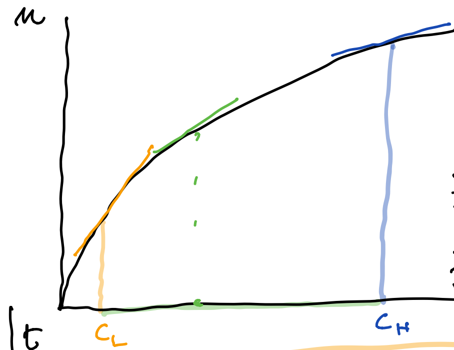
Chromatographic column — adsorption isotherm

from the PDE

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

$$\sigma = \frac{dt}{dz} \qquad \lambda(c) = \frac{1}{\sigma(c)} = \frac{dz}{dt}$$

$\frac{d\sigma}{dc} < 0$

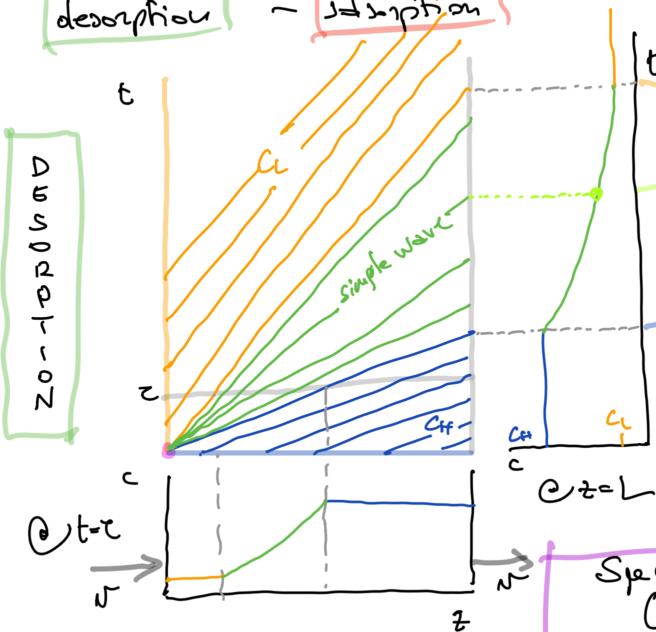


$$f(c) = \frac{Hc}{1+Kc}$$

$$f'(c) = \frac{H}{(1+Kc)^2}$$

$$f'' < 0$$

desorption — adsorption



$$t_{L,\text{breakthrough}} = \sigma(c_L)\,L$$

$$t = \sigma(c)\,L \qquad \sigma(c) = \frac{t}{L}$$

$$f'(c) = \left(\frac{vt}{L} - 1\right)\frac{1}{\nu}$$

$$t_{H,\text{eluted}} = \sigma(c_H)\,L$$

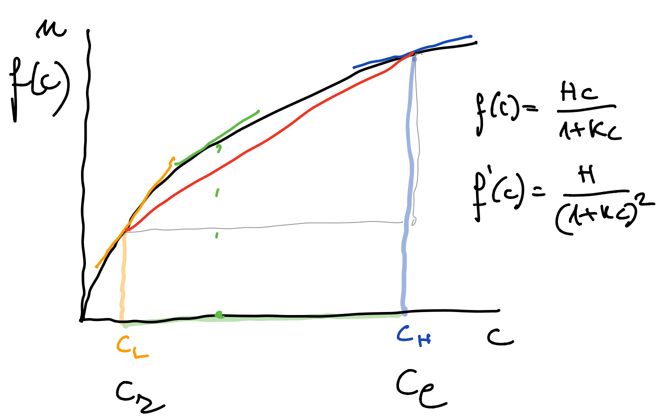
$$Kc = \sqrt{\frac{\nu H}{\frac{vt}{L} - 1}} - 1$$

$\hookrightarrow c(t, z=L)$

Special case: $c_L = 0$
(desorption = regeneration)

$$t_{\text{regeneration}} = \frac{L}{v}\left(1 + \nu f'(0)\right)$$

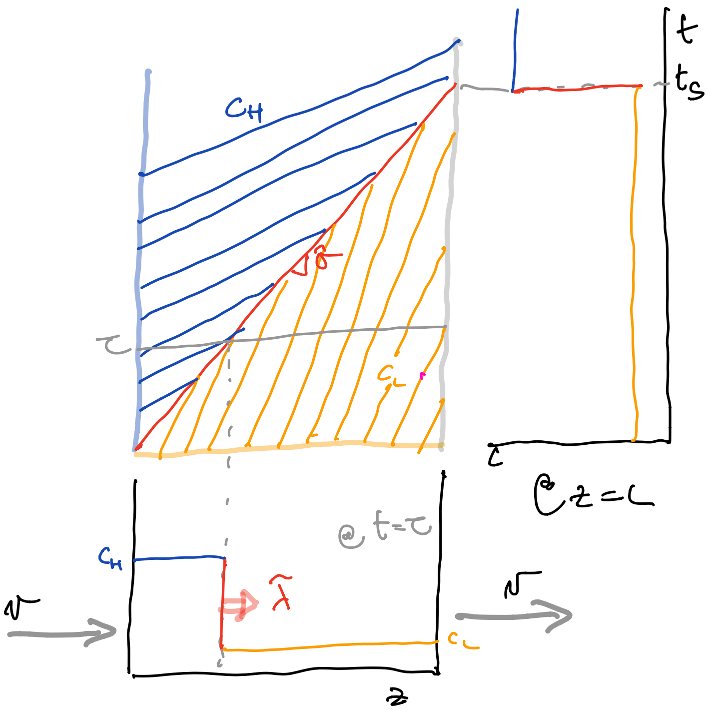
regeneration time does not depend on initial concentration



$$f(c) = \frac{Hc}{1+Kc}$$

$$f'(c) = \frac{H}{(1+Kc)^2}$$

ADSORPTION



$t_s = \tilde{\sigma} L$ s = shock

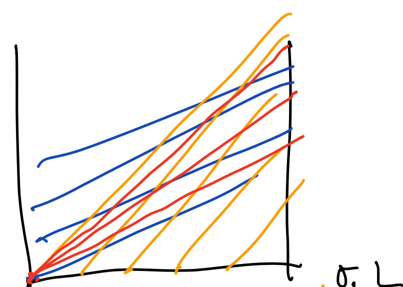
$\tilde{\lambda} = \frac{1}{\tilde{\sigma}}$

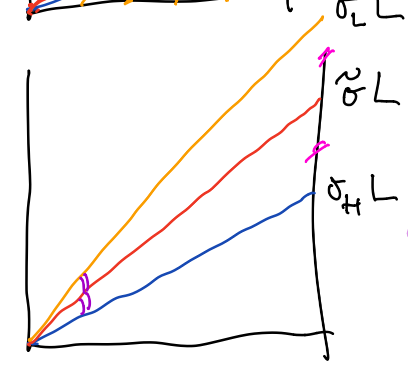
$$\tilde{\sigma}(c_L, c_H) = \frac{1}{v}\left(1 + \nu \frac{\Delta f}{\Delta c}\right)$$

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

special case $c_L = 0$
(adsorption on a clean column)

$$\tilde{\sigma} = \frac{1}{v}\left(1 + \nu \frac{f(c_H)}{c_H}\right)$$





① $\tilde{\sigma}$ could be many different values

$$\sigma(c_H) \le \tilde{\sigma} \le \sigma(c_L)$$

② what is the principle governing the choice of $\tilde{\sigma}$?

(i) $\tilde{\sigma} = \frac{1}{2}\left(\sigma(c_H) + \sigma(c_L)\right)$

(ii) equal areas !?

? (iii) equal angles → TJ checks

(iv) conservation of mass!! in finite form

$M(c)$ hold up
$F(c)$ flux

conservation law differential form (it requires continuity and differentiability):

$$\frac{\partial M}{\partial t} + \frac{\partial F}{\partial z} = 0$$

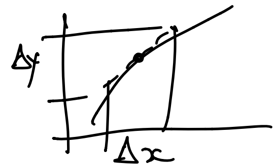
$$M'(c)\frac{\partial c}{\partial t} + F'(c)\frac{\partial c}{\partial z} = 0$$

PDE is incompatible with the "shock"

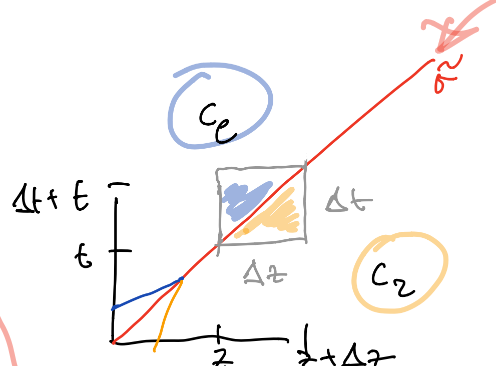
conservation law in finite form

$$\underbrace{\cancel{A}\,\Delta z\,\big(M(t+\Delta t) - M(t)\big)}_{A\ CC} = \underbrace{\cancel{A}\,\Delta t\,\big(F(z) - F(z+\Delta z)\big)}_{\text{FLOW-IN} - \text{FLOW-OUT}}$$ finite form

$$\frac{dy}{dx} \simeq \frac{\Delta y}{\Delta x}$$



$$M = \varepsilon c + (1-\varepsilon) f(c)$$
$$F = \varepsilon v c$$



$$\tilde{\sigma} = \frac{\Delta t}{\Delta z}$$

$$\Delta z\,\underbrace{\big(M(c_e) - M(c_z)\big)}_{} = \Delta t\,\underbrace{\big(F(c_e) - F(c_z)\big)}_{}$$

$$\Delta z \quad \Delta M \quad = \Delta t \quad \Delta F$$

$$\tilde{\sigma} = \frac{\Delta t}{\Delta z} = \frac{\boxed{\Delta M}}{\boxed{\Delta F}} = \frac{\varepsilon \Delta c + (1-\varepsilon)\Delta f}{\varepsilon v \Delta c} = \boxed{\frac{1}{v}\left(1 + \nu \frac{\Delta f}{\Delta c}\right) = \tilde{\sigma}}$$

what is fixed, and what is calculated?

$$\boxed{\begin{array}{c} c_e \\ c_z \\ M(c), F(c) \\ \frac{\Delta t}{\Delta z} = \tilde{\sigma} \end{array}} \qquad \boxed{\tilde{\sigma}}$$

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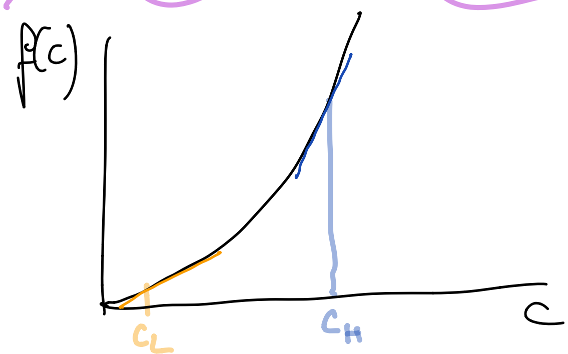
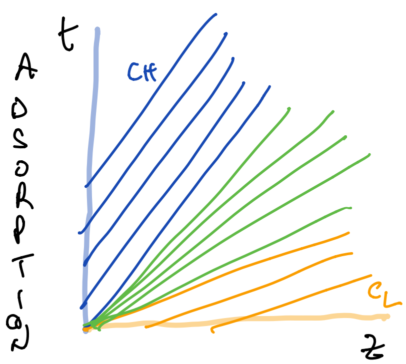
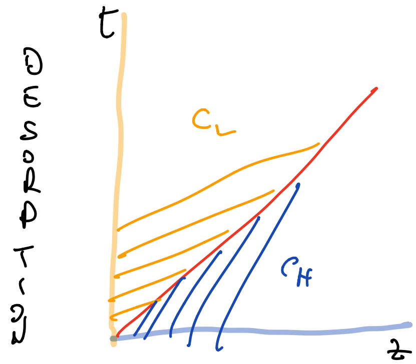


$$f(c) = \frac{Hc}{1-Kc} \qquad f'' > 0$$

$$f(c) = ac + bc^2 \quad (a, b > 0) \qquad f'' > 0$$

$$\frac{d\sigma}{dc} > 0$$

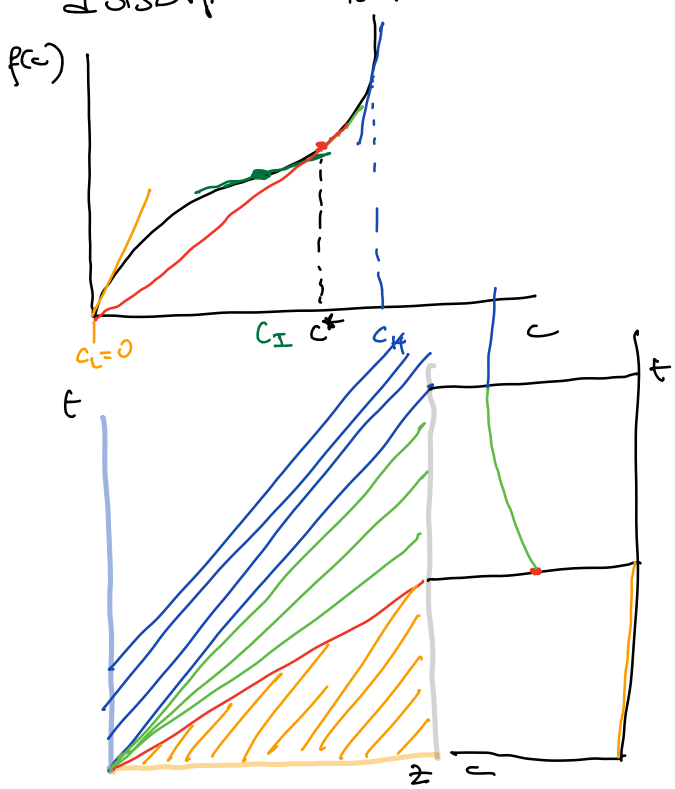


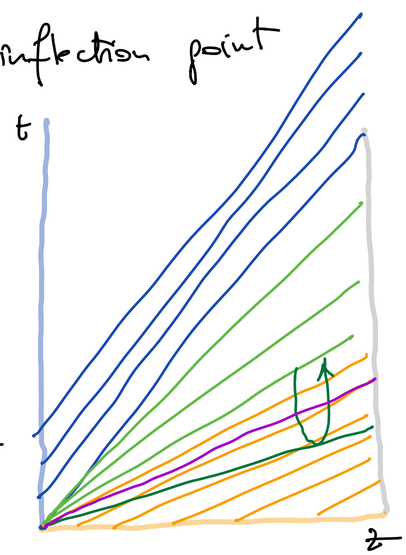


(B.E.T.)

→ Rate Controlled Separation

Adsorption isotherm with inflection point





semi-shock: combination of shock and simple wave.