Stage Operation Material Balances

1. Simple Mass Balance and Units

Consider a cocurrent process (Figure 1), the overall (in the sense of the entire unit) material balance of a species, A, which can be transferred from one phase to another is (without the subscript A)

\[ y_1 \left( \frac{\text{moles } A}{\text{total moles}} \right) V_1 \left( \frac{\text{total moles}}{\text{time}} \right) + x_1 L_1 = y_2 V_2 + x_2 L_2, \left( \frac{\text{moles } A}{\text{time}} \right) \]  

(1)

where \( x \) and \( y \) can be mole or mass fractions, and \( L \) and \( V \) are the total liquid and vapor molal (molar) or mass flow rates. When \( L_1 = L_2 = L \) and \( V_1 = V_2 = V \),

\[ y_1 + \frac{L}{V} x_1 = y_2 + \frac{L}{V} x_2 \]  

(2)

The total flow rates \( L \) and \( V \) remain constant only if the transfer species is present in very low concentrations. Many analytical procedures (e.g. the McCabe-Thiele diagram) are based on constant flow rates. (In later sections, we shall see that the ratio \( L/V \) is the slope of what is called the operating line. Constant \( L \) and \( V \) are required to give a straight operating line.)

When there is significant mass transfer (in what we call concentrated systems), it is unlikely that the molar flow rates \( L \) and \( V \) will remain constant through the system. (This is what we will call curved operating lines.) But with a slight alteration in our choice of notations, we can still obtain a straight operating line by employing mass or mole ratios and the flow of inert species. (Inert here means components which will not be transferred from one phase to another.) Eqn. (1) can now be expressed as

\[ Y_1 \left[ \frac{\text{moles } A}{\text{moles } B, C \text{ etc. only}} \right] V' \left[ \frac{\text{moles } B, C \text{ etc. only}}{\text{time}} \right] + X_1 L' = Y_2 V' + X_2 L', \left( \frac{\text{moles } A}{\text{time}} \right) \]

or

\[ Y_1 + \frac{L'}{V'} X_1 = Y_2 + \frac{L'}{V'} X_2 \]  

(3)

where \( X \) and \( Y \) are mass or mole ratios of the transferable species (A) to that of all other inert species (B, C, etc.) in the two phases: (Subscripts for the species A are omitted.)

\[ Y = \frac{y}{(1-y)}, \quad X = \frac{x}{(1-x)} \]  

(4)

or
\[ \frac{Y}{1+Y}, \quad \frac{X}{1+X} \]

A few redundant notes: \( V_1 \) is the total flow rate entering stage 1 according to Fig. 1 and \( y_1 \) is the concentration of A in the stream \( V_1 \). When the concentration is low, eqn. (4) indicates that \( Y = y \) and \( X = x \). Mass or mole ratios are very useful in analysis and design of gas absorption and liquid extraction processes.

Also, the total flow rates in eqn. (1) can be calculated as

\[ V_1 = \frac{V'}{(1-y_1)}, \quad L_1 = \frac{L'}{(1-x_1)}, \text{ etc.} \]

The mass or molar flow rates of the inert species are denoted by \( L' \) and \( V' \) and they remain constant through the process no matter how many moles of A are being transferred between the two phases. (The simplest scenario is a binary mixture in either phase such that \( L' \) and \( V' \) are just pure solvent flow rates, and \( X \) and \( Y \) are mole ratios of the solute A to the solvents in either phase.)

For ease of typing, all material balances below are only in terms of mass or mole fractions, and in the form of constant total flow rates. You should change the notations accordingly to mass or mole ratios when you know that constant total flow rates may not apply.

That is, you make the decision on the choice of \( x \) or \( X \). For dilute systems, the mathematics is really the same. We just change the notations from \( x \) to \( X \), \( L \) to \( L' \), etc. For concentrated systems, you know that the use of mole fractions will not give you a linear operating line. If we are using a computer, it does not really matter. We will do very well with \( x \) no matter what. Remember that most of these methods in this class were developed in the slide-rule age and we are aiming toward developing simple (but actually rather ingenious) graphical solutions to our mass balances.

In the following equations, the notation we used is common to gas-liquid operations. The gas flow rate and concentration are \( V \) and \( y \) and the corresponding variables for the liquid phase are \( L \) and \( x \).
2. Cocurrent Processes

Consider again the cocurrent process in Figure 1. Eqn. (1) is the overall material balance. We rewrite eqn. (2), with \( L \) and \( V \) constant, to represent in general the concentrations of the two streams at any point within the process (the black box) as related to the inlet:

\[
\frac{L}{V} (x_1 - x) = y - y_1
\]

or

\[
y = -\frac{L}{V} x + \left( y_1 + \frac{L}{V} x_1 \right)
\]  

(2a)

This relation is referred to as the operating line and has a negative slope on a \( y \)-\( x \) diagram. (Note that this is different from the equilibrium line which provides the relation between exiting streams of an equilibrium stage. This will be cleared up later when we have to write the balance equations of an equilibrium stage process. An equilibrium stage is also called an ideal or theoretical stage; these terms are interchangeable.)

**Question:** Where should the operating line lie?

For a transfer of the species \( A \) from the \( L \) (liquid) to \( V \) (gas) phase (stripping), \( x_2 < x_1 \) and \( y_2 > y_1 \), and the driving force \((x - x^*)\) has to be positive. Hence the operating line is below the equilibrium line.

For a transfer of the species \( A \) from the \( V \) to \( L \) phase (absorption), \( y_2 < y_1 \) and \( x_2 > x_1 \), and the driving force \((y - y^*)\) has to be positive. Hence the operating line is above the equilibrium line.

**Question:** What is the form of eqn. (2a) when the process is an equilibrium stage operation?

In this case, \( y_2 = mx_2 \), and equation (2a) is usually rearranged to the form

\[
x_2 = \frac{x_1 + (1/A) x_{in}^*}{1 + (1/A)}, \quad x_{in}^* = \frac{y_1}{m} \quad (\text{Stripping})
\]

(5a)

or

\[
y_2 = \frac{y_1 + Ay_{in}^*}{1 + A}, \quad y_{in}^* = mx_1 \quad (\text{Absorption})
\]

(5b)

where

\[
A = \frac{L}{mV}
\]

is the absorption factor. (As far as nomenclature goes, do not confuse the absorption factor \( A \) with the species \( A \).) The stripping factor, \( S \), is sometimes used to denote \( 1/A \).
**NOTE:** In this development, we have assumed that the phase equilibrium can be described by the simple linear relation \( y^* = mx^* \). This is usually adequate for gas absorption operations. We shall consider nonlinear equilibrium lines in later chapters.

**Question:** What is the thermodynamic relation which provides the linear equilibrium relation?

**Question:** Why is \( A \) called the absorption factor? Why are there two different forms of equations for stripping and absorption?

### 3. Countercurrent Processes

The operating line equation for Figure 2, based on the left end, is

\[
\frac{L}{V} (x_1 - x) = y_1 - y
\]

or

\[
y = \frac{L}{V} x + \left( y_1 - \frac{L}{V} x_1 \right)
\]  

(6)

When there is a single stage and is in equilibrium, \( y_1 = mx_2 \), the corresponding equations to Figure 2 are

\[
x_2 = \frac{x_1 + (1/A) x^{*_{out}}}{1 + (1/A)}, \quad x^{*_{out}} = \frac{y_2}{m}
\]  

(7a)

\[
y_1 = \frac{y_2 + Ay^{*_{out}}}{1 + A}, \quad y^{*_{out}} = mx_1
\]  

(7b)

The absorption factor is defined as above. (Note that the subscripts here are very different from what we shall use later in section 5.)

**Question:** Show that the operating line for a countercurrent stripping process is below the equilibrium line, while the operation line of countercurrent absorption is above the equilibrium line.

**Question:** Sketch the \( y \) and \( y^* \) profiles for both cocurrent and countercurrent equilibrium multistage processes.

**Question:** If the liquid and gas inlet concentrations and the gas outlet concentration are specified, what is the minimum liquid flow rate (or minimum operating line slope)?
4. Cross-Flow Cascades

The material balance of the transfer species of stage \(i\) in Figure 3 is

\[
Lx_{i-1} + Vy_o = Lx_i + Vy_i
\]

or

\[
y_i = -\frac{L}{V} x_i + \left( y_o + \frac{L}{V} x_{i-1} \right)
\]  \hspace{1cm} (8)

where \(V\) is now the gas flow rate to each individual stage. If the stage reaches phase equilibrium, \(y_i = mx_i\), and

\[
x_i = \frac{x_{i-1} + (1/A)x_{in}^*}{1 + (1/A)}, \quad x_{in}^* = \frac{y_o}{m}
\]  \hspace{1cm} (9a)

\[
y_i = \frac{y_o + Ay_{in}^*}{1 + A}, \quad y_{in}^* = mx_{i-1}
\]  \hspace{1cm} (9b)

**Question:** Sketch the operating lines for stripping and absorption processes.

**Question:** Sketch the operating lines for a cross-flow cascade with equilibrium stages.

**Question:** Repeat with non-equilibrium stages.

**Question:** Compare the separation "efficiency" of cocurrent, countercurrent and crosscurrent processes. Why is countercurrent processes more effective?

5. Kremser, Souders and Brown (KSB) Equation

In unit operation design calculations, it is useful to find out the quality of separation for a given number of stages. It is also useful to find the required number of stages if the product recovery is specified. The development was first given by Kremser in 1930, and by Souders and Brown in 1932. The resulting equations are referred to as the KSB or Kremser equations.

Consider a countercurrent process with equilibrium stages (Figure 4). We define
the absorption factor $A = \frac{L}{mV}$,

or the stripping factor $S = \frac{mV}{L} = \frac{1}{A}$

and

\[x_{\text{out}}^* = \frac{y_{Ao}}{m} = \frac{y_{Ain}}{m}\]

For stage 1:

\[x_{A1} + V y_{A1} = L x_{A2} + V y_{A0}, \quad y_{A1} = m x_{A1}\]

or

\[x_{A2} - x_{A1} = S (x_{A1} - x_{\text{out}}^*)\] (10)

The material balance over stage 2 and the bottom:

\[x_{A1} + V y_{A2} = L x_{A3} + V y_{A0}\]

or

\[x_{A3} - x_{A1} = S (x_{A2} - x_{\text{out}}^*)\] (11)

Now subtract eqn. (10) from (11):

\[x_{A3} - x_{A2} = S (x_{A2} - x_{A1})\] (11a)

(Note that this is a clumsy way to get eqn. (11a). This equation is nothing but the material balance of stage 2 in equilibrium. The derivation is just to show that there are more ways than one to do things, but we are dealing with simple mass balances and the result has to be the same.)

Substitute eqn. (10) in (11a):

\[\frac{x_{A3} - x_{A2}}{x_{A1} - x_{\text{out}}^*} = S^2\] (11b)

Now try this one more time with stage number 3. We should get

\[x_{A4} - x_{A1} = S (x_{A3} - x_{\text{out}}^*)\]

and

\[x_{A4} - x_{A3} = S (x_{A3} - x_{A2})\]

\[= (x_{A1} - x_{\text{out}}^*) S^3\]

With similar procedures, for any stage \(i\),

\[\frac{x_{i+1} - x_i}{x_{A1} - x_{\text{out}}^*} = S^i\] (12)

Now add up all the balances of stages 1 to \(n\):
\[
\frac{x_{An+1} - x_A1}{x_A1 - x_{\text{out}}} = \sum_{k=1}^{n} S^k
\]  
(13)

We can rearrange eqn. (13) by adding and subtracting the term \(x_{An+1}\sum S^k\) and writing

\(x_{An+1} = x_{Ain}\) and \(x_A1 = x_{Aout}\):

\[
\frac{x_{Ain} - x_{Aout}}{x_{Ain} - x_{\text{out}}} = \frac{1}{1 + \sum_{k=1}^{n} S^k}
\]

\[
= \frac{\sum_{k=0}^{n} S^k - 1}{\sum_{k=1}^{n} S^k}
\]

(13a)

The final result is

\[
\frac{x_{Ain} - x_{Aout}}{x_{Ain} - x_{\text{out}}} = \frac{S - S^{n+1}}{1 - S^{n+1}}
\]

(14)

Equation (14) can further be rearranged to the forms

\[
\frac{x_{Aout} - x_{Aout}^*}{x_{Ain} - x_{\text{out}}} = \frac{1 - S}{1 - S^{n+1}}
\]

(14a)

and

\[
\ln \left[ \frac{1}{1 - A} \left( \frac{x_{Ain} - x_{Aout}^*}{x_{Aout} - x_{Aout}^*} \right) + A \right] = \ln \left[ \frac{S}{S^{n+1}} \right]
\]

(14b)

The entire derivation can be carried out turning the procedure upside down, i.e., starting with stage \(N\) and the material balances in terms of \(y\). The corresponding equations to eqns. (10) and (11b) are eqns. (15a) and (15b).

For stage \(N\):

\[
\frac{y_{An-1} - y_{An}}{y_{An} - y_{\text{out}}^*} = A, \quad y_{\text{out}}^* = m_{Ain}
\]

(15a)

and stage \(N-1\):

\[
\frac{y_{An-2} - y_{An-1}}{y_{An} - y_{\text{out}}^*} = A^2
\]

(15b)

The corresponding form of eqn. (12) for any stage \(i\) is

\[
\frac{y_{Ai} - y_{Ai+1}}{y_{An} - y_{\text{out}}^*} = A^{n-i}
\]

(16)

Sum up all the stages:
The final results corresponding to eqns. (14), (14a) and (14b) are

\[ \frac{y_{A0} - y_{An}}{y_{An} - y^{*}_{out}} = \sum_{k=1}^{n} A^n \] (17)

and

\[ \frac{y_{Ain} - y_{Aout}}{y_{Ain} - y^{*}_{out}} = \frac{A - A^{n+1}}{1 - A^{n+1}} \] (17a)

and

\[ \frac{y_{Aout} - y^{*}_{out}}{y_{Ain} - y^{*}_{out}} = \frac{1 - A}{1 - A^{n+1}} \] (17b)

Note that eqns. (14) and (17) are very similar (and mathematically identical). All you have to do is interchange \( x \) and \( y \), \( S \) and \( A \).

**Question**: When you solve either a stripping or an absorption problem, does it matter whether you use eqn. (14) or (17)?

**Question**: Derive the corresponding form of the Kremser equation for the cross-flow cascade. Show that when \( y_0 = 0 \), how the equation simplifies. (The answer is below, but try to do it yourself first.)

**Question**: What about a similar analysis for a cocurrent multistage process?

### 6. Kremser Equation for Cross-Flow Cascade

Refer back to Fig. 3. The derivation will continue onto stage \( N \) on the right. Derive in terms of \( X \) (i.e. stripping), and define

\[ S = \frac{1}{A} = \frac{V'm}{L'} \]

and

\[ X^* = \frac{Y_o}{m} \]

**Stage \( N \):**

\[ V'Y_o + L'X_{N-1} = V'Y_N + L'X_N, \quad Y_N = mX_N \]

\[ X_{N-1} + S \frac{Y_o}{m} = SX_N + X_N \]

\[ X_{N-1} = X_N(1+S) - SX^* \] (18)

**Stage \( N-1 \):**

\[ X_{N-1} - X_N = S (X_N - X^*) \] (18a)
\[ Y_o + L'X_{N-2} = V'Y_{N-1} + L'X_{N-1} \]

\[ S \frac{Y_o}{m} + X_{N-2} = SX_{N-1} + X_{N-1} \]

\[ X_{N-2} = X_{N-1} (1+S) - SX^* \]  \hspace{1cm} (19)

Subtract eqn. (18) from (19):

\[ X_{N-2} - X_{N-1} = (X_{N-1} - X_N) (1+S) \]  \hspace{1cm} (19a)

Substitute eqn. (18a) in (19a):

\[ X_{N-2} - X_{N-1} = (X_N - X^*) (1+S)S \]  \hspace{1cm} (19b)

Now for stage \( N-2 \):

\[ Y_o + L'X_{N-3} = V'Y_{N-2} + L'X_{N-2} \]

\[ X_{N-3} = X_{N-2} (1+S) - SX^* \]  \hspace{1cm} (20)

Subtract eqn. (19) from (20):

\[ X_{N-3} - X_{N-2} = (X_{N-2} - X_{N-1}) (1 + S) \]  \hspace{1cm} (20a)

Substitute eqn. (19a) in (20a):

\[ X_{N-3} - X_{N-2} = (X_N - X^*) (1 + S)^2 S \]  \hspace{1cm} (20b)

By induction,

\[ \frac{X_o - X_1}{X_N - X^*} = S(1 + S)^{N-1} \]  \hspace{1cm} (20c)

Sum up the (b) form of all the stages:

\[ \frac{X_o - X_N}{X_N - X^*} = S + S \sum_{k=0}^{N-1} (1 + S)^k \]  \hspace{1cm} (21)

\[ S \left[ 1 + \sum_{k=0}^{N-1} (1 + S)^k \right] \]

\[ = S \sum_{k=0}^{N-1} (1 + S)^k \]

\[ = S \left[ \frac{1-(1+S)^N}{-S} \right] \]

\[ = S (1 + S)^N - 1 \]

This leads to
\[ \frac{X_o - X^*}{X_N - X^*} = (1 + S)^N \]  

or

\[ N = \frac{\ln \left( \frac{X_o - X^*}{X_N - X^*} \right)}{\ln (1 + S)} \]  

When \( Y_o = 0, \) \( X^* = 0, \) and

\[ N = \frac{\ln \left( \frac{X_o}{X_N} \right)}{\ln (1 + S)} \]  

or

\[ \frac{X_N}{X_o} = (1 + S)^{-N} \]

This is one of many ways to derive the equation. Try to derive the results a different way. Try to use \( x, L, \) etc.