On the Synthesis of Distillation Sequences for Mixtures of Water, Hydrogen Chloride and Hydrogen Fluoride

P. Pöllmann, SGL GROUP
A.J. Gerbino, AQSIm (Speaker)
Problem Statement

Given ...

An aqueous feed mixture, which contains 13 wt-% HCl and 0.5 wt-% HF

Question ...

Is it possible, to produce an hydrochloric acid of 31 wt-% HCl, with an HF impurity of 50 ppm maximum?

Solution ...

... see the following presentation
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- Ordinary Distillation, Splits and Products
- Simple Distillation (Open Evaporation)
- Simple vs. Ordinary Distillation

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- Topological Structure of OE Diagrams
- Singular Points (Pure Components and Azeotropes)
- Examples of Possible OE Diagram Structures
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Mixtures of substances A, B and C can be represented in a triangular diagram. In the figure, two edges of the triangle coincide with the axes of a co-ordinate system. The pure components are the corners, binary mixtures are the edges, and ternary mixtures fill the inner area of the triangle.

For the mixture M the mass fractions of components B and C, $x_{BM}$ and $x_{CM}$, can be read directly from the abscissa or ordinate. These two mass fractions are enough to specify the mixture composition, since $x_A + x_B + x_C = 1$.

If necessary, the composition of component A in the mixture M can be determined from the diagram by establishing the ratio $m/a$. This way of finding compositions works in general, even if the triangle is not rectangular or does not have equal side lengths.
When, in the following, concentration scales are not needed for discussion of matter, the composition triangle will look like shown here.

The diagram shall be isobaric. If necessary, the constant pressure will be given somewhere near or inside it.

The names of the pure components, if necessary along with their boiling points in parentheses, will be given at the corners.

The volatilities of the components shall be A (most volatile) - B - C (least volatile).
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By material balance, the points of feed F, distillate D and bottoms W of a distillation column are located on a straight line.

Three qualitatively different splits are possible:

1 - recovery of the most volatile component A in the distillate product D₁,

2 - recovery of least volatile C in the bottoms product W₂, and

3 - none of the former, i.e., distribution of the medium volatile component B between distillate and bottoms products.
The straight line through the point of component C and the point of the feed F is the locus of mixtures having the same ratio of components A and B as the feed.

By nature of distillation,

• from the feed location to the top of the column, the ratio of more volatile A increases to the expense of B,

• and from the feed to the bottoms less volatile B is enriched compared to A. This way, the horizontally shaded areas are found.

By analogous reasoning, the vertical shading follows.
Determination of Ternary Distillation Product Composition Regions

The shaded two-fold triangular region is the locus of possible distillate and bottoms products.

It can easily be constructed, even by a rough sketch made free-hand ("pen-and-paper" method), and is very useful for distillation process synthesis.
Very interesting for process synthesis are the products, which are practically free of at least one component.

Following the rule of construction, i.e., drawing straight lines through the points of the feed and the components with extreme volatility, the point B will never be part of the shaded areas.

The component B with intermediate volatility can never be a product, whatever composition the feed F might have.

To symbolise this, the point B has got an open circle.
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A liquid L shall be submit to open evaporation in a heated pot. Above the surface of the liquid L with composition x a vapour V with composition y is formed in thermodynamic equilibrium. The vapour that is removed at the moment of formation, carries volatile matter with itself.

By mass balance, liquid L changes composition as indicated by a short arrow being co-linear with the dashed line being tangent to the liquid composition profile.

After infinite time, the last drop in the pot will be least volatile component C. During the process between L and C, the boiling temperature in the pot can increase only.

The composition profile of the liquid in the heated pot of open evaporation is called residue curve.
Depending on the initial composition $L_1$, $L_2$ or $L_3$ of the mixture in the pot, the residue curves proceed on different paths, but all terminate at least volatile component $C$.

If the practical process of open evaporation could be inverted, then the profile starting at $L$ would run through $L_1$ and terminate at most volatile $A$.

If a binary mixture is evaporated, then an edge will be the profile. Profiles inside follow the pattern described by the edges.

There is no ternary profile, that is able to meet $B$. To symbolise this, the point $B$ is an open circle.

There is no ternary profile, that is able to cross the boundary of the triangle.
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Simple vs. Ordinary Distillation

The liquid composition profiles of open evaporation (residue curves) and ordinary distillation are similar. The difference is the curvature, being stronger for the ordinary distillation profiles.

Two different liquid composition profiles in the rectifying section of an ordinary distillation column are shown. Both originate at the same distillate product D.

Clearly, if there is no distillation at all, then the column will be filled with liquid D. The larger the reboiler and condenser loads are chosen, the further proceeds the distillation, the longer extends its profile.

In the limit of infinite reflux ratio, or, equivalently, equal L and V inside the column, which also means zero amount of D, the profile of ordinary distillation approaches the residue curve.
There is evidence in literature, that the boundary of the “non-interesting” ordinary distillation products can be well approximated by the residue curve running through the point of the feed.

Consequently, the straight-line sketch of the product composition regions (dashed lines) yields a rough superset of the correct regions.

More rigorous is the yellow area.
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This diagram does no longer show residue curves inside it. By just tracing the boundaries of the region, within which the open evaporation process takes place, it is reduced to the information content from a qualitative point of view. It does not matter how the residue curves run inside the triangle - if necessary, they could easily be sketched using the information given by arrows.

The shape of this structural diagram is determined by the characters of the singular points at the corners - the singular points can be classified into

- ones having arrows only pointing in or out (C or A),
- and others (only one in this case - B) having both kinds of arrows.
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The “Mathematics” of Open Evaporation (OE)

• Topological Structure of OE Diagrams

• **Singular Points (Pure Comps and Azeotropes)**

• Examples of Possible OE Diagram Structures
The locations of singular points are not limited to corners only (pure components). They also can be located on edges (binary azeotropes) or in the interior (ternary azeotropes) of the composition triangle. Speaking in terms of open evaporation, singular points are pure components or mixtures, which evaporate at constant temperature, sending out a vapour with same composition as the liquid.
Types of Singular Points of Open Evaporation Diagrams

Singular points (pure components or azeotropes) of ternary open evaporation can be classified with respect to where the process will run (residue curves shown with arrows), after the process has been initiated close by the singular point.

Points which the process can nothing but run into (stable nodes) or nothing but leave (unstable nodes) are shown as full circles ●. All other singular points (saddle points) have open circles ○.

Every singular point has dividing lines attached to it (shown as thick lines), which are clearly visible at saddle points, but which could not be found out at nodes if they were not drawn using thick lines.
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Examples of Possible OE Diagram Structures

A (56)  C (61)  M (65)
(65)  B (80)
(61)  (54)

A = Acetone
B = Benzene
C = Chloroform
EB = Ethyl Benzene
EG = Ethylene Glycol
M = Methanol
O = Octane

(...) = boiling temperature (°C) of singular point
## The HCl-HF-Water Mixture

### Known Facts
- Open Evaporation (OE) Experiments
- Measurements vs. OLI MSE Calculations

### Distillation Process Synthesis for HCl-HF-Water
- Topological Structure of the OE Diagram
- Distillation Products and Boundaries
- Suggested Distillation Column Sequence
What commonly is known about the system of HCl, HF and water, is given in the composition triangle shown here.

There are two azeotropes with maximum temperature “Az.” and water associated,

- at 20 % HCl
- and 37% HF.

If already possible, the correct arrows and types of singular points have been indicated.

But there is lack of information ...
Starting Point of Thermodynamic Topological Analysis

There is lack of information at all places with question marks.

A single ? asks, how open evaporation behaves in the close surroundings of the singular point. Should it be a node ● or a saddle point ○?

A double ?? asks the additional question, “does an azeotrope exist at all”.

X<sub>HF</sub> HF (20°C)

Az. (113°C)

p = 1.013 bar

HCl (-85°C)

H<sub>2</sub>O (100°C) Az. (109°C) 

X<sub>HCl</sub>
Potential Open Evaporation Structures for HCl-HF-water Mixtures

Based on
- the previously given theoretical background
- the known facts about the HCl-HF-water system
- some combinatorics

there exist 10 different potential candidates for open evaporation diagrams of the HCl-HF-water system.

At this point, an experiment is inevitable ...
Planning Open Evaporation Experiments

The HCl-water azeotrope - is it
• a saddle point  ○ ?
• or a node  ● ?

The following slides will focus on the subset

\[ 0 < x_{\text{HCl}}, x_{\text{HF}} < 0.2 \]

of the composition triangle.

(... = boiling temperature (°C) of singular point (@ 1 atm)
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An open evaporation experiment be initiated with liquid $L_1$. During a certain time of evaporation, the liquid be in the point $L_2$. All the vapour that is released be collected, accumulated and analysed. The liquids concentrations be measured as well.

$L_1$, $L_2$ and further measurements of the liquid in the pot are single points of the, by nature, continuous residue curve.

$L_1$ or $L_2$ has an equilibrium vapour $V_1$ or $V_2$, respectively. Clearly, the composition of the accumulated vapour, which is the only information on vapour compositions the experiment has brought, is located somewhere in between $V_1$ and $V_2$. The accumulated vapour composition cannot be taken as a measurement of the equilibrium vapour composition $V_1$ or $V_2$. 

\[ p = \text{constant} \]
Open Evaporation Experimental Results

In order to find out the nature of the HCl-water azeotrope in the system of HCl, HF and water, open evaporation experiments have been performed in the chemical laboratory at SGL Carbon, Meitingen.

Mixtures at the origins of arrows in the diagram were initial liquids of open evaporations. The arrows indicate the change of liquid composition during each experiment. The final states near the pointers of the arrows were measured.

As can be seen, the liquid mixtures are enriched with respect to HF during each and every experiment. In terms of open evaporation, the HCl-water azeotrope is a saddle point.

In terms of ordinary distillation, this means, that mixtures rich in HF are to be expected as bottoms products, and mixtures free from HF as distillates.
Postulated Structure of the HCl-HF-water OE Diagram

Based on the assumptions

• there is no binary HCl-HF azeotrope

• there is no ternary azeotrope

and following the experimental results, one open evaporation diagram structure can be identified.

The validity of the assumptions will have to be checked in further work.

(...)= boiling temperature (°C) of singular point (@ 1 atm)
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Comparing Measured and Simulated Residue Curves

One of the residue curves, that have been measured by SGL Carbon, Meitingen, has been recalculated using the AspenPlus process simulator and a special model provided to SGL Carbon by OLI Systems.

As can be clearly seen, the qualitative shape of the measured profile is met by the OLI model, but missed by AspenPlus.

In terms of ordinary distillation (bottoms product is found where temperature increases), AspenPlus predicts bottoms product near the HCl-water azeotrope, whereas OLI and experiment see it near the HF-water azeotrope.

(A note on the difference between measured and OLI - What has been calculated was a sequence of flashes, taking every y as the new x, which is not a residue curve, but topologically equivalent w.r.t starting and ending points or dividing lines.)
Problem Statement (repeated)

Given ...

An aqueous feed mixture, which contains 13 wt-% HCl and 0.5 wt-% HF

Question ...

Is it possible, to produce an hydrochloric acid of 31 wt-% HCl, with an HF impurity of 50 ppm maximum?

Solution ...

... see the remainder of the presentation
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Under atmospheric pressure, hydrochloric acid of 20 mass-% HCl has the maximum boiling temperature of 109°C (azeotrope). Hydrofluoric acid exhibits a maximum azeotrope at 37% HF and 113°C. If other azeotropes do not exist, then the shown diagram represents the structure of open evaporation.

For example, the structure of the system octane - ethylene glycol (EG) - ethyl benzene (EB) is reciprocal, as shown below.
Open evaporations of HCl-HF-water mixtures can only proceed along paths, a few of which are shown qualitatively.

The line of junction between the azeotropes acts as a dividing line, which - like an edge of the composition triangle - cannot be traversed by any profile of open evaporation.

It is like the H₂O-Az.-Az. triangle makes up a composition triangle of its own.
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Because of interrelations between open evaporation and ordinary distillation, the material balance line of a ternary (ordinary) distillation column cannot be located across the distillation boundary.

In analogy to the HCl-water azeotrope, the distillation boundary is the reason why the mixture cannot be separated by ordinary distillation.

But ...
The sensitivity of the HCl-water azeotrope on pressure is sufficient for pressure-swing distillation presenting a practical process variant for “breaking the azeotrope”.

What if HF is associated? - The pressure will not be able to change the structure of the open evaporation diagram.

Calculations indicate the HF-water azeotrope will be unchanged by pressure (whether or not it changes, does not matter for the following), but the shift of the HCl-water azeotrope state lets the distillation boundary follow in the indicated way.
The “pen-and-paper” sketch of distillation product regions can be applied to the small triangle by full analogy ...
The regions of distillate D and bottoms product B of ordinary atmospheric distillation, that can be obtained from the feed F, are shaded.

It should be possible to obtain a distillate practically free of HF impurities, which, in turn, can be separated by pressure swing distillation to obtain concentrated hydrochloric acid.

The bottoms product is small in amount and expected to be somewhat like the HF-water azeotrope.
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An aqueous feed mixture, which contains 13 wt-% HCl and 0.5 wt-% HF

Question ...

Is it possible, to produce an hydrochloric acid of 31 wt-% HCl, with an HF impurity of 50 ppm maximum?

Solution ...

The following process should work in principle!
Distillation Process for Purifying Hydrochloric Acid from HF

The first column has the task of purifying the feed mixed acid. By reasoning as outlined in the preceding slides, this first separation is feasible. In addition, a practical design of the first column has been obtained using the ESP simulator of OLI Systems.

The remainder of the process is conventional pressure-swing distillation for separating hydrochloric acid.
Summary

For mixtures of HCl, HF and water ...

... Open evaporation experiments have been performed by SGL Carbon, Meitingen, Germany

... The OLI MSE VLE model is supported by the measurements

... The topological structure of open evaporation has been postulated

... A distillation process for removing HF impurities from hydrochloric acid has been suggested

... A preliminary design of the HF column was possible using OLI’s ESP simulator