Absorption

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Agenda

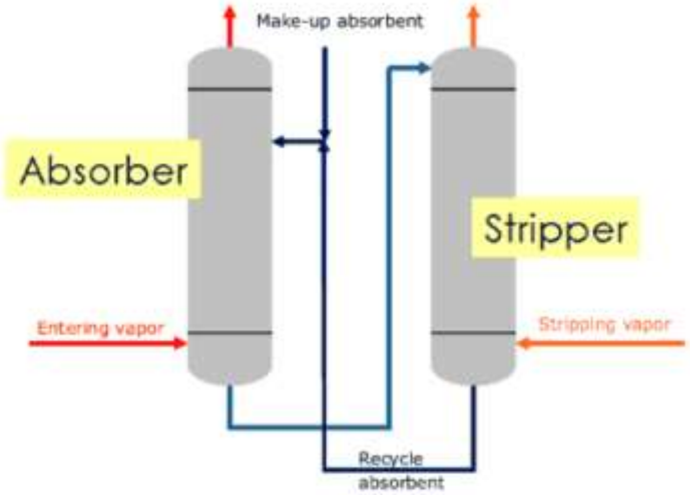
- Absorption and stripping: introduction
- Absorption process fundamentals
- Henry’s law and phase equilibrium
- Absorption: McCabe Thiele solution for dilute solutions
- Stripping analysis for dilute systems
- Analytical solution for dilute systems: Kremser equation
- Relationship of HETP and HTU
- Absorption: general case of non dilute solutions
- Absorption: calculation of equilibrium and material balances
- Degrees of freedom
- Recycling of the solvent
- Energy balances and adiabatic process
- The Kremse-Brown-Souders equation
- Absorption with Radfrac

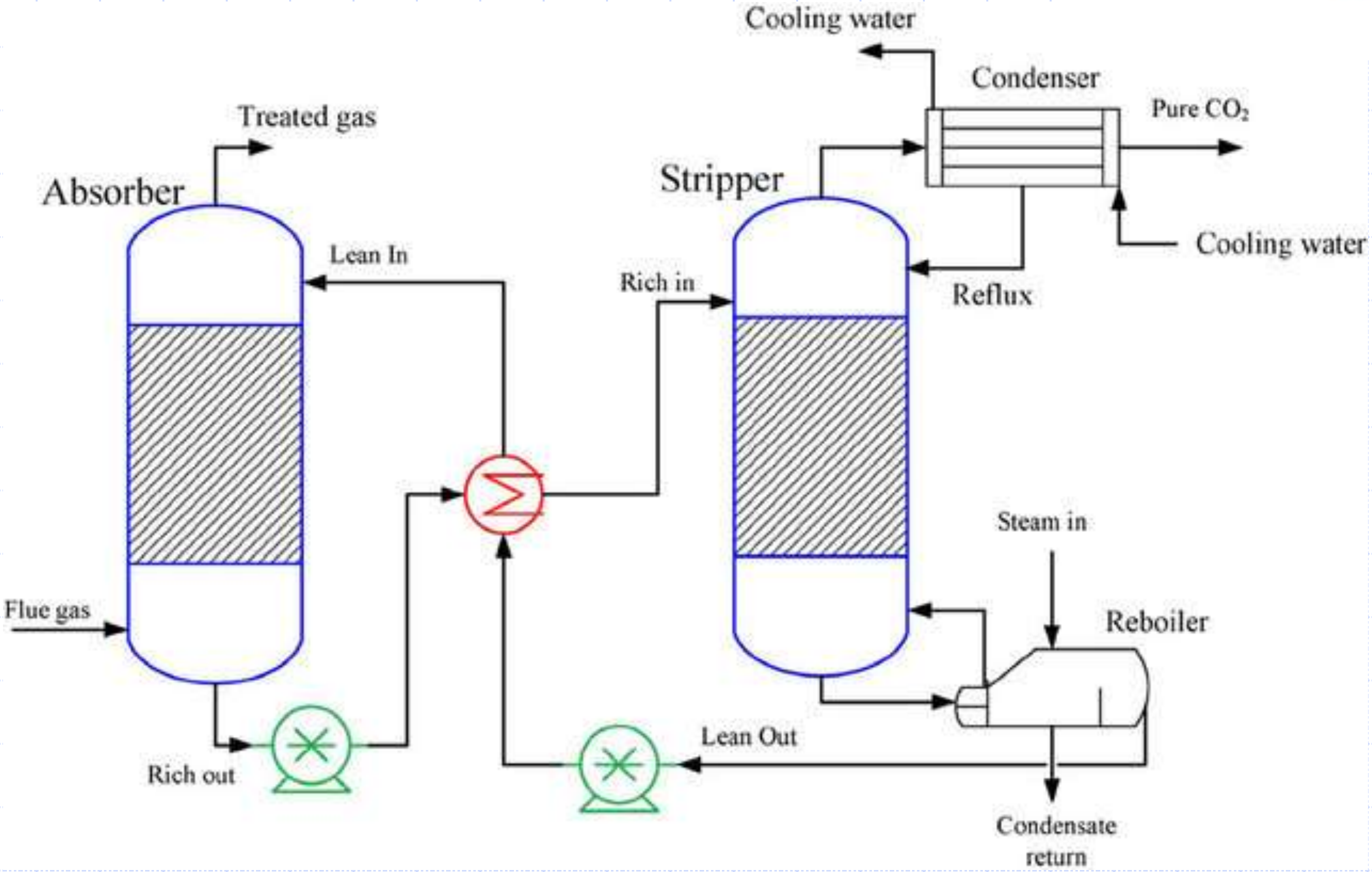
Absorption and Stripping

- Absorption (or scrubbing) is the removal of a component (the solute or absorbate) from a gas stream via uptake by a nonvolatile liquid (the solvent or absorbent).
- Desorption (or stripping) is the removal of a component from a liquid stream via vaporization and uptake by an insoluble gas stream.
- Thus, absorption and stripping are opposite unit operations, and are often used together as a cycle.
- Both absorption and stripping can be operated as equilibrium stage processes using trayed columns or, more commonly, using packed columns.

Absorber/Stripper Cycle

- Absorber + stripper





Absorption Systems – Physical

- **Physical absorption** relies on the solubility of a particular gas in a liquid.
  - This **solubility is often quite low**; consequently, a relatively **large amount of liquid solvent** is needed to obtain the required separation.
  - This liquid solvent containing the solute is typically **regenerated by heating or stripping** to drive the solute back out.
  - Because of the low solubility and large solvent amounts required in physical absorption, **chemical absorption is also used**…

- Examples:
  - CO_2 and water
  - CO and water
  - H_2S and water
  - NH_3 and water
  - NO_2 and water

Acetylene and acetic acid
NH_3 and acetone
Ethane and carbon disulfide
N_2 and methyl acetate
NO and ethanol

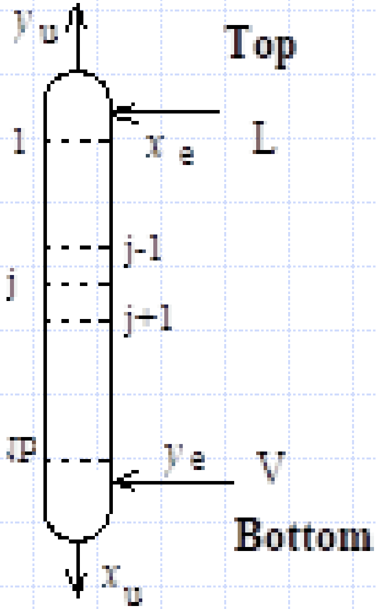
Absorption Systems – Chemical

- **Chemical absorption** relies on reaction of a particular gas with a reagent in a liquid.
  - This absorption **can often be quite high**; consequently, **a smaller amount of liquid solvent/reagent** is needed to obtain the required separation.
  - However, the reagent may be **relatively expensive**, and it is often desirable to regenerate when possible.

- Examples:
  - CO_2 / H_2S and aqueous ethanol amines
  - CO_2 / H_2S and aqueous hydroxides
  - CO and aqueous Cu ammonium salt
  - SO_2 and aqueous dimethyl aniline
  - HCN and aqueous NaOH
  - HCl / HF and aqueous NaOH

Absorption: how to perform the process

- The best option is to contact the gas (vapor) stream with the solvent stream in a **counter-current pattern**.
- From the process standpoint, separation by absorption requires a certain **number of ideal stages** in series.
- As far as the equipment is concerned, an absorption process is carried out **in a column**, which can be either a **tray column or a packed column**.
- We refer to x and y as molar fractions. Note that the **flow rates L and V are NOT constant** along the column.



Absorption and Stripping – the Problem

- The principal difference in handling adsorption and stripping, compared to distillation, is how we represent the equilibria (**equilibrium curve**) and mass balances (**operating lines**).
  - In distillation, the liquid and vapor streams were assumed to remain constant under CMO.
  - In absorption, we have removal of the solute from the gas stream and uptake by the solvent liquid stream; thus, the total liquid and gas stream amounts or flow rates can change.
  - Due to absorption, at the bottom the flow rates are larger than at the top.
  - So, it is **impossible to obtain an operating line which is a straight line**.

Absorption and Stripping Assumptions

- If we **use mole fractions** of the solute and assume that the gas and liquid stream amounts or flow rates remain constant, significant error can result if the solute concentration in the inlet gas stream is greater than about 1%.
  - If we can set up our equilibrium curve and operating line to account for this change in the overall gas and liquid flow rates, we can use the McCabe-Thiele method to solve absorption and stripping problems.
- **We assume that**:
  - The carrier gas is insoluble (or it has a very low solubility), e.g, N_2 or Ar in water.
  - The solvent is nonvolatile (or it has a low vapor pressure), e.g., water in air at low temperatures.
  - The system is isothermal. e.g., the effects of heat of solution or reaction are low or there is a cooling or heating system in the column.
  - The system is isobaric.
  - The concentration of the solute is low, say <10% – this is the limit for the use of Henry’s Law.

Absorption fundamentals

- **The separation of components from a gaseous mixture** can be achieved in various ways.
    - For example, the fractionation of oxygen and nitrogen from an air stream is carried out by **distillation at a low temperature**. This requires a refrigeration cycle but is an economically sustainable process anyway.
    - In other cases, when it is desired to **separate only one** or some components, it is not possible to recover the components of interest by condensation because the temperature required would be too low, and a **thermal separation process** would not be economically convenient.
- An alternative option is a non-thermal separation process such as absorption.
- In absorption, **a second phase is added** to the starting gas (or vapor) mixture, which is a liquid phase often referred to as the solvent.
    - This liquid solvent is chosen so that to **maximize its affinity with respect to one** (or more) components of the gas (vapor) phase to be separated from the rest of the gas (vapor).
- In a chemical engineering language, the solvent is selected to obtain a **favorable distribution of the components** of interest between the two phases.

Absorption fundamentals

- The separation by absorption is obtained by suitably contacting the gas stream with the liquid solvent. With this operation some components can be transferred from a gaseous to a liquid phase in a selective way.
- The aim of an absorption process may be:

1. To recover valuable components by condensing them in the solvent
2. To purify a gas (vapor) stream by separating unwanted heavier components
3. To achieve both 1 and 2 goals

- The minimum number of components in an absorption process is 3:

- the component to be recovered by direct condensation in the liquid
- one component in the gas(vapor) phase, which is not condensed
- the solvent, which is heavy enough not to be significantly present in the gas phase

Absorption: equilibrium curve

- In a three-component system with two co-existing phases 3 iso-fugacity conditions can be written to calculate the thermodynamic equilibrium:

$$f_1^v = f_1^l$$

$$f_2^v = f_2^l$$

$$f_3^v = f_3^l$$

- With 1 we indicate the vapor component not subject to condensation and with 3 the solvent, which is assumed not to evaporate.
  - Therefore, component 2 is the only one distributed between the two co-existing phases, for which the iso-fugacity condition has a practical application.
- Accordingly, components 1 and 3 are referred to as "inert" components
  - "inert gas" and "inert liquid", respectively.
- If the pressure is relatively low, a γ-φ approach can be used to express the equilibrium condition for component 2.

Fugacity from Henry's law

- Vapor phase fugacity $\hat{f}_i^V = P y_i \hat{\phi}_i^V$
- Liquid phase fugacity: $\hat{f}_i^L = \left(f_i^L\right)_{id} \gamma_i$
- Where $\left(f_i^L\right)_{id} = R_i(T,P) x_i$
- Since pure liquid does not exist $R_i = \lim_{x_i \to 0} \frac{f_i^L}{x_i} = \frac{H_i^{sol}}{\gamma_i^\infty}$

$$\hat{f}_i^L = x_i \gamma_i^* H_i \qquad \gamma_i^* = \gamma_i / \gamma_i^\infty \Rightarrow 1 \, as \, x_i \Rightarrow 0$$

GLE: $P y_i \hat{\phi}_i^V = x_i H_i \gamma_i^* \xrightarrow{\text{Low P}} P y_i = x_i H_i \qquad P y_2 = x_2 H_2$

- Henry's law is used to determine the amount of a supercritical component or light gas in the liquid phase
- Only used with Ideal and Activity Coefficient models
- H_i is calculated from temperature-dependent Henry's constants for each solute-solvent pair

Absorption: equilibrium curve

- H_2 is the Henry constant of component 2: $H_2 = \lim_{x_2 \to 0} \frac{f_2}{x_2}$
- Note that, if the component is condensable at the absorption temperature and pressure, the Henry constant depend on the infinite-dilution activity coefficient:
  - Remember the expression of liquid f at low pressure: $\mathrm{f}_2 = P_2^o x_2 \gamma_2$

$$H_2 = P_2^0 \gamma_2^\infty$$

- Under the assumption that the liquid solution is diluted (i.e. $x_2<0.10$) the equilibrium condition for component 2 can be written as:

$$y_2 = m_2 x_2, \text{ with } m_2 = \frac{H_2}{P}$$

- which represents a straight line if absorption is carried out at constant T and P

Henry's Law Constants

- Absorption data is typically available in the form of solute mole fractions, y_i vs. x_i, or in terms of the Henry's constant.
- Henry's Law, in terms of the mole fractions of solute i and the total pressure, is:

$$y_i = \frac{H_i}{P_{Tot}} x_i$$

- The higher H the lower the solubility x (with P and y constant)
- Henry's Law is valid at low concentrations of solute i, approximately less than 10%.

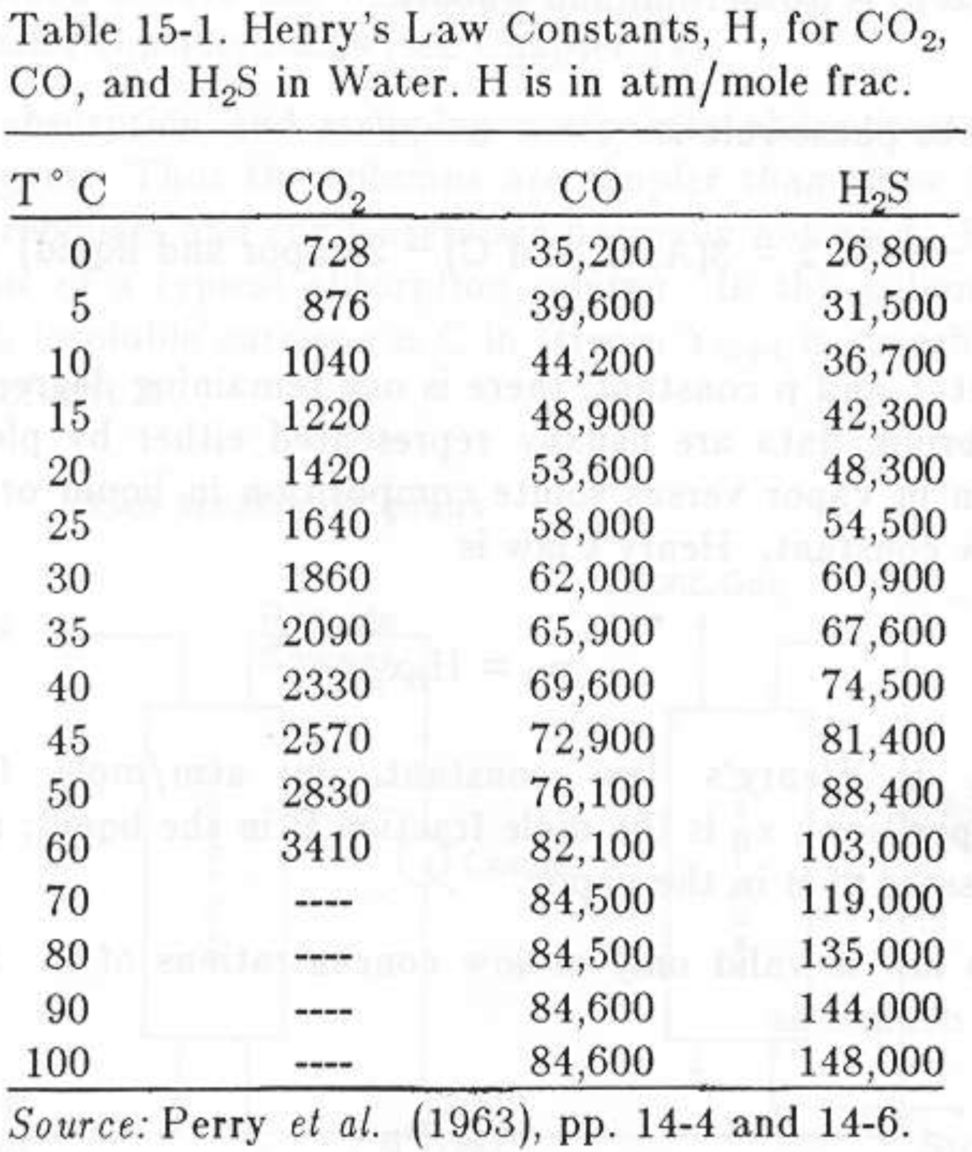


Table 15-1. Henry's Law Constants, H, for CO_2, CO, and H_2S in Water. H is in atm/mole frac.

T °C	CO_2	CO	H_2S
0	728	35,200	26,800
5	876	39,600	31,500
10	1040	44,200	36,700
15	1220	48,900	42,300
20	1420	53,600	48,300
25	1640	58,000	54,500
30	1860	62,000	60,900
35	2090	65,900	67,600
40	2330	69,600	74,500
45	2570	72,900	81,400
50	2830	76,100	88,400
60	3410	82,100	103,000
70	----	84,500	119,000
80	----	84,500	135,000
90	----	84,600	144,000
100	----	84,600	148,000

Source: Perry *et al.* (1963), pp. 14-4 and 14-6.

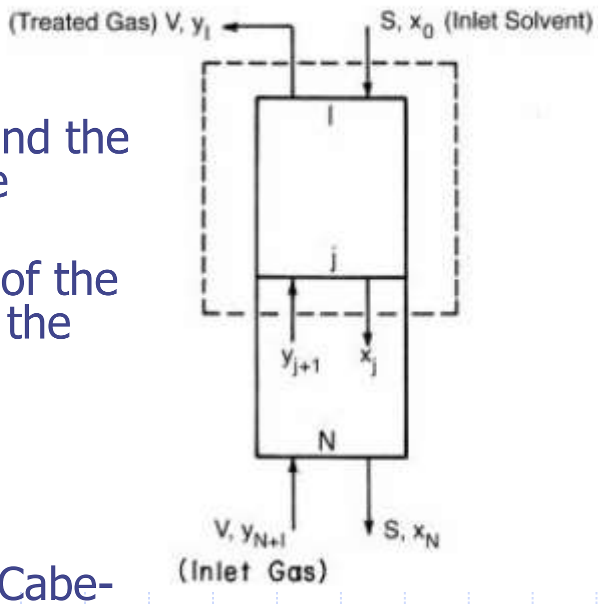
Absorption: different cases

- Different approximations are available for absorption calculations
- In terms of HETP
  - Dilute absorption with OL constant
    - Both OL and equilibrium lines are linear and parallel
    - Both OL and equilibrium lines are linear but not parallel
  - General case with OL not linear in terms of L and V
    - Material balances are rewritten in terms of inert gas and liquid solute.
- In terms of HTU - NTU
  - General case with OL not linear in terms of L and V
    - Material balances are rewritten in terms of inert gas and liquid solute.

Absorption: McCabe Thiele solution

- For dilute absorption
  - The McCabe-Thiele diagram is useful when the OL is straight. This requires that liquid flow rate/vapor flow rate = const.
  - Further assumptions:
  - **1.** The heat of absorption is negligible.
  - **2.** Operation is isothermal.
  - These two assumptions will guarantee satisfaction of the energy balances.
  - When the gas and liquid streams are both fairly dilute, the assumptions will probably be satisfied. If the solute mole fraction in the feed $y_{B,N+1}$ is very low, then transferring most or even all of the solute to the liquid will have very little effect on the overall vapor flow rate V or on the overall liquid flow rate L.

Absorption: McCabe Thiele solution



- For dilute absorption
  - We can assume that L and V are both constant, and the operating line on a McCabe-Thiele diagram will be straight.
  - Using the mass balance envelope around the top of the absorption column shown in Figure, we can write the solute mass balance for constant L and V.

$$y_{i+1}V + x_0L = y_1 + x_yL$$

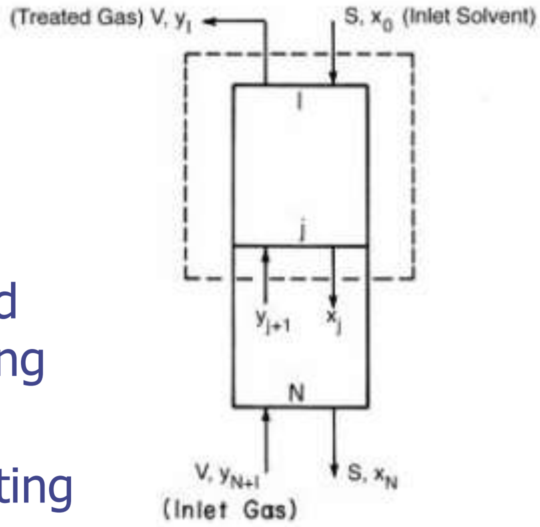
  - Solving for y_{j+1} we obtain the equation for the McCabe-Thiele operating line.

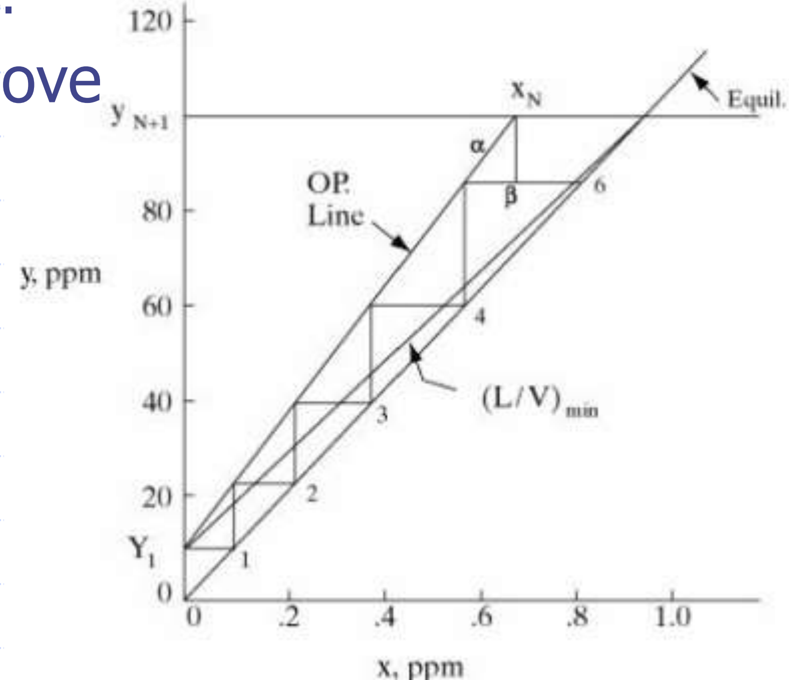
$$y_{i+1} = \left(\frac{L}{V}\right)x_j + [y_1 - \left(\frac{L}{V}\right)x_0]$$

  - With slope L/V and y-intercept $[y_1 - (L/V)x_0]$.
  - All possible passing streams with compositions (x_j, y_{j+1}) must lie on the operating line.
  - This includes the two streams at the top of the absorber (x_0, y_1) and the two streams at the bottom of the absorber (x_N, y_{N+1}).

Absorption: McCabe Thiele solution

- For dilute absorption
  - The procedure for a dilute absorption problem is:
  - **1.** Plot the y versus x equilibrium data.
  - **2.** For a design problem, typically x_0, y_{N+1}, y_1, and L/V will be known. Point (x_0, y_1) is on the operating line and the slope is L/V. Plot the operating line.
  - **3.** Start at stage 1 and step off stages by alternating between equilibrium and operating lines.
- Note that the operating line is above the equilibrium line.
  - This occurs because solute is being transferred from gas to liquid.
  - In distillation the more volatile component was transferred from liquid to gas and the operating line was below the equilibrium curve.



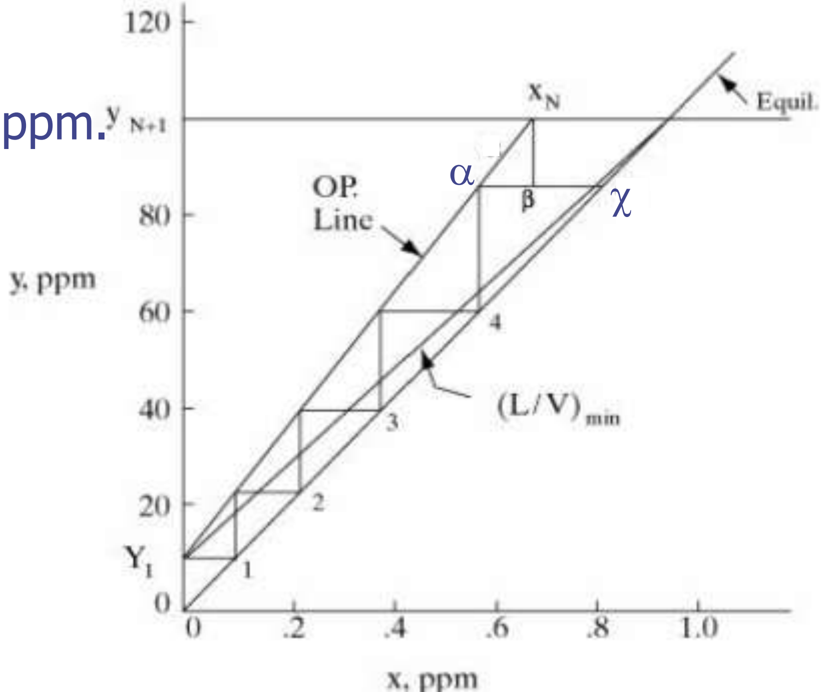


Example: dilute absorption

- 1000 kmol/h of air containing 100 ppm (mol) of chloroform at 25°C and 2.0 atmosphere is to be processed.
- We plan to absorb the chloroform with pure water at 25°C.
- Operation is at L/V = 1.4 (L/V)min.
- If we want an outlet air stream containing 10.0 ppm chloroform, how many equilibrium stages are required?

Example: dilute absorption

- Solution
  - Equilibrium is $y = H\,x/P = 211.19\,x / 2.0 = 105.6\,x$ with y and x in ppm.
    - This is a straight line of slope 105.6 that goes through the origin.
  - Plot this line on a y versus x plot, as shown in Figure.
    - calculate x_{equil} at $y = 100$ as $x_{equil} = 100/105.6 = 0.947$ ppm and plot this point.
  - The operating line goes through point $(x_0, y_1) = (0, 10\text{ ppm})$.
  - The minimum operating line goes through this point and the point on the equilibrium line at $y_{N+1} = 100$ ppm.
  - At this value of y, $x_{min\_L/V} = y_{N+1}/\text{slope} = 100/105.6 = 0.947$ ppm.
  - The slope of the minimum OL is
  - $\left(\frac{L}{V}\right)_{min} = \frac{(y_{N+1}-y_1)}{(x_{min-L/V}-x_0)} = \frac{100-10}{0.947-0} = 95.0$
  - $\left(\frac{L}{V}\right) = 1.4\left(\frac{L}{V}\right)_{min} = 133$
  - OL can be plotted.

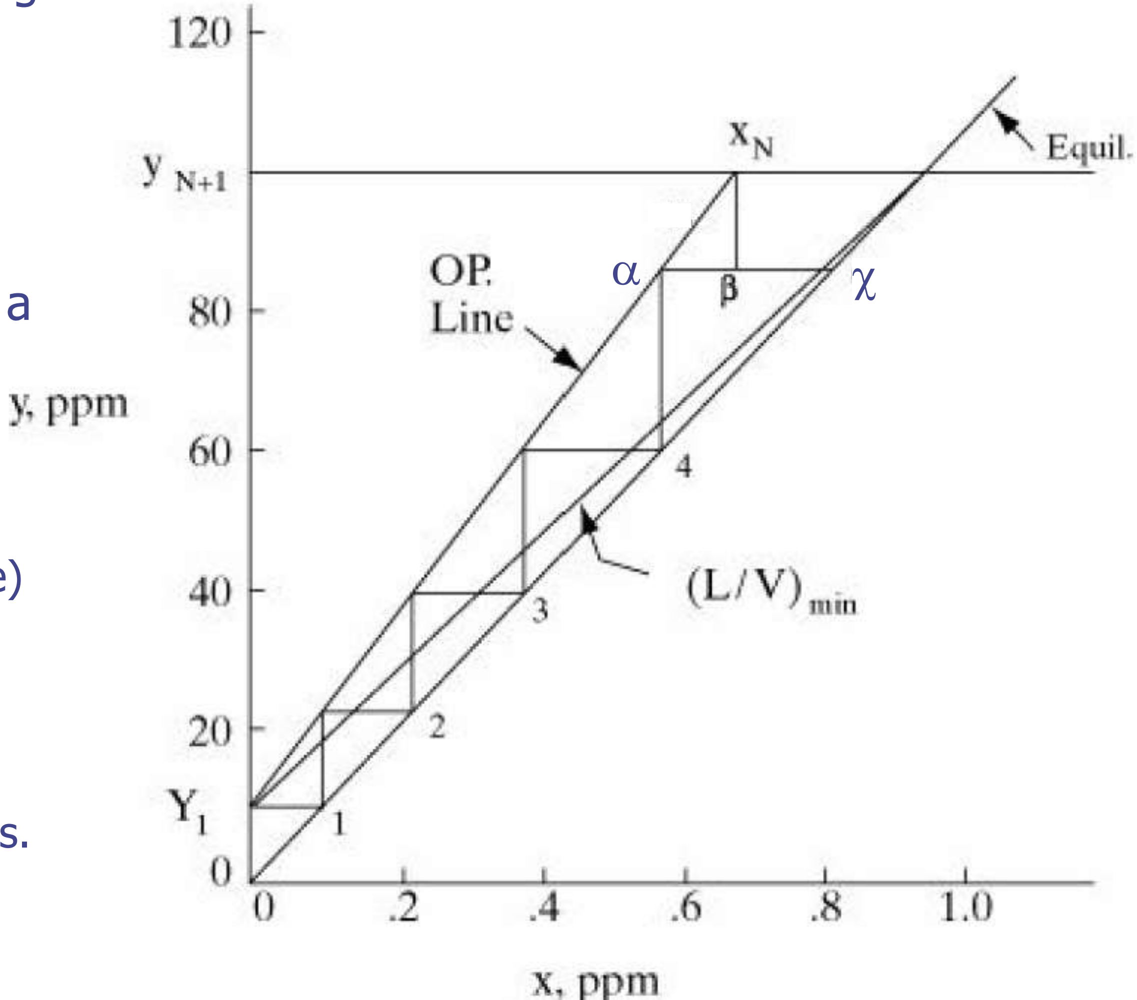


Example: dilute absorption

- Equation of OL is valid when j=N.

$$y_{i+1} = \left(\frac{L}{V}\right) x_j + [y_1 - \left(\frac{L}{V}\right) x_0]$$

- Solving for x_N with $x_0=0$ we get.
- $x_N= (y_{N+1}-y_1) / (L/V) = (100-10) / 133 = .68$ ppm
- Five equilibrium stages are more than sufficient.
- If desired, we can estimate a fractional number of equilibrium contacts:



Fraction = (distance from OL to x_N)/ (distance from OL to equilibrium line)

= (distance α to β)/(distance α to χ)
= 0.08/0.2 = 0.4

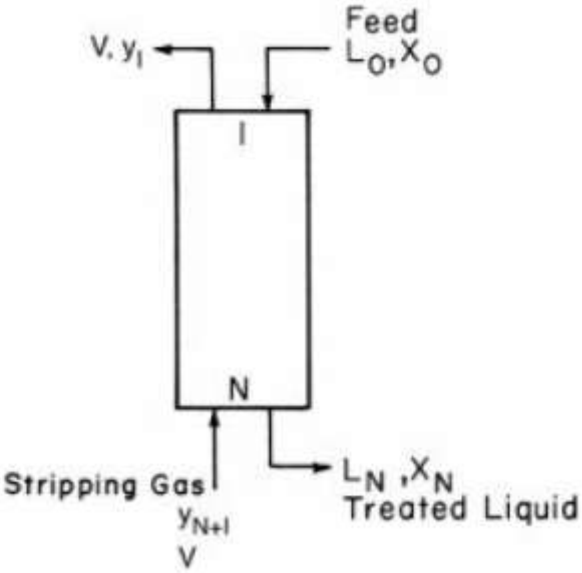
Thus, we need 4.4 equilibrium contacts.

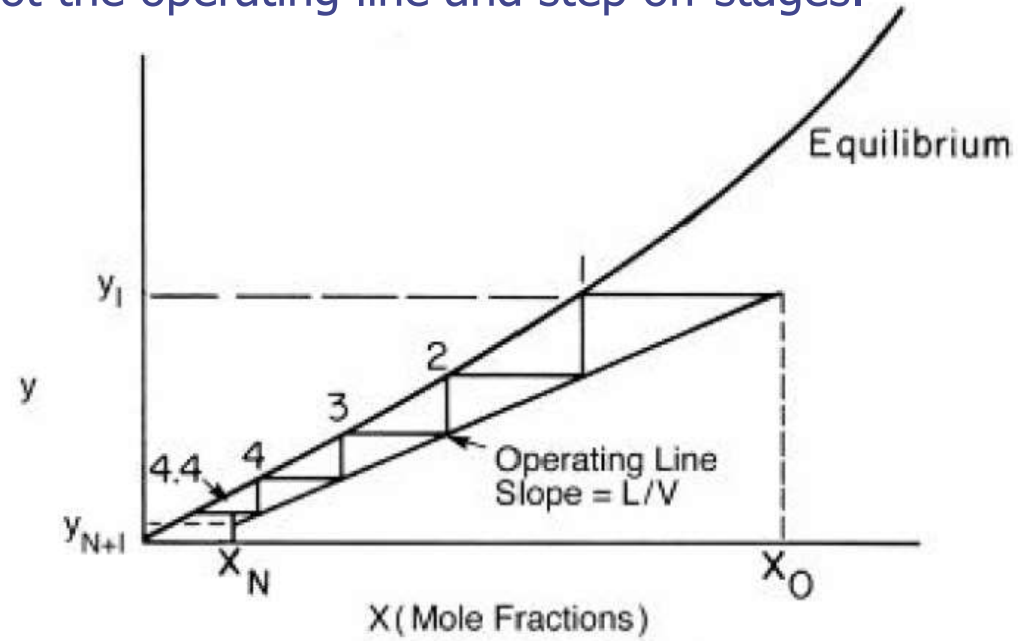
Stripping analysis for dilute systems

- Since stripping is very similar to absorption we expect the method to be similar.
    - The mass balance for the column is the same and the OL is the same:

$$y_{i+1} = \left(\frac{L}{V}\right) x_j + \left[y_1 - \left(\frac{L}{V}\right) x_0\right]$$

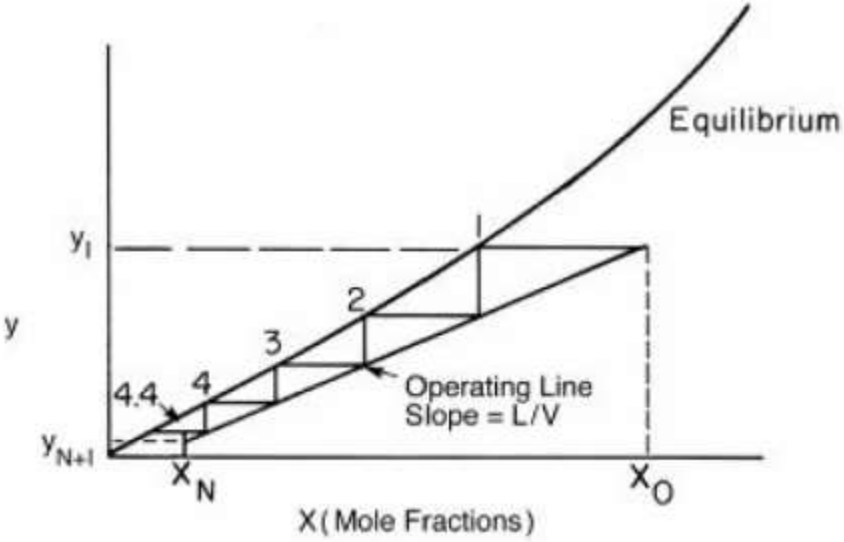
    - For stripping we know x_0, x_N, y_{N+1}, and L/V. Since (x_N, y_{N+1}) is a point on the operating line, we can plot the operating line and step off stages.





Stripping analysis for dilute systems

- Note that the **operating line is below the equilibrium** curve because solute is transferred from liquid to gas.
- This is therefore **similar to the stripping section** of a distillation column.
- A **maximum L/V** ratio can be defined; this corresponds to the minimum amount of stripping gas.
- Start from the known point (y_{N+1}, x_N), and draw a line to the intersection of $x = x_0$ and the equilibrium curve. Alternatively, there may be a tangent pinch point.
- For a stripper, $y_1 > y_{N+1}$, while the reverse is true in absorption.
- Thus, the top of the column is on the right side in this figure but on the left side absorption figure.
- Stripping often has large temperature changes, so the calculation method used here is often appropriate only for very dilute systems.

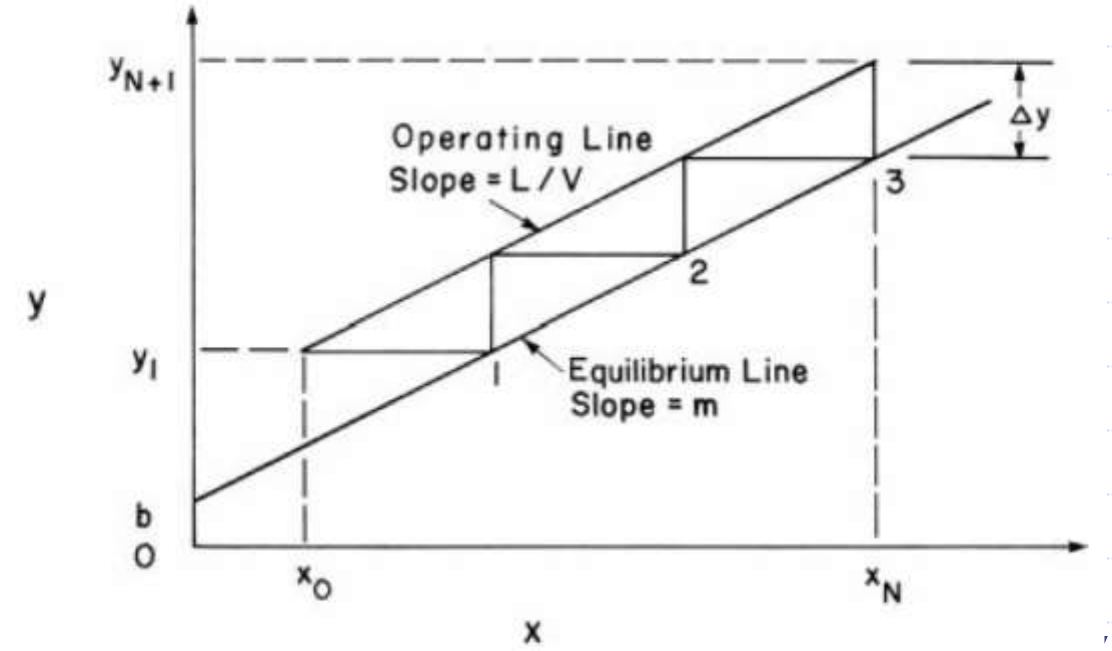


Analytical solution for dilute systems: Kremser equation

- When the **solution is quite dilute** (say less than 1% solute in both gas and liquid), the total liquid and gas flow rates will not change significantly since little solute is transferred.
  - The column and the OL are the same as above:
  - To use OL equation in McCabe-Thiele diagram, we assume the following:
  - **1.** L/V (total flows) is constant.
  - **2.** Isothermal system.
  - **3.** Isobaric system.
  - **4.** Negligible heat of absorption.
  - These are reasonable assumptions for dilute absorbers and strippers.
  - **5.** Equilibrium line is straight → $y_j = m\, x_j + b$
- An analytical solution for absorption is derived for the special case where the operating and equilibrium **lines are parallel**.
  - Now the distance between operating and equilibrium lines, Δy, is constant. To go from outlet to inlet concentrations with N stages, we have
  - $\Delta y = y_{N+1} - y_1$

Analytical solution for dilute systems: Kremser equation

- Δy may be obtained subtracting eq. equation from the OL equation, with L/V constant and parallel lines (L/V=m):
  - $\Delta y = y_i - L/V\, x_0 - b$ = constant
  - And combining with $\Delta y = y_{N+1} - y_1$
  - $N = \frac{y_{N+1} - y_1}{\left(y_1 - \frac{L}{V} x_0 - b\right)}$ for L/(mV)=1 (Kremser equation)
  - The ratio **A=L/(mV)** is defined as the absorption factor.

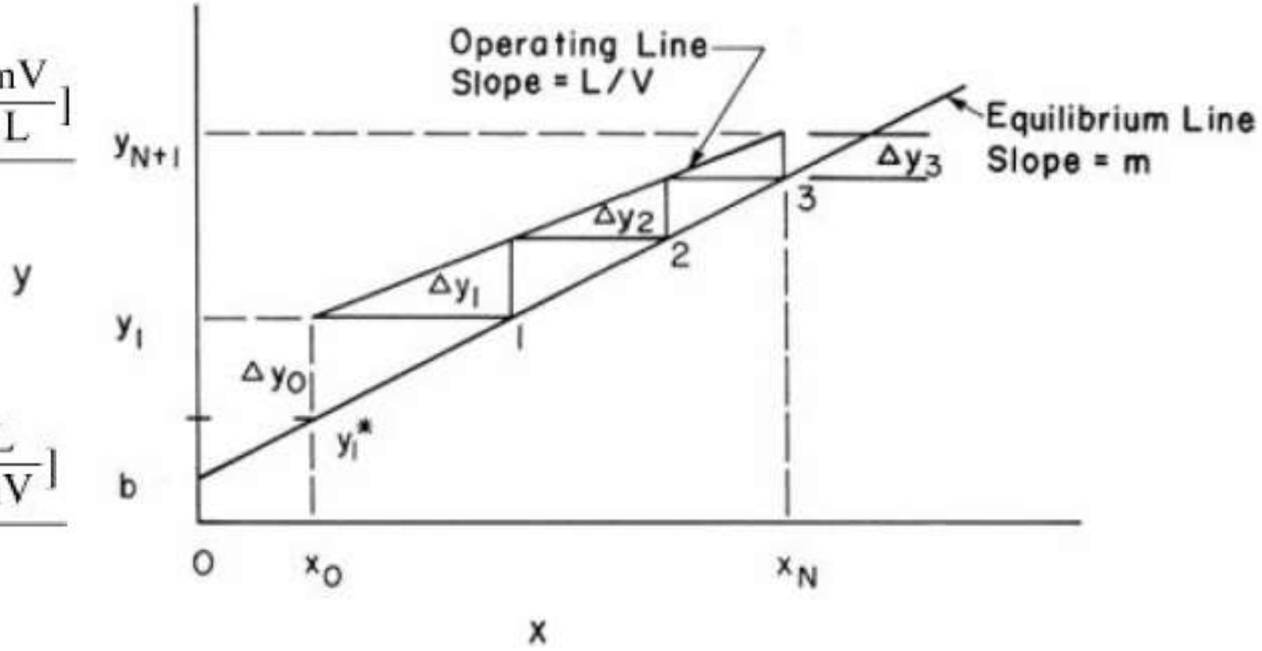


Analytical solution for dilute systems: Kremser equation

- More general case is when the two lines are not parallel.
    - Now Δy_j varies from stage to stage. The Δy_j values can be determined as before using the equilibrium equation: $x_j = (y_j - b)/m$
    - The difference between inlet and outlet gas concentrations must be the sum of the Δy_j values shown in Figure.
    - After algebraic manipulation one obtains (in the vapor or liquid phase):

$$N = \frac{\ln\left[\left(1 - \frac{mV}{L}\right)\left(\frac{y_{N+1} - y_1^*}{y_1 - y_1^*}\right) + \frac{mV}{L}\right]}{\ln\left(\frac{L}{mV}\right)}$$

$$N = \frac{\ln\left[\left(1 - \frac{L}{mV}\right)\left(\frac{x_0 - x_N^*}{x_N - x_N^*}\right) + \frac{L}{mV}\right]}{\ln\left(mV/L\right)}$$

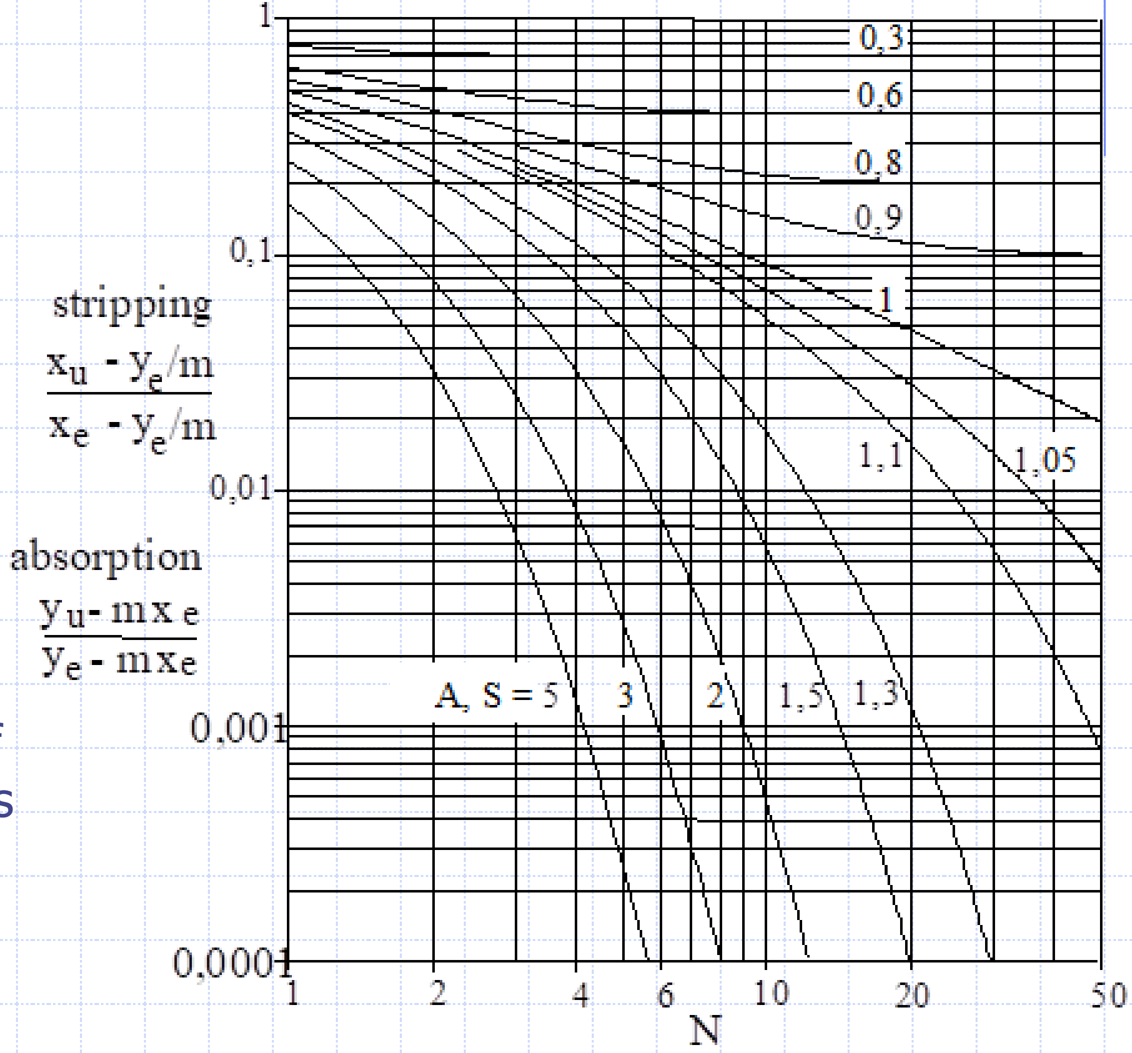


Absorption: the Kremse-Brown-Souders equation

- The Y axes is the left hand side of the Kremser eq.:

$$\frac{y_e - y_u}{y_e - mx_e} = \frac{A^{NP+1} - A}{A^{NP+1} - 1}$$

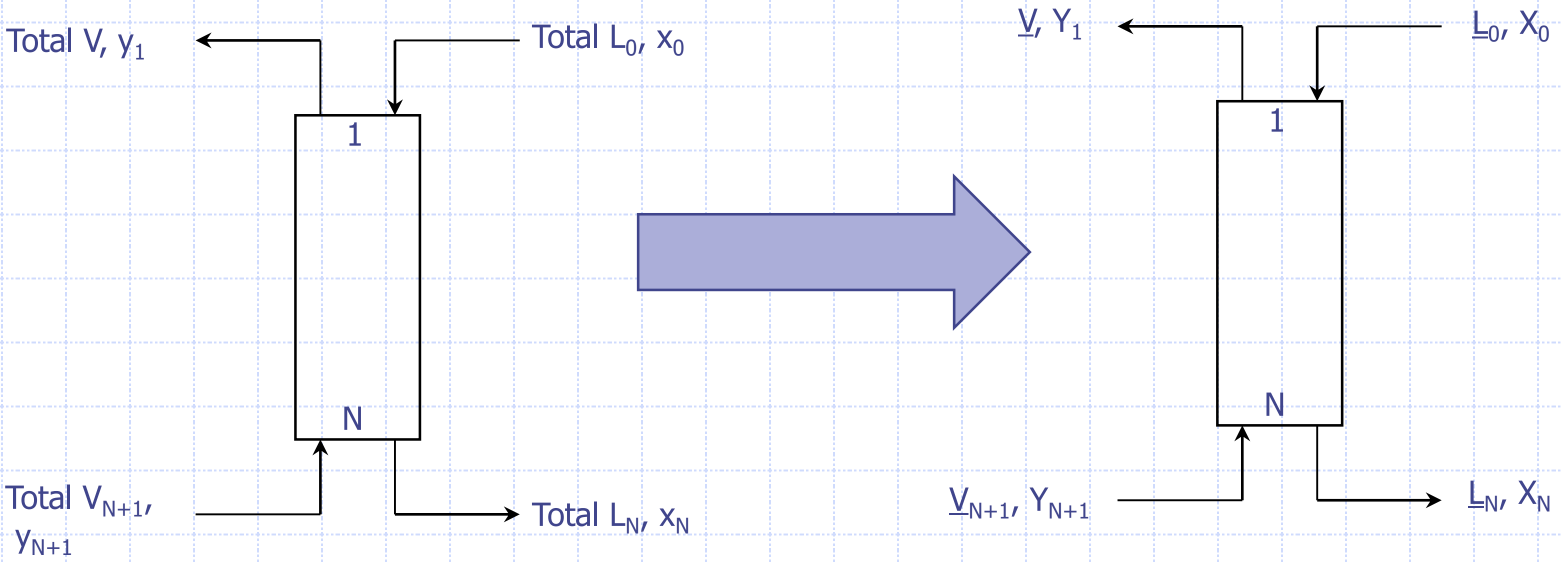
- With A=L/(mV) the absorption factor
- Note that, when the absorption factor is too low, the desired separation might not be achieved independently of the number of ideal stages
- Remember that this is an approximated solution



Absorption and Stripping: circumventing the Problem

- While the **total gas and liquid streams can change** in absorption, the flow rate of the carrier gas, which we assume to be insoluble in the solvent, does not change.
- Similarly, **the flow rate of the solvent**, which we assume to be nonvolatile, **does not change**.
- Consequently, we can define our equilibrium curve and operating line in terms of **mole ratios** with respect to the carrier gas and solvent, instead of mole fractions as we did in distillation.
- Doing so **circumvents the problem** of the changing total gas and liquid stream amounts or flow rates in absorption and stripping.

Absorption – Variable Specification



Total V, y_1

Total L_0, x_0

1

N

Total V_{N+1}, y_{N+1}

Total L_N, x_N

$\underline{V}$, Y_1

$\underline{L}_0$, X_0

1

N

$\underline{V}_{N+1}$, Y_{N+1}

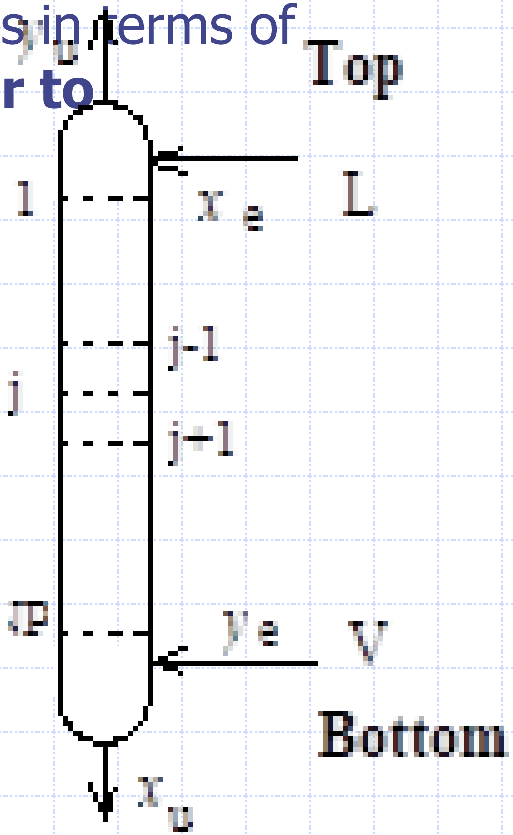
$\underline{L}_N$, X_N

Total Vapor (V) and Total Liquid (L) Flows Rates and Mole Fractions

Carrier Gas ($\underline{V}$) and Solvent ($\underline{L}$) Flow Rates and Mole Ratios

Absorption: material balances

- Therefore, it is preferred to refer to **the "inert" flow rates** rater than to the total ones.
- In fact the "inert" flow rates $\underline{L}$ and $\underline{V}$ remain constant along the column.
- However, in order to express the material balances in terms of component flow rates (as usual), we need to **refer to molar ratios** rather than to molar fractions:



$$X = \frac{mol\ comp\ 2}{mol\ \ pure\_liquid\ \ solvent}$$

$$Y = \frac{mol\ comp\ 2}{mol\ \ pure\_carrier\ \ gas}$$

$$X = \frac{x}{1-x} \quad ; \qquad Y = \frac{y}{1-y}$$

- Note that X and Y may be greater than 1.

Absorption: material balances

- With reference to molar ratios, the overall mass balance reads:

$$\underline{L}(X_u - X_e) = \underline{V}(Y_e - Y_u)$$

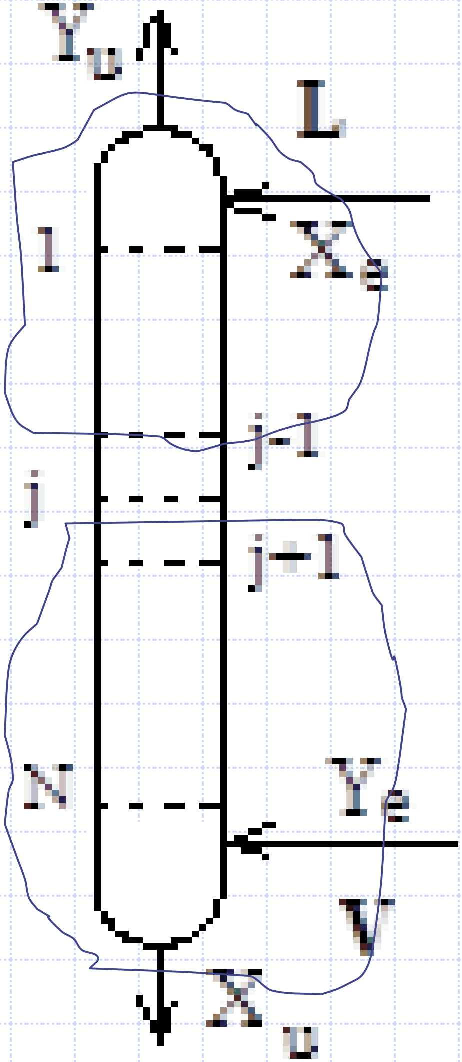
- With respect to the top:

$$\bar{L}(X_{j-1} - X_e) = \bar{V}(Y_j - Y_u)$$

- With respect to the bottom:

$$\bar{L}(X_u - X_j) = \bar{V}(Y_e - Y_{j+1})$$

- They can be plotted as a straight line in the X-Y diagram.



Absorption: plotting equilibrium curve

- However, the equilibrium relationship is not a straight line any more.
- In fact, molar ratios have to be used instead of molar fractions.
  - Considering Y=y/(1-y); x=X/(1+X) and $y_2 = m_2 x_2,\ with\ m_2 = \frac{H_2}{P}$

$$Y = \frac{mX}{1 + (1 - m)X} = \frac{H_2 X}{P + (P - H_2)X}$$

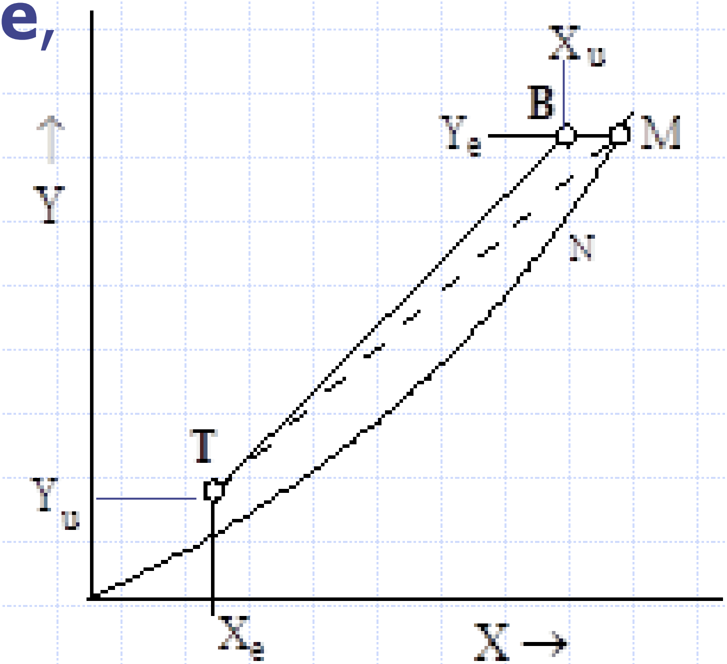
- This equation has a vertical asymptote at:

$$X_{asymptote} = \frac{1}{m - 1} = \frac{P}{H_2 - P}$$

- Note that the asymptotic condition occurs for a value of *X* which is positive if *m>1*, and negative if *m<1*, thus the concavity of the equilibrium curve may be positive or negative.

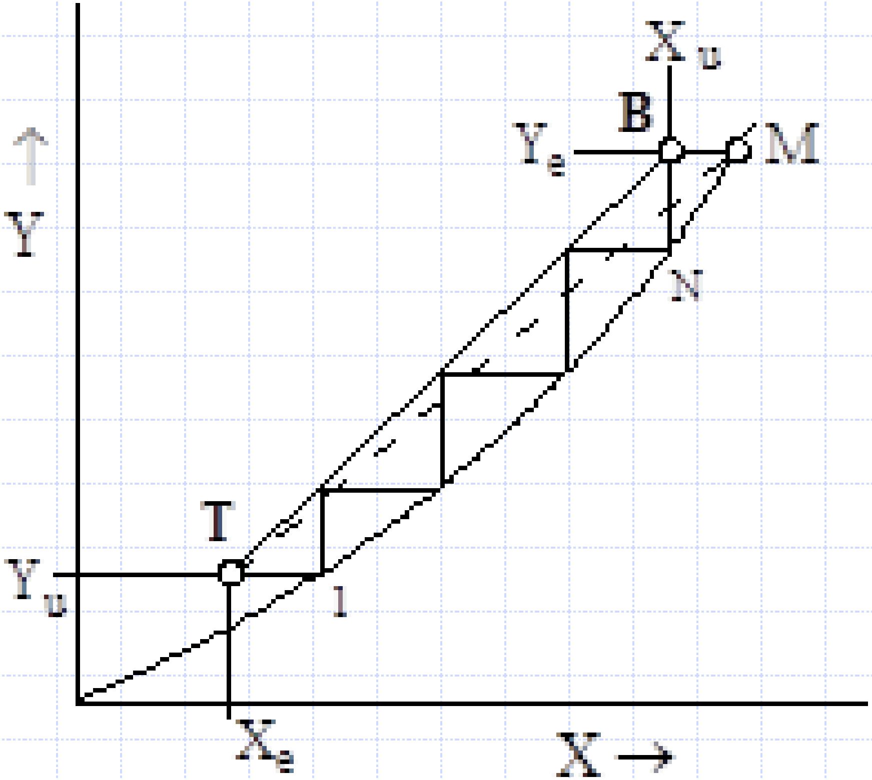
Absorption: plotting equilibrium curve

- Figure shows the first case m>1: **the composition of the liquid must be less than that of equilibrium with the gas**, in each section of the column,
  - The mass transfer of component 2 is from the gas to the liquid phase, which is typical of any absorption process.
- It follows that **absorption is favored by low temperature and high pressure**,
  - because the distance between operating line and equilibrium curve are maximized in these conditions.

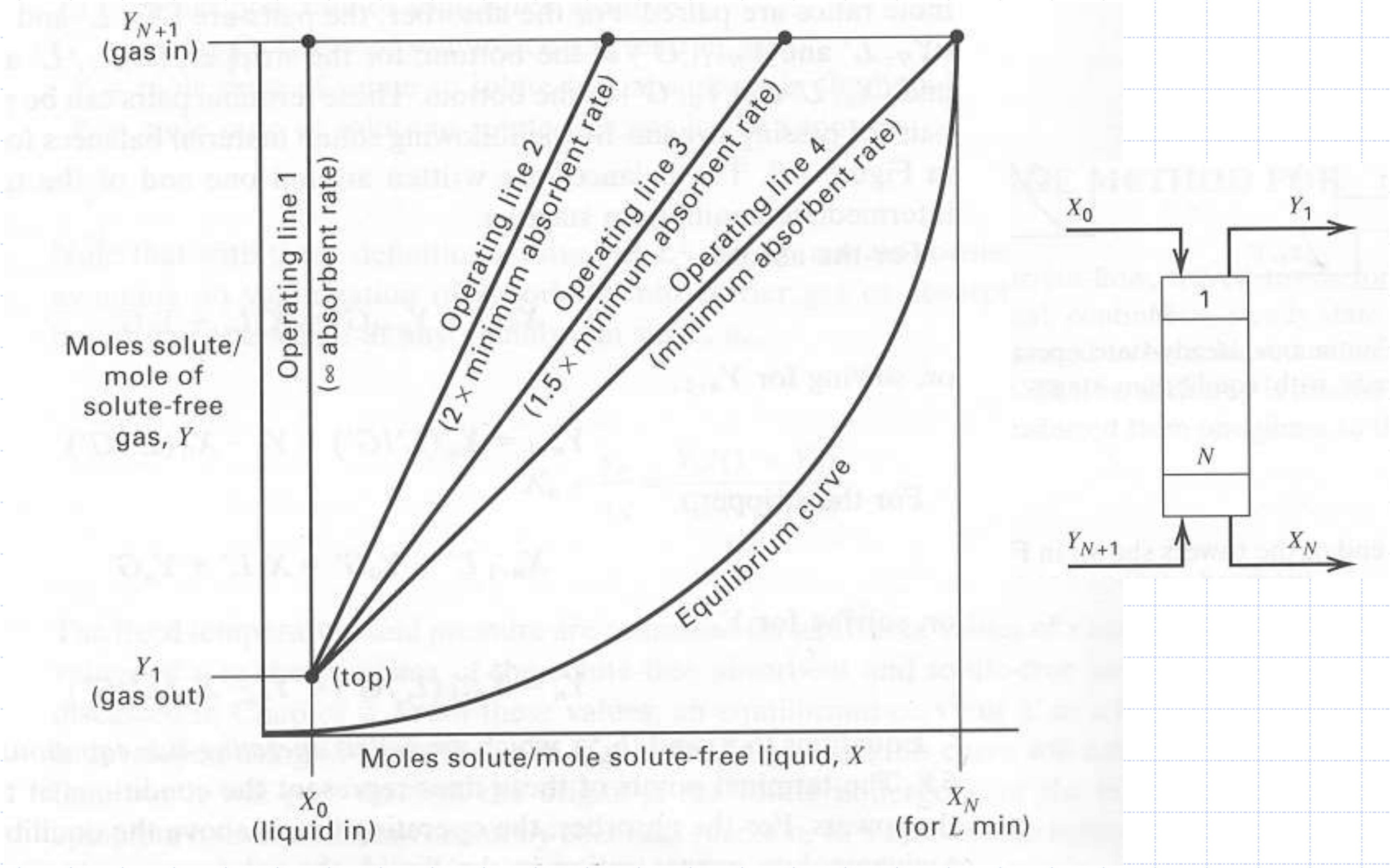


Absorption: plotting equilibrium curve & operating line

- The absorber operating line is the following: $Y_{j+1} = \frac{\underline{L}}{\underline{V}} X_j + \left(Y_u - \frac{\underline{L}}{\underline{V}} X_e \right)$
  - The slope of the operating line is L/V.
  - Note that with the slope of the operating line equal to $(\underline{L}/\underline{V}_{\text{min}})$, N → ∞
- The design specification is given
  - in terms of outlet gas (or vapor) composition,
  - as a recovery, i.e. 1- ($\underline{VY}_u$ / $\underline{VY}_e$): that is the ratio (Y_u/Y_e).
- For given Y_e and Y_u it is possible to identify the (L/V min),
  - corresponding to the minimum consumption of absorbent liquid to reduce the composition in the gas of component 2 from Y_e to Y_u.
  - In the figure this condition is represented by segment TM.



Minimum Absorbent Rate – L_{min}



Degrees of Freedom (DoF)

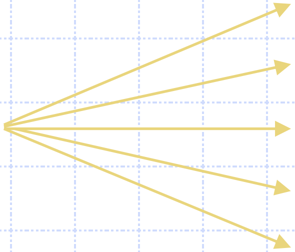
- Intensive variables:
  - Temperature, Pressure, concentration, …
- Extensive variables
  - mass flow, energy flow, …
- Iterative variables
  - n° of stages in a distillation column

$$N_i = N_v - N_r$$

N_i = independent variables

N_v = total variables

N_r = independent equations



- Inherent relations (specific of the system)
- Mass balance relations
- Energy balance relations
- Phase equilibria relations
- Chemical equilibria relations

- $\boldsymbol{N\_i>0}$: "problem is underspecified and additional variables must be specified in order to determine the remaining variables"
- $\boldsymbol{N\_i=0}$: problem can be solved
- $\boldsymbol{N\_i<0}$: problem is overdetermined with redundant and possibly inconsistent relations

Stream

$$N_v = T, P, \dot{m}, H_{stream}, x_i = 1 + 1 + 1 + 1 + (c - 1) = c + 3$$
$$N_r = 1$$

Enthalpy is a function of
composition, T and P

or

$$N_v = T, P, \dot{m}, H_{stream}, x_i = 1 + 1 + 1 + 1 + c = c + 4$$
$$N_r = 1 + 1$$

$$\sum_{i}^{c} x_i = 1$$

Enthalpy is a function of
composition, T and P

$$N_i = c + 2$$

e.g.
c-1: components
1: temperature
1: pressure
1: mass flow

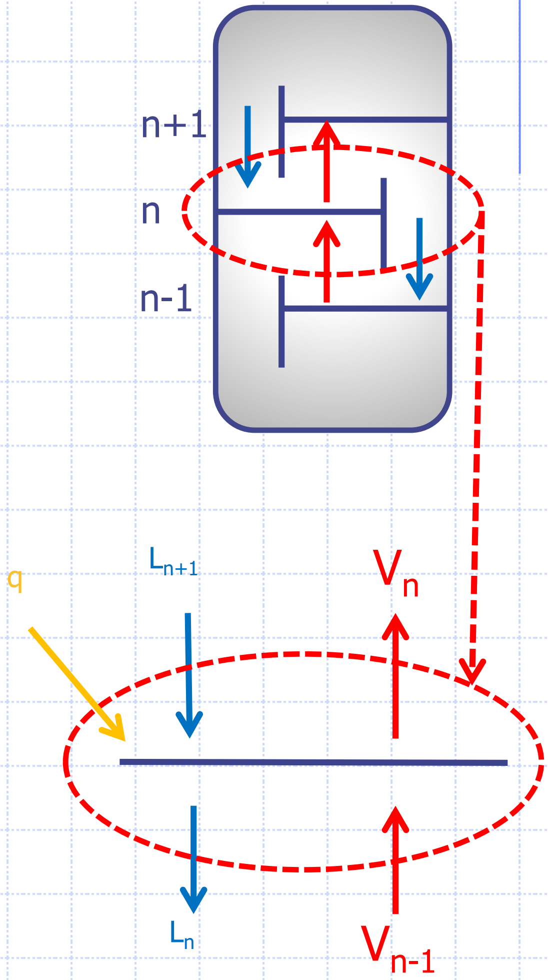
Separation column: Equilibrium stage

$$N_v = \underset{\text{Number of streams}}{\underset{\uparrow}{4}} * (c+2) + \underset{\text{Heat exchanged}}{\underset{\uparrow}{1}} = 4c+9$$

$$N_r = \underset{\text{Mass balance}}{\underset{\nearrow}{c}} + \underset{\text{Energy balance}}{\underset{\nwarrow}{1}} + \underset{\text{Phase equilibria}}{\underset{\nwarrow}{c}} + \underset{\text{T,P equivalence}}{\underset{\nwarrow}{2}} = 2c+3$$

$$N_i = 2c + 6$$

e.g.
2(c+2): definition of inlet streams
1: temperature
1: pressure



Absorption column

$$N_v = n * (2c + 6) + 1$$

Number of stages

DoF for each stage

Heat exchanged

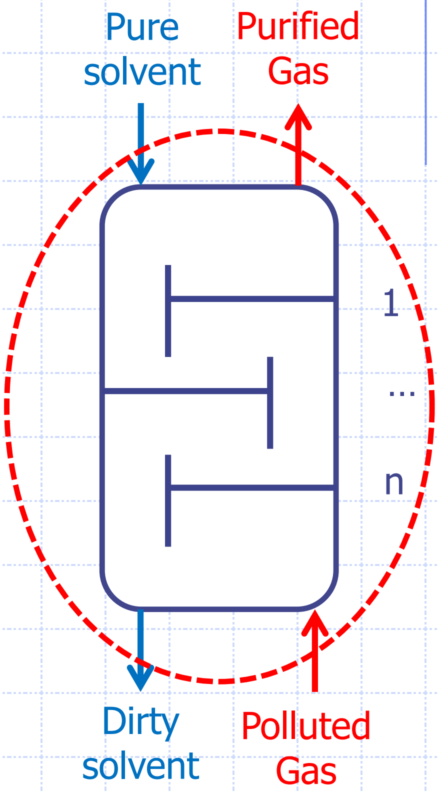
$$N_r = 2 * (c + 2) * (n - 1)$$

Streams ∀ stage

DoF for each stream

n-1 independent stages

$$N_i = 2n + 2c + 5$$



e.g.
2(c+2): definition of inlet streams
n: P ∀ stage
n: Heat loss ∀ stage
1: number of stages

Absorption: number of degrees of freedom

- For an absorption stack of NP ideal contact stages, the number of degrees of freedom is given by:

$$N_i = 2n + 2c + 5$$

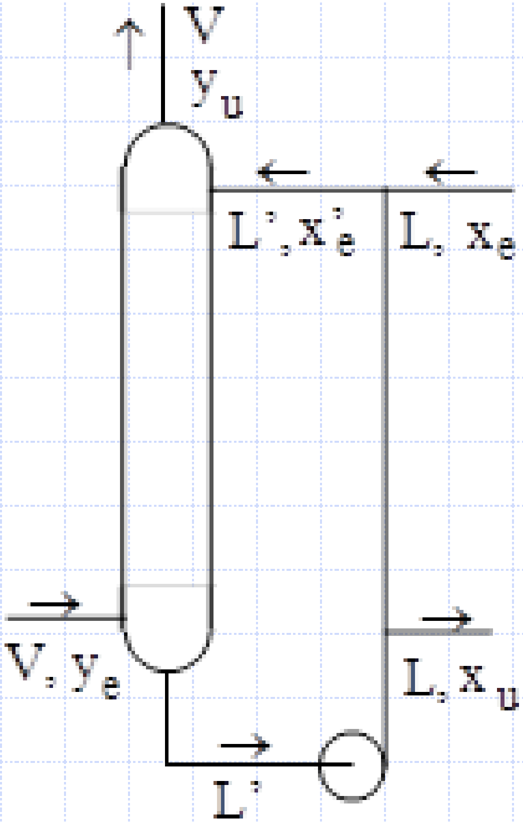
- Usually, the values of **n thermal dispersions** are known, and those of **n pressures** must be assigned, as well as **C + 2 variables of the two feeds** are set, so that only 1 degree of freedom remains.
- This is an uncomfortable situation, leading to no degrees of freedom in rating problems.
- So, it is decided to increase this number by 1, considering the inlet liquid flow rate as the second degree of freedom.
- So, an absorption column has two degrees of freedom in process design (for instance Y_u and L) and one in process rating (for instance Y_u).

Absorption: selection of degrees of freedom

- In design mode:
  - When designing a continuous counter-current absorption process, Y_u is usually the design specification.
  - The flow rate L of the liquid absorbent (the solvent) is the second degree of freedom, and is usually kept a lower as possible, to reduce costs related to the solvent purification and product recovery downstream.
- In rating mode:
  - In the case of rating, the only available degree of freedom is set on Y_u, which is again the design specification, and the liquid flow rate is the one resulting from calculation.
- It is noteworthy that, differently from a distillation process, an absorption process is more complicated because it requires at least two steps:
  - the absorption one, followed by a step to regenerate the solvent, and to recover the product of interest from the mixture with the solvent.
  - This second step can be achieved in a number of ways.

Absorption: saving solvent by recycling it

- In absorption operation it is usually desired to reduce the liquid duty for a given separation,
  - in order to save money in the following stage of liquid purification.
  - However, a low liquid flowrate may have the disadvantage of insufficient wetting in packed column (not the case of a tray column).
  - Therefore, in the current absorption practice, a fraction of the liquid is often recycled back to the column before the purification stage.

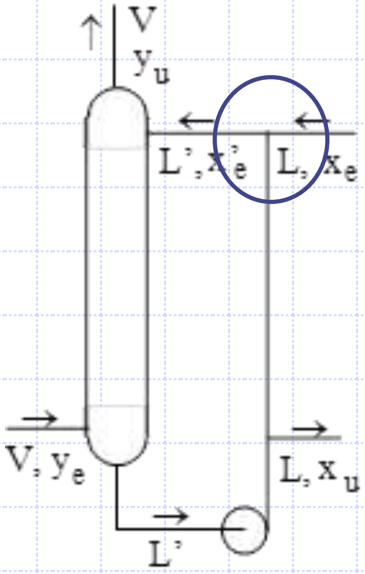


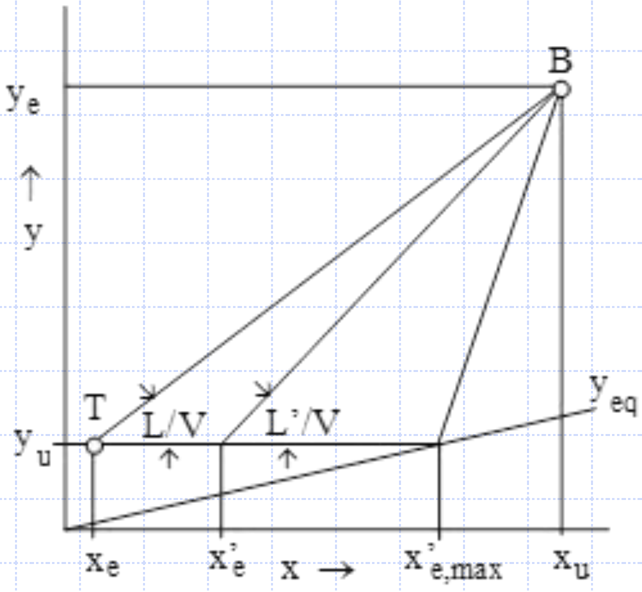
Absorption: saving solvent by recycling it

- The balance at the mixing point before the liquid inlet in the column reads:

$$L'x'_e = (L' - L)x_u + Lx_e$$

- The maximum recycle flow rate allowed to respect the design specification, L'_{max}, corresponds to the equilibrium condition of the liquid concentration x'_e with y_u, represented by $x'_{e,max}$ in the Figure. For values of $L'>L'_{max}$ a larger value of y_u has to be accepted (or a smaller value of x_u, or both of them).





Absorption: overall energy balance

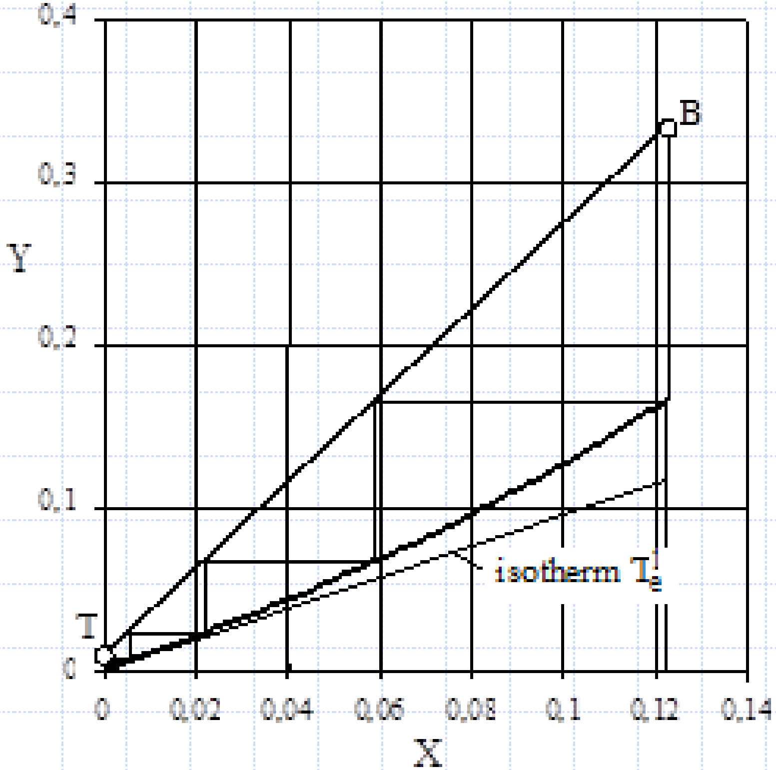
- The absorption of gaseous components in a liquid phase is an exothermic process, as **absorption is a partial condensation** by direct contact.
  - So, the energy released upon condensation has to be disposed of in some way.
- If the column is assumed to be **adiabatic**, as occurs in practice, this energy **increases the temperature** inside the column.
  - The resulting temperature profile increases from the top to the bottom of the column.
  - The simplified overall energy balance around an adiabatic absorption column is:

$$\lambda_B \bar{L}(X_u - X_e) = \bar{L}\, C_p^L \left(T_u^L - T_e^L\right) + \bar{V}\, C_p^V \left(T_u^V - T_e^V\right)$$

  - remember that $\bar{L}(X_u - X_e) = \bar{V}(Y_e - Y_u)$
  - This energy balance is written on a molar basis, so that the specific heat of condensation and the specific heat capacities of both the vapor and the liquid are in molar basis as well.
  - If we account for real property values and real flow rates, we can see that both of the terms in the right hand side contribute to the calculation of temperatures.

Absorption: adiabatic versus isothermal process

- Therefore, the energy balance equation has to be used together with material balances and to the equilibrium relationship to calculate an adiabatic absorption process.
  - The solution of this model requires an **iterative procedure**.
- As a result, in an adiabatic absorption column the outlet streams may be at a **higher temperature** than the inlet ones.
  - Increase in temperature from top to bottom of an absorption column brings a decrease in solubility.
- With respect to the isothermal operation,
  - higher value of the ratio $(\underline{L}/\underline{V})_{min}$ will be required or, with the same ratio $(\underline{L}/\underline{V})$, a greater number of ideal stages will be needed for the desired separation.



Notes on Absorbers (1)

- Note that the **operating line** for an absorber is above the equilibrium curve.
  - For a given solute concentration in the liquid, the solute concentration in the gas is always greater than the equilibrium value, which provides the driving force for the separation.
- The solute is transferred **from the gas to the liquid** in absorption.
  - In distillation, we plotted the more volatile component, which was transferred from the liquid to the gas.
  - In distillation, if we had plotted the less volatile component, which was transferred from the gas to the liquid, the OL would also lie above the equilibrium curve.

Notes on Absorbers (2)

- Also note that the **OL is linear** if we use mole ratios.
  - This results because of the form of the operating line where L/V is a constant.
  - L and V are based upon the nonvolatile solvent and insoluble carrier gas, respectively, which do not change.
  - If we had used mole fractions and total gas and liquid rates, the OL would be curved because the total gas and liquid rates would change since we are removing the solute from the gas and absorbing it into the liquid.
- One could use mole fractions and the total gas and liquid streams in our calculations only if the solute is in low concentrations, say < 1%, in most systems.
  - Don’t confuse this requirement with that for the use of Henry’s Law, which requires low solute concentrations, < 10%, to be valid.

Notes on Absorbers (3)

- Note the location of the top and bottom of the column on the McCabe Thiele diagram.
  - We will typically **step down from the top of the column**, which is equivalent to **stepping up on the McCabe-Thiele plot** for absorption.
- Since we are starting on the OL, we need to express the equilibrium curve in terms of $X_{Eq} = X_{Eq}(Y_{Eq})$.
  - Although this appears to be opposite of what we did in distillation, where we used $y_{Eq} = y_{Eq}(x_{Eq})$ when stepping up the plot, remember that we are still stepping down from the top of the column on the absorption plot.
- We use Y_{Eq} vs. X_{Eq} to plot the equilibrium curve, but we also need X_{Eq} vs Y_{Eq} to actually solve the problem analytically.

Temperature and pressure effects

- Why low temperatures? $P y_2 = x_2 H_2$
  - Since H increases with T, according to the Henry's law, x decreases with increasing T. For a good solubility T should be low.
  - Vapor pressure of a solvent increases with T: higher the solvent evaporation: at high temperatures, this will cause the loss of solvent For stability of the solvent the temperature should be low.
- Why high Pressure? $P y_2 = x_2 H_2$
  - Henry's law → higher the partial pressure (Py), higher the solubility x (at constant H): high total P means high gas solubility and increased mass transfer rates.
  - High total P prevents the solvent to evaporate.
- So, both high P and low T are for the same 2 reasons.
  - to increase the amount of component dissolved in liquid
  - to prevent the evaporation of the solvent.

Absorption with Radfrac

- It is desired to absorb acetone from air into water.
    - The column and feed streams are at 1 atm.
    - The inlet gas stream is 3.2 mol% acetone.
    - Flow of inlet gas is 100 kmol/h.
    - Inlet gas is at 30°C.
    - Water flow rate is 200 kmol/h.
    - Inlet water is pure and temperature is 20°C.
    - N = 6.
- Desired specification: 0.003 max mole fraction in gas out
- Find the outlet concentrations and flow rates.

Absorption with Radfrac

- Base case:
  - Look at the **temperature profile** and note the temperature maximum. Look at the concentration profiles. Does the outlet vapor meet the acetone requirement?
  - Where does all the water in the outlet gas come from?
- Case 1:
  - **Decrease the water flow rate** to 100 kmol/h and run again. Do you meet the required acetone concentration in the gas?
- Case 2:
  - **Double the number of stages** to 12 with L = 100. Does this help reduce the outlet vapor mole frac of acetone significantly?
- Case 3:
  - Return to N = 6 with L = 100. **Reduce the temperature** of both the feed gas and the inlet water to 10°C.
  - Did this allow you to meet the outlet specifications for air?
  - Did the amount of water in the air decrease? (Why?)
  - Do you see much change in the outlet concentration of the liquid stream?
- Case 4:
  - Repeat case 3 but with feed, solvent, and absorber **all at 2.0 atm**.