

# Modelling and Mathematical Methods in Process and Chemical Engineering

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## Binary chromatography

The derivation of the conservation equations for binary chromatography for each of the species  $i = 1, 2$  is equivalent to the derivation of the conservation equation for one component chromatography. Starting from a species balance

$$\text{ACC}_i = \text{IN}_i - \text{OUT}_i$$

we obtain the conservation law in differential form

$$\frac{\partial M_i}{\partial t} + \frac{\partial F_i}{\partial z} = 0$$

for species  $i$ . This leads to the conservation equations for the two species, namely

$$\frac{\partial c_1}{\partial t} + \nu \frac{\partial n_1}{\partial t} + V \frac{\partial c_1}{\partial z} = 0 \quad (1)$$

$$\frac{\partial c_2}{\partial t} + \nu \frac{\partial n_2}{\partial t} + V \frac{\partial c_2}{\partial z} = 0 \quad (2)$$

### Case 1: the two equations are uncoupled

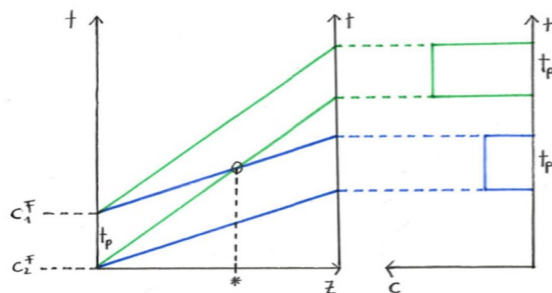
In this simple case, the adsorption of species  $i$  is independent of the concentration of species  $j$ :

$$n_i = f_i(c_i)$$

Assuming a simple Henry's law dependency  $n_i = H_i c_i$  (this typically happens when the species are very diluted and a linear adsorption isotherm can be used) and inserting it into equations 1 and 2, the conservation equation for species  $i$  (where  $i = 1, 2$ ) follows as

$$(1 + \nu H_i) \frac{\partial c_i}{\partial t} + V \frac{\partial c_i}{\partial z} = 0$$

Therefore, the species are independent of each other and each species behaves like a single species. We emphasize here that this assumption is valid only for very dilute solutions where the two species do not influence each other.



$$H_1 < H_2$$

$$\sigma_i = \frac{1 + \nu H_i}{V}$$

$$\Rightarrow \sigma_1 < \sigma_2$$

\* base line separation

## Case 2: the two equations are coupled

In this considerably more complex case, the concentration of species  $i$  is a function of both concentrations  $c_1$  and  $c_2$ , i.e.,

$$n_i = f_i(c_1, c_2)$$

In the following, we use the relation

$$n_i = \frac{H_i c_i}{1 + K_1 c_1 + K_2 c_2}$$

which is known as the Langmuir model for competitive adsorption. Then, equation 1 becomes

$$\begin{aligned} \frac{\partial c_1}{\partial t} + \nu \frac{\partial n_1(c_1, c_2)}{\partial t} + V \frac{\partial c_1}{\partial z} &= 0 \\ \frac{\partial c_1}{\partial t} + \nu \left( \frac{\partial n_1}{\partial c_1} \frac{\partial c_1}{\partial t} + \frac{\partial n_1}{\partial c_2} \frac{\partial c_2}{\partial t} \right) + V \frac{\partial c_1}{\partial z} &= 0 \end{aligned} \quad (3)$$

Analogously, for equation 2, we have

$$\begin{aligned} \frac{\partial c_2}{\partial t} + \nu \frac{\partial n_2(c_1, c_2)}{\partial t} + V \frac{\partial c_2}{\partial z} &= 0 \\ \frac{\partial c_2}{\partial t} + \nu \left( \frac{\partial n_2}{\partial c_1} \frac{\partial c_1}{\partial t} + \frac{\partial n_2}{\partial c_2} \frac{\partial c_2}{\partial t} \right) + V \frac{\partial c_2}{\partial z} &= 0 \end{aligned} \quad (4)$$

The conservation equations 3 and 4 for the two species are now coupled through  $n_i$ .

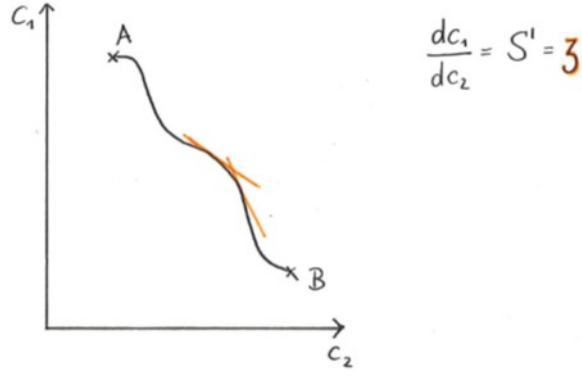
As for a chromatographic process with a single component, our aim is again to derive the concentration profiles as a function of time and space, i.e.,  $c_i = \text{function}(t, z)$ . However, since now we have a system of two PDEs, we cannot apply the method of characteristics straight away. Instead, we approach the problem as follows:

- In a first step, we derive two sets of characteristics  $\Gamma_1$  and  $\Gamma_2$  in the so-called **Hodograph plane** ( $c_1, c_2$ -plane). These characteristics describe the mapping of the solution of the system of PDEs (i.e., the mapping of the elution profiles) in the  $c_1, c_2$ -plane. They indicate how  $c_2$  changes as a function of  $c_1$  (or vice versa) for any possible state  $(c_1, c_2)$ . By determining the relationship between  $c_1$  and  $c_2$ , we can reduce the number of PDEs to solve from two to one. We will find that for any state  $(c_1, c_2)$ , there are two characteristics (one of each set;  $\Gamma_1$  and  $\Gamma_2$ ), suggesting two different possible paths.
- Having reduced the system to a single PDE, we can apply the method of characteristics to obtain the slopes in the physical  $t, z$ -plane. The reciprocal of these slopes corresponds to the propagation velocities, and each state  $(c_1, c_2)$  on a characteristic ( $\Gamma_i$ ) travels with a characteristic propagation velocity.
- Finally, we have to find the physically correct path (there is only one) in the hodograph plane, which connects the initial state to the feed state, and calculate the corresponding propagation velocities. From the information provided by the hodograph plane (relationship  $c_1$  between  $c_2$ ) and the physical plane (propagation velocities), we can construct the concentration profiles as a function of space and time.

## 1 The Hodograph plane and the characteristics $\Gamma_1$ and $\Gamma_2$

### 1.1 Derivation of $\zeta$

The solutions of equations 3 and 4 can be mapped into the  $c_1, c_2$ -plane, the so called **Hodograph plane**.



We are interested in the path connecting the two states. Therefore, we need to know the function  $S$  that relates  $c_1$  to  $c_2$ .

$$c_1 = S(c_2) \quad (5)$$

We define  $\zeta$  as the derivative of the function  $S$ , i.e.,

$$\boxed{\frac{dc_1}{dc_2} = S' =: \zeta} \quad (6)$$

$\frac{\partial c_1}{\partial t}$  and  $\frac{\partial c_2}{\partial t}$  are now connected through  $\zeta$ , namely

$$\frac{\partial c_1}{\partial t} = \frac{dc_1}{dc_2} \frac{\partial c_2}{\partial t} = \zeta \frac{\partial c_2}{\partial t}$$

With this relation and the abbreviation  $\frac{\partial n_i}{\partial c_j} = n_{ij}$ , equations 3 and 4 can be rewritten as a function of the concentration of only one species,  $c_2$ , and  $\zeta$ , as

$$\zeta \frac{\partial c_2}{\partial t} + \nu \left( \zeta n_{11} \frac{\partial c_2}{\partial t} + n_{12} \frac{\partial c_2}{\partial t} \right) + V \zeta \frac{\partial c_2}{\partial z} = 0 \quad (7)$$

$$\frac{\partial c_2}{\partial t} + \nu \left( \zeta n_{21} \frac{\partial c_2}{\partial t} + n_{22} \frac{\partial c_2}{\partial t} \right) + V \frac{\partial c_2}{\partial z} = 0 \quad (8)$$

Thus, we now have two equations in a single unknown  $c_2$ . For the problem to have a solution, equations 7 and 8 must be identical. This identity can be enforced via a condition on  $\zeta$ . Namely, dividing equation 7 by  $\zeta$  and then comparing coefficients with equation 8 yields

$$n_{11} + \frac{n_{12}}{\zeta} = \zeta n_{21} + n_{22} \quad (9)$$

By rearranging, we obtain

$$\boxed{n_{21}\zeta^2 - (n_{11} - n_{22})\zeta - n_{12} = 0} \quad (10)$$

which can be used to calculate  $\zeta$ . Solving equation 10 leads to two solutions for  $\zeta$ . These are

$$\zeta_{1,2} = \frac{1}{2n_{21}} \left[ (n_{11} - n_{22}) \pm \sqrt{\Delta_\zeta} \right]$$

where

$$\Delta_\zeta := (n_{11} - n_{22})^2 + 4n_{12}n_{21}$$

For our example of competitive Langmuir adsorption ( $n_i = \frac{H_i c_i}{1 + K_1 c_1 + K_2 c_2} = \frac{H_i c_i}{d}$ ), we know that  $\Delta_\zeta$  is positive, since we have

$$n_{ii} = \frac{\partial n_i}{\partial c_i} = \frac{H_i(d - K_i c_i)}{d^2} = \frac{H_i(1 + K_j c_j)}{d^2} > 0 \quad (11)$$

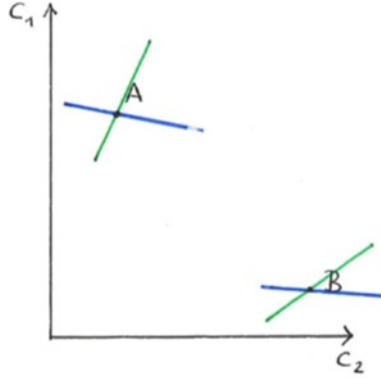
$$n_{ij} = \frac{\partial n_i}{\partial c_j} = \frac{-H_i c_i K_j}{d^2} < 0 \quad (12)$$

Because  $\Delta_\zeta$  is positive and  $\sqrt{\Delta_\zeta}$  is greater than  $(n_{11} - n_{22})$ , we get one positive and one negative solution for  $\zeta$ . These solutions are given by

$$\zeta_1 = \frac{1}{2n_{21}} \left[ (n_{11} - n_{22}) + \sqrt{\Delta_\zeta} \right] < 0 \quad (13)$$

$$\zeta_2 = \frac{1}{2n_{21}} \left[ (n_{11} - n_{22}) - \sqrt{\Delta_\zeta} \right] > 0 \quad (14)$$

This means that for every point in the *Hodograph plane*, there are two possible directions, one with a positive and one with a negative slope.



## 1.2 Derivation of $c_1 = S(c_2)$ and of the characteristics $\Gamma_i$

Now that we have calculated  $\zeta$ , an equation for  $S$  (cf. equation 5) could be derived by integrating equation 6, but this procedure is complicated and time consuming. Therefore, we choose an alternative route. Inserting equations 11 and 12 into equation 9 yields

$$H_1(1 + K_2c_2) - \frac{H_1K_2c_1}{\zeta} = -H_2K_1c_2\zeta + H_2(1 + K_1c_1)$$

This equation can be solved for  $c_1$ , i.e.,

$$c_1 = \zeta c_2 - \frac{(H_2 - H_1)\zeta}{H_1K_2 + H_2K_1\zeta} = \zeta c_2 - \frac{k\zeta}{\zeta + h} \quad (15)$$

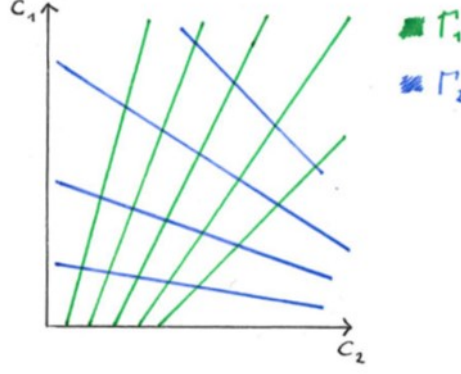
where

$$k := \frac{H_2 - H_1}{H_2K_1} > 0$$

$$h := \frac{H_1K_2}{H_2K_1} > 0$$

$$\gamma := \frac{H_2}{H_1} > 1$$

We now assume that  $\zeta$  is constant and test if this assumption is consistent with equation 15. Since this is the case, we know that  $\zeta$  **constant** is a possible solution. This type of PDE is called *Clairaut equation*. The solution to equation 5 therefore consists of straight lines in the *Hodograph plane*.



For a constant value of  $\zeta_2$  and varying  $\zeta_1$ , the equation for the series of straight lines  $\Gamma_1$  is given by

$$\Gamma_1 : \quad c_1 = \zeta_2 c_2 - \frac{k\zeta_2}{\zeta_2 + h} \quad (16)$$

and for a constant value of  $\zeta_1$  and varying  $\zeta_2$ , the equation for the series of straight lines  $\Gamma_2$  is given by

$$\Gamma_2 : \quad c_1 = \zeta_1 c_2 - \frac{k\zeta_1}{\zeta_1 + h} \quad (17)$$

By solving the last two equations for  $c_1$  and  $c_2$  as a function of  $\zeta_1$  and  $\zeta_2$  (linear system), we obtain the following equations for  $c_1$  and  $c_2$ , and then  $d$  from its definition:

$$c_1 = \frac{-k\zeta_1\zeta_2}{(\zeta_1 + h)(\zeta_2 + h)} \quad (18)$$

$$c_2 = \frac{kh}{(\zeta_1 + h)(\zeta_2 + h)} \quad (19)$$

$$d = \frac{1}{\gamma} \left( \frac{\zeta_1 + h\gamma}{\zeta_1 + h} \right) \left( \frac{\zeta_2 + h\gamma}{\zeta_2 + h} \right) \quad (20)$$

### 1.3 Connecting $\zeta_i$ to the eigenvalues $\vartheta_i$

We now examine the relation between  $\zeta$  and the eigenvalues of the problem. The Jacobian of the concentrations  $n_i$  is given by

$$\underline{J} = \begin{bmatrix} n_{11} & n_{12} \\ n_{21} & n_{22} \end{bmatrix}$$

For the eigenvalues  $\vartheta$  of this Jacobian, we know that

$$\vartheta^2 - (n_{11} + n_{22})\vartheta + (n_{11}n_{22} - n_{12}n_{21}) = 0 \quad (21)$$

Furthermore, the discriminant of equation 10 is

$$\Delta_\zeta = (n_{11} - n_{22})^2 + 4n_{12}n_{21}$$

and the discriminant of equation 21 is

$$\Delta_\vartheta = (n_{11} + n_{22})^2 + 4n_{12}n_{21} - 4n_{11}n_{22} = (n_{11} - n_{22})^2 + 4n_{12}n_{21}$$

Therefore, the discriminants of equations 10 and 21 are the same, i.e.,

$$\Delta_\zeta = \Delta_\vartheta$$

Let us assume for the relation between  $\vartheta$  and  $\zeta$  that

$$\vartheta = n_{11} + \frac{n_{12}}{\zeta} = n_{22} + \zeta n_{21} \quad (22)$$

In order to prove this assumption, we insert equation 22 into equation 21

$$\begin{aligned}
& (n_{22} + \zeta n_{21})^2 - (n_{11} + n_{22})(n_{22} + \zeta n_{21}) + n_{11}n_{22} - n_{12}n_{21} = \\
= & n_{21}^2 \zeta^2 + \zeta(n_{21}n_{22} - n_{11}n_{21}) - n_{12}n_{21} = \\
= & n_{21}(n_{21}\zeta^2 - \zeta(n_{11} - n_{22}) - n_{12}) \stackrel{10}{=} 0
\end{aligned}$$

Thus, the assumption is correct.

For the corresponding  $\vartheta$ , we get

$$\boxed{\begin{array}{ccccc} \zeta_1 & < & 0 & < & \zeta_2 \\ \updownarrow & & & & \updownarrow \\ \vartheta_2 & & & & \vartheta_1 & > & 0 \end{array}} \text{ since } \vartheta_1 \vartheta_2 = n_{11}n_{22} - n_{12}n_{21} > 0 \Rightarrow \vartheta_i > 0$$

Another way of writing equation 22 using total differentials is

$$\begin{aligned}
\vartheta &= \frac{\partial n_2}{\partial c_2} + \frac{\partial n_2}{\partial c_1} \frac{dc_1}{dc_2} = \left. \frac{Dn_2}{Dc_2} \right|_{\Gamma} \\
\vartheta &= \frac{\partial n_1}{\partial c_1} + \frac{\partial n_1}{\partial c_2} \frac{dc_2}{dc_1} = \left. \frac{Dn_1}{Dc_1} \right|_{\Gamma}
\end{aligned}$$

and therefore

$$\left. \frac{Dn_2}{Dc_2} \right|_{\Gamma} = \left. \frac{Dn_1}{Dc_1} \right|_{\Gamma}$$

Using this insight and the eigenvalue  $\vartheta_i$ , the system of PDEs (equations 7 and 8) can be reduced to the single PDE

$$\boxed{[1 + \nu \vartheta_i] \frac{\partial c_2}{\partial t} + V \frac{\partial c_2}{\partial z} = 0} \tag{23}$$

with  $i = 1, 2$ . The corresponding slopes  $\sigma_i$  in the physical  $t, z$ -plane are

$$\sigma_i = \frac{1}{V} (1 + \nu \vartheta_i) \tag{24}$$

## 2 Introduction of the $\omega_1, \omega_2$ -plane

The derivations in the previous section enable us to obtain the representation in the **Hodograph plane** independently of the initial and the feed state. Still, we do not know yet the correct path that connects the initial and the feed state. To identify this path, we introduce a new plane with a new set of variables  $\omega_1$  and  $\omega_2$ , which are defined as

$$\boxed{\omega_j := \frac{H_2(\zeta_j + h)}{\zeta_j + h\gamma}}$$

Therefore, we have

$$\boxed{\zeta_j = \frac{h(\omega_j \gamma - H_2)}{H_2 - \omega_j}} \tag{25}$$

with

$$\frac{d\omega_j}{d\zeta_j} = \frac{H_2(\gamma - 1)h}{(\zeta_j + h\gamma)^2} > 0 \tag{26}$$

as  $\gamma = \frac{H_2}{H_1} > 1$ . This means that  $\omega$  is a monotonically increasing function of  $\zeta$ . From equations 18, 19, and 20, and using equation 25, we derive

$$K_1 c_1 = \frac{-H_2(\omega_1 - H_1)(\omega_2 - H_2)}{\omega_1 \omega_2 (H_2 - H_1)} \tag{27}$$

$$K_2 c_2 = \frac{H_1(\omega_1 - H_2)(\omega_2 - H_2)}{\omega_1 \omega_2 (H_2 - H_1)} \tag{28}$$

$$d = 1 + K_1 c_1 + K_2 c_2 = \frac{H_1 H_2}{\omega_1 \omega_2} \tag{29}$$

for the concentrations, and

$$\boxed{\vartheta_j = n_{22} + n_{21}\zeta_{3-j} \stackrel{11\&12}{=} \frac{H_2(1 + K_1c_1)}{d^2} - \frac{H_2K_1c_2}{d^2}\zeta_{3-j} = \dots = \frac{\omega_j}{d} = \frac{\omega_j^2\omega_{3-j}}{H_1H_2}} \quad (30)$$

for the eigenvalue  $\vartheta$ . The relation  $\vartheta_j = f(\omega_1, \omega_2)$  is thus established by equation 30. Also, it follows that

$$\boxed{\begin{array}{ccccc} \zeta_1 & < & 0 & < & \zeta_2 \\ \updownarrow & & & & \updownarrow \\ \vartheta_2 & & & & \vartheta_1 & > & 0 \\ \updownarrow & & & & \updownarrow & & \\ \omega_2 & & & & \omega_1 & > & 0 \end{array}}$$

Multiplying equation 21 by  $d^2$  yields

$$d^2\vartheta^2 - d^2(n_{11} + n_{22})\vartheta + d^2(n_{11}n_{22} - n_{12}n_{21}) = 0$$

where

$$\begin{aligned} d^2(n_{11} + n_{22}) &\stackrel{11}{=} H_1(1 + K_2c_2) + H_2(1 + K_1c_1) \\ d^2(n_{11}n_{22} - n_{12}n_{21}) &\stackrel{11\&12}{=} \frac{H_1H_2}{d} \end{aligned}$$

Multiplying equation 21 with  $d^3$  and inserting  $d = f(\omega)$  yields

$$d\omega^2 - \omega[H_1(1 + K_2c_2) + H_2(1 + K_1c_1)] + H_1H_2 = 0$$

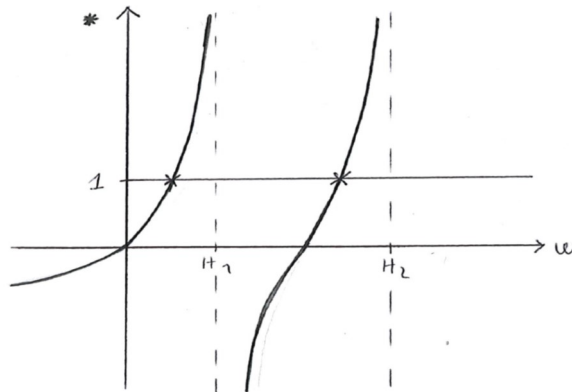
which we can rearrange

$$(\omega - H_1)(\omega - H_2) + \omega K_2c_2(\omega - H_1) + \omega K_1c_1(\omega - H_2) = 0$$

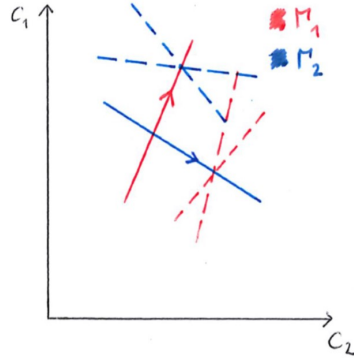
and finally divide by  $(\omega - H_1)(\omega - H_2)$  to obtain

$$\boxed{\underbrace{\frac{\omega K_2c_2}{H_2 - \omega} + \frac{\omega K_1c_1}{H_1 - \omega}}_* = 1} \quad (31)$$

By plotting equation 31, we can see that  $0 < \omega_1 \leq H_1 \leq \omega_2 \leq H_2$ . Furthermore, for  $c_1 = 0 \Rightarrow \omega_j = H_1$  with  $j = 1$  or  $j = 2$  (or  $j = 1$  and  $j = 2$  in the watershed point W, see below), and for  $c_2 = 0 \Rightarrow \omega_2 = H_2$ .



As a next step, we further examine the *Hodograph plane*: how does the slope of the  $\Gamma_1$  lines change along  $\Gamma_2$ , and vice versa?



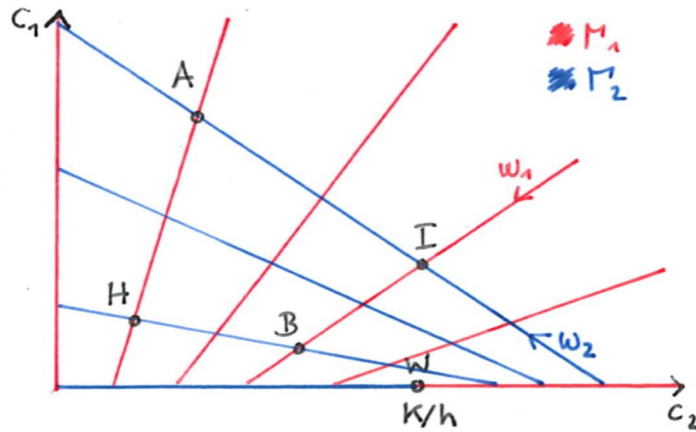
From equations 18 and 19, we derive

$$\zeta_1 \zeta_2 = -\frac{c_1 h}{c_2}$$

Moving along a  $\Gamma_2$  characteristic in positive  $c_2$  direction (same  $\Gamma_2$  with a constant, negative slope  $\zeta_1$  passing different  $\Gamma_1$  characteristics with different, positive slopes  $\zeta_2$ ),  $c_2$  increases and  $c_1$  decreases. Therefore (as  $\zeta_1 < 0$ )  $\zeta_2 = -\frac{c_1 h}{c_2 \zeta_1}$  decreases. On the other hand, when moving along a  $\Gamma_1$  characteristic in positive  $c_2$  direction (same  $\Gamma_1$  with a constant, positive slope  $\zeta_2$  passing different  $\Gamma_2$  characteristics with a different negative slopes  $\zeta_1$ ), we have

$$\zeta_1 = -\frac{c_1 h}{c_2 \zeta_2} \stackrel{16}{=} -h + \frac{hk}{c_2(\zeta_2 + h)}$$

Therefore, for increasing  $c_2$ ,  $\zeta_1$  decreases (it increases in magnitude, as it is negative, and thus  $\Gamma_2$  becomes steeper). In summary,  $\Gamma_1$  becomes less steep and  $\Gamma_2$  becomes steeper as we move in positive  $c_2$  direction.



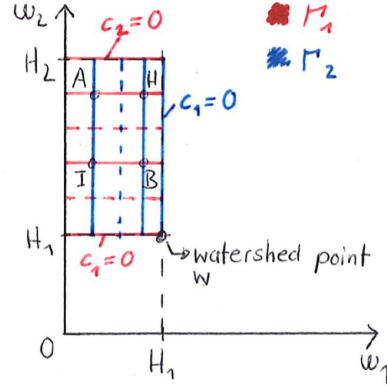
Let us now examine the point where the discriminant of equation 15 becomes zero. For this point, the so called watershed point W, there is only one solution for  $\zeta$ , which can be obtained by solving

$$\Delta_\zeta = (k - hc_2 + c_1)^2 + 4c_1c_2h = 0$$

which yields  $c_1 = 0$  and  $c_2 = \frac{k}{h}$ .

Also, let us map the characteristics from the *Hodograph plane* into the  $\omega$ -plane (or *characteristic plane*). We have seen that  $\omega_j$  is a monotonically increasing function of  $\zeta_j$ . Therefore, for the characteristics  $\Gamma_i$  with  $\zeta_{3-i} = \text{const.}$ , we also have  $\omega_{3-i} = \text{const.}$





The  $\omega$ -plane is particularly useful because it is directly related to the physical plane ( $t, z$ -plane), as the slope  $\sigma$  of the characteristics in the physical plane is a linear function of the eigenvalues  $\vartheta$  and therefore also of  $\omega$ :

$$(1 + \nu\vartheta) \frac{\partial c_2}{\partial t} + V \frac{\partial c_2}{\partial z} = 0 \quad (32)$$

$$\sigma = \frac{1}{V}(1 + \nu\vartheta) = f(\vartheta) = f\left(\frac{\omega}{d}\right) \quad (33)$$

### 3 Solving the Riemann problem in the physical plane

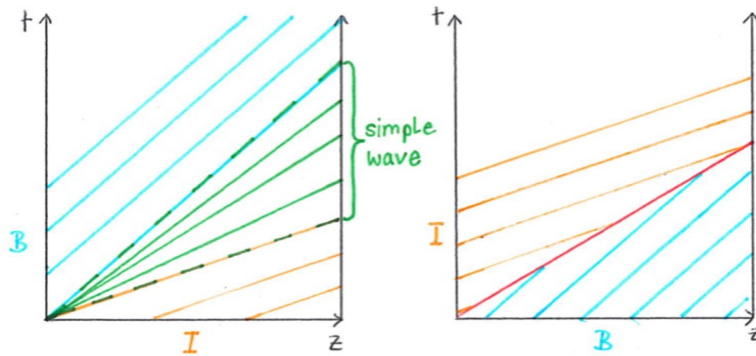
In the previous two sections, the knowledge required to solve the Riemann problem in the physical plane was developed.

#### 3.1 Case 1: the two states are on the same characteristic

First, consider the points I and B which are connected via a  $\Gamma_1$  characteristic ( $\zeta_1$  varies,  $\zeta_2 = \text{const.}$ ).

$$\begin{aligned} \vartheta_1^I &= \frac{(\omega_1^I)^2 \omega_2}{H_1 H_2} \\ \vartheta_1^B &= \frac{(\omega_1^B)^2 \omega_2}{H_1 H_2} > \vartheta_1^I \\ \Rightarrow \sigma_1^B &> \sigma_1^I \end{aligned}$$

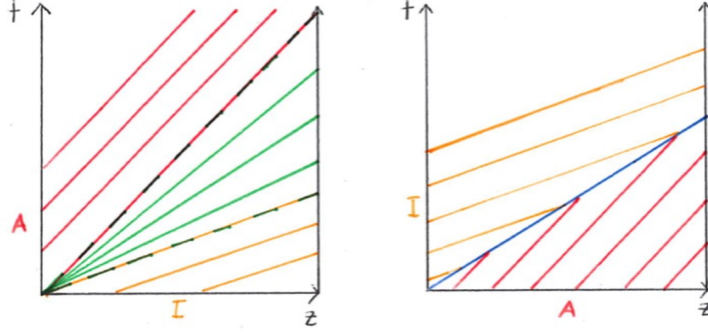
Going from the initial state I to the state B, we therefore get a simple wave, and going from the initial state B to the state I, we get a shock.



Now, let us consider the states I and A that are connected via a  $\Gamma_2$  characteristic ( $\zeta_2$  varies,  $\zeta_1 = \text{const.}$ ).

$$\begin{aligned} \vartheta_2^A &= \frac{(\omega_2^A)^2 \omega_1}{H_1 H_2} \\ \vartheta_2^I &= \frac{(\omega_2^I)^2 \omega_1}{H_1 H_2} < \vartheta_2^A \\ \Rightarrow \sigma_2^A &> \sigma_2^I \end{aligned}$$

Therefore, going from the initial state I to the state A, we obtain a simple wave, and going from the initial state A to the state I, we get a shock.



**Question 1:** What is the slope of the characteristics for the simple wave  $\sigma_i$ ?

For the simple wave from I to B, the eigenvalue is given by  $\vartheta_1 = \frac{\omega_1^2 \omega_2}{H_1 H_2}$  with  $\omega_1^I < \omega_1 < \omega_1^B$ . For the simple wave from I to A, the eigenvalue is given by  $\vartheta_2 = \frac{\omega_1 \omega_2^2}{H_1 H_2}$  with  $\omega_2^I < \omega_2 < \omega_2^A$ .

**Question 2:** What is the slope of the shock  $\tilde{\sigma}$ ?

Recall that for single-component chromatography, the slope of the shock is given by  $\tilde{\sigma} = \frac{1}{V} \left(1 + \nu \frac{\Delta n}{\Delta c}\right)$ . For binary chromatography, due to the mathematical analogy, we have

$$\tilde{\sigma}_i = \frac{1}{V} \left(1 + \nu \frac{\Delta n_i}{\Delta c_i}\right)$$

The slope of the shock has to be the same for both the components 1 and 2, i.e.,

$$\begin{aligned} \frac{1}{V} \left(1 + \nu \frac{\Delta n_1}{\Delta c_1}\right) &= \frac{1}{V} \left(1 + \nu \frac{\Delta n_2}{\Delta c_2}\right) \\ \frac{\Delta n_1}{\Delta c_1} &= \frac{\Delta n_2}{\Delta c_2} \end{aligned}$$

This reminds us of the differential condition we derived above:  $\left. \frac{Dn_2}{Dc_2} \right|_{\Gamma} = \left. \frac{Dn_1}{Dc_1} \right|_{\Gamma}$ . However, here we have a finite condition. Therefore the idea is that the same characteristics that are a solution for the differential condition are also a solution for the new, finite condition.

Proof:

$$\begin{aligned} \frac{Dn_2}{Dc_2} &= \frac{Dn_1}{Dc_1} \\ \Rightarrow Dn_1 &= \zeta Dn_2 \end{aligned}$$

For binary Langmuir Isotherm, the dependency of  $n_1$  on  $n_2$  is linear, i.e.,

$$\Delta n_1 = \zeta \Delta n_2 \quad (34)$$

From the definition of  $\zeta$  follows

$$\begin{aligned} \frac{Dc_1}{Dc_2} &= \zeta \\ \Rightarrow Dc_1 &= \zeta Dc_2 \end{aligned}$$

Since the solutions of this equation are straight lines in the hodograph plane, we also know that

$$\Delta c_1 = \zeta \Delta c_2 \quad (35)$$

Finally, dividing equation 34 by equation 35 yields

$$\frac{\Delta n_1}{\Delta c_1} = \frac{\Delta n_2}{\Delta c_2}$$

which is what we wanted to show. Therefore, the  $\Gamma_i$  characteristics are a solution.

Now, we derive an equation for the shock eigenvalues  $\tilde{\vartheta}_i$  through straightforward though cumbersome algebra, and obtain

$$\tilde{\vartheta}_j = \frac{\Delta n_i K_i}{\Delta c_i K_i} = \frac{\omega_j^L \omega_j^R \omega_{3-j}}{H_1 H_2} = \frac{\omega_j^L}{d^R} = \frac{\omega_j^R}{d^L}$$

and therefore with  $\omega_1^I < \omega_1^B$  the slopes of, e.g. the state I, the shock, and the state B are related as follows:

$$\vartheta_1^I = \frac{(\omega_1^I)^2 \omega_2}{H_1 H_2} < \tilde{\vartheta}_1 = \frac{\omega_1^I \omega_1^B \omega_2}{H_1 H_2} < \vartheta_1^B = \frac{(\omega_1^B)^2 \omega_2}{H_1 H_2} \quad (36)$$

### 3.2 Case 2: the two states are not on the same characteristic

We also want to construct a solution for the case that the two states are not on the same characteristic. For instance, this is the case when B and A are the initial and the feed state, respectively. Initially, it seems that there is an infinite number of paths in the Hodograph plane that connect these two states, but we are going to see that, from a physical point of view, most of these possibilities are infeasible. In fact, there is only one physically feasible way of connecting B and A. Here, we follow the convention of going from “left to right” in the physical plane, i.e., we start from the feed state A and move to the initial state B. Let us now examine the two possibilities  $A \rightarrow I \rightarrow B$  and  $A \rightarrow H \rightarrow B$ .

Recall the following equations, which we will use below:

$$\begin{aligned} \sigma_j &= \frac{1}{V} (1 + \nu \vartheta_j) \\ \vartheta_j &= \frac{\omega_j}{d} = \frac{\omega_j^2 \omega_{3-j}}{H_1 H_2} \\ d &= \frac{H_1 H_2}{\omega_1 \omega_2} \end{aligned}$$

**A  $\rightarrow$  H  $\rightarrow$  B:** Let us show that this path is infeasible from a physical point of view.

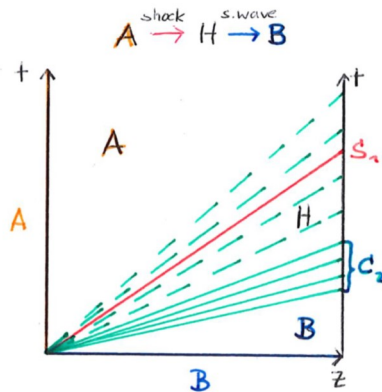
In the physical plane, from A to H, we have a shock with

$$\tilde{\vartheta}_1^{AH} = \frac{\omega_1^A \omega_1^H \omega_2^H}{H_1 H_2}$$

and from H to B we have a simple wave with

$$\begin{aligned} \vartheta_2^B &= \frac{\omega_1^B (\omega_2^B)^2}{H_1 H_2} \\ \vartheta_2^H &= \frac{\omega_1^H (\omega_2^H)^2}{H_1 H_2} \end{aligned}$$

Since  $\omega_1 < \omega_2$ , it is clear that  $\vartheta_2^H > \tilde{\vartheta}_1^{AH}$ . The simple wave transition would therefore overlap the shock transition.



This is physically not possible, but would always be the case when we have a transition from a  $\Gamma_1$  (red) characteristic to a  $\Gamma_2$  (blue) characteristic (same argumentation as above, independent of the form of the transition, i.e., simple wave or shock). Therefore, turns from a  $\Gamma_1$  (red) characteristic to a  $\Gamma_2$  (blue) characteristic are always forbidden. This leaves only one possible path connecting A and B, namely  $A \rightarrow I \rightarrow B$ .

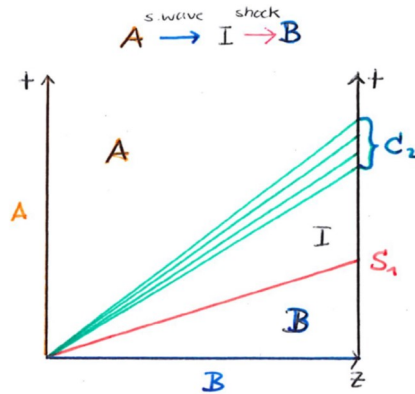
$A \rightarrow I \rightarrow B$ : With the slope of the simple wave transition at I given by

$$\vartheta_2^I = \frac{\omega_1^I (\omega_2^I)^2}{H_1 H_2} = \frac{\omega_1^A (\omega_2^B)^2}{H_1 H_2}$$

and the slope of the shock transition from I to B given by

$$\tilde{\vartheta}_2^{IB} = \frac{\omega_1^I \omega_1^B \omega_2^B}{H_1 H_2} = \frac{\omega_1^A \omega_1^B \omega_2^B}{H_1 H_2}$$

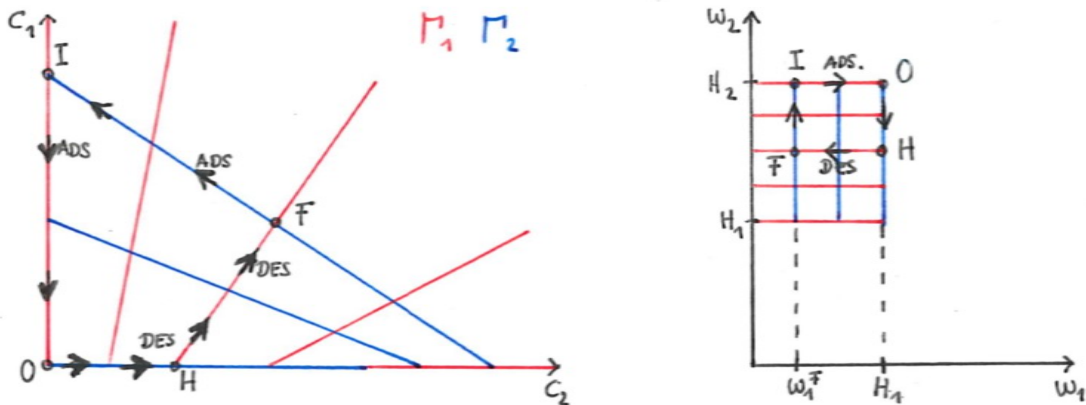
we see that the slope of the simple wave transition is greater than the slope of the shock. In summary, as only turns from blue to red characteristics are allowed, the path  $A \rightarrow I \rightarrow B$  is the only physically correct path connecting the feed state A with the initial state B.



In the final part of this chapter, we present an example. Keep in mind the following notational convention: a shock of type  $i$  (along a  $\Gamma_i$  characteristics) is called  $S_i$ , and a simple wave of type  $i$  is called  $C_i$ .

**Example:** Preparative chromatography (separation and purification of two components)

We have a given feed state F that can be located in the Hodograph plane, and also in the  $\omega_1, \omega_2$ -plane, and we want to connect it with the origin 0 representing an empty (i.e., completely desorbed) column. We know that the only transitions allowed are from blue to red characteristics, so we can immediately draw the path connecting the two states for adsorption and desorption in both planes.



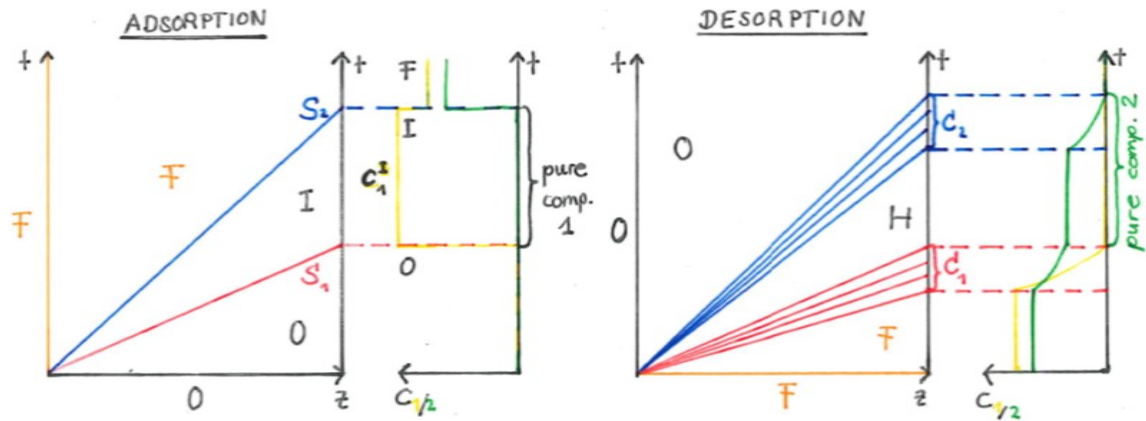
To calculate the slopes, we construct the following table for the eigenvalues:

	$c_1$	$c_2$	$\omega_1$	$\omega_2$	
0	0	0	$H_1$	$H_2$	Des.
H	0	$c_2^H$	$H_1$	$\omega_2^F$	
F	$c_1^F$	$c_2^F$	$\omega_1^F$	$\omega_2^F$	Ads.
I	$c_1^I$	0	$\omega_1^F$	$H_2$	
0	0	0	$H_1$	$H_2$	

$$\left. \begin{array}{l} \vartheta_2 = \frac{(\omega_2^F)^2}{H_2} \\ \vartheta_1 = \frac{(\omega_1^F)^2 \omega_2^F}{H_1 H_2} \\ \tilde{\vartheta}_2 = \frac{\omega_1^F \omega_2^F}{H_1} \\ \tilde{\vartheta}_1 = \omega_1^F \end{array} \right\}$$

The transitions for the adsorption and the desorption step can be plotted in the physical plane.



These plots show that pure component 1 can be obtained during adsorption and that pure component 2 can be obtained during desorption. However, in the desorption case, there is a time-span ( $C_1$ ) during which the two components are mixed. Note that the concentration of component 1 during adsorption is higher than the concentration of the same component in the feed.