this linearity prevailing until the corrosion by-products contribute an additional cell intensity increase term and then we have $W=K'O_2+K''\log O_2$. The effect of temperature can be determined from handbook values for oxygen solubility, while for pressure the dissolved oxygen follows Henry's Law, $O_2=KP$. Also, the alpha point will vary slightly for various steels depending upon the particular oxygen cell systems thereof.

The above criteria might serve as first guides for the extrapolation of these results to other oxygen-steel-electrolyte systems not only in aerobic corrosion fatigue but also to the oxygen cell corrosion of steels of whatever kind.

A more complete account of this work is to be published in *Corrosion*.

FREDERICK J. RADD
L. HUGH CROWDER
LOUIS H. WOLFE

Ponca City,
Oklahoma.
Nov. 6.

[1] Whitman, W. G., Russell, R. P., and Davis, G. H. B., *J. Amer. Chem., Soc.*, **47**, 70 (1925).

CHEMISTRY

Comparison of Efficiency and Separating Power of Packed and Capillary Gas Chromatographic Columns

THE distinction between the efficiency and the separating power of gas chromatographic columns has been widely appreciated for some time. Recently[1], I have shown that a *separation factor* S can be defined by :

$$S=36\left(\frac{\alpha}{\alpha-1}\right)^2 \qquad (1)$$

where $\alpha=(V_{R_2}/V_{R1})>1$, that is, the true relative retention volume (or time) of a given pair of substances. The value of S deduced from equation 1 corresponds to the exact separation of the two substances and is equal to the number of theoretical plates required to give the separation when the true retention volume is much greater than the free gas or dead volume, V_d, of a column. The apparent retention volume, V'_R, used in the usual theoretical plate equations is the sum of V_d and V_R for a given substance.

In practice, V_R is often not much greater than V_d and may well be less for some things. In these circumstances it is possible to show[1] that the theoretical plate requirement for separation is related to S by :

$$N=S\left\{1+2\left(\frac{V_d}{V_{R_2}}\right)+\left(\frac{V_d}{V_{R_2}}\right)^2\right\} \qquad (2)$$

N increases very rapidly as the ratio V_d/V_{R_2} increases. For example, consider the separation of two substances for which $\alpha=3$. In conditions such that $V_R\gg V_d$, then $N=S=81$, whereas, if $V_d=10V_R$, while S again is 81, $N\sim10{,}000$. Comparing two columns differing only in the ratio V_d/V_R, we see from this example that, at the same theoretical plate height H, the latter column in the example would need to be 120 times as long as the former column to achieve the same end.

Packed columns normally operate in conditions such that V_R is at least as big as V_d whereas capillary columns are frequently used with ratios of V_d/V_R as high as 30. Thus, if we take the earlier example as being a comparison between a packed and a capillary column we see that the performance of an 8 ft. long packed column could only be reproduced with 1,000 ft. of capillary. Not all comparisons reflect so badly upon capillary columns, but it is certain that the enormous theoretical plate efficiencies recently reported with such columns must be viewed with caution and a real appreciation of their performance arrived at by use of the equation :

$$S=16\left(\frac{V_{R_2}}{W}\right)^2 \qquad (3)$$

which is similar in form to the widely used theoretical plate equation[3].

What is evident from equation 2 is that any separation which can be achieved in a packed column can be achieved with a capillary and *vice versa*. The real difference between the two types of column lies in the possible speed of analysis. Purnell and Quinn[2] have extended equation 2 and find that the time of analysis for the exact separation of any pair of substances of given α is :

$$t=\frac{SH}{\bar{u}}\,\frac{(1+V_{R_2}/V_d)^3}{(V_{R_2}/V_d)^2} \qquad (4)$$

where $\bar{u}$ is the average carrier gas velocity. At any given ratio of $H/\bar{u}$ there is a minimum analysis time, $t_{\min}$, which is achieved when $V_{R_2}=2V_d$ and so we can say that :

$$t_{\min}=\frac{243\ SH}{\bar{u}} \qquad (5)$$

The limiting low value of $H/\bar{u}$ is, to a reasonable approximation, the mass transfer constant C in the van Deemter equation[3] and so we have :

$$t_{\min}=243.S.C. \qquad (6)$$

The condition that $V_R=2V_d$ can be more readily achieved in packed than capillary columns, due to the porous nature of the packing, which permits higher ratios of solvent to free space volumes without, at the same time, significantly increasing the value of C. Presumably, a porous walled capillary might overcome this difficulty. An alternative view is that unless the ratio V_{R_2}/V_d is the same for both types of column different lengths will be needed to carry out the same separation. Generally, the capillary must be the longer, and since the optimum velocity is about the same for either column, analysis must be slower with the capillary.

In conclusion, it may be pointed out that provided packed and capillary columns are operated under identical conditions they will be equally effective both in speed and separating power. In these circumstances the choice between them depends upon other factors, such as ease of construction, maximum sample size, and so on.

Equations 5 and 6 indicate the times of analysis which may be attainable. For example, for the separation of, say, propane and n-butane at room temperature with a column containing squalane, $\alpha\sim3$ and if $C=10^{-3}$ sec., which is a reasonable estimate, $t_{\min}=0{\cdot}55$ sec. With diminishing α the analysis time increases, but even at $\alpha=1{\cdot}08$, as found for *m*- and *p*-xylene eluted from benzquinoline at 78° a time of 50 sec. should be attainable.

J. H. PURNELL

Department of Physical Chemistry,
Lensfield Road,
Cambridge.
Nov. 10.

[1] Purnell, J. H. (in course of publication).
[2] Purnell, J. H., and Quinn, C. P. (in course of publication).
[3] van Deemter, J. J., Zuiderweg, F. J., and Klinkenberg, A., *Chem. Eng. Sci.*, **5**, 271 (1956).