

EXTRACTION

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1. GENERAL

In this work only continuous extraction is considered. Extraction as a continuous and industrial unit operation is usually done in one unit, which is called an extraction column. After the extraction the solvent has to be separated from the products (usually by distillation), so the whole process includes several steps.

Extraction as a unit operation means separating the components of a mixture. Separation is based on the difference of solubility of components when a certain solvent is used. Notice the certain analogy between extraction and other column operations.

1.1 STREAMS IN EXTRACTION

No recycle flow is used in this work, so the extraction apparatus looks like the schematic representation in figure 1. The process is counter current. It is common practice to call the flow of the extraction column as follows. The feed F and the solvent S enter the column from different ends. The idea of the extraction process is to capture the desired components from the feed into the solvent which is then called the extract. The feed stream leaving the column from which the desired component has been extracted is called raffinate.

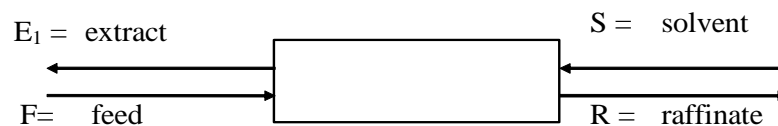


Figure 1. Extraction apparatus

2. THEORY

The following notions are assumed to be familiar:

- Ideal stage, ideal stage model, calculation of the amount of ideal stages
- Phase equilibrium
- Saturated flow

2.1 PHASE EQUILIBRIUM

Only three-component systems are discussed here. Equilibrium data of such a system can always be represented in triangular coordinates as in figure 20.10 in McCabe et al. (1993). Though, a more useful method to plot three-component data is to use rectangular coordinates as in figure 2. Tie lines in figure 2 connect extract and raffinate compositions, which are in equilibrium state together. A diagram based on these points gives the equilibrium line in the x,y -coordinates.

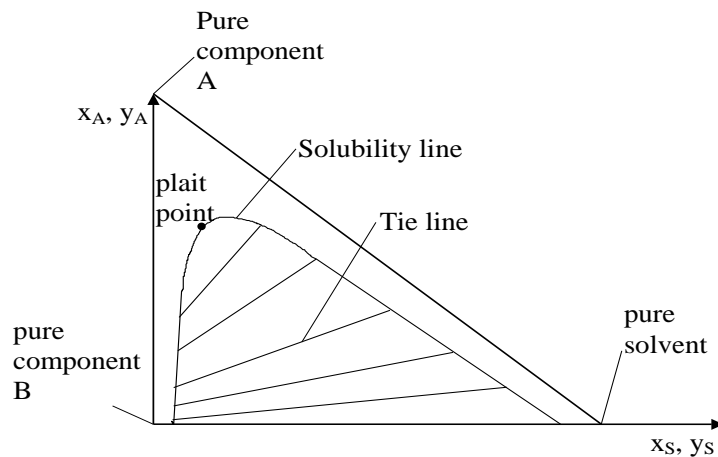


Figure 2. Rectangular coordinates of three-component system.

2.3 CALCULATION MODELS

The schematic figure of the multicomponent liquid liquid extractor is the following

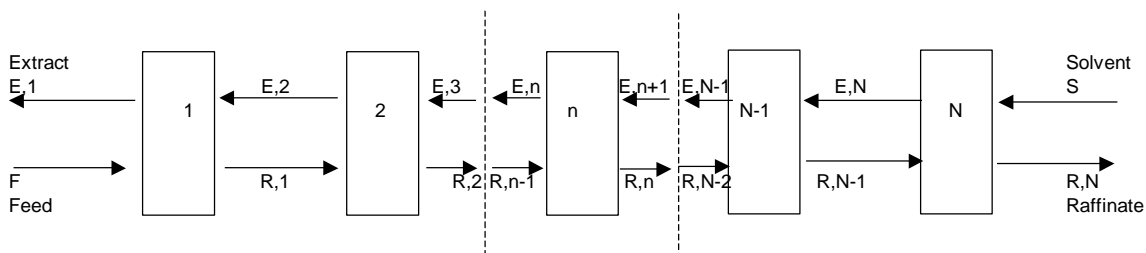


Figure 4. Schematic diagram of countercurrent ideal liquid liquid stage

The boxes are ideal stages and indexing starting from the feed end.

The balances are written for each ideal stage. As an example for the first stage the total balance is

$$F + E_2 = R_1 + E_1$$

the component balance for the component i

$$F x_{F,i} + E_2 x_{E_2,i} = R_1 x_{R_1,i} + E_1 x_{E_1,i}$$

The total balance for stage n

$$R_{n-1} + E_{n+1} = R_n + E_n$$

the component balance for the component i

$$R_{n-1} x_{R_{n-1},i} + E_{n+1} x_{E_{n+1},i} = R_n x_{R_n,i} + E_n x_{E_n,i}$$

The total balance for the last stage N

$$R_{N-1} + S = R_N + E_N$$

the component balance for the component i

$$R_{N-1}x_{R,N-1,i} + Sx_{S,i} = R_Nx_{R,N,i} + E_Nx_{E,N,i}$$

The above presentation leads to four balance equations per stage in case of ternary system. Because the fourth equation per stage can be derived from the rest of the three equations per stage there is only three equations needed: for example

- a) total balance and component balances of two components.
- b) component balance of three components

The above balances need also the thermodynamic model to mathematically present the equilibrium between phases, i.e. leaving streams from a stage are in equilibrium.

The model can be for example the activity coefficient model NRTL or UNIQUAC. These are capable for model the liquid liquid equilibrium.

The three thermodynamic equations for each component for the first stage

$$K_{1,i} = \frac{x_{E1,i}}{x_{R1,i}} = \frac{\gamma_i(T, x_{R1,1}, x_{R1,2}, x_{R1,3})}{\gamma_i(T, x_{E1,1}, x_{E1,2}, x_{E1,3})}$$

and the mole fraction definitions

$$\sum_{n=1}^3 x_{R1,i} = 1$$

$$\sum_{n=1}^3 x_{E1,i} = 1$$

for the n'th stage

$$K_{n,i} = \frac{x_{En,i}}{x_{Rn,i}} = \frac{\gamma_i(T, x_{Rn,1}, x_{Rn,2}, x_{Rn,3})}{\gamma_i(T, x_{En,1}, x_{En,2}, x_{En,3})}$$

and the mole fraction definitions

$$\sum_{n=1}^3 x_{Rn,i} = 1$$

$$\sum_{n=1}^3 x_{En,i} = 1$$

and for the last stage N

$$K_{N,i} = \frac{x_{EN,i}}{x_{RN,i}} = \frac{\gamma_i(T, x_{RN,1}, x_{RN,2}, x_{RN,3})}{\gamma_i(T, x_{EN,1}, x_{EN,2}, x_{EN,3})}$$

and the mole fraction definitions

$$\sum_{n=1}^3 x_{RN,i} = 1$$

$$\sum_{n=1}^3 x_{EN,i} = 1$$

These gave 5 additional equations per stage. Totally there are 8 equations per ideal stage. Sounds complicated but it is not. Solving this kind on set of equations is relatively straightforward at the spreadsheet program like Excel, or mathematics software like Matlab, Mathcad, Maple, etc.

If the systems contains more than three components, naturally the number of equations increases.

2.6 OVERALL EFFICIENCY

If the real process is a stage process, the change from the ideal stage model to the actual stage process is done with the efficiency ε of an actual stage. There are many different definitions for efficiencies but the simplest one is the overall efficiency ε_{TOT} , which is defined as:

$$\varepsilon_{TOT} = \frac{N_{IDEAL}}{N_{ACTUAL}} \quad (1)$$

3. EQUIPMENT

3.1 COLUMN

The extraction column used to this work is a York-Scheibel column. It is a countercurrent multistage extraction column developed by E. G. Scheibel in the late 40's and made by Otto H. York Inc. in 1952. One mixing zone and one settling zone form one actual stage. According to the data sheet of the device the efficiency of an actual stage for MIK-water-HAc system was measured to be 0.5 – 0.9 when flow rate was between 0 – 0.06 m³ / sm² and the diameter of the column was 12 in. The mixing speed was not told. According to Scheibel (1948) the mixing speeds of other substances have varied between 1000 and 1600 rpm.

According to the data sheet the nominal capacity of a 1-inch (25 mm) column in MIK-water-HAc system is a gallon per hour or 1*10⁻⁶ m³ / s, which gives a liquid load of 0.02 m³/m²/s.

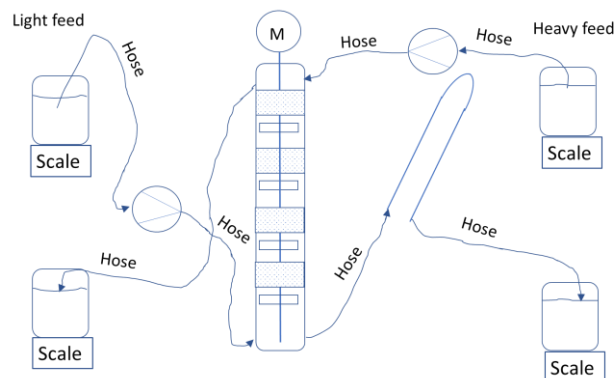


Figure 3. Schematic of the extraction equipment

3.2 MEASURING EQUIPMENT

Scales are connected to a datalogging equipment, and the masses of the scales are logged during the operation.

Also

- A stopwatch
- Tachometer for defining mixing speeds
- NaOH-burette for defining concentrations + NaOH solution and an indicator.
- Magnetic mixer and a magnet
- 3 x 100 ml Erlenmeyer-bottles for titration
- 2 x 500 ml Erlenmeyer-bottles for defining the flow rates

4. OPERATING THE COLUMN

4.1 ARRANGEMENTS

Water is used to extract acetic acid (HAc) from methyl isobutyl ketone (MIK). So, the extracted component is HAc, the diluent is MIK and water is the solvent:

component A = HAc
component B = MIK
solvent S = water

The continuous phase is the water phase into which the MIK phase is dispersed by mixing. Water is led to the column from top and MIK-HAc mixture from the bottom. Flow from the feed tanks to the column is achieved with compressed air. The feed rates are controlled with valves and measured with the rotameters.

The phase boundary is adjusted to the upper part of column, below the exit point of the lighter phase. Adjusting is done with an overflow pipe.

The solvent fed to the system is pure water, so $y_{S,b} = 1.0$.

The feed is a mixture of pure MIK and pure HAc.

CAUTION!

MIK-HAc mixture is corrosive! Watch out for skin contact. Use safety gloves if needed!

4.2 STARTING THE WORK

- Define the concentration of NaOH solution with 0,1 M HCl solution.
- Define the concentration of the HAc-MIK feed twice.
- Open the pressure air valve and adjust the pressure to 0,3 bar.
- Remove the air from the rotameters by opening the feed valves almost completely open for a moment.
- Fill up the column with water so that the water level is about 10 cm below the water feeding point.
- Adjust both the feed flow rates to their desired values.
- Switch the mixer on.

- Keep the phase boundary between the uppermost settling zone and the exit point of the lighter phase.

4.3 MEASUREMENTS

- Calculate the amount of ideal stages.
- Assistant gives the flow rates and the mixing speed.
- Adjust the feed rates and the mixing speed to their desired values.
- Take a sample every 10 minutes from the extract phase and define its HAc concentration.
- When the HAc concentration is not changing remarkably, take the other measurements:
- Take samples from the products and titrate them.
- Define the product rates by collecting a sample at least for 10 minutes and by weighting it.
- Check and note the mixing speed.
- Adjust the feed rates and the mixing speed to their desired values and repeat the measurements.

4.4 FINISHING THE WORK

- Show your results to the assistant and after permission:
- Close the pressure air valve and the feed valves.
- Empty the column to the canister in the fume cupboard.
- Empty the collector bottles of the extract and raffinate to the same canister.
- Clean up the surroundings.

5. REPORTING

The reporting is done as told in general instructions. The both members of work pair take care of one stabilized state measurements of the column.

- Show the stabilization of column graphically.
- Summarize the results.
- Use mass fraction coordinates.

- Draw with Aspen the triangular equilibrium diagram. Show the diagram in the report
Comment the diagram.

- Define by trial and error the number of ideal stages N . Use mass fractions.

- Calculate the overall tray efficiency $\varepsilon = \frac{N}{N_{ACT}}$. Here an actual tray is one mixer + one settler part of the column

- Conclusions. What can you say about the results? Why the results are like they are? Do the results fit the theory? If not, why?

6. NOMENCLATURE

F	total mass flow in the feed, kg/s
E	total mass flow in the extract, kg/s
R	total mass flow in the raffinate, kg/s
S	total mass flow in the solvent, kg/s
x	mass fraction dimensionless

Subindexes

E	Extract
F	Feed
i	internal flow
n	tray n
N	tray N
R	Raffinate
S	solvent

Superscripts

7. REFERENCES

- McCabe, W.L., Smith, J.C. and Harriot, P., Unit Operations of Chemical Engineering, 5th ed., McGraw-Hill, 1993.
Treyball, R.E., Mass-Transfer Operations, 3rd ed., McGraw-Hill, 1980

8. APPENDIXES

1. The solubility and equilibrium data of the HAc-MIK-H₂O –system.
2. Matching the balances of extraction

The solubility and equilibrium data for HAc – MIK – water system.

A	B	S
HAc	MIK	water
C ₂ H ₄ O ₂	C ₆ H ₁₂ O	H ₂ O
60.05	100.16	18

w = weight fraction
 wy = weight fraction in water phase
 wx = weight fraction in MIK phase

SOLUBILITY		
A	B	S
0.000	0.020	0.980
0.242	0.053	0.705
0.286	0.073	0.641
0.311	0.094	0.595
0.329	0.125	0.546
0.342	0.172	0.486
0.341	0.254	0.405
0.333	0.322	0.345
0.322	0.402	0.276
0.312	0.432	0.256
0.295	0.492	0.213
0.279	0.535	0.186
0.260	0.580	0.160
0.237	0.624	0.139
0.217	0.661	0.122
0.193	0.698	0.109
0.167	0.741	0.093
0.136	0.790	0.074
0.000	0.977	0.023

Linearization of the solubility line			
S(calc)	difference	Relative difference	% relative difference
0.98	0.00	0.00	0.11
0.70	0.01	0.01	0.97
0.65	0.01	0.01	0.90

$$m = -1.17$$

$$b = 0.98$$

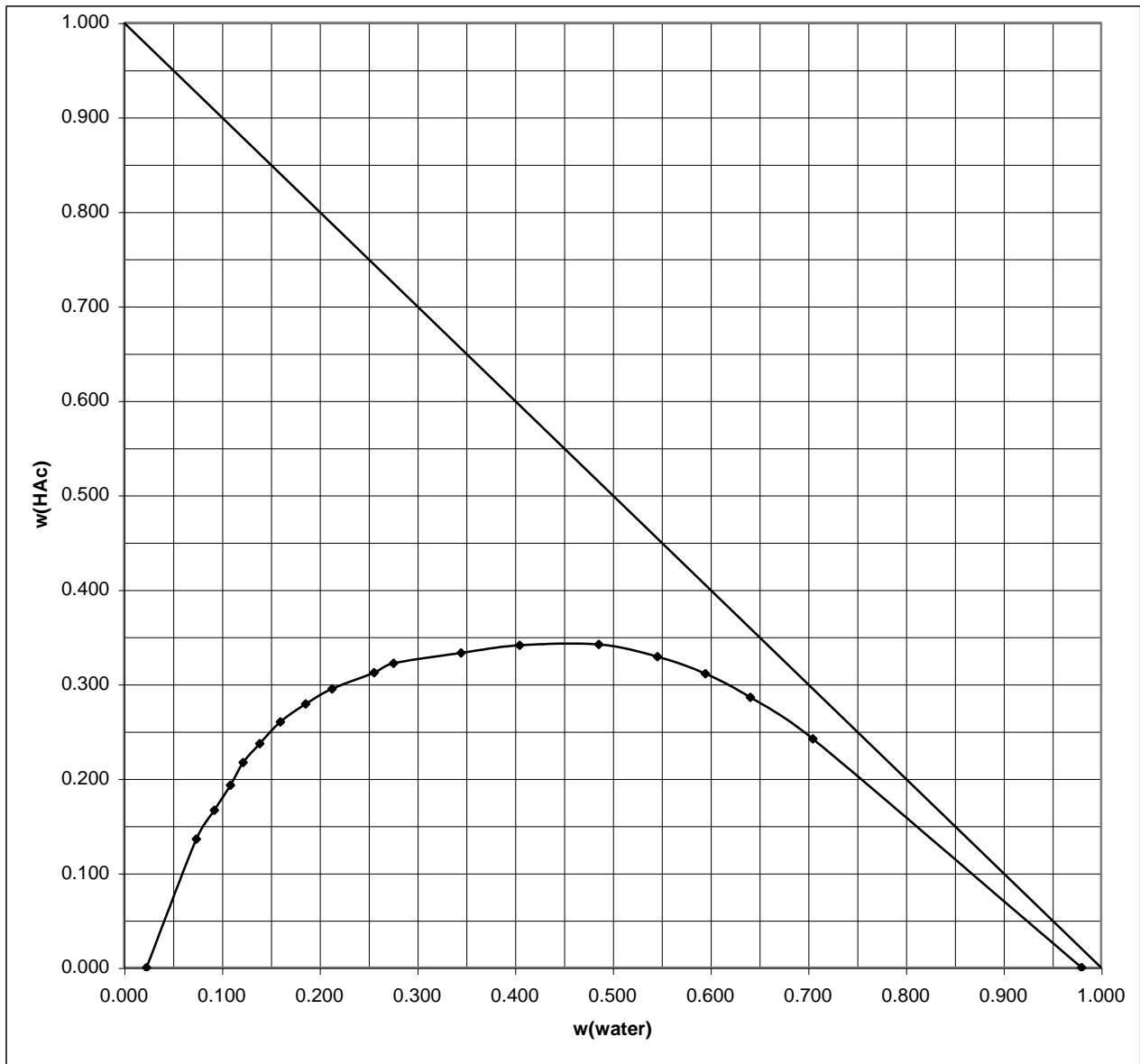
S(calc)	difference	Relative difference	% relative difference
0.17	0.02	0.11	11.15
0.15	0.01	0.03	3.37
0.14	0.00	0.02	1.96
0.13	0.01	0.07	6.98
0.12	0.01	0.07	7.41
0.10	0.01	0.11	10.52
0.09	0.01	0.15	15.05
0.01	0.01	0.61	61.12

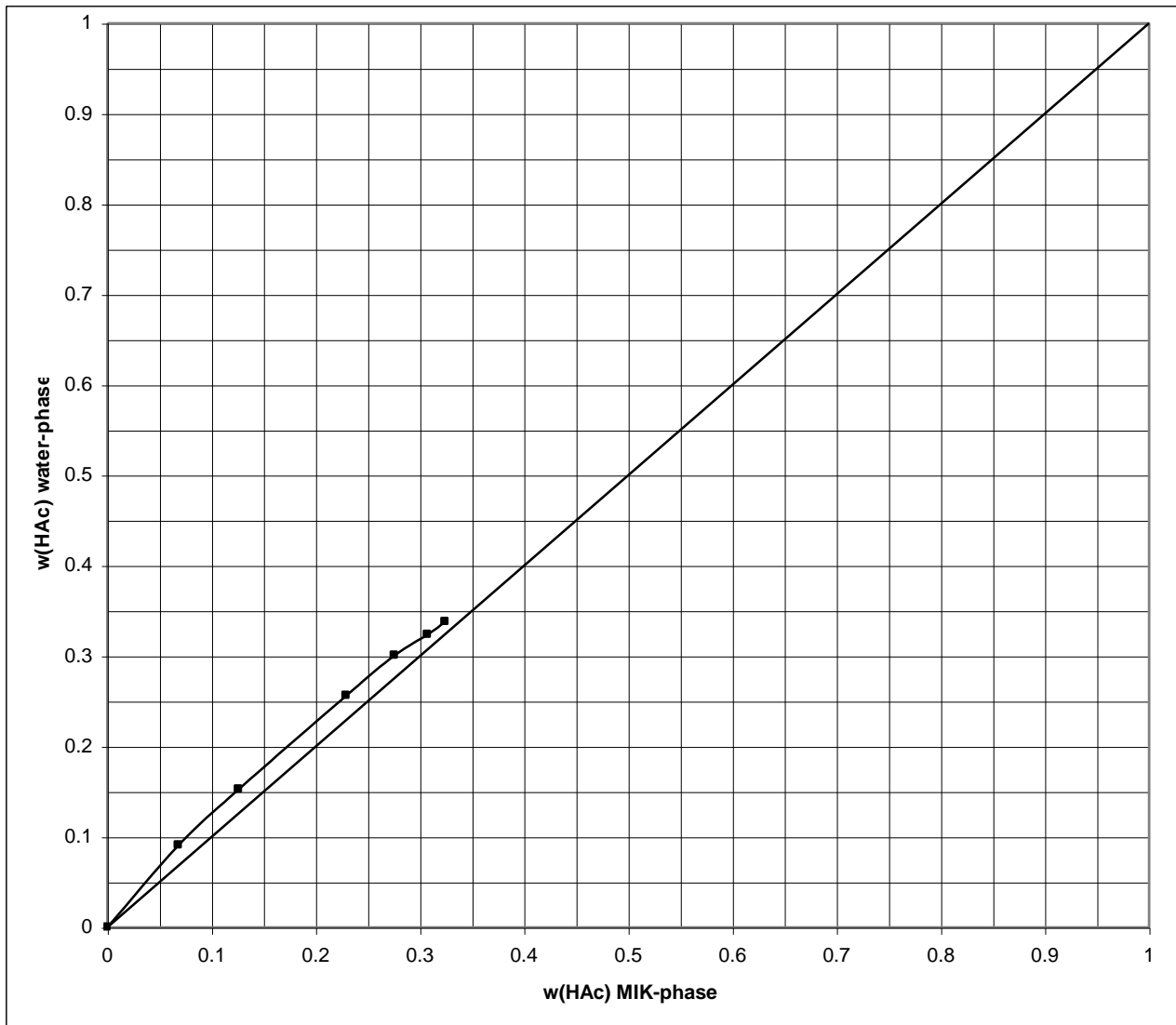
$$m = 0.56$$

$$b = 0.01$$

EQUILIBRIUM	
wx	wy
0	0
0.069	0.091
0.126	0.153
0.229	0.256
0.276	0.301
0.308	0.324
0.324	0.338

Source: Othmer, D.F., White, R.E., Trueger, E., Liquid-liquid Extraction data, Ind. Eng. Chem. 33(1941) 1240-8

Solubility of HAc-MIK-H₂O -system

Equilibrium of HAc-MIK-H₂O -system

MATCHING THE BALANCES						8.4.2005
This workbook contains the following sheets:						Color codes
MENU	This sheet.					GIVE
BASIC CASE	Protected therefore Solver does not work.					MATCHED
EXTRACTION	Protected therefore Solver does not work.					CONSTRAINTS
BINARY DISTILLATION	Protected therefore Solver does not work.					TARGET FUNCTION
MACRO	Contains the macros.					
GENERAL PRINCIPLE OF MATCHING THE BALANCES						
The sum $S = \sum (P_i * ((x_i - X_i) / x_i)^2)$ is minimized						
xi = measured value of quantity i						
Xi = matched value of quantity i						
Pi = weighting coefficient of quantity i						
so that total and component balances hold true and the sum of mole fractions is one.						
The task at hand is a constrained optimization task, which constraints are the balances and the sum of mole fractions						
and the minimized function is the weighted sum of relative differences of						
matched and measured values.						
There is no universal algorithm to solve a problem like this, which would always lead to a solution.						
Therefore matching should be done with few different initial values.						
INSTRUCTIONS						
0 Go to sheet and use the macro CopyPage to make an unprotected sheet.						
1 Give the measured values to cells: MEASURED						
2 If needed give the weighing coefficients to cells: WEIGHT						
The greater the weighting coefficient the smaller is the difference between matched and measured values.						
Weighting coefficient of an accurate measurement should be large.						
Weighting coefficient of an inaccurate measurement should be small.						
Weighting coefficient can be in the range (0, positive infinity). Here the coefficients should be ≥ 1 .						
If there is no special need for weighting, use 1.						
3 Give initial values (e.g. measured values) to cells: INITIAL VALUES						
Leave all other cells UNTOUCHED!						
4 Choose Tools / Solver / Solve: Solver starts the optimization.						
The target cell of the optimization becomes active.						
The constraints are:						
Balances hold true, in other words the cells IN-OUT = 0						
Sum of mole fractions equals to 1, cells $\sum x = 1$						
All matched values are positive, MATCHED ≥ 0						
5 If the result is not reasonable, try other initial values or change the weighting coefficients.						
Notice that the best result is obtained only by trial and error.						
6 If a reasonable result is not found, save the result and restart solver.						
If a reasonable result is not found after a few times, return to 5 and try other initial values.						
7 Extraction:						
Substance A (component to be extracted) = HAc						
Substance B (diluter) = MIK						
Substance S (solvent) = vesi						
if HAc, of which the feed is made, contains water p -weight %, feed contains $x_B = 1.0 - (1.0 + p / (100 - p)) * x_A$,						
since x_S / x_A is always $p / (100 - p)$ in feed, which is made by adding substance B						
In the solvent $y_S = 1.0$ because it is pure water.						
Raffinate and extract are saturated, so x_S is obtained from the saturation curve.						
In raffinate $x_S = 0.56 * x_A + 0.01$ and in extract $x_S = -1.17 * x_A + 0.98$.						
In both $x_B = 1.0 - x_A - x_S$						
Extra constraint: in raffinate and extract $x_A \geq 0.001$						
8 Binary distillation						
Notice that $x_B = 1.0 - x_A$						

MATCHING THE BALANCES			EXTRACTION (A: HAc - B: MIK - S: water)								
			← Extract				Solvent				
				PROCESS							
			Feed →				Raffinate →				
Water in HAc=		20.000	weight%								
WEIGHTING COEFFICIENTS											
	IN				OUT					COLOR CODES	
	Feed	Solvent	Raffinate	Extract					GIVE		
TOTAL	1.0	1.0	1.0	1.0					MATCHED		
xA	1.0		1.0		1.0		1.0		CONSTRAINTS		
xB	1.0		1.0		1.0		1.0		TARGET FUNCTION		
xS	1.0		1.0		1.0		1.0				
MEASURED											
	IN				OUT						
	Feed	Solvent	Raffinate	Extract					IN-OUT		
TOTAL	2.000	2.000	3.000	3.000					-2.000		
xA	0.200	0.400	0.300	0.900	0.000	0.000	0.300	0.900	-1.400		
xB	0.750	1.500	0.522	1.566	0.000	0.000	0.522	1.566	-0.279		
xS	0.050	0.100	0.178	0.629	1.000	2.000	0.178	0.629	-0.321		
SUMx	1.000	1.000	1.000	1.000							
MATCHED											
	IN				OUT						
	Feed	Solvent	Raffinate	Extract					IN-OUT		
TOTAL	1.100	2.200	3.300	4.400					-4.400		
xA	0.110	0.121	0.330	1.089	0.000	0.000	0.330	1.089	-2.904		
xB	0.863	0.949	0.475	1.568	0.000	0.000	0.475	1.568	-1.037		
xS	0.028	0.030	0.195	0.643	1.000	2.200	0.195	0.643	-0.459		
SUMx	1.000	1.000	1.000	1.000							
RELATIVE DIFFERENCE											
	IN				OUT						
	Feed	Solvent	Raffinate	Extract							
TOTAL	0.450	-0.100	-0.100	-0.467							
xA	0.450		-0.100	-0.467							
xB	-0.150		0.090	-0.335							
xS	0.450		-0.094	0.260							
WEIGHTING COEFFICIENT * SQUARE OF RELATIVE DIFFERENCE											
	IN				OUT						
	Feed	Solvent	Raffinate	Extract							
TOTAL	0.203	0.010	0.010	0.218							
xA	0.203		0.010	0.218							
xB	0.023		0.008	0.112					SUM		
xS	0.203		0.009	0.068					1.293		