Control of Gaseous Air Pollutant Emissions by Absorption into Liquid

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In general, the control of gaseous air pollutant emissions (at low pollutant concentrations such as less than 0.5% or 0.5/100 or 5000 ppm by gaseous volume) is most efficiently accomplished using liquid spray towers and a liquid which has a good absorption capacity for the air pollutant (ie low magnitude of the Henry's law constant or involves a chemical reaction which removes the air pollutant from the liquid phase). The text books usually go into great detail about the design and operation of countercurrent packed absorption towers which are commonly used in industrial chemical processing (and are covered in detail in chemical engineering books) but do not cover the design and operation of gaseous absorption *spray towers* - probably because authors are not able to copy this information from other chemical engineering books.

I. Equilibrium Solubility of a (pollutant) gas in a liquid

The solubility of an air pollutant gas (such as sulfur dioxide or SO_2) can be measured at equilibrium conditions of constant temperature and constant total pressure until the concentrations of the pollutant gas in the gas phase and in the liquid phase are constant. When a gas mixture is in equilibrium with an ideal liquid solution, the equilibrium partial pressure of the pollutant gas "A" is related to the liquid phase concentration X_A and the total pressure P by Raoult's law p_A, atm = X_A (P_{total}, atm). The literature often uses the asterick * to denote that the partial pressure is at equilibrium (see eq 12.1 p 437 Noll) so p_A* would indicate the equilibrium partial pressure of substance or pollutant A.

For non ideal liquid solutions, Henry's law relates the partial pressure of the pollutant gas or the mole fraction of the pollutant gas to the liquid phase concentration of the pollutant gas. Note that Henry's law constants do have *different units* - depending on the units of the gas phase concentration and the liquid phase concentration. Unfortunately, many texts, books, and articles are not clear regarding the units.

Two examples of Henry's law constant units are shown below (in Mathcad equation format)

First identify that a gas is dissolved in the liquid and that the mole fraction of pollutant gas dissolved in liquid is X

X = (mole gas)/(total moles in the liquid)

$$\text{moleliquid} := \text{mole} \qquad \text{molegasinliq} := \text{mole}$$

$$\text{totalmoleliquid} := \text{molegasinliq} + \text{moleliquid}$$

Then writing the equation for the Henry's law constant H note that it has units (in other words, it is easy to cancel out the moles/moles - *but these are not the same moles!!!)*

$$X := 0.2\cdot\frac{\text{molegasinliq}}{\text{molegasinliq} + \text{moleliquid}} \qquad X = 0.2\,\frac{\text{molegasinliq}}{\text{totalmoleliquid}}$$

$$H := 0.1\cdot\frac{\text{atm}}{\left(\frac{\text{molegasinliq}}{\text{totalmoleliquid}}\right)}$$

$$\text{partialpressuregas} := (H)\cdot(X)$$

$$\text{partialpressuregas} = 0.02\,\text{atm}$$

The partial pressure gas = H X and it would be niceto have an asterick * but * means multiply in Mathcad. At any rate, the partial pressure result is inpressure units - such as atm or inches Hg

$$\text{partialpressuregas} = 0.60011\,\text{in\_Hg}$$

Another form of Henry's law is the gas phase mole fraction of pollutant
y* = (m, mole fraction of pollutant in gas phase / mole fraction of pollutant in liq phase)
(X, mole fraction pollutant in liquid phase)

$$\text{ypollutantgas} := (m)\cdot(X) \qquad X = 0.2\,\frac{\text{molegasinliq}}{\text{totalmoleliquid}}$$

$$\text{molegasingas} := \text{mole}$$

$$m := 0.3\cdot\left(\frac{\text{molegasingas}}{\text{molegasinliq}}\right)$$

$$\text{totalmolegas} := \text{mole}$$

Note that m is also a Henry's Law constant, with units different from the first Henry's law constant H

$$\text{moleothergas} := \text{mole}$$

$$\text{totalmolegas} := \text{molegasingas} + \text{moleothergas}$$

$$\text{ypollutantgas} = 0.2\,m\,\frac{\text{molegasingas}}{\text{totalmolegas}} \qquad \text{ypollutantgas} = 0.2\,m\,\frac{\text{molegasingas}}{\text{molegasingas} + \text{moleothergas}}$$

It is recognized that carrying all of these units can be a burden, but it is appropriate to at least understand that these units exist because they do affect mass transfer and absorption calculation equation results. And there is not an uniform way to label the two Henry's law constants (in this example, H and m).

Making an equilibrium y-x graph for SO_2 in pure water at Temp 30C and 1 atm

$i := 0 .. 5$

There are six values of x in the table , so i = 0 to 5

$$x := \begin{pmatrix} 0.0014 \\ 0.0028 \\ 0.0042 \\ 0.0056 \\ 0.0070 \\ 0.0084 \end{pmatrix}$$

The Henry's law constant for SO_2 at 30C is given in as 0.0034 atm/mole fraction but we need
H = 42,7 moleSO_2 in gas phase/mole SO_2 dissoved in water.

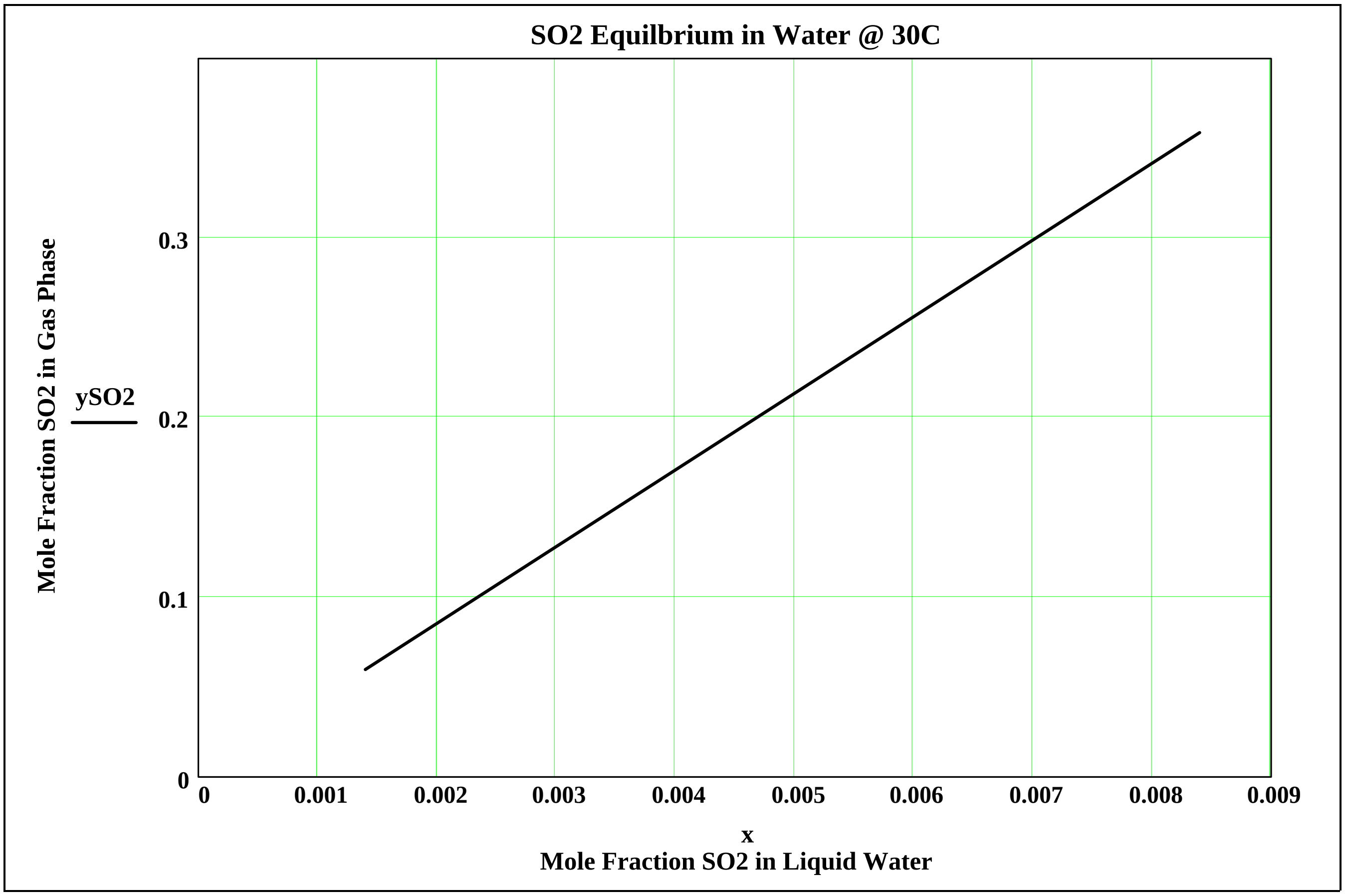
$$ySO2_i := 42.7 \cdot (x_i)$$

$$ySO2 = \begin{pmatrix} 0.06 \\ 0.12 \\ 0.179 \\ 0.239 \\ 0.299 \\ 0.359 \end{pmatrix}$$

$$ppmSO2 := (10^6) \cdot ySO2$$

$$ppmSO2 = \begin{pmatrix} 5.978 \times 10^4 \\ 1.196 \times 10^5 \\ 1.793 \times 10^5 \\ 2.391 \times 10^5 \\ 2.989 \times 10^5 \\ 3.587 \times 10^5 \end{pmatrix}$$

Shown below is the equilibrium Y-X diagram for SO_2 in equilibrium with SO_2 dissolved in water



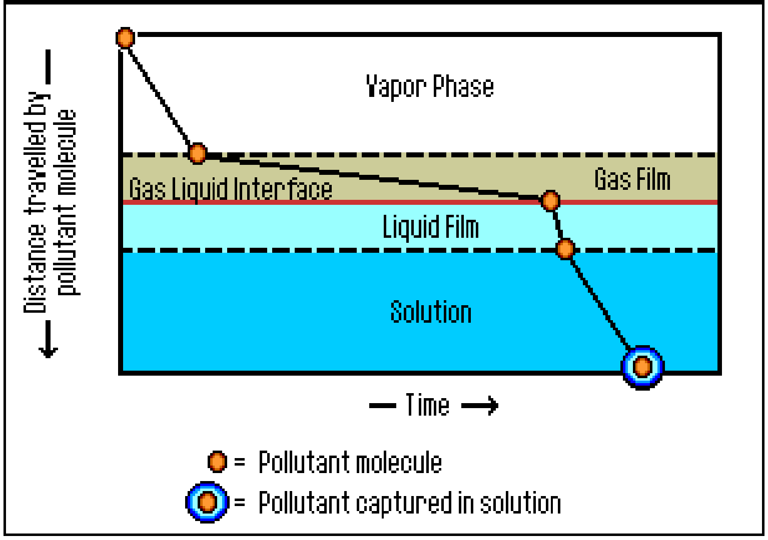
Note that the SO_2 gaseous phase concentrations is in this example are in the 60,000 to 360,000 ppm range whereas air pollutant SO_2 stack gas concentrations are more likely in the 200 to 2000 ppm & perhaps as high as 8% or 80,000 ppm for SO_2 emissions from some processes in copper smelting. In other words, Henry's law constants usually hold OK for the dilute air pollutant concentrations seen in air pollutant absorption control devices.

II. Mass Transfer

A. Fick's First Law of diffusion (Adolf Fick did research on the diffusion of salt in water and published an article in Ann Physik Vol 89 pp 59 1855 at the age of 26). For unidirectional binary diffusion, Fick's First Law describes the diffusion of a component (pollutant molecule in our case) A in a media B (a gaseous media in our case) where D_{AB} is the diffusion coefficienct of pollutant A in the fluid media B (B is a gas in our case) and dC_A/dx is the pollutant concentration gradient ("driving force") of the pollutant A from the bulk gas to the gas-liquid interface (for our caseof absorption of a gaseous pollutant A into a liquid). A digram of the Two-Film theory concentration gradients is shown in many texts and shown below (the 2 films are the gas film and the liquid film with the gas-liquid interface in between).

The air pollutant concentration gradient dConc / dx causes the air pollutant molecules to diffuse downward from the vapor phase across the gas film and then across the liquid film and into the solution. This illustration shows that the air pollutant travels slowly across the gas film (takes longer time) and fast across the liquid film and then into the bulk solution. This graph is for a gas phase controlled mass transfer case.

Figure 2. Graph (A)



D_{AB} is the diffusion coefficient or diffusivity of the pollutant gas A through fluid (gas) B

$$D_{AB} := 0.2 \cdot \frac{cm^2}{sec}$$

$$dC_A := 0.001 \cdot \frac{mole}{cm^3}$$

$$dx := 0.001 \cdot cm$$

$$pollutant := 1$$

dC_A is the concentration gradient of pollutant A over the distance dx

$$J_A := -\left(D_{AB}\right) \cdot \left(\frac{dC_A}{dx}\right)$$

Fick's First Law for the flux of pollutant A or J_A

$$J_A = -0.2 \frac{mole \cdot pollutant}{cm^2 \cdot sec}$$

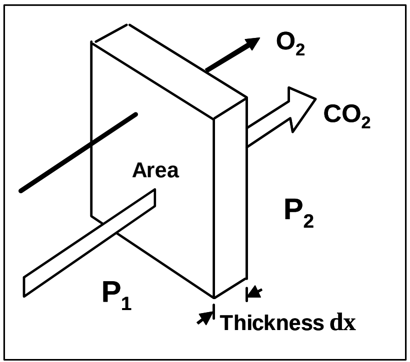
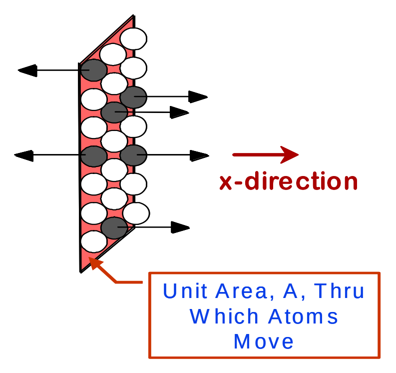


Illustration at left shows O_2 and CO_2 diffusing through Area of Thickness dx



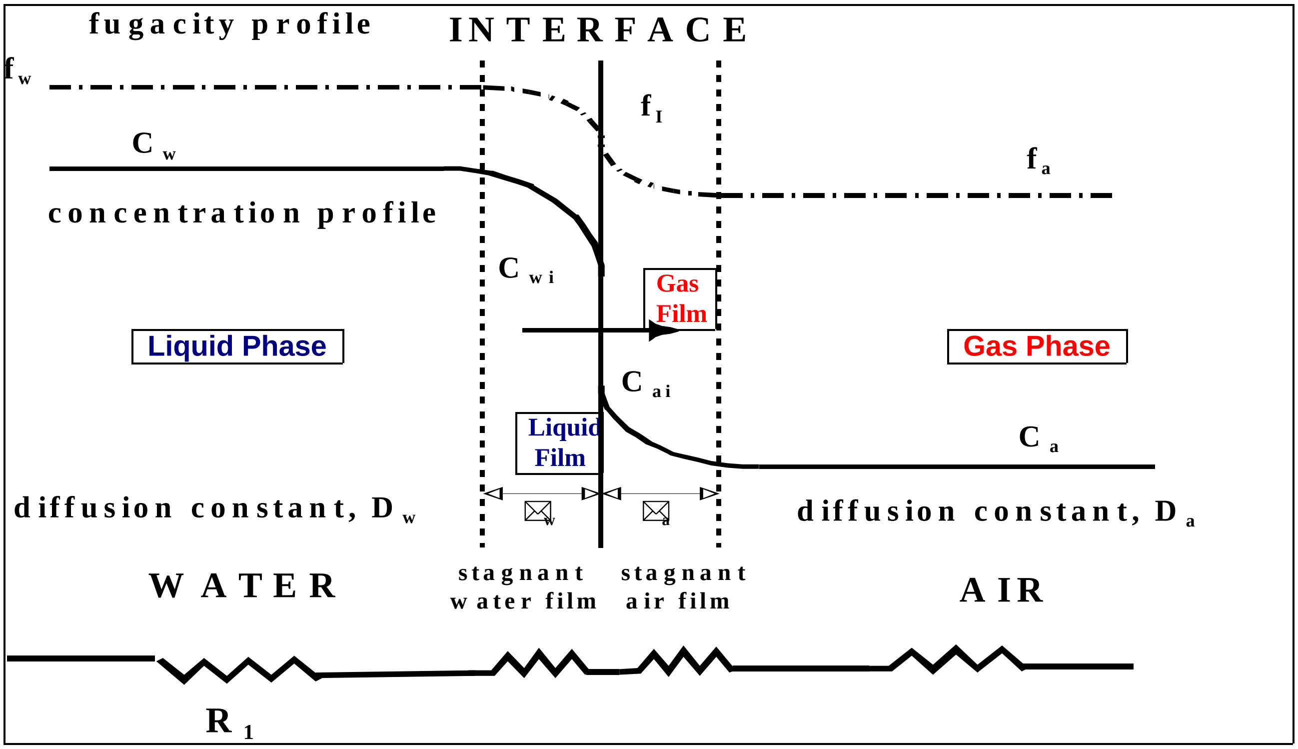
The illustration to the right shows 4 gray colored spheres moving or diffusing to the right and 2 gray spheres diffusing to the right, for a net diffusion to the right of 2 gray spheres which in this illustration are "atoms" but in the case of air pollutant gases are molecules.

This prior example calculation shows the mass transfer or flux of pollutant A through fluid B as

0.2 moles of pollutant A /cm^2 second

Why is the flux quantity negative in the text definitions for Fick's First Law?
Perhaps because the conc. gradient for the compound being absorbed from the gas phase into the liquid phase is a negative (decreasing concentration towards the liquid phase)

Evaporation of Liquid Water into Gaseous Air (2 Film Diagram below)



$N := K_{Liquid} \cdot (C_{Liquid} - C_{LiquidInterface})$

$K_{Gas} := 2.0 \cdot \frac{mole}{cm^2 \cdot sec}$

$molepollutant := mole$

Overall Liquid Phase mass transfer coefficient = K_{Liquid}

$Y_{Gas} := 0.1 \cdot \left(\frac{molepollutant}{mole}\right)$

$Y_{Star} := 0.01 \cdot \left(\frac{molepollutant}{mole}\right)$

$\frac{1}{K_{Liquid}} := \frac{1}{k_{Liquid}} + \frac{1}{k_{Gas} \cdot H}$

$N := (K_{Gas}) \cdot (Y_{Gas} - Y_{Star})$

Overall Gas Phase mass transfer coefficient = K_{Gas}

$\frac{1}{K_{Gas}} := \frac{1}{k_{Gas}} + \frac{H}{k_{Liquid}}$

$N := \left(2.0 \cdot \frac{mole}{cm^2 \cdot sec}\right) \cdot \left[\left[0.1 \cdot \left(\frac{molepollutant}{mole}\right)\right] - \left[0.01 \cdot \left(\frac{molepollutant}{mole}\right)\right]\right]$

Note that the K_{Gas} units are mole/cm^2 sec or lbmole/ft^2 hr

$N = 0.18 \frac{molepollutant}{cm^2 \cdot sec}$

H is the Henry's Law Constant in appropriate units

k_{Liquid} is the liquid film mass transfer coefficient (lbmole/ft^2 hr atm) or (cm/sec)

k_{Gas} is the gas film mass transfer coefficient (lbmole/ft^2 hr atm) or (cm/sec)

Ficks First Law of diffusion is similar to Fourier's Law of heat conduction

q, Btu/hr = - (k, Btu/hr ft F^o) [(Δ Temp, F^o) / (Δ y, ft)]

where k is the thermal conductivity of the material and ΔT / dy is the temp gradient

B. Absorption Tower Mass Balance

$\text{lbmole} := (\text{mole})\cdot(453.6)$

At steady state conditions, a mass balance on an absorption tower shows that mass pollutant A into the tower = mass pollutant A out assuming there is no chemical reaction which generates or destroys pollutant A. Using G_m and L_m for the molar flow rates of the gaseous and liquid media streams in an absorption tower (perhaps in units like lb-moles/ft^2 hr) and X and Y as the mole fractions of pollutant A in the liquid and gas streams, the steady state mass balance (where M_G = gas molecular wt, RG = universal gas constant R, M_L = liguid molecular wt, ra = gas density, L = liquid mass flow in lb/ft^2 hr, Lm = liquid molar flow, lbmole/ft^2 hr) can be written as

$G_m := 50\cdot\frac{\text{lbmole}}{\text{ft}^2\cdot\text{hr}}$

$T := (460 + 68)\cdot R$

$P := 1\cdot\text{atm}$

$M_G := \frac{29\cdot\text{gm}}{\text{mole}}$

$RG := 0.082054\cdot\frac{\text{liter}\cdot\text{atm}}{\text{mole}\cdot K}$

$\rho_G := \frac{P\cdot M_G}{RG\cdot T}$

$L := \left(15\cdot\frac{\text{gal}}{1000\cdot\text{ft}^3}\right)\cdot\left(8.34\cdot\frac{\text{lb}}{\text{gal}}\right)\cdot\left(\frac{1}{\rho_G}\right)\cdot(G)$

$G := G_m\cdot M_G$

$G = 1450.02\frac{\text{lb}}{\text{ft}^2\cdot\text{hr}}$

$M_L := 18\cdot\text{gm}\cdot\text{mole}^{-1}$

$L_m := \frac{L}{M_L}$

$L = 2411.66\frac{\text{lb}}{\text{ft}^2\cdot\text{hr}}$

$L_m = 133.979\frac{\text{lbmole}}{\text{ft}^2\cdot\text{hr}}$

$\rho_G = 0.07522\frac{\text{lb}}{\text{ft}^3}$

Above is presented the liquid and gas flow rates in lbmole/ft^2 hr and lb/ft^2 hr along with the relationship between the Liquid /Gas flow rate ratio in gallons liquid/1000 ft^3 gas and the flow rates. Also, it is nice to have the gas velocity (superficial velocity which assumes the tower is empty) in the absorption tower as this can give a good indication of the approximate gas residence in the tower.

$\text{GasVelocity} := \frac{G}{\rho_G}$

$\text{GasVelocity} = 5.355\frac{\text{ft}}{\text{sec}}$

C. Equation for the Operating Line - Pollutant Mass Balance on Absorption Tower

The operating line provides a graphical representation of the actual pollutant concentrations in the gas and liquid phases throughout a steady state absorption tower. In other words, if samples of the gas and liquid are extracted from the absorption tower, the measured pollutant concentrations in the gas y and in the liquid x should agree with the operating line concentrations on the graph. At steady state operation (which is when the gas flow, liquid flow, y_{in}, and x_{in} are all constant), the y and x concentrations change only with distance along the axis of the absorption tower (one-dimensional variation in concentrations).

Using a pollutant mass balance around the absorption tower

Mass of pollutant into tower = Mass of pollutant out from tower

$(x_{in}\cdot L_{in}) + (y_{in}\cdot G_{in}) := (x_{out}\cdot L_{out}) + (y_{out}\cdot G_{out})$

Assumptions are:

1) Steady state flow. No change in gas or liquid flow rates through the tower
2) No chemical reactions to create pollutant inside the tower.
3) $L_{in} = L_{out}$ and $G_{in} = G_{out}$
4) Constant temperature

$L(x_{out} - x_{in}) := G(y_{in} - y_{out})$

Solving for y_{in}

$y_{in} := \left(\frac{L}{G}\right)\cdot(x_{out} - x_{in}) + y_{out}$

This is the equation for the operating line plotted on a y - x diagram

Question Does this mass balance equation work for both co-current and countercurrent flow? Yes. In co-current flow, both the liquid and gas enter at the top of the tower and the liquid flows down because of gravity, the gas flows down because of the pressure drop.

D. Number of Mass Transfer Units

$$N_{OG} := \int_{y_{out}}^{y_{in}} \frac{1}{y - y_{star}}\, dy$$

y_{star} is gas phase concentration of pollutant in equilibrium with the liquid pollutant concentration x. In books y_{star} is shown as y*

To calculate the number of mass transfer units NOG, it is suggested that you:

1) First assume that the equilibrium conc. y* or $y_{star} = 0$ Then NOG = $\int_{y_{out}}^{y_{in}} \frac{1}{y}\, dy = \ln\left(\frac{y_{in}}{y_{out}}\right)$

This will give you the minimum N_{OG} needed for this situation

2) Next assume that both the equilibrium and operating lines are straight

Be careful when calculating the ystar values

$$N_{OG} := \left[\frac{(y_{in} - y_{out})}{(y - \text{ystar})\text{in} - (y - \text{ystar})\text{out}}\right]\left[\ln\cdot\left[\frac{(y - \text{ystar})\text{in}}{(y - \text{ystar})\text{out}}\right]\right]$$

The above equations for N_{OG} work for both countercurrent and co-current towers. Note that the Colburn Chart which is in many texts (used to get N_{OG}) *works only for countercurrent towers* & it is Mike Pilat's recommendation that this Colburn Chart *not* be used (too easy to mess it up).

Question Are co-current absorption towers used for air pollution control?
Answer: Yes, many spray droplet scrubbers have co-current flow as the droplets flow along with the gases Look at the spray droplet scrubbers at Colstrip Montana coal-fired power plant or the wet-dry spray tower at the Spokane Municipal Incinerator which are co-current absorption systems. Unfortunately, very few books cover co-current absorption towers.

See the Mathcad file AmmoniaAbsorption.mcd for an example calculation for absorption of ammonia gas NH_3 into water and it uses the data of Fellinger who was an U of W chemical engr student working on ammonia sulfite pulping research. Fellinger's data is for the H_{OG} or height of overall mass transfer unit for 1.5 inch Raschig ring packing for absorption towers.

E. Overall Mass Transfer Coefficients

$$N := (K_{Gas})\cdot(Y_{Gas} - Y_{Star})$$

Overall Gas Phase mass transfer coefficient = K_{Gas}

Overall Gas Phase mass transfer coefficient = K_{Gas}

$$\frac{1}{K_{Gas}} := \frac{1}{k_{Gas}} + \frac{H}{k_{Liquid}}$$

$$N := \left(2.0\cdot\frac{\text{mole}}{\text{cm}^2\cdot\text{sec}}\right)\cdot\left[\left[0.1\cdot\left(\frac{\text{molepollutant}}{\text{mole}}\right)\right] - \left[0.01\cdot\left(\frac{\text{molepollutant}}{\text{mole}}\right)\right]\right]$$

Note that the K_{Gas} units are mole/cm^2 sec or lbmole/ft^2 hr and not molepollutant / cm^2 sec or lbmolepollutant /ft^2 hr

$$N = 0.18\,\frac{\text{molepollutant}}{\text{cm}^2\cdot\text{sec}}$$

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