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Constant pattern (shock layer)

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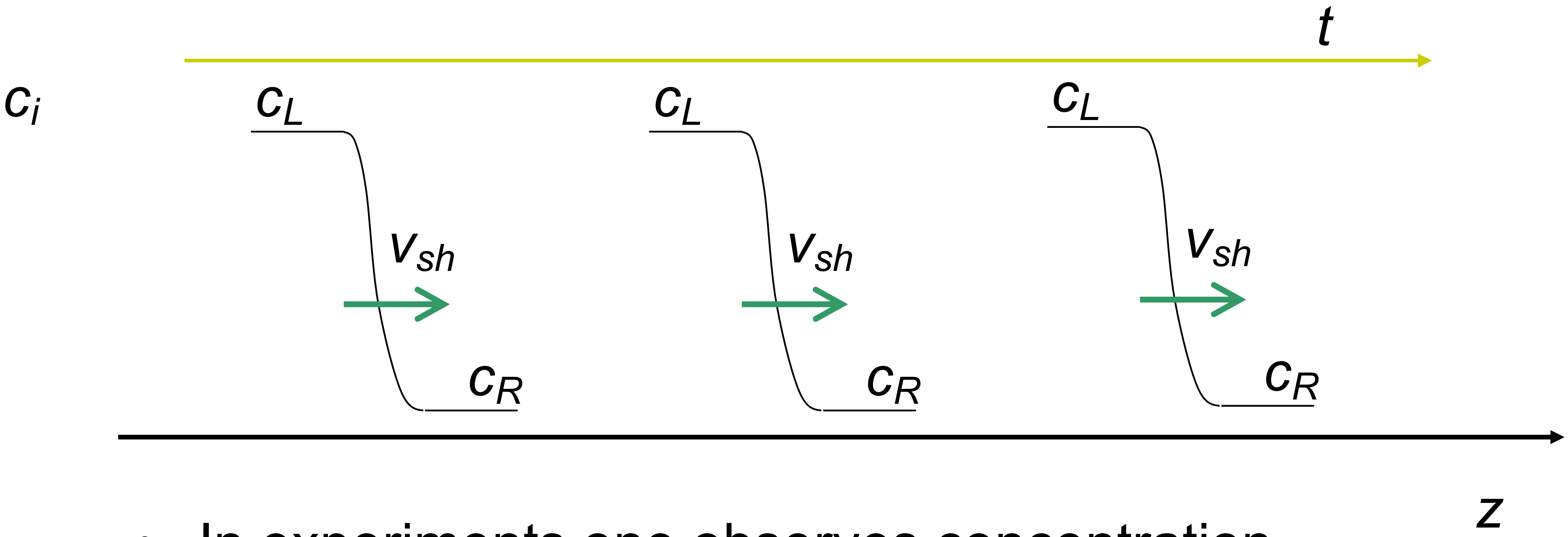
Learning objectives

1. Is the discontinuity in the solution of a conservation law (Equilibrium Theory of chromatography) physically meaningful?
2. How can one answer such question, via experiments or through theory?
3. What is a constant pattern, and how can one calculate it?

Exp: shock propagation and constant pattern



- In experiments one observes concentration fronts that propagate at constant velocity without changing shape → ***constant pattern***
- Comparison between E.T. model and experiments is tricky; we'd better use a detailed model → ***rate model***

Rate model and E.T. model

Rate model

$$\varepsilon \frac{\partial c_i}{\partial t} + (1-\varepsilon)\frac{\partial n_i}{\partial t} + u\frac{\partial c_i}{\partial z} = \varepsilon (D_i + E_i)\frac{\partial^2 c_i}{\partial z^2}$$

$(D_i + E_i) \rightarrow 0$

$$\frac{\partial n_i}{\partial t} = a_p k_i \left(n_i^* - n_i\right)$$

$k_i \rightarrow \infty$

$$n_i^* = f(c_i)$$

Equilibrium theory model

$$\varepsilon \frac{\partial c_i}{\partial t} + (1-\varepsilon)\frac{\partial n_i^*}{\partial t} + u\frac{\partial c_i}{\partial z} = 0$$

$$\frac{\partial n_i}{\partial t} = a_p k_i \left(n_i^* - n_i\right)$$

$$n_i^* = f(c_i)$$

- Longitudinal flux is due to convection, diffusion and axial mixing.
- Adsorption and desorption are mass transfer limited and described by a Linear Driving Force model.
- Rate model and E.T. model are linked.

$$\tilde{\sigma} = \frac{1}{V}\left(1 + \nu \frac{f_L - f_R}{c_L - c_R}\right) = $$
$$= \frac{1}{V}\left(1 + \nu \frac{[f]}{[c]}\right) = \frac{1}{v_{sh}}$$

Rate model, dimensionless

Rate model

$$\varepsilon \frac{\partial c_i}{\partial t} + (1-\varepsilon)\frac{\partial n_i}{\partial t} + u\frac{\partial c_i}{\partial z} = \varepsilon (D_i + E_i)\frac{\partial^2 c_i}{\partial z^2}$$

$$\frac{\partial n_i}{\partial t} = a_p k_i \left(n_i^* - n_i\right)$$

$$n_i^* = f(c_i)$$

Dimensionless model (1-comp)

$$\frac{\partial c}{\partial \tau} + \nu \frac{\partial n}{\partial \tau} + \frac{\partial c}{\partial x} = \frac{1}{Pe}\frac{\partial^2 c}{\partial x^2}$$

$$\frac{\partial n}{\partial \tau} = St\left(f - n\right)$$

$$\tau = \frac{tu}{\varepsilon L}; \quad x = \frac{z}{L}; \quad \nu = \frac{1-\varepsilon}{\varepsilon};$$

$$Pe = \frac{L^2/(D+E)}{L\varepsilon/u}; \quad St = \frac{L\varepsilon/u}{1/(a_p k)}$$

$$\tilde{\sigma}_{dimensionless} = 1 + \nu\frac{[f]}{[c]} = \frac{1}{v_{sh,dimensionless}}$$

Do these equations admit a constant pattern solution?

If yes, under which conditions?

Rate model, and constant pattern

Dimensionless model (1-comp)

$$\frac{\partial c}{\partial \tau} + \nu \frac{\partial n}{\partial \tau} + \frac{\partial c}{\partial x} = \frac{1}{Pe}\frac{\partial^2 c}{\partial x^2}$$

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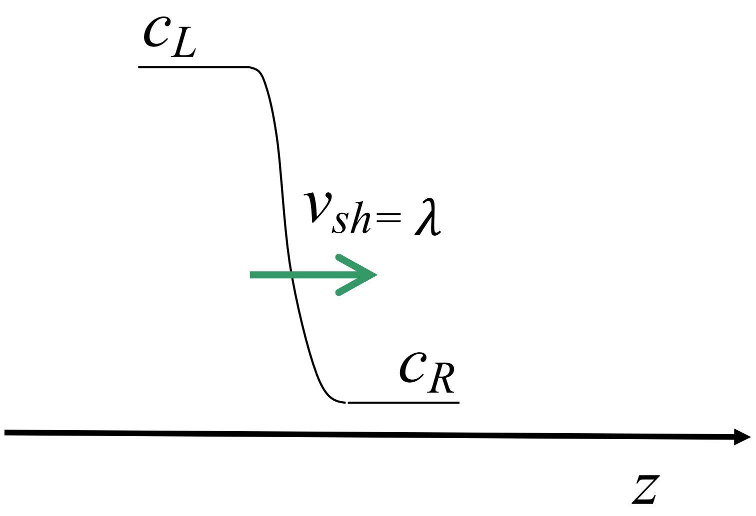

Assumptions

- Dimensionless shock velocity: λ
- Infinitely long column
- Moving coordinate system: $\xi = x - \lambda\tau$

$$\frac{\partial}{\partial x} = \frac{d}{d\xi}\frac{\partial \xi}{\partial x} = \frac{d}{d\xi}$$

$$\frac{\partial}{\partial \tau} = \frac{d}{d\xi}\frac{\partial \xi}{\partial \tau} = -\lambda\frac{d}{d\xi}$$

- Boundary conditions

$$\xi \to -\infty \qquad c \to c_L \qquad c', c'' \to 0$$

$$\xi \to +\infty \qquad c \to c_R \qquad c', c'' \to 0$$

Rate model, and constant pattern

Dimensionless model (1-comp)

$$\frac{\partial c}{\partial \tau} + \nu \frac{\partial n}{\partial \tau} + \frac{\partial c}{\partial x} = \frac{1}{Pe}\frac{\partial^2 c}{\partial x^2}$$

$$\frac{\partial n}{\partial \tau} = St\left(f - n\right)$$

$$\begin{cases} -\lambda c' - \nu\lambda n' + c' = c''/Pe \\ -\lambda n' = St\left(f - n\right) \end{cases}$$

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

$$c''\left(1-\lambda\right) + \nu St\left(f' - n'\right) = c'''/Pe$$

$$c''\left(1-\lambda\right) + \nu St\ f' = St\left[c'\left(1-\lambda\right) - c''/Pe\right]/\lambda + c'''/Pe$$

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

Assumptions

- Dimensionless shock velocity: λ
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$$\frac{\partial}{\partial x} = \frac{d}{d\xi}\frac{\partial \xi}{\partial x} = \frac{d}{d\xi}$$

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Constant pattern

$$\frac{1}{Pe\,St}c''' - \left(\frac{1}{\lambda\,Pe} + \frac{1-\lambda}{St}\right)c'' + \frac{1-\lambda}{\lambda}c' - \nu f' = 0 \qquad \text{2nd B.C.}$$

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

$\frac{1}{Pe\,St}$ → ≈ 0

$\left(\frac{1}{\lambda\,Pe} + \frac{1-\lambda}{St}\right)$ → $1/\alpha$

Boundary conditions

$$\xi \to -\infty \qquad c \to c_L \qquad c', c'' \to 0$$

$$\xi \to +\infty \qquad c \to c_R \qquad c', c'' \to 0$$

$$\frac{dc}{d\xi} = \alpha\left[\frac{1-\lambda}{\lambda}(c - c_R) - \nu(f - f_R)\right] \qquad \text{1st order ODE}$$

$$0 = \alpha\left[\frac{1-\lambda}{\lambda}(c_L - c_R) - \nu(f_L - f_R)\right] \qquad \text{1st B.C.}$$

$$\lambda = \left(1 + \nu\frac{[f]}{[c]}\right)^{-1} = \tilde{\sigma}^{-1} = v_{sh} \quad \text{(dimensionless)}$$

$$\frac{dc}{d\xi} = \alpha\nu\left[\frac{[f]}{[c]}(c - c_R) - (f - f_R)\right] = F(c)$$

Constant pattern

$$\frac{dc}{d\xi} = \alpha v \left[\frac{[f]}{[c]} (c - c_R) - (f - f_R) \right] = F(c)$$

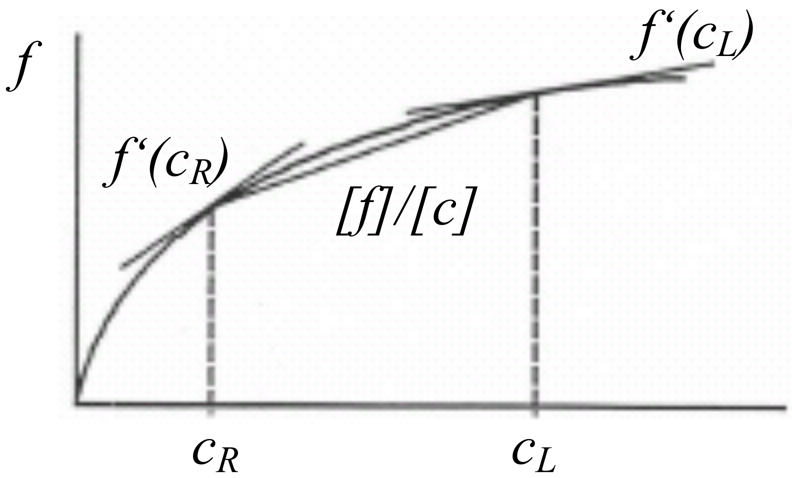
Boundary conditions

$$\xi \to -\infty \quad c \to c_L \quad c', c'' \to 0$$
$$\xi \to +\infty \quad c \to c_R \quad c', c'' \to 0$$

Boundary conditions require that c_L be an unstable steady state ($F'(c_L) > 0$), and c_R be a stable steady state ($F'(c_R) < 0$).

$$F'(c) = \alpha v \left[\frac{[f]}{[c]} - f' \right]$$

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



Constant pattern

$$\frac{dc}{d\xi} = \alpha v\left[\frac{[f]}{[c]}(c-c_R)-(f-f_R)\right] = F(c)$$

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

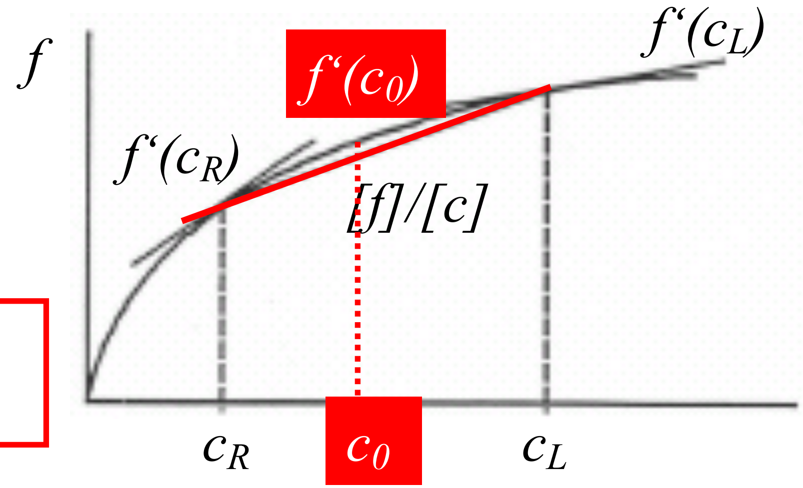
$$\frac{1+Kc}{(c-c_R)(c-c_L)}dc = \alpha v K\frac{[f]}{[c]}d\xi$$

$$\frac{1}{[c]}\left(\frac{1+Kc_L}{c-c_L}-\frac{1+Kc_R}{c-c_R}\right)dc = \alpha v K\frac{[f]}{[c]}d\xi$$

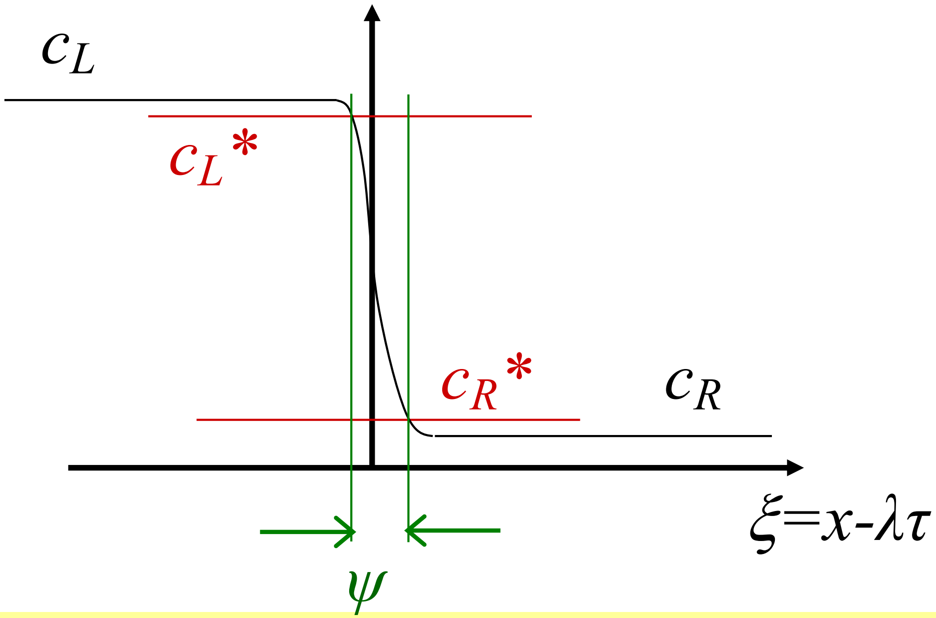
$$(1+Kc_L)\ln\left(\frac{c-c_L}{c_0-c_L}\right)-(1+Kc_R)\ln\left(\frac{c-c_R}{c_0-c_R}\right) = \alpha v K[f]\xi$$

c_0 is where $\frac{d^2c}{d\xi^2} = F'(c_0) = 0$, i.e. $\frac{[f]}{[c]} = f'(c_0)$, or:

$$(1+Kc_0) = \sqrt{(1+Kc_L)(1+Kc_R)}$$



Shock layer thickness



distance from plateau: $\beta = \dfrac{c_L - c_L^*}{c_L - c_R} = \dfrac{c_R^* - c_R}{c_L - c_R}$

shock layer thickness: $\psi = \xi\left(c_R^*\right) - \xi\left(c_L^*\right)$

earlier breakthrough: $\Delta\tau = \dfrac{\psi}{2\lambda}$

Shock layer thickness

$$\left(1+Kc_L\right)\ln\left(\frac{c-c_L}{c_0-c_L}\right)-\left(1+Kc_R\right)\ln\left(\frac{c-c_R}{c_0-c_R}\right)=\alpha\nu K\left[f\right]\xi$$

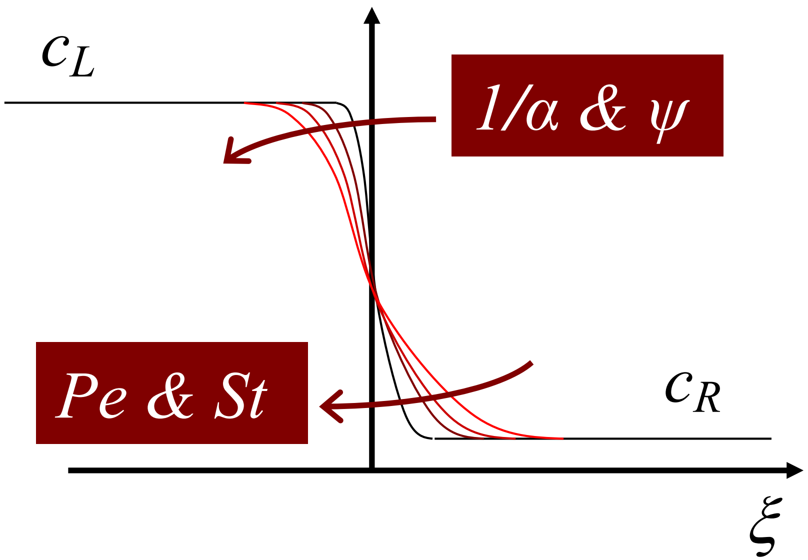
$$\psi=\xi\left(c_R^*\right)-\xi\left(c_L^*\right)=\frac{1+Kc_L}{\alpha\nu K\left[f\right]}\ln\left(\frac{c_R^*-c_L}{c_L^*-c_L}\right)-\frac{1+Kc_R}{\alpha\nu K\left[f\right]}\ln\left(\frac{c_R^*-c_R}{c_L^*-c_R}\right)=$$

$$=\left(\frac{1+Kc_L}{\alpha\nu K\left[f\right]}+\frac{1+Kc_R}{\alpha\nu K\left[f\right]}\right)\ln\left(\frac{1-\beta}{\beta}\right)=\frac{2+K\left(c_L+c_R\right)}{\alpha\nu K\left(f_L-f_R\right)}\ln\left(\frac{1-\beta}{\beta}\right)$$

Shock layer thickness

$$\psi = \frac{2 + K\left(c_L + c_R\right)}{\alpha v K\left(f_L - f_R\right)} \ln\left(\frac{1-\beta}{\beta}\right) \qquad \Delta\tau = \frac{\psi}{2\lambda}$$

$$\frac{d\psi}{d\left(1/\alpha\right)} > 0 \qquad \frac{1}{\alpha} = \frac{1}{\lambda\, Pe} + \frac{1-\lambda}{St}$$



Learning objectives

- ✓The discontinuity in the solution of a conservation law (Equilibrium Theory of chromatography) is indeed physically meaningful → E.T. predicts existence and propagation velocity.
- ✓One can answer such question, through theory and mathematical analysis of a detailed model, where experiments motivate assumptions.
- ✓A constant pattern is what one can see in experiments, and what the shck layer theory allows calculating (isotherm independent).