

A GUIDANCE MANUAL FOR MODELING HYPOTHETICAL ACCIDENTAL RELEASES TO THE ATMOSPHERE

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A Guidance Manual For Modeling Hypothetical Accidental Releases to the Atmosphere

Health and Environmental Sciences Department

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PREFACE

This manual presents methods for modeling hypothetical accidental releases of fluids into the atmosphere from petroleum process operations. Given a particular type of release (e.g., pipe break, evaporating pool) and the chemicals or petroleum fractions involved, methods for modeling the release and subsequent dispersion phenomena are treated in a step-wise, comprehensive manner. The reader is presumed to be technically oriented, but not a specialist in the various disciplines represented.

Release phenomena, germane meteorological concepts, and after-the-fact mitigation countermeasures are presented for ready reference in this document. First, fluid dynamic and thermodynamic procedures best used to calculate flow rates and initial fluid states for a material being released into the atmosphere are given in some detail, including numerical examples. Next, the essential information required to characterize the atmosphere for dispersion modeling is presented, along with recommended default parameters. Lastly, available quantitative methods for incorporating vapor cloud mitigation methods into the dispersion modeling are presented.

To demonstrate how a number of the modeling procedures can be implemented, detailed simulation of eight hypothetical release scenarios are presented. The assumptions made, the calculation and/or selection of appropriate modeling parameters, use of several well-known modeling programs, and graphical presentation of results obtained are discussed.

It is not possible to present all the information that might be required for the various disciplines involved; however, extensive references are provided.

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NOMENCLATURE

NOMENCLATURE

Symbol	Quantity	SI Units of Measure ^a
L	Length	meters, m
M	Mass	kilogram, kg
F	Force	newton, N
τ	Time	seconds, s
E	Energy	joules, J
T	Temperature	kelvin, K
P	Pressure	Pascal (derived)
kmol ^b	Moles	kilogram molecular weight

a: If blank, the quantity is dimensionless, a fraction, or a count.

b: "mol" is defined as one gram molecular weight.

Symbol	Description	Units of Measure
A	Throat area, pool area, etc.	L^2
A_s	Effective area for air entrainment by sprays	L^2
B	Buoyancy factor for evaporation	
C_p	Heat capacity at constant pressure (+ subscripts l or v)	$E/[M \cdot T]$
C_D	Discharge coefficient	
C_I	Cloudiness index	
c	Concentration	M/L^3
D	Diameter (e.g. orifice, evaporating pool)	L
d	Ordinary differential operator	
E	Energy	E/M
E_{int}	Internal energy	E/M
E_{kin}	Kinetic energy	E/M
E_{pot}	Potential energy	E/M
F_N	Nozzle flow number for Equation 5-1	
FDF	Finite duration factor	
f_{ns}	Mole fraction in cloud entering spray barrier	
f_s	Mole fraction in cloud leaving spray barrier	
f_{rm}	Mole fraction released material	
f_v	Mole fraction vapor (or weight for pure component)	
G	Mass flux	$M/[L^2 \cdot \tau]$
G_{max}	Maximum mass flux	$M/[L^2 \tau]$
G'	Normalized mass flux, Leung/Epstein model	$M/[L^2 \tau]$
g	Gravitational constant (= 9.807 m/s ²)	L/τ^2
H	Enthalpy	E/M
h	Heat transfer coefficient, air-to-pool	$E/[T \tau]$
h_f	Vapor barrier fence height	L
h_l	Liquid head	L
hpool	Height of evaporating pool	L
K	Equilibrium vapor/liquid mole fraction ratio (Chapter 3)	
K	Empirical nozzle constant (Chapter 5)	
k	Specific heat ratio	
k	von Karman's constant (0.41)	
k_c	Convective mass transfer coefficient	L/τ

Nomenclature

Symbol	Description	Units of Measure
k_s	Thermal conductivity of ground	$E/[LT\tau]$
L	Length of water curtain, Equation 5-1	L
L_{ns}	Lateral spray nozzle separation distance	L
M	Molecular weight	$M/kmol$
$\dot{M}$	Momentum flow rate per unit length of barrier	F/L
m	Number of spray nozzles	
N_{Pr}	Prandtl number	
N_{Re}	Reynolds number	
N_s	Number of chemical species	
N_{Sc}	Schmidt number	
N_{sh}	Sherwood number	
n	Number of intervals, samples	
n_{mol}	Number of moles	
ndf	Number of degrees of freedom (Phase Rule)	
P	Pressure	F/L^2
$\mathcal{P}$	An intensive property, a variable quantity	
p	Exponent in wind speed power law	
Q	Amount of heat	E
q	Heat rate	E/τ
R	Ideal gas constant	$[F \cdot L]/[kmol \cdot T]$
Ri	Release Richardson Number	
r	Evaporating pool radius	L
r	Pressure ratio (defined with various subscripts)	
r_c	Critical pressure ratio	
S	Entropy	$E/[M \cdot T]$
s	Downwind dimension of spray barrier	L
T	Temperature	T
t	Time	τ
tol	Numerical equation solution tolerance	
U	Volumetric flow rate	L^3/τ
u	Velocity of fluid	L/τ
u_f	Air entrainment velocity	L/τ
u_f	Wind speed at vapor barrier fence height	L/τ
u_{wind}	Wind speed	L/τ
u_*	Friction velocity	L/τ
V	Volume	V
v	Specific volume (volume per unit mass)	L^3/M
v_c^m	Specific molal volume (volume per mole)	$L^3/kmol$
W	Mass	M
w	Mass flow rate	M/τ
X	Evaporation surface roughness correction factor	none
x	Downwind distance	L
x_i	Mole fraction of a component in the liquid phase	
y	Crosswind distance	L

Nomenclature

Symbol	Description	Units of Measure
y_i	Mole fraction of a component in the vapor phase	
z	Vertical distance (elevation)	L
z_l	Liquid head	L
z_{meas}	Wind speed measurement height	L

Greek and Other Letters

α_1	Void fraction (fraction vapor in a vapor/liquid stream)	
α	Before/after concentration ratio for barriers	
α_T	Thermal diffusivity	L^2/τ
γ	Convergence filter or "accelerator"	
Δ	Finite difference operator	
∂	Partial differential operator	
κ	Fraction material remaining in the plume after curtain	
ε	Scrubbing (removal) efficiency fraction	
ϵ	Error of equation solution	
ϵ_{fl}	Radiation emissivity (average)	none
ζ	Heat flux	$E/[L^2\tau]$
η	Number of phases in equilibrium	
Θ	Heat of conduction factor	$E/[L^2\tau^{1/2}]$
λ	Monin-Obukov length	L
λ_T	Thermal conductivity	$E/[LT\tau]$
μ	Absolute viscosity	Pa*s (pressure/time)
ξ	Vapor barrier fence porosity	
ν	Kinematic viscosity of the vapor in air	L^2/τ
ρ	Density	M/L^3
$\sigma_x, \sigma_y, \sigma_z$	Atmospheric dispersion coefficients	L
σ	Surface tension	FL/L
σ_{sb}	Stefan-Boltzman constant	$E/[L^2T_4]$
Φ	Monin-Obukov length function	
ϕ	Downward pointing spray correlation parameter	
ϕ_s	Sun angle	degrees
χ	Mass fraction	
ψ	Rain out mass fraction	
Ω	Net work (includes expansion)	E
Ω_{shaft}	Shaft work	E
ω	Correlating parameter for Leung/Epstein model	
$\mathcal{D}$	Molecular diffusivity of the vapor in air	L^2/τ
h	Henry's Law constant	P

Subscripts

*	denotes friction velocity
▼	low superheat
1.25	wind speed at 1.25 meters elevation
2	stagnant reservoir (flow models) orifice throat (flow models)

Nomenclature

Symbol	Description	Units of Measure
3	atmosphere (flow models)	
a	atmospheric	
avg	average	
BP	bubble point temperature	
b	mitigation barrier location	
bulk	bulk property, pseudo-pure component	
c	critical (temperature, pressure, volume)	
DP	dew point temperature	
e	air entrainment	
i	component index	
int	internal (energy)	
j	phase index	
key	key component in a mixture	
kin	kinetic	
l	liquid phase	
lh	liquid head	
lv	liquid-to-vapor, heat of vaporization	
max	maximum (choked)	
ms	mean value specific to entropy calculations	
N	Maximum value of index n	
NBP	Normal boiling point	
n	index, count	
ns	for the plume (= cloud), just before entering the spray	
p	initial plume (except for C_p)	
pool	evaporating pool	
pot	potential (energy)	
pxs	plume cross-section entering the spray	
rev	reversible process	
rm	released material	
s	saturation conditions	
s	spray interaction surface	
sat	saturated	
sauter	Sauter mean particle diameter	
si	spray impact area	
spray	after the spray	
surf	surface value	
T	thermal	
v	vapor phase	
vap	of vaporization	
wind	wind	
x	for downwind distance axis	
y	for crosswind distance axis	
z	for vertical distance (elevation)	
↓	Into the pool	
↑	Upward out of the pool	

CHAPTER 1

CHAPTER ONE

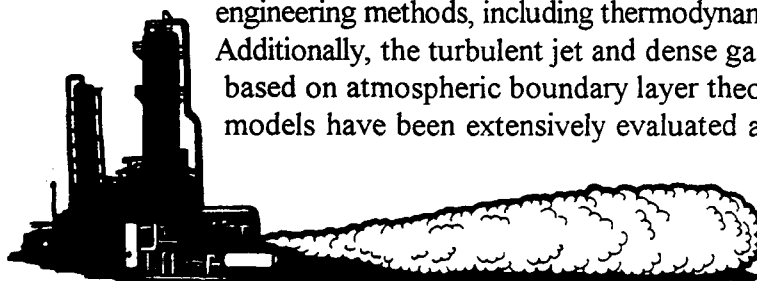
Introduction

The purpose of this Guidance Manual is to provide methodologies for consequence analysis purposes. That is, given a potential or after-the-fact set of circumstances for the accidental release of a chemical fluid into the atmosphere (the “*scenario*”), what are the appropriate methods to estimate spatial and time dependent concentrations of the material over a particular geographical area?

Scenarios may be generated within the hazard analysis parts of overall risk assessment studies. Techniques such as HAZOPS, fault tree, and “what if” analyses are used to discover potential hazardous situations which lead to an accidental release. Concentrations predicted for an identified release scenario may then be used to estimate possible impact of the shock waves and thermal damage from vapor cloud explosions, or potential toxic effects. The impact of toxic dispersed vapor clouds requires interpretation by specialists such as toxicologists and industrial hygienists. Thus the person or persons doing the source/release and dispersion modeling must interact “upstream” with those doing hazard analyses and with those “downstream” who interpret health or flammability aspects.

The modeling methodologies presented and recommended are intended for use in risk assessment studies for refinery/chemical plants during design or operation as well as for emergency response planning purposes. Also, available quantitative or semi-quantitative methods for mitigating a release after or during its occurrence are discussed. The product of any modeling exercise is an estimate of concentrations of the released material over a potentially affected geographic area so that possible toxic and/or flammability impact can be estimated. Modeling procedures are recommended on the basis of applicability to the particular situation being considered, required accuracy of results, simplicity, and availability of computer codes. If comparable modeling methods are available, they are discussed and used selectively in the example release scenarios. The calculational procedures and computer programs discussed are in the public domain. To limit the extent of the demonstrative simulation work, only SLAB, HGSYSTEM and DEGADIS program systems were used.

The release/dispersion scenarios described and exemplified are hypothetical; that is, they do not describe any particular accident that has occurred, nor a known situation for which an accident is liable to occur. However, the treatment and examples are realistic, for they have been drawn from the experience and knowledge of many technical personnel working in industry, government and academia. Calculational procedures used and recommended are well-accepted and are state-of-the-art in terms of readily available methods in the public domain; for example, the calculations for initial fluid release amount/flow rate and its concomitant physical state use standard chemical engineering methods, including thermodynamic and physical property estimation. Additionally, the turbulent jet and dense gas atmospheric dispersion models are based on atmospheric boundary layer theory and other physical principles; the models have been extensively evaluated against small and large scale experiments.



This Manual does not cover the origination of release scenarios, nor the interpretation of concen-

tration estimates, except to demonstrate the concepts. These factors should be established separately for each individual modeling application. Effects criteria, such as flammability limits and references to toxic materials, toxicities, or toxic concentrations levels, (*concentration of concern*), are used only to impart a sense of reality to the various examples and should not be used without review. Estimation and/or interpretation of possible toxic effects of model-predicted chemical concentrations are outside the scope and purpose of this Manual. The sidebar suggests a method for selection of flammability limit concentrations if no other information is available and/or for screening purposes.

The scope of the manual does not include model development and evaluation. Use of a specific modeling program for a type of application does not imply that program is particularly recommended. In general, problems encountered by the author in using a program were made known to the program author.

Manual Organization

Chapter 2 of the Manual provides an overview of phenomena which must be considered in defining release/dispersion scenarios. The phenomena involved are discussed qualitatively so that the applicability of modeling methods described in later chapters can be appreciated. Eight representative scenarios are described for the purpose of previewing types of problems, which will be analyzed, simulated and discussed in *Chapter 6*.

Chapter 3 provides working methods for estimating the rates and physical states of released substances on entering the atmosphere. Because chemical engineering thermodynamics is extensively used, a working overview to this subject provides the basic concepts involved, as well as references to sources of physical and thermodynamic data required for the calculations. Calculational methods follow for releases from process equipment (valves, openings in vessel walls, sudden vessel failure, etc.). The releases may form "clouds" consisting of vapor, and vapor plus liquid aerosols. In some cases, evaporating pools of liquids may be formed on water or ground surfaces. The best, *practical*, calculational methods are presented for the current state-of-the-art. The results of these calculations are needed as parameters for the atmospheric dispersion models.

Chapter 4 provides an brief overview of meteorological phenomena which affect vapor cloud transport and dispersion as well as descriptions of associated characterization parameters used in dispersion modeling. Recommendations are made for selection of parameter values.

Flammability Criteria

Published flammability limits are determined in the laboratory by means of experiments in which the fuel/air concentrations are uniform and precisely known. Thus measured, the lower flammability limit ("LFL") for most hydrocarbons ranges from about 2% to 6% by volume. So, to be conservative, a LFL of 2% can be taken as a nominal, global value for the purposes of this Guidance Manual.

Actually, the concentration at any point and time in a real cloud, such as that being considered here, will be highly variable. There will be "fingering," "holes," and other inhomogeneities caused by terrain, structures and general turbulence.

In a number of field tests, it has been found that peak concentrations are generally about twice that of average concentrations in vapor clouds. On this basis, the LFL of 1% should be considered for general use. However, dispersion models do not predict concentrations more accurately than a factor of 2 at best. For these reasons, a range of concentrations for the lower flammability limits must be considered. Therefore, for these purposes, **if a model calculates a released material concentration less than 0.5%v, the corresponding real cloud will be taken as non-flammable.**

Also, an upper flammability limit need not be considered, as it must be for a closed system. With a cloud, there is always an "edge" in which a flammable mixture exists, thus the cloud can be ignited if the edge encounters an ignition source.

Chapter 5 describes mitigation of accidental releases into the atmosphere from the standpoint of modeling after-the-fact actions with estimates of their effectiveness. This information can be used with dispersion modeling to help in the selection and design of mitigation measures.

Chapter 6 presents the purposes, statement, analysis, simulation methods and results for eight release scenarios. Recommendations are made within each presentation for selection and analysis of modeling parameters for the problem at hand.

The *Nomenclature* (follows the Table of Contents) lists the symbols with their generalized units-of-measure used in the Manual. The *SI* units-of-measure system is used for all equations and examples. The three modeling program systems use various mixtures of the metric system units; conversions to and from SI units by the user are implied. ★

Appendix I summarizes the suggested default values for selected modeling parameters.

Appendix II is an overview of the features and input data requirements of the three modeling program systems, SLAB, HGSYSTEM and DEGADIS. These are used for demonstrating the modeling techniques and typical results for the demonstration scenarios in Chapter 6. User's Manuals should be consulted for detailed descriptions of program theory, operation, data requirements, file formats, and results generated.

Appendix III contains listings of germane modeling program input and intermediate result files referenced in the time dependent release simulation of Scenario 7 of Chapter 6.

Quick References

In addition to the Table of Contents and the Subject Index, several techniques have been used to aid the reader in locating particular information or methods to use in modeling applications. Chapters 3 through 5 each have a *Quick Reference* text box showing the page and/or equation where a particular subject or algorithm is most directly discussed.

In the scenario descriptions of Chapter 6, a text box summarizes the major *Release Attributes* by which the scenario's type and principal parameters may be readily identified. A *RECAP* summarizes the parameters used in the modeling. Additional methods, noted in the introduction of that chapter, are also used to aid quick referencing.

Equations which are primarily used for calculations have the symbol ◇ appended to the equation number.

Conventions

Within each chapter, tables, figures and equations are each numbered sequentially from the top of the chapter. If reference to these items is made from one chapter to another, the chapter number is prefixed. For example, Figure 3-12 is the 12th figure in Chapter 3. Pages are numbered according to *Chapter number-Page number*. To avoid confusion, the tables and figures for each scenario in Chapter 6 are prefixed by Sn, where n is the scenario number and S designates "Scenario." For example, Figure S6-2 denotes the second figure in Scenario 6.

★

Perry's Chemical Engineering Handbook, Sixth Edition, Chapter 1, contains a complete definition of the SI quantities, the relationships between them, and tables of conversion factors to other units-of-measure systems. This will be called "Perry's Sixth" for brevity. See *References* for further information on the handbook.

References, listed after Chapter 8, are presented according to chapter number. Within a chapter, a particular reference is made according to *author [reference number]*. If a citation is made from within one chapter to a reference listed under another chapter heading, the chapter number is prefixed.

Terminology

Not all of the terminology used in this field is precisely defined or used. In this manual, “*substance*” is used to denote a pure chemical, chemical mixture, or other material which can or might be released to the atmosphere. “*Fluid*” is used for a substance capable of flowing, which may be gas, liquid, a gas/liquid mixture or aerosol suspension, or even a suspension containing solids in a flowing stream.

It is common practice to use the term “*vapor cloud*” for any visible or invisible body of substance moving with, and/or through, the atmosphere. Such a cloud may actually contain released liquid (in addition to its vapor) or even suspensions of solid particles. Although “*plume*” may most often refer to elevated releases from stack, it is used herein also for ground level or vapor clouds. “*Gas blanket*” is sometimes used to describe a surface level, dense vapor cloud in the early stages of its release. These terms are used more or less synonymously in this manual to mean the bounded, fluid entity of released substance (mixing with air) flowing through the atmosphere.

The symbol “ppm” refers to parts-per-million by volume [mole] in the gas, unless otherwise stated. Also, if at all possible, standard mathematical symbols as in the disciplinary literature are used for the parameters and variables. However, the same symbol or letter is often used in this text for many different items; this can be very confusing. Therefore, to help minimize possible misinterpretations, some different-than-standard symbols are used.

Subject Index Development

The subject index is based upon Chapters 1 - 6 and Appendix II. Not every appearance of a particular word or phrase is listed; a usage which is of minor importance does not appear in the index. The Nomenclature, References, Appendix I and Appendix III are not indexed.

In Chapter 6 demonstration scenario simulations, the words/phrases *pressure*, *temperature*, *wind speed*, and *stability class* are not indexed because they appear a large number of times in the text for each scenario.

CHAPTER 2



Documents

Document Sharing Hub

CHAPTER TWO

Overview of Release/Dispersion Processes and Demonstration Scenarios

The Overall Modeling Process

Every modeling study involves six major steps:

1. State the objective(s) of the study, including consideration of the material and mechanism, or *scenario*, by which it could be released. A scenario may also define initial ranges for parameters to be studied, such as release rates and modes, meteorology, etc.;
2. Devise or select appropriate release/dispersion modeling method(s);
3. Calculate the source parameters such as the amount released or mass flow rate(s) as well as physical state(s) of the released fluid for the next step;
4. Model the initial transport and mixing of the fluid with the atmosphere;
5. Model the transport and dispersion of the formed plume or cloud in the atmosphere; this produces concentration estimates over the space and time of interest; and
6. Document the work and report the results in a clearly understandable manner.

The goal of a modeling study is to answer the question: “What are the safety implications of a particular hypothetical release?” This must be considered in light of the local area involved, *e.g.*, population density, structures, terrain, weather, etc. In a real study, **Step 1** above must address the local situation.

Given the objective and the hypothesized circumstances of a release, modeling methods can be selected in **Step 2** to best (or adequately) represent the scenario. Sometimes, particular phenomena can only be modeled in a very approximate, or bounding, manner because of lack of a valid model, experimental information, time allowed to do the study, etc. In such situations, it may be necessary to modify originally chosen scenarios to fit the available resources. Since modeling of an entire scenario often requires sequential use of submodels, results from a particular model may change or influence the choice and use of following model(s).

Calculation of release rates/amounts via **Step 3** may be fairly straightforward. In some cases, the rate may be given as a result of a preceding risk analysis or “what if” study. However, most of the time these values will need to be calculated by accepted engineering methods and thermodynamics.

After the fluid enters the atmosphere, a “*transition*” modeling method may be required as **Step 4** to define the initial mixing of the fluid with the air. This will represent phenomena such as cooling of the cloud or jet by gas expansion, state phase changes, etc. A common example is a fluid at high temperature and pressure being released through a hole. Intense mixing, which occurs in jets, can markedly affect downwind concentration results when compared with the case where a jet is not formed.

Step 5 is the final dispersion modeling process for a scenario. For example, the selection of a particular dispersion model will be based upon whether an elevated plume proceeds into the “far

field” under the influence of wind and atmospheric dispersion phenomena, or whether a dense gas cloud is formed from an area source, or perhaps where a jet is ignited to flare. These models, which may be steady state or time dependent, will generate concentration isopleths (constant value loci) over the geographical area and time of interest.

Step 6, documenting the work and proper presentation of the results, is very important. The manner of presentation should be designed with the background of the intended audience in mind. The presentation of results by means of extensive tables of numbers, *e.g.*, concentration vs. downwind distance, is usually very ineffective. Well-prepared plots and other figures designed with the intended audience in mind are preferred.

Near vs Far Field Modeling

Consider the release of a fluid for which the plume or cloud remains near the ground as it travels downwind. Close to the source, the detailed “mechanism” by which the fluid leaves its containment to form a plume at atmospheric pressure must be modeled to obtain accurate concentration estimates. For example, release of a turbulent jet will immediately entrain large amounts of air. On the other hand, at sufficiently long downwind distances, the amount of air entrained into the plume by the turbulent jet becomes insignificant relative to the amount subsequently entrained by atmospheric mixing processes.

Therefore, the term *near field* is generally used to mean the area close to a source where the details of the release mechanism phenomena still *significantly affect* the concentrations. The term *far field* denotes the area beyond the near field.

If a particular modeling application is concerned only with the far field, it may be possible to simplify the modeling procedures. To estimate the approximate distance for the beginning of the far field, modeling with and without detailed source effects can be used; the distance at which plume centerline concentration curves approach each other is the beginning of the far field as a first approximation; the far field is where the original substance concentration becomes less than about 1/1000 of the release concentration.

Note that the above definitions apply only to releases occurring near the ground (or sea) for which the plume remains near the ground. For elevated plumes, the near versus far field concept is not as useful. Plume rise has a significant effect on all calculated ground-level concentrations.

To summarize, *if near field receptor locations are of interest for ground level releases:*

- The mechanism of the release source effects should be modeled (*e.g.*, for released chemicals the particular reactions and phase equilibria should be appropriately modeled);
- Time dependent modeling should be used if the release is of short duration (varies rapidly with time).

If far field receptor locations are of interest for ground level releases:

- Concentrations are functions of release rate only, not the specific mechanism of the release (*e.g.*, once chemical reactions and phase equilibria effects disappear in the far field, inert gas thermodynamics may be used in the modeling);
- Steady state modeling of finite duration releases may often be used with appropriate correction for concentration averaging time with respect to travel time.

Mitigation effects on the cloud can be important, particularly if pollutant is removed from the cloud. However, air entrainment which dilutes the pollutant concentrations in the cloud are generally only important in the near-field. Cloud mitigation systems are discussed in Chapter 5 and Scenario 7 of Chapter 6.

Release-to-Dispersion Phenomena

The phenomena associated with an accidental release of a petroleum or chemical material into the atmosphere and its subsequent dispersion is, in general, a complex process. To properly model the final dispersion process, which is primarily controlled by atmospheric forces, all release phenomena must be appropriately modeled so the correct release rates and fluid states are used for dispersed concentration estimates. Without this, serious over- and under-predictions can be obtained.

Figure 1 broadly summarizes most of the sequences of processes, or paths, through which a discharged material can pass until its dispersion is controlled completely by atmospheric boundary layer phenomena. (Key words or phrases corresponding to the boxes in the figure are shown in bold type below.)

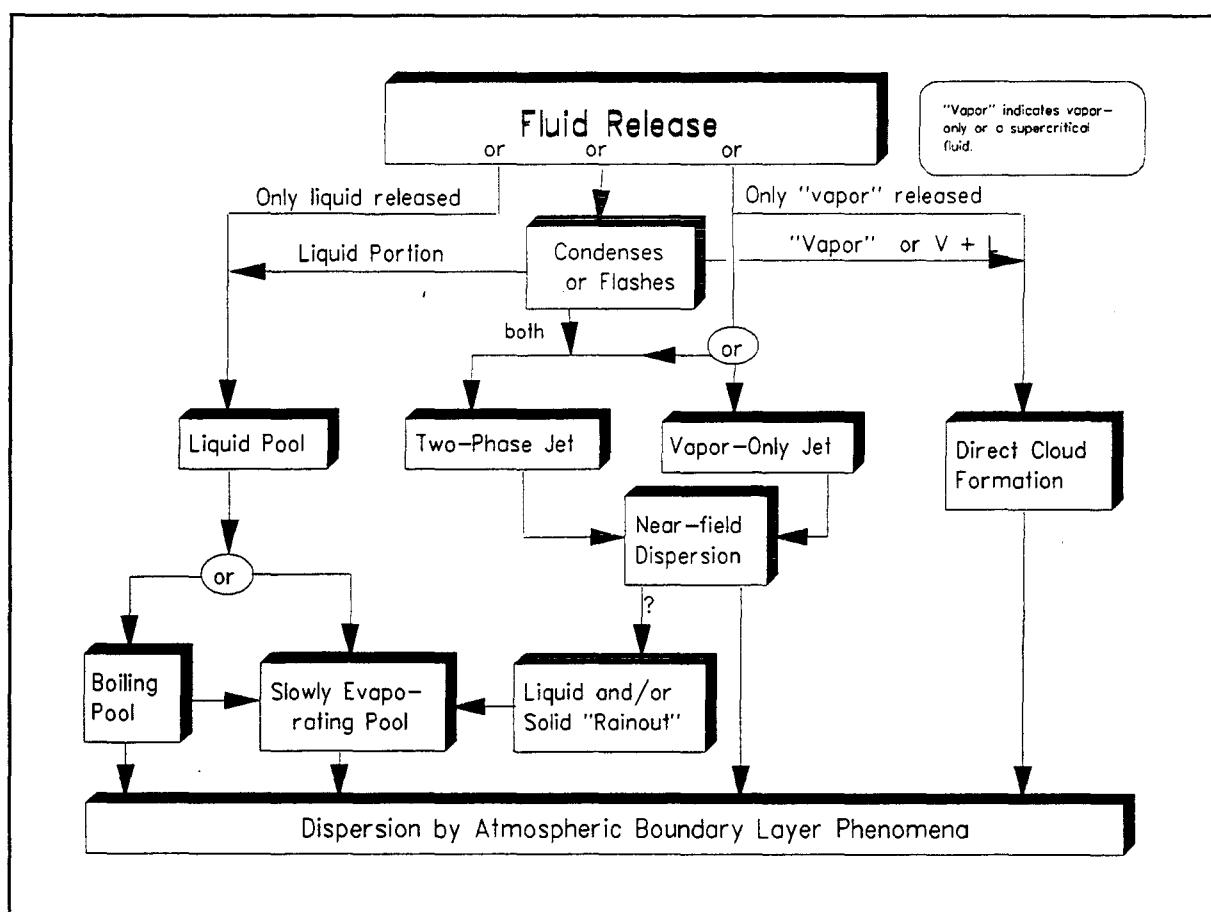


Figure 1. Paths to Air Dispersion near the release point.

Starting at the top of the figure, the fluid[★] release may be from a bursting, or large, opening in a vessel, or from a valve, a small hole in a vessel or pipe, and so forth. If the fluid is a liquid superheated above its normal boiling point, it will flash to form a **vapor/liquid mixture**; this is a high energy process, so much or all of the liquid may remain suspended in the gas phase as an **aerosol** of very fine droplets. If the fluid is condensable vapor, the cooling caused by expansion from storage to atmospheric pressure may cause a liquid phase to form. This liquid may remain all suspended as an aerosol, or some can “rain out” to form a **pool**.

If the fluid is released at high pressure through a hole, nozzle, orifice or pipe-end, a **turbulent jet** will be formed. Turbulent jets rapidly mix the fluid with the air. Thermodynamic processes mentioned above are also acting. Thus dispersion in the near source is primarily controlled by these mechanisms. However, for a vertical release, the plume will bend over to an extent, depending upon its density relative to air. A **dense gas, ground level cloud** may be formed by the plume sinking to the ground.^{★★}

If the original fluid is below its boiling point at atmospheric pressure (*i.e.*, its normal boiling point), is a non-boiling solution, is a cryogenic liquid, or is a liquid formed by condensation from the adiabatic release, a pool of liquid may be formed upon release. (The cases where all the fluid is absorbed by the ground or drops to the bottom of a water body are not treated in this Manual.) Pool evaporation may occur by two modes: 1) **Boiling evaporation** takes place if the ground is, and remains, warmer than a liquid which is below its normal boiling point; 2) mass-transfer limited **slow evaporation** occurs from the turbulent action of the wind over the surface of a liquid or solution which is a non-boiling liquid. Since the boiling process requires heat, a spill may start as a boiling liquid, but as the ground is cooled, the evaporation may become mass transfer limited.

Finally, the released cloud becomes subject to dispersion by **atmospheric** turbulence, as indicated in the lowest box in the figure. If an elevated jet-plume is formed above the ground, its velocity will slow to the wind speed, and the temperature and density of the plume will asymptotically approach that of air. If the jet directly impacts the ground, the cloud formed will spread horizontally and then disperse in the atmosphere. If the cloud is from a boiling pool, *usually* a dense cloud is formed, which will initially spread due to its density, and then disperse downwind through normal atmospheric processes. For surface area releases in which the emission rate is small enough not to affect significantly the density of the air at the source, a neutrally buoyant cloud will be formed at ground level and disperse through normal atmospheric processes.

It is common practice to refer to all the modeling processes above the bottom box in Figure 1 as “source modeling,” while the dispersion by atmospheric-only process is often called “dispersion modeling.”

Demonstration Scenarios

Eight hypothetical release scenarios have been developed to demonstrate methods recommended for modeling. These scenarios were selected to encompass many of the paths shown in Figure 1, and to demonstrate the atmospheric variables required (to estimate concentrations) for a given situation.

Table 1 summarizes the source/release, interpretation, boundary layer, and attributes for all eight

-
- ★ “Fluid” refers to gas-only, liquid-only, vapor plus liquid and/or solid mixtures (aerosols), etc. The material may be a pure chemical or a multicomponent system.
 - ★★ “Ground” will be generally used to denote the earth's surface, either sea or ground.

scenarios.

In the following descriptions, only minimum details are given. Full scenario descriptions, their analyses, simulation results, and summary discussions are provided in Chapter 6. Excerpts from Figure 1 show the particular analysis path for each scenario; those scenarios with similar paths are grouped in a single figure.

Table 1. Summary of Scenario Attributes

No.	SCENARIO							
8	Liquid benzene from tank bottom outlet							
7	Anhydrous HCl vapor jet - water spray mitigation							
6	Ammonia loading hose or pipe break							
5	Liquified chlorine tank truck accident							
4	Oil well blowout							
3	Supercritical propane pipe hole release							
2	H2S in CO2 from safety relief stack							
1	H2S from unlit flare stack							

ATTRIBUTE	1	2	3	4	5	6	7	8
SOURCE CHARACTERIZATION								
Release method:								
"Hole" (orifice, nozzle, pipe-end, etc.)	X	X	X	X		X	X	X
Vessel burst					X			
Area flux								X
Flow rate given	X	X		X				
Released fluid state:								
Liquid						X		
Vapor	X	X			X		X	
Liquid + Vapor				X	X			
Supercritical fluid			X					
Chemical reactions:								
Time characterization:								
Steady state	X	X	X	X				X
Finite					X	X	X	
Short transient (fast decay)							X	
TRANSITIONAL								
Turbulent Jet:								
Vertical upwards orientation	X	X		X				
Horizontal orientation			X			X	X	
Other orientation								
Pools, ponds, etc. (areas):								
Boiling ("cryogenic")								
Non-boiling					X			X
ATMOSPHERIC ATTRIBUTES								
(Flat, level terrain assumed.)								
Cloud or plume elevation:								
On the surface				X	X	X	X	X
Elevated	X	X	X	X				
Roughness type:								
Rural		X		X	X			
Urban						X		X
Industrial	X					X	X	X
Other			X					
Stability:								
Stable	X	X		X	X	X	X	
Neutral	X	X	X	X		X		X
Unstable	X	X		X				
INTERPRETATION								
Averaging time:								
Instantaneous			X			X	X	
1 minute	X	X		X		X		
10 minute								X
Other					X	X		
Hazard type:								
Toxic	X	X		X	X	X	X	X
Flammable			X	X				X

Scenario 1: Hydrogen Sulfide from Unlit Flare Stack

This scenario demonstrates the effects of two important variables on the dispersion behavior of vertically-directed turbulent jets (plumes): 1) the *momentum*, which is the product of the initial fluid mass flow rate and its density; and 2) the *atmospheric conditions*, which govern the wind speed and air density. In addition, the method for treating a multi-component gas release using the properties of a pseudo-pure component gas will be shown.

For a hazard analysis, maximum ground level concentrations of H_2S are to be estimated for a range of potential pressure relief valve discharges of sour process gas from a 26.8 m tall flare stack. Flared gas has greatly increased plume buoyancy as well as air dilution rates compared with the non-burned gas. Of concern here is the possibility that the released gas is not ignited or that the flame goes out, thus causing potentially hazardous concentrations of H_2S at ground level.

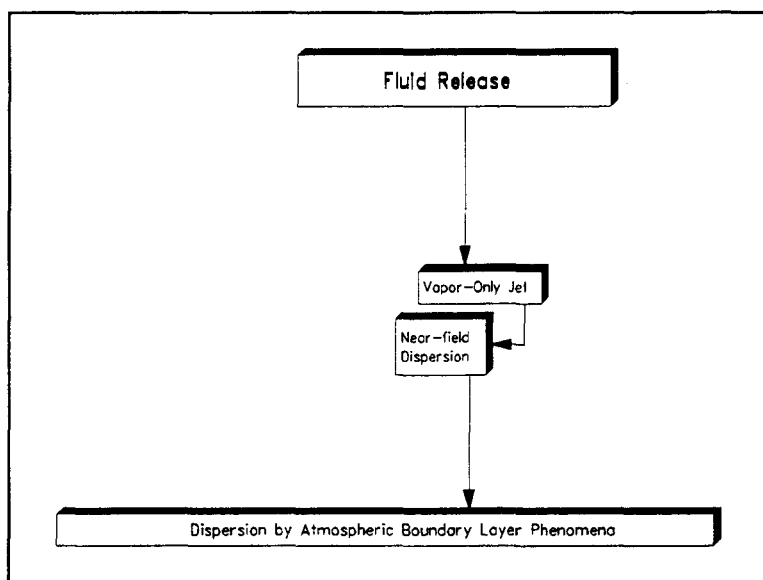


Figure 1. Release paths for Scenarios 1, 2, and 3.

The design maximum flow rate for the stack is 16 kg/s, the minimum flow rate is 1.6 kg/s, the flow regime is non-choked, and the stack exit temperature is 300K. The exit diameter of the stack is 0.20 m. The chemical composition of the stack gas, which contains methane, ethane, propane and hydrogen sulfide is given.

The process unit is in a large oil refinery surrounded by urban and suburban areas with trees.

Scenario 2: Hydrogen Sulfide and Carbon Dioxide from a Safety Relief Stack

For an oil field located in a rural area, secondary recovery operations use carbon dioxide as the flooding agent to maintain reservoir pressure. The separation plant produces a recycled stream containing about 1.3%v H_2S with the balance being essentially all CO_2 . This stream is representative of the gas discharged to a new safety relief stack being designed for the unit. The maximum flow rate of 12 kg/s is to be used to estimate the required stack height and exit diameter. For the diameter calculations, assume an internal pressure of 70 kPa (gauge) at 275 K.

For this example, assume that the ground level concentrations for H_2S and CO_2 should not exceed 10 ppm and 2.0 %v, respectively, on an averaging time basis of 60 seconds.

Scenario 3: Supercritical Propane Pipe Hole Release

Supercritical propane at 340 K and 7.0 MPa is heated in a gas-fired process preheater to a temperature of 540 K. Assume that the pressure in the outlet line is the same as for the feed line, and that a 19 mm diameter hole can develop from some type of failure on either line. Either hole would be about 3 meters above grade. How far downwind could a vapor cloud remain flammable? The most likely ignition source is about 15 m from the heater. Could the jet's vapor be ignited if it happened to be directed towards the ignition source?

Scenario 4: Oil Well Blowout

The 0.35 m diameter well casing of a sour crude production well breaks off at ground level to cause a blowout which spews oil and gas vertically into the air at about 23,000 kg/hr. The temperature of the mixture just before discharge into the atmosphere is 316 K (108 F). It is expected that the discharge would continue at this rate for some time, perhaps several days, before it could be shut off. The results of the crude assay analysis and flash calculation are known. From these, the H_2S concentration in the vapor phase of the released fluid is about 12%v.

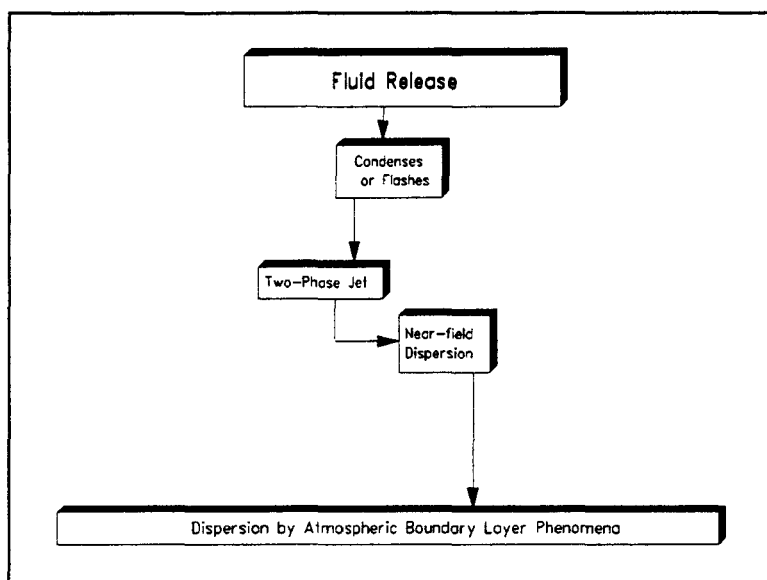


Figure 1. Release paths for Scenarios 4, 6, and 7.

Dispersion modeling is required to estimate “worst case” estimates of H_2S concentrations vs the radial distance from the well. Or, stated another way, what would be the radius from the source for which the H_2S concentration would always be less than 10 ppm, for all expected meteorological conditions?

The meteorological conditions typical for the location are hot, humid days when the atmosphere becomes very unstable during the day, with maximum instability occurring in the early afternoon. At night, the earth cools to cause stable conditions. Daytime winds and cloud cover produce neutral stability conditions.

Scenario 5: Liquefied Chlorine Tank Truck Accident

On a partly cloudy night with light winds, a tank truck, filled with liquid chlorine to its full 16

metric ton capacity, jack-knives, then overturns in tall grass adjacent to the highway. The tank ruptures and empties in 30 minutes in a manner so that the rapidly expanding fluid forms a cloud of vapor and liquid aerosol as it enters the atmosphere. No liquid pool forms. Assume that the internal tank storage temperature equals the ambient temperature, 303 K. For this locale in the Midwest prairie/farm country, forecasts call for daytime high temperatures of 303 K with winds from 4 to 8 m/s with moderate insolation and minimum nighttime temperatures near 223 K with

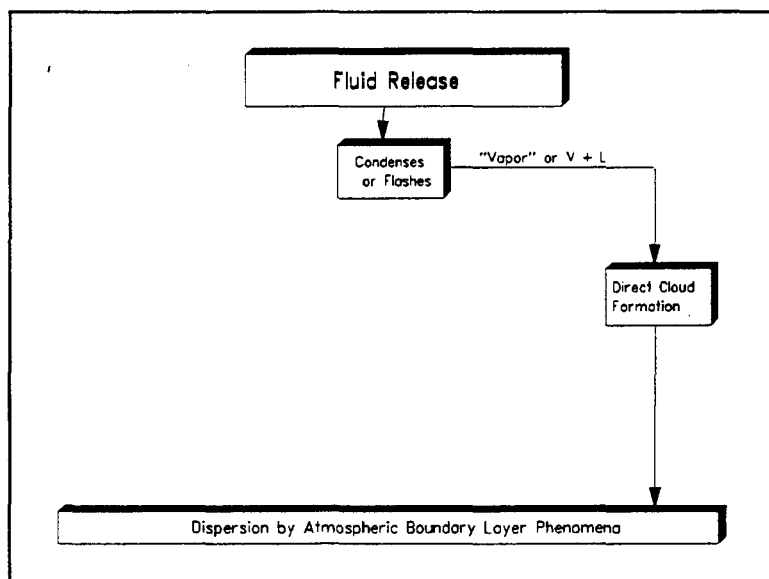


Figure 1. Release path for Scenario 5.

winds ranging from calm to 3 m/s with less than 40% ($< 3/8$) cloud cover.

To assist emergency response personnel, estimates of downwind chlorine concentrations along with the areas potentially affected are required.

Scenario 6: Ammonia Hose or Pipe Break

As part of a study to design the site of a new railroad tank car and tank truck ammonia loading facility for a very large refinery/chemical plant complex, the hazard analysis indicates the consequences of hose breakage or accidental disconnection that should be investigated. The hose end could whip around to discharge liquid ammonia in any direction, or the pipe to which the hose was connected could discharge the stream in any direction.

Upstream automatic control systems are being designed so that if a release such as this occurs, flow can be stopped quickly (several minutes or less). To assist the control system designers in deciding the maximum automatic shut-off time, a modeling study was requested to estimate the effect of shut-off time, and therefore release duration, on downwind cloud travel from the facility.

Assume the ammonia is stored in pressure vessels which are in temperature equilibrium with the surroundings, and that the pipes and hoses have inside diameters of 5 cm.

Demonstrate how different release durations and associated averaging times can affect analysis results.

Scenario 7: Hydrogen Chloride Pipe Break

This exercise demonstrates typical procedures that may be used to model water spray barrier mitigation effects by means of a ground level hydrogen chloride plume release. The presentation differs from other scenarios in this chapter in that it is a step-by-step presentation of methods, rather than an analysis and solution of a given problem. These methods are, in general, applicable to the removal of other chemicals and/or the use of other barriers (*e.g.*, steam curtains, vapor fences) provided their specific effects can be quantified.

Scenario 8: Evaporating Pool of Liquid Benzene

During construction operations, an outlet line on the bottom of a benzene storage tank is sheared off. The discharge continues for 30 minutes before it is stopped. The diked tank is located in the tank farm of a large refinery/chemical plant complex surrounded by urban and suburban populated areas. The minimum distance from this particular tank through the complex to the company fence line is 195 meters. Tank size and information needed for discharge rates as well as dike dimensions are given. Assume the potential release occurred in the morning of a warm day

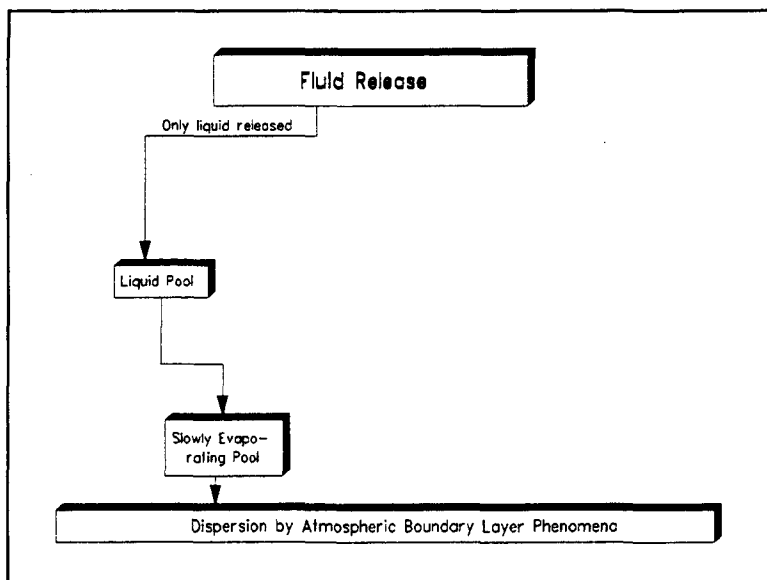


Figure 1. Release path for Scenario 8.

with full cloud cover.

Required are estimates of downwind maximum concentrations of benzene as comparative plume areas shown by 1 and 50 ppm benzene concentration isopleths. The effect of wind speed is also of interest. A 10-minute averaging time needs to be used for all concentration estimates.

CHAPTER 3



Documents

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CHAPTER THREE

Source Modeling

Overview

This chapter presents methods for calculating release rates and fluid conditions for substances accidentally released to the atmosphere; this information is required by atmospheric dispersion models to calculate downwind chemical concentrations. The *substances* may be pure chemical compounds or mixtures thereof, and the fluid stream may be vapor, liquid, or a suspension of a vapor and a liquid (“aerosols”). Parameters needed to characterize a released substance are: Source type (*e.g.*, jet, evaporating pool, “instantaneously” formed cloud[★]), mass flow rate, physical state (vapor, liquid, or both), stream temperature and composition. Parameters can be estimated by methods drawn from Chemical Thermodynamics and Fluid Mechanics.

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Commonly used calculational methods, with overviews of background theory, are presented. Derivations of most equations are not provided; references are given so the methods may be expanded or modified to suit specific circumstances which are beyond the scope of this Manual. Concepts applicable to systems in thermodynamic equilibrium are reviewed, starting with phase equilibria.

Methods for obtaining and/or calculating generally required physical and thermodynamic properties of gas and liquid phases are presented. For releases involving large flow rates, such as rapid flow through a hole, or an instantaneous rupture of a vessel containing supercooled fluids, the thermodynamic equilibrium and fluid momentum concepts for calculation of flow rates are presented. Finally, methods for calculation of evaporation rates from boiling and non-boiling pools are discussed. Example calculations for the various methods are given.

Release Characterization Complexities

Most incidents start with a substance being released from containment, owing to either failure of the storage vessel or pipe, or an abnormal discharge from an engineered device such as a relief valve, vent stack, or other device. Superheated liquids will expand into the atmosphere as a cooled vapor and/or liquid stream, and if both, usually an aerosol cloud. Liquids with normal (atmospheric) boiling points below their storage temperature will form evaporating pools on the ground. If the container fails by means of a relatively small opening, the mass flow rate through this “hole” can be estimated by well-known equations, provided the temperature, pressure, and physical properties are known (*e.g.*, liquid or gas density). For a chemical system involving vaporizable components, vapor/liquid equilibria calculations are required to calculate the relative amounts of the vapor and liquid phases, as well as to establish instantaneous phase compositions. Physical and thermodynamic properties are temperature, pressure, and composition dependent.

★ Releases in which all of the available substance is released into the atmosphere in less than roughly one minute are often called “instantaneous” releases.

Also, as flow continues to decrease the amount of stored substance, the pressure and temperature (and composition, if applicable) in the vessel will change to satisfy conservation of mass and energy. In some applications, these time dependent changes should be considered in modeling a specific release scenario.

Most release scenarios can be modeled by assuming that the processes involved are *reversible and in thermodynamic equilibrium*, considering the large uncertainties of scenario definitions and dispersion models. Although this assumption is generally not true in the strict sense, some processes are so fast that equilibrium calculations provide adequate results. Also, use of this assumption may be the only way estimates can be obtained, because sufficient detailed knowledge of the phenomena is rarely available for more accurate calculations.

Units of Measure

The SI units-of-measure system is used for all calculations in this manual; see Smith and Van Ness [8], Perry's Sixth [6]. A list of all symbols with units-of-measure is presented in the *Nomenclature* which precedes Chapter 1. The SI *pascal* unit of pressure is primarily used, but other common units are often used in scenario discussions (1 atm = 14.7 psia = 101,325 Pa = 0.101 MPa). When pressure in pascals is used in the various equations involving energy balances, the gravitational constant, $g = 9.807 \text{ m/s}^2$, usually does not appear explicitly because of SI definitions. In other units-of-measure systems, such as English and Metric, g appears explicitly. Finally, because of common usage, degrees Celsius and atmospheres, for temperature and pressure, respectively, will often be used in example problems and release scenarios throughout the Manual.

Phase Equilibria

A frequent calculational problem is: "Given the composition of a system, its temperature and pressure, what are the relative amounts of vapor and liquid, and what are the compositions of each phase?" The methodology of solution is called "VLE" (for Vapor-Liquid Equilibrium) or a "flash" calculation. The general methods for calculating phase equilibria are beyond the scope of this discussion. However, introductory methods to solve this problem for "well-behaved" substances (e.g., certain hydrocarbons at low pressure) are presented to give an overview of the techniques involved. Further, these equations can be used in some accidental release modeling applications. For comprehensive information on this subject, please refer to texts such as Smith & Van Ness, Chapter 13. Reid, Prausnitz and Poling [7] also provides a table of references.

Phase Rule

A *phase* is a homogeneous region of matter. A gas or mixture of gases, a liquid or liquid solution, and a solid crystal are examples of phases. A phase need not be continuous; examples of homogeneous phases are a *gas* (e.g., CO_2) dispersed as bubbles in a *liquid* (soda water), and *liquid* droplets suspended in a vapor cloud. Abrupt changes in physical properties occur in the interface between phases. Consider a vessel containing one or more phases in thermodynamic equilibrium; the relative amount and composition of each phase remain constant with time, and all phases have the same temperature and pressure. The *phase rule* governs the number of *intensive* variables which can be independently specified – the *number of degrees of freedom (ndf)*. (Intensive properties are those which are independent of the extent of the system and of the individual phases.) The phase rule for non-reacting systems is

$$ndf = N_{cs} - \eta + 2$$

where N_{cs} = number of species and η = number of phases in the system.

For the case of a single substance, or "pure component," $N_{cs} = 1$. Thus if the system contains only liquid or vapor, *but not both*, then $ndf = 2$. This means that both temperature and pressure may be specified (manipulated), as long as another phase does not appear. However, suppose *pure liquid is in equilibrium with its vapor*, then $\eta = 2$ and $ndf = 1$. This means that either temperature or pressure may be specified (manipulated), *but not both*. That is, if temperature is specified, then the pressure of the gas phase above the liquid in the vessel is the *vapor pressure* at that temperature.

For multicomponent systems, $N_{cs} > 1$ and the degrees of freedom increase, so more knowledge (e.g., independent equations) must be applied to completely specify the state of a system. Some examples are shown in the box.

Phase Rule Examples

Degrees of Freedom	Number of Species	Number of Phases	Allowed Specifications, Typical Situations
$ndf =$	N_{cs}	$\eta + 2$	
2	1	1	Can specify T <u>and</u> P; e.g., for vapor only
1	1	2	Specify T <u>or</u> P; Use vapor pressure curve for non-specified variable
2	2	2	Specify T <u>and</u> P, then the phase compositions are determined.
3	3	2	Specify T <u>and</u> P, the mole fraction of one component in a phase may be set.

The degrees of freedom determines the number of independent equations which must be solved to find the phase compositions and overall vapor/liquid mole ratio. Also, for example, if temperature is an unknown variable, another relation such as the overall vessel energy balance must be invoked [Smith & Van Ness, p 362 *et seq*].

Pure Component Systems

For a pure substance contained in a vessel, specification of either temperature or pressure determines whether the single phase is liquid or vapor. *Figure 1* shows vapor pressure vs temperature plots for several pure chemical compounds. At constant pressure (e.g., the atmosphere), all of a given sub-

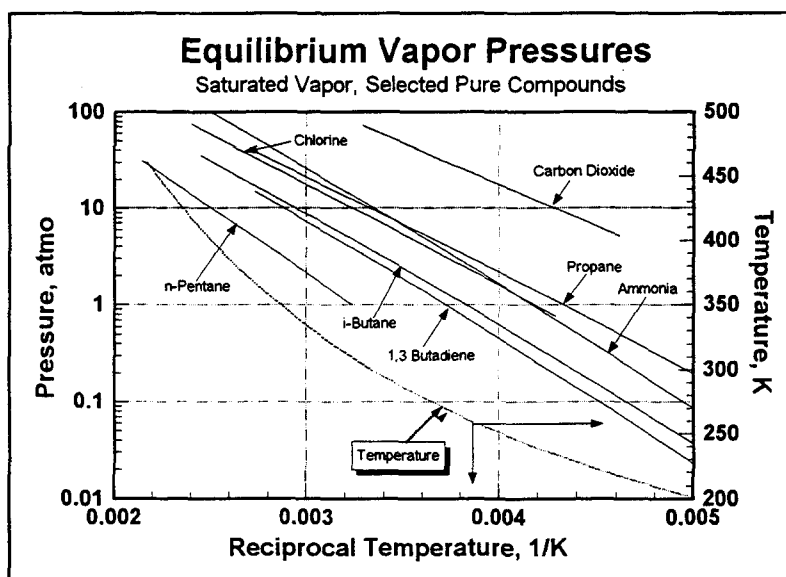


Figure 1.

stance is vapor at temperatures to the right of its curve, and it is all liquid to the left. The temperature at which the vapor pressure equals 1 atm is called the *Normal* boiling point (T_{NBP}).

As shown in Figure 1, the example plots of the logarithm of the equilibrium ("saturation") pressures (P_s) vs the reciprocal of absolute temperatures ($1/T$) gives straight or nearly straight lines for the ranges shown. For vaporization at low pressures, the Clausius/Clapeyron equation [Smith & Van Ness p. 182] may be used to relate the vapor pressure to the temperature and the latent heat of vaporization (ΔH_{lv}):

$$\Delta H_{lv} = -R \left(\frac{d \ln P_{sat}}{d(1/T)} \right) \quad (2) \diamond$$

The derivation of this equation assumes the gas is ideal and that molar volume of the liquid is negligible with respect to that of the vapor. (The SLAB dense gas dispersion model uses this equation.) If the pressure (temperature) is high enough for the gas to be significantly non-ideal, the Clapeyron equation (not presented) should be used using numerical solution techniques.

Multicomponent Vapor-Liquid Equilibria

Almost all substances in industrial applications are multicomponent streams. If a stream consists of one major component, with small amounts of other components ("trace" substances)[★], then it can be thermodynamically treated as a pure component. For multicomponent streams that can

form vapor and liquid, there may be a range of pressures (at constant temperature) in which liquid and vapor co-exist. An example is shown in Figure 2. It shows temperature (T) vs. phase concentrations for a two component mixture. Shown are the mole fractions of component 1 in the liquid and vapor phases, x_1 and y_1 , respectively. (Because the sum of mole fractions of all components in a phase must always sum to 1, x_2 and y_2 can be found by difference; this is in accordance with the phase rule.) The horizontal dashed line shows the liquid and vapor composition in equilibrium at 80 C; the liquid phase is at its bubble point and the vapor phase is at its dew point for this particular pressure.

Raoult's Law connects the vapor and liquid concentrations for ideal gases in equilibrium with ideal solutions:

$$P_i = x_i P_{sat,i} = y_i P \quad (3)$$

★ "Small" usually means less than about 1%. The concentration(s) of trace compounds are such that the physical, chemical and thermodynamic properties of the major component of interest are not significantly affected.

Heat of Vaporization Example

The SLAB dense gas dispersion model is to be used in an application concerned with the release of chlorine to the atmosphere. The latent heat of vaporization, a required input parameter if a two phase system is possible in the turbulent jet expansion, can be estimated from Figure 3-1 as follows: Using the finite difference approximation,

$$slope = \frac{d \ln P_{sat}}{d(1/T)} \approx \frac{(\ln P_1) - (\ln P_2)}{(1/T_1) - (1/T_2)} = \frac{\ln 18 - \ln 1.6}{0.003 - 0.004} = -2420.$$

The ideal gas constant in SI units is 8313 (Pa - K - kg - m - Joules), thus the approximate heat of vaporization is:

$$\Delta H_{lv} = -R \cdot slope = (-8313) \cdot (-2420) = 20.12 \text{ MJ/kg}.$$

SLAB requires J/kgmol; dividing the above value by the molecular weight of chlorine, 70.91, gives 283 KJ/kgmol.

That is, the partial pressure of the component in the vapor (P_i) is proportional to its mole fraction in the liquid times its pure component, saturated vapor pressure value. Because the partial pressures must sum to the total pressure (P),

$$\sum_i y_i P = P \sum_i y_i = P \cdot 1 \quad (4)$$

The vapor/liquid equilibrium “K-value” is defined as

$$\frac{y_i}{x_i} \equiv K_i \quad (5)$$

For non-ideal systems, the K-values depend on composition, and the vapor and liquid mole fractions are multiplied by concentration dependent vapor and liquid phase *activity coefficients*. These coefficients are obtained by empirical correlations developed from measured data, and their use is beyond the scope of this chapter.

In some applications, the full curve of Figure 2 does not exist in the ranges of temperature, pressure and composition conditions of interest. For example, the solubility of a gas in a solute is very low. In that case, *Henry's Law* may be used:

$$P_1 = h_1 x_1 \quad (6)$$

in which subscript 1 denotes the solute, and h_1 is the Henry's law constant, which may be a strong function of temperature. Note that the constant is found by extrapolation of solubility data to infinite dilution; activity coefficients are applied when the concentration becomes great enough to be significant. For this situation, special techniques must be used in setting up the VLE equations to be solved.

Discussion

The following VLE methods should be useful for understanding the types of governing sets of equations; an example solution of a simple, well-behaved VLE problem is presented later. For accidental release modeling purposes, the required accuracies of solution are less than those needed for typical chemical engineering design purposes. That is, applications which involve pure components, or mixtures of substances may be solved by ideal gas and ideal liquid assumptions. In general, these substances will be of

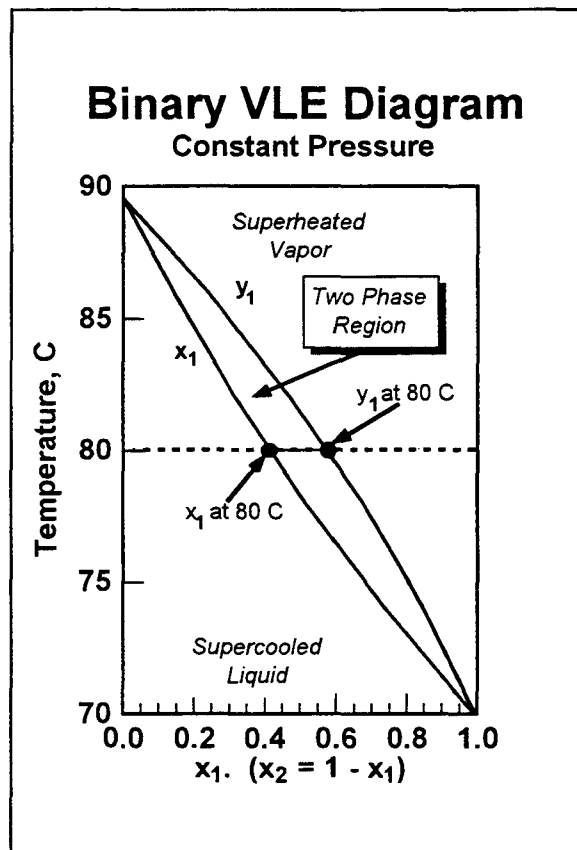


Figure 2.

low molecular polarity, such as hydrogen-saturated hydrocarbons, and the vessel will be at low pressures. As the compounds become more polar, molecular interaction increases (as may pressure), thus mixing and compositional effects must be accounted for. Thus, to obtain adequate accuracy, more complete thermodynamic equations are used which employ liquid and vapor component *concentration activity coefficients*; these are based on measured deviations from ideality. The best advanced methods are based on *equations of state* which, in some way, account for molecular size and attraction (*i.e.*, the ideal gas law does not).

Because VLE calculations for real streams are complex and require a database of characterizing parameters for all substances of interest, computer programs are used. Many organizations, such as petroleum and chemical companies as well as process engineering organizations, have stand-alone VLE computer programs. Programs are available from several vendors. Process engineering flowchart simulation programs usually contain complete thermodynamic and physical properties for substances, and may be used just to obtain VLE solutions along with physical properties.

The VLE concepts discussed here are limited to constant temperature and pressure applications. In the more general problem, temperature and/or pressure is unknown, so, in addition to the conservation of mass equation, energy and/or momentum balance equations must be used for implicit specification of these variables. For example, a stream of constant bulk composition and mass in equilibrium at conditions $[T_1, P_1]$ isenthalpically changes to $[T_2, P_2]$, with T_1 , P_1 , and P_2 being known. A VLE calculation is performed for the mixture from which the enthalpy (H_1) is directly calculated. Then, T_2 is iteratively adjusted by the algorithm until the specific enthalpy (H_2) matches the first value, H_1 . Of course, for the general case, the VLE computational part of the computer program must always determine the number and kind of phases existing before proceeding with the flash calculation. This is usually done by calculation of the dew point temperature (T_{DP}) and the bubble point temperature (T_{BP}); if a trial solution for T_2 is between T_{DP} and T_{BP} , then a two-phase solution exists. Smith & Van Ness has complete discussions on these topics, including detailed computational flow charts for bubble and dew temperature/pressure calculations.

Ideal VLE (Flash) Calculations. Consider a multicomponent mixture for which the temperature, pressure and overall (bulk) composition are known for N_{cs} chemical species (components). The moles (mass) of each component must be equal to the sum of the moles in the vapor and liquid phases:

$$z_i(n_v + n_l) = y_i n_v + x_i n_l \quad (7)$$

where z_i = mole fraction of i^{th} component for the total system ("bulk"), n_v = total moles in the vapor phase, and n_l = total moles in the liquid phase. This equation may be put on a single total mole basis by dividing it by the quantity $n_v + n_l$ to obtain:

$$z_i = y_i f_v + x_i f_l \quad (8)$$

where f_v = mole fraction vapor and f_l = mole fraction liquid in the system. By definition,

$$f_v + f_l = 1 \quad (9)$$

Substitution of Equations 7 and 8 into 9 and rearranging yields

$$x_i = \frac{z_i}{[f_v (K_i - 1) + 1]} \quad (10)$$

To maintain material balance in the liquid phase,

$$\sum_i x_i = 1 \quad (11)$$

must be satisfied. (Summations with respect to I are always made over all N_{cs} unless otherwise stated.) Thus, given the z_i and K_i values (the latter are generally known as a function of temperature), the problem is to find f_v while satisfying Equation 11. However, a real solution to the set of equations (10 and 11) does not exist if two phases do not exist; *e.g.*, as depicted in Figure 2.

If the system is just at the *dew point* of the vapor, then $f_v = 1$; substituting this into Equation 10 and then the result into Equation 11 yields

$$\sum_i \frac{z_i}{K_i} \leq 1 : \text{ True for all vapor} \quad (12) \diamond$$

In the preceding, equality holds at the dew point (saturated vapor), and if the summation is less than 1, the system is all superheated vapor. Equations equivalent to 10 to 12 may be derived using f_l and y_i from which it may be shown that if the system is at or below the *bubble point* of the liquid (thus the system is all liquid), then

$$\sum_i z_i K_i \leq 1 : \text{ True for all liquid} \quad (13) \diamond$$

For chemical systems for which the K -values are very weakly dependent upon concentrations, the non-linear Equations 10 and 11 may be numerically solved for f_v with Newton's Method. Define the error for the j^{th} iteration for Equation 11 to be

$$\epsilon_j = 1 - \sum_i x_{i,j} \quad (14)$$

the value of which is to be reduced below some small constant, *tol*. Given a positive, real value for $f_{v,j}$, an improved value can be calculated by Newton's Method by

$$f_{v,j+1} = f_{v,j} + \gamma \cdot \left[\frac{\epsilon_j}{(d\epsilon/df_v)_j} \right] \quad (15)$$

where γ is a convergence "accelerator" or "filter" coefficient ($0.1 < \gamma \leq 1$). From Equations 10 and 11, the derivative in Equation 15 is

$$\left(\frac{d\epsilon}{df_v} \right)_j = - \sum_i \frac{z_i (K_i - 1)}{[f_{v,j} (K_i - 1) + 1]^2} \quad (16)$$

Flash Calculation Algorithm

Using the above equations for a stream in which the K-values are independent of phase compositions, and are known for the given temperature and pressure, the equilibrium amount of liquid and vapor, as well as their compositions, may be found. The following algorithm assumes that a two phase solution exists.

1. Given the bulk composition (z-values) and the K-values, choose a starting value for f_v . Use 0.9 if no other information is available; do not use a value near zero or else the algorithm may march into zero or negative territory. Assign $j = 1$ and tol (a very small number, e.g., 1E-06).
2. Calculate ϵ_j by Equations 10, 11, and 12, and the derivative by Equation 16.
3. If $\epsilon_j < tol$, then go to Step 5, else go to Step 4.
4. Calculate an improved value, $f_{v,j+1}$, by Equation 17, and go to Step 2.
5. The solution is complete. Calculate the vapor component mole fractions by Equation 7, if required.

An example flash calculation for a three component system is presented on the next page.

Multicomponent Vapor-Liquid Equilibrium Calculation Examples

For three components in the bulk mixture; constant K-values

Component	1	2	3	
K-value K	0.10	0.50	10.00	
				Component Sums
Case 1: The mixture is all liquid				
Bulk mole fraction z	0.99	0.01	0.01	1
z/K quotient =	9.90	0.01	0.00	9.911 = Sum(z/K) < 1 for all vapor: FALSE
zK product =	0.10	0.00	0.05	0.152 = Sum(zK) < 1 for all liquid: TRUE
Case 2: The mixture is all vapor				
Bulk mole fraction z	0.01	0.01	0.99	1
z/K quotient =	0.05	0.01	0.10	0.159 = Sum(z/K) < 1 for all vapor: TRUE
zK product =	0.00	0.00	9.90	9.903 = Sum(zK) < 1 for all liquid: FALSE
Case 3: Vapor and liquid phases exist in equilibrium				
Bulk mole fraction	0.20	0.30	0.50	1 << These bulk mole fractions are used in the VLE calculation below.
z/K quotient =	2.00	0.60	0.05	2.65 = Sum(z/K) < 1 for all vapor: FALSE
zK product =	0.02	0.15	5.00	5.17 = Sum(zK) < 1 for all liquid: FALSE

Typographical Note:
 Given constant values are shown in *italic type*.
 Values of special interest are shown in **bold type**.
 Calculated values are given in non-italic type.

Vapor-Liquid Equilibrium Calculations for Case 3:

Terms and equations are developed from left to right. See Equations 10 to 16.

Equation 15 Filter = 0.2

Iteration No.	Fraction Vapor fv	Mole fraction in liquid, x(i) (Equation 10) Component			Sum x(i)	Error of Eq. 14	Derivative terms for Equation 16 Component			Neg. Error Derivative Eq. 16	Error/ Err. Der. Quotient Eq. 15	Filtered fv Correction Eq. 15
		1	2	3			1	2	3			
Initial guess	0.9	1.0000	0.5455	0.0549	1.600400	-0.60040	-4.986150	-0.495868	0.054341	5.427676	-0.110618	-0.022124
1	0.877876	0.9528	0.5347	0.0562	1.543658	-0.54366	-45.389822	-0.476508	0.056800	45.809530	-0.011868	-0.002374
2	0.875503	0.9432	0.5336	0.0563	1.533066	-0.53307	-0.444799	-0.474498	0.057073	0.862224	-0.618246	-0.123649
3	0.751854	0.6186	0.4807	0.0644	1.163650	-0.16365	0	-0.385141	0.074600	0.310541	-0.526984	-0.105397
4	0.646457	0.4783	0.4433	0.0733	0.994868	0.00513	0	-0.327497	0.096802	0.230695	0.022246	0.004449
5	0.650906	0.4829	0.4447	0.0729	1.000525	-5.254E-04	0	-0.329660	0.095675	0.233986	-2.245E-03	-4.491E-04
6	0.650457	0.4824	0.4446	0.0729	0.999950	5.036E-05	0	-0.329441	0.095788	0.233653	2.155E-04	4.310E-05
7	0.650500	0.4825	0.4446	0.0729	1.000005	-4.859E-06	0	-0.329462	0.095777	0.233685	-2.079E-05	-4.158E-06
8	0.650496	0.4824	0.4446	0.0729	1.000000	4.685E-07	0	-0.329460	0.095778	0.233682	2.005E-06	4.010E-07
9	0.650496	0.4824	0.4446	0.0729	1.000000	-4.517E-08	0	-0.329460	0.095778	0.233682	-1.933E-07	-3.866E-08
10	0.650496	0.4824	0.4446	0.0729	1.000000	4.356E-09	0	-0.329460	0.095778	0.233682	1.864E-08	3.728E-09

Note that the process has converged to three significant figure accuracy in five iterations, and to five significant figure accuracy in seven iterations. Also, the ninth iteration has converged to within the number of digits used by the computer (about 8). If further iterations are continued, then the solution will probably stabilize at the above solution, within the computational real number word size.

The value of the convergence filter coefficient must be chosen to obtain a valid solution, i.e., $0 < \text{fraction vapor} < 1$. For this example, a coefficient between about 0.15 and 0.35 works. The validity of solution should always be checked in this manner.

Fluid Properties

Volumetric Properties of Pure Fluids.

The calculation of release rates into the atmosphere, and the state of the fluid (liquid, vapor, or both) requires certain physical properties (e.g., density) and thermodynamic quantities (e.g., internal energy, enthalpy, entropy). The latter quantities are derived from volumetric and thermal data. Quantitative knowledge of the pressure-volume-temperature ("PVT") relationship for a pure component or a mixture is key to understanding and calculating phase existence, phase equilibria, flow rates, and fluid expansion parameters into the atmosphere. The basic concepts and equations of state are summarized below. The last section of this Fluid Properties part provides general references from which property values and estimation methods may be obtained.

Homogeneous substances are *liquids*, *vapors*, or *solids* for which physical and thermodynamic properties are markedly different between the three states for a given chemical compound. However, the differences in properties become indistinguishable at the *critical point*. The critical point is determined experimentally, and is characterized by the critical temperature (T_c) and critical pressure (P_c). Above this point, the substance is totally homogeneous and is neither liquid or gas or solid; it is called a *supercritical fluid*. These fluids are beyond the scope of this chapter, as are solids.

The Virial Equation of State for Gases. It has been experimentally determined that the PV product for a pure gas is more nearly constant, at a constant temperature, than for either P or V alone. A form of the generalized empirical *Virial* equation of state for gases is:

$$\frac{PV}{RT} = Z = 1 + k_1P + k_2P^2 + k_3P^3 + \dots \quad (17)$$

where P is the *pressure*, V is the volume per mole, R is the *ideal gas constant* (8314.4 for SI units), T is the absolute temperature, Z is the *compressibility factor*, and k_1 , k_2 , k_3 are constants, termed the *virial coefficients*. This is the basis for the *ideal gas law*, for it has been determined that as P tends to zero, the PV product tends to the same value for all gases in the limit (at a constant temperature). A number of useful correlations have been developed in which the compressibility factor is presented as a function of pressure along isothermal curves for pure gases and mixtures. The *API Technical Data Book*, Vol. I [2] contains graphical compressibility factor data for many petroleum-type hydrocarbons.

The Ideal Gas Law. As pressure is decreased, all terms on the right hand side of the preceding equation except for the first approach zero, so in the limit $Z = 1$, thus $PV = RT$, where the constant R is based on one mole of the substance. For n moles, the ideal gas law is

$$PV = nRT \quad (18) \diamond$$

from which molal and mass density may be readily derived. The ideal gas is generally used in all atmospheric dispersion programs. For calculation of current vessel contents ("holdups"), and flow through pipes and orifices, the ideal gas law *may* provide sufficient accuracy *for these purposes* if the system is not near the critical point.

Cubic Equations of State. Polynomial equations cubic in molar volume have been found the simplest of those capable of well representing both liquid and vapor behavior; this dual phase

applicability is required for general thermodynamic use. Some well-known equations have been developed by *van der Waals*, *Redlich/Kwong*, *Soave*, *Benedict-Webb-Rubin* and *Peng/Robinson*. Solution of the cubic equations with concomitant calculation of physical and thermodynamic properties are iterative and usually require computer methods. In some process simulator programs used to obtain properties for release modeling, the user may be required to select the equation of state method. Descriptions can be found in references [3,5,7,8].

Generalized Correlations for Liquids. Because of the uncertainties in modeling accidental releases, where the major uncertainties are specification of the release scenarios and stochastic variations caused by atmospheric processes, the *variation* of liquid specific volume (reciprocal density) with temperature and pressure should not be significant in many applications. For example, hydrocarbons will change volume by about 1 to 2 percent with change of 10 degrees kelvin. Thus it may be sufficient to use a single average value, taken from tables or correlations for the temperature range of interest. Also, liquid specific volume is usually a weak function of pressure, so this variation can often be neglected. If the temperature range of interest is large, it might be necessary to fit a simple linear or quadratic function of temperature to tabulated densities. Densities for multicomponent liquids can often be obtained from general purpose VLE/physical properties computer programs.

If liquid density data is not available for a particular compound, Rackett's equation (Smith and Van Ness, p. 97) is probably the simplest available. The specific molal volume for a saturated pure liquid is found by

$$v_{sat}^m = v_c^m Z_c^{(1 - T_r)^{0.2857}} \quad (19)$$

where v_c^m is the critical molal volume, Z_c is the compressibility calculated from the ideal gas law using the critical volume, temperature, and pressure, and T_r is the reduced temperature (T/T_c). Critical constants are given for selected compounds in Smith and Van Ness, Appendix B, and for an extensive number of compounds in Appendix A of Reid, Prausnitz and Poling [7]. The latter authors present (p.67) a modified form of the above equation which is accurate, but requires an additional, empirically fitted constant unique to each compound. Smith and Van Ness also discuss the Lydersen et al correlation, which is also based upon corresponding states with which the reduced density is found graphically for given reduced temperatures and pressures. Reid, Prausnitz and Poling present several other, more complex methods designed for accurate liquid density estimation over wide ranges of temperature and pressure.

Thermodynamic Properties

The *primary* thermodynamic properties are pressure (P), volume (V), temperature (T), internal energy (E^*), and entropy (S). These quantities may be related through the first and second laws of thermodynamics by means of differential equations for particular applications. For convenience, three additional properties have been defined:

$$\begin{aligned} \text{Enthalpy: } H &= E + PV \\ \text{Helmholtz energy: } A &= E - TS \\ \text{Gibbs energy: } G &= H - TS \end{aligned} \quad (20)$$

★ Smith and Van Ness use the symbol U .

These quantities, and/or differential quantities *derived* from them, are used to develop sets of equations to represent particular applications (*e.g.*, a VLE calculation).

In release applications, *heat capacities* are often involved. The *heat capacity at constant pressure* is defined as

$$C_p = \left(\frac{\partial H}{\partial T} \right)_p \quad (21) \diamond$$

and the *heat capacity at constant volume* is defined as

$$C_v = \left(\frac{\partial E}{\partial T} \right)_v \quad (22)$$

These important parameters are required for the calculation heat content and temperatures of mixtures from individual component values, adiabatically expanded gas properties, and flashing choked flow rates, for examples.

Experimentally obtained values of specific or molal volumes, enthalpies, and entropies as functions of temperature and pressure are available in the literature and computerized databases for many substances. For some of these substances, heat capacities at constant pressure can be found. Heat capacities at constant volume are seldom found in the literature, but may be derived from the other available quantities. If, for example, the enthalpy for a substance is available as a function of temperature at a given pressure, then the data may be fitted to an empirical equation, and Equation 21 used to calculate the temperature slope (C_p) at a particular temperature, or, more simply, finite differences can be used to calculate the approximate value from a table.

As will be seen, the ratio $k = C_p/C_v$ is used in certain equations to calculate choked flow. For ideal gases *only*,

$$C_v = C_p - R \quad (23)$$

If the gas departs significantly from ideality, spurious values can be obtained by using the preceding equation. (*e.g.*, $C_v < 0$). If k is not available from reliable sources, a value of 1.4 is recommended for screening purposes in release scenario modeling.

Other Properties

Viscosity. For calculations involving the flow of fluids through pipes and other devices where frictional energy losses need be considered, the *viscosity* (ν) fluid property is required; examples are pipe flow and pool evaporation. Viscosity is defined as the ratio of shearing stress divided by a velocity gradient, so its dimensions[★] are $\text{F}\tau/\text{L}^2$; the *poise* is $0.1 \text{ Pa}\cdot\text{s}$. The *kinematic viscosity* is the ratio of viscosity to density with units $\text{L}^2\tau$.

Perry's Sixth, Chapter 3, has nomographs for obtaining the viscosities of a number of pure compound gases and liquids. A number of estimation methods for gas viscosities, based on molecular theory of gases coupled with empirical correlations, are available; their number and

★ See *Nomenclature* for dimension symbols.