Phenomenological Coefficients.—The coefficients $(L_{ij})_V$ and $(L_{ij})_0$ defined for the volume-fixed and solvent-fixed frames of reference by equations 12 and 11, respectively, can now be calculated from the quantities in Tables V and VI. Because the L_{ij} are coefficients of forces in flow equations for isothermal diffusion, they may be considered more basic than the diffusion coefficients D_{ij} which are coefficients of concentration gradients. From the values of μ_{kj} and α_{lk} the a_{jl} defined by equation 26 were computed and are given in Table VIII; the relation[5] $a_{12} = a_{21}$ provides a check on these calculations. Then the $(D_{ij})_V$ of Table V and the a_{jl} were used with equations 28 and 24 to obtain the $(L_{ij})_V$ which are shown in Table VIII. Also shown in that table are values of $(L_{ij})_0$; they can be obtained from the $(L_{ij})_V$ by using equation 17, or they may be calculated from the $(\hat{D}_{ij})_0$ of Table V and the μ_{kj} by using equations presented elsewhere.[94]

It should be noted that each $(L_{ij})_V$ differs significantly from the corresponding $(L_{ij})_0$ at most of the compositions considered. Inspection of equations 10 and 17 shows that in general these coefficients become identical only at zero concentration of both solutes. Because the values of L_{ij} depend on the frame of reference chosen for the flows and on the choice of forces, it is evident that values of zero for the cross-term coefficients (with $i \neq j$) do not imply an inherent "ideality" of the system. There exists no unique, absolute, standard for describing diffusion in a given system as "ideal" or "without coupled diffusion"; such terms can be useful in classifying systems but they must be assigned arbitrary definitions.

Values of the $(L_{ij})_V$ and $(L_{ij})_0$ in Table VIII provide a direct test of the Onsager reciprocal relations for each of the six compositions studied. According to the ORR these coefficients should satisfy equations 13 and 14 in the forms $(L_{12})_0 = (L_{21})_0$ and $(L_{12})_V = (L_{21})_V$; the agreement between L_{12} and L_{21} is seen to be fairly good for either frame of reference. However, in this paper we do not use this agreement as our main test of the ORR. The accuracy of this test is not indicated directly by estimates of the probable error in L_{12} and L_{21} because errors in the activity coefficient derivatives contribute some uncertainty to both the numerator and the denominator of the expression for each L_{ij}; only the errors in the numerators contribute uncertainty to tests of the ORR because the denominators (the A of equations 28) cancel. The following section presents our main tests of the ORR.

Tests of the Validity of the Onsager Reciprocal Relation.—For these tests we used equation 24 to convert the $(D_{ij})_V$ in columns H-M of Table V to $(\hat{D}_{ij})_V$; then these values and those for the a_{jl} were used to calculate values of the left-hand side (l.h.s.) and the right-hand side (r.h.s.) of equation 29 for each composition. (It is seen from Table VIII that equation 29a is satisfied, so to satisfy the ORR it is necessary and sufficient that l.h.s.

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[88] Ref. 64, Appendix 8.3, Table I.

[89] K. S. Kunz, "Numerical Analysis," McGraw-Hill Book Co., Inc., New York, N. Y., 1957.

[90] H. E. Salzer, "Table of Coefficients for Obtaining the First Derivative without Differences," National Bureau of Standards Applied Mathematics Series-2, U. S. Government Printing Office, Washington, D. C., 1948 (to 7 points).

[91] J. Kuntzmann, "Formules de Dérivation Approchée au Moyen de Points Équidistants," Societé d'Electionique et d'Automatisme, Courbevoie (Seine), 1954 (to 11 points).

[92] D. G. Miller, *J. Phys. Chem.*, **60**, 1296 (1956).

[93] Equation 6 of ref. 29. The constants of that equation had been evaluated using Table 11 in Appendix 8.10, instead of Table 1 of Appendix 8.3, of ref. 64.

[94] Equations 1d–1i of ref. 4.

TABLE VIII[a]

PHENOMENOLOGICAL COEFFICIENTS[b] $(L_{ij})_V$ AND $(L_{ij})_0$ FOR SIX COMPOSITIONS OF THE SYSTEM H_2O–GLYCINE–KCl AT 25°

1 = glycine; 2 = KCl

	H	I	J	K	L	M
a_{11}/RT[c]	3.91730	3.92984	3.94832	1.94280	1.95641	1.97602
a_{12}/RT	−0.11833	−0.07328	−0.02598	−0.08885	−0.04946	−0.01081
a_{21}/RT	−0.11833	−0.07328	−0.02598	−0.08885	−0.04946	−0.01081
a_{22}/RT	14.67605	7.31904	3.70406	14.79655	7.37646	3.73346
$A/(RT)^2$[d]	57.47644	28.75728	14.62414	28.73885	14.42897	7.37727
$(L_{11})_V \times RT \times 10^8$	0.25899	0.25889	0.25797	0.50207	0.50110	0.49806
$(L_{12})_V \times RT \times 10^8$	.00064	.00017	− .00027	.00058	− .00029	− .00008
$(L_{21})_V \times RT \times 10^8$	.00096	− .00018	− .00030	.00166	− .00217	− .00423
$(L_{22})_V \times RT \times 10^8$	.12219	.24531	.48605	.11839	.23768	.46724
$(L_{11})_0 \times RT \times 10^8$	.26482	.26475	.26394	.52525	.52441	.52167
$(L_{12})_0 \times RT \times 10^8$	.00300	.00493	.00942	.00528	.00919	.01918
$(L_{21})_0 \times RT \times 10^8$	.00332	.00457	.00939	.00638	.00725	.01488
$(L_{22})_0 \times RT \times 10^8$	.12309	.24895	.50093	.11929	.24130	.48199

[a] More figures than are significant are retained in this table to be consistent with the numbers shown in Table VI and to reduce accumulation of errors in future calculations. From the errors indicated in footnote *c* of Table IX, it may be estimated that the values shown for the $(L_{ij})_V \times RT \times 10^8$ and $(L_{ij})_0 \times RT \times 10^8$ are correct within a few parts in the third figure after the decimal point. It is seen that $(L_{12})_V = (L_{21})_V$ and $(L_{12})_0 = (L_{21})_0$ within this approximate estimate of error and also that the $(L_{12})_V$ and $(L_{21})_V$ for this system are not significantly different from zero in the range of composition studied. As indicated in the text, these values of zero for $(L_{12})_V$ and $(L_{21})_V$ do not necessarily indicate the absence of "coupling" of the solute flows in any absolute sense. [b] The coefficients $(L_{ij})_V$ and $(L_{ij})_0$ are for flow equations expressed in moles of the components. [c] The a_{ij} are defined by equation 26. [d] Defined by equation 28a.

TABLE IX

TESTS OF THE ONSAGER RECIPROCAL RELATION FOR SIX COMPOSITIONS OF THE SYSTEM H_2O–GLYCINE–KCl AT 25°

	H	I	J	K	L	M
(l.h.s. 29) × $(10^8/RT)$[a]	−0.295	−0.201	−0.077	−0.226	−0.139	−0.030
(r.h.s. 29) × $(10^8/RT)$	− .277	− .211	− .077	− .195	− .166	− .061
Difference[b]	.018	− .010	.000	.031	− .027	− .031
Probable error[c]	± .076	± .043	± .027	± .075	± .039	± .036

[a] See equation 29. [b] This difference is (r.h.s. 29 − l.h.s. 29) × $(10^8/RT)$. [c] Based on an estimated error of $\pm 0.005 \times 10^{-5}$ in each $(D_{ij})_V$ and on errors given in Table VII for the activity coefficient derivatives; the errors in the $\bar{V}_i$ and the c_i were neglected as they were too small to affect the probable errors shown.

29 = r.h.s. 29.) Values of the two sides of equation 29 for each composition are given in the first and second lines of Table IX; the difference (r.h.s. − l.h.s.) is recorded in the third line. This simple difference is shown instead of, for example, the per cent. difference because it is independent of how equation 29 is written: the difference expressed as a percentage would depend on the magnitudes of l.h.s. 29 and r.h.s. 29 (*i.e.*, on how the terms from equation 28 are arbitrarily grouped when forming the two sides of equation 29). To indicate whether the differences reported in the third line exceed those expected from the estimated errors of measurement, the probable error[95] in each difference is shown in the fourth line. These estimated errors were calculated from the errors indicated in footnote *c* of Table IX; errors in the activity coefficient derivatives contributed a negligible amount except in column M where they represented about 2/3 of the total probable error. As an indication of how much the terms $\partial \ln \gamma_k / \partial m_l$ contribute to the tests of the ORR, we note that if all four of these molal activity coefficient derivatives are arbitrarily set equal to zero the values of the differences (r.h.s. 29 − l.h.s. 29) × $(10^8/RT)$ for columns H-M become −0.178, −0.173, −0.122, −0.137, −0.169 and −0.140, respectively.

It is seen from Table IX that the experimental data satisfy the ORR within the estimated error for each of the six compositions chosen for the present study of this system. These tests represent some improvement over earlier tests: the estimated error ($\pm 0.005 \times 10^{-5}$) in each $(D_{ij})_V$ for this system is somewhat less than that for most systems studied previously,[4-7] and the activity coefficient data were available for the same range of concentrations as the data from the diffusion measurements.

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(95) Defined by equation 74 of ref. 5.