ion, and (*c*) as a catalyst for the electron transfer process:

$$d[\mathrm{Coen}_3]^{3+}\ \text{spin-paired} + l[\mathrm{Coen}_3]^{2+}\ \text{spin-free} \rightarrow$$
$$l[\mathrm{Coen}_3]^{3+} + d[\mathrm{Coen}_3]^{2+} \rightleftharpoons l[\mathrm{Coen}_3]^{2+}$$

Activated carbon is known to be capable of effecting mild reductions in aqueous solution, for example, ferric to ferrous ion, but would not be expected to reduce the spin-paired $[\mathrm{Coen}_3]^{3+}$ ion because of the negative potential of couple $[\mathrm{Coen}_3]^{3+}$ spin-paired/$[\mathrm{Coen}_3]^{2+}$ spin-free ($E_0 = -0{\cdot}232$ V.)[3]. The potential of the couple $[\mathrm{Coen}_3]^{3+}$ spin-free/$[\mathrm{Coen}_3]^{2+}$ spin-free, in which both oxidation states are electronically equivalent, would be expected to be very much more positive.

Because of electronic non-equivalence, electron transfer between cobalt(II) and cobalt(III) complexes in aqueous solution is usually slow[6]. For example, the complete electron-transfer racemization of $d[\mathrm{Coen}_3]\mathrm{Cl}_3$ ($0{\cdot}0551\ M$) in the presence of d,l-$[\mathrm{Coen}_3]\mathrm{SO}_4$ ($0{\cdot}02\ M$) and ethylenediamine ($0{\cdot}24\ M$) in a nitrogen atmosphere at 25° C. required 8 days[7]. Activated carbon (2 gm. in 100 ml. of solution) catalysed the above reaction strongly, and all activity was lost in 2 min. at 25° C.

Racemization was also catalysed by freshly prepared platinum, palladium and rhodium black, and small amounts of cobalt(II) complex could be detected. In the presence of these metals a reducing agent was necessary. This could be adsorbed hydrogen, sulphite ion or even alcohol.

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'Eddy' Diffusion in Chromatography

Under the above title, J. Calvin Giddings[1] has discussed the axial spreading of the solute in chromatographic columns which is responsible for the smearing of zones and in particular the contribution made to this by 'eddy' diffusion.

In 'eddy' diffusion the spreading of the solute is less than could be derived from random walk considerations applied to the carrier fluid, since the uneven velocity distribution causes radial concentration gradients, which by radial molecular diffusion tend to keep the solute closer together in the axial direction.

For turbulent flow in unpacked tubes the appropriate theory has been worked out by Taylor[2]. The velocity distribution in laminar flow also produces a spreading effect which is counteracted by radial diffusion. This case has also been examined by Taylor[3]. A generalized treatment for tubes of arbitrary cross-section and for arbitrary velocity profiles is due to Aris[4].

In our publication[5] on the statistical treatment of mechanisms causing axial spreading we have expressed the view (*loc. cit.*, p. 267) that the velocity distribution (in this case a parabolic one) and the radial molecular diffusion cannot be considered as being statistically independent, the reason being that the second process reduces the effect of the first. Giddings (*loc. cit.*) states that the two processes are independent.

For independent processes, when variances must be added, as we have explained, both the apparent diffusion coefficient D and the height H corresponding to an ideal stage have conserved the property of additivity, since they are proportional to the variance.

However, in order to obtain a reduction in D (or H), Giddings has introduced the additivity in a factor n occurring in the denominator in his equation (1) on the strength of a statement that n is the sum of numbers of steps for the two supposedly independent processes. We fail to see the statistical justification for this procedure.

The fact that, for proper a and b, the form:

$$1\bigg/\left(\frac{1}{a}+\frac{1}{b}\right)$$

has the correct limits for $b \rightarrow \infty$ and $a \rightarrow \infty$ is of course insufficient to justify the treatment.

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Variances add[1], for certain independent processes which, by virtue of an elementary random event, contribute directly to the variance. Lateral diffusion is not such a process. The variance is caused by non-equilibrium established by the difference in downstream velocity from point to point. Lateral diffusion acts to reduce this variance as can be seen by the inverse relationship between variance or plate height and diffusion coefficient. The random change in velocity which occurs along a given stream path, as found in packed columns but not in capillary columns, also reduces the variance. Both factors act independently to exchange molecules between fast- and slow-moving regions.

The fact that independent processes do not necessarily contribute additive terms to the variance can be seen by use of a simple example which, unlike the above, can be accounted for in an exact fashion. Let the transition between two discrete species, A_1 and A_2, with downstream velocities v_1 and v_2 occur by two independent mechanisms. The forward and reverse rate constant for the first mechanism are k_1 and k_2, respectively, and for the second mechanism, k_1' and k_2'.

Using a method developed elsewhere[2] for obtaining asymptotic expressions for plate height with complex kinetics, we obtain:

$$H = \frac{2R\,(1-R)\,(v_1-v_2)}{k_2 + k_2'}$$

where R, the ratio of average solute to average fluid velocity, is an equilibrium property. Rate effects appear only in the denominator, and, in fact, are additive in the denominator as proposed for eddy diffusion[3]. We see that "the second process reduces the effect of the first"[1], but the processes are, none