Rate Theory of Chromatography

$$H = H_L + H_S + H_M + H_{SM}$$

H = height equivalent to theoretical plate (as in Plate Theory)

H_L = contribution due to longitudinal diffusion

H_S = stationary phase mass transfer contribution

H_M = diffusion associated with mobile phase effects

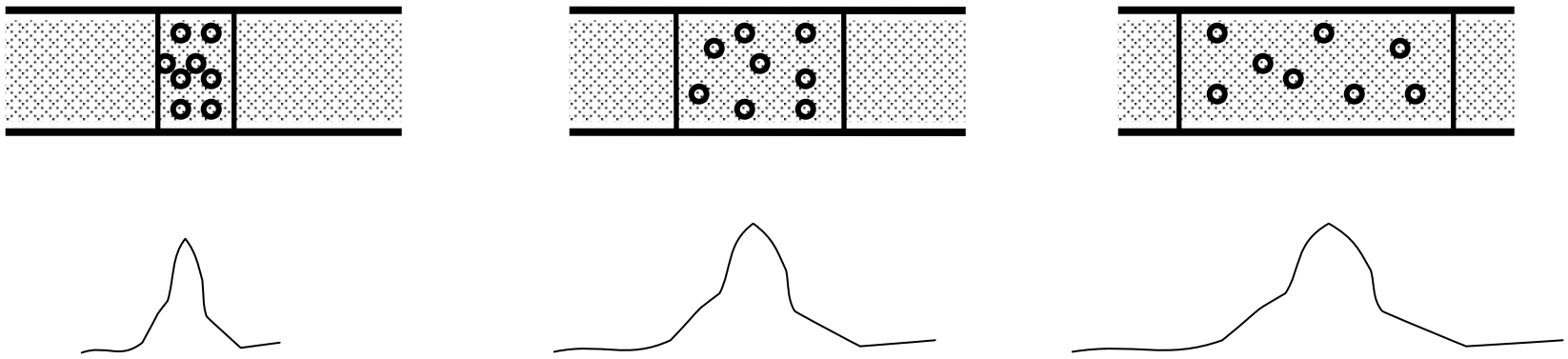
H_{SM} = diffusion into or mass transfer across a stagnant layer of mobile phase (neglect)

$$H = B/\mu + C\mu + A$$

van Deemter Equation A, B & C are coefficients, μ = velocity

1) Longitudinal Diffusion $H_L = (B/\mu)$

$t = 0$ $0 < t < t_R$ t_R

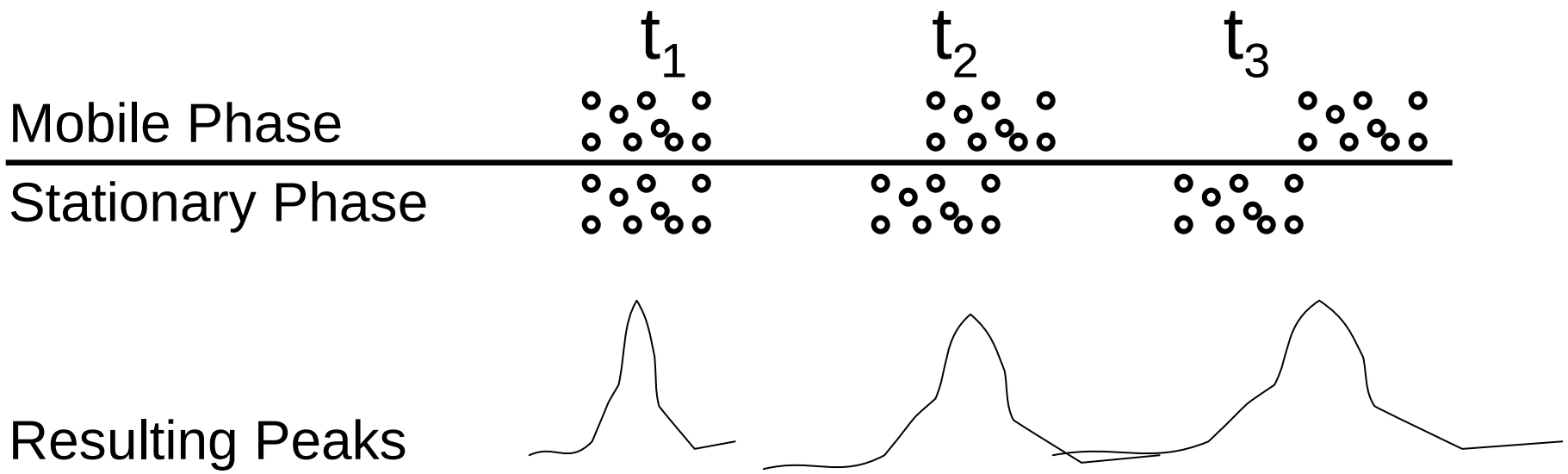


$\sigma_L^2 = 0$ $\sigma_L^2 = 2 D_M t_M$

Variance due to longitudinal diffusion = 0 at start

Variance increases with time & diffusion coefficient D

2) Mass transfer in & out of stationary phase

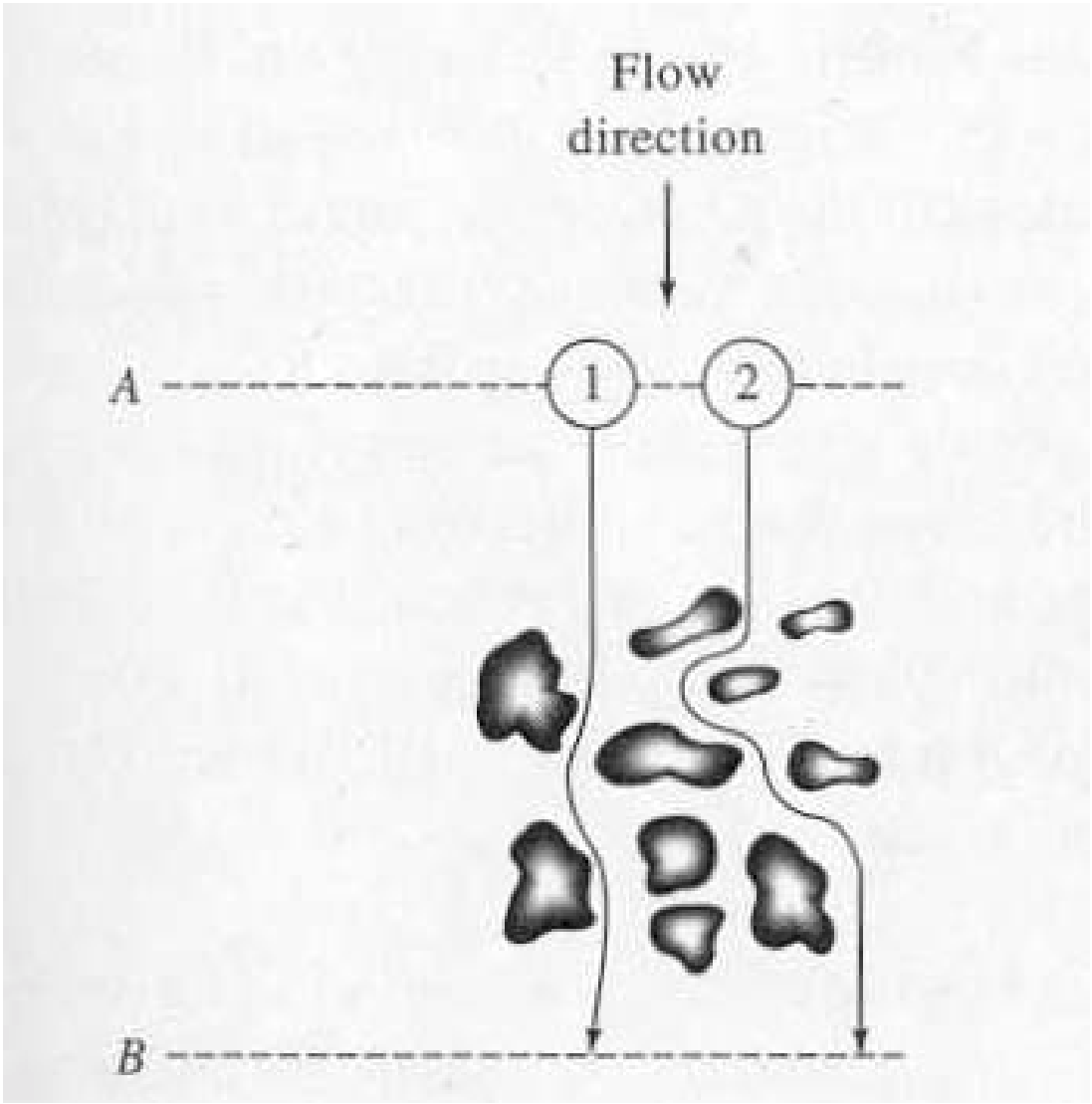


Broadening of peaks is a function of mobile phase velocity (moving molecules faster than those in stationary phase)

Not the same as longitudinal diffusion $H_S = C\mu$

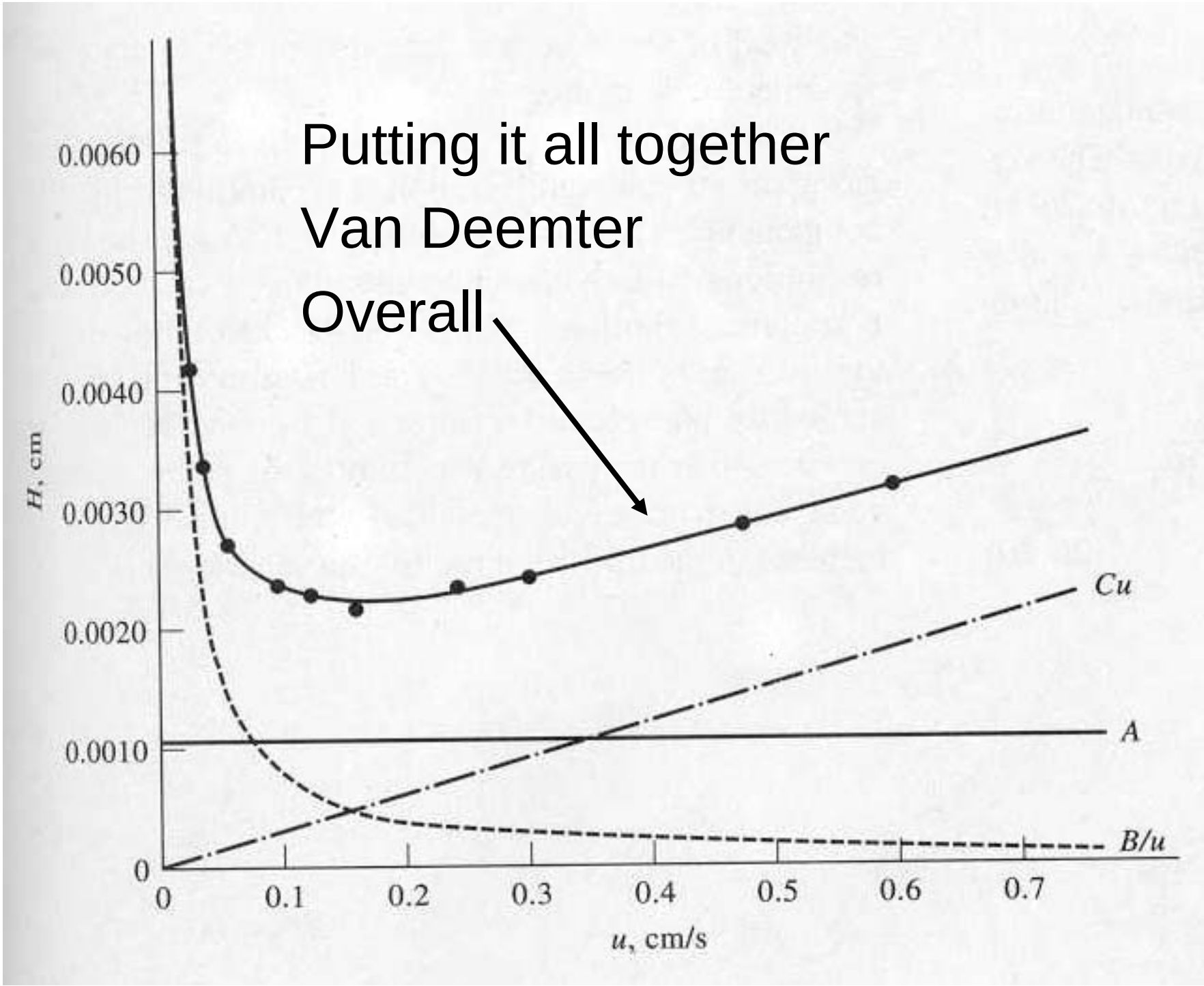
In Plate Theory condition at t_1 assumed to hold throughout

3) Uneven Flow or Eddy Diffusion



Path 1 is shorter than path 2

$H_M = A$


Putting it all together
Van Deemter
Overall
0.0060
0.0050
0.0040
0.0030
0.0020
0.0010
0
H, cm
Cu
A
B/u
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
u, cm/s

Optimizing Column Performance – seldom operate at optimum → too slow

Normally want to get required separation in shortest time, this may be at 2X μ_{opt}

Can optimize a separation by varying experimental conditions, usually goals are

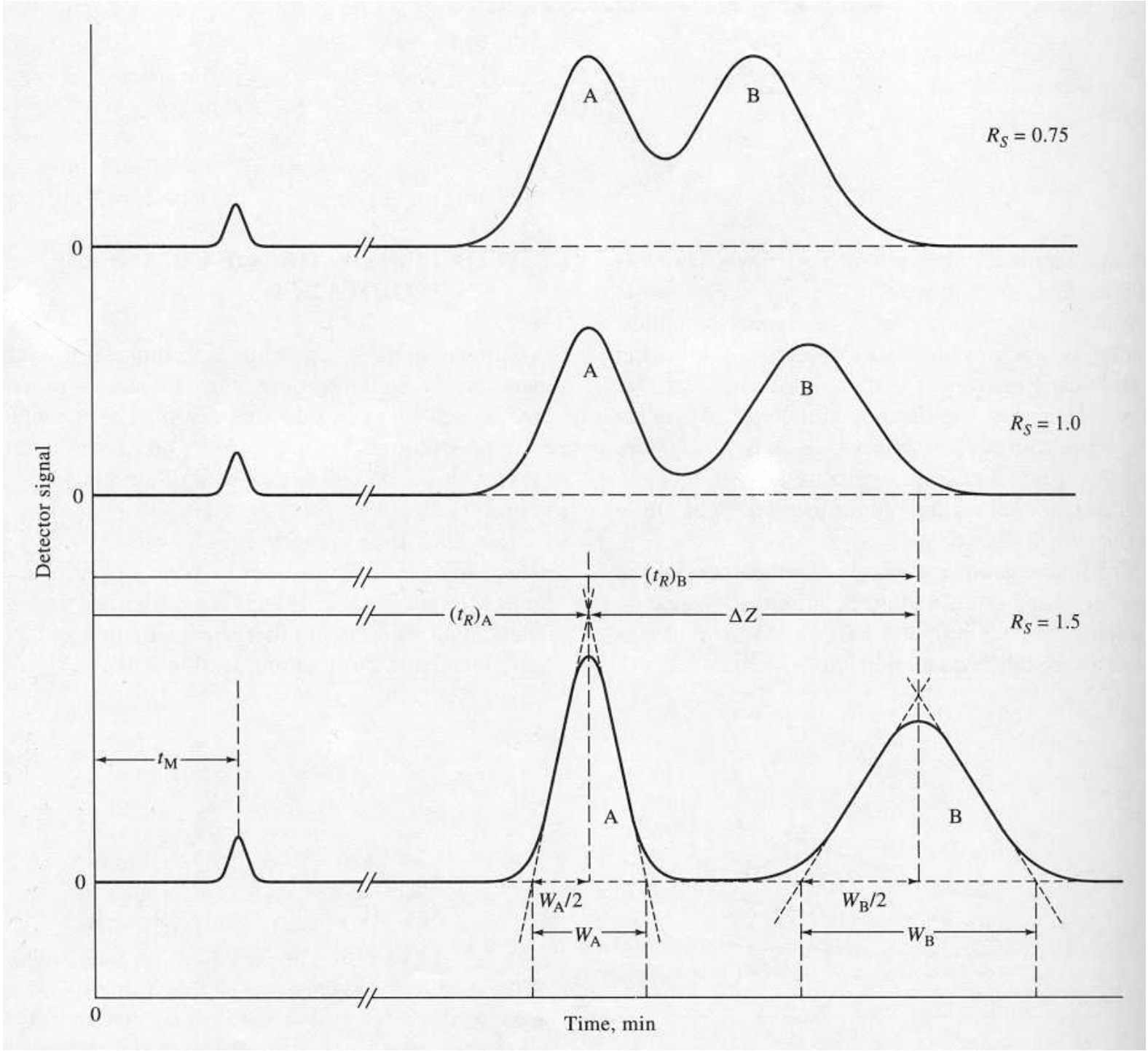
1) reduce band broadening (zone)

2) alter relative migration rates of components (allowing better separation of two components)

Variable	Symbol	Usual Units
Linear velocity of mobile phase	u	$cm \cdot s^{-1}$
Diffusion coefficient in mobile phase	D_M	$cm^2 \cdot s^{-1}$
Diffusion coefficient in stationary phase	D_S	$cm^2 \cdot s^{-1}$
Retention factor (Equation 26-8)	k'	unitless
Diameter of packing particle	d_p	cm
Thickness of liquid coating on stationary phase	d_f	cm

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	$\frac{B}{u} = \frac{2\gamma D_M}{u}$
Mass transfer to and from liquid stationary phase	$C_S u$	$C_S u = \frac{f_S(k')d_f^2}{D_S} u$
Mass transfer in mobile phase	$C_M u$	$C_M u = \frac{f_M(k')d_p^2}{D_M} u$



This brings us to Resolution (R_S) = Measure of columns ability to separate 2 analytes

Note ΔZ = spread of peaks & W or W/2 = peak width

$$R_S = \frac{\Delta Z}{W_A/2 + W_B/2} = \frac{2\,\Delta Z}{W_A + W_B} = \frac{2[(t_R)_B - (t_R)_A]}{W_A + W_B}$$

If $R_S = 1.0$ then $\Delta Z = W_A/2 + W_B/2$

and peaks touch with about 4% overlap

This is too big an error to tolerate

If $R_S = 1.5$ then about 0.3% overlap

Can lengthen column to improve resolution by increasing N → this also increases time for analysis

In terms of capacity factor (k') & selectivity factor (α)

$$R_S = \frac{\sqrt{N}}{4}\left(\frac{\alpha - 1}{\alpha}\right)\left(\frac{k_B'}{1 + k_B'}\right)$$

Usually choose k_B' for 2nd eluting peak, so

$$N = 16\, R_s^2 \left(\frac{\alpha}{\alpha + 1}\right)^2 \left(\frac{1 + k_B'}{k_B'}\right)^2$$

Last of all relate t_R to R_S

$$(t_R)_B = \frac{16\, R_s^2\, H}{\mu} \left(\frac{\alpha}{\alpha + 1} \right)^2 \left(\frac{1 + k_B'}{k_B'} \right)^2$$

Allows calculation of retention time for a desired resolution with known capacity factor

Normally want highest possible resolution in shortest time – always a compromise

Can look at equation in two parts

$$(t_R)_B = \frac{16\, R_s^2\, H}{\mu} \left(\frac{\alpha}{\alpha + 1}\right)^2 \left(\frac{1 + k_B'}{k_B'}\right)^2$$

H/μ (or N)

Kinetic effects for band broadening related to N, H & L also μ → change Flow rate or length

Thermodynamic part because α & k' are related to partitioning - equilibrium process change temp or comp

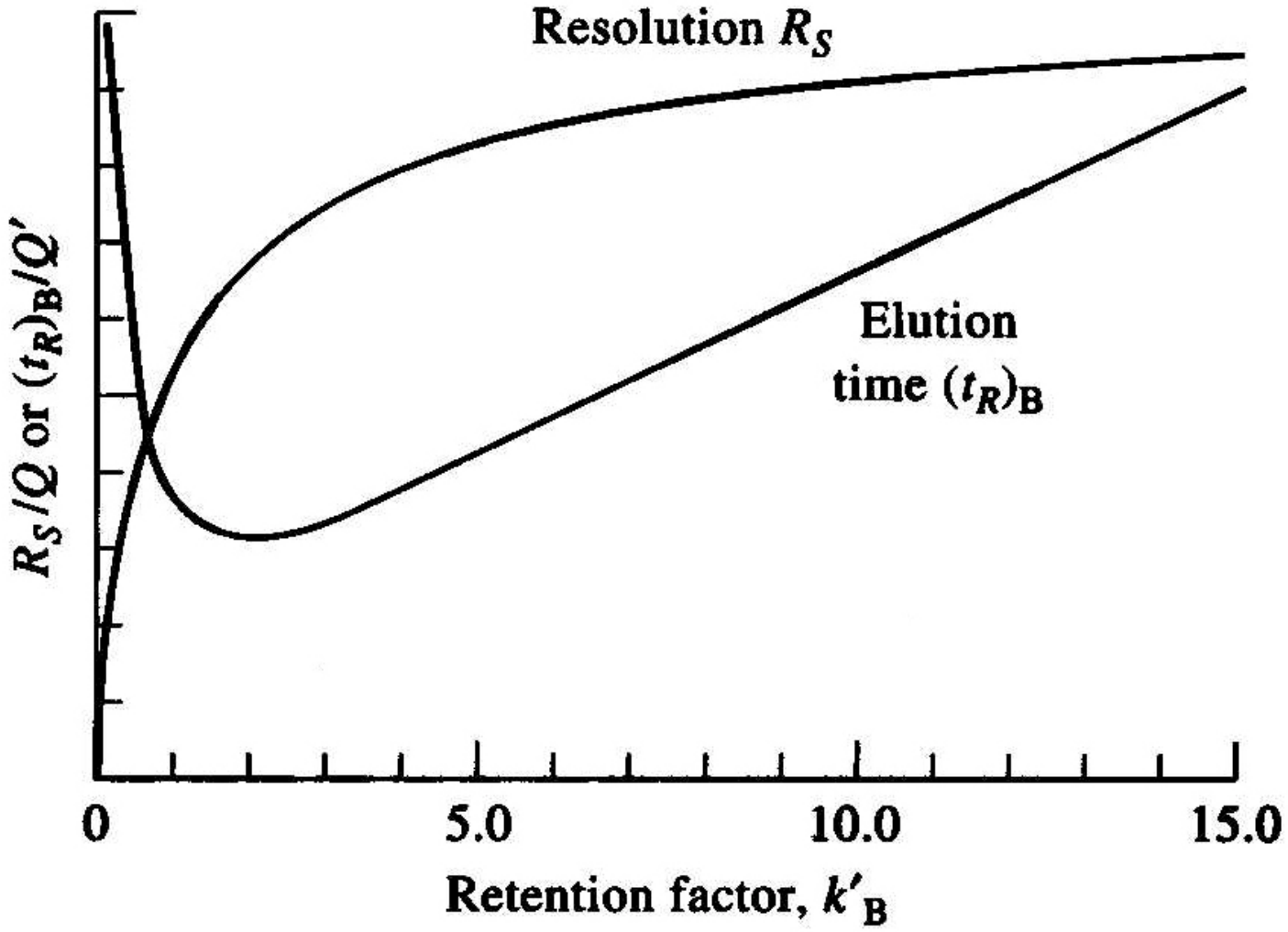
From resolution equation given above

$$R_S = \frac{\sqrt{N}}{4} \left(\frac{\alpha - 1}{\alpha} \right) \left(\frac{k_B'}{1 + k_B'} \right)$$

Can simplify

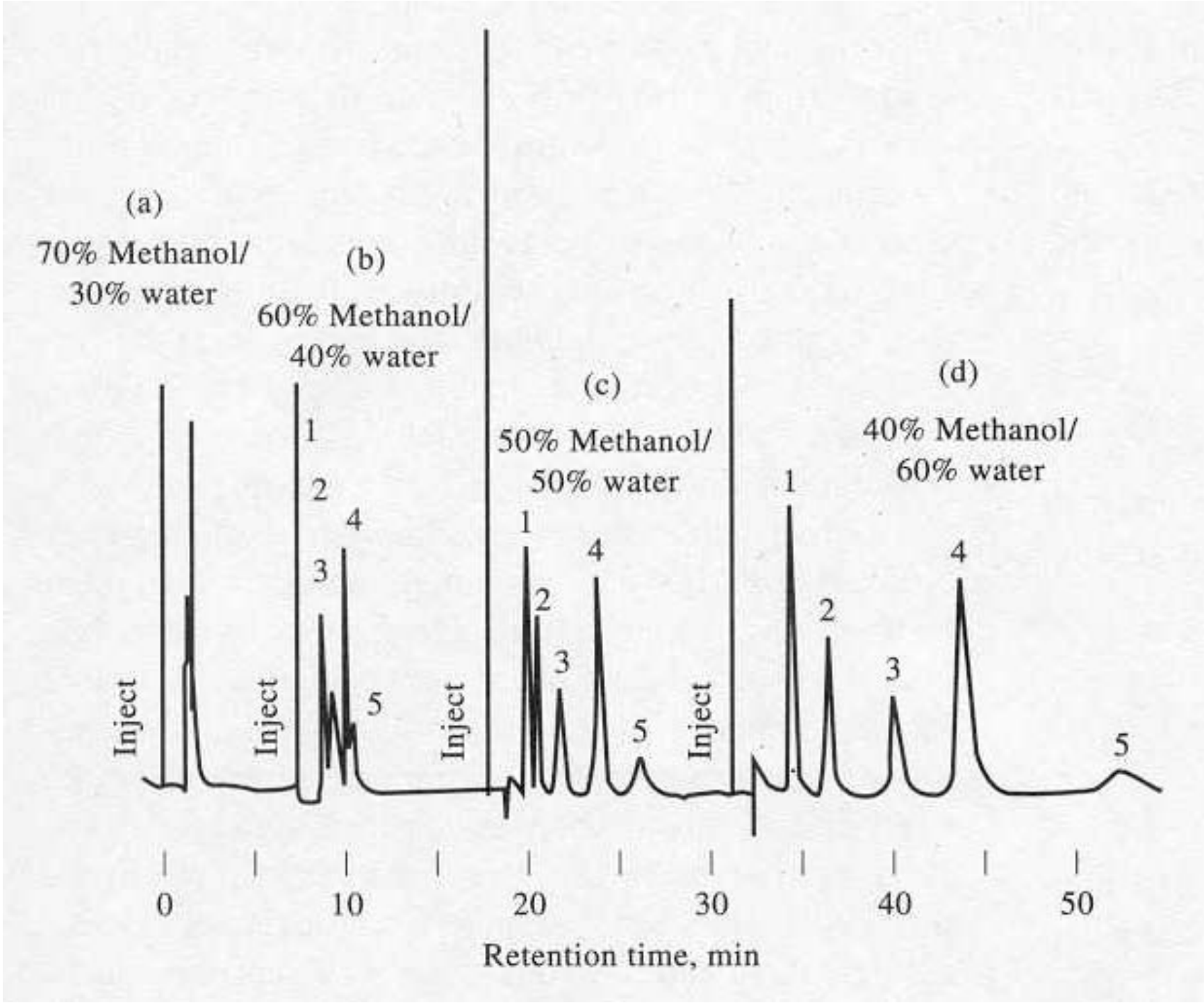
$$R_s = Q \left(\frac{k_B'}{1 + k_B'} \right)$$

Where Q represents all other parameters



Avoid values above 10

Figure 26-12 Effect of retention factor k'_B on resolution R_s and elution time $(t_R)_B$. It is assumed that Q and Q' remain constant with variation in k'_B.


(a)
70% Methanol/
30% water
(b)
60% Methanol/
40% water
(c)
50% Methanol/
50% water
(d)
40% Methanol/
60% water
Inject
Inject
Inject
Inject
1
2
3
4
5
0
10
20
30
40
50
Retention time, min

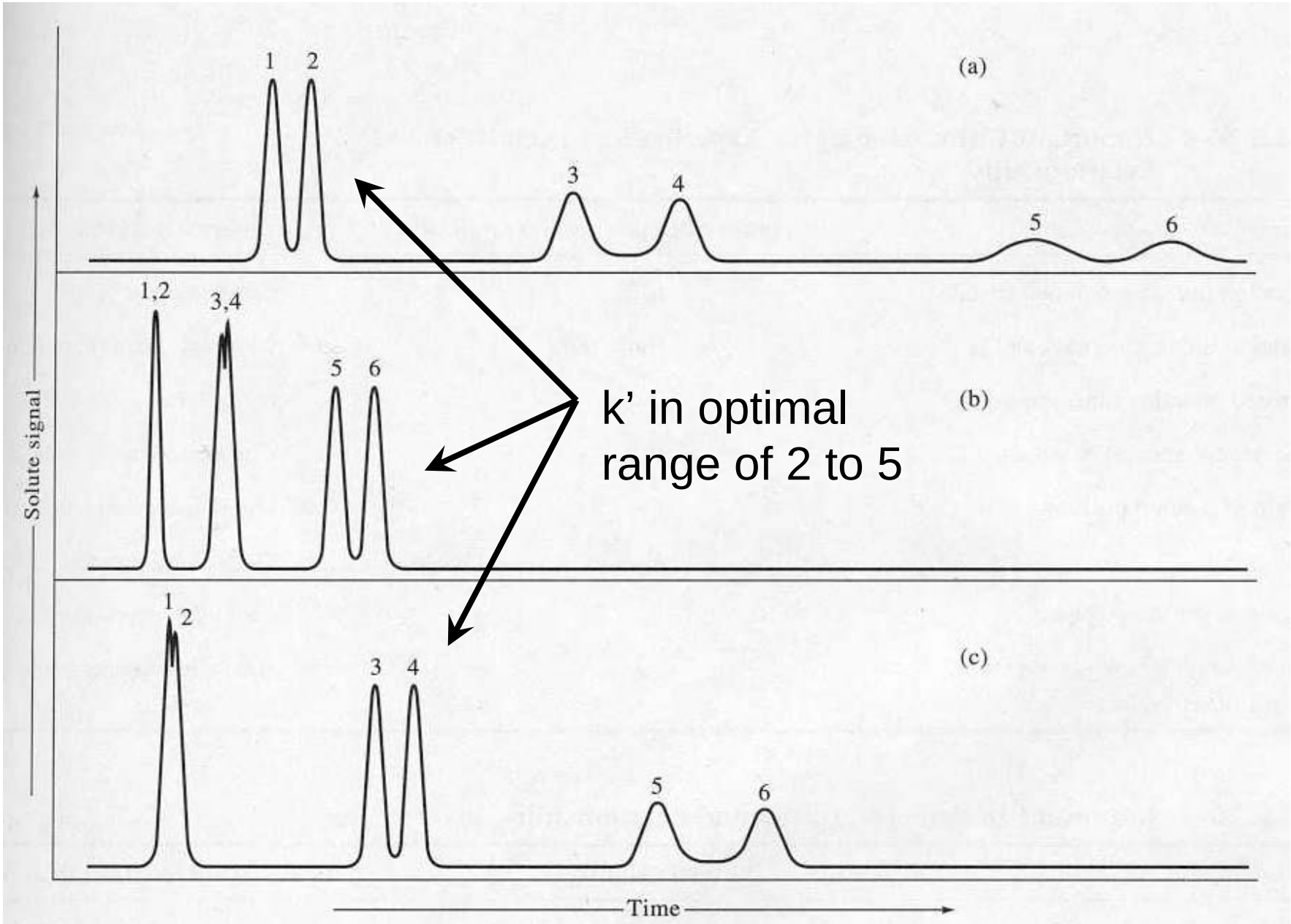


Figure 26-14 Illustration of the general elution problem in chromatography.

Commonly found problem in chromatography

General Elution Problem

Solution – change conditions during chromatographic run so that k' changes

Start with conditions for chromatogram (a), after 1 & 2 elute

Change to conditions for chromatogram (c), after 3 & 4 elute

Change to conditions for chromatogram (b) to get 5 & 6

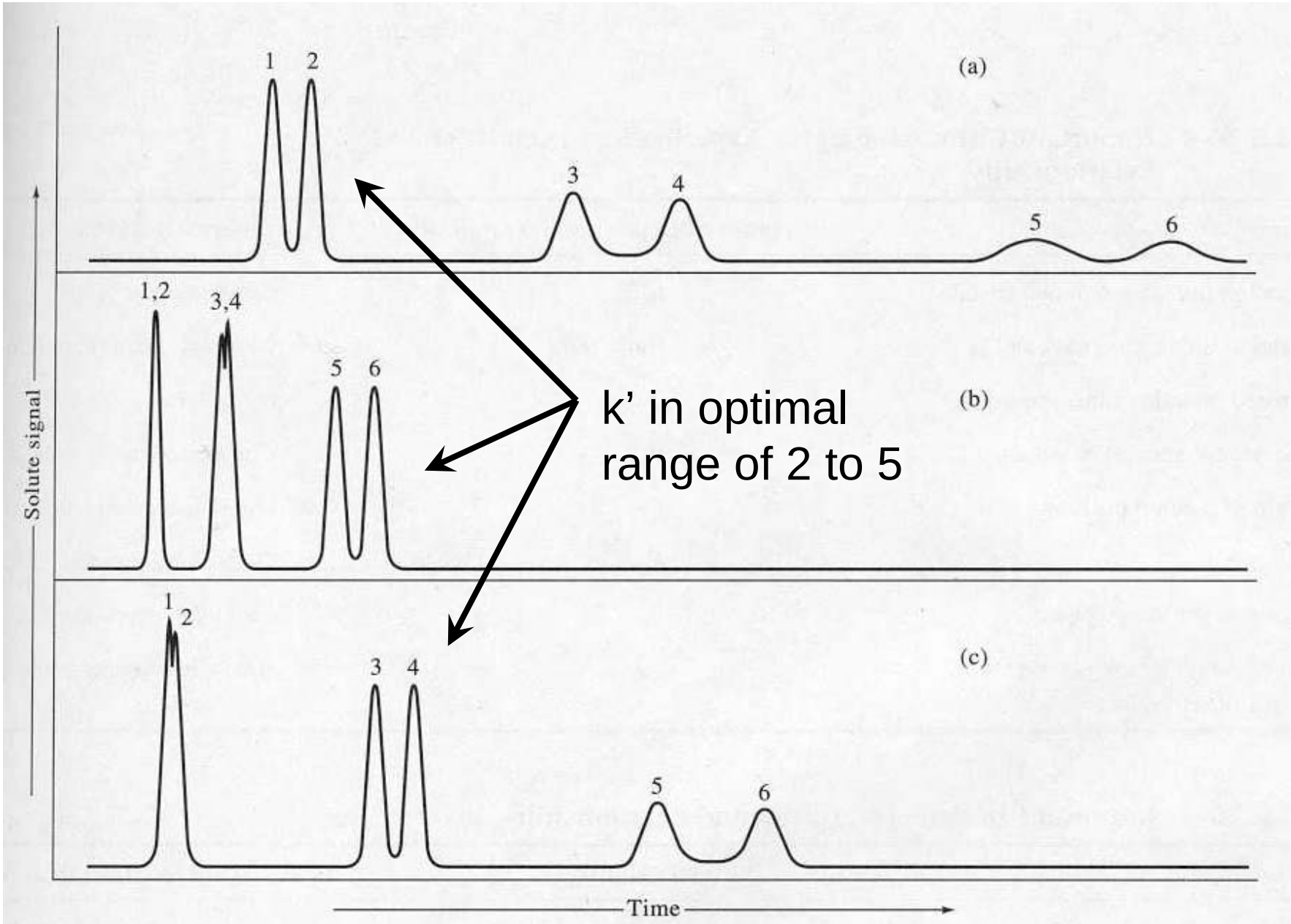


Figure 26-14 Illustration of the general elution problem in chromatography.

Since k’ is related to partitioning of solute between mobile phase and stationary phase, can easily change mobile phase

In GC do temperature programming

In HPLC do solvent programming (a.k.a. gradient elution)

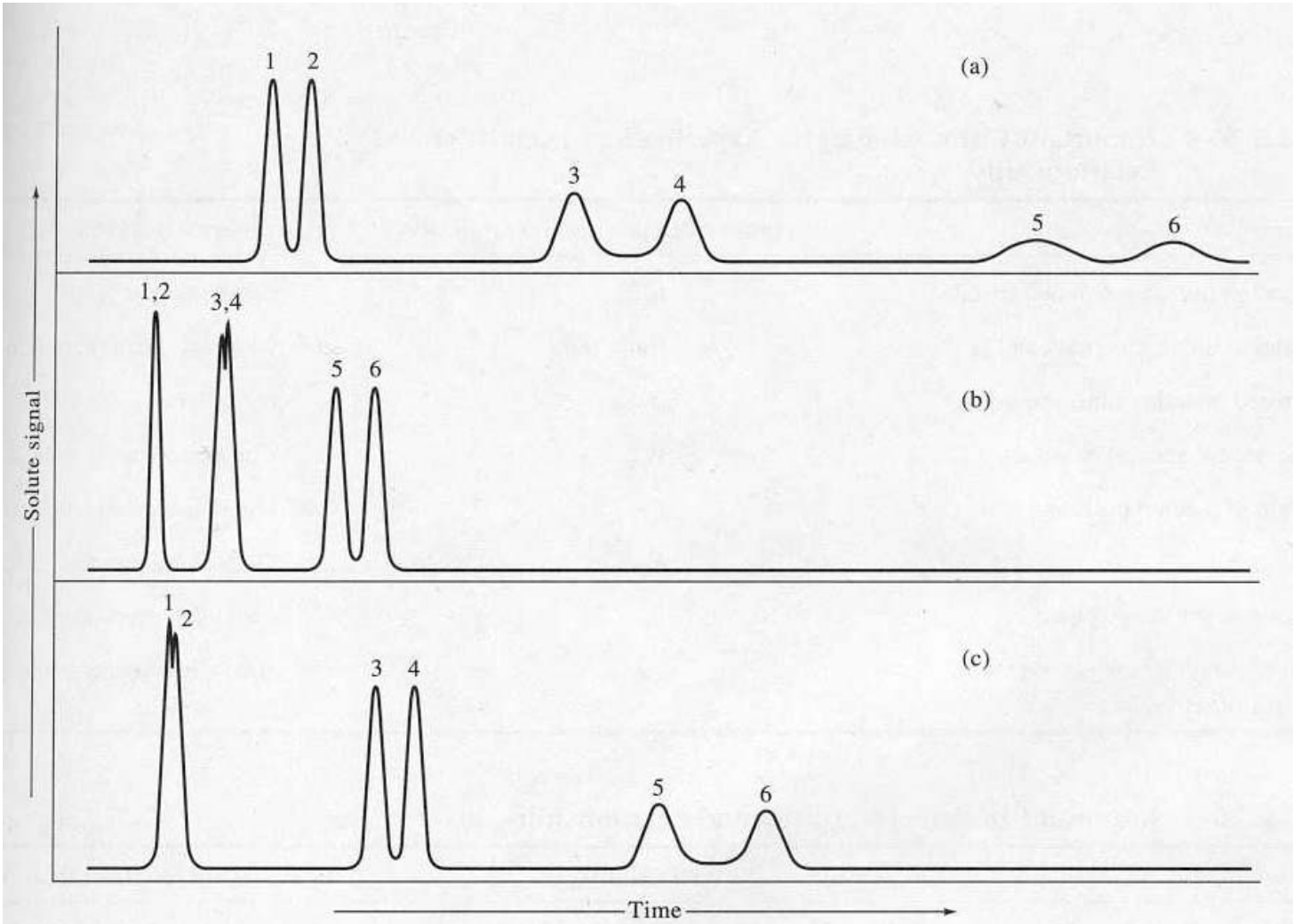


Figure 26-14 Illustration of the general elution problem in chromatography.