PattersonHarker Maps of Molecular Crystals

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point, the procedure is repeated, and a little consideration shows that this technique leads to the minimization of R_n.

Two expressions are available for the change ϵ_{rj} in any coordinate x_{rj}:

$$\epsilon_{rj} = -2R_n(\partial R_n/\partial x_{rj})/\sum_{rj}(\partial R_n/\partial x_{rj})^2$$

or:

$$\epsilon_{rj} = -[\sum_{rj}(\partial R_n/\partial x_{rj})^2](\partial R_n/\partial x_{rj})/$$

$$\sum_{rj,\,r'j'}(\partial^2 R_n/\partial x_{rj}\cdot\partial x_{r'j'})(\partial R_n/\partial x_{rj})(\partial R_n/\partial x_{r'j'}).$$

The first expression should be used only so long as the coordinates are far from their final values and is particularly simple to compute; whilst the second equation applies up to the minimum itself.

A particularly interesting variant of the method is available when a sufficiently large number of planes of zero observed intensity is available (excluding zeros due to symmetry elements). In this case the expressions:

$$O_1 = \sum_{hkl} |F_{calc}|$$

$$O_2 = \sum_{hkl} F_{calc}^2$$

taken over all planes of zero observed intensity can be minimized, and the resulting calculations are much simplified.

Simple extensions enable the position of a fixed molecular shape to be found such that R_n is minimized. This is done either by referring the molecule to an axial system, whose orientation and origin are then varied, or by taking three atoms of the molecule as standards and minimizing R_n in such a way that all inter-atomic distances remain fixed. When a molecule contains known groupings related to one another by free rotations, a slightly more general approach enables the same methods to be applied.

Finally, it is possible to use the technique to obtain density distributions which minimize R_n, although there, particular care has to be taken to obtain a stereo-chemically plausible starting distribution.

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Upper Limit to the Tritium Content of Ordinary Water

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IN 1938 Sherr, Smith, and Bleakney[1] concluded from mass spectrographic measurements, using deuterium gas, that the tritium content of ordinary water is less than one part in 10^{12}. It has been established by the experiments described below that the tritium atom fraction in ordinary water is less than one part in 10^{17}. An extension of this technique should lead to a smaller upper limit to the abundance of this isotope.

22-mm partial pressure of deuterium gas, having a D content greater than 95 percent,[2] was added to a glass envelope copper gauze cathode Geiger-counter tube having a diameter of 42 mm, an effective counting volume of 200 cc and containing 23-mm partial pressure each of argon and ethyl alcohol. The normal background count, employing a $\frac{3}{8}''$ lead shield was 2.85 counts per second. The addition of the deuterium gas did not change the the counting rate within the precision of the measurements. The average deviation of this measurement (based upon four independent experiments) was 0.03 counts per second. The latter value was used in calculating the upper limit to tritium abundance.

Using the above data and a tritium half-life of 31 years,[3] the tritium atom fraction in ordinary water is less than $1.5\times10^{-13}(T^\circ/T)$, where (T/T°) is the factor by which the tritium was enriched in the electrolysis of normal water from 99.98 percent H to the final D content. Using 95 percent for the latter, the initial-volume/final-volume water ratio was calculated from the $H-D$ cathodic separation factor. The ratio (T/T°) was calculated from this volume ratio and the $H-T$ separation factor.[4] For $H-D$ and $H-T$ separation factors of 5 and 10, respectively, (T/T°) equals 2.0×10^4. For corresponding factors 6.5 and 13, respectively, (T/T°) equals 1.3×10^4. Taking (T/T°) as 1.5×10^4, the tritium atom fraction in ordinary water is less than one part in 10^{17}. By exhaustive electrolysis of heavy water, it will be possible to decrease the magnitude of this upper limit. The latter is of interest, inasmuch as tritium is a possible reaction product in nuclear processes taking place in the earth's atmosphere.[5]

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Patterson-Harker Maps of Molecular Crystals

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THE interpretation of the x-ray data obtained from megamolecular crystals presents a new and difficult problem in cases where the structure and even the composition of the molecular units are unknown. If an attack be attempted by way of Patterson and Patterson-Harker maps, computed from the experimental data, a useful, even necessary preliminary is the study of the Patterson maps of various structure types.[1] A fundamental difficulty, however, arises at the outset owing to the overlapping in Patterson space S_2 of the Pattersons of individual molecules in the crystal in atomic space S_1^2. The purpose of this note is to draw attention to and indicate some of the implications of the fact that there is always a region about the
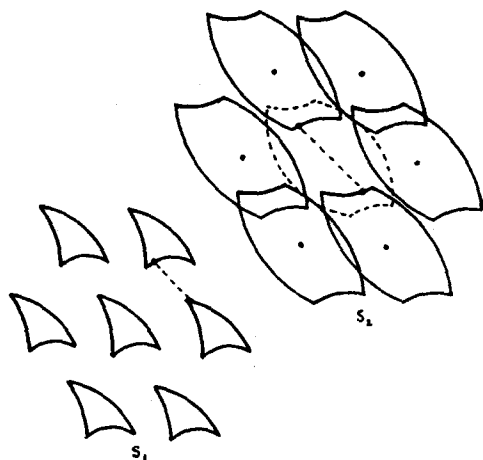
FIG. 1.

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
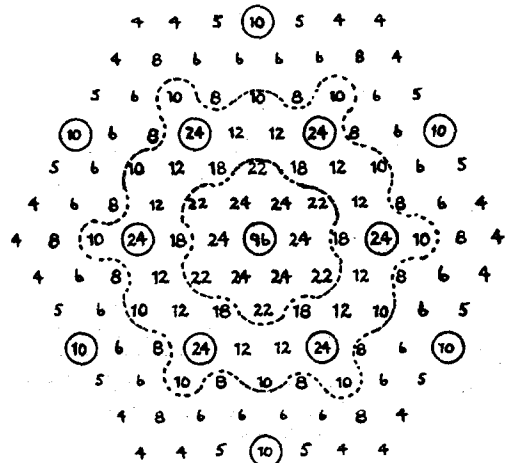

FIG. 2.

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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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

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