

ments on palladium, nickel, rhodium and platinum, and we intend to extend our measurements to other metals, and to investigate how the Fermi-level changes during an actual catalytic reaction. The foregoing theoretical treatment with further development should enable us to correlate resistance and magnetic measurements during chemisorption, which has not been satisfactorily achieved to date.

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### Study of some of the Parameters involved in Split-stream Chromatographic Injection

THE two essential requirements placed on a split-stream injector are that: (1) the injected sample be uniformly distributed in the split stream as the splitting point is reached; (2) the width of the splitted portion entering the column be appreciably smaller than the eventual width of all the eluted components.

It will be assumed in the investigation that follows that the injected sample, if liquid, is not vaporized sluggishly, and that the wall of the mixing tube connecting the injected point to the splitting point does not retain the sample. The first of these effects would interfere with good sample distribution in the split stream, and the second would cause tailing of the portion injected in the column.

Let  $L$ ,  $S$ ,  $D$  and  $F$  designate the length and cross-section of a round mixing tube, the diffusion constant of some component of interest and the volumetric flow of the split stream. The time required for substantial diffusion of a molecule packet across the mixing tube is of the order of  $S/D$  and the time  $aS/D$  will be allotted to this event,  $a$  being a 'safety factor' larger than unity intended to allow for nearly completely uniform diffusion of the component in the mixing tube. The velocity of the carrier gas being  $F/S$ , the length of an adequately long mixing tube should be at least the product of that velocity times the allotted diffusion time, that is:

$$L \geq a \frac{S}{D} \cdot \frac{F}{S} = a \frac{F}{D} \quad (1)$$

This length is notably independent of tube size.

The height equivalent to a theoretical plate ( $H$ ) of the mixing tube is given by the expression:

$$H = 2 \frac{DS}{F} + \frac{F}{24\pi D}$$

and since fairly large splitting ratios will be aimed at, for which the velocity will be appreciably higher than that required for minimizing the expression above,  $H$  will be given with sufficient accuracy by:

$$H \approx \frac{F}{24\pi D}$$

The space variance of any component distribution after travelling along the mixing tube of length  $L$  will be  $LH$  and the volumetric variance will be:

$$W = S^2 L H = S^2 a \frac{F}{D} \frac{F}{24\pi D} = \frac{a S^2 F^2}{24\pi D^2}$$

Let  $N$  designate the splitting ratio. The volumetric variance  $w$  of the component entering the column will be:

$$w = W = \frac{a S^2 F^2}{24\pi N^2 D^2}$$

and its space variance will be:

$$\frac{w}{s^2} = \frac{a S^2 F^2}{24\pi N^2 D^2 s^2}$$

where  $s$  designates the open tubular column cross-section. This variance should be appreciably smaller than the variance of the inert component eluting from the column, which is itself smaller than the variance of the retarded components. This variance is, at optimum velocity:

$$l \sqrt{\frac{s}{3\pi}} = \frac{1}{3\pi} n s$$

where  $l$  designates the column length, and  $n$  its number of plates.

At optimum velocity for any component, the column flow is a fraction  $1/c$  of the optimum flow for the inert component,  $c$  being usually between 2 and 3:

$$f = \frac{1}{c} D \sqrt{48\pi s}$$

hence:

$$F = N f = \frac{N D}{c} \sqrt{48\pi s} \quad (2)$$

and we should have:

$$\frac{a S^2 F^2}{24\pi N^2 D^2 s^2} = \frac{a S^2 48\pi N^2 D^2 s}{24\pi c^2 N^2 D^2 s^2} \leq \frac{1}{b} \frac{n s}{3\pi}$$

or:

$$S \leq c s \sqrt{\frac{n}{6\pi a b}} \quad (3)$$

where  $b$  designates a second 'safety factor', larger than unity, designed to ensure that the main contribution to any band variance is that due to the band passage in the column.

Substituting the value of  $F$  from equation (2) in equation (1) we obtain:

$$L \geq a N \sqrt{48\pi s} \quad (4)$$

Equations (3) and (4) constitute two essential constraints on the mixing tube, giving as they do an upper bound on its cross-section and a lower bound on its length.

M. J. E. GOLAY

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### Stereospecific Catalytic Labelling of Amino-acids and Mandelic Acid with Isotopic Hydrogen

A COMPARISON has been made between the catalytic labelling<sup>1</sup> of organic compounds with deuterium and tritium and radiation-induced techniques<sup>2</sup>. Of fundamental importance in deciding the choice of method, particularly for tracer applications, is the possible change in configuration which may occur during substitution by isotopic hydrogen. In radiation-induced procedures, a preference for retention of configuration has been observed in crystalline systems such as the octyl phthalates<sup>3</sup> and inositols<sup>4</sup>, whereas a predominance of inversion occurs in the liquid octanols and inositol ethers<sup>5</sup> and in simple amino-acids<sup>6</sup>. In the catalytic technique, results from the only heavy-water system studied show that, in optically active lactic acid, deuteration of the  $\alpha$ -position is generally accompanied by inversion<sup>7</sup>.