

Analysis of Chromatographic Theories and Thermodynamics Calculation Procedure

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Abstract—This paper presents the development of chromatography, two mathematical methods for describing chromatographic phenomena, band broadening processes as well as the procedure for retention volume measurement and calculation. The plate and the rate theories for gas chromatographic phenomena are comprehensively discussed. The reduction of infinite dilution activity coefficients from retention data is explained. While the rate theory can predict the influence of various factors on column performance, the plate theory is more useful in the calculation of thermodynamic properties such as infinite dilution activity coefficients, enthalpy and entropy of mixtures.

Keywords—Band broadening, chromatographic phenomena, column performance, plate theory, retention volume, thermodynamic properties

I. INTRODUCTION

ALTHOUGH the word chromatography was employed as early as 1731, the first published work was in 1906 by Tswett [1]. Tswett (1906) [1] was the first to recognize that the chromatographic process consists of sequential sorption – desorption interactions. This was visualized in the original experiments in which plant pigments were separated into coloured bands by elution with petroleum ether through a bed of powdered calcium carbonate. The name chromatography was suggested for this separation procedure. In 1931, Kuhn et. al. in [1] rediscovered the same technique when resolving plant carotene into its components. This technique called liquid – solid chromatography was further developed between 1940 and 1946 mainly by Tiselius and Claesson as discussed by [1]. Wilson (1940) [2] was the first to describe the chromatographic process mathematically assuming complete solute sorption – desorption equilibrium. The elution process was then treated as the passage of a concentration profile through the chromatographic system. Reference [2] also recognized that bandwidth phenomena were most likely dependent on column void space, diffusion as well as finite rates of sorption – desorption.

The most important development in the history of chromatography was in 1941 when Martin and Synge [3]

developed a theory based on packed column distillation for liquid – liquid chromatography. Equilibration of solute between the mobile and stationary phases in each plate was assumed to be complete. Plate to plate diffusion was considered to be negligible and the ratio of solute concentration in the phases (partition coefficient) was taken to be constant irrespective of the amount of solute present (linear isotherm). Reference [4] offered a promising improvement to Wilson's earlier treatment by correcting several of the physical impossibilities, which developed from the theory. De Vault's [4] treatment was superior to that of Martin and Synge [3] in that it was based on the continuous distribution of the solute between the stationary and mobile phases along the length of the column. Thus avoiding the hypothetical discontinuity of the plate model and this treatment was later confirmed by [5].

Thomas (1944) [6] made an important contribution to the continuous distribution model. He examined ion exchange process in flowing systems and demonstrated that if the flow rate is slow enough the rate – controlled sorption – desorption column processes will approach equilibrium. This can then be treated with mathematical precision. Investigations of rate controlled kinetic processes such as diffusion and mass transfer were carried by many workers. Lapidus and Amundson (1952) [7] developed a mathematical model that introduced explicitly concepts of eddy and longitudinal diffusion as well as mass transfer non equilibrium contributions. These studies formed the basis of the well – known treatments of Van Deemter et. al. (1956) [8] as they simplified the mathematics of Lapidus and Amundson (1952) [7]. The result was the clarification and popularisation of what is known today as the 'rate theory of chromatography'.

After the publication of the successful experiments of James and Martin (1952) [9], the gas liquid chromatography (GLC) received great response as the simple and powerful technique in separation and analysis work. The GLC technique has progressed rapidly in theory and practice since in 1952. Earlier important contributions to the GLC are due to James and Martin [9], James and Phillips (1953) [10], Ray (1954) [11] and Bradford et. al. (1955) [12]. Golay (1957) [13] introduced a new version of the GLC by replacing the packed chromatographic column with high efficiency capillary column in which the liquid phase is supported by the inside wall of the capillary tube. Reference [13] developed a theory for the capillary column based on the electrical analogy of resistors and condensers.

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Several mathematical methods have been developed to describe the chromatographic phenomena. For gas liquid chromatography the applicable methods can be divided into two basic theories. One of these theories is based on equilibrium and is called the 'plate theory' while the other one is the 'rate theory' based on kinetics and these are discussed in section II of this paper.

II. CHROMATOGRAPHIC THEORIES

A. The Plate Theory

Martin and Synge [3] introduced the plate theory by applying the 'theoretical plate' concept of distillation to a liquid – liquid chromatographic column. This theory was expanded by [14] who illustrated the calculation of the number of theoretical plates. James and Martin [9] modified the theory by deriving the correction factor for the compressibility of the carrier gas in the case of gas – liquid chromatography. The theory is based on the following assumptions (i) instantaneous equilibrium takes on the first and on each successive theoretical plate (ii) the distribution isotherm is linear, that is at equilibrium the distribution ratio of one solute between the two phases is independent of both the absolute value of its concentration and the presence of other solutes (iii) the diffusion effects of the solute along the length of the column are negligible (iv) the solute volume is negligibly small (v) the molecules of the solute are distinguishable in the carrier gas (vi) the pressure is constant throughout the column (vii) the support material is completely inert and exerts no adsorption effect.

According to the plate theory the GLC column is considered to consist of a number of thin layers and each is such that true equilibrium exists between the mean concentration of the solute in the stationary phase in that layer and its vapour in the gas phase leaving that layer. Consequently each layer is equivalent to one theoretical plate. The height of each plate is called the height equivalent to a theoretical plate (HETP). The passage of a solute through the column can be treated mathematically by making material balances around each plate during the continuous flow. A binomial expansion is developed to express the amount of solute left in each plate after successive infinitesimal volumes of the gas phase has passed. The Gaussian distribution is used to approximate the binomial distribution through the use of Bernoulli's theorem. This treatment finally leads to (1) for the shape of the elution curve on a column of n plates.

$$Q_n = \frac{1}{\sqrt{2\pi n}} \left(\frac{V}{V_m + KV_L} \right)^{ne^n - \frac{V}{V_h}} \quad (1)$$

Q_n , V_m , V_L , K and V_h are the amount of solute in the n th plate when V of gas passed, the volume of gas holdup in the column, the liquid phase volume, the partition coefficient defined as the ratio of the solute concentration per unit volume

in the liquid phase to that in the gas phase and the effective volume of each plate respectively. The effective volume of each plate is equal to $h(a + Kb)$ where h the height equivalent to a theoretical plate, a and b are cross sectional areas of the gas and liquid phases respectively. At maximum concentration;

$$Q_n = \frac{1}{\sqrt{2\pi n}} \quad (2)$$

$$n = \frac{V}{V_h} \quad (3)$$

In (3) V is the volume of gas required to elute the maximum peak of the solute through the column and this by definition equal to the retention volume (V_R). Therefore:

$$V_R = V = nV_h = nh(a + Kb) \quad (4)$$

Or

$$V_R = V_M + KV_L \quad (5)$$

Equation (5) is the fundamental equation in GLC through which thermodynamic functions can be calculated. The number of theoretical plates can be derived by making use of (1) [15]. The two points of inflection of the Gaussian distribution curve of the equation are at $V = (2 \pm \sqrt{n})V_h$ and the intersections with the base line of the tangents to these points are at $V = (n \pm 2\sqrt{n})V_h$. The section of the baseline between these two points of intersection is the peak width V_p , Fig. 1 and is calculated as in (6).

$$V_p = (n + 2\sqrt{n})V_h - (n - 2\sqrt{n})V_h = V_h \sqrt{n} \quad (6)$$

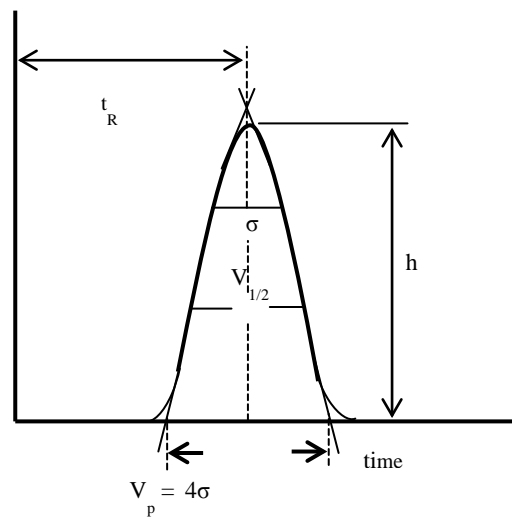


Fig. 1 Measurement of N

The number of theoretical plates (n) which is essentially a measure of peak sharpness can be calculated from the volume of gas corresponding to peak maximum (V_R) and the peak width (V_p) of the chromatogram using (7) or (8).

$$\frac{V_R}{V_p} = \frac{nV_h}{4V_h\sqrt{n}} = \frac{1}{4}\sqrt{n} \quad (7)$$

Or

$$n = 16 \left(\frac{V_R}{V_p} \right)^2 \quad (8)$$

The height equivalent to a theoretical plate (HETP) is given by (9) where L is the length of the column.

$$HETP = \frac{L}{n} \quad (9)$$

B. The Rate Theory

Van Deemter et. al. [8] developed the rate theory for linear isotherm by considering the chromatographic column as a continuous medium and also took into account diffusional operations of mass transfer. The theory shows that the distribution curve of a single solute can be approximated by a Gaussian curve of the same type as that of the 'plate' theory. According to the plate theory as presented by [8], the following processes describe the phenomena taking place in the chromatographic column; (i) Eddy diffusion caused by the irregular paths of gas molecules as a result of the presence of packing material (ii) Molecular diffusion of the solute in the vapour takes place longitudinally. Molecular diffusion in the liquid phase is very small and can be neglected. (iii) Equilibrium between the two phases does not take place instantaneously because of resistance to mass transfer. These processes are related to the height equivalent to a theoretical plate through (10).

$$HETP = 2\lambda d_p + \frac{2MD_g}{u} + \frac{8k'}{\pi^2(1+k')^2} \frac{d_f^2}{D_L} u \quad (10)$$

In (10) λ , M , D_g , u , k' , d_f and D_L are the correction factor, diffusion coefficient in the gas phase, correction factor for the tortuosity of the interparticle spaces, linear gas velocity,

a factor given by $\frac{KF_l}{F_g}$, the effective thickness of liquid film on the support and the diffusion coefficient in the liquid phase respectively. Equation (3) can be expressed using three constants only (11).

$$HETP = A + \frac{B}{u} + C_s u \quad (11)$$

Equation (11) is the abbreviated form of the well-known Van

Deemter equation. A , B and $C_s u$ are the eddy diffusion, molecular diffusion and mass transfer terms. The 'rate' theory

as presented by [8] was tested experimentally and found to be correct [16], [17]. However [17] indicated that the diffusion term is not independent of flow rate but inversely proportional to it. The Van Demeeter equation was also modified by including the fourth term to account for the resistance to mass transfer in the gas phase [18]. The 'plate' theory is the simpler of the two and is suitable in describing the shape of the elution curves, calculating the number of theoretical plates and HETP. The combination of the 'plate' and 'rate' theories can be made through the HETP of (9), (10) and (11). The resulting equation is very useful in discussing the various factors affecting GLC operation and performance.

III. BAND BROADENING PROCESSES

The three main contributions to band broadening are eddy diffusion, longitudinal molecular diffusion and mass transfer. The variances of each of the band broadening processes are additive to give the overall variance of the system and this is a measure of column efficiency. Column efficiency is expressed in terms of plate height (H) and is a function of the average

linear velocity of the mobile phase, u .

$$H = \left(\frac{1}{A} + \frac{1}{C_m u} \right)^{-1} + \frac{B}{u} + C_s u + C_{sm} u \quad (12)$$

A. Eddy Diffusion

The A term represent eddy diffusion or the multiple paths effect. The flow pattern through a bed of granular material is very tortuous as solute and mobile phase follow a path of least resistance to flow. The velocity of a single particle through the packed bed will fluctuate between wide limits and the total distances travelled by individual particles will also vary. The fluctuations are random because the structure of the bed which causes them is random. Particles travelling through open pathways will travel rapidly compared in narrow pathways. The simple theory of eddy diffusion assumes that the particle will remain in a single flow path. This is not the case in practice as the particle can diffuse laterally from one flow path to another. This process is called coupling and it averages out the two flow paths and reduces the amount of band broadening so that the final bandwidth, although still greater than the initial band width is less compared to a situation where coupling had not occurred. The contribution to the overall plate height, H , from multiple paths effect is expressed as in (13).

$$A = 2\lambda d_p \quad (13)$$

In (13) λ is packing constant which is ≈ 0.5 for well packed columns and d_p is the particle diameter.

B. Molecular Diffusion

As the solute band moves through the column, diffusion in the direction of flow (longitudinal or axial) also occurs. Besides occurring in the fluid phase, this diffusion also takes at the interface. The contribution of molecular diffusion to plate height is given by (14).

$$B = 2\gamma D_M \quad (14)$$

In (14), γ is the obstruction factor which accounts for column packing hindrance to diffusion. For packed columns, typical values range from 0.6 – 0.8. D_M is the coefficient of diffusion of the solute species in the mobile phase.

C. Mass Transfer

Mass transfer (C terms) relates to the rates at which solute species are sorbed and desorbed as well diffusion within each phase. This rate is controlled by sorption – desorption and diffusion controlled kinetics. Sorption – desorption kinetics refers to the intermittent capture and release of solute species by the stationary phase. Diffusion controlled kinetics may originate from either the liquid stationary phase or the mobile phase. The mass transfer effects are divided into stationary (C_s) and mobile (C_m) phase terms. The rate at which solute species transfer into and out of the stationary phase makes significant contribution to band broadening and the rate is mainly controlled by diffusion in the liquid stationary phase. As a result of statistical fluctuations, individual solute species will spend different time in the stationary phase. Those particles which spend most time in the stationary phase, will when they re-join the mobile phase would have been left behind resulting in band broadening. The contribution to the overall plate height is given by (15).

$$C_s = \frac{d_f^2}{D_s} \frac{k'}{(1+k')^2} \quad (15)$$

In (14) k' , d_f and D_s are the capacity factor, liquid film thickness and the rate of diffusion respectively. The liquid film thickness should be small and the liquid stationary phase should be chosen to give high solute diffusion coefficients. Film thickness is controlled by both the quantity of stationary phase used as well as the surface area of the support material. The mobile phase mass transfer is made up of the moving mobile and the stagnant mobile phase's contributions.

- **Moving mobile phase:** The solute species in the same flow path do not move with same velocity. Those in the centre will move more rapidly than those at the column walls which are slowed as a result of frictional forces and this gives rise to band broadening. The contribution to the overall plate height is expressed as in (16).

$$C_m = \frac{\Omega^2}{D_M} \quad (16)$$

In (16), Ω , d_p , D_M are a function of packing structure, particle diameter and the coefficient of diffusion of the solute species in the mobile phase respectively.

- **Stagnant mobile phase:** If the stationary phase is made up of porous material, the pores (the intra particle void) is filled with mobile phase at rest and there is very little interchange between this 'stagnant' mobile phase in the pores and the moving mobile phase outside the pores i.e. in the interparticle void volume. To reach the stationary phase, solute particles will have to diffuse into this stagnant pool of fluid. Some solute molecules will diffuse deeper into the stagnant pool than others and will be left behind. When these molecules finally join the stream again, a band broadening of the chromatographic band occurs. In a packing of porous spherical particles, the contribution to the overall plate height is given by (17).

$$C_{sm} = \frac{(1-\phi+k')^2 d_p^2}{30(1-\phi)(1+k')^2 \gamma D_M} \quad (17)$$

ϕ is the fraction of the total mobile phase in the inter-particle space.

IV. RETENTION VOLUMES

A. Gas Holdup Volume (V_m)

The gas hold volume is a measure of the total volume of space available to the mobile phase in the system, that is column dead void volume, injector and detector volumes as well as the volumes of any connecting tubing for example from column to detector. The gas holdup volume (V_m) is defined in (18), F and t_m are carrier gas flow rate and retention time respectively.

$$V_M = Ft_m \quad (18)$$

In a well-defined system, the extra column dead volume is small compared to the column dead volume. The column itself is not completely filled with stationary phase. The fraction of free (non-solid) space within a certain volume element of a porous material is called its porosity which is a measure of space available to the mobile phase. Gas occupies both the space between particles where it is moving and pores within particles where it is stagnant. A non-sorbed molecule spends part of its time in each space.

B. Uncorrected Retention Volume (V_R)

This is the mobile phase volume required to elute the sample from the column and is usually referred to as the retention volume without any qualification as it is properly called the uncorrected retention volume (V_R) (19).

$$V_R = Ft_R \quad (19)$$

C. Adjusted Retention Volume (V'_R)

The retention time t_R is made up of t_m , the time the solute spends in the mobile phase and time, t_s , the time the solute spends in the stationary phase. Separations are due to different times solutes spend in the stationary phase. The adjusted retention time, t'_R is the time the solute spends in the stationary phase. The adjusted retention volume V'_R is defined as in (20).

$$V'_R = Ft'_R = V_R - V_M \quad (20)$$

D. Net Retention Volume (V_N)

This is the adjusted retention volume corrected for the compressibility of the gaseous mobile phase.

$$V_N = jV'_R = j(V_R - V_M) \quad (21)$$

j is the gas compressibility factor and it is defined as in (22)

$$j = \frac{3}{2} \left[\frac{\left(\frac{P_i}{P_o}\right)^2 - 1}{\left(\frac{P_i}{P_o}\right)^3 - 1} \right] \quad (22)$$

$\frac{P_i}{P_o}$ is the ratio of the inlet and outlet pressures

E. Specific Retention Volume (V_g)

This is defined as the net retention volume per gram of stationary phase at 0°C. This is very important as it allows the comparison of retention data obtained at different temperatures and with different weight of the same stationary phase.

$$V_g = \frac{273.16V_N}{W_s T_c} \quad (23)$$

In (23) W_s , T_c and V_N are weight of stationary phase, column temperature and the net retention volume corresponding to that measured at column temperature, corrected for gas hold-up in the column and for pressure drop from inlet to outlet of the column respectively.

F. Retention Time Measurement

Retention is measured from the point of injection to the maximum of the chromatographic peak. For very sharp peaks, the maximum is easily determined but for broad peaks tangents to the peak have to be drawn and the retention time will be the point of intersection as shown in Fig. 2. The use of retention volume (V_R) is preferred as it allows comparison of retention data obtained under different flow conditions. The

measurement of t_m requires a solute that has a distribution coefficient $K = 0$. Since K is dependent on temperature, a change in column temperature will result in a change in

t_R unless if $K = 0$.

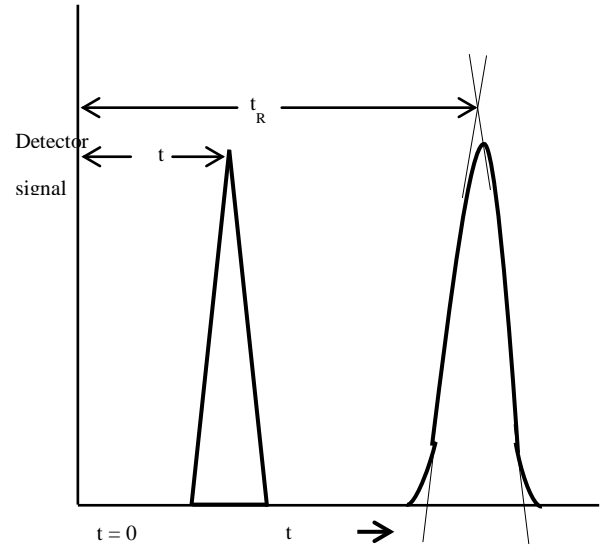


Fig. 2 Retention time measurement

G. Activity Coefficients from GLC

Infinite dilution activity coefficient γ^∞ can be expressed in terms of gas chromatographic data and saturation vapour pressure as in (24).

$$\gamma_i^\infty = \frac{273R}{V_g^o P_i^o M_2} \quad (24)$$

In (24) R , M_2 , V_g^o and P_i^o are the universal gas constant, stationary phase molecular weight, specific retention volume and solute vapour pressure.

To correct for the vapour phase deviation from ideal behaviour, we can conveniently make use of the second virial coefficient (B) as defined in (25).

$$B = \lim_{P \rightarrow 0} \left(V - \frac{RT}{P} \right) \quad (25)$$

When the corrections for vapour phase deviation from ideal behaviour are taken into account, the activity coefficient at infinite dilution can be expressed as in (26).

$$\ln \gamma^\infty = \ln \left[\frac{273.16R}{P_i^o V_g^o M_2} \right] - \frac{P_i^o}{RT} (B_{11} - V_1) \quad (26)$$

B_{11} is the gas – state second virial coefficient of component 1 and V_1 is the liquid state molar volume. When the carrier gas is helium at no more than 6 psi above atmospheric pressure corresponding to a flow rate of 10 – 50 cm³ min⁻¹, the solute-carrier virial coefficients are negligible.

V. CONCLUSION

Two approaches can be used to explain chromatographic

separation process. The 'plate' theory proposed by Martin and Synge [3] was based on an analogy with distillation and counter current extraction. The 'rate' theory of Van Demeter et al [8] accounts for the dynamics of separation and can predict many aspects of chromatographic performance. The 'plate' theory neglected the concepts of solute diffusion and flow paths and these are accounted for in the 'rate' theory. The 'rate' theory can predict the effect on column performance of factors such as phase properties, phase thickness, solute diffusivities, partition coefficients, phase velocity, phase thickness, support size, support porosity and flow rates. Each theory has its own advantages and limitations. The 'plate' theory is more useful in the derivation of thermodynamic properties such as infinite dilution activity coefficients as well as enthalpy and entropy of mixing through the measured retention volumes.

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