

Silent discharge at low pressures and corona discharge at atmospheric pressure both respond to the presence of vapour in a manner similar to the devices previously described. They suffer, however, the disadvantage that the emission of electrons from their electrodes is disturbed by the presence of vapour and it is difficult in practice to obtain consistent and reproducible operation.

The methods of vapour concentration measurement just described possess the advantages of exceptional sensitivity and freedom from disturbance by changes in ambient temperature, pressure and gas flow-rate. They are particularly suitable for use with gas chromatography apparatus.

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April 8.

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³ Lovelock, J. E., James, A. T., and Piper, E. A., *Ann. N.Y. Acad. Sci.* (in the press).

Conditions for Differential Reaction of 'Identical' Chemical Groups

ATTENTION was first directed to the principles involved in explaining the differential reaction of two 'identical' groups in a single molecule by Ogston¹, and they have been further discussed and generalized by Wilcox², Schwartz and Carter³ and most recently by Hirschmann⁴. Since a recent review⁵ seems to hold that the views of these authors (in particular those of Ogston and of Schwartz and Carter) are in some ways contradictory, and since Hirschmann's excellent article appears to be too little known, a brief re-statement is attempted. Ogston's and Schwartz and Carter's views are in fact complementary (as Hirschmann shows), each being explicit about an aspect of the matter which the other takes for granted.

The molecules under discussion are all of the type in which the two 'identical' groups are so by virtue of a symmetry operation of the molecule as a whole, which changes an object into its mirror image. For example, each *a* group in the molecule *Caabd* is, in relation to the surrounding *a*, *b* and *d* groups, the mirror image of the other. However, two such enantiomorphic situations can be discriminated only by means of an asymmetric agent as, for example, an asymmetric observer who contemplates a model of the molecule, an enzyme (as discussed by Ogston), or an optically active amine in the reactions discussed by Schwartz and Carter.

The actual process of discrimination may take one of several forms. It may involve reaction or response by the asymmetric agent, for example, by a sign of recognition on the part of the observer of the model; or reaction by the molecule which contains the 'identical groups', as in the cases considered by Ogston: or reaction of both, as in the cases considered by Schwarz and Carter. In each case, the essential feature is the dependence of the reactivity of the system upon the mutual orientation of its parts. The phenomenon of discrimination is not ascribable to either part separately, but to the relationship between both.

This consideration shows that the notion of 'three-point-attachment' used by Ogston is not misleading, though it is not, of course, to be taken as a literal description of the forces acting between two mole-

cules. It does correctly express the uniqueness of any particular mutual orientation of an asymmetric molecule and one which contains two 'identical' groups, upon which the reactivity must depend; it does not matter whether this dependence is absolute or relative.

I am grateful to Dr. D. M. Hodgkin for discussion.
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March 28.

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³ Schwartz, P., and Carter, H. E., *Proc. U.S. Nat. Acad. Sci.*, **40**, 499 (1954).

⁴ Hirschmann, H., in "Essays in Biochemistry", 156, edit. by Graff, S. (John Wiley and Sons, Inc., New York, 1955).

⁵ Korke, S., "Ann. Rev. Biochem.", **25**, 685 (1956).

An Ultrasonic Investigation of Chemical Kinetics in Manganous Sulphate Solutions

EXCESS sound absorption in magnesium sulphate solutions was ascribed by Liebermann¹ to either a unimolecular or dissociation-type process involving magnesium sulphate molecules or its ions. Wilson² found the process to be unimolecular. Barthel³ modified the work of Wilson and found that Wilson's work fitted equally well to the unimolecular or dissociation type process.

In order to determine the mechanism responsible for excess sound absorption in manganous sulphate the effect on sound absorption of varying the concentration of the salt and dielectric constant of the solvent has been studied. This should shift the dissociation equilibrium and so have a marked effect on sound absorption. Theoretical interpretation of the results follows that of Bies⁴ for magnesium sulphate solutions.

The exact nature of the relationship between the excess sound absorption and concentration in the case of manganous sulphate is not well known, as the results of Kurtze and Tamm⁵ and of Wilson differ for sound absorption in electrolytic solutions. Hence the variation with concentration of the excess sound absorption in manganous sulphate solution was studied in great detail in the range 0.0025–1 *M*. The graph of a/v^2 against frequency (Fig. 1) shows that the absorption a/v^2 decreases with increase in frequency. The plot of $a'\lambda$ (excess sound absorption \times wave-length) against frequency reveals the existence of a relaxation frequency near 3 Mc./s., which increases in the range 0.0025–0.02 *M* but is independent of the concentration in the range 0.02–0.1 *M* and again varies slightly above 0.1 *M*.

In order to determine the mechanism responsible for excess sound absorption in manganous sulphate solutions, ultrasonic absorption in water-dioxan mixtures of dielectric constant equal to 56.5 and 48.0 e.s.u. was studied at different concentrations of manganous sulphate. Absorption was found to increase considerably with the decrease in the dielectric constant of the solvent which is also the case with $a'\lambda$. This supports the dissociation hypothesis, as the variation of the dielectric constant of the solvent should lead to the disturbance of the equilibrium in the case of dissociation reaction and influence the absorption.

In order to confirm the dissociation hypothesis further in the case of manganous sulphate, variation of the specific rate of association (K_2) with the change in the reciprocal of the dielectric constant