Source Term Determination for Spills of Binary Liquid Solutions

by

A. Blanchard

Westinghouse Savannah River Company
Savannah River Site
Aiken, South Carolina 29808

D. Hadlock

Westinghouse Safety Management Solutions
SC USA

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

MASTED

DOE Contract No. **DE-AC09-96SR18500**

This paper was prepared in connection with work done under the above contract number with the U. S. Department of Energy. By acceptance of this paper, the publisher and/or recipient acknowledges the U. S. Government's right to retain a nonexclusive, royalty-free license in and to any copyright covering this paper, along with the right to reproduce and to authorize others to reproduce all or part of the copyrighted paper.

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

This report has been reproduced directly from the best available copy.

Available to DOE and DOE contractors from the Office of Scientific and Technical Information, P. O. Box 62, Oak Ridge, TN 37831; prices available from (423) 576-8401.

Available to the public from the National Technical Information Service, U. S. Department of Commerce, 5285 Port Royal Road, Springfield, VA 22161.

DISCLAIMER

**Portions of this document may be illegible
electronic image products. Images are
produced from the best available original
document.**

SOURCE TERM DETERMINATION FOR SPILLS OF BINARY LIQUID SOLUTIONS (U)

Dennis Hadlock

1/6/97

DOES NOT CONTAIN
UNCLASSIFIED CONTROLLED
NUCLEAR INFORMATION

Reviewing
Official: *D. Hadlock* Sr. Eng.

(Name and Title)

Date: 1/6/97

Westinghouse Savannah River Company
Safety Engineering Department
Aiken, SC 29808

Keywords: Solutions
Chemical
Source Term

AUTHOR/TECHNICAL REVIEW

D. J. Hadlock - Safety Analysis Engineering Section

1/6/97

Date

B. V. Nguyen - Technical Reviewer

1/6/97

Date

APPROVALS:

J. W. Lightner - Manager SAES-ESTG

1/6/97

Date

M. J. Hitchler - Manager SED-SAES

4/8/97

Date

SUMMARY

Source term determination for spills of binary liquid solutions pose a unique dilemma as the partial vapor pressures of the constituents change as the spill evaporates. The change in partial pressures is more pronounced as the difference in the constituent vapor pressures increases. Past practices have been to conservatively analyze these solutions by either of the following two methods:

- (1) Calculate the source term based on the partial pressure of the most limiting constituent (from a toxicological standpoint) when the partial pressure of that constituent will decrease as the spill evaporates.
- (2) Calculate the theoretical mass transfer equilibrium concentration of the solution and use the partial pressure of the most limiting constituent (from a toxicological standpoint) at the equilibrium concentration when the partial pressure of that constituent will increase as the spill evaporates.

The drawback to the above practices are that they can greatly overestimate the source term when the partial pressure of the most limiting constituent decreases rapidly or increases slowly after the spill begins to evaporate. The methodology in this report takes advantage of the physical properties of the binary solution and the methodology used in calculating evaluation criteria for the solution of concern to provide a technical basis to remove some of this conservatism.

The methodology in this report results in the determination of an average vapor pressure over a predetermined time period of interest. The time period of interest is based on whether the most limiting constituent partial pressure increases or decreases over time. This average partial pressure is then used for determination of source terms for spills of the solution.

CONTENTS

INTRODUCTION	1
DISCUSSION	1
Examples	6
CONCLUSION	7
REFERENCES	8

TABLES

Table 1: Partial pressures for HCl Solutions	1
Table 2: Partial pressures for HNO ₃ Solutions	2
Table 3: HCl release rates - Kawamura and Mackay	4
Table 4: HCl release rates - Eckert-Drake	5

APPENDICES

Appendix 1: EXCEL™ Spreadsheet of Source Term Model	
Appendix 2: EXCEL™ Spreadsheet of Eckert-Drake Source Term Model	
Appendix 3: Pp Curves for HCl Solutions	
Appendix 4: 36 Weight Percent HCl Analytical Dilution Steps for a 1000 lb Spill	
Appendix 5: Pp Curves for HNO ₃ Solutions	
Appendix 6: 50 Weight Percent HNO ₃ Analytical Concentration Steps for a 1000 lb Spill	

INTRODUCTION

Binary liquid solutions pose a unique situation when determining the release rate (source term) from a spill of the solution. The vapor pressure of each of the two components, commonly referred to as the partial pressure (Pp), can vary widely over the range on concentration. This situation is encountered when calculating source terms for dilute acid mixtures. In this case one of the components, water, poses no toxicological hazard, while the other is the hazard of interest. Due to this difference in partial pressures, the solution can either dilute or concentrate over time. As the solution dilutes or concentrates, the Pp of the hazard will change accordingly. This change in Pp is directly related to the evaporation rate of the hazardous material in the solution.

A previous method (Ref. 1) of calculating the isothermal mass transfer equilibrium condition of a binary liquid mixture has been employed for safety analysis. A drawback to this method is that the answer is independent of the time it takes to reach the equilibrium mass transfer. Many times in safety analysis work, this length of time may be used as a mitigating feature for the accident being analyzed.

This report documents a method where the change in the Pp of each component is calculated over a period of time. The calculation yields an average Pp over the time period selected which allows the physical properties of the resulting average Pp to be used in the safety analysis.

DISCUSSION

Two solutions will be used for examples throughout this report. The two solutions are 36 weight percent hydrochloric acid (HCl) and 50 weight percent nitric acid (HNO₃). These solutions were chosen as they represent the two possible endpoints of a solution over time, dilution and concentration. The partial pressures of HCl and water over aqueous solutions of HCl @30°C are (Ref. 2):

Table 1: Partial pressures for HCl Solutions

HCl Concentration (wt %)	Pp H ₂ O (mmHg)	Pp HCl (mmHg)
36	6.08	188.0
34	7.32	92.0
32	8.70	44.5
30	10.20	21.0
28	11.80	9.9

As the Pp of the HCl is much greater than the Pp of water, the solution would be expected to dilute over time (in the case of HCl, the large disparity between the two component Pp's would cause a relatively fast dilution over the first few minutes) until some equilibrium is reached. The use of the Pp at 36 weight % for source term determination would result in an overestimation over a relatively long duration.

The partial pressures of HNO_3 and water over aqueous solutions of HNO_3 @ 30°C are (Ref. 2):

Table 2: Partial pressures for HNO_3 Solutions

HNO_3 Concentration (wt %)	Pp H_2O (mmHg)	Pp HNO_3 (mmHg)
50	14.4	0.56
55	12.2	0.93
60	10.3	1.66
65	8.8	3.17
70	7.4	5.50

As the Pp of HNO_3 is much smaller than the Pp of water, the solution would be expected to concentrate over time until some equilibrium is reached. The use of the Pp at 50 weight % for source term determination could result in an underestimation for a relatively long duration.

In order to calculate the change in the solution, and thus the change in Pp, over time, it is necessary to choose a model for calculating source terms. For the purposes of this report, a manual model that could easily be adapted to an EXCEL™ spreadsheet was selected (Ref. 3). This model is commonly referred to as the Kawamura and Mackay Model. The formula used are as follows:

$$ST = (A)(K_M) \left(\frac{M_w P_v}{RT} \right) \quad [\text{Eq. 1.0}]$$

where: ST = source term ($\text{kg}\cdot\text{sec}^{-1}$)

A = area of the evaporating puddle (m^2)

K_M = mass transfer coefficient ($\text{m}\cdot\text{sec}^{-1}$)

M_w = molecular weight of substance ($\text{kg}\cdot\text{kmol}^{-1}$)

P_v = vapor pressure (Pa)

R = universal gas constant ($8314 \text{ J}\cdot\text{kmol}^{-1}\cdot\text{K}^{-1}$)

T = ambient temperature (K)

The mass transfer coefficient, K_M , is calculated by:

$$K_M = 0.0048 \left(U^{7/9} \right) \left(Z^{-1/9} \right) \left(S_c^{-2/3} \right) \quad [\text{Eq. 2.0}]$$

where: U = wind speed at a height of 10 m ($\text{m}\cdot\text{sec}^{-1}$)

Z = pool diameter in the wind direction (m)

S_c = the laminar Schmidt number

The laminar Schmidt number is calculated by:

$$Sc = \nu / D_M \quad [\text{Eq. 3.0}]$$

where: ν = the kinematic viscosity of the air ($\text{m}^2\text{sec}^{-1}$)

D_M = The molecular diffusivity of HCl in air ($\text{m}^2\text{sec}^{-1}$)

The molecular diffusivity of HCl is approximated by:

$$D_M = D_{H_2O} \sqrt{\frac{Mw_{H_2O}}{Mw_{HCl}}} \quad [\text{Eq. 4.0}]$$

Appendix 1 shows the final spreadsheet setup for equations 1.0 through 4.0.

As stated previously, the concept is to determine the average Pp of the solution over a pre-determined time period and then use this Pp to obtain input data for the accident analysis. The general methodology to calculate the average Pp is as follows:

1. The partial pressures of the solute and solvent are graphed in order to interpolate values between those given from a standard reference (as in Tables 1 and 2 of this report).
2. Using the source term spreadsheet (Appendix 1), calculate the release rate of the solution components for a predetermined spill volume.
3. The amount of each component evaporated for the time duration of choice is determined and subtracted from the original amounts of each component.
4. The new weight percent of the solution is calculated for the remaining solution, the proper Pp for each component is obtained from step 1 above and then input for the next time period. The change in density of the solution should be considered but can normally be ignored.
5. The process is continued through the time period of interest for the release.
6. The total amount of the hazardous component (e.g., HCl or HNO_3) released over the time period is calculated and divided by the time period to obtain the average release rate.
7. The Pp input into Appendix 1 is iterated until the release rate in step 6 is achieved. This Pp input is the "average" Pp over the time period of interest.

In the above methodology, there are three basic assumptions the analyst needs to decide upon prior to performing the analysis, they are (1) the predetermined spill volume, (2) analytic time period for each dilution/concentration step, and (3) the total time period of interest to calculate the average Pp. These three assumptions are arrived at as follows:

(1) Predetermined Spill Volume

If only one accident is being analyzed, it is logical that the accident spill size would be used. However, if it is desired to calculate an average Pp that can be used for varying spill volumes more information is needed. Some source term models are more sensitive to the spill volume input than others (related to the complexity of the model). As an example, the model used in this report shows the following sensitivity (normalized to the release rate per square meter) for various spills of HCl at a Pp of 10225 Pa:

Table 3: HCl release rates - Kawamura and Mackay

Volume (gal)	Release Rate (g·min ⁻¹ m ⁻²)
100	37.1
500	34.0
1000	32.8
2000	31.5

Using the results in table 3 and depending on the range of accidents to be analyzed, selecting a predetermined spill size of 500 to 1000 gallons should be sufficient to cover a large range of spills.

For comparison, another model suitable for spreadsheet adaptation, the Eckert-Drake model (Ref. 4), was also looked at. The spreadsheet for this model is contained in Appendix 2. The formulas used within the Eckert Drake spreadsheet are as follows:

$$m = h_d A \left(\frac{M \Delta p}{R_g T} \right) \quad [\text{Eq. 5.0}]$$

where: m = mass transfer rate (release rate)

h_d = mass transfer coefficient

A = surface area of pool (m²)

Δp = difference between the liquid phase vapor pressure and the gas phase partial pressure

R_g = gas law constant

T = air temperature (K)

The variable h_d above is calculated by:

$$hd = 0.644 \frac{D}{L} Re^{1/2} Sc^{1/2} \quad (\text{laminar}) \quad \text{for } Re < 500,000$$

$$hd = \frac{D}{L} [0.037 Re^{0.8} - 871] Sc^{1/3} \quad (\text{mixed}) \quad \text{for } Re \geq 500,000$$
[Eq. 6.0]

where D = diffusion coefficient of volatile component in air

L = pool length parallel to direction of flow

Re = Reynolds number

Sc = Schmidt number

The Reynolds and Schmidt numbers are defined as:

$$Re = \frac{Lu\rho}{\mu} \quad \text{and} \quad Sc = \frac{\mu}{D\rho}$$
[Eq. 7.0]

where: L = pool length parallel to direction of flow

u = wind velocity (m-sec⁻¹)

ρ = density of air

μ = viscosity of air

Performing the same modeling as for Table 3, the results with the Eckert-Drake model are:

Table 4: HCl release rates - Eckert-Drake

Volume (gal)	Release Rate (g-min ⁻¹ m ⁻²)
100	8.9
500	13.3
1000	14.2
2000	14.6

The Eckert-Drake model shows a greater sensitivity to pool size due to the input for the mass transfer coefficient changing from the 100 to the 500 gallon spill size (the Reynolds number transitions above the 500,000 trigger point between these two spill sizes). As such, greater care should be taken for selection of the pool size.

(2) Analytic Time Period for Dilution/Concentration Step

Selecting this time period is dependent on whether or not the solution of interest is diluting (more hazardous material evaporating) or concentrating (less hazardous material evaporating). As most analysis desire to show a level of conservatism it is important to select time periods that can

support this desire. For a solution that is diluting, use of a relatively long time period would overemphasize the initial high Pp of the component of interest thus not showing a "conservative" analysis. For a solution that is concentrating, use of a long time period would overemphasize the high Pp of the non (or less) toxic component which would result in a more conservative (faster) concentration time. In all cases the smaller the time intervals, the better the analysis. Practical application of the methodology forces the analyst to choose the desired conservatism in the analysis and thus the actual time interval used.

As the methodology for finding the average Pp is an iterative process, it is possible to start with a small time period and then base any increase in the time period on the results of the first few analyses.

(3) Total Time Period of Interest

Again, selection of this time period will depend greatly on whether or not the solution of interest is diluting or concentrating. In the case of a diluting solution (e.g., 36 weight % HCl), the average Pp from the time of the spill to the desired endpoint will produce the highest results. At WSRC, most analyses for chemical source terms and dispersion are compared to the Emergency Response Planning Guideline (ERPG) or Temporary Emergency Exposure Limits (TEEL) value (Ref. 5). The averaging time for calculating the ERPG/TEEL is normally 15 minutes (Ref. 6). As such, a 15 minute time period for a diluting solution is a logical choice.

If a solution is concentrating (e.g., 50 weight % HNO₃), there are actually two time periods of interest. The first is the time period for the calculation of the Pp. Again using the logic from above, 15 minutes is the logical choice. The second time period is, within the accident scenarios being analyzed, the time period between the spill and when mitigative actions are taken. For example, if the assumption is that mitigative actions can be assured within 8 hours, the material would be concentrated for 8 hours with the time period of 7.75 to 8.00 hours post-spill being used to calculate the average Pp to be used in analyzing the scenario.

Examples

The first example is the dilution of concentrated HCl after a spill. The HCl is assumed to be at 36 weight percent at the time of the spill. The Kawamura and Mackay model is used for source term determination. The spill size to be analyzed is 1000 lbs (101.63 gallons), the analytic time period is one minute and the period of analysis is fifteen minutes. The Pp of the HCl and H₂O were graphed using EXCEL™. The graph was used to manually determine the Pp of HCl and H₂O after each analytical step. The graphs are contained within Appendix 3. The results from the analysis of each time step is contained within Appendix 4.

From Appendix 4, the total amount of HCl released over the 15 minute period is calculated by subtracting the final HCl mass from the initial mass of 360 lb. This results in:

$$360 \text{ lb} - 288.7 \text{ lb} = 71.3 \text{ lb of HCl vaporized over the first 15 minutes}$$

The average source term is calculated by dividing by the time period of interest (15 minutes) and converting to grams as follows:

$$71.3 \text{ lb}/15 \text{ min} (454 \text{ g/lb}) = 2158 \text{ g/min release rate (source term)}.$$

An "average" HCl partial pressure is calculated for the first 15 minutes through iteration of the Kawamura and Mackay EXCELTM spreadsheet to attain the average source term. An average source term of 2158 g/min results in an average Pp of 76.7 mmHg for 36 weight percent HCl. This represents a reduction of greater than one-half of the original Pp (188 mmHg) that would be used in other methods (Ref. 3).

The next example is the concentration of a 1000 lb (92.3 gallon) spill of 50 weight percent HNO₃. In this scenario, no mitigation is assumed for the first eight hours after the spill. Therefore, the concentration is calculated for the first 8 hours prior to performing any average Pp calculations. Appendix 5 contains the Pp curves for solutions of HNO₃. Appendix 6 contains the results from the analysis at each time step. The time step initially selected was 30 minutes (as this is a concentration calculation, longer time steps are quicker and more conservative). Based on the concentration over the first three hours (50.0% to 50.3%), the time step was increased to one hour for the remainder of the analysis. In this example, the weight percent concentration/Pp of the HNO₃ was increased from 50%/0.56 mmHg to 50.9%/0.62 mmHg. As the trend of concentration show a very small slope, the calculation of a 15 minute average for post mitigation time is not necessary. In this case the 0.62 mmHg Pp would suffice.

The results of this methodology for 50 weight % HNO₃ shows a significant difference when compared to the methodology contained within reference 1. Using reference 1 and thus ignoring the time factor to reach equilibrium, the 50 weight % HNO₃ is assumed to concentrate to 66.56 weight % (ref. 7). The use of the Pp at 66.56 weight % for source term analysis equates to a Pp for HNO₃ of 3.8 mmHg, a six fold increase.

CONCLUSION

The use of the methodology contained within this report will calculate an average Pp for a binary chemical mixture that is less restrictive than the use of the initial Pp for binary mixtures that are diluting or the use of the mass transfer equilibrium Pp when the time of interest is less than the time to reach equilibrium.

All of the methodology in the report was performed manually in order to show the various steps in sufficient detail. This methodology utilizes source term codes easily adaptable to spreadsheets. The Pp curves could easily be input into common software (e.g., CricketGraphTM) to generate a function specific to the graph. As such, putting this methodology into simple code in order to facilitate quicker results should not be a difficult task.

REFERENCES

1. Kalinich, D. A., *Determination of Isothermal Mass Transfer Equilibrium Conditions of Binary Liquid Mixtures*, M-CLC-S-00383, 8/16/94.
2. R. H Perry and D. W. Green, *Perry's Chemical Engineers' Handbook*, sixth edition, McGraw-Hill Book Company, New York, 1984.
3. Evans, M, *Modeling Hydrochloric Acid Evaporation in ALOHA™*, HAZMAT 93-3, July, 1993.
4. Eckert, E. R. G. and R. M. Drake, *Heat and Mass Transfer*, McGraw Hill Book Co, 1959.
5. Craig, D. K., *ERPGs and TEELs for Chemicals of Concern at SRS: Rev. 11 (October 31, 1996)*, ECS-CAT-96-0095, November 14, 1996.
6. Craig, D. K., WSRC-MS-92-206, *Toxic Chemical Hazard Classification and Risk Acceptance Guidelines for use in DOE Facilities (U)*, Rev. 2, November 16, 1994.
7. Kalinich, D. A., *Nitric Acid-Water Isothermal Mass Transfer Equilibrium at 35 °C*, M-CLC-S-00384, Revision 0, 8/18/94.

Appendix 1 - EXCEL™ Spreadsheet of Kawamura and Mackay Source Term Model

	A	B	C
1	Parameter	Value	Dimensions
2	E (Evaporation Rate)	=A*Km*MW*Pv/(Rg*T)	kg/s
3	MW (Molecular Weight)	36.5	kg/kg-mole
4	Pv (Vapor Pressure)	10225	Pa
5	Rg (Gas Law Constant)	8314	J/kgmole-K
6	Temperature	30	°C
7	Volume of Spill	6.1	gal
8	d (Depth of Pool)	0.01	m
9	A (Surface Area of Spill)	=V/Depth	m^2
10	Km (Mass Transfer Coeff)	=0.0048*U^(7/9)*Z^(-1/9)*Sc^(-2/3)	m/s
11	Z (Pool Diameter in Wind Direction)	=SQRT(4*A/PI())	m
12	Sc (Schmidt Number)	=nu/Dm	
13	U (wind velocity)	1.7	m/s
14	nu (kinematic viscosity of air)	0.000015	m^2/sec
15	mu (viscosity of air)	0.000019	kg/m-s
16	Dm (Molecular Diffusivity of Solute in Air)	=D_H2O*SQRT(MW_H20/MW)	m^2/sec
17	D_H20 (Molecular Diffusivity of Water)	0.000024	
18	MW_H20	18	kg/kg-mole
19			
20	Conversions		
21	T (Absolute)	=B6+273.15	K
22	V (Volume)	=B7*0.0037853	m^3
23	Pv (Vapor Pressure)	=Pv/133.32	mm Hg
24	Evaporation Rate	=E*1000*60	g/min

Appendix 2 - EXCEL™ Spreadsheet of Eckert-Drake Source Term Model

	A	B	C
1	Parameter	Value	Dimensions
2	mdot (Mass Transfer Rate)	$=hd*A*MW*dp/(Rg*T)$	kg/s
3	MW (Molecular Weight)	37	g/g-mole
4	Vapor Pressure	76.7	mm Hg
5	Rg (Gas Law Constant)	0.0831451	bar-m ³ /kg-mole-°K
6	Temperature	30	°C
7	Volume of Spill	1000	gal
8	d (Depth of Pool)	0.01	m
9	A (Surface Area of Spill)	$=V/Depth$	m ²
10	hd (Mass Transfer Coeff)	$=IF(Re<500000,B20,B21)$	m/s
11	D (Diffusion Coeff)	0.0000162	m ² /s
12	L (Pool Length)	$(4*B9/3.14159)^{(1/2)}$	m
13	Re (Reynolds Number)	$=L*u*rho/mu$	
14	Sc (Schmidt Number)	$=mu/(D*rho)$	
15	u (wind velocity)	1	m/s
16	rho (density of air)	1.2	kg/m ³
17	mu (viscosity of air)	0.000019	kg/m-s
18			
19	Conditional		
20	hd (if laminar)	$=0.644*(D/L)*Re^{0.5}*Sc^{(1/3)}$	
21	hd (if mixed)	$=(D/L)*(0.037*Re^{0.8-871})*Sc^{(1/3)}$	
22			
23	Conversions		
24	T (Absolute)	$=B6+273.15$	°K
25	V (Volume)	$=B7*0.0037853$	m ³
26	dp ()	$=B4/750.06$	bar
27	Evaporation Rate	$=E*1000*60$	g/min
28	2 hr evaporation	$=(B27*120)/1000$	kg

Appendix 3 - Pp Curves for HCl Solutions

Pvp of H₂O over HCl Solution

Pvp of HCl Over HCl Solution

Appendix 4 - 36 Weight Percent HCl Analytical Dilution Steps for a 1000 lb Spill

0-1 min.: Pp HCl = 188 mmHg Pp H₂O = 6.08 mmHg

Evaporative rate HCl = 5290 g/min = 11.65 lb released

Evaporative rate H₂O = 107 g/min = 0.24 lb released

360 lb HCl - 11.65 lb = 348.35

640 lb H₂O - 0.24 lb = 639.76

new weight percent = 35.3

1-2 min.: Pp HCl = 152 mmHg Pp H₂O = 6.5 mmHg

Evaporative rate HCl = 4277 g/min = 9.42 lb released

Evaporative rate H₂O = 114 g/min = 0.25 lb released

348.35 lb HCl - 9.42 lb = 338.93

639.76 lb H₂O - 0.25 lb = 639.51

new weight percent = 34.6

2-3 min.: Pp HCl = 116 mmHg Pp H₂O = 6.9 mmHg

Evaporative rate HCl = 3264 g/min = 7.20 lb released

Evaporative rate H₂O = 121 g/min = 0.27 lb released

338.93 lb HCl - 7.20 lb = 331.73

639.51 lb H₂O - 0.27 lb = 639.24

new weight percent = 34.2

3-4 min.: Pp HCl = 100 mmHg Pp H₂O = 7.2 mmHg

Evaporative rate HCl = 2814 g/min = 6.20 lb released

Evaporative rate H₂O = 126 g/min = 0.28 lb released

331.73 lb HCl - 6.20 lb = 325.53

639.24 lb H₂O - 0.28 lb = 638.97

new weight percent = 33.8

4-5 min.: Pp HCl = 88 mmHg Pp H₂O = 7.5 mmHg

Evaporative rate HCl = 2476 g/min = 5.45 lb released

Evaporative rate H₂O = 126 g/min = 0.29 lb released

325.53 lb HCl - 5.45 lb = 320.08

638.97 lb H₂O - 0.29 lb = 638.68

new weight percent = 33.4

5-6 min.: Pp HCl = 72 mmHg Pp H₂O = 7.7 mmHg

Evaporative rate HCl = 2026 g/min = 4.46 lb released

Evaporative rate H₂O = 135 g/min = 0.30 lb released

320.08 lb HCl - 5.45 lb = 315.62

638.68 lb H₂O - 0.30 lb = 638.38

new weight percent = 33.1

6-7 min.: Pp HCl = 66 mmHg Pp H₂O = 7.9 mmHg

Evaporative rate HCl = 1857 g/min = 4.10 lb released

Evaporative rate H₂O = 139 g/min = 0.31 lb released

315.62 lb HCl - 4.10 lb = 311.52

638.38 lb H₂O - 0.31 lb = 638.07

new weight percent = 32.8

7-8 min.: Pp HCl = 60 mmHg Pp H₂O = 8.1 mmHg

Evaporative rate HCl = 1688 g/min = 3.72 lb released

Evaporative rate H₂O = 142 g/min = 0.31 lb released

311.52 lb HCl - 3.72 lb = 307.80

638.07 lb H₂O - 0.31 lb = 637.76

new weight percent = 32.6

8-9 min.: Pp HCl = 56 mmHg Pp H₂O = 8.3 mmHg

Evaporative rate HCl = 1576 g/min = 3.47 lb released

Evaporative rate H₂O = 146 g/min = 0.32 lb released

307.80 lb HCl - 3.47 lb = 304.33

637.76 lb H₂O - 0.32 lb = 637.44

new weight percent = 32.3

9-10 min.: Pp HCl = 50 mmHg Pp H₂O = 8.5 mmHg

Evaporative rate HCl = 1407 g/min = 3.10 lb released

Evaporative rate H₂O = 149 g/min = 0.33 lb released

304.33 lb HCl - 3.10 lb = 301.23

637.44 lb H₂O - 0.33 lb = 637.11

new weight percent = 32.1

10-11 min.: Pp HCl = 46 mmHg Pp H₂O = 8.6 mmHg

Evaporative rate HCl = 1294 g/min = 2.85 lb released

Evaporative rate H₂O = 151 g/min = 0.33 lb released

301.23 lb HCl - 2.85 lb = 298.38

637.11 lb H₂O - 0.33 lb = 636.78

new weight percent = 31.9

11-12 min.: Pp HCl = 43 mmHg Pp H₂O = 8.8 mmHg

Evaporative rate HCl = 1210 g/min = 2.67 lb released

Evaporative rate H₂O = 155 g/min = 0.34 lb released

298.38 lb HCl - 2.67 lb = 295.71

636.78 lb H₂O - 0.34 lb = 636.44

new weight percent = 31.7

12-13 min.: Pp HCl = 40 mmHg Pp H₂O = 8.9 mmHg

Evaporative rate HCl = 1126 g/min = 2.48 lb released

Evaporative rate H₂O = 156 g/min = 0.34 lb released

295.71 lb HCl - 2.67 lb = 293.23

636.44 lb H₂O - 0.34 lb = 636.10

new weight percent = 31.6

13-14 min.: Pp HCl = 38 mmHg Pp H₂O = 9.0 mmHg

Evaporative rate HCl = 1069 g/min = 2.36 lb released

Evaporative rate H₂O = 158 g/min = 0.35 lb released

293.23 lb HCl - 2.36 lb = 290.87

636.10 lb H₂O - 0.35 lb = 635.75

new weight percent = 31.4

14-15 min.: Pp HCl = 35 mmHg Pp H₂O = 9.1 mmHg

Evaporative rate HCl = 985 g/min = 2.17 lb released

Evaporative rate H₂O = 160 g/min = 0.35 lb released

290.87 lb HCl - 2.17 lb = 288.70

635.75 lb H₂O - 0.35 lb = 635.40

new weight percent = 31.2

Appendix 5 - Pp Curves for HNO₃ SolutionsPvp of H₂O over HNO₃ Solution Pvp of HNO₃ over HNO₃ Solution

Appendix 6 - 50 Weight Percent HNO_3 Analytical Concentration Steps for a 1000 lb Spill

0-30 min.: Pp HNO_3 = 0.56 mmHg Pp H_2O = 14.4 mmHg

30 min total Evaporation of HNO_3 = 0.11 lb released

30 min total Evaporation of H_2O = 1.17 lb released

500 lb HNO_3 - 0.11 lb = 499.89

500 lb H_2O - 1.17 lb = 498.83

new weight percent = 50.1

30-60 min.: Pp HNO_3 = 0.56 mmHg Pp H_2O = 14.4 mmHg

30 min total Evaporation of HNO_3 = 0.11 lb released

30 min total Evaporation of H_2O = 1.17 lb released

499.89 lb HNO_3 - 0.11 lb = 499.78

498.83 lb H_2O - 1.17 lb = 497.66

new weight percent = 50.1

60-90 min.: Pp HNO_3 = 0.56 mmHg Pp H_2O = 14.4 mmHg

30 min total Evaporation of HNO_3 = 0.11 lb released

30 min total Evaporation of H_2O = 1.17 lb released

499.78 lb HNO_3 - 0.11 lb = 499.67

497.66 lb H_2O - 1.17 lb = 496.49

new weight percent = 50.2

90-120 min.: Pp HNO_3 = 0.57 mmHg Pp H_2O = 14.3 mmHg

30 min total Evaporation of HNO_3 = 0.11 lb released

30 min total Evaporation of H_2O = 1.17 lb released

499.67 lb HNO_3 - 0.11 lb = 499.56

496.49 lb H_2O - 1.17 lb = 495.32

new weight percent = 50.2

120-150 min.: Pp HNO₃ = 0.57 mmHg Pp H₂O = 14.3 mmHg

30 min total Evaporation of HNO₃ = 0.11 lb released

30 min total Evaporation of H₂O = 1.17 lb released

499.56 lb HNO₃ - 0.11 lb = 499.45

495.32 lb H₂O - 1.17 lb = 494.15

new weight percent = 50.3

150-180 min.: Pp HNO₃ = 0.58 mmHg Pp H₂O = 14.3 mmHg

30 min total Evaporation of HNO₃ = 0.11 lb released

30 min total Evaporation of H₂O = 1.17 lb released

499.45 lb HNO₃ - 0.11 lb = 499.34

494.15 lb H₂O - 1.17 lb = 492.98

new weight percent = 50.4

180-240 min.: Pp HNO₃ = 0.58 mmHg Pp H₂O = 14.3 mmHg

30 min total Evaporation of HNO₃ = 0.22 lb released

30 min total Evaporation of H₂O = 2.33 lb released

499.34 lb HNO₃ - 0.22 lb = 499.12

492.98 lb H₂O - 2.33 lb = 490.65

new weight percent = 50.4

240-300 min.: Pp HNO₃ = 0.58 mmHg Pp H₂O = 14.3 mmHg

30 min total Evaporation of HNO₃ = 0.22 lb released

30 min total Evaporation of H₂O = 2.33 lb released

499.12 lb HNO₃ - 0.22 lb = 498.90

490.65 lb H₂O - 2.33 lb = 488.32

new weight percent = 50.5

300-360 min.: Pp HNO₃ = 0.59 mmHg Pp H₂O = 14.25 mmHg

30 min total Evaporation of HNO₃ = 0.22 lb released

30 min total Evaporation of H₂O = 2.32 lb released

498.90 lb HNO₃ - 0.22 lb = 498.68

488.32 lb H₂O - 2.32 lb = 486.00

new weight percent = 50.6

360-420 min.: Pp HNO₃ = 0.60 mmHg Pp H₂O = 14.2 mmHg

30 min total Evaporation of HNO₃ = 0.23 lb released

30 min total Evaporation of H₂O = 2.32 lb released

498.68 lb HNO₃ - 0.23 lb = 498.45

486.00 lb H₂O - 2.32 lb = 483.68

new weight percent = 50.8

420-480 min.: Pp HNO₃ = 0.62 mmHg Pp H₂O = 14.1 mmHg

30 min total Evaporation of HNO₃ = 0.23 lb released

30 min total Evaporation of H₂O = 2.30 lb released

498.45 lb HNO₃ - 0.23 lb = 498.22

483.68 lb H₂O - 2.30 lb = 481.38

new weight percent = 50.9