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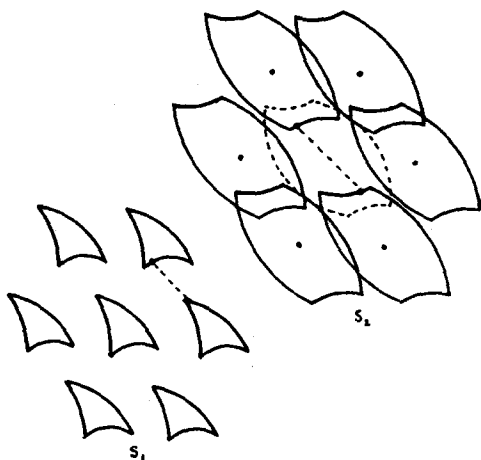

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FIG. 1.

origin in S_2 which records the Patterson of a single unit of pattern, provided there is a minimum distance of approach of the units of pattern in neighboring cells in S_1.

Figure 1 depicts the case of a two-dimensional crystal with a single molecule as its unit of pattern. With a minimum approach k between molecules, there is an "intra-molecular" region about the origin in S_2 which extends at least to a circle of radius k. To define this region more precisely, we take a number of directions in turn and observe the closest approach of molecules in each case. Erecting these vectors at the origin in S_2, we get points on the boundary of the region—actually pairs of points, since the Patterson map has a center of symmetry in the origin. For the corresponding three-dimensional cases, the situation may be described in similar terms.

The question then arises as to the type of information, if any, which is implicit in this restricted part of the Patterson map of an individual molecule. The answer is clear on general grounds. All entries in a Patterson map in the neighborhood of the origin are caused by local situations within the molecule, i.e., by the fine structure of the
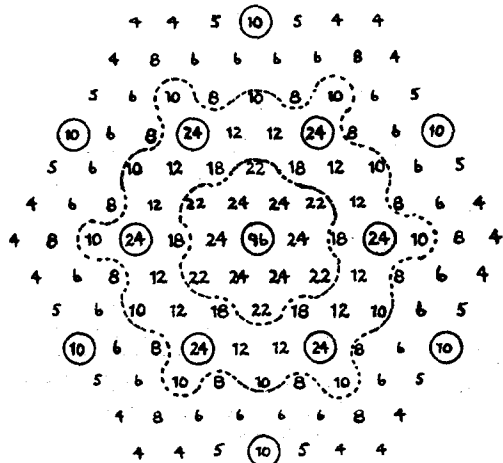

FIG. 2.

molecule. As an example of a case in which the Patterson near the origin bears marks of the fine structure of a point set in S_1, we give in Fig. 2 the central section of the Patterson normal to a trigonal axis of a 96-point set on the surface of an octahedron.[3]

In the case of a molecular crystal with more than a single molecule in its unit of pattern, the case is more complicated but there is still the possibility of obtaining some hint from the Patterson map of the crystal regarding the fine structure, if any, of the molecules. It is still true that the Patterson near enough to the origin depends only upon local situations within the unit of pattern, i.e., upon neighborhood situations within the individual molecules. For, suppose there are two molecules A and B in the unit of pattern which are not necessarily parallel displacements of one another and may even be different structures. The Patterson of $A+B$ is the Patterson of A plus the Patterson of B plus the Patterson interactions of A on B and of B on A.[4] If the nearest approach of A and B is k', the cross interactions do not come nearer to the origin than k'. There is, therefore, a region around the origin in which the Patterson is simply the sum of the individual Pattersons of A and B; the same type of situation obtains with any number of molecules in the unit of pattern.

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[2] D. Wrinch, Phil. Mag. 27, 490 (1939).
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Application of Radioactive Isotopes to the Problem of Diffusion of Electrolytes in Aqueous Solutions

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THE diaphragm cell has been used extensively in studying the problem of the diffusion of ions in solution. The method reduces the problem to a one dimensional case. The starting point in one dimensional diffusion studies is usually

$$\frac{\partial c}{\partial t} = \frac{\partial}{\partial x}\left(\mathfrak{D}\frac{\partial c}{\partial x}\right), \tag{1}$$

where $\mathfrak{D}$ is the diffusion coefficient. $\mathfrak{D}$ is then taken as a first approximation to be independent of concentration, whence Fick's law results:

$$\frac{\partial c}{\partial t} = \mathfrak{D}\frac{\partial^2 c}{\partial x^2}. \tag{2}$$

Equation (2) has been integrated in many forms, and it is evident the equation involves an average or integral diffusion coefficient, as it is known experimentally that $\mathfrak{D}$ is not independent of c. The diffusion coefficient of an electrolyte at infinite dilution was first calculated by Nernst[1] to be

$$\mathfrak{D}° = 17.863\times10^{-10}T\left(\frac{\lambda_+°\lambda_-}{\Lambda°}\right), \tag{3}$$

where the symbols have their usual meaning. By using the Debye-Hueckel theory, Onsager and Fuoss[2] were able to obtain the following equation for the dependence of the diffusion coefficient on concentration:

$$\mathfrak{D} = 16.632 \times 10^{+10} T \left(\frac{\tilde{m}}{c}\right)\left(1 + c\,\frac{\partial \ln y_{\pm}}{\partial c}\right), \qquad (4)$$

where $y_{\pm}$ is the mean ionic activity coefficient, and the mobility term $(\tilde{m}/c)$ is a complicated function of the viscosity, the concentration, and the equivalent conductance at infinite dilution of the ions and compound. The slowness of diffusion makes it so that experiments are quite difficult and of long duration. Because of the difficulty in obtaining accurate analytical data, experiments in the region where the Debye-Hueckel theory is taken to be valid have been heretofore almost impossible. Onsager and Fuoss[2] were unable to obtain results below $0.05N$ with which to test their equation. Greater dilutions have been studied by experimenters, using optical methods for analysis, but Longsworth[3] says: ". . . This probably indicates that the optical methods in current use for the study of free diffusion, while capable of yielding results that are accurate within a few percent, we are not yet sufficiently sensitive for work of high precision, especially in the regent of dilute solutions for which the theory is valid."

In the Physics Laboratory at Howard, studies on diffusion of ions in solution have been undertaken using the radioactivity of isotopes as the analytical tool. The explicit assumption is made that the radioactive isotope behaves in exactly the same way as the non-radioactive isotope (in spite of the slight difference in mass). A given amount of active salt was added to a liter of $0.1M$ solution, in preliminary tests, and several more dilute solutions were prepared from this. It was found that the counts per minute, registered on a Geiger-Mueller counter and scaling circuits, from a definite quantity of each solution were a linear function of the concentration, as would be expected. Preliminary trials have indicated that this technique will give better results than any of the previous analytical methods. We have found it possible to work with solutions of $10^{-6}M$ without difficulty. Results obtained will be reported to this journal soon.

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Propagation of Ultrasonic Waves Through Liquid Mixtures and the Dynamics of Their Molecular Interaction

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IN some previous papers,[1,2] a theoretical background was developed for discussing the variation of ultrasonic velocity with molecular structure of pure liquids and liquid mixtures. It was shown that it is compressibility and not sound velocity that is a fundamental property from the point of view of molecular structure. One significant conclusion was that association would raise the value of compressibility. The mixtures analysed were water alcohol (methyl ethyl, propyl), benzene-ethyl alcohol, benzene-carbon tetrachloride, butyl alcohol-heptane, benzene-ether, ethyl acetate-carbon tetrachloride, chloroform-acetone, and chloroform-ether.[1,3,4] On the experimental side, maxima of velocity (and minima of compressibility) were obtained for water alcohols, a minimum of velocity for chloroform-ether, and inflexion of velocity curve for benzene-alcohol. It was shown that in water-alcohol mixtures, there is mutual depolymerization of the components that gives rise to minima of compressibility.

Experimental data for a number of other mixtures were taken as far back as in 1940, at the Bose Institute, Calcutta, and their analysis has recently been completed.[5] They are ethyl alcohol-chloroform, ethyl alcohol-carbon tetrachloride, benzene-chloroform, ether-alcohol, water-glycerine, chloroform-carbon tetrachloride and sodium chloride+water+ethyl alcohol. Moreover, analysis of experimental data of other workers for acetone-water and acetic acid-water[7] has also been attempted. In the following we state some of the more important experimental facts and derivations therefrom.

Alcohol-Chloroform.—The velocity and compressibility curves are inflected, the compressibility being less than the ideal values on the alcohol-rich side, and greater than the ideal on the chloroform-rich side. It is concluded that the chloroform molecules can partially depolymerize alcohol association on the alcohol-rich side, without all the molecules so dissociated being attached to chloroform molecules. These dissociated molecules are in strong force-fields and cause lowering of compressibility. The finding is in direct contrast to that of Raymond and Scatchard.[8] Because of the tendency of alcohol molecules to associate with themselves and, simultaneously, with chloroform, a dynamical equilibrium results, resulting in part of the moecules being dissociated. Because of tendencies for a particular class of molecules to associate in two different systems, what actually results depends upon the strength of the two tendencies, and the structure of the different possible association systems. The name "dynamics of liquid mixtures" has been proposed to denote this sort of dynamical interaction.

Water-Glycerine.—The velocity is more and compressibility less than the ideal values all through the range. It is derived that the association of water is broken down, but that of glycerine incompletely, because of its relatively great strength.

Chloroform-Carbon Tetrachloride.—The velocity curve shows a slight minimum, and the compressibility is greater than the ideal values. It is derived that the value of compressibility of chloroform in the pure state, lower than that of carbon tetrachloride, is not directly due to its dipolar activity, but due to the greater intermolecular action involved because of its particular molecular shape. Two Cl atoms of a chloroform molecule can approach two Cl atoms of another molecule because of the dip in its otherwise symmetrical molecular shape, caused by the small size