# Quantitative Methods in Chemistry

Week 10, Lecture 3

This week: Theoretical basis of chromatography (concept of plates, theoretical plate height, plate count, resolution, retention time, retention factor, selectivity factor)

This lecture: Theoretical basis of chromatography – Comparison between Rate theory and plate theory

Plate Theory – Success and Pitfalls

Imaginary plates that result in separation
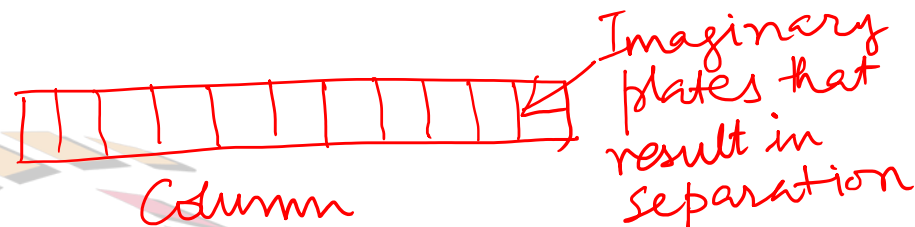
Column

- Has a **thermodynamic** basis (relies on attainment of equilibria between mobile and stationary phases). *on the plates*

R_s = resolution
N = plate count

- Was successful in predicting **band broadening**. Remember $H = \sigma^2/L$. This can be re-written as $H \cdot L = \sigma^2$. As the length of column increases, the variance of the peak increases as well.

- Resolution increases with plate count - $R_s \propto \sqrt{N}$ $H\downarrow$ => $N\uparrow$ for the same length of column. So, it aimed to achieve **small HETP values** to achieve **high resolutions**.

- Plate theory assumes **establishment of equilibrium** by the solute between the mobile and the stationary phases. However, this is **not** at all **true**, especially under rapid eluting conditions that give the best resolutions.

Invariant of solute conc'n.

$$K_c = \frac{C_S}{C_M}$$

- The distribution constant presumes the **adsorption isotherm to be linear**. However, most solutes exhibit **Langmuir-type adsorption isotherms** between the stationary phase and the mobile phase, which are not linear.

Isocratic elution

- Presumes that chromatographic **conditions remain constant** throughout the analysis. However, this will not be true under **gradient elution** conditions. → two or more solvents are mixed together in different proportions to achieve faster elution of the solute.

Rate theory of Chromatography

- Is the more refined theory for chromatographic separations

- Proposed in 1956 by van Deemter.

- Relies on the **rate** at which solute partitions between the stationary and mobile phases.

- Takes into consideration the changes in **column efficiencies** with **flow-rate** of mobile phase.

- Provides optimized solvent flow rates to achieve highest efficiencies

Plate theory - Thermodynamic
Rate theory - Kinetic

Jan Jozef van Deemter

Change in plate height with flow-rate of mobile phase

Gas chromatography
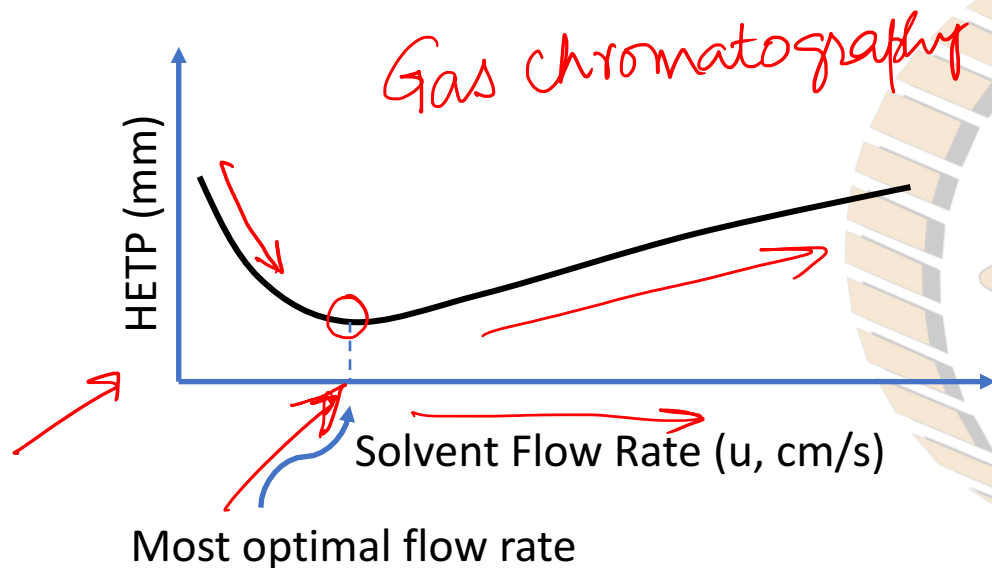
- Increasing flow rate of the mobile phase brings about a decrease in the plate height initially. This corresponds to increased efficiency of separation.

- As the flow rate is increased further, the plate height increases and the efficiency decreases.

- Why does this happen and how to explain this?

HETP (mm)

Solvent Flow Rate (u, cm/s)

Most optimal flow rate

The Van Deemter Equation

$$\text{HETP} = A + B/u + Cu$$

Reduce all these terms to achieve smallest HETP values.

Where, u is the linear velocity or flow rate of the mobile phase

A, B and C are terms in the equation

C_s is the stationary phase resistance-to-mass-transfer coefficient

C_m is the mobile phase resistance-to-mass-transfer coefficient

$$C = (C_S + C_M)$$

HETP

Cu

A

B/u

← Composite effect of the three terms.

Linear flow rate of mobile phase (u, cm/s)
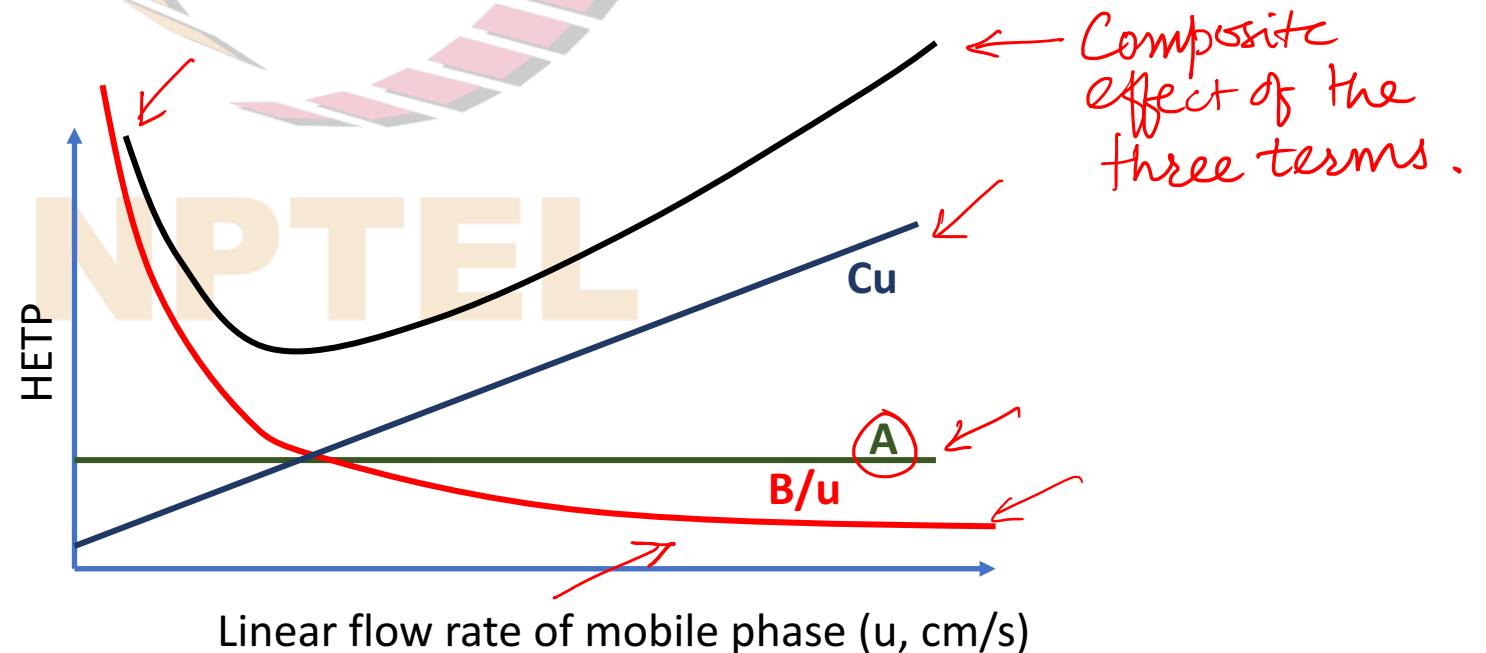
Term A in Van Deemter Equation

1st term

Packed chromatographic column

- The coefficient A is also known as the **Eddy Diffusion Term**.

- It is also called the **Packing Parameter Term**.

- It is independent of the flow rate and is the **inherent property of the column**.

- Occurs due to the multiple paths of flow for the solute inside a packed column.

W_i

W_o

$$A = 2 \cdot \lambda \cdot d_p$$

$$A \propto d_p$$
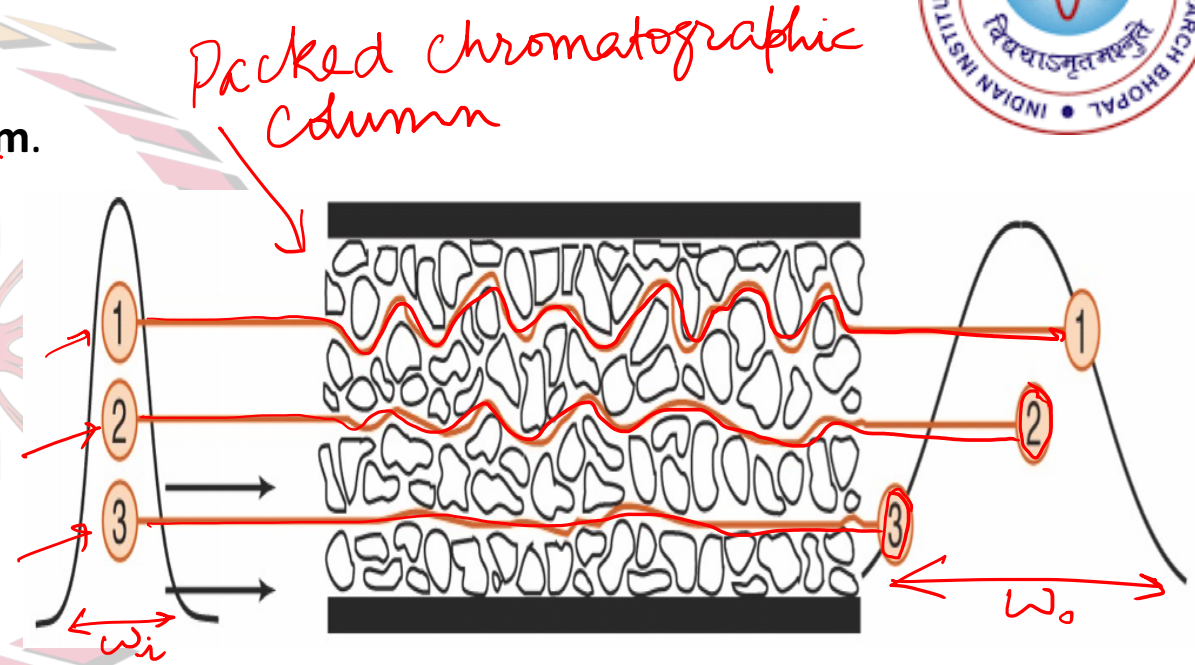
Where λ = dimensionless constant characteristic of packing of column,

And d_p = diameter of the particles employed in packing

Factors influencing A-term ('eddy' diffusion or multiple-path term)

Particle size d_p – Smaller the particle size, smaller is the path dispersion effect

Particle shape (regular or irregular?) – Regular (spherical) particles provide more uniform path to the solute

Particle pore structure / shape

Quality of the column packing – well packed columns provide better resolutions!

Wall effects (material, roughness, column diameter) – preferably thin columns with smooth walls

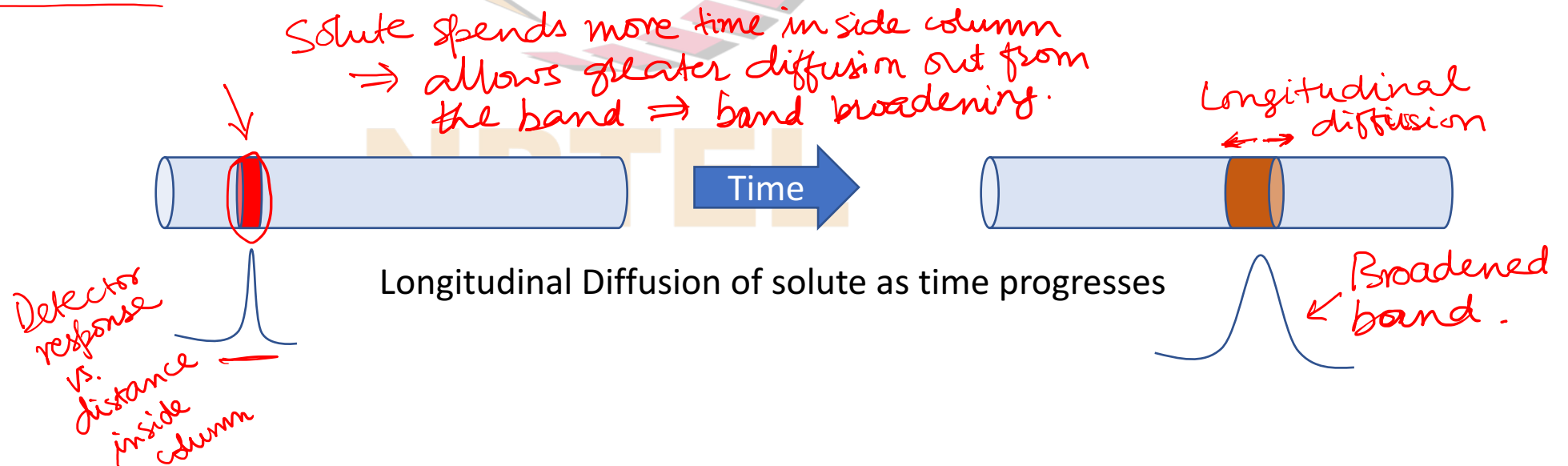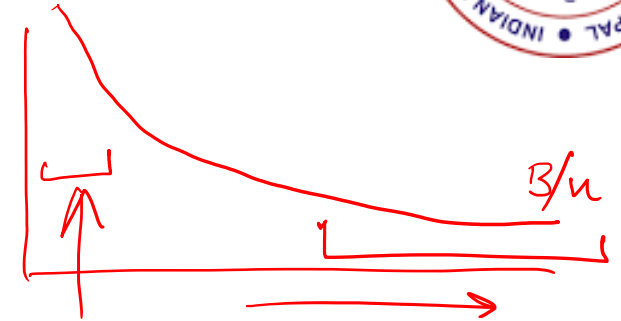*mobile phase flows unobstructed*

A-term can be removed if there is **no packing** in the column! $A \rightarrow 0$

Is it possible? ←

Term B/u in Van Deemter Equation

- Also known as the **Longitudinal Diffusion Term**.

- Arises due to concentration of the solute into a **thin band** during elution.

- The solute has natural tendency to **diffuse out** of the band.

- Very important in Gas Chromatography because of faster diffusion in gases.

- Dominates during low flow rates for mobile phase because the solute gets more time to diffuse out.

B/u

Solute spends more time inside column ⇒ allows greater diffusion out from the band ⇒ band broadening.

Longitudinal diffusion

Time

Longitudinal Diffusion of solute as time progresses

Detector response vs. distance inside column

Broadened band.

Peak broadening due to Diffusion

Variance (σ^2) due to diffusion is given as:

$\sigma^2 = 2 \cdot D_M \cdot t_M$ where, D_M is the diffusion constant of solute in the mobile phase and t_M is the dead time or void time.

$\sigma^2 = 2 \cdot D_M \cdot L/u$ where u is the average linear velocity of the solvent.

Now, Plate Height due to longitudinal diffusion is:

$H_D = \sigma^2/L = 2 \cdot D_M / u$ where $2 \cdot D_M = B$

Factors influencing the Longitudinal Diffusion term

- Linear velocity of the mobile phase
- Diffusion coefficient of analyte in the mobile phase D_M
- Mobile phase viscosity γ
- Temperature
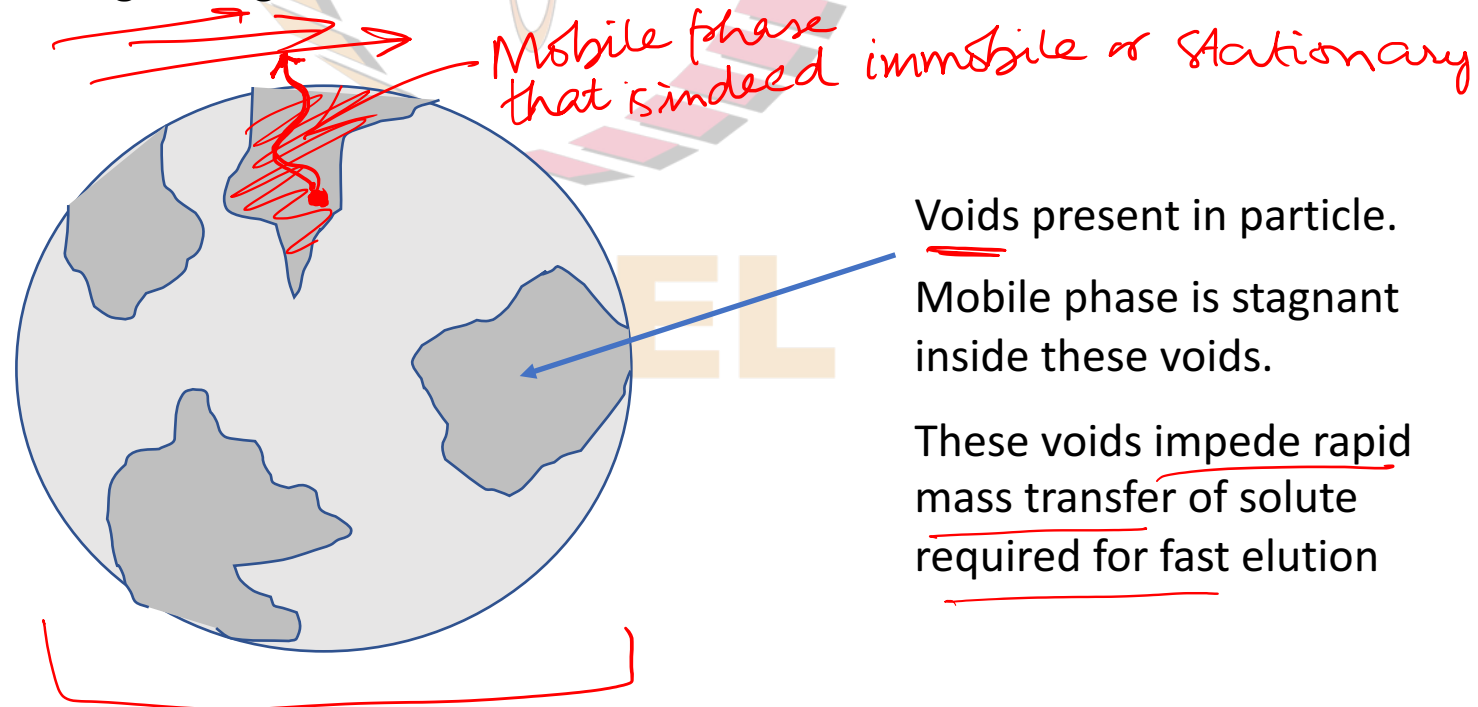- Type of analyte (molecular mass)

$\gamma \propto \dfrac{1}{B/u}$

Term C in Van Deemter Equation

- Also called the "**Resistance to Mass Transfer**" term.

- Occurs due to **Non-equilibrium** conditions occurring during chromatography.

- The solute resists transfer to the mobile phase if **entrapped in the voids** present in the particle of stationary phase

- **Slower flow rate** allows sufficient time for the solute to diffuse out of the voids, thus decreases the band broadening arising due to this term.

Cu

reduce flow rates to reduce Cu term

Mobile phase that is indeed immobile or Stationary

Voids present in particle.

Mobile phase is stagnant inside these voids.

These voids impede rapid mass transfer of solute required for fast elution

Factors effecting Term C in Van Deemter Equation

lower resistance → faster diffusing solute into the mobile phase

- The mobile phase resistance-to-mass-transfer coefficient C_M is inversely proportional to the Diffusion Coefficient of the solute in the mobile phase.

- For packed columns, C_M is proportional to the particle size d_p used in the stationary phase.

- A slow flow rate for the mobile phase allow for sufficient equilibration/ diffusion of the solute into the moving mobile phase.

- Retention Factor k

$$k = \frac{t_s}{t_M}$$

- Viscosity and Velocity of the mobile phase

- Quality and porosity of the stationary phase

Minimal pores & Small particle sizes for smallest C·u term

- Temperature at which chromatography is undertaken

Influences diffusion coefficient, viscosity