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## GAS CHROMATOGRAPHIC MEASUREMENT OF TRANSPORT PROPERTIES\*

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(Received March 28th, 1974)

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### 1. INTRODUCTION

The greatest emphasis during the past 15 years in the application of gas chromatography to physical-analytical measurements has been placed on the determination of activity coefficients, vapour pressures, thermodynamic quantities, boiling points, second virial coefficients of gas mixtures, kinetic constants, solid surface properties, inter- and intra-phase mass transfer coefficients, etc.<sup>1-12</sup>. Choudhary and Doraiswamy<sup>12</sup> presented a critical review of the applications of gas chromatography in catalysis.

In this paper, a comprehensive review of the literature published during the past 15 years on the use of gas chromatography in the evaluation of binary diffusion coefficients of gases and organic vapours, effective diffusivities of catalysts and adsorbents, intra-particle and intra-crystalline mass transfer coefficients, surface diffusion coefficients and heat transfer coefficients, is presented.

\* NCL Communication No. 1790.

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## 2. BINARY DIFFUSION COEFFICIENTS OF GASES

Numerous techniques have been described for the measurement of binary diffusion coefficients of gases and organic vapours. Most of these methods, however, are time consuming in the evaluation of quantitative results<sup>13</sup>. Recent developments in the theory of chromatography<sup>14-18</sup> have made it possible to develop techniques<sup>13,19</sup> for the rapid and accurate measurement of diffusion coefficients.

### A. Method of Giddings and Seager

Giddings and Seager<sup>13,20-22</sup> were among the first workers to apply gas chromatography in order to measure gas-phase diffusion coefficients. The method is based on the special case<sup>13</sup> of the more general theory of chromatography first derived by Taylor<sup>23,24</sup>.

According to generalized chromatographic theory<sup>13,25,26</sup>, the height equivalent to a theoretical plate (HETP,  $H$ ) of a packed column can be written as

$$H = 1/[(1/2 \lambda d_p) + (1/C_u v)] + \frac{2 \gamma D_u}{v} + C_l v + C_k v \quad (1)$$

This equation is simplified by replacing the packed column by an empty tube of uniform circular cross-section and assuming that adsorption at the wall is negligible, so that  $C_k = 0$ . As there is no liquid in the tube,  $C_l = 0$ . Further, the quantity  $2 \lambda d_p$  approaches infinity because there are no mixing stages in the tube, and for this precise geometry  $\gamma$  is unity. Thus, eqn. 1, in the case of an empty tube of uniform cross-section, reduces to

$$H = \frac{r_0^2 v}{24 D_u} + \frac{2 D_u}{v} \quad (2)$$

where the expression for a circular tube,  $r_0^2/24 D_u$ , replaces  $C_u$ .

An equivalent form of eqn. 2, as derived by Taylor<sup>23</sup>, can be written as

$$D_u = \frac{v}{4} \left( H \pm \sqrt{H^2 - \frac{r_0^2}{3}} \right) \quad (3)$$

For low flow-rates ( $v$ ), eqn. 3 can be simplified<sup>27</sup> to

$$D_u = v \left( \frac{H}{2} \right) \quad (4)$$

which would be valid for low-molecular-weight gases.

The HETP can be obtained from chromatographic data by the relationship

$$H = \frac{L}{n} = \frac{L}{16} \left( \frac{m}{t_R} \right)^2 = \frac{L}{16} \left( \frac{m}{t} \right)^2 \quad (5)$$

or

$$H = L \left( \frac{\tau}{t_R} \right)^2 \quad (6)$$

Eqns. 3 and 5 (or 6) imply that only three quantities, the peak width (or peak variance), the retention time and the average carrier flow velocity, are required for estimating the gas phase diffusivity. The positive root of eqn. 3 is valid up to a certain critical velocity  $v_c$  given by<sup>13</sup>:

$$v_c = 4 \sqrt{3} D_{AB}/r_0 \quad (7)$$

At velocities greater than  $v_c$ , the negative root becomes valid. For the case when  $v \gg v_c$ , the Taylor limit becomes valid.

The apparatus consists of a commercially available gas chromatographic unit, with an empty tube of uniform circular cross-section replacing the packed column. In order to correct for the end-effects and for diffusion occurring in the instrument dead volume, Giddings and Seager<sup>13</sup> collected data using both the long tube and the short tube separately, and the data for the short tube are subtracted from those for the long tube. Thus

$$H = (L_l - L_s)(\tau_l^2 - \tau_s^2)/(t_l - t_s)^2 \quad (8)$$

The need for this cumbersome two-column procedure was eliminated by Fuller *et al.*<sup>28</sup> through direct on-column sample introduction and a rigorous reduction of the detector dead volume. The oven dimensions were increased so as to accommodate the diffusion tube without tight coils and bends, which tend to distort tube cross-sections and otherwise alter the peak dispersion. Their gas chromatographic broadening apparatus for diffusion measurements is illustrated in Fig. 1.

Arnikar and co-workers<sup>29,30</sup> made use of an electrodeless discharge tube as a detector in the rapid determination of binary diffusion coefficients of some organic vapours into nitrogen.

Hargrave and Sawyer<sup>31</sup> applied a similar gas chromatographic method for the determination of gaseous inter-diffusion coefficients for solute vapour-carrier gas pairs in the temperature range 25–250° by using eqn. 4. The plate height is calculated from the relationship

$$H = \frac{L}{5.545} \left[ \frac{w}{t_R} \right] \quad (9)$$

and the flow velocity ( $v$ ) at the column outlet is calculated from

$$v = \frac{L}{t_R} \quad (10)$$

as there is no measurable pressure drop across an open column.

Fuller *et al.*<sup>28</sup> determined experimental binary diffusion coefficients for some halogenated hydrocarbon compounds diffusing into helium by utilizing the gas chromatographic peak broadening technique, and described certain modifications that have improved the speed and accuracy of the technique. A critical discussion of the validity of the method is also given.

Huang *et al.*<sup>32</sup> obtained experimental diffusivities for several gas-gas, gas-

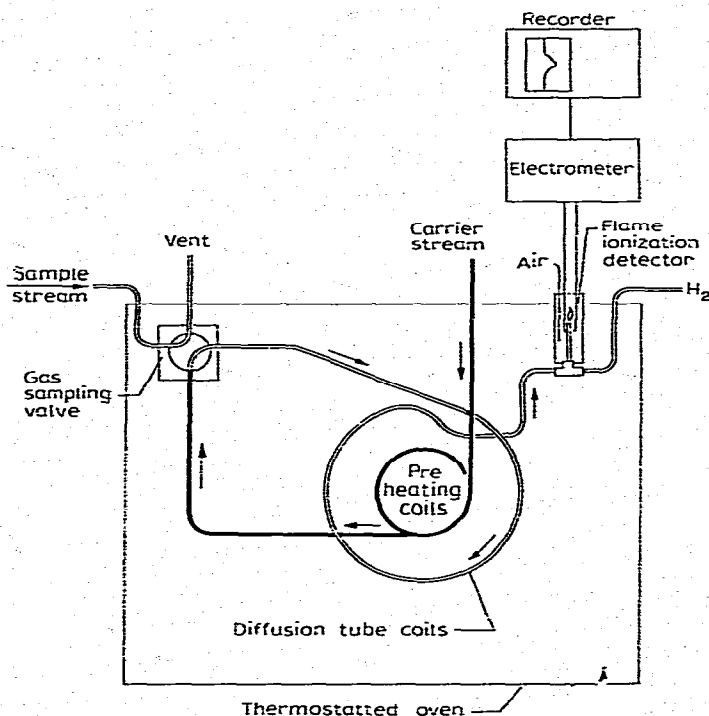


Fig. 1. GC broadening apparatus for diffusion measurements<sup>28</sup>.

liquid vapour and gas-solid vapour systems, using the above method. On the basis of the experimental results, a generalised semi-empirical equation:

$$D_{AB} = \frac{5.06 T^{1.73}}{(V_A^{1/3} + V_B^{1/3})^2 \rho^{1.286}} \left( \frac{1}{M_A} + \frac{1}{M_B} \right)^{1/2} \quad (11)$$

has been developed to predict the diffusivities of binary gas-gas and gas-liquid vapour systems as a function of pressure and temperature. A comparison of this equation with data appearing in the literature yields an average error of 3.5%, which is less than that predicted by many other methods.

Kwok *et al.*<sup>28</sup> suggested that the normal plate height expression can still be used if proper modification of the diffusion coefficient is made in the case of linear adsorption. Several investigators<sup>27,31,34-38</sup> have established the validity of the above gas chromatographic open-tube method for the measurement of the inter-diffusion coefficients of gases and vapours of volatile organic compounds.

### B. Method of Carberry and Bretton

Carberry and Bretton<sup>39</sup> suggested a pulse-flow method, according to which the inter-diffusion coefficient can be obtained from the concentration-time distribution data or from the mean retention time as measured at the diffuse pulse maxima:

$$t_m = \frac{D_a}{v^2} \left[ \left( 1 + \frac{L v}{D_a} \right)^{1/2} - 1 \right] \quad (12)$$

For beds of more than several particle diameters in length, eqn. 12 becomes a simple function of  $D_g$ , tube length ( $L$ ) and velocity ( $v$ ):

$$t_m = \frac{L}{v} - \frac{D_g}{v^2} = \theta - \frac{D_g}{v^2} \quad (13)$$

or

$$\frac{t_m}{\theta} = - \frac{D_g}{L v} \quad (14)$$

Thus a plot of the ratio of the pulse retention time to that of carrier velocity,  $t_m/\theta$ , is a function of  $1/Lv$ , the slope being equal to the diffusion coefficient. Beyond the flow regime where molecular transport governs axial dispersion,  $D_g$  is directly proportional to  $Lv$ , and  $t_m/\theta$  therefore becomes constant with the onset of turbulent diffusion.

Frontal analysis was also used by Fejes and Schay<sup>10</sup> for the determination of gaseous inter-diffusion coefficients.

All the methods discussed above are applicable to both open and packed tubes, but suffer from the disadvantages inherent in operating at low flow-rates from the uncertainty as to the role of "eddy diffusion", which may interact in a complex way with gas-phase mass transfer<sup>11</sup>.

### C. Arrested elution method

Knox and McLaren<sup>12</sup> suggested an arrested elution method that by-passes most of the experimental and theoretical difficulties which occur in the continuous elution method of Giddings and Seager<sup>13</sup> and Giddings<sup>14-18</sup>. It is applicable equally to open and packed columns and is of intrinsically higher precision than the continuous method based upon HETP measurement.

In this method, a sharp band of an unadsorbed gas is injected into the column and eluted at a controlled and measurable velocity. When the band is about half way down the column, the gas flow is arrested for a time  $t$ , during which spreading can occur only by diffusion. Finally, the band is eluted from the column and its profile and standard deviation are determined by the detector. The diffusion spreading for empty and packed tubes is given by

$$\frac{d \delta_t^2}{d t} = 2 D_g/v^2 \quad (\text{for an empty tube}) \quad (15)$$

and

$$\frac{d \delta_t^2}{d t} = 2 \gamma D_g/v^2 \quad (\text{for a packed tube}) \quad (16)$$

Hence, a plot of  $\delta_t^2$  against the time of residence in the column is a straight line of slope  $2 D_g/v^2$  (for an empty tube) or  $2 \gamma D_g/v^2$  (for a packed column), from which the inter-diffusion coefficient can be calculated. Details of the method and the theoretical interpretation of  $\gamma$  are discussed in the original paper<sup>12</sup>.

### D. Multi-flow-rate and one-flow-rate methods

Huber and van Vught<sup>36</sup> and Kobayashi and co-workers<sup>43-45</sup> studied the gaseous diffusion coefficients of dilute and moderately dense gases by perturbation chromatography. Their measurements were based on the dispersion model for laminar flow in a long circular tube at up to 60 atm at 25° for tritiated methane in methane and in tetrafluoromethane by the multi-flow-rate method using the relationship<sup>45</sup>

$$\frac{\Delta[\delta^2]}{\Delta t} = \frac{2}{v^2} \cdot D_g + \frac{\beta}{D_g} \quad (17)$$

The diffusion of argon, methane, nitrogen and carbon dioxide in helium at 50°, 25°, 0° and -25°, respectively, at up to 60 atm was measured by the one-flow-rate method using the relationship<sup>45</sup>

$$\frac{\Delta\delta^2}{\Delta t} = \frac{2}{v^2} \cdot D_g + \frac{r_0}{24 D_g} \quad (18)$$

A representative plot of the rate of change of variance  $\Delta\delta^2/\Delta t$  versus  $2/v^2$  is given in Fig. 2.

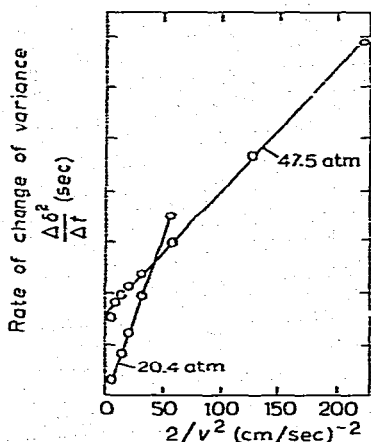


Fig. 2. Determination of diffusivity of tritiated  $\text{CH}_4$  in  $\text{CF}_4$  at 25° (ref. 45).  $\Delta\delta^2/\Delta t = (2/v^2)D_g + \beta/D_g$ .

Hu<sup>44</sup> and Hu and Kobayashi<sup>45</sup> improved perturbation detection by using a small-volume ionization chamber for radioactive detection and a micro-scale thermal conductivity cell for non-radioactive detection. Agreement between their experimental and theoretical values was good for variance calculations. Some results were obtained by using both the multi-flow-rate method, which used several velocities at the same temperature and pressure, and the one-flow-rate method, which required measurement at only one flow-rate.

Apart from the literature discussed above, several investigations have been reported on the use of gas chromatographic methods for measuring gas-phase diffusion coefficients using packed or unpacked columns<sup>46-49</sup>.

## 3. EFFECTIVE DIFFUSIVITY OF CATALYSTS

The measurement of effective diffusion coefficients is based on the well known equation developed by Van Deemter *et al.*<sup>50</sup> for a gas chromatographic column:

$$H = A + B/v + C v \quad (19)$$

where  $H$  is the HETP and  $v$  is the interstitial carrier gas velocity. The terms  $A$ ,  $B$  and  $C$  are constants of the column, gases and operating conditions. The term  $A$  is due to turbulence in the gas stream caused by the particles of packing and is the so-called "eddy diffusion" term. The term  $B$  is due to longitudinal diffusion of gas in the pulse both forwards and backwards in the carrier gas stream. The  $C$  term is due to mass transfer between the gas and solid phases. It can be seen from eqn. 19 that at high gas velocities the term  $C$  is dominant and the  $B$  term becomes unimportant. Thus, the equation for  $H$  at high carrier gas velocities reduces to

$$H = A + C v \quad (20)$$

Habgood and Hanlan<sup>51</sup> obtained the following expression for  $C$ :

$$C = \frac{d_p^2}{\sqrt{2} \pi^2} \cdot \frac{F_1}{F_2} \cdot \frac{1}{p_r D_e} \cdot \frac{1}{[1 + 273 F_1 / (\alpha' T q_b)]^2} \quad (21)$$

where

$$\alpha' = \frac{[V_R^0 - V_d^0]}{W} \cdot \frac{273}{T} \quad (22)$$

They calculated the HETP for very small sample volumes giving symmetrical Gaussian peaks by the relationship

$$H = \frac{L}{16} \left( \frac{1.5 S^0}{1.1 V_R^0} \right)^2 \quad (23)$$

and attempted a tentative interpretation of  $C$  in terms of an apparent gas phase diffusion in the charcoal pores.

The term  $C$  can also be expressed<sup>52</sup> as

$$C = \frac{d_p^2}{\sqrt{2} \pi^2} \cdot \frac{F_1}{F_2} \cdot \frac{1}{p_r D_e} \cdot \frac{1}{[1 + K_0 F_1 / F_2]^2} \quad (24)$$

where

$$K_0 = 1/[\epsilon + (t_m - t_d) v F_1 / F_2 L] \quad (25)$$

and the HETP calculated by measuring the pulse broadening of a non-chemically interacting gas at various flow velocities that occur in a column packed with catalyst using eqn. 5, 6 or 23.

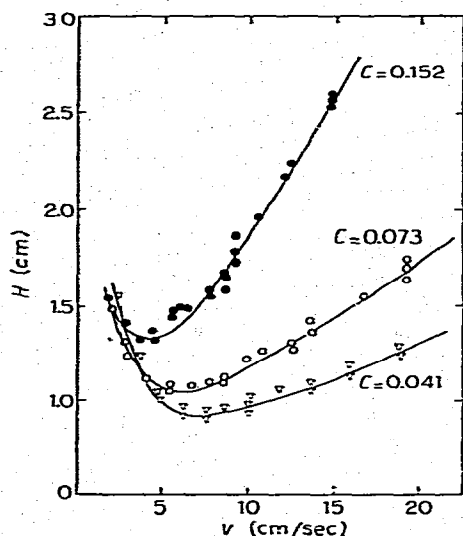


Fig. 3. HETP as a function of interstitial gas velocity for  $\text{SO}_2$  on Na-mordenite<sup>53</sup>. Temperature: ●, 133°; ○, 210°; ▽, 261°.

Using the values of  $H$  as a function of flow velocity, the term  $C$  (and also  $A$  and  $B$ ) of the Van Deemter equation can be calculated by plotting the HETP,  $H$ , against the flow velocity (or by the least-squares method); the slope of the linear portion of the curve in the region of high gas velocities corresponds to the value of the term  $C$  (a representative plot of  $H$  versus  $v$  is shown in Fig. 3<sup>53</sup>). Hence, as all the terms in eqn. 24 except  $D_e$  can be determined experimentally, the effective diffusivity of the catalyst can be calculated with sufficient accuracy.

Leffler<sup>52</sup> applied this method to alumina H-51 using nitrogen as the adsorbed gas at  $-78^\circ$  and found reasonable agreement between the results obtained from this method and the Weisz and Schwartz relationship<sup>54</sup>. Davis and Scott<sup>55</sup>, using gas chromatography, also reported good agreement between the values of  $D_e$  and steady-state results for solids that are reasonably homogeneous.

Szlaur<sup>56</sup> measured the adsorption kinetics of polar compounds on molecular sieves in order to determine the effective diffusion coefficients into granules. Values of the coefficients of mass transfer for packed capillary gas-solid chromatographic columns were measured from the dependence of HETP on flow-rate and used to explain the low values of zone diffusion<sup>57</sup>.

Eberly<sup>58</sup> and Ma and Mancel<sup>53</sup> studied the effective diffusivity of inert gases (argon, krypton and sulphur hexafluoride) in a series of Na- and H-mordenites, Na-faujasite and amorphous silica-alumina catalysts and of carbon dioxide, nitrogen dioxide and sulphur dioxide in molecular sieve zeolites. They found that this gas chromatographic pulse technique is especially suitable for measurement of effective diffusivities of solid catalysts at high temperatures and low concentrations. It is very difficult to make measurements under these conditions by the conventional vacuum technique<sup>59</sup>. Trimm and Corrie<sup>58</sup> employed this method for the measurement of the diffusivity of various gases in catalyst pellets as a function of temperature. They found



that the results obtained at low temperatures for some gases cannot be extrapolated to the higher temperatures at which the catalyst operates. At temperatures below 400° the variation of  $D_e$  with temperature showed predictable behaviour, but above 400° a marked increase in the dependence of  $D_e$  on temperature was observed, the magnitude of which depended on the nature of the gas. They explained this anomalous effect in terms of a surface diffusion model. As surface mobility is known to increase exponentially with temperature, surface diffusion provides a good explanation of their results.

This gas chromatographic method for the determination of  $D_e$  has the inherent advantage that measurements are made at temperatures which approach those used in commercial processes. Detailed procedures for the determination of the experimental values of the terms in the expression used for calculating effective diffusion coefficients have been given by Leffler<sup>52</sup>, Eberly<sup>58</sup> and Ma and Mancel<sup>53</sup>.

#### 4. MASS TRANSFER COEFFICIENTS FOR PACKED BEDS

##### A. General

The advanced theory of gas chromatography permits the estimation of the mass transfer resistances such as axial diffusion, interphase diffusion, film diffusion and intra-particle (or intra-crystalline) diffusion, by chromatographic measurements<sup>60-61</sup>. Recent developments in gas chromatographic theory, with emphasis on the mass transfer processes that occur in the packed column, are summarized below.

Following the simple approach of Giddings<sup>65</sup> and Van Deemter *et al.*<sup>59</sup>, Jones<sup>25</sup> derived a generalized expression for the HETP including the effect of gas-phase mass transfer. Van Deemter's original equation (eqn. 19) was modified by Kambara and co-workers<sup>66,67</sup>, who gave a mathematical treatment of the kinetic role of diffusion and the pressure drop in gas chromatography. There are a number of papers and theories suggesting different modifications of Van Deemter's equation<sup>68-71</sup>. Takács<sup>70</sup> developed an approximation equation which involves the use of a simple mathematical method for numerically determining the coefficients of the approximation equation by means of a computer.

Giddings<sup>15,71</sup> carried out theoretical studies of band spreading in chromatography by a non-equilibrium method<sup>14,16</sup> and examined the contribution of lateral diffusion to plate height. Khan<sup>72</sup> presented a non-equilibrium treatment which includes interfacial mass transfer resistance. Kubin<sup>73</sup> contributed to the theory of chromatography in a detailed analysis of diffusion outside and inside the support particles.

At low concentrations, the shapes of the peaks deviate from a Gaussian distribution<sup>74</sup> and may be sensitive to the detailed kinetics. Bock and Parke<sup>75</sup> calculated the first four moments of the distribution function on the assumption that the rates of sorption and desorption do not play significant roles, and the distribution functions were found from these moments. Chromatographic peaks were treated mathematically by Kaminskii *et al.*<sup>76</sup> and the first six moments of the peak were derived on the assumption that peak spreading is determined solely by diffusion in the stationary phase and the sorption coefficient is large; a method for the recalculation of the distribution function from the moment was also suggested. Linear non-

equilibrium chromatography was treated mathematically independently by Kučera<sup>77</sup>, and five moments of the chromatographic peak were calculated and their physical significance was discussed. Grubner<sup>78</sup> applied the statistical moments theory to the solution of a system of partial differential equations describing a model based on diffusion-controlled kinetics for gas-solid chromatography. Grubner and Underhill<sup>79</sup> used a standard mathematical method of analysis by moments to compare the most common equations for mass transfer in a packed bed, and the first six moments were given for four equations (for a theoretical chamber model, film-limited mass transfer, intra-particle diffusion and inter-particle diffusion). In each instance, the first ordinary moment was found to be independent of the mechanism of mass transfer.

Grubner *et al.*<sup>80</sup> studied mass transfer phenomena in gas-solid systems with special emphasis on the internal porosity of the stationary phase, and the mass transfer coefficients were obtained from a more exact treatment of gas-solid chromatography<sup>81</sup>.

Analysis of moments is a very powerful mathematical technique and can be used as a means of comparing the previously derived equations for break-through curves<sup>60,61,79</sup>. From an experimental viewpoint, only the first five or six moments need be calculated; the higher moments are difficult to determine from experimental data<sup>79</sup>.

### B. Method based on moment analysis

Schneider and Smith<sup>60,61</sup> presented a new method for determining adsorption equilibrium constants, rate constants, mass transfer coefficients, axial or longitudinal diffusivity, intra-particle diffusivity and surface diffusivity from gas chromatographic data. The method was based upon the theory of chromatography developed by Kubin<sup>73</sup> and Kučera<sup>77</sup> for relating the moments of the effluent concentration wave from a bed of adsorbent particles to the rate constants associated with various steps in the overall adsorption process. Basically, a pulse of the adsorbate is injected into the column (packed with catalyst particles) head and the first and second moments of the outlet peak are measured. Theory permits the calculation of the mass transfer coefficients from these measurements. The principles of the method are as follows.

The first absolute moment ( $\mu'_1$ ) of the chromatographic curve is defined as

$$\mu'_1 = m_1/m_0 \quad (26a)$$

where

$$m_n = \int_0^x t^n c(z,t) dt \quad (n = 0, 1, 2, \dots) \quad (26b)$$

The first moment is of basic significance in the determination of retention time and depends only on the partition coefficient and on the longitudinal diffusion, and is not affected by transport phenomena on the grain and across the surface film or by the shape and size of the grain.

The second central moment ( $\mu_2$ ) of the chromatographic curve is defined as

$$\mu_2 = \frac{1}{m_0} \int_0^x (t - \mu'_1)^2 c(z,t) dt \quad (27)$$

The second central moment has significance in the determination of the peak width and, as with all higher moments, it depends on all factors that characterize the transport of a given compound through the column.

The moments  $\mu'_1$  and  $\mu_2$  can be evaluated explicitly, using Laplace-Carson transforms<sup>60,61</sup>, as

$$\mu'_1 = \frac{\bar{z}}{v} (1 + \delta_0) + \frac{t_{0,1}}{2} \quad (28)$$

and

$$\mu_2 = \frac{2\bar{z}}{v} \left[ \delta_1 + \frac{E_A}{\alpha} (1 + \delta_0)^2 \frac{1}{v^2} \right] + \frac{t_{0,1}^2}{12} \quad (29)$$

where

$$\delta_0 = \frac{1 - \alpha}{\alpha} \cdot \beta \left( 1 + \frac{u_p}{\beta} \cdot K_A \right) \quad (30)$$

and

$$\delta_1 = \frac{1 - \alpha}{\alpha} \cdot \frac{R^2 \beta^2}{15} \cdot \left( 1 + \frac{u_p}{\beta} K_A \right)^2 \cdot \left( \frac{1}{D_p} + \frac{5}{k_f R} \right) \quad (31)$$

Further, the effective intraparticle diffusion coefficient,  $D_p$ , is related to the effective surface diffusion coefficient,  $D_s$ , by the relationship

$$D_p = D_k + \frac{u_p}{\beta} \cdot K_A D_s \quad (32)$$

and the effective gas diffusion coefficient (Knudsen),  $D_k$ , is given by

$$D_k = \frac{\beta}{q_{\text{int}}} \cdot \mathcal{D}_k \quad (33)$$

where

$$\mathcal{D}_k = 4/3 r_p \sqrt{2 RT/\pi M} \quad (34)$$

The effective surface diffusion coefficient,  $D_s$ , is related to the true surface diffusion coefficient,  $\mathcal{D}_s$ , by the relationship

$$D_s = \frac{\beta}{q_{\text{sur}}} \cdot \mathcal{D}_s \quad (35)$$

It has been shown that the external mass transfer coefficient,  $k_f$ , does not depend on the carrier gas velocity at low Reynolds number<sup>60</sup>. Hence  $k_f$  can be calculated from the relationship  $N_{\text{sh},AB} = 2.0$ , where the Sherwood number is  $N_{\text{sh},AB} = 2 R k_f / D_{AB}$ .

By using the resulting relationship  $k_f R = D_{AB}$  in eqn. 31, the effective intraparticle diffusion coefficient,  $D_p$ , can be calculated from the experimental second central moment ( $\mu_2$ ) for a series of chromatographic curves measured for different

carrier gas velocities,  $v$ . The adsorption coefficient,  $K_A$ , can be evaluated by means of eqns. 28 and 30 from the experimental first absolute moment ( $\mu_1$ ) using the same series of chromatographic curves. The binary diffusion coefficient,  $D_{AB}$ , can be calculated from theoretical equations<sup>52</sup> if the experimental values are not available.

Further, the axial diffusion coefficient ( $D_{ax}$ ) can be obtained from the experimental second central moments measured at high carrier gas velocities (*i.e.*, high Reynolds numbers) by eqn. 29. Finally, eqns. 32–35 are used to evaluate the effective and true surface diffusivities from the effective intra-particle diffusion coefficient,  $D_p$ .

Schneider and Smith<sup>60,61</sup> used the above gas chromatographic method for measuring axial dispersion coefficients, intra-particle diffusivities, external mass transfer coefficients and surface diffusivities for ethane, propane and *n*-butane on silica gel at 50–200° and at atmospheric pressure. Good agreement was obtained between the experimental and calculated breakthrough curves, which confirmed the theory of gas–solid chromatography as well as the model used for the adsorber. This fact also suggested that the rate constants determined by gas chromatography have a physical significance and are not simply empirical constants.

As the average surface coverage is very low, the surface diffusion coefficients obtained by this method are very close to the limiting values. The detailed experimental procedures, evaluation of moments of the chromatographic curves and estimation of mass transport coefficients are discussed in the original papers<sup>60,61</sup>.

### C. Method based on Fourier analysis

Gangwal *et al.*<sup>64</sup> obtained transport rate coefficients by determining the coefficients of the Fourier series which describes chromatographic peaks rather than the moments themselves, arguing that these can be determined more accurately than the moments, particularly higher moments. The principles of this method are as follows.

A function  $f(t)$  in an interval in time,  $t$ , of period  $T$ , can be represented by a Fourier series as

$$f(t) = \sum_{n=1}^{\infty} a_n \sin(n\pi t/T) + \sum_{n=0}^{\infty} b_n \cos(n\pi t/T) \quad (36)$$

where the coefficients  $a_n$ ,  $b_n$  and  $b_0$  are

$$a_n = \frac{1}{T} \int_0^{2T} f(t) \sin(n\pi t/T) dt \quad (37)$$

$$b_n = \frac{1}{T} \int_0^{2T} f(t) \cos(n\pi t/T) dt \quad (38)$$

$$b_0 = \frac{1}{2T} \int_0^{2T} f(t) dt \quad (39)$$

There will be just one peak for chromatographic curves of interest in rate measurement and the period  $T$  is a time sufficiently long to allow the tail of the peak to vanish. With injection of a sample in the carrier gas, the peak measures  $c(t)$ . Assuming that

the injection is closely approximated by the Kronecker delta function  $\delta(t = 0)$ , the normalized response is  $E(t)$ , the probability density function of residence time. The Fourier transform of  $E(t)$  is

$$\bar{E}(i\omega) = \int_0^{2T'} E(t) \cos(n\pi t/T') dt - i \int_0^{2T'} E(t) \sin(n\pi t/T') dt \quad (40)$$

$$= T' b_n - i T' a_n \quad (41)$$

By employing the amplitude ratio,  $A_n$ , and the phase lag,  $q_n$ , for the  $n$ th-harmonic component in place of  $a_n$  and  $b_n$ , we obtain

$$A_n = T' \sqrt{a_n^2 + b_n^2} \quad (42)$$

$$q = \arctan(b_n/a_n) \quad (43)$$

The coefficients  $a_n$ ,  $b_n$  and subsequently  $A_n$  and  $q_n$  are to be evaluated from the normalized chromatographic curve by eqns. 37, 38, 42 and 43. The partial differential equations and boundary conditions for the system (assuming a  $\delta$  input) are normalized and subjected to a Fourier transform and the coefficients  $a_n$  and  $b_n$  are obtained from the imaginary and real parts of eqn. 41. Expressions for  $A_n$  and  $q_n$  are obtained through eqns. 42 and 43. Model parameters are then evaluated by minimizing  $[(A_n)_{\text{exptl.}} - (A_n)_{\text{model}}]^2$  or  $[(q_n)_{\text{exptl.}} - (q_n)_{\text{model}}]^2$  or their sum by a suitable search technique.

Gangwal *et al.*<sup>64</sup> obtained the system properties from the amplitude ratio by a five-dimensional search using the modified simplex method of Nelder and Mead<sup>63</sup>. The parameters evaluated were relatively independent of the choice of the Fourier coefficient but the dispersion coefficient seemed to be sensitive to the choice of amplitude ratio or phase lag. The detailed theory and the procedures for the evaluation of the parameters  $D$ ,  $D_c$ ,  $k_f$ ,  $K_A$  and  $k_u$  of gas-solid systems from  $A_n$  (or  $q_n$ ) for a chromatographic peak by a five-dimensional search were described in the original paper<sup>64</sup>.

The advantage of Fourier analysis over moment analysis is that it permits more information to be extracted from a curve. The higher moments (third to fifth) which are subject to increasingly large errors, or additional measurements, as Schneider and Smith<sup>60</sup> undertook, are necessary for moment analysis to give the same result.

Moment analysis and Fourier analysis are limited to systems that can be described by linear differential equations.

#### D. Method based on the passage of a pulse through a stirred reactor

The above two gas chromatographic techniques<sup>60,61,64</sup> can be used to study any reactant or product that emerges from the column as a reasonably well defined peak. In the study of a reactant under actual catalytic (or reaction) conditions, the product peak may interfere with that of the reactant.

Kelly and Fuller<sup>63</sup> proposed a method based on the passage of a pulse through

a stirred reactor to overcome this difficulty by using a more specific detector. A dynamic mathematical model of an isothermal heterogeneous continuously stirred tank catalytic reactor for a first-order reaction was developed and employed for the experimental determination of intra-granular diffusivities, binary sorption isotherms and reaction rate constants under actual reaction conditions. This method is rapid and only zero- and first-moment calculations of the transient response are required for the data analysis.

### *E. Study of mass transfer resistances in molecular sieves*

Zikanova<sup>54</sup> determined the radial coefficient of internal diffusion of pentane in granulated zeolites from the dependence of statistical moments of the elution curve on the linear flow velocity of the carrier gas. The results obtained provide evidence that the overall transport rate of the sorbate molecules from the surface of the granule to the adsorption site is limited by activated diffusion within zeolite crystallites. Several investigations have been reported on the measurement of effective diffusivities of synthetic zeolite and molecular sieve catalysts using gas chromatography<sup>53,56,58</sup>.

MacDonald and Habgood<sup>62</sup> described a gas chromatographic method based on the theory of Giddings and Schettler<sup>55</sup> for the determination of intra-crystalline mass transfer resistances in zeolite catalysts. They reported experimental results for benzene, octane and decane on an NaX zeolite catalyst at about 400°. The method is based on the following considerations:

The mass transfer in a microporous solid (such as molecular sieve and zeolite catalysts) takes place by two distinct processes: (i) mass transfer from the moving gas stream through the stationary gas film and within the macropore system of the granule to the external surface of the crystallite, and (ii) mass transfer through the micropores of the crystallite to reaction sites on the walls of the micropores. These two processes of mass transport in the regular crystal structure of the zeolites can be studied by the method of Giddings and Schettler<sup>55</sup>, which involves measurements of the total mass transfer resistances using two carrier gases of different diffusivities. The resistance due to process *i* depends upon the nature of the carrier gas, while that due to process *ii* does not, provided that the carrier gas is not significantly adsorbed. The relative contributions of film and macropore resistances to process *i* could be obtained to some extent from results with granules of different size ranges.

According to Giddings and Schettler<sup>55</sup>, the expression for HETP is

$$H/f_1 = H_g + C_s v_0 (f_2/f_1) \quad (44)$$

where  $H_g$  is the sum of all gas-phase contributions to the HETP,  $C_s$  the intra-crystalline mass transfer coefficient,  $v_0$  the column outlet velocity,  $f_2$  the James-Martin pressure gradient correction used in gas chromatography to allow for the variation in local gas velocity along the column, and  $f_1$  a factor to allow for decompression along the column. The terms contained in  $H_g$  are a function of  $v_0/D_g$ . The principle of the method lies in the fact that a known change in  $D_g$  which gives a corresponding change in  $H_g$  is produced, while not affecting  $C_s$ . By introducing a variable

$$X = v P_0/D_g' \quad (45)$$

eqn. 44 becomes

$$H/f_1 = H_g(X) + C_s X f_2 D_g/f_1 P_0 \quad (46)$$

Either by varying  $P_0$  using the same carrier gas, or by choosing two carrier gases of different diffusivities, two different curves of  $H/f_1$  versus  $X$  can be obtained. The HETP can be obtained by using the relationship

$$H = L f_2 / (f_1^2) \quad (47)$$

based on the more refined theories<sup>28</sup> from the statistical moments of the peak, which can readily be calculated by computer from a digitized peak<sup>62</sup>. By determining the HETPs over a range of flow-rates in each carrier gas, under conditions such that the range of  $X$  is the same for each gas,  $H_g(X)$  will have an identical value in each carrier and hence the term  $C_s$  can be obtained from the relationship

$$C_s = [(H/f_1)_1 - (H/f_1)_2] / [X(Z_1 - Z_2)] \quad (48)$$

where

$$Z = f_2 D_g / f_1 P_0 \quad (49)$$

Hence, from the plots of  $H/f_1$  versus  $X$  and  $Z$  versus  $X$ , one can obtain  $C_s$  from the differences in  $H/f_1$  and  $Z$  for two carrier gases at a given value of  $X$ . Typical plots of data<sup>62</sup> according to eqn. 48 are shown in Fig. 4.

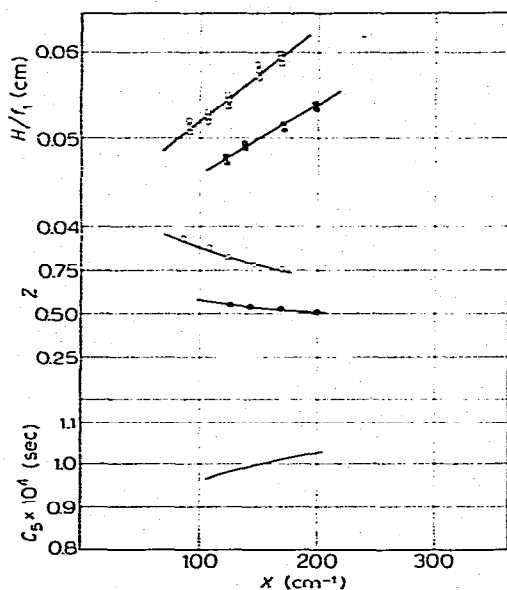


Fig. 4. Typical plots of data<sup>62</sup> according to eqn. 48, for benzene. Temperature = 430°. ●, Nitrogen; ○, hydrogen.

For a homogeneous spherical crystallite, an apparent diffusion coefficient,  $D_c$ , of the sorbate within the crystallite can be obtained from<sup>15</sup>

$$D_c = \frac{1}{30} \cdot \frac{k}{[1+k]^2} \cdot \frac{d_c^2}{C_s} \quad (50)$$

where  $k$  is the partition ratio and  $d_c$  the diameter of the zeolite crystallite. For large values of  $k$ , eqn. 50 reduces to

$$D_c = \frac{1}{30} \cdot \frac{d_c^2}{k C_s} \quad (51)$$

Based on their experience, MacDonald and Habgood<sup>62</sup> suggested criteria to indicate acceptable results.

## 5. HEAT TRANSFER PARAMETERS FOR PACKED BEDS

Sagara *et al.*<sup>56</sup> developed a temperature pulse method based on the chromatographic theory of Kubin<sup>73</sup> for the determination of heat transfer parameters for flow in packed beds of porous or non-porous solid particles. The method is based on the assumption that heat is dispersed axially and heat transfer occurs between fluid and particle, and intra-particle. The contribution to heat transfer due to solid-to-solid conduction, which is significant for small particle sizes, is neglected and hence this method is not suitable for beds of small particles.

The moments of the response of the column effluent temperature to a pulse in the inlet temperature are related to the thermal parameters by simple algebraic equations, so that the functional relationships of the parameters and variables are directly displaced: by varying the conditions, some of the coefficients can be determined. The first moment of the temperature curve from the bed gives reasonable estimates of the specific heat, while the second moment provides information on rate parameters (such as fluid-to-particle heat transfer coefficient, effective thermal conductivity of the particles and axial conductivity of the fluid phase). The method is rapid and interpretation of the data can easily be carried out as only elementary calculations are involved.

## 6. ACKNOWLEDGEMENT

The author thanks Dr. L. K. Doraiswamy, Deputy Director and Head of the Division of Chemical Engineering and Process Development, National Chemical Laboratory, Poona, for his encouragement throughout this work.

## 7. SUMMARY

A comprehensive review on the use of gas chromatographic techniques in the measurement of binary diffusion coefficients of gases and vapours, effective diffusivities of catalysts, intra-particle and intra-crystalline mass transfer coefficients, axial diffusion coefficients, surface diffusivities and heat transfer coefficients is presented.



## 8. NOMENCLATURE

$a_n$	Fourier coefficient defined by eqn. 37.
$A, B, C$	constants of eqn. 19.
$A_n$	amplitude ratio defined by eqn. 42.
$b_0, b_n$	Fourier coefficients defined by eqns. 38 and 39.
$c$	chart paper speed of recorder.
$C_g$	non-equilibrium term for gaseous diffusion.
$C_k$	non-equilibrium term for kinetic processes.
$C_l$	non-equilibrium term for liquid diffusion.
$C_s$	mass transfer resistance within crystallite.
$d_c$	crystallite diameter.
$d_p$	particle diameter.
$D$	dispersion coefficient.
$D_{AB}, D_d$	gas-phase diffusion coefficients.
$D_r$	intra-crystalline diffusion coefficient.
$D_e$	effective diffusivity of catalyst.
$D_u$	binary diffusion coefficient (at 1 atm pressure).
$D_k$	effective gas (Knudsen) diffusion coefficient.
$\mathcal{D}_k$	Knudsen diffusion coefficient.
$D_s$	effective surface diffusion coefficient.
$\mathcal{D}_s$	true surface diffusion coefficient.
$E_A$	apparent activation energy.
$E(i\omega')$	Fourier transform of $E(t)$ .
$E(t)$	probability density residence time.
$f_1, f_2$	pressure correction terms.
$F_1$	void fraction in packing.
$F_2$	solid fraction in packing ( $1 - F_1$ ).
$H$	height equivalent to a theoretical plate (HETP).
$H_g$	plate height to gas phase contribution.
$k$	partition ratio.
$k_a$	adsorption rate constant.
$k_f$	external mass transfer coefficient.
$K_A$	adsorption coefficient.
$l$	distance on recorder chart measured from the point corresponding to the start of the chromatogram to the peak maximum.
$L$	length of packed column.
$L_t$	length of long diffusion tube.
$L_s$	length of short diffusion tube.
$m$	distance on the base line between points where the two tangents (to the point of inflection of peak) intersect.
$M, M_A, M_B$	molecular weights.
$n$	number of plates.
$p$	pressure.
$p_c$	pore volume.
$P_0$	ratio of outlet pressure to unit pressure.
$q_{int}$	tortuosity factor for intra-particle gas diffusion.

$q_{sur}$	tortuosity factor for intra-particle surface diffusion.
$r_0$	tube radius.
$r_p$	average pore radius.
$R$	gas constant.
$\Delta V_R^0$	volume of carrier gas corresponding to the maximum of the peak.
$\Delta S^0$	volume of carrier gas corresponding to the base of the elution peak.
$t$	time.
$t_m, t_d$	retention times for adsorbate and non-adsorbate.
$t_{0,t}$	injection time for adsorbable substance.
$t_R$	retention time of peak measured at its centre.
$T$	temperature.
$T'$	period.
$v$	average carrier gas velocity.
$v_c$	critical velocity.
$v_0$	outlet velocity.
$V_A, V_B$	molar volumes.
$V_d^0$	retention volume for non-adsorbate.
$V_R^0$	retention volume for adsorbate.
$W$	weight of adsorbent.
$X$	reduced velocity equal to $v_0 P_0 / D_g$ .
$z$	coordinate along the length of chromatographic column.
$Z$	$f_2 D_g / f_1 P_0$ .
$\alpha$	external void fraction.
$\alpha'$	distribution coefficient.
$\beta$	intra-particle void fraction.
$\gamma, \bar{z}$	constants (of the order of unity).
$\mu_1'$	first absolute moment.
$\mu_2, \mu_3$	second and third central moments.
$\rho_b$	density of packed bed.
$\rho_p$	particle density.
$\delta^2$	variance.
$\tau$	standard deviation.
$\omega$	peak width.
$\omega'$	frequency (equal to $n\pi/T'$ ).
$\theta$	equal to $L/v$ .
$\varepsilon$	pellet porosity.

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