## CE 407 Notes <br> Binary distillation theory of Murphree tray efficiency

Consider a binary distillation process.
Octanol ("OCT") is the light component (more volatile, lower boiling); its boiling point at e.g. 14 mm Hg is $94^{\circ} \mathrm{C}$.

Lactic acid ("LA") is the heavy component (less volatile, higher boiling); its boiling point at e.g. 14 mm Hg is $132^{\circ} \mathrm{C}$.

Comment: In this set of notes we focus on the heavy component, lactic acid, and mole fractions $x$ and $y$ refer to it. This departs form the usual convention according to which $x$ and $y$ refer to the light component. In general, please go by the usual convention.

## Q: How does the falling liquid reflux absorb lactic acid from the rising vapor?

A: Lactic acid transfers from the interior of each vapor bubble to the liquid-vapor interface, and from there to the bulk liquid.


Let's focus on one bubble of vapor surrounded by liquid.


Equilibrium distribution of lactic acid at interface:

$$
y^{*}=x_{\text {bulk }} \gamma P^{\text {sat }} / P
$$

(Raoult's law modified by activity coefficient; mole fractions, activity coefficient and saturated vapor pressure refer to lactic acid)

What equation describes the physics?

$$
d(\text { moles of lactic acid in bubble }) / d t=-\left(4 \pi R^{2}\right) \times k_{y}\left(y_{\text {bulk }}-y^{*}\right)
$$

where

$$
\begin{aligned}
a & =\text { radius of bubble, } \\
k_{y} & =\text { mass transfer coefficient for transfer of lactic acid through octanol-rich gas, } \\
y_{\text {bulk }} & =\text { gas-phase mole fraction of lactic acid in bulk of bubble, } \\
y^{*} & =y^{*}\left(x_{\text {bulk }}\right)=\text { gas-phase mole fraction of lactic acid at liquid-vapor interface } \\
& =x_{\text {bulk }} \gamma P^{\text {sat }} / P \text { (Raoult's law modified by activity coefficient), and } \\
x_{\text {bulk }} & =\text { mole fraction of lactic acid in liquid (assumed well-mixed). }
\end{aligned}
$$

The bubble forms at one of the holes at the bottom of the tray at time $t=0$. It rises through the liquid, and pops through the surface at time $L / u_{\text {bubble }}$, where $L$ is the depth of liquid on the tray, and $u_{\text {bubble }}$ is the speed at which the bubble rises due to buoyancy. In other words, the residence time of the bubble in the liquid is $L / u_{\text {bubble }}$.

## Q: What's the upshot of all this?

A: E.V. Murphree showed in 1925 that

$$
\frac{y_{1}-y_{2}}{y^{*}-y_{2}}=1-\exp \left(-\frac{k_{y} A L}{u_{\text {bubble }}}\right)=\eta_{M}
$$

(with slight differences in notation and formulation; cf. Eq. (6) in Murphree (1925)), where $A$ is the interfacial area per mole of vapor on the tray. The quantity $\eta_{M}$ is called the Murphree efficiency or tray efficiency. The larger the mass transfer coefficient $\left(k_{y}\right)$, the larger the interfacial area ( $A$ ) or the longer the residence time of the bubble spends on the tray ( $L / u_{\text {bubble }}$ ), the closer $\eta_{M}$ is to unity, and the more nearly equal $y_{1}$ is to $y^{*}$. A tray for which the vapor leaving the tray has a lactic acid mole fraction perfectly in equilibrium with that of the liquid leaving the tray (i.e., $y_{1}=y^{*}\left(x_{1}\right)$ ) is called an ideal or theoretical tray ( $\eta_{M}=1=100 \%$ ).

## Q: What is the take-home message we want to remember here?

A: In distillation (and other staged operations), we are usually given a tray efficiency $\eta_{M}$. When we work in terms of $\eta_{M}$, mass transfer seems not to enter distillation calculations. However, the joy of mass transfer is actually embedded in $\eta_{M}$.

Problem: Suppose the volume fraction of bubbles in the froth (bubbly liquid on tray) is $\phi=0.4$. What is $A$, the interfacial area per mole of vapor on the tray, for a bubble diameter of (a) 2 mm and (b) 2 cm ? (The important parameter $A$ appears in the equation for $\eta_{M}$ at the top of the previous page.) Assume atmospheric pressure.

Solution: One bubble has volume $4 \pi a^{3} / 3$ and surface (interfacial) area $4 \pi a^{2}$. For a given total volume of froth (bubbly liquid on the tray) $V$,

Vapor volume in total volume $V=\phi V$
Moles of vapor in total volume $V=$ (vapor volume $) \times($ molar density from ideal gas law $)$ $=(\phi V) \times(P / R T)$.
Also,
Number of bubbles $N_{\text {bubble }}$ in total volume $V=$ (vapor volume) $/$ (volume of one bubble)

$$
=(\phi V) /\left(4 \pi a^{3} / 3\right)
$$

Surface area of bubbles in total volume $V=N_{\text {bubble }} \times\left(4 \pi a^{2}\right)=\left[\phi V /\left(4 \pi a^{3} / 3\right)\right] \times\left(4 \pi a^{2}\right)$

$$
=3 \phi V / a
$$

With these intermediate results,

$$
\begin{aligned}
A & =(\text { surface area of bubbles in total volume } V) /(\text { moles of vapor in total volume } V) \\
& =(3 \phi V / a) /[(\phi V) \times(P / R T)]=3 R T /(a P)
\end{aligned}
$$

Note that the volume fraction of bubbles in the froth actually cancels out of the calculation, and is therefore not needed. The desired numerical answers are
(a) $A=3 \times[8.314 \mathrm{~J} /(\mathrm{mol} \mathrm{K})] \times(298.15 \mathrm{~K}) /[(0.001 \mathrm{~m}) \times(101325 \mathrm{~Pa})]$
$=73.4 \mathrm{~m}^{2} / \mathrm{mol} \leqslant$ look at that high surface area, Batman!
(b) $A=3 \times[8.314 \mathrm{~J} /(\mathrm{mol} \mathrm{K})] \times(298.15 \mathrm{~K}) /[(0.01 \mathrm{~m}) \times(101325 \mathrm{~Pa})]$
$=7.34 \mathrm{~m}^{2} / \mathrm{mol} \leftarrow$ look at that low surface area, Batman!

