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 were mass balance techniques are not easily obtained. Several cases are presented that illustrate the methods of calculation for actual aerospace conditions of operation and the results of these method applications are summarized.

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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 is needed. For purposes of this calculation, this pipe is considered straight and 6 inches in diameter. The R123 reservoir is considered to be at 70°F (294.3K).

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:

$$\Delta P = 1/2\varrho(V_1^2 - V_2^2)$$
(1)

Given the density of air³⁴ at 70°F to be 1.21 kg/m³, a 10-mph (4.47 m/sec) wind speed would then produce a pressure drop of only $0.5(1.21)(4.47^2 - 0) = 12.1$ Pa, which is a very small pressure differential (less than 0.002 psia) and need <u>not</u> 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 equimolal 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 determined³³.

$$N_{A} = D_{G}(p - p_{i})/RTZ$$
(2)

The gas diffusion coefficient is estimated²⁶ by use of the molecular weights of the gases of interest, temperature, and various constants^{*} (determined by thermodynamic properties of each gas).

$$D_{G} = \{BT^{3/2}[(1/M_{1}) + (1/M_{2})]^{1/2}\}/Pr_{12}{}^{2}I_{d}$$
(3)

where,

T = absolute temperature, 294.3 K M_1 = molecular weight of air, 28.84 g/mole M_2 = molecular weight of R123, 152.93 g/mole P = absolute pressure, atm

This method (equation 3) is suggested for studying collisions of polar and nonpolar molecules which is the case for air and a solvent vapor^{33, 36}. Needed thermodynamic data has been found for R123 refrigerant⁶ but requires more laborious calculations than the readily available data for air.

The constants to be determined are:

$$\begin{split} &I_d, \text{ collision integral, } = \text{fcn}(\text{kT}/\epsilon_{12}) \\ &r_o = \text{collision diameters} \\ &V_b = \text{molal volume (liquid volume at the normal boiling point)} \\ &\rho_b = \text{liquid density at the normal boiling point} \\ &(r_0)_1 = 3.617 \text{ angstroms}^{26} \\ &(r_0)_2 = 1.18 V_b^{-1/3} = 5.567 \text{ angstroms} \\ &V_b = M_2/\rho_b = 152.93/1.456 = 105.03 \text{ cm}^3/\text{g-mole}^{-26} \\ &r_{12}, \text{ collision diameter average, } = [(r_0)_1 + (r_0)_2]/2 = 4.592 \text{ angstroms} \\ &B, \text{HBS constant}^{**}, = \{10.85 - 2.5[(1/M_1) + (1/M_2)]^{1/2}\} \times 10^{-4} = 10.34 \times 10^{-4}. \end{split}$$

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

Using values from Perry & Chilton (Chemical Engineering Handbook)²⁶, for air, gives $\varepsilon_1/k = 97.0$ K. Determining the same for R123 requires use of the Wilke and Lee approximations³⁶.

$$\epsilon/k = 0.77T_c$$
, where T_c is the critical temperature (4)
 $\epsilon/k = 1.15T_b$, where T_b is the normal boiling point (5)

Thus two estimates for ε_2/k can be calculated by use of data from a CRC (Handbook of Chemistry and Physics)¹⁷; $0.77T_c = 0.77(456.8K) = 351.7K$ and $1.15T_b = 1.15(301K) = 346.2K$. Both these values are very close, so using the average has $\varepsilon_2/k = 349K$. So $\varepsilon_{12}/k = [(\varepsilon_1/k)(\varepsilon_2/k)]^{1/2} = 184$; and $kT/\varepsilon_{12} = 1.60$. Using a table again from Perry & Chilton²⁶, finds I_d to be 0.5837.

^{*} Subscript * refers to air and subscript ** refers to R123.

Hirshfelder-Bird-Spotz

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

 $D_{G} = (10.34 \times 10^{-4})(294.3)^{3/2}[(1/28.84) + (1/152.98)]^{1/2}/1(4.592)^{2}(0.5837) = 0.0861$ cm²/sec

This value is consistent with listed values²⁷ for other air-gas binary pairs. Further confidence is established for this diffusion coefficient value when calculated by the Fuller²⁶ method:

$$D_{G} = \{0.001T^{1.75}[(1/M_{1}) + (1/M_{2})]^{1/2}\} / P[(\Sigma \nu_{1})^{1/3} + (\Sigma \nu_{2})^{1/3}]^{2}$$
(6)

This alternative method makes use of atomic and molecular diffusion volumes. Based on listed values^{26, 33, 35} for carbon, hydrogen, chlorine and an estimated value for fluorine, the diffusion coefficient per equation 6 is $0.0847 \text{cm}^2/\text{sec}$. 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 then use equation (2), the vapor pressures of R123 at the liquid interface and at the pipe exit level are necessary. The corresponding vapor pressure²⁷, Table 2-326 provides an interpolated and converted vapor pressure of 0.81 atm at 70°F. At ~52 feet (1585 cm) from the liquid surface, the R123 vapor pressure is assumed to be ~0.

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

 $N_{A} = [(0.0861 \text{ cm}^{2}/\text{sec})(0.81 - 0)]/[(82.06 \text{ cm}^{3}-\text{atm/mole-K})(294.3 \text{ K})(1585 \text{ cm})]$ = 1.82×10⁻⁹ moles/cm²-sec

A 6" pipe diameter converts to an area of 182.4 cm^2 . For the time interest of 2 days, the amount of R123 to pass through the plane 52 feet above the R123 fluid is estimated to be:

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

Discussion

The value of 0.0574 moles is relatively small (8.8g). However, this amount should be thought of in context of vapor that <u>passes</u> through the plane of interest, <u>not</u> 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-hour 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 ~0. 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.

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 work⁹ 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 generated literature³⁷ concluded that the vapor over a methyldiethanolamine (MDEA)-water mixture is 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 quantitatively establish the belief that heated TEA-water mixtures emit essentially zero VOC's, vapor liquid equilibria (VLE) and associated thermodynamic data is required. There are several methods that can be employed for predicting Henry's Law constants^{21,25}. Utilizing the "Bond Estimation Method" from available software, the Henry's law constant is calculated to be 4.18×10^{-12} atm-m³/mole at the standard temperature of 298 K. Lacking vapor pressures 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. EPA⁸, is necessary to obtain extrapolated values of the Henry's law constant at elevated temperatures of interest (~140°F).

The method chosen is by using the van't Hoff equation^{1, 30},

$$k_{\rm H} = k_{\rm H}^{*} \exp[(-\Delta_{\rm soln} H/R)(1/T^{'} - 1/T^{*})]$$
(7)

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

$$\Delta_{\rm soln} H/R = -d\ln(k_{\rm H})/d(1/T)$$
(8)

These temperature dependent factors are available from Sander³⁰. 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 find¹⁴, 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 is found to be, 1.42×10^{-10} atm-m³/mole after requisite conversion factors

are 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 mole/kg, this "salting effect"³² is considered minimal.

With this Henry's law constant, the method prescribed from an EPA report⁸ was utilized to determine a vapor weight fraction (see appendix 1) of 3.4×10^{-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 expression¹⁵. The calculated water loss for a large tank (88 ft² surface area) of this size, results in a likely value of ~8.8 gallons/hour, which corresponds with known water adds made on a daily basis. The final result is,

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

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 straight forward²². However, for solutions such as nitric acid, the method of estimation must take into account solution non-ideality. An expression which is useful for gases that exhibit large solubility even at low pressures is the "extended Henry's law"^{3,4,23}:

$$\gamma_i \mathbf{x}_i = \mathbf{H}_i \mathbf{y}_i \boldsymbol{\phi}_i \mathbf{P} \tag{9}$$

where,

 γ_i = activity coefficient

 x_i = mole fraction in liquid

 $H_i =$ Henry's Law constant

 y_i = mole fraction in vapor

 ϕ_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:

$$\mathbf{p}_{i} = \gamma_{i} \mathbf{x}_{i} / \mathbf{H}_{i} \tag{10}$$

where,

 $p_i = y_i P$ = 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_{HNO_3}) and dissociation constant (k_a) can be represented in terms of chemical equilibria by equations (11) and (12).

$$\mathbf{a}_{\mathrm{HNO}_3} = \gamma_{\mathrm{HNO}_3} \mathbf{x}_{\mathrm{HNO}_3} \tag{11}$$

$$k_a = a_{H^+} a_{NO_3} / a_{HNO_3}$$
 (12)

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

$$(a_{H^{+}} a_{NO_3}) = a_{\pm}^2 = (\gamma_{\pm} c_{\pm})^2 = (\gamma_{\pm} \alpha c_{HNO_3})^2$$
(13)

where,

 α = fractional dissociation

 γ_{\pm} = mean molal activity coefficient

 c_{\pm} = ionic concentration, molal

 c_{HNO_2} = stoichiometric concentration of nitric acid

What must be considered next is that in concentrated solutions the unionized portion of the nitric acid may affect the activity coefficient of the ionized part. From the Setchénov relation, MacKay¹⁸ provides an expression that <u>modifies</u> the activity coefficient, since there is an expected "salting effect" of the electrolytes on the non-electrolyte.

$$\log \gamma_{\eta} = \log \left(\gamma_{\pm} / \alpha \right) - 1 / 2 \lambda_{c} (1 - \alpha) m_{s}$$
(14)

where,

 γ_h = hypothetical activity coefficient

 λ_{c} = salting coefficient,

 $m_s = \underline{molality}$ of the solute, moles 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^{18, 31} in terms of activity coefficient, fractional dissociation, stoichiometric concentration, and dissociation constant as:

$$\mathbf{a}_{\mathrm{HNO}_{2}} = (\gamma_{\mathrm{h}} \alpha \mathbf{c}_{\mathrm{HNO}_{2}})^{2} / \mathbf{k}_{\mathrm{a}}$$
(15)

At this point it would be most useful to illustrate an example. Consider a nitric acid solution (25°C) made up of 40 gallons of 42° Bé nitric acid with the balance being water for a total of 100 gallons. 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 table²⁶. This acid solution corresponds to being 31.47% by weight or 5.68M(molar) or 7.0m(molal). By interpolation, Redlich²⁸ has the degree of

dissociation for this concentration to be 0.812. Again, by interpolation, the CRC¹⁷ provides a stoichiometric mean activity coefficient of 1.295 which correlates well with the figure provided by MacKay¹⁸.

Since this is a concentrated acid, the salting effect on the activity coefficient can be determined by use of equation (14), which calculates $\gamma_h = 1.513$. There are several reported values for the dissociation constant^{5, 7, 31}; the value used in this example is from Redlich et. al.,²⁸ is $k_a = 20M$. There are also several reported values^{7, 29, 30, 31} for the Henry's Law constant at standard temperature (T = 298.15K), for this example let $H_{HNO_3}^{e} = 8.9 \times 10^4$ M/atm.

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

$$p_{HNO_3} = [(\gamma_h \alpha c_{HNO_3})^2 / k_a] / H_{HNO_3}$$
(16)
$$\gamma_h \alpha c_{HNO_3} = (1.513 \cdot 0.812 \cdot 7.0m) = 8.6m (6.75M)$$
$$p_{HNO_3} = [(6.75M)^2 / 20M] / 8.9 \times 10^4 M / atm = 2.56 \times 10^{-5} atm (0.019 mmHg)$$

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 Rauolt's Law, the reduction of the partial pressure of water can be determined by equation (17).

$$p_{H_{2}O} = (1 - \gamma_{\pm} x_{HNO_{2}})^{2} \cdot P^{*}_{H_{2}O}$$
(17)

where,

 x_{HNO_3} = the stoichiometric mole fraction of nitric acid in solution $P^*_{H_2O}$ = the saturation vapor pressure of water γ_{\pm} = mean activity coefficient p_{H_2O} = (1 - 1.295 \cdot 0.112)² · 23.756 = 17.4 mm Hg

This value agrees precisely with what can be interpolated from Table 3-16 of Perry & Chilton²⁶. However, if γ_h is used instead of γ_{\pm} in equation (17), then $p_{H_2O} = 16.4 \text{ mm Hg}$. The vapor mole fraction of nitric acid is, $y_{HNO_3} = p_{HNO_3}/p_{H_2O} = 0.019/16.4 = 0.00116$. As already mentioned, the evaporation rate cannot assume that the partial pressures of water to be unchanged from that of pure water. The acid solution vapor pressure is $p_{H_2O} + p_{HNO_3} = (16.4 + 0.019) = 16.419 \text{ mmHg}$ (2189 Pa). Following the same method, as illustrated in the appendix, the emission rate is then calculated to be 0.0021 lb/hour of HNO₃.

Nitric Acid Emissions – Empirical Method

An alternative method was developed^{16, 19} 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).

$$\mathbf{E}_{s} = \mathbf{A} \cdot \mathbf{K}_{m} \cdot (\mathbf{M}_{w_{s}} \cdot \mathbf{P}_{s}/\mathbf{R} \cdot \mathbf{T})$$
(18)

$$\mathbf{K}_{\rm m} = 0.0292 \cdot \mathbf{U}^{7/9} \cdot \mathbf{Z}^{-1/9} \cdot \mathbf{S}c^{-2/3} \tag{19}$$

$$Sc = \nu/D_s \tag{20}$$

$$D_{s} = D_{12} \cdot (M_{w_{H_{4}0}}/M_{w_{s}})^{1/2}$$
(21)

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

A = surface area of solution, = 2.23 m^2

 M_{w_s} = molecular weight of the solute, = 63 g/mole

 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/s)

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

v = kinematic viscosity of air = 1.5×10^{-5} m²/s

 D_{12} = molecular diffusivity of H_2O in air = 2.5×10^{-5} m²/s

 $M_{w_{H_{2}0}}$ = molecular weight of water = 18 g/mole

 $R = 8.314 \text{ Pa-m}^3/\text{mol-K}$

The calculated parameters are:

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

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/hour. After unit conversions, the evaporation rate is 0.0024 lb/hour. 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, however, 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 type of calculations for other non-ideal solutions where partial pressure tables are <u>not</u> 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. Carroll² 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 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):

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

where,

 $H_{i,mix}$ = 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.

1) 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.



Emission Factors were Developed to Estimate Losses from Solvent Wiping Operations

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. Conventional emission estimates methods 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 \$100K. Having provided defendable emission estimates allowed the clean and paint work packages to be moved to the new site as planned¹¹. Also, management may have off-loaded this work package, due to the long flow time to obtain a federal permit had that been required.

2) Hybrid-Etch

Emissions from a planned 'hybrid-etch" tank was needed for a Notice of Construction (NoC) application. A detailed calculation using vapor-liquidequilibria (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 tabular 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. Detailed cost estimates to perform a scrubber install ranged from \$667K to \$845K. This planned cost was able to be avoided.



Large Chemical Tanks and Scrubbers

3) Delta IV Cr Seal Scrubber

Delta IV operations 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 action¹² that has the best chance of long-term success was to implement a dilute chrome 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 is not required to implement this process change. Cost avoidance estimates are ~\$500K for purchase and installation and ~\$50K annual recurring for operation and maintenance. Added schedule pressures were also avoided.



Delta IV Heavy

4) Refrigerant Escape - Frederickson

A chiller unit had an incident involving R-123 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 R-123 vapor that would potentially exit a long straight pipe. An appropriate modeled approach is to perform the subject estimate as a result of binary mixing of gases theory. Steady state equimolal counter-diffusion at a plane equivalent to the pipe length (~52

feet) was 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 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 minimal¹³. 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.



R123 Chiller Unit

5) Auburn Machined Structures Nitric-HF Exposure

An acid scrubber to be shutdown 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 <u>and</u> binary diffusion of gases theory. The value calculated was relatively small but should be thought of in 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 the amount of gas that passes through the plane just above (2 cm) above the liquid surface, will be 100 times greater than 2 meters above the tank. This is why dangerous acid process tanks are

recessed. 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-hour time period studied. In summary, a diffusion gradient, over a 2 meter distance, is assumed to not develop enough to impede the rate of diffusion. Detailed calculations were shown so that additional computations, for differing conditions, can be readily obtained by using this same method; consequently, sound recommendations were made for inclusion in the emergency action plan¹⁰.



Nitric - Hydrofluoric Hard Metal Etch Tank

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 available²⁴. 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.



Emission Estimate Methodology Tree

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Appendix

TEA, triethanolamine, (OHCH₂CH₂)₃-N

Molecular weight of TEA, 149.19 g/g-mole

Molecular weight of water, 18 g/g-mole

 H^*_{TEA} , Henry's law constant at 298 K = 4.18×10^{-12} atm-m³/mole (per Bond Estimation Method)

 H'_{TEA} , Henry's law constant at 333 K = 1.42×10^{-10} atm-m³/mole (per application of van't Hoff equation)

Henry's Law: $\dot{p}_{TEA} = H_{TEA}(C_{TEA})$ simple form applicable at low concentrations

Volume of tank = 3484 gallons or (13.19 m³)

Area of tank = 88 ft^2

Process solution concentration = 10%

Concentration of TEA in process solution = 8%

Specific gravity of process solution = 1.05

Weight of process solution = (3484 gallons)(1.05)(8.345 lb/gallon) = 30528 lb

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

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

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

 $\dot{p}_{TEA} = (H_{TEA})(C_{TEA}) = (1.42 \times 10^{-10} \text{ atm-m}^3/\text{mole})(56.3 \text{ g-moles}/\text{ m}^3) = 8.0 \times 10^{-9} \text{ atm}$

 $\dot{p_T}$, 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)^{*}

 y_{TEA} , vapor mole fraction of TEA at 60 C, = $\dot{p}_{TEA}/\dot{p}_{T}$ = (8.0×10⁻⁹ atm)/(0.197 atm) = 4.06×10⁻⁸

 Z_{TEA} , vapor weight fraction of TEA, = $(y_{\text{TEA}})(M_{\text{TEA}})/M_{\text{H2O}}$ = $(4.06 \times 10^{-8})(149.19 \text{ g/g-mole})/(18 \text{ g/g-mole}) = 3.4 \times 10^{-7}$

Emission rate of process solution:

 $E = 1.857 T_o^{-0.4} v^{0.5} ((P_s(T_w)/T_w) - (H P_s(T_o)/T_o))$

^{*}Chemical Engineering Handbook, Perry & Chilton, 5th Ed.

Where,

E = evaporation rate, mg/cm²-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/M² or (149.4 mm Hg) P_s(T_o), saturated vapor pressure at T_o, = 3167 N/M² or (23.8 mm Hg) v, air speed at water surface, = 0.4 m/s H, relative humidity, = 0.3 or (30%)

 $E = [(1.857)(298)^{-0.4}(0.4)^{0.5}]\{(19915/333) - [(0.3)(3167)/298]\} = 6.81 \text{ mg/cm}^2 \text{-min}$ $L_t = \text{total losses} = E^*[(88 \text{ ft}^2)(929 \text{ cm}^2/\text{ft}^2)](525600 \text{ min/year})/(453720 \text{ mg/lb}) = 644930 \text{ lb/year}$ (or ~ 8.82 gallons/hour)

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