(2) ↓ t_r of late-eluting i's by ↓ K_i

How?

GC: ramp up T during elution

$\left(K_i = \frac{[i]_s}{[i]_m} \right.$ ← if adsorption to stat phase, $[i]_s$ ↓ with ↑ T (Josie's comment) $\left.\right)$

↳ He or N_2 interacts negligibly with i's
⇒ T has no effect

eg Harris Fig 24-7 (handout)

LC: change polarity of mobile phase during elution

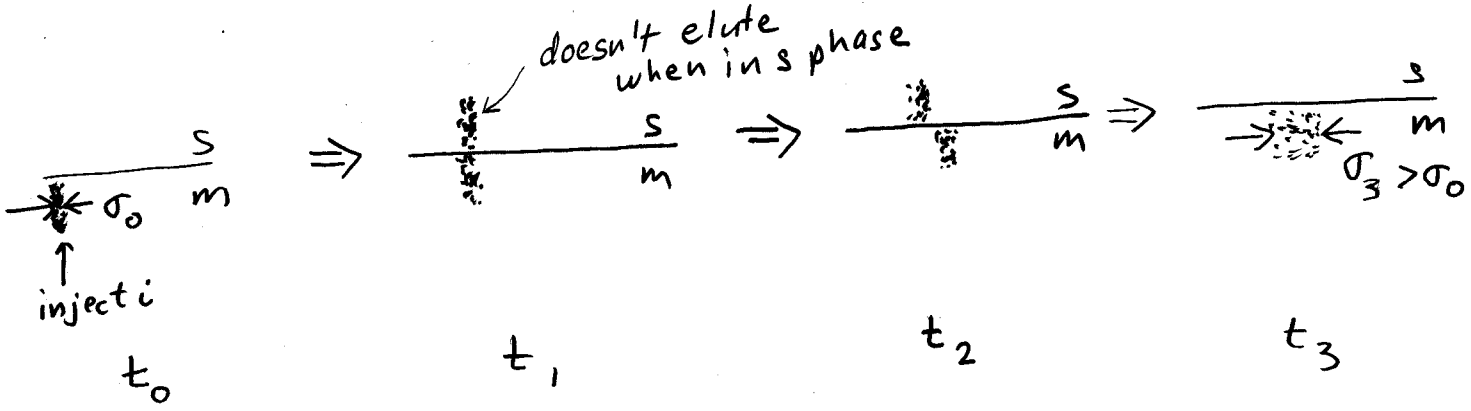
eg Harris Figs 25-10, 11 (handout)

$B = 2D_m$, where $D_m \equiv$ diffusion coefficient of i in mobile phase

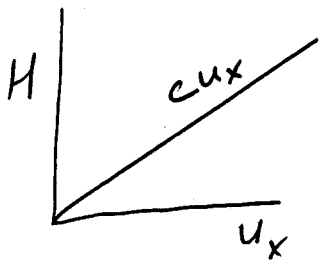
↑ D_m ⇒ faster diffusion

D_m (gas) vs. D_m (liq) ?? (DEMO)

• $C u_x$: Delayed movement of i btwn mobile and stationary phases



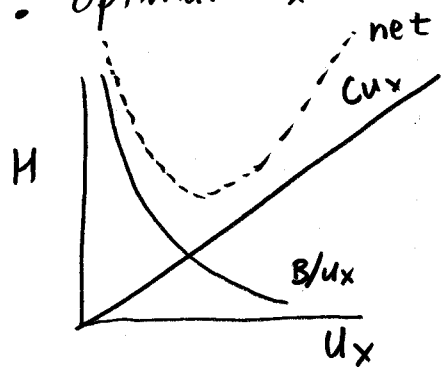
i in m phase gets ahead of i in s phase



broadening <u>increases</u> with $\uparrow u_x$

(the faster m moves, the more i in s phase gets left behind)

∴ optimal u_x at some intermediate value:



What affects C? (DEMO)

↓ C (i.e. increase equilibration rate) by...

(1) ↓ distance btwn i and phase boundaries

gc: thin open-tubular columns (0.1-0.5mm diam.)
thin stat phase coatings (0.1-5um thick)

lc: no open-tubular columns! (Gretchen's comment)
* diffusion in liq phase much too slow *
(small D_m (liq) great for $\frac{B}{u_x}$; awful for $C u_x$!)
⇒ use packed columns (A term notwithstanding)
↳ silica particles coated with stat phase

(2) ↑ Temp (esp. w/ gc)
eg Harris 24-7 (a) and (b) (handout)

For gc, ↑T is a two-fer
↓ $\frac{B}{u_x}$ (↓ K_i ⇒ ↓ t_{r_i})
↓ $C u_x$ (faster diffusion (!) btwn phases) (Nick's comment)

(a T high enough to speed up mass transfer on a ~50um length scale not high enough to broaden peaks measurably (~1mm) in the elution (x) direction)