



Fig. 3.—Difference synthesis showing electronic anisotropy. Contours at intervals of $0.5 \text{ e.}\text{\AA}^{-2}$, zero contour omitted, negative contour broken.

the bond lengths differs significantly from expected values, and all bond angles are close to expected values.

The hydrogen bond arrangement is of particular interest. Difference syntheses and C—O bond lengths confirm the expectation of a neutral carboxyl and a charged amino group inferred from the fact that the crystals were grown from a highly acid solution. One H atom is bonded to the O₂ atom and three to the N atom. Each of these H atoms is involved in a hydrogen bond to Cl⁻ and together make essentially a tetrahedral matrix of H atoms about each Cl⁻.

A Cl⁻ which is hydrogen bonded to three appropriately spaced charged amino groups may have some significance in protein structures. Three such groups would strongly attract chloride ions and bind them more tightly than widely spaced groups.

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A Generalization of the Frit Method for the Measurement of Diffusion Coefficients

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The frit method for determining diffusion coefficients, which was originally developed for cylindrical frits with sealed edges, applies for frits of any shape.

1. Wall, Grieger and Childers have described a simple method for measuring diffusion coefficients of substances in liquid solutions.¹ It consists of soaking a circular disc of porous material with sealed edges (or a thin, non-sealed disc) in the solution of the diffusing substance and then suspending the disc in a bath of pure solvent. The apparent weight of the suspended disc is determined at various times. The change of weight corresponds to the loss of solute by diffusion. For large t the amount of solute in the disc, $Q(t)$, decreases exponentially with t , *i.e.*

$$\log Q(t) \sim -\alpha Dt + \beta \quad (t \rightarrow \infty) \quad (1)$$

where the constant α depends on the thickness and porosity of the disc used. It is obvious that from such an experiment the value of D can be calculated after determining α by a calibration experiment.

(1) F. T. Wall, P. F. Grieger and C. W. Childers, *THIS JOURNAL*, **74**, 3562 (1952); see also F. T. Wall, *et al.*, *ibid.*, **75**, 3550, 6340 (1953).

2. As indicated in Wall's paper, the theoretical basis of this method is as follows. For "one-dimensional diffusion" out of a homogeneous cylindrical disc we have (see *c.g.*)²

$$Q(t) = Fdc_0 \frac{8}{\pi^2} \sum_{\nu=0}^{\infty} \frac{1}{(2\nu+1)^2} \exp[-Dt(2\nu+1)^2\pi^2/d^2] \quad (2)$$

where $Q(t)$ is the amount of diffusing substance in the disc at time t as before, F and d are area and thickness of the disc, respectively, and c_0 is the uniform initial concentration of the diffusing substance in the disc.

It is safe to assume that (2) applies to a porous disc as well, if only d is replaced by the "effective thickness" d' and similarly F by F' . Then from

(2) P. Frank, R. v. Mises, "Differential- und Integralgleichungen der Physik," Vol. II, M. S. Rosenberg, New York, N. Y., Reprint, 1943, p. 557f.

(2) the relation 1 follows immediately, and we have

$$\alpha = \frac{\pi^2}{d'^2 \cdot 2.303} \tag{3}$$

“One-dimensional diffusion” is achieved experimentally by sealing the edges of the disc so that there is no sideward diffusion. If the edges are not sealed, equation 2 has to be replaced by a more complicated one. However, an examination of this equation shows—we are quoting Wall’s paper—“that for thin frits $\log Q(t)$ should be still linear in Dt . For the thickest frits used a correction of only 3% was necessary because of sideward diffusion. In any event, if measurements are made on two different solutions using the same frit, the ratio of slopes should be equal to the ratio of diffusion coefficients.”

3. It would seem from what has been published about the frit method, that it is limited to frits of special shape, *i.e.*, thin cylindrical discs, if possible with sealed edges. In this communication we shall show that such a limitation does not exist; *i.e.*, that the above procedure can be performed with frits of any shape (even irregular and unknown) and the experiment is evaluated by using formula 1 as before. The basis of this generalization is the following mathematical theorem.

4. *Theorem.* Let T be a three-dimensional body, *e.g.*, with a piecewise continuously curved surface S and the initial concentration $c_0(\xi)$ of the diffusing substance be twice continuously differentiable for $\xi \in T$. Then, if diffusion takes place in T and for all $t > 0$ the boundary condition

$$c(\xi, t) = 0 \quad (\xi \in S, t > 0) \tag{4}$$

holds, $Q(t)$ is given by

$$Q(t) = \sum_{\nu=0}^{\infty} Q_{\nu} e^{-\lambda_{\nu} Dt} \tag{5}$$

From this (1) follows immediately.

Proof. The diffusion equation to solve is

$$\frac{\partial c}{\partial t} = D \Delta c \quad (\xi \in T, t \geq 0) \tag{6}$$

with initial concentration $c_0(\xi)$ and boundary condition (4). Now it is seen easily that for any fixed λ the function

$$c = u(\xi) e^{-\lambda Dt}$$

is a solution of (6) and (4), if $u(\xi)$ satisfies the relations

(3) ξ stands symbolically for (x, y, z) .

$$\Delta u + \lambda u = 0 \quad (\xi \in T) \tag{7}$$

$$u(\xi) = 0 \quad (\xi \in S) \tag{8}$$

The treatment of equations 7 and 8 leads, as known, to the following result.⁴

There exists an infinite sequence of positive eigenvalues λ_{ν} ($\nu = 0, 1, \dots$) for which (7) has solutions $\varphi_{\nu}(\xi)$ satisfying (8). Furthermore any function $c_0(\xi)$ with the above properties⁵ can be developed into an uniformly convergent Fourier series in terms of $\varphi_{\nu}(\xi)$; *i.e.*

$$c_0(\xi) = \sum_{\nu=0}^{\infty} a_{\nu} \varphi_{\nu}(\xi) \quad (\xi \in T) \tag{9}$$

So the (unique) solution of our diffusion problem becomes

$$c(\xi, t) = \sum_{\nu=0}^{\infty} a_{\nu} \varphi_{\nu}(\xi) e^{-\lambda_{\nu} Dt} \tag{10}$$

If we now put

$$Q_{\nu} = \int_T a_{\nu} \varphi_{\nu}(\xi) d\tau \tag{11}$$

we have at once the stated relation (5).

As in section 2 we may apply these formulas not only for homogeneous bodies but for porous bodies as well.⁶ Therefore from (5) it follows that the relation 1 applies to porous frits of any shape as stated above.

We have not investigated so far, how long it takes for bodies of different shape but of equal volume to “reach” the asymptotic behavior (1), although this problem would be of interest.

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(4) Ref. 2, Vol. I, p. 829ff.

(5) In the case of the frit method $c_0(\xi)$ is of course a constant c_0 .

(6) The argument on porosity given in section 2 is no longer necessary; because of its generality the stated theorem may be applied directly to the pores of the frit.