Chemistry 4631

Instrumental Analysis
Lecture 23

Introduction to Chromatography

Rate Theory

- Focuses on the contributions of various kinetic factors to zone or band broadening.

- Column Dispensivity, H, is assumed to be the sum of the individual contributions of the kinetic factors.

Introduction to Chromatography

Rate Theory

$$H = A + B/u + Cu \text{ (van Deemter equation)}$$

- u – average linear mobile phase velocity

- A – represents the contribution to zone broadening by eddy diffusion

- B – represents the contribution of longitudinal diffusion

- C – represents the contribution of resistance to mass transfer in both the stationary and mobile phases.

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Rate Theory

- Eddy Diffusion – (A term) – results from the inhomogeneity of flow velocities and path lengths around the packing particles (individual flow paths for packed columns are of different lengths).

- Small uniformly packed particles in columns are the most efficient and A is very small.

- A is zero for open tubular columns.

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Flow direction
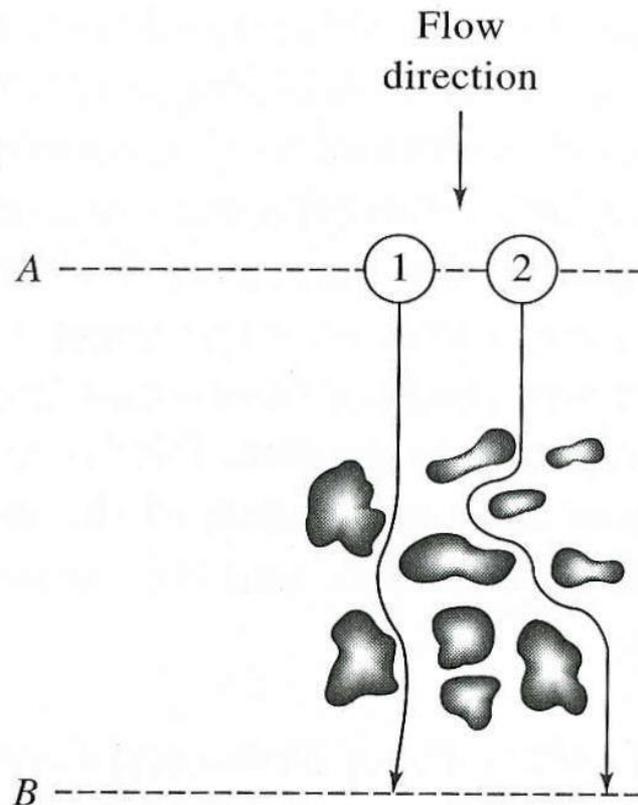
Figure 26-8 Typical pathways of two molecules during elution. Note that distance traveled by molecule 2 is greater than that traveled by molecule 1. Thus, molecule 2 would arrive at B later than molecule 1.

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TABLE 26-3 Kinetic Processes That Contribute to Peak Broadening

Process	Term in Equation 26-19	Relationship to Column* and Analyte Properties
Multiple flow paths	A	$A = 2\lambda d_P$
Longitudinal diffusion	B/u	$\dfrac{B}{u} = \dfrac{2\gamma D_M}{u}$
Mass transfer to and from liquid stationary phase	$C_S u$	$C_S u = \dfrac{f_S(k')d_f^2}{D_S}u$
Mass transfer in mobile phase	$C_M u$	$C_M u = \dfrac{f_M(k')d_p^2}{D_M}u$

*u, D_S, D_M, d_f, d_p, k' are as defined in Table 26-2.
$f(x)$ = function of x.
λ, γ: constants that depend on the quality of the packing.
B: coefficient of longitudinal diffusion.
C_S, C_M: coefficients of mass transfer in stationary and mobile phases, respectively.

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Rate Theory

$H = A + B/u + Cu$ (van Deemter equation)

- u – average linear mobile phase velocity

- A – represents the contribution to zone broadening by eddy diffusion

- B – represents the contribution of longitudinal diffusion

- C – represents the contribution of resistance to mass transfer in both the stationary and mobile phases.

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Rate Theory

- Longitudinal (molecular) Diffusion – (B term) – arises from the random molecular motion of analyte molecules in the mobile phase. Longitudinal diffusion along the axis of the column results in zone broadening.
- $ß = 2\gamma\, D_m$.

- Obstructive factor, γ – is unity for coated capillary columns. Longitudinal diffusion is hindered by packing.

- D_m – solute diffusion coefficient in the mobile phase.

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Rate Theory

- Diffusion rate depends on temperature and pressure of the mobile phase.

- D_m decreases with decreasing temperature and increasing pressure.

- LC has a much lower β than GC since diffusion rates are much larger in gases.

- So gases of higher MW's are favored as mobile phases since diffusion is lower.

- As mobile phase velocity increases β becomes less.

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TABLE 26-3 Processes That Contribute to Band Broadening

Process	Term in Equation 26-23	Relationship to Column* and Analyte Properties
Multiple flow paths	A	$A = 2\lambda d_p$
Longitudinal diffusion	B/u	$\dfrac{B}{u} = \dfrac{2\gamma D_M}{u}$
Mass transfer to and from stationary phase	$C_S u$	$C_S u = \dfrac{f(k)d_f^2}{D_S}u$
Mass transfer in mobile phase	$C_M u$	$C_M u = \dfrac{f'(k)d_p^2}{D_M}u$

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Rate Theory

$$H = A + B/u + Cu \text{ (van Deemter equation)}$$

- u – average linear mobile phase velocity

- A – represents the contribution to zone broadening by eddy diffusion

- B – represents the contribution of longitudinal diffusion

- C – represents the contribution of resistance to mass transfer in both the stationary and mobile phases.

$$H = A + B/u + Cu = A + B/u + (C_s + C_m)\,u$$

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Rate Theory

Mass Transfer – (C term) – most important term in GC, LC, and SFC.

- For a stationary phase – C_s is small for solid phases (since transfer of analyte on and off a surface is rapid), but is a factor for liquid stationary phases.

- C for liquids depends on thickness of the film, the diffusion coefficient of the analyte in the stationary phase and geometric nature of the packing.

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Rate Theory

- For a mobile phase – C_m – depends on the capacity factor of the analyte and the particle diameter of the stationary phase (packed) or internal diameter of the column (open tubular). Efficiency increases as particle size or column diameter decreases.
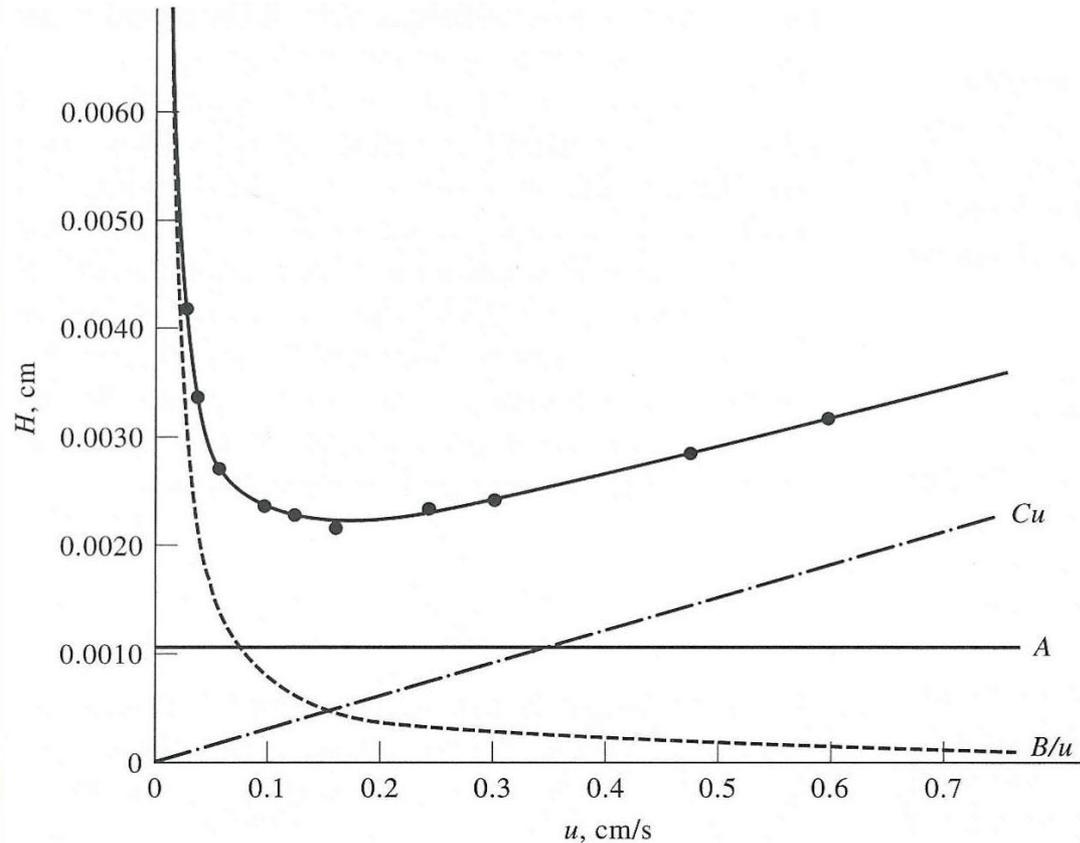
$$H = A + B/u + Cu = A + B/u + (C_s + C_m)\, u$$

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TABLE 26-3 Processes That Contribute to Band Broadening

Process	Term in Equation 26-23	Relationship to Column* and Analyte Properties
Multiple flow paths	A	$A = 2\lambda d_{\mathrm{p}}$
Longitudinal diffusion	B/u	$\dfrac{B}{u} = \dfrac{2\gamma D_{\mathrm{M}}}{u}$
Mass transfer to and from stationary phase	$C_{\mathrm{S}}u$	$C_{\mathrm{S}}u = \dfrac{f(k)d_{\mathrm{f}}^{2}}{D_{\mathrm{S}}}u$
Mass transfer in mobile phase	$C_{\mathrm{M}}u$	$C_{\mathrm{M}}u = \dfrac{f'(k)d_{\mathrm{p}}^{2}}{D_{\mathrm{M}}}u$

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Figure 26-9 A van Deemter plot for a packed liquid chromatographic column. The points on the upper curve are experimental. The contributions of the various rate terms are shown by the lower curves: A, multipath effect; B/u, longitudinal diffusion; Cu, mass transfer for both phases. *(From E. Katz, K. L. Ogan, and R. P. W. Scott, J. Chromatogr., 1983, 270, 51. With permission.)*

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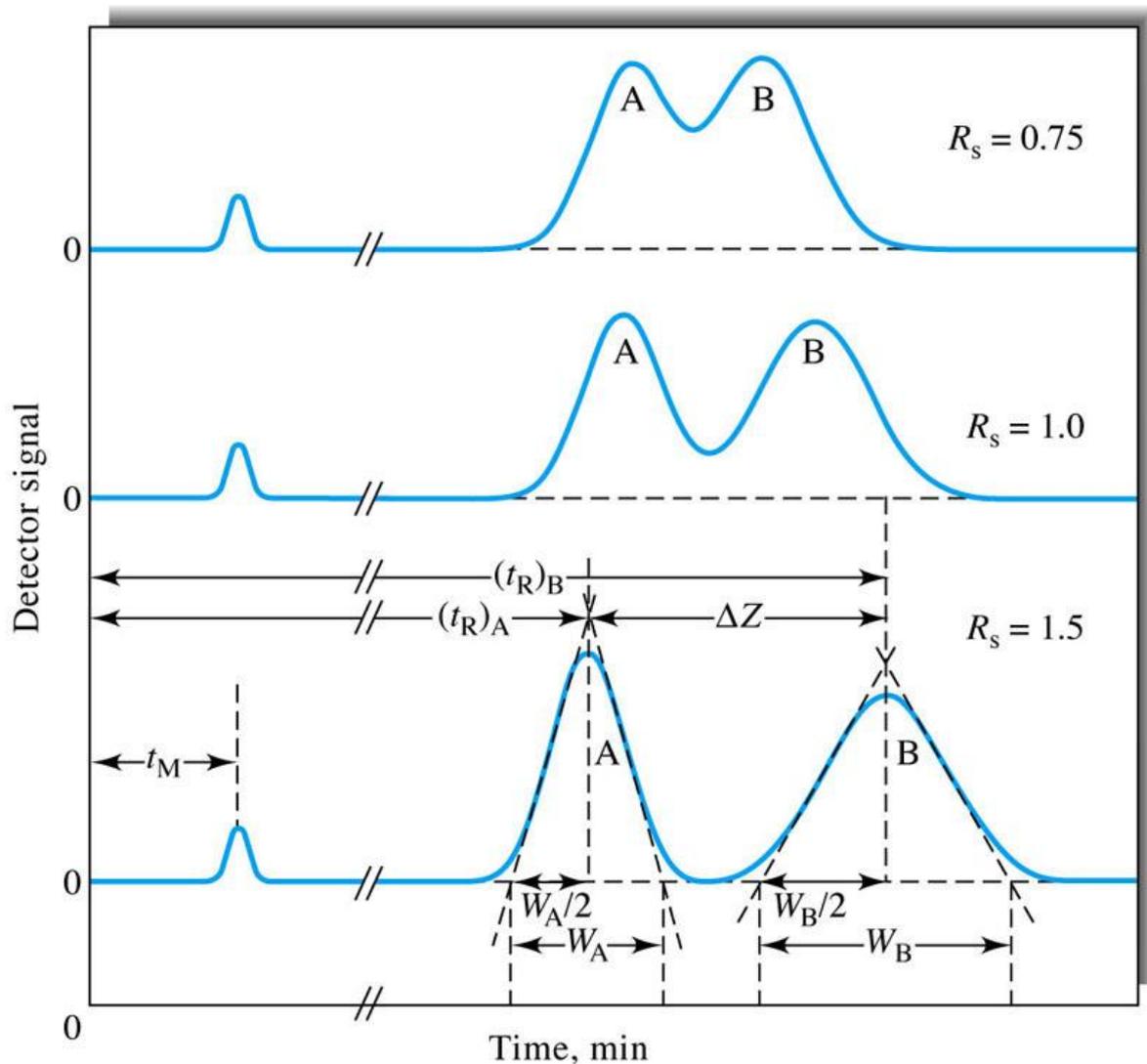
Optimization of Chromatographic Performance

A chromatographic separation is optimized by varying the experimental conditions.

Resolution

- For symmetrical peaks

$$\mathbf{R}_s = \frac{2(\mathbf{t_{r2}} - \mathbf{t_{r1}})}{\mathbf{w_{b1}} + \mathbf{w_{b2}}}$$

R_s - resolution

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Optimization of Chromatographic Performance

Resolution Equation

$$R = \tfrac{1}{4}\sqrt{N} \times (k/(k+1)) \times (\alpha - 1)$$

Efficiency   *Retention Factor*   *Selectivity*

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Resolution Equation

$$R = \tfrac{1}{4}\sqrt{N} \times (k/(k+1)) \times (\alpha - 1)$$

$$\text{Efficiency} \quad \text{Retention Factor} \quad \text{Selectivity}$$

The first part relates to the kinetic effects that lead to band broadening … $(N)^{1/2}$ or H/u.

The second and third terms are related to the thermodynamics of the separation.

Second term which contains k, depends on the properties of both the solute and the column.

Third term which contains, α, the selectivity term, depends on the properties of the mobile and stationary phases.

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Resolution Equation

$$R = \tfrac{1}{4}\sqrt{N} \times (k/(k+1)) \times (\alpha-1)$$

Efficiency   *Retention Factor*   *Selectivity*

The parameters N (or H), k, α, can be adjusted.

α and k can be varied by varying the temperature or composition of the mobile phase. Or a different column packing can be used.

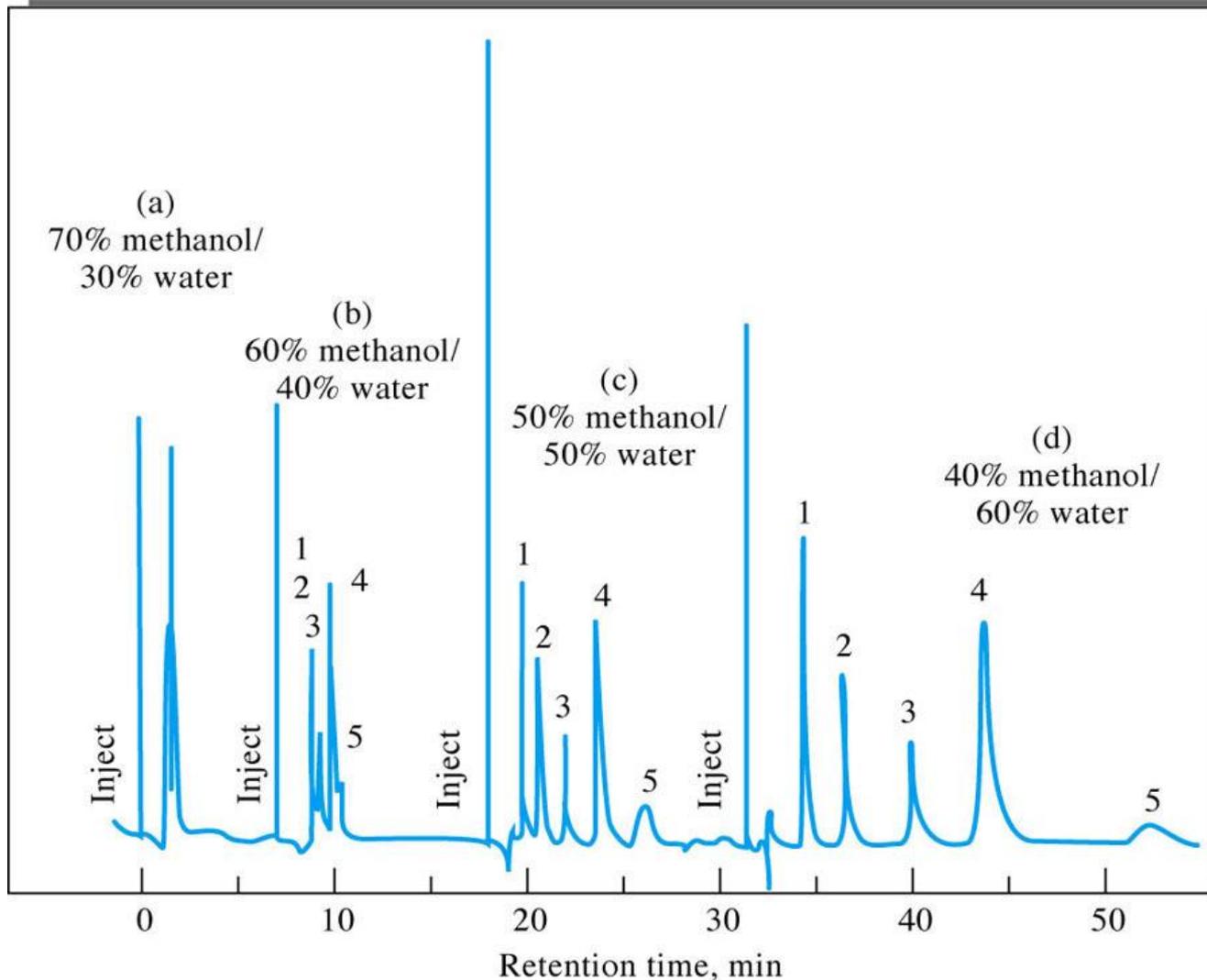N can be changed by altering the length of the column.

H can be changed by altering the flow of the mobile phase, the particle size of the packing, the viscosity of the mobile phase, and thickness of the liquid stationary phase.

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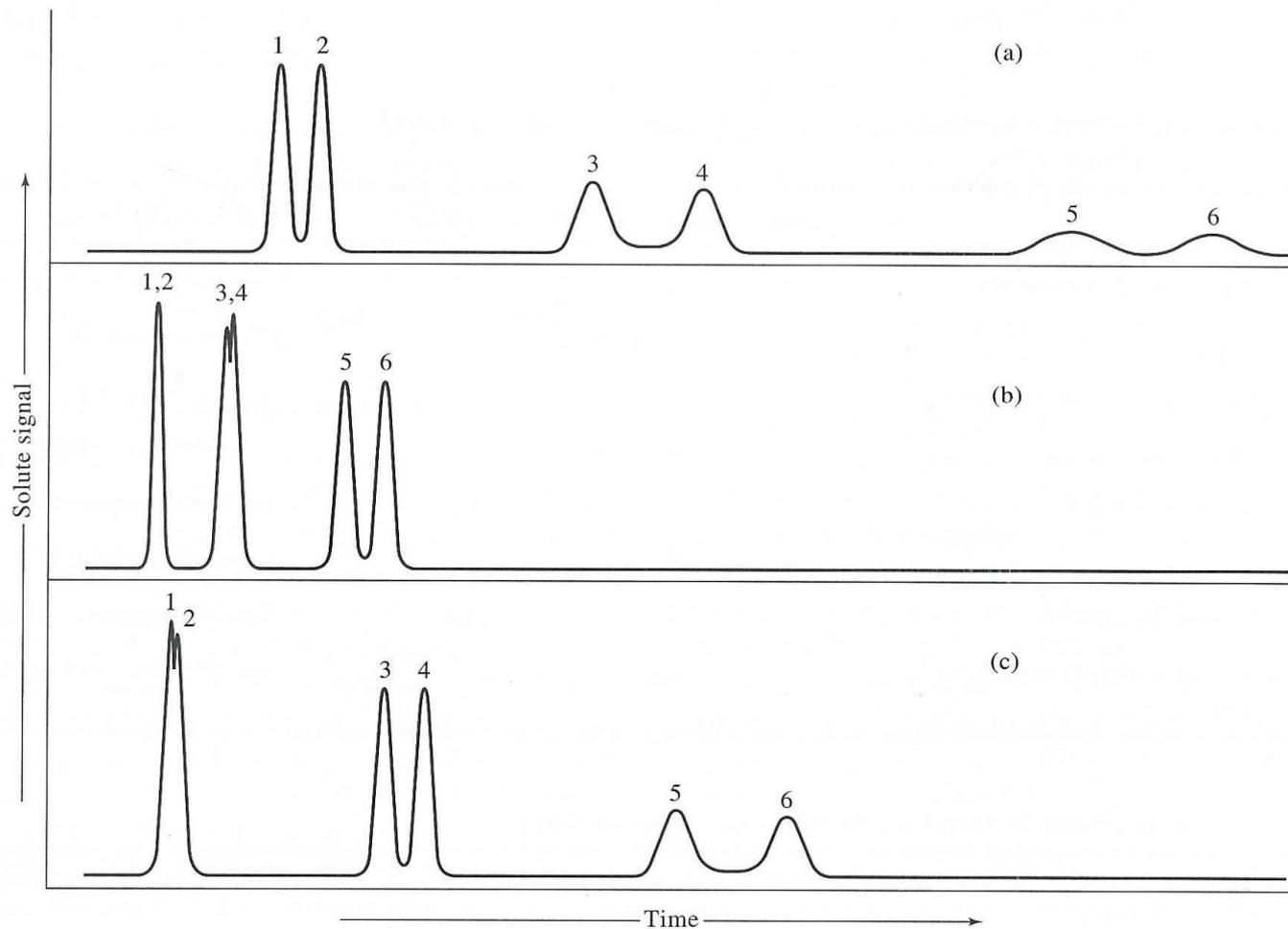
Figure 26-14 Illustration of the general elution problem in chromatography.

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TABLE 26-4 Important Chromatographic Quantities and Relationships

Name	Symbol of Experimental Quantity	Determined From
Migration time, unretained species	t_M	Chromatogram (Figure 26-7)
Retention time, species A and B	$(t_R)_A$, $(t_R)_B$	Chromatogram (Figures 26-7 and 26-12)
Adjusted retention time for A	$(t'_R)_A$	$(t'_R)_A = (t_R)_A - t_M$
Peak widths for A and B	W_A, W_B	Chromatogram (Figures 26-7 and 26-12)
Length of column packing	L	Direct measurement
Volumetric flow rate	F	Direct measurement
Linear flow velocity	u	F and column dimensions (Equations 26-6 and 26-7)
Stationary-phase volume	V_S	Packing preparation data
Concentration of analyte in mobile and stationary phases	c_M, c_S	Analysis and preparation data

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TABLE 26-5 Important Derived Quantities and Relationships

Name	Calculation of Derived Quantities	Relationship to Other Quantities
Linear mobile-phase velocity	$u = \dfrac{L}{t_M}$	
Volume of mobile phase	$V_M = t_M F$	
Retention factor	$k = \dfrac{t_R - t_M}{t_M}$	$k = \dfrac{K V_S}{V_M}$
Distribution constant	$K = \dfrac{k V_M}{V_S}$	$K = \dfrac{c_S}{c_M}$
Selectivity factor	$\alpha = \dfrac{(t_R)_B - t_M}{(t_R)_A - t_M}$	$\alpha = \dfrac{k_B}{k_A} = \dfrac{K_B}{K_A}$
Resolution	$R_s = \dfrac{2[(t_R)_B - (t_R)_A]}{W_A + W_B}$	$R_s = \dfrac{\sqrt{N}}{4}\left(\dfrac{\alpha - 1}{\alpha}\right)\left(\dfrac{k_B}{1 + k_B}\right)$
Number of plates	$N = 16\left(\dfrac{t_R}{W}\right)^2$	$N = 16 R_s^2 \left(\dfrac{\alpha}{\alpha - 1}\right)^2 \left(\dfrac{1 + k_B}{k_B}\right)^2$
Plate height	$H = \dfrac{L}{N}$	
Retention time	$(t_R)_B = \dfrac{16 R_s^2 H}{u}\left(\dfrac{\alpha}{\alpha - 1}\right)^2 \dfrac{(1 + k_B)^3}{(k_B)^2}$	

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Objectives

- **Qualitative Applications
  Confirm presence or absence of compounds in samples. Screening unknowns.**

- **Quantitative Applications
  Establish the amount of individual components in a sample by comparing with standards used for quality control.**

- **Preparative Applications
  Purifying samples.**

Assignment

- Read Chapter 23
- HW12 Chapter 23: 2, 4, 7, 8, and 11
- HW12 Chapter 23 Due 3/29/24

- Read Chapter 25
- HW13 Chapter 25: 1-8 and 10
- HW13 Chapter 25 Due 04/01/24

- Read Chapter 26
- HW14 Chapter 26: 1- 17
- HW14 Chapter 26 Due 04/03/24

- Test 3 – PPT Lectures 15-21 - Friday April 5th