A Spreadsheet for the Estimation of Chemical Exposure

By THOMAS R. KOWAR

This article presents a spreadsheet for the calculation of exposure estimates for pure liquid chemicals; these estimates are based on equations reported in the literature. In addition, exposure estimates for sampling, drumming and open reactor manway operations with liquid chemicals are calculated. The calculations are based on the molecular weight and vapor pressure of the subject chemical. The spreadsheet also estimates vapor pressure from the boiling point of the chemical and the estimated vapor pressure is used for the exposure calculations for chemicals without a known vapor pressure.

Liquids evaporate. A pure liquid chemical is in equilibrium with its vapor in a closed system. The vapor is a gas and it exerts pressure. Therefore, the term "vapor pressure" is used to characterize the amount of chemical that exists as a gas in this equilibrium. Vapor pressure is a physical property of a pure liquid chemical that increases as temperature increases. For many chemicals, vapor pressures are available in the literature. Typically, this pressure is reported along with the temperature at which it is measured; it is expressed in units of millimeters of mer-

cury (mm Hg) or atmospheres (atm). One atmosphere of pressure (atm) is equivalent to 760 mm Hg.

A liquid in an open system cannot achieve equilibrium with its vapor because vapor disperses away from its source. Consequently, the liquid continuously evaporates and presents vapor to the surrounding space. This is why a liquid slowly disappears upon standing. In most industrial settings, liquid chemicals are not handled in closed systems. Typically, they are poured, drained or pumped as used for various purposes. These uses present opportunities for occupational exposure to the liquids and their vapors.

Agencies such as OSHA and the American Conference of Industrial and Government Hygienists (ACGIH) establish occupational exposure guidelines for chemicals. Such guidelines define a safe level for human exposure in an industrial environment. A hierarchy of engineering controls, administrative controls and personal protective equipment (PPE) is used to limit human exposure below the level of the chemical's exposure guideline.

Recently, OSHA promulgated a regulation that requires an employer to measure or estimate employee exposure to a chemical as part of its PPE policy (Hubbard 22+). The direct measurement of chemical exposure requires the development and validation of both sampling protocols and analytical methods. These activities require substantial time and may be impractical in environments where a

chemical is only used for a limited time. The estimation of chemical exposure liability is intuitive in a qualitative sense. Volatile, low-boiling liquids with a high vapor pressure present higher concentrations of vapor to the atmosphere than do liquids with a high boiling point and lower vapor pressure. However, quantitative estimates of chemical vapor exposure are not readily available.

Various industrial operations that involve chemicals result in different exposure potential. The rate of a chemical's evaporation is a function of the liquid's surface area and molecular weight, the temperature and the rate of airflow over the liquid (Hummel, et al 519+). Generally, exposure is greater for larger amounts of a chemical; however, small quantities distributed over a large surface area or presented at a high temperature may also present an opportunity for high exposure. Thus, the context in which a chemical is handled determines potential exposure.

A method for the calculation of exposure estimates has been presented by Hubbard (22+). Environmental Protection Agency (EPA) engineers also have developed equations for estimating inhalation exposures (Matthiessen 30+). These equations calculate a range of exposure for humans conducting sampling, drumming and open reactor manway operations that involve pure liquid chemicals. These operations are typical industrial activities that represent low, medium and high chemical exposure scenarios, respectively.

Equations from the Matthiessen article are based on physical chemistry and chemical engineering principles and on a set of reasonable assumptions regarding ventilation rate, air mixing, surface area and operation-specific factors.

Inhalation exposure estimates are reported as concentrations (C) in units of parts per million (ppm) and are calculated from the vapor pressure (P^0) and the molecular weight (MW) of the subject chemical. Calculations assume that temperatures of the liquid chemical and its vapor are equal.

Equations 1 and 2 calculate the lower and upper limits of the exposure range estimate for the sampling scenario.

1) $C = 46P^0[18/MW]^{0.33}$
2) $C = 459P^0[18/MW]^{0.33}$

Equations 3 and 4 calculate the lower and upper limits of the exposure range estimate for the drumming scenario.

3) $C = 800P^0$
4) $C = 12,000P^0$

Equations 5 and 6 calculate the lower and upper limits of the exposure range estimate for the open reactor manway scenario.

5) $C = 7,452P^0[18/MW]^{0.33}$
6) $C = 37,262P^0[18/MW]^{0.33}$

RESULTS & DISCUSSION

The present article reports on an Excel spreadsheet that calculates inhalation exposure estimates for pure liquid chemicals based on the methods reported by Matthiessen. The critical input data for the spreadsheet are the chemical's MW and vapor pressure, and the temperature at which vapor pressure is determined. Alternatively, if vapor pressure is unknown, the spreadsheet calculates an estimate of vapor pressure using the chemical's boiling point.

Estimation of vapor pressure from the boiling point is based on Trouton's rule and the Clausius-Clapeyron equation (Barrow 206, 386+). Trouton's rule is expressed in equation 7 and it states that the molar heat of vaporization, ΔH_v (cal/mole), divided by boiling point, T_b in degrees Kelvin (°K), for liquids is approximately constant. This constant is actually the molar entropy of vaporization ΔS_v (cal/°K-mole).

The molar heat of vaporization is the amount of heat required to convert one mole of liquid chemical to one mole of gaseous chemical. The molar entropy of vaporization is the change in entropy, or disorder, achieved by conversion of one mole of liquid chemical to one mole of gaseous chemical. Stated somewhat differently, Trouton's rule says that the molar entropy of vaporization is approximately the same for all liquids and this conclusion is intuitively reasonable. The spreadsheet uses the subject chemical boiling point in

FIGURE 1 Exposure Estimate for Toluene

Inputs					
Enter the Compound Name	Toluene				
Enter the Molecular Weight of the Compound	92.14 daltons		Enter the CAS Number for the Compound		108-88-3
Enter the Boiling Point of the Compound	111.00 degrees Centigrade	=	384.15 degrees Kelvin		
Enter the Temperature of Estimates	20.00 degrees Centigrade	=	293.15 degrees Kelvin		
Enter the Known Vapor Pressure at the Temperature of Estimates	22.00 mm Hg	=	0.0289 atmosphere		

From Trouton's Rule and the Clausius-Clapeyron Equation

Estimated Heat of Vaporization	8,451.30 calories/mole			
Estimated Vapor Pressure	24.45 mm Hg	=	0.0322 atmosphere	

From Known Vapor Pressure

	Low		High			Low		High	
Estimated Exposure Range for Sampling	0.78	to	7.77 ppm	or	2.98	to	29.76 mg/m3
Estimated Exposure Range for Drumming	23.16	to	347.37 ppm	or	88.70	to	1,330.55 mg/m3
Estimated Exposure Range for Open Manway	125.85	to	629.25 ppm	or	482.05	to	2,410.26 mg/m3

From Estimated Vapor Pressure

	Low		High			Low		High	
Estimated Exposure Range for Sampling	0.86	to	8.63 ppm	or	3.31	to	33.07 mg/m3
Estimated Exposure Range for Drumming	25.74	to	386.06 ppm	or	98.58	to	1,478.73 mg/m3
Estimated Exposure Range for Open Manway	139.87	to	699.33 ppm	or	535.74	to	2,678.70 mg/m3

Source: Matthiessen, R. Craig Estimating Chemical Exposure Levels in the Workplace, *Chem. Eng. Prog.* **1986**, *82(4)*, 30-34.   04/30/01

FIGURE 2 Exposure Estimate for Methanol

Inputs					
Enter the Compound Name	Methanol				
Enter the Molecular Weight of the Compound	32.04 daltons		Enter the CAS Number for the Compound		67-56-1
Enter the Boiling Point of the Compound	65.00 degrees Centigrade	=	338.15 degrees Kelvin		
Enter the Temperature of Estimates	20.00 degrees Centigrade	=	293.15 degrees Kelvin		
Enter the Known Vapor Pressure at the Temperature of Estimates	97.25 mm Hg	=	0.1280 atmosphere		

From Trouton's Rule and the Clausius-Clapeyron Equation

Estimated Heat of Vaporization	7,439.30 calories/mole			
Estimated Vapor Pressure	138.91 mm Hg	=	0.1828 atmosphere	

From Known Vapor Pressure

	Low		High			Low		High	
Estimated Exposure Range for Sampling	4.87	to	48.66 ppm	or	6.48	to	64.82 mg/m3
Estimated Exposure Range for Drumming	102.37	to	1,535.53 ppm	or	136.35	to	2,045.23 mg/m3
Estimated Exposure Range for Open Manway	788.33	to	3,941.67 ppm	or	1,050.01	to	5,250.06 mg/m3

From Estimated Vapor Pressure

	Low		High			Low		High	
Estimated Exposure Range for Sampling	6.95	to	69.51 ppm	or	9.26	to	92.58 mg/m3
Estimated Exposure Range for Drumming	146.23	to	2,193.39 ppm	or	194.76	to	2,921.46 mg/m3
Estimated Exposure Range for Open Manway	1,126.08	to	5,630.40 ppm	or	1,499.87	to	7,499.35 mg/m3

Source: Matthiessen, R. Craig Estimating Chemical Exposure Levels in the Workplace, *Chem. Eng. Prog.* **1986**, *82(4)*, 30-34.   04/30/01

equation 7 to calculate a rough estimate of the molar heat of vaporization.

7) $\Delta H_v / T_b = \Delta S_v \approx 22$

The Clausius-Clapeyron equation (equation 8) relates the natural logarithm of the ratio of two vapor pressures, P_2 (atm) and P_1 (atm), for a chemical to its molar heat of vaporization, ΔH_v (cal/mole), the universal gas constant, R (cal/mole-°K), and the two temperatures, T_2 (°K) and T_1 (°K) associated with the vapor pressures, respectively.

8) $\ln[P_2/P_1] = -(\Delta H_v/R)[[1/T_2]-[1/T_1]]$

The spreadsheet uses the rough estimate of a chemical's molar heat of vaporization, its boiling point and the temperature for the vapor pressure estimate (equation 8) to calculate vapor pressure. If one stipulates T_1 as the chemical's boiling point, then the corresponding vapor pressure P_1 will be one atmosphere and the left side of equation 8 reduces to $\ln P_2$. Exponentiation of both sides of equation 8 provides P_2 as the vapor pres-

TABLE 1 Summary of Open Reactor Manway Exposure Estimates for Organic Solvents

Chemical Name	Temperature (°C)	Vapor Pressure (mm Hg)	Manway Low Exposure (ppm)	Manway High Exposure (ppm)
Acetic Acid	20	11.8	78	389
Acetone	20	180.0	1,199	5,995
Acetonitrile	20	73.0	545	2,726
2-Butanone	25	100.0	620	3,101
Diethyl Ether	20	442.0	2,716	13,584
Dimethylformamide	25	3.7	23	114
Dimethyl Sulfoxide	20	0.4	2	12
Ethanol	19	40.0	288	1,438
Ethyl Acetate	20	73.0	424	2,119
Heptane	20	40.0	223	1,113
Isopropanol	24	40.0	263	1,317
Methanol	20	97.2	788	3,942
2-Methoxyethanol	25	6.0	36	183
Methylene Chloride	24	400.0	2,350	11,752
Tetrahydrofuran	20	145.0	899	4,497
Toluene	20	22.0	126	629

sure of the chemical at temperature T_2. This coarse method of estimating vapor pressure works surprisingly well. However, it is weak for chemical compounds that are capable of hydrogen bonding; such compounds tend to have higher molar heats of vaporization than predicted by Trouton's rule. Consequently, the spreadsheet calculates exposure estimates that are higher than those determined experimentally. These estimates are conservative and err on the side of safety for such compounds.

Figures 1 and 2 provide examples of the spreadsheet for toluene and methanol, respectively. The "inputs" section provides for acquisition of data required for the calculation. The user inputs the name and Chemical Abstracts Service (CAS) number identifiers for the subject chemical. The CAS number is included on the spreadsheet for clarity because the use of chemical nomenclature is not always precise. The chemical's MW (daltons), boiling point (°C) and vapor pressure (mm Hg), if known, are also input.

The "Temperature of Estimates" entry is the temperature (°C) at which vapor pressure is determined for compounds with known vapor pressure. If this pressure is to be estimated, this entry serves to define the temperature for which the estimate is to be made. Erroneous exposure estimates will result from the use of a temperature that does not correspond to a known vapor pressure entry. The spreadsheet displays the boiling point and Temperature of Estimates in °K and the known vapor pressure in atm.

The "From Trouton's Rule" and "Clausius-Clapyeron Equation" section of the spreadsheet display the estimated molar heat of vaporization in cal/mole

and the estimated vapor pressure in both mm Hg and atm.

The "From Known Vapor Pressure" section displays estimated exposure ranges for sampling, drumming and open reactor manway operations; these are calculated using known vapor pressure and associated Temperature of Estimates. The low and high values of the ranges are displayed for each operating scenario in ppm and in milligram per cubic meter (mg/m³). The two sets of units are used to present the exposure estimates because exposure guidelines are defined in one or the other of these units.

The "From Estimated Vapor Pressure" section displays the estimated exposure ranges calculated using estimated vapor pressure. Note that the mg/m³ displays are temperature-adjusted using the Temperature of Estimates temperature value. The mg/m³ values are calculated from ppm values using equation 9, where MW (daltons) is the molecular weight, T_2 (°K) is the Temperature of the Estimates and R (liter-atm/mole-°K) is the universal gas constant.

9) $mg/m^3 = [ppm*MW/RT_2]$

Table 1 summarizes exposure estimates for the open reactor manway operation scenario for various organic solvents. The table includes vapor pressure and corresponding temperature used for the exposure estimates.

CONCLUSION

This article has presented a spreadsheet that can be used to calculate exposure estimates for pure liquid chemicals. Estimates are based on the equations reported by Matthiessen. Exposure estimate ranges for sampling, drumming and open reactor

manway operations with pure liquid chemicals are calculated and displayed in ppm and mg/m³.

Calculations are based on the subject chemical's molecular weight and vapor pressure. The spreadsheet also estimates vapor pressure from the chemical's boiling point; this estimated pressure is used for exposure calculations for chemicals without a known vapor pressure.

The spreadsheet presented serves as a tool in evaluating potential exposure to pure liquid chemicals under several handling scenarios. Such information is useful for the selection of proper PPE. ■

REFERENCES

Hubbard, G. "OSHA's Respiratory Protection Standard: Calculating Reasonable Exposure Estimates." *Professional Safety.* Nov. 2000: 22-24.

Hummel, A.A., et al. "Evaporation of a Liquid in a Flowing Airstream." *American Industrial Hygiene Assn. Journal.* 57(1996): 519-525.

Matthiessen, R.C. "Estimating Chemical Exposure Levels in the Workplace." *Chemical Engineering Progress.* 82(1986): 30-34.

Barrow, G.M. *Physical Chemistry.* 5th ed. New York: McGraw-Hill, 1988.

Thomas R. Kowar, *Ph.D., is an organic chemist with Pharmacia Corp. in Skokie, IL. In this position, he manages the development and preparation of new pharmaceutical products. Prior to joining Pharmacia, he was a process development chemist for Story Chemical Corp. and Chemetron Corp. Kowar holds a B.S. in Chemistry from Kent State University and a Ph.D. in Chemistry from Michigan State University.*