

# Emission Estimate Methods

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Determinations of emissions for certain chemical process operations are often needed when 1) obtaining environmental permits, 2) planning for pollution control equipment for new operations, 3) reacting to the impact of new environmental regulations or 4) assessing impact of possible equipment failure. Consequently, a substantial number of chemical engineering calculations are needed to answer fundamental questions of environmental pollution such as: 1) Where does the pollutant go? and 2) How fast does it get there? There are many documented methods that use best practices based on mass balance measures. However, there are occasions where simple mass balances cannot be conducted. Thus ostensible methods are needed to estimate emissions where mass balance techniques are not easily obtained. Several cases are presented here that illustrate the methods of calculation for actual aerospace conditions of operation and the results of these method applications are summarized.

**Keywords:** Chemical process emissions, pollution control, environmental issues

## Introduction

Determinations of emissions for certain chemical process operations are often needed when 1) obtaining environmental permits, 2) planning for pollution control equipment for new operations, 3) reacting to the impact of new environmental regulations or 4) assessing impact of possible equipment failure. Consequently, a substantial number of chemical engineering calculations are needed to answer fundamental questions of environmental pollution such as: 1) Where does the pollutant go? and 2) How fast does it get there? There are many documented methods that use best practices based on mass balance measures. However, there are occasions where simple mass balances cannot be conducted. Thus ostensible methods are needed to estimate emissions where mass balance techniques are not easily obtained. Several cases are presented here that illustrate the methods of calculation for actual aerospace conditions of operation and the results of these method applications are summarized.

## Chiller unit refrigerant escape — Gaseous diffusion method

A chiller unit had an incident involving R123 refrigerant.\*\* Over a two-day period, an estimate of the amount of R123 vapor that would potentially exit a long pipe was needed. For purposes of this calculation, this pipe is considered to be straight and 15.2 cm (6 in.) in diameter. The R123 reservoir is considered to be at 21°C (70°F; 294.3 K).

### Calculation

Initially, consideration needs to be given to pressure drop effects at the pipe exit due to ambient wind conditions on the roof. A simplified version of the Bernoulli equation can be used:

$$\Delta P = \frac{1}{2} \rho (V_1^2 - V_2^2) \quad (1)$$

Given the density of air<sup>1</sup> at 21°C (70°F) to be 1.21 kg/m<sup>3</sup>, a 4.47-m/sec (10-mph) wind speed would then produce a pressure drop of only  $0.5 \times 1.21 \times (4.47^2 - 0) = 12.1$  Pa, which is a very small pressure differential (less than 0.002 psia) and need not be considered as a mass transfer driving force.

A more appropriate modeled approach is to perform the subject estimate as a result of binary mixing of gases theory. Steady state equimolar counter-diffusion at a plane equivalent to the pipe length (~52 feet) can be calculated and is related by the difference of partial pressures at two positions, temperature and distance between the liquid surface and the position of interest. Use of the gas constant,  $R$ , and the gas diffusion coefficient,  $D_G$ , must be determined.<sup>2</sup>

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\*\* 1,1 Dichloro-2,2,2-trifluoroethane,  $\text{CHCl}_2\text{CF}_3$

$$N_A = \frac{D_G(p - p_i)}{RTZ} \quad (2)$$

The gas diffusion coefficient is estimated<sup>3</sup> by use of the molecular weights of the gases of interest, temperature and various constants,<sup>\*\*\*</sup> determined by thermodynamic properties of each gas.

$$D_G = \frac{BT^{\frac{3}{2}} \left( \frac{1}{M_1} + \frac{1}{M_2} \right)^{\frac{1}{2}}}{Pr_{12}^2 I_d} \quad (3)$$

where,

$T$  = absolute temperature, 294.3 K

$M_1$  = molecular weight of air, 28.84 g/mol

$M_2$  = molecular weight of R123, 152.93 g/mol

$P$  = absolute pressure, atm

This method (Equation 3) is suggested for studying collisions of polar and non-polar molecules which is the case for air and a solvent vapor.<sup>2,4</sup> Needed thermodynamic data has been found for R123 refrigerant<sup>5</sup> but the readily available data for air is insufficient for the more laborious calculations.

The constants to be determined are:

$I_d$ , collision integral = fcn( $kT/\epsilon_{12}$ )

$r_o$  = collision diameters

$V_b$  = molal volume (liquid volume at the normal boiling point)

$\rho_b$  = liquid density at the normal boiling point

$(r_o)_1 = 3.617$  angstroms<sup>3</sup>

$(r_o)_2 = 1.18 V_b^{1/3} = 5.567$  angstroms

$V_b = M_2/\rho_b = 152.93/1.456 = 105.03$  cm<sup>3</sup>/g-mol<sup>3</sup>

$r_{12}$ , collision diameter average, =  $\frac{1}{2}[(r_o)_1 + (r_o)_2] = 4.592$  angstroms

$B$ , HBS constant\*\*\*\* =  $\{10.85 - 2.5[(1/M_1) + (1/M_2)]^{1/2}\} \times 10^{-4} = 10.34 \times 10^{-4}$ .

The collision integral ( $I_d$ ) is determined as a function of the Boltzman constant ( $k$ ), the energy of molecular attraction ( $\epsilon$ ) and temperature ( $T$ ).

Using values from Perry & Chilton (*Chemical Engineering Handbook*)<sup>3</sup>, for air, gives  $\epsilon_1/k = 97.0$  K. Determining the same for R123 requires use of the Wilke and Lee approximations.<sup>4</sup>

$$\epsilon/k = 0.77T_c, \text{ where } T_c \text{ is the critical temperature} \quad (4)$$

$$\epsilon/k = 1.15T_b, \text{ where } T_b \text{ is the critical temperature} \quad (5)$$

Thus two estimates for  $\epsilon_2/k$  can be calculated by use of data from a *CRC Handbook of Chemistry and Physics*:<sup>6</sup>

$$0.77T_c = 0.77(456.8 \text{ K}) = 351.7 \text{ K and}$$

$$1.15T_b = 1.15(301 \text{ K}) = 346.2 \text{ K.}$$

Both these values are very close, so using the average has  $\epsilon_2/k = 349$  K. So:

$$\epsilon_{12}/k = [(\epsilon_1/k)(\epsilon_2/k)]^{1/2} = 184 \text{ and}$$

$$kT/\epsilon_{12} = 1.60.$$

Using a table again from Perry & Chilton<sup>3</sup> finds  $I_d$  to be 0.5837.

Finally, the diffusion coefficient for air and counter-diffusing R123 is calculated as:

$$D_G = (10.34 \times 10^{-4})(294.3)^{3/2} [(1/28.84) + (1/152.98)]^{1/2} / (4.592)^2 (0.5837) = 0.0861 \text{ cm}^2/\text{sec.}$$

This value is consistent with listed values<sup>7</sup> for other air-gas binary pairs. Further confidence is established for this diffusion coefficient value when calculated by the Fuller<sup>3</sup> method:

$$D_G = \{0.001T^{1.75} [(1/M_1) + (1/M_2)]^{1/2} / P [(\Sigma v_1)^{1/3} + (\Sigma v_2)^{1/3}]^2 \} \quad (6)$$

This alternative method makes use of atomic and molecular diffusion volumes. Based on listed values<sup>2,3,8</sup> for carbon, hydrogen, chlorine and an estimated value for fluorine, the diffusion coefficient per Equation 6 is 0.0847 cm<sup>2</sup>/sec. The  $D_G$  values (from Equations 3 and 6) agree to within 2%, giving good confidence in the validity of the diffusion coefficient for an air/R123 counter-diffusing system.

To use Equation (2) then, the vapor pressures of R123 at the liquid interface and at the pipe exit level are necessary. The corresponding vapor pressure, found in Table 2-326 of Ref. 7, is an interpolated and converted vapor pressure value of 0.81 atm at 21°C (70°F). At approximately 15.85 m (52 ft) from the liquid surface, the R123 vapor pressure is assumed to be about zero.

Using a gas constant consistent with the units involved, Equation (2) calculates the rate of diffusion as:

$$N_A = [(0.0861 \text{ cm}^2/\text{sec})(0.81 - 0)] / [(82.06 \text{ cm}^3\text{-atm/mole-K})(294.3 \text{ K})(1585 \text{ cm})] = 1.82 \times 10^{-9} \text{ moles/cm}^2\text{-sec}$$

A 6" pipe diameter converts to an area of 182.4 cm<sup>2</sup>. For the time interest of two days, the amount of R123 to pass through the plane 15.85 m (52 ft) above the R123 fluid is estimated to be:

$$(1.82 \times 10^{-9} \text{ moles/cm}^2\text{-sec})(182.4 \text{ cm}^2)(48 \text{ hr})(3600 \text{ sec/hr}) = 0.0574 \text{ moles}$$

## Discussion

The value of 0.0574 moles is relatively small (8.8 g). However, this amount should be thought of in the context of vapor that passes through the plane of interest, not the total amount of R123 vapor that leaves the liquid surface. For instance, considering the diffusion rate for R123 vapor just ~6" above the liquid surface calculates to be 100 times greater. However, the driving force of gas diffusion, being the partial pressure differences at the planes of interest, is far enough apart to be nearly unchanged over a 48-hr time period. Thus, using the steady state estimation of Equation (2) is appropriate, especially since ambient wind will move R123 vapor from the pipe exit so that the vapor pressure of R123, at the pipe exit remains nearly zero. Also, complicating this calculation with a time dependent vapor pressure gradient would result in a smaller final value so this estimate is actually conservative.

In summary, the estimated amount of potential R123 vapor, exiting the long roof pipe, is minimal.

\*\*\* Subscript 1 refers to air and subscript 2 refers to R123.

\*\*\*\* Hirschfelder-Bird-Spotz constant

## Emulsion degrease emissions — Simple Henry's Law method

A heated emulsion cleaner containing triethanolamine (TEA) as an organic constituent is included for corrosion inhibition. TEA is a large molecule with a very low pure component vapor pressure. Believing that TEA does not possess appreciable volatile behavior, past work<sup>9</sup> used Quality Assurance TEA add records as a means to calculate drag-out volumes. This method correlated well with an alternate tracer element analysis using inductively-coupled plasma (ICP). Furthermore, academic literature<sup>10</sup> concluded that the vapor over a methyldiethanolamine (MDEA)-water mixture was essentially pure water even at very high temperatures. MDEA has a higher vapor pressure than TEA and thus the same could then be concluded for TEA.

However, to establish quantitatively the belief that heated TEA-water mixtures emit essentially zero VOCs, vapor liquid equilibria (VLE) and associated thermodynamic data are required. There are several methods that can be employed for predicting Henry's Law constants.<sup>11,12,13</sup> Utilizing the "Bond Estimation Method" from available software, the Henry's law constant is calculated to be  $4.18 \times 10^{-12}$  atm-m<sup>3</sup>/mol at the standard temperature of 298 K (24.9°C; 76.7°F). Lacking vapor pressure values at elevated temperatures and even less so thermodynamic data such as virial coefficients, critical temperature or critical pressure, an alternative method from that provided by the U.S. EPA<sup>14</sup> is necessary to obtain extrapolated values of the Henry's law constant at elevated temperatures of interest (~60°C; 140°F).

The method chosen is by using the van't Hoff equation,<sup>15,16</sup>

$$k_H = k_H^* \exp \left[ \left( -\Delta_{sol} \ln \frac{H}{R} \right) \left( \frac{1}{T'} - \frac{1}{T^*} \right) \right] \quad (7)$$

The enthalpy of solution divided by the gas law constant can be found by plotting  $\ln(k_H)$  versus  $1/T$ .

$$\Delta_{sol} \ln \frac{H}{R} = - \frac{d \ln(k_H)}{d \left( \frac{1}{T} \right)} \quad (8)$$

These temperature dependent factors are available from Sander.<sup>16</sup> Unfortunately, of the hundreds of compounds listed, TEA is not among them. However, many amines are listed and a range of Equation (8) factors can be considered (2400 - 10,000). In another academic literature find,<sup>17</sup> Henry's law constants for n-alcohols were studied for their temperature dependence. Applying Equation (8), a C6 alcohol was found to have a factor of ~7400, which is in the range found for amines. To be conservative, a large factor (10,000) for Equation (8) was chosen to apply to Equation (7) and the resulting Henry's law constant for solutions at 333 K (60°C; 140°F) was found to be  $1.42 \times 10^{-10}$  atm-m<sup>3</sup>/mol, after requisite conversion factors were applied. The effect of also having a salt in solution would tend to raise the Henry's law constant. However, with the sodium sulfide concentration at only ~0.24 mol/kg, this "salting effect"<sup>18</sup> is considered minimal.

With this Henry's law constant, the method prescribed from an EPA report<sup>14</sup> was utilized to determine a vapor weight fraction (see the Appendix) of  $3.4 \times 10^{-7}$  for TEA over the degreaser tank of interest. Now the total losses of vapor can be determined. Knowing

that the vast majority of vapor lost will be water, an estimate of the water evaporated was determined by use of a derived expression.<sup>19</sup> The calculated water loss for a large tank (8.2 m<sup>2</sup>; 88 ft<sup>2</sup> surface area) of this size, results in a likely value of ~33 L/hr (~8.8 gal/hr), which corresponds with known water adds made on a daily basis. The final result is:

$$L_{TEA} (\text{loss of TEA}) = (Z_{TEA})(L_v) = (3.4 \times 10^{-7})(644930 \text{ lb./yr}) = 0.22 \text{ lb./yr (98 g/yr)}.$$

Given this value, even with numerous degreasing tanks, the TEA emissions can be considered to be essentially zero.

## Nitric acid emissions — Chemical equilibria method

Emission estimates for ideal solution and gas conditions (*e.g.*, soluble organics) are relatively straightforward.<sup>20</sup> However, for solutions such as nitric acid, the method of estimation must take solution non-ideality into account. An expression which is useful for gases that exhibit large solubility even at low pressures is the "extended Henry's Law";<sup>21-23</sup>

$$\gamma_i x_i = H_i y_i \phi_i P \quad (9)$$

where,

$\gamma_i$  = activity coefficient  
 $x_i$  = mole fraction in liquid  
 $H_i$  = Henry's Law constant  
 $y_i$  = mole fraction in vapor  
 $\phi_i$  = fugacity coefficient  
 $P$  = total pressure

However, since the total pressure is relatively low, the fugacity coefficient is often equal to unity and the vapor pressure can be used as a representation of the total pressure and mole fraction in the vapor phase. So for a nitric acid solution, a simplistic expression for vapor-liquid-equilibrium is:

$$P_i = \frac{\gamma_i x_i}{H_i} \quad (10)$$

where,

$$P_i = y_i P = \text{solute vapor pressure}$$

From chemical thermodynamics, it is known that the activity of a solution can be equated to the product of its activity coefficient and mole fraction. Specific to nitric acid, the activity coefficient ( $a_{\text{HNO}_3}$ ) and dissociation constant ( $k_a$ ) can be represented in terms of chemical equilibria by equations (11) and (12).

$$a_{\text{HNO}_3} = \gamma_{\text{HNO}_3} x_{\text{HNO}_3} \quad (11)$$

$$k_a = a_{\text{H}^+} \cdot a_{\text{NO}_3^-} / a_{\text{HNO}_3} \quad (12)$$

Furthermore, since the concentrations of both ions in solution are stoichiometrically equivalent, the activities can be written as:

$$(a_{\text{H}^+} \cdot a_{\text{NO}_3^-}) = a_{\pm}^2 = (\gamma_{\pm} c_{\pm})^2 = (\gamma_{\pm} \alpha c_{\text{HNO}_3})^2 \quad (13)$$

where,

$\alpha$  = fractional dissociation

$\gamma_{\pm}$  = mean molal activity coefficient

$c_{\pm}$  = ionic concentration, molal

$c_{\text{HNO}_3}$  = stoichiometric concentration of nitric acid

What must be considered next is that in concentrated solutions, the non-ionized portion of the nitric acid may affect the activity coefficient of the ionized part. From the Setchénov relation, MacKay<sup>24</sup> provides an expression that modifies the activity coefficient, since there is an expected "salting effect" of the electrolytes on the non-electrolyte.

$$\log \gamma_{\pm} = \log (\gamma_{\pm}/\alpha) - \frac{1}{2}\lambda_c(1 - \alpha)m_s \quad (14)$$

where,

$\gamma_{\pm}$  = hypothetical activity coefficient

$\lambda_c$  = salting coefficient,

$m_s$  = molality of the solute, mols solute/kg solvent

and according to MacKay,  $\lambda_c = 0.048 \pm 0.005$  for nitric acid.

By combining Equations (11) through (14), the activity of nitric acid can best be represented<sup>24,25</sup> in terms of activity coefficient, fractional dissociation, stoichiometric concentration and dissociation constant as:

$$a_{\text{HNO}_3} = (\gamma_{\pm}\alpha c_{\text{HNO}_3})^2 / k_a \quad (15)$$

At this point it would be most useful to illustrate an example. Consider a nitric acid solution (25°C) made up of 40 gal of 42° Bé nitric acid with the balance being water for a total of 100 gal. To determine representative concentrations would require use of the Gibbs-Duhem equation and constituent partial molal volumes. A simpler method is by iteration, using a nitric acid density and weight percent table.<sup>3</sup> This acid solution corresponds to being 31.47% by weight or 5.68M (molar) or 7.0m (molal). By interpolation, Redlich<sup>26</sup> has the degree of dissociation for this concentration to be 0.812. Again, by interpolation, the CRC<sup>6</sup> provides a stoichiometric mean activity coefficient of 1.295 which correlates well with the figure provided by MacKay.<sup>24</sup>

Since this is a concentrated acid, the salting effect on the activity coefficient can be determined by use of Equation (14), which calculates  $\gamma_{\pm} = 1.513$ . There are several reported values for the dissociation constant.<sup>25,27,28</sup> The value used in this example from Redlich, *et. al*<sup>26</sup> is  $k_a = 20\text{M}$ . There are also several reported values<sup>16,25,28,29</sup> for the Henry's Law constant at standard temperature ( $T = 298.15\text{ K}$ ). For this example let  $H^{\circ}_{\text{HNO}_3} = 8.9 \times 10^4 \text{ M/atm}$ .

Now all the pieces are ready to fit together in determining the partial pressure of nitric acid for these sample conditions.

$$p_{\text{HNO}_3} = [(\gamma_{\pm}\alpha c_{\text{HNO}_3})^2 / k_a] / H_{\text{HNO}_3} \quad (16)$$

$$\gamma_{\pm}\alpha c_{\text{HNO}_3} = (1.513 \cdot 0.812 \cdot 7.0\text{m}) = 8.6\text{m} \text{ (6.75M)}$$

$$p_{\text{HNO}_3} = [(6.75\text{M})^2 / 20\text{M}] / 8.9 \times 10^4 \text{ M/atm} = 2.56 \times 10^{-5} \text{ atm (0.019 mm Hg)}$$

This partial pressure of nitric acid is quite small, so the expected emission rate is also likely to be small.

In order to obtain a nitric acid mole fraction, the partial pressure of water is also needed. Of course, the solution partial pressure from water is less than the saturation vapor pressure of water due to the colligative properties of a solution. By use of Raoult's Law,

the reduction of the partial pressure of water can be determined by Equation (17).

$$p_{\text{H}_2\text{O}} = (1 - \gamma_{\pm}x_{\text{HNO}_3})^2 \cdot P^*_{\text{H}_2\text{O}} \quad (17)$$

where,

$x_{\text{HNO}_3}$  = the stoichiometric mole fraction of nitric acid in solution

$P^*_{\text{H}_2\text{O}}$  = the saturation vapor pressure of water

$\gamma_{\pm}$  = mean activity coefficient

$$p_{\text{H}_2\text{O}} = (1 - 1.295 \cdot 0.112)^2 \cdot 23.756 = 17.4 \text{ mm Hg}$$

This value agrees precisely with what can be interpolated from Table 3-16 of Perry & Chilton.<sup>3</sup> However, if  $\gamma_{\pm}$  is used instead of  $\gamma_{\pm}$  in Equation (17), then  $p_{\text{H}_2\text{O}} = 16.4 \text{ mm Hg}$ . The vapor mole fraction of nitric acid is,  $y_{\text{HNO}_3} = p_{\text{HNO}_3} / p_{\text{H}_2\text{O}} = 0.019 / 16.4 = 0.00116$ . As already mentioned, from the evaporation rate, one cannot assume that the partial pressures of water are unchanged from that of pure water. The acid solution vapor pressure is  $p_{\text{H}_2\text{O}} + p_{\text{HNO}_3} = (16.4 + 0.019) = 16.419 \text{ mm Hg (2189 Pa)}$ . Following the same method, as illustrated in the Appendix, the emission rate is then calculated to be 0.0021 lb./hour of  $\text{HNO}_3$ .

## Nitric acid emissions — Empirical method

An alternative method was developed<sup>30,31</sup> which uses an empirical model, which through a series of equations, calculates directly the evaporation rate of the solute in an aqueous solution, making use of a mass transfer coefficient ( $K_m$ ), the unitless Schmidt number ( $Sc$ ), and molecular diffusivity ( $D_s$ ).

$$E_s = A \cdot K_m \cdot (M_{w_s} \cdot P_s / R \cdot T) \quad (18)$$

$$K_m = 0.0292 \cdot U^{7/9} \cdot Z^{1/9} \cdot Sc^{-2/3} \quad (19)$$

$$Sc = \nu / D_s \quad (20)$$

$$D_s = D_{12} \cdot (M_{w_{\text{H}_2\text{O}}} / M_{w_s})^{1/2} \quad (21)$$

To compare directly with the previous nitric acid example, the known parameters are:

$A$  = surface area of solution = 2.23 m<sup>2</sup>

$M_{w_s}$  = molecular weight of the solute = 63 g/mol

$P_s$  = partial pressure of the solute = (0.019/760)/101325 = 2.53 Pa

$T$  = ambient temperature = 298.15 K

$U$  = ambient air speed over the solution surface = 1440 m/hr (0.4 m/sec)

$Z$  = distance of solution surface in the along-wind air movement direction = 1.28 m

$\nu$  = kinematic viscosity of air =  $1.5 \times 10^{-5} \text{ m}^2/\text{sec}$

$D_{12}$  = molecular diffusivity of  $\text{H}_2\text{O}$  in air =  $2.5 \times 10^{-5} \text{ m}^2/\text{sec}$

$M_{w_{\text{H}_2\text{O}}}$  = molecular weight of water = 18 g/mol

$R$  = 8.314 Pa-m<sup>3</sup>/mol-K

The calculated parameters are:

$D_s$  = molecular diffusivity of the solute, =  $1.34 \times 10^{-5} \text{ m}^2/\text{sec}$

$Sc$  = laminar Schmidt number for solute = 1.1225

$K_m$  = mass transfer coefficient = 7.647 m/hr

The evaporation rate of the solute ( $E_s$ ) is then calculated to be 1.096 g/hr. After unit conversions, the evaporation rate is 0.0024 lb/hr. This empirical model provides a value that is remarkably close to

the method used with a chemical equilibria approach. This approach is simpler than the chemical equilibria method, but requires already knowing the solute vapor pressure at the concentration of interest and does not appear to account for ambient humidity.

The rigors of these methods are shown in detail to illustrate how to perform these types of calculations for other non-ideal solutions where partial pressure tables are not readily available. The example of nitric acid was chosen so that an easy check could be made with known values.

## Mixed solutes

Beyond the scope of the examples illustrated are the further complications that arise when accounting for the effect of mixed solutes. Carroll<sup>32</sup> explains that it is safe to assume that there is no interaction of the solutes in the liquid phase when the solutes are not very soluble. That is, the partial pressures of each species can be determined independently as if the other species were not present. However, for highly soluble gases, each of the Henry's law constants must be determined, taking into account salting effects, activity coefficients and solute interaction effects. For highly soluble gases, it may be more appropriate to approach the estimate as being multi-solvent instead of multi-solute. For the case of a solute in a binary solvent, use Equation (22):

$$\ln H_{i,\text{mix}} = x_g \ln H_{ig} + x_k \ln H_{ik} + a_{gk} x_g x_k \quad (22)$$

where,

$H_{i,\text{mix}}$  = Henry's law constant for solute i in the mixture

$H_{ig}$  = Henry's law constant for solute i in solvent g

$H_{ik}$  = Henry's law constant for solute i in solvent k

$a_{gk}$  = interaction parameter between g and k for mixed solvent

$x_g$  = mole fraction of component g in liquid

$x_k$  = mole fraction of component k in liquid

The use of Equation (22) depends on having either binary equilibrium data for solvents g and k or having specific experimental data. Demonstrating the use of this method is beyond the scope of this paper.

## Applications

At Boeing, these emission estimate techniques have been used in various situations. What follows are brief situation descriptions and results.

## Operation expansion

Detailed chemical engineering analysis was performed to satisfy required justification to the Air Quality Management District for the Boeing Auburn site, Puget Sound Clean Air Agency (PSCAA) and allowed a planned building expansion to occur. Potential emissions were calculated as required for a Notice of Construction (NoC) specific to the planned expansion in support of added work statement. The emission estimates for pre-paint solvent cleaning and immersion aqueous degreasing used chemical engineering methods that employed vapor-liquid-equilibria data via Henry's Law and Raoult's Law.

To estimate solvent emissions, an empirical relationship was determined using production hazardous waste data. Through regression analysis, emission factors (EF) were equated to the quotient of constituent solvent vapor pressures and a maximum solvent vapor pressure (Fig. 1). Conventional emission estimates methods, which may have yielded values close to the 40-ton limit, would have triggered a federal permit exercise as opposed to a local permit. This effort provided the technical basis for a successful Potential-to-Emit (PTE) calculation methodology. The consequence of alternatively needing a federal permit (includes Environmental Engineering labor, consultant labor and permit application fees) would have been over \$100,000. Having provided defensible emission estimates allowed the clean and paint work packages to be moved to the new site as planned.<sup>33</sup> Also, management may have off-loaded this work package, due to the long flow time to obtain a federal permit had that been required.

## Hybrid-etch

Emissions from a planned "hybrid-etch" tank was needed for a Notice of Construction (NoC) application. A detailed calculation using vapor-liquid-equilibria (VLE) data resulted in emission rates for two constituent acids and one organic component. The calculation was displayed on a spreadsheet which also included a regression equation extrapolated from used tubular water vapor pressure data. Based on these estimates, Environmental Engineering was able to determine that a scrubber and associated infrastructure and labor were not required (Fig. 2). Detailed cost estimates to perform a scrubber install ranged from \$667,000 to \$845,000. This planned cost was able to be avoided.

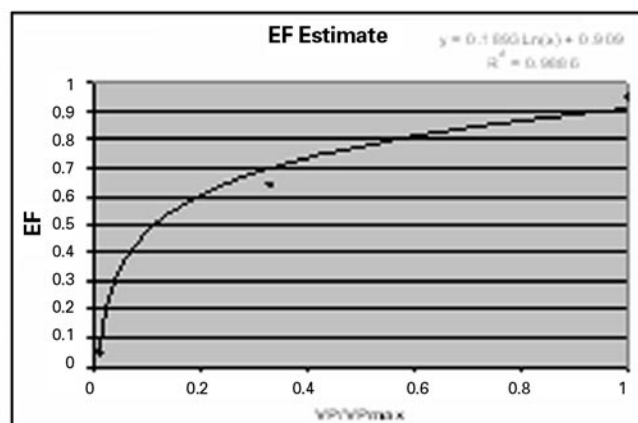


Figure 1—Emission factors were developed to estimate losses from solvent wiping operations.

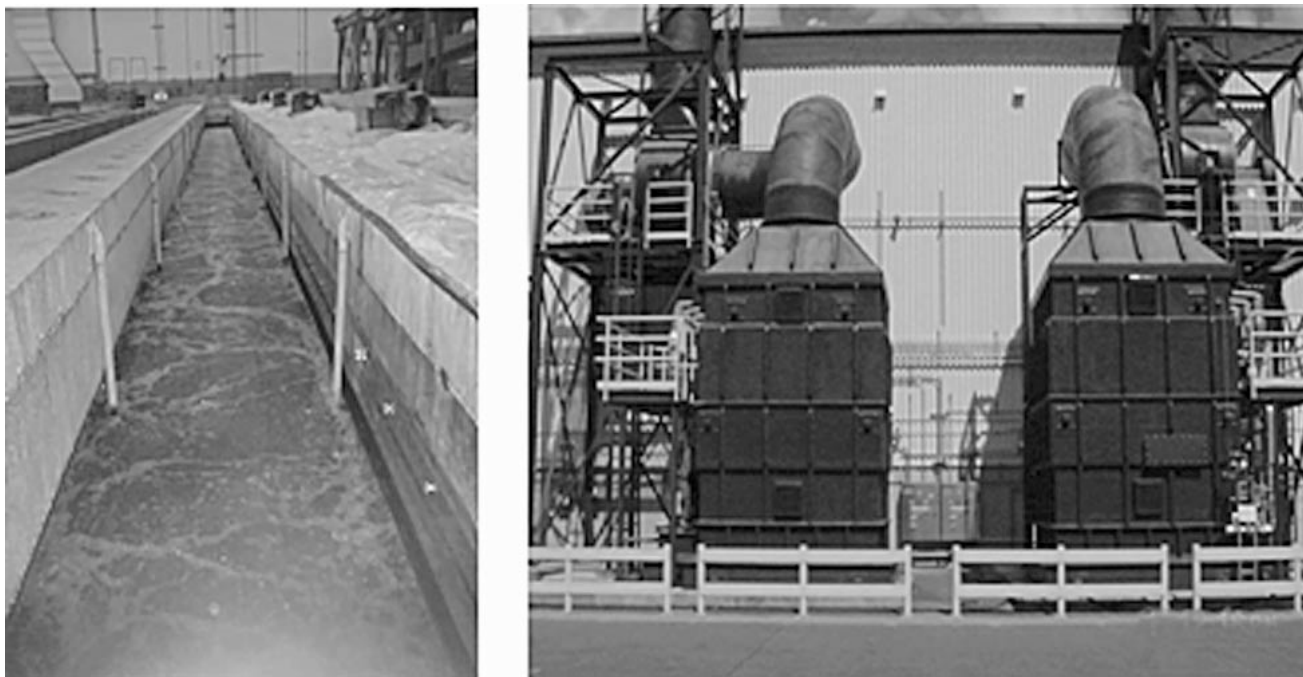


Figure 2—Large chemical tanks and scrubbers.

### ***Delta IV Cr seal scrubber***

Delta IV operations (Fig. 3) were impacted due to the Sulfuric Acid Anodizing (SAA) process not passing salt spray. A Corporate-wide team was assembled and has been providing technical assistance on a variety of issues all aimed at making this process operational and trying to understand the root cause. One corrective action<sup>34</sup> that had the best chance of long-term success was to implement a dilute chromate seal solution in place of the current de-ionized water seal tank. Part of the site implementation plan (for this planned chemistry change) was to provide a scrubber that would service the hot seal tank. A detailed recommendation and background information were provided such that local (Alabama) regulatory agencies agreed that a scrubber was not required to implement this process change. Cost avoidance estimates were ~\$500,000 for purchase and installation and ~\$50,000 annual recurring for operation and maintenance. Added schedule pressures were also avoided.

### ***Refrigerant escape - Frederickson***

A chiller unit (Fig. 4) had an incident involving R123 refrigerant in which the initial volume was unknown; therefore a simple mass balance could not be performed to provide a loss estimate. The task was to estimate, over a two-day period, the amount of R123 vapor that would potentially exit a long straight pipe. An appropriate modeled approach was to perform the subject estimate as a result of binary mixing of gases theory. Steady-state equimolar counter-diffusion at a plane equivalent to the pipe length (~52 feet) was calculated and was related by the difference of partial pressures at two positions: temperature and distance between the liquid surface and the position of interest. Use of the gas constant and the gas diffusion coefficient was determined. Thus a gas diffusion coefficient was also required and was estimated by use of the molecular weights of the gases of interest, temperature and various constants (determined by the thermodynamic properties of each

gas). The estimated amount of potential R123 vapor, exiting the long roof pipe, was determined to be minimal.<sup>35</sup> The consequences of this effort were that Boeing was enabled to assess environmental impact as low risk. Alternatively, a conservative estimate might have resulted in a much higher risk assessment, which would likely have then required outside engineering consultation.



Figure 3—Delta IV heavy.



Figure 4—R123 chiller unit.



Figure 5—Nitric-hydrofluoric hard metal etch tank.

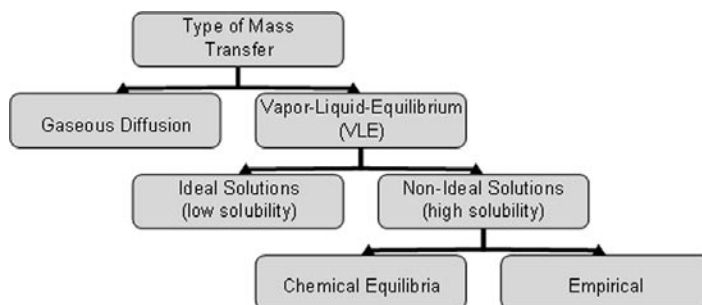


Figure 6—Emission estimate methodology tree.

### Auburn machined structures nitric-HF exposure

An acid scrubber to be shut down for maintenance needed an estimate of acidic gases movement into the immediate area. This was a difficult problem because it required the use of Henry's law and binary diffusion of gases theory. The value calculated was relatively small but should be thought of in the context of the amount of gas that passes through a plane of interest, not the total amount of gas that is emitted from the liquid surface. For instance, consider that the amount of gas that passes through the plane just above (2 cm) above the liquid surface will be 100 times greater than 2 m above the tank. This is why dangerous acid process tanks are recessed (Fig. 5). Of course, as time passes, a diffused gas gradient will develop. However the driving force of gas diffusion, being the partial pressure differences at the planes of interest, is far enough apart to be nearly unchanged over the 5-hr time period studied. In summary, a diffusion gradient, over a 2-m distance, is assumed not to develop enough to impede the rate of diffusion. Detailed calculations were provided so that additional computations, for differing conditions, could be readily obtained by using this same method; consequently, sound recommendations were made for inclusion in the emergency action plan.<sup>36</sup>

### Summary

Important first steps toward understanding the estimate of an emission calculation are assessing the mode of mass transfer and therefore how to properly use the chemical property and thermodynamic information available (Fig. 6).<sup>37</sup> Gas that is moving through stagnant air can be modeled using binary diffusion theory. A gas emission from a liquid source requires understanding the vapor-liquid equilibrium (VLE) system. This can be complicated if the solute of interest is highly soluble or if little physical property data is available. Non-ideal solutions (high solubility) can be approached with chemical equilibria and thermodynamic information or one can make use of empirical methods if solute vapor pressures are known.

The methods provided, illustrate how some emission estimates can be determined. The applications provided show that substantial benefit can be realized by use of these methods.

### Acknowledgements

I am thankful to the Boeing Technical Library Staff for providing the many references requested in a timely fashion. I appreciate the technical review of John Jones and the editorial technical writing of Harry Larsen, Lynn Breda and Jim Lindsay. Mostly, I am grateful to Jack Fullen for providing encouragement and then inspiration in the pursuit of a career in Chemical Engineering.

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## About the Author



W. John Fullen, CEF has been with the Boeing Company for more than 20 years, at present in the Material and Process Technology area, first in advanced composites and more recently in chemical technology and support of solvent research and tankline operations. Prior to that, he worked at H.B. Fuller Co. in the area of adhesives. He holds a B.S. in Chemical Engineering from the University of Minnesota.



## Appendix

TEA, triethanolamine,  $(\text{OHCH}_2\text{CH}_2)_3\text{-N}$

Molecular weight of TEA, 149.19 g/g-mol

Molecular weight of water, 18 g/g-mol

$H^*_{\text{TEA}}$ , Henry's law constant at 298 K =  $4.18 \times 10^{-12}$  atm-m<sup>3</sup>/mol (per Bond Estimation Method)

$H^*_{\text{TEA}}$ , Henry's law constant at 333 K =  $1.42 \times 10^{-10}$  atm-m<sup>3</sup>/mol (per application of van't Hoff equation)

Henry's Law:  $p^*_{\text{TEA}} = H^*_{\text{TEA}} (C_{\text{TEA}})$  simple form applicable at low concentrations

Volume of tank = 13.19 m<sup>3</sup> (3484 gal)

Area of tank = 8.18 m<sup>2</sup> (88 ft<sup>2</sup>)

Process solution concentration = 10%

Concentration of TEA in process solution = 8%

Specific gravity of process solution = 1.05

Weight of process solution = (3484 gal)(1.05)(8.345 lb/gal) = 13.8 tonnes (30528 lb.)

Weight of TEA in tank = (0.1)(0.08)(30528 lb)(453.7 g/lb) = 110804 g (244 lb.)

Moles of TEA in tank = 110804 g/(149.19 g/g-mol) = 743 g-mol

$C_{\text{TEA}} = (743 \text{ g-mol})/(13.19 \text{ m}^3) = 56.3 \text{ g-mol/m}^3$

$p^*_{\text{TEA}} = (H^*_{\text{TEA}})(C_{\text{TEA}}) = (1.42 \times 10^{-10} \text{ atm-m}^3/\text{mol})(56.3 \text{ g-mol/m}^3) = 8.0 \times 10^{-9} \text{ atm}$

$p^*_T$ , vapor pressure of process solution at 60°C, = (149.38 mm Hg)(1 atm/760 mm Hg) = 0.197 atm (used vapor pressure of water at 60°C) (Ref. 3).

$y_{\text{TEA}}$ , vapor mole fraction of TEA at 60°C, =  $p^*_{\text{TEA}}/p^*_T = (8.0 \times 10^{-9} \text{ atm})/(0.197 \text{ atm}) = 4.06 \times 10^{-8}$

$Z_{\text{TEA}}$ , vapor weight fraction of TEA, =  $(y_{\text{TEA}})(M_{\text{TEA}})/M_{\text{H}_2\text{O}} = (4.06 \times 10^{-8})(149.19 \text{ g/g-mol})/(18 \text{ g/g-mol}) = 3.4 \times 10^{-7}$

### **Emission rate of process solution:**

$$E = 1.857 T_o^{-0.4} \sqrt{0.5} [(P_s(T_w)/T_w) - (H P_s(T_o)/T_o)]$$

where,

E = evaporation rate, mg/cm<sup>2</sup>-min

$T_o$ , ambient air temperature = 298 K

$T_w$ , water surface temperature = 333 K

$P_s(T_w)$ , saturated vapor pressure at  $T_w$  = 19915 N/M<sup>2</sup> or 149.4 mm Hg.

$P_s(T_o)$ , saturated vapor pressure at  $T_o$  = 3167 N/M<sup>2</sup> or 23.8 mm Hg.

v, air speed at water surface = 0.4 m/sec

H, relative humidity = 0.3 or 30%

$$E = [(1.857)(298)^{-0.4}(0.4)^{0.5}]\{(19915/333) - [(0.3)(3167)/298]\} = 6.81 \text{ mg/cm}^2\text{-min}$$

$L_t$  = total losses =  $E^*[(88 \text{ ft}^2)(929 \text{ cm}^2/\text{ft}^2)](525600 \text{ min/yr})/(453720 \text{ mg/lb}) = 644930 \text{ lb/yr}$   
(or ~ 8.82 gal/hr)

$L_{\text{TEA}}$ , loss of TEA =  $(Z_{\text{TEA}})(L_t) = (3.4 \times 10^{-7})(644930 \text{ lb/yr}) = 0.22 \text{ lb/yr}$  (or 98 g/yr)