

Absorption

Separation of gaseous mixture by dissolving one or more components in a liquid. Reverse process is called **desorption**. Absorption accompanied by chemical reaction is **chemisorption**. Absorption is usually favored by low temperature and elevated pressure.

Absorbers can be:

- i) **staged devices** – columns containing plates
- ii) **devices with continuous contact of phases** – columns with packed bed of **particles (rings, saddles)** or with a **structured packing** (metal construction with a high surface/volume ratio); also **spray towers** and **bubbled columns** are used.

In staged columns equilibrium in each stage can be attained. In devices with continuous contact a non-equilibrium mass transfer occurs. All these devices operate as **flow-through counter-current systems**.

Staged counter-current absorbers

Description is formally the same as in the case of counter-current extractors. Because of a large difference between densities of the two phases (gas/liquid), the counter-current flow is easy to maintain in gravitational field, unlike with extractors.

We assume three components:

A ... **absorbed component**

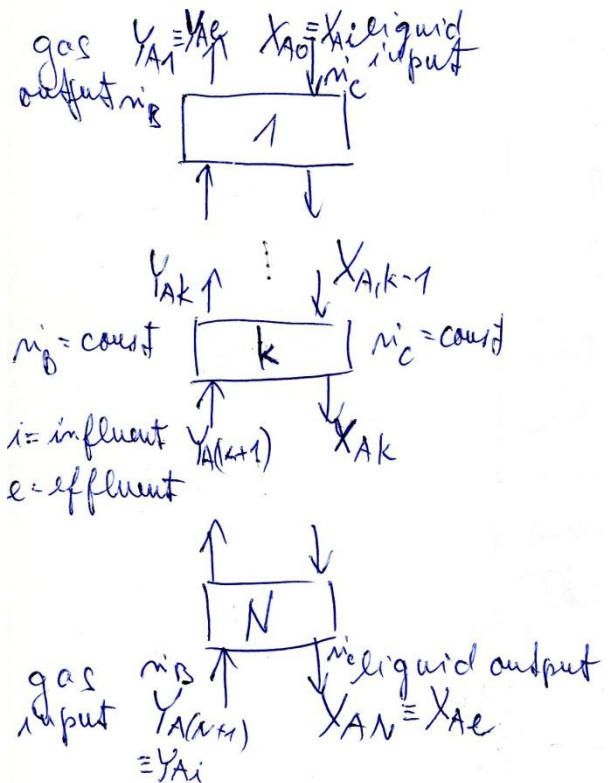
B ... **gaseous solvent**

C ... **liquid solvent**

Let us assume that **B and C do not mix**, i.e. V does not dissolve and C does not evaporate (or only negligibly). The **relative molar fractions** are useful:

$$X_A = \frac{\dot{n}_A}{\dot{n}_C} ; Y_A = \frac{\dot{n}_A}{\dot{n}_B}$$

phase	X_A	... relative molar fraction of A in liquid
phase	Y_A	... relative molar fraction of A in gaseous
	\dot{n}_B	... flow of gaseous inert
	\dot{n}_C	... flow of inert liquid



The flow of inert gas can be related to volumetric flow at the input \dot{V}_{gi} , which is a measurable quantity, by assuming ideal gaseous mixture:

$$\dot{n}_B = (1 - y_{Ai}) \dot{n}_{gi} = (1 - y_{Ai}) \frac{p \dot{V}_{gi}}{RT} = (1 - y_{Ai}) c_{gi} \dot{V}_{gi}$$

where

y_{Ai} is (normal) molar fraction of A at the input

\dot{n}_{gi} is total molar flow at the input

p, T are pressure and temperature (at input)

$c_{gi} = \frac{p}{RT}$ is overall molar density of the gas (at input)

Relations between normal and relative molar fractions are:

$$Y_A = \frac{n_A}{n_B} = \frac{n_A}{n - n_A} \frac{1}{\frac{1}{n}} = \frac{y_A}{1 - y_A}$$

$$X_A = \frac{x_A}{1 - x_A} \left(\text{reverse: } y_A = \frac{Y_A}{1 + Y_A}; x_A = \frac{X_A}{1 + X_A} \right)$$

Overall balance on moles of A (balances of B,C are useless)

From the scheme we have:

$$\dot{n}_B Y_{Ai} + \dot{n}_C X_{Ai} = \dot{n}_B Y_{Ae} + \dot{n}_C X_{Ae}$$

or in a difference form:

$$\dot{n}_B (Y_{Ai} - Y_{Ae}) = \dot{n}_C (X_{Ae} - X_{Ai}) = \dot{n}_A$$

\dot{n}_A is flow of A across the interface in the entire column

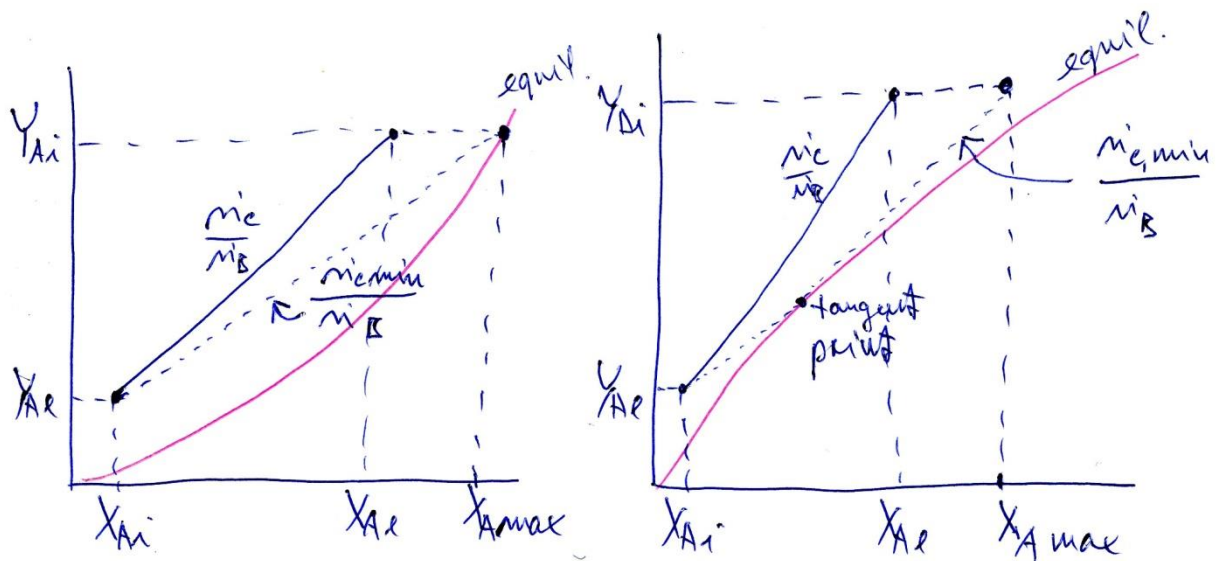
Minimal consumption of the liquid solvent

By writing the balance on A from stage 1 to stage k (anywhere in the column) we get:

$$\dot{n}_B (Y_{A,k+1} - Y_{Ae}) = \dot{n}_C (X_{Ak} - X_{Ai})$$

$$Y_{A,k+1} = \frac{\dot{n}_C}{\dot{n}_B} (X_{Ak} - X_{Ai}) + Y_{Ae}$$

which is an **operating line** having slope $\frac{\dot{n}_C}{\dot{n}_B}$ and passing through point $[X_{Ai}, Y_{Ae}]$. This is analogous to the situation in extraction, only now in the graph the operating line is **above** the equilibrium line.



The minimal slope of the operating line defines minimal consumption of C, which can be calculated from

$$\frac{\dot{n}_{C,min}}{\dot{n}_B} = \frac{Y_{Ai} - Y_{Ae}}{X_{A,max} - X_{Ai}}$$

and the maximal output composition in liquid $X_{A,max}$ is found from the graph. **Real consumption** is then $\dot{n}_C = \gamma \dot{n}_{C,min}$ where $\gamma = 1.2 - 1.5$ is an empirical factor.

Remarks:

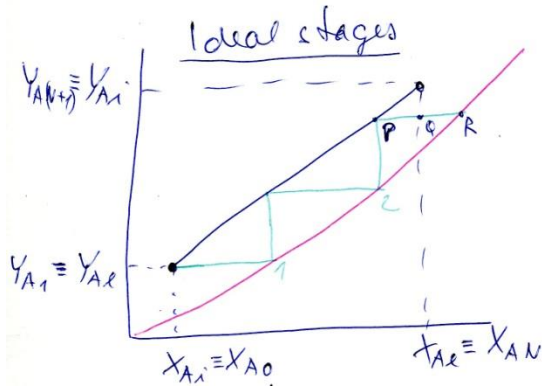
- i) If the equilibrium line is linear: $Y_A = \varphi_A X_A$ then graph is not needed because $X_{A,max} = \frac{Y_{Ai}}{\varphi_A}$ (the equilibrium coefficient $\varphi_A = const$ is known or can be found as shown below)
- ii) At low concentrations Henry's law applies: $y_A = \frac{p_A}{p} = \frac{H_A}{p} x_A = \Psi_A x_A$; p_A is partial pressure of A in gas and H_A is Henry constant

In general $\varphi_A = \frac{\Psi_A}{1 - (\Psi_A - 1)x_A}$ but at low concentrations $\varphi_A \doteq \Psi_A = const$.

Number of stages is obtained by combining molar balance at each stage and equilibrium equation relating outputs from each stage. Correction can be made if the stages are not equilibrium ones by making use of **Murphree's efficiency**.

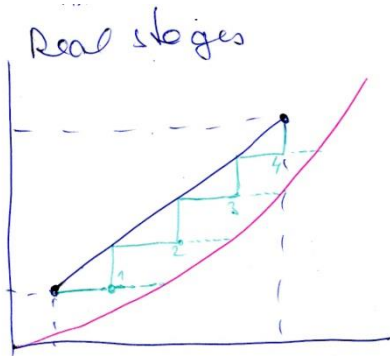
Graphical solution is convenient:

Ideal stages



Number of equilibrium (ideal) stages: $2 + \frac{\overline{PQ}}{\overline{PR}} = N_{ideal}$

Real stages



for example if Murphree efficiency $E_x = 0.5$ then horizontal lines from operating line to equilibrium are divided into halves. If E_y is given, vertical lines are used instead. In general $E_x \neq E_y$.

Algebraic solution

Formally the same as in extraction. For ideal stages the result is

$$X_{A,k-1} = \frac{\varphi_{Ak} \dot{n}_B}{\dot{n}_C} X_{A,k} + \frac{\Delta \dot{n}_A}{\dot{n}_C}$$

where $\Delta \dot{n}_A = \dot{n}_C X_{A,i} - \dot{n}_B Y_{Ae} = \dot{n}_C X_{A,e} - \dot{n}_B Y_{Ai}$ is the “cross-flow” of A (the same for each stage) see details in chapter on extraction.

Remark: Instead of Murphree efficiency a global efficiency E_g can be given and the number of real stages then is (the number should be rounded up to the nearest whole number)

$$N_{real} = \frac{N_{ideal}}{E_g}$$

Calculation of number of stages for linear equilibrium line

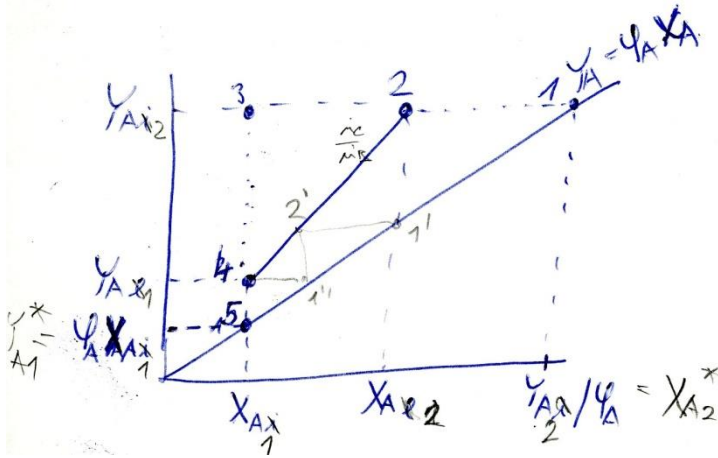
As in extraction in counter-current cascade, we introduce **factor of mass exchange**

$$\zeta_X = \frac{\varphi_A \dot{n}_B}{\dot{n}_C} \text{ or } \zeta_Y = \frac{\dot{n}_C}{\varphi_A \dot{n}_B}$$

and effectiveness factors

$$\eta_X = \frac{X_{Ae} - X_{Ai}}{Y_{Ai}/\varphi_A - X_{Ai}}; \eta_Y = \frac{Y_{Ai} - Y_{Ae}}{Y_{Ai} - \varphi_A X_{Ai}}$$

Graphical representation:



For $\eta_X = 1$ or $\eta_Y = 1$ the number of stages $N \rightarrow \infty$. It can be shown that

$$\frac{1 - \eta_X}{1 - \eta_Y} = \left(\frac{1}{\zeta_X}\right)^N = \zeta_Y^N \text{ and } \eta_X = \frac{\eta_Y}{\zeta_Y}; \eta_Y = \frac{\eta_X}{\zeta_X}$$

thus:

$$N = \frac{\ln \frac{1 - \eta_Z}{\zeta_Z}}{\ln \zeta_Z} \text{ where } Z \text{ is } X \text{ or } Y$$

$$\text{for } \zeta_Z = 1: N = \frac{\eta_Z}{1 - \eta_Z}$$

Absorption in columns with continuous mass exchange

- packed beds, spray towers, bubbled columns

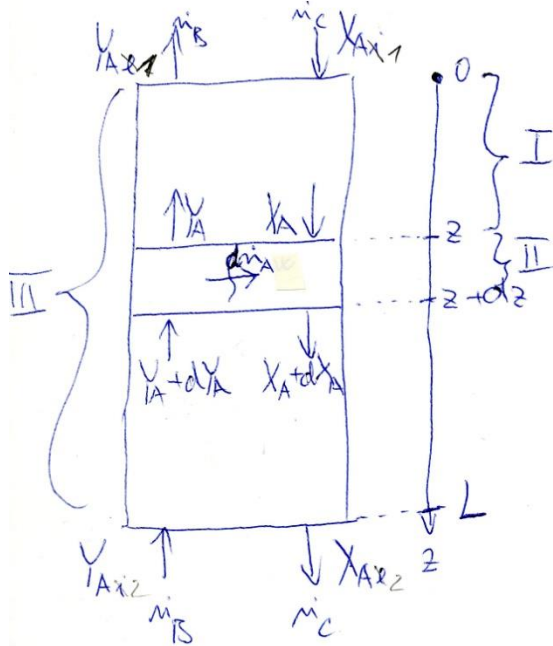
No stages or plate no equilibrium. We have to use **mass transfer rate equations** and **local balance equations**

Balance of A in I: $\dot{n}_B(Y_A - Y_{Ae}) = \dot{n}_C(X_A - X_{Ai})$

Balance of A in II: $d\dot{n}_A = \dot{n}_B(Y_A + dY_A - Y_A) = \dot{n}_C(X_A + dX_A - X_A)$

$$d\dot{n}_A = \dot{n}_B dY_A = \dot{n}_C dX_A$$

Balance of A in III: $\dot{n}_B(Y_{Ai} - Y_{Ae}) = \dot{n}_C(X_{Ae} - X_{Ai}) = \dot{n}_A$



The flow of A across the interface in the differential system II, $d\dot{n}_A$, can be expressed also by overall mass transfer equation:

$$d\dot{n}_A = K_Y(Y_A - Y_A^*)dA = K_X(X_A^* - X_A)dA$$

where dA is area of the interface between phases in II. This area can be conveniently expressed as

$$dA = a dV = a S dz$$

where

a is density of the interface surface [$\text{m}^2 \text{m}^{-3}$] = [m^{-1}] (per volume)

S is cross-sectional area of the column [m^2]

By comparing $d\dot{n}_A$ expressed from mass balance and from mass transfer we get

$$K_Y(Y_A - Y_A^*) a S dz = \dot{n}_B dY_A$$

$$K_X(X_A^* - X_A) a S dz = \dot{n}_C dX_A$$

Upon separation and integration from $z = 0$ to $z = L$:

$$L = \int_0^L dz = \frac{\dot{n}_B}{K_Y a S} \int_{Y_{Ai}}^{Y_{Ae}} \frac{dY_A}{Y_A - Y_A^*} \quad \text{or} \quad L = \frac{\dot{n}_C}{K_X a S} \int_{X_{Ai}}^{X_{Ae}} \frac{dX_A}{X_A^* - X_A}$$

$$L = H_Y N_Y \quad \text{or} \quad L = H_X N_X$$

H_Y, H_X ... height of the transfer unit

N_Y, N_X ... number of the transfer units

The integral is evaluated as follows:

- a) $Y_A^* = \varphi_A X_A$ and X_A is expressed as a function of Y_A from mass balance of A in I
 b) $X_A^* = \frac{Y_A}{\varphi_A}$ and Y_A is expressed as a function of X_A from the balance of A in I

If φ_A depends on X_A the integral must be calculated numerically on a computer.

If $\varphi_A = \text{const}$ (= linear equilibrium) then the integral can be calculated analytically with the following results

$$N_Y = \frac{Y_{Ai} - Y_{Ae}}{\Delta Y_{l,m}} \text{ or } N_X = \frac{X_{Ae} - X_{Ai}}{\Delta X_{l,m}}$$

where $\Delta Y_{l,m}$ and $\Delta X_{l,m}$ are **logarithmic mean driving forces**:

$$\Delta Y_{l,m} = \frac{(Y_{Ai} - Y_{Ai}^*) - (Y_{Ae} - Y_{Ae}^*)}{\ln \frac{Y_{Ai} - Y_{Ai}^*}{Y_{Ae} - Y_{Ae}^*}} \text{ and } \Delta X_{l,m} = \frac{(X_{Ae}^* - X_{Ae}) - (X_{Ai}^* - X_{Ai})}{\ln \frac{X_{Ae}^* - X_{Ae}}{X_{Ai}^* - X_{Ai}}}$$

here $Y_{Ai}^* = \varphi_A X_{Ai}$; $Y_{Ae}^* = \varphi_A X_{Ae}$ and $X_{Ai}^* = \frac{Y_{Ae}}{\varphi_A}$; $X_{Ae}^* = \frac{Y_{Ai}}{\varphi_A}$

Remarks:

- In calculating N_Y or N_X the value of K_Y or K_X varies along the absorber if φ_A depends on X_A (or Y_A) \rightarrow we need to take an geometric average: $\bar{\varphi}_A = \sqrt{\varphi_{A,z=0} \cdot \varphi_{A,z=L}}$
- In packed beds the value of surface to volume ration of the packing a_t is found in tables. But the surface may not be all wetted \rightarrow the real value $a = sa_t$ where s is a fraction of wetted surface.
- The cross-sectional area S must be large enough to avoid flooding of the column or even entrainment of the liquid by fast flow of gas. Thus

$$S \geq \frac{\dot{V}_{gi}}{v_{g,max}}$$

where $v_{g,max}$ is **maximal superficial velocity** of the gas which corresponds to flooding conditions.

- For $\varphi_A = \text{const}$ one can instead of the logarithmic mean approach also use the **effectiveness factor** defined as for a staged column. Thus

$$N_Z = \frac{1 - \frac{\eta_Z}{\zeta_Z}}{\ln \frac{1 - \eta_Z}{\zeta_Z}} \text{ where } Z \text{ is } X \text{ or } Y$$

for $\zeta_Z = 1$: $N = \frac{\eta_Z}{1 - \eta_Z}$

η_Z is the effectiveness factor

ζ_Z is the mass exchange factor