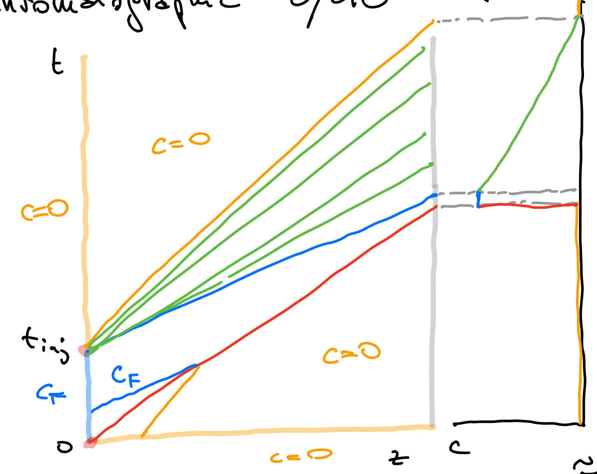
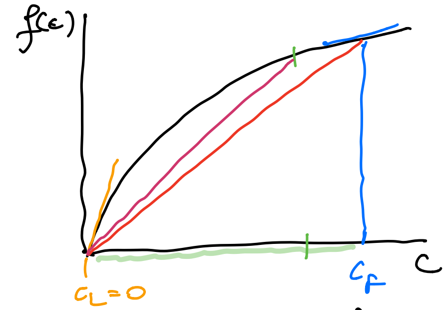
# [1] Chromatographic cycle : initial value problem




$$\sigma(c) = \frac{1}{v}\left(1+\nu\frac{df}{dc}\right)$$

$$\tilde{\sigma}(c_F,0) = \frac{1}{v}\left(1+\nu\frac{\Delta f}{\Delta c}\right) = \frac{1}{v}\left(1+\nu\frac{f(c_F)}{c_F}\right)$$

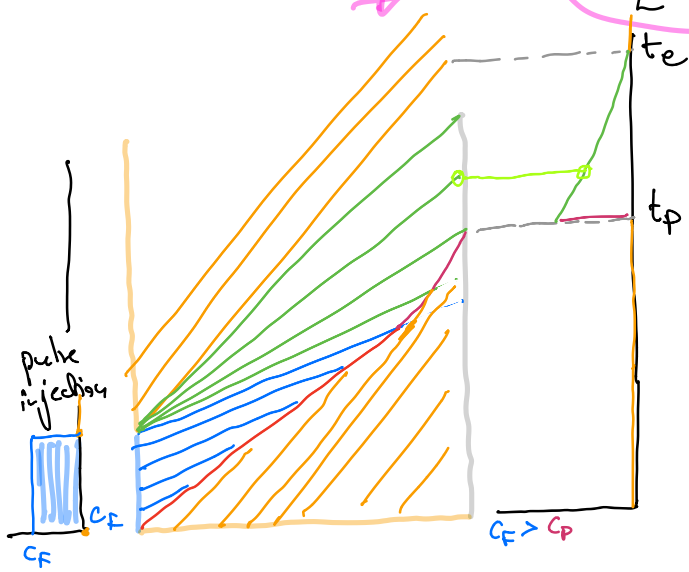
blue : $\boxed{t = t_{inj} + \sigma(c_F)\, z}$ ⊕

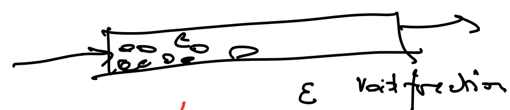
red : $\boxed{t = \tilde{\sigma}\, z}$ ⊖

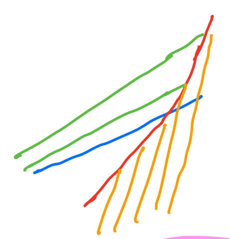
$$0 = t_{inj} + (\sigma_F - \tilde{\sigma})\, z = t_{inj} + \frac{\nu}{v}\left(f'(c_F) - \frac{f(c_F)}{c_F}\right) z$$

$$\Rightarrow z = \frac{t_{inj}\, v}{\nu}\left(\frac{f(c_F)}{c_F} - f'(c_F)\right)^{-1} < L$$

$$\frac{t_{inj}\, v}{L} < \nu\left(\frac{f(c_F)}{c_F} - f'(c_F)\right)$$ for interaction



$c_p$ ? $t_p$ ?

square pulse

overall material balance

$$IN = \cancel{Q}\, c_F\, t_{inj} = \cancel{Q}\int_{t_p}^{t_e} c(t)\,dt = OUT =$$

$$t = \sigma(c)\, L = \frac{L}{v}\left(1+\nu f'(c)\right)$$

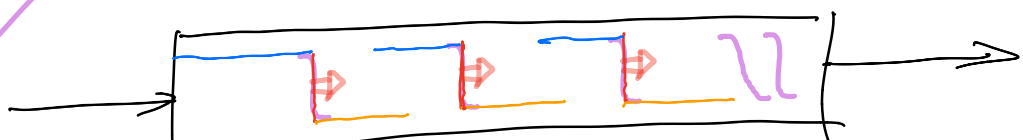
$$dt = \frac{L}{v}\,\nu f''(c)\,dc$$

$$= \frac{L\nu}{v}\int_{c_p}^{0} c\, f''(c)\, dc = c_p\, t_{inj}$$

$$\int_{c_p}^{0} c\, f''(c)\, dc = \Big[c\, f'(c)\Big]_{c_p}^{0} - \int_{c_p}^{0} f'(c)\, dc = \Big[c\, f'(c) - f(c)\Big]_{c_p}^{0} = \boxed{f(c_p) - c_p f'(c_p)}$$

$$f(c_p) = \frac{H c_p}{1+K c_p} \qquad f'(c_p) = \frac{H}{(1+K c_p)^2} \qquad \boxed{\frac{K H c_p^2}{(1+K c_p)^2}}$$

# 2 Constant pattern



smooth concentration front, traveling at constant velocity, without changing shape

challenge: can we model a constant pattern?

Equilibrium theory (method of characteristics) →
- Ass. 1: no mass transfer resistances = phase equilibrium
- Ass 2: transport through convection only (no diffusion)

$$\boxed{\frac{\partial}{\partial t}\big(\varepsilon c + (1-\varepsilon) f(c)\big) + \varepsilon v \frac{\partial c}{\partial z} = 0}$$

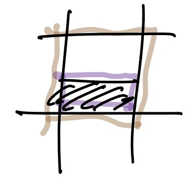
Rate model of chromatography: ① $n \neq f(c)$

② $F = u c - \varepsilon D \frac{\partial c}{\partial z}$

convection — diffusion

$$\left\{\begin{array}{l} \dfrac{\partial}{\partial t}\left(\varepsilon c + (1-\varepsilon)n\right) + \varepsilon v \dfrac{\partial c}{\partial z} = \varepsilon D \dfrac{\partial^2 c}{\partial z^2} \\[2ex] \dfrac{\partial n}{\partial t} = a_p k \left(f(c) - n\right) \end{array}\right.$$

$a_p$: $\left[\dfrac{m^2}{m^3}\right]$ $\quad k$: $\left[\dfrac{m}{s}\right]$



$$\left\{\begin{array}{l} \dfrac{\partial c}{\partial \tau} + \nu \dfrac{\partial n}{\partial \tau} + \dfrac{\partial c}{\partial x} = \dfrac{1}{Pe} \dfrac{\partial^2 c}{\partial x^2} \\[2ex] \dfrac{\partial n}{\partial \tau} = St \left(f(c) - n\right) \end{array}\right.$$

Eq. Theory

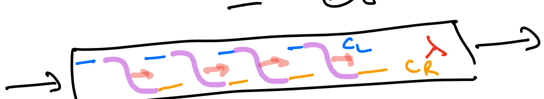
$$\frac{\partial n}{\partial t} = \frac{\partial f}{\partial t} = \frac{df}{dc}\frac{\partial c}{\partial t}$$

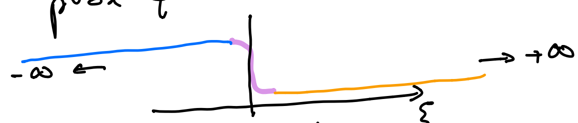
$$\tau = \frac{tv}{L} \qquad x = \frac{z}{L} \qquad \nu = \frac{1-\varepsilon}{\varepsilon}$$

$$Pe = \frac{L^2/D}{L/v} = \frac{\text{char. diffusion time}}{\text{residence time}} \qquad St = \frac{L/v}{1/(a_p k)} = \frac{\text{residence time}}{\text{char. mass transfer time}}$$

Equilibrium theory is the limit for:

- $Pe \to \infty$ no diffusion
- $St \to \infty$ phase equilibrium




dimensionless form of the rate model $\xrightarrow{?}$ constant pattern solution

Assumptions

(1) constant velocity: $\lambda$

(2) infinitely long column $\quad -\infty < x < +\infty$

(3) moving coordinate system $\quad \xi = x - \lambda\tau$

$$\frac{dc}{d\xi} = c' \qquad \frac{d^2c}{d\xi^2} = c''$$

$$\frac{\partial}{\partial x} = \frac{d}{d\xi}\frac{\partial \xi}{\partial x} = \frac{d}{d\xi} \qquad \frac{\partial^2}{\partial x^2} = \frac{d^2}{d\xi^2} \qquad \frac{\partial}{\partial \tau} = \frac{d}{d\xi}\frac{\partial \xi}{\partial \tau} = -\lambda\frac{d}{d\xi}$$

(4) B.C. $\quad \xi \to -\infty \quad c \to c_L, \; c', c'' \to 0 \qquad \xi \to +\infty \quad c \to c_R, \; c', c'' \to 0$

$$\begin{cases} -\lambda c' - \nu\lambda m' + c' = \frac{1}{Pe} c'' \\ -\lambda m' = St\,(f-m) \end{cases}$$

PDEs $\rightarrow$ ODEs

$(\tau, x)$ $(\xi)$

$f = f(c)$

$$\begin{cases} \nu m' = \frac{1}{\lambda}\left\{ c'(1-\lambda) - c''/Pe \right] \\ c'(1-\lambda) + \nu\, St\,(f-m) = c''/Pe \end{cases}$$

this determines $m$!

$\frac{d}{d\xi}$

$$c''(1-\lambda) + \nu\, St\,(f'-m') = c'''/Pe$$

$$c''(1-\lambda) + \nu\, St\, f' = \frac{St}{\lambda}\left\{ c'(1-\lambda) - c''/Pe \right\} + c'''/Pe$$

in $c$ only!

$$\boxed{\frac{1}{Pe\, St} c''' - \left(\frac{1}{\lambda Pe} + \frac{1-\lambda}{St}\right) c'' + \frac{1-\lambda}{\lambda} c' - \nu f' = 0} \rightarrow c$$

$\lambda$ is unknown!!