CHAPTER 12
PLATE HEIGHT AND OPTIMIZATION
IN CHROMATOGRAPHY

12.1 PLATE HEIGHT EQUATIONS

given

\[ H = \frac{B}{v} + \sum \left( \frac{1}{A_i \cdot v} + \frac{1}{C_{mi} \cdot v} \right) + C_s \cdot v \]

where

for packed columns

at low and medium velocity range, diffusion dominates.
\[ A_i \] term dropped out. (\( H_f \) term)

\[ H \] becomes

at high velocity, flow dominates.
\[ H_D \] term dropped.

\[ H \] becomes

\[ \text{van Deemter equation} \]
for capillary columns (GC, SFC)

simple
1. st. phase - uniform film

2. no obstacles in column

3. only one flow (uniform space)

4. constant velocity

5. flow property - parabolic (well-known)

thus \( H \) becomes

\[
H = \frac{2D_m}{v} + \frac{1}{24} (6R^2 - 16R + 11) \frac{r_c^2v}{D_m} + \frac{2}{3} R(1 - R) \frac{d^2v}{D_s}
\]

or
12.2 PLATE HEIGHT AND GAS CHROMATOGRAPHY

In GC,

\[ \text{gas compression} \quad \rightarrow \quad \text{velocity gradients} \quad \text{affect} \quad H \]

\[ D_m \quad \text{scaled to} \quad D_g \quad \text{for GC} \]

\( o: \text{outlet} \)

since \( pv = \text{const.} \)

\[ \text{high} \, v \quad \rightarrow \quad \text{high} \, D_g \]  \hspace{1cm} (12.15)

at inlet, compression \( \rightarrow \) slow \( v \), slow \( D_g \)

Based on 12.15

thus

\[ H_s = C_s \, v \]

consider av. velocity as: \( \tilde{v} \)

\[ H_s = C_s \tilde{v} \quad \text{time av. velocity} \]

\[ \tilde{v} = v_o \, j \quad \text{observed plate height} \]
observed plate height

is the sum of the last two expressions

as

fully corrected eq.

12.3 REDUCED PLATE HEIGHT

universal curve by reduced variables (by J.C. Giddings)

$c$: critical point

\[ v_r = \frac{v}{v_c}, \quad T_r = \frac{T}{T_c}, \quad P_r = \frac{P}{P_c} \]
for chromatography, $H_f$ and $H_D$

when $H_f = H_D$, transition between flow controlled and diffusion controlled random walk.

occurs at $v_c' = v$

$v_c'$ gives as

use simpler parameter
(dues to the complexity of $\lambda$ and $\omega$)

reduced velocity

(12.23)

reduce plate height as dimensionless form by $d_p$

$$h = \frac{H}{d_p}$$
plate height in 12.1

for all well packed column

\[ h \text{ is function of only } v_r, \gamma (\text{packing structure}), \omega_i, \lambda_i \]

for poorly packed columns

small \( \Omega \), large \( \gamma \)

mobile phase term gives \( \propto v_r^n \quad n \sim 1/3 \)

\[ h = \frac{2\gamma}{v_r} + \alpha v_r^n + \Omega v_r \]
12.4 OPTIMIZATION: HIGHER RESOLUTION

resolution given in eq 5.58

thus

when $\Delta R$ gets small --- $dR$

rearrangement gives

from eq. 10.9

its reciprocal

we find

combine 12.35 with 12.37
gives

$$R \Delta \left( \frac{1}{R} \right) = \Delta K \frac{V_s}{V_m} \frac{V_m}{V_m + KV_s}$$
finally
to increase $R_s$

1. keep $R$ small
2. increase $N$

$$N = \frac{L}{H}$$

decrease $H$ or increase $L$

resolution and thermodynamics - $\Delta K/K$ term

by differentiation

$dK = \ldots$

thus

rearrange $R_s$ into $N$
Table 12.2  Number of plates required to obtain unit resolution for different $\Delta(\Delta\mu^o)$ values at 300K and $R=0.2$.

\[
\begin{array}{ccc}
N & \text{cal/mol} & \text{j/mol} \\
400 & 150 & 620 \\
2500 & 60 & 250 \\
10,000 & 30 & 125 \\
40,000 & 15 & 62 \\
250,000 & 6 & 25 \\
1,000,000 & 3 & 12 \\
\end{array}
\]

3 cal/mol gives $R_s = 1$ in column of $10^6$ plates.
(intermolecular interaction)

isomers (small structural differences)
-- can be separated in high N columns

complex multicomponent separation

consider $n_c$ rather than $R_s$

separate multicomponents?

need much more space along the sep. axis than that required to hold the peaks.
(Due to overlap of peaks)
Need to consider peak isolated successfully

when \( n_c = 200, m = 100 \) gives only \( s = 37 \)

\[ n_c >> m \]

high \( n_c \) needs large \( N \), small \( H \)

minimizing plate height

plate height \( H \) depends on
flow velocity \( d_p \)
packing non-uniformity \( \lambda \)
diffusivity \( D_m, D_s \)
degree of retention
st. phase structure
temperature
pressure drop
Optimization?

choose velocity $v$

to get min. $v$

$v_{opt}$ gives

$H_{min} =$
if \( C_s \gg C_m \) st. ph. noneq. Dominated

\[
C = C_m + C_s \approx C_s \\
B = 2 \gamma D_m
\]

Now, \( H_{\text{min}} = 2(BC)^{1/2} \)

\[
H_{\text{min}} = \left\{ 8\gamma \left( \omega d_p^2 + qR(1 - R) \frac{D_m}{D_s} d^2 \right) \right\}^{1/2}
\]

Figure 12.4. Plate height versus flow velocity plot for negligible stationary phase non-equilibrium effects (bottom curve) and for dominant stationary phase effects (top).

In general case,

\[
H_{\text{min}} = \left\{ 8\gamma \left( \omega d_p^2 + qR(1 - R) \frac{D_m}{D_s} d^2 \right) \right\}^{1/2}
\]

without considering speed of separation

think parameters other than \( v \)

1) st. ph. Effect

2) mob. ph. Effect

3) extracolumn effect
12.5 OPTIMIZATION: FASTER SEPARATION

from the simple theory \[ N = \frac{L}{H} \]

increase \( N \) \( \leftrightarrow \) increase \( L \)
impractical due to sep. time increase

\[ L = NH \]

separation time \( t \)
the time to separate comp. \( m \) in column \( L \) at sample velo. \( V = Rv \)

\[ t = \frac{L}{V} = \]

\[ N = \frac{16R_s^2}{(\Delta K / K)^2(1 - R)} \]

consider
1. use small \( N \) - gives small \( t \)
   needs high ratio of \( \Delta K / K \)
2. \( N/R \) ratio

for a given column, mo.phase., and \( T \)
\( N/R \) fixed

\[ t \propto \frac{H}{v} \]
$H/v$ becomes smaller as $v$ increases

Figure 12.5. The $H/v$ ratio shown as a slope for the two operating velocities $v_i$ and $v_1$.

as $v$ increases, $\Delta p$ increases

Basic equation: \hspace{1cm} (12.60)

Allow $d_p$ to vary

1) $H$ is scaled to $d_p$

2) $v$ is scaled to $D_m/d_p$

thus $H/v$ curve changes

remedy: convert to reduced variables

\hspace{1cm} (12.64)
\[ t = \frac{N H}{R \sqrt{d_p}} = \frac{N h d_p}{R \sqrt{D_m / d_p}} = \frac{N h d_p^2}{R \sqrt{D_m}} \]

Thus \( t \) (and \( \Delta p \)) increase with \( d_p \)

since: \( \Delta p = \frac{\phi \eta \sqrt{L}}{d_p^2} \) (12.63) and \( L = NH \) (12.59)

\( d_p \) is (12.65)

however: thus:

\( t \) becomes: (12.66)

Conclusions
\( t \) proportional to
- \( 1/\Delta p \) (increase \( \Delta p \))
- \( h \) (reduce to minimum)
- \( \eta \) (minimize)

only well packed columns with a minimum stationary phase contribution to \( H \)