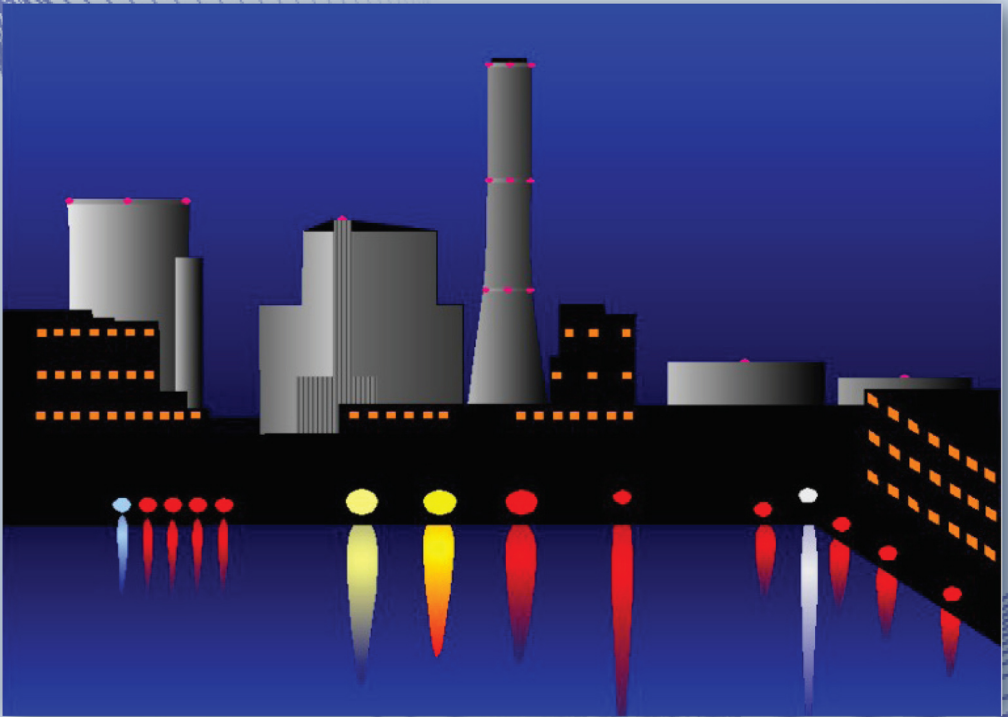


SECOND EDITION

INDUSTRIAL HYGIENE CONTROL OF AIRBORNE CHEMICAL HAZARDS



WILLIAM POPENDORF



CRC Press
Taylor & Francis Group

Industrial Hygiene Control of Airborne Chemical Hazards

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Second Edition

William Popendorf



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Preface

While the author's main goal in writing *Industrial Hygiene Control of Airborne Chemical Hazards* was for it to serve as a textbook, it is applicable to many audiences. For example:

- a practicing occupational hygienist wondering how to choose a substitute organic solvent that is safer to use than the hazardous one his or her company or client is currently using.
- a hygienist needing to learn about local exhaust ventilation without becoming an engineer.
- a hygienist looking to understand respirators, their selection, and program management.

Industrial hygiene [IH] is typically taught in a distinct sequence of anticipation, recognition, evaluation, and control. In that sense, this book focuses squarely on the control of chemical hazards. Its title implies a further focus on airborne chemical hazards, although many of the principles presented herein also apply to both airborne biological hazards and dermal chemical hazards.

While this book is based on science and is often quantitative, very little day-to-day IH work is quantitative. Therefore, the book also attempts to introduce the student to the kinds of judgment needed to control exposures within the diverse settings in which people actually work. The ability of industrial hygienists to extend their knowledge and apply judgment, rather than just plugging data into a formula, is one of several personally satisfying rewards of practicing the profession that this book tries to illuminate.

The approach to chemical hazard control taken within this book tries to bridge the gap between our existing knowledge of the physical principles and mechanisms that underlie the generation and dispersion of airborne chemicals and the wealth of recommendations, techniques, and tools accumulated by prior generations of IH practitioners. Thus, this book assumes that the reader is academically trained in science and math and has seen at least a small number of manufacturing or other work settings with chemical hazards, but is inexperienced in the selection, design, implementation, or management of chemical exposure controls.

The approach taken to explaining nonventilation controls relies on knowledge from physical chemistry and basic Newtonian physics that the student should be able to recall with appropriate prompting. While much of ventilation as a “control” has its origins in engineering and this book does try to introduce students to some engineering tools, no engineering background is expected from the reader. Where the book is quantitative, there are lots of formulae; however, in contrast to most engineering texts, the author has tried to avoid using mathematical abbreviations that are *without meaning* and has tried to present derivations as a tool to transition from the basic science to the formula that industrial hygienists use. One goal of the second edition was to amplify those distinctions via formatting.

Each technical chapter herein is preceded by specific learning goals. Each learning goal is preceded by a symbol and incorporates a key phrase loosely adapted from Bloom's “cognitive domains.” These symbols, phrases, and keys are explained in detail at the end of Chapter 1 (Table 1.2). The idea behind these key phrases is that one does not need to know everything at the same level. Each key phrase implies a level of learning that should be sought at this time in a novice industrial hygienist's education.

The first chapter of this book explains the approach taken by the author in teaching IH control, and an overview of salient features contained within the book specifically to aid learning. The first few chapters cover the important principles and mechanisms of physical chemistry that affect gases, vapors, aerosols, and their plumes in more detail than other texts. Chapter 4 provides unique insights that link those principles and mechanisms to some occupational health and safety regulations and exposure limits. Chapters 8 and 9 are virtually unique in their coverage of nonventilation controls (chemical or process substitution, work practice modifications, and other pathway

controls). The next two chapters are devoted to the principles and tools used in ventilation control, five chapters to local exhaust ventilation design, two chapters to the costs to operate a ventilation system and provide system management, and two more chapters to the ability and limitations of general ventilation to control airborne chemical hazards. The final two chapters discuss the ability and limitations of administrative controls, personal protective equipment in general, and respirators in particular.

This book attempts to cover all the basic ventilation topics without getting too advanced. At the same time, this book goes well beyond any other single textbook on the topics of nonventilation controls and receiver controls. Taken as a whole, this book provides a unique, comprehensive tool to learn the challenging yet rewarding role that IH can play in controlling airborne chemical hazards at work.

Acknowledgments

We don't get a second chance to learn from our own fatal mistakes. And disabling mistakes are expensive lessons. But we can all learn by reading from and listening to those who have preceded us. I thank many predecessors from many fields of knowledge for passing on their wisdom, and my wife Joyce for encouraging and sustaining me in this contribution to passing on a little more knowledge that might improve the practice of industrial hygiene.

William Popenorf



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Author

William Pependorf was a professor of industrial hygiene at Utah State University from 1995 until he retired in 2010 and became a *professor emeritus*. Prior to that he was a tenured professor at the University of California, Berkeley and the University of Iowa, Iowa City, served on the board of the American Industrial Hygiene Association, and was a director of the American Board of Industrial Hygiene. Dr. Pependorf taught and conducted research for over 40 years and published more than 75 papers and book chapters beginning with pesticide hazards to farm workers 1972–1992, inorganic dusts 1978–1982, organic dusts from grains and livestock 1982–1995, automotive industry foundries and metal working fluids 1987–1994, and broader reviews since 1991. His general interest has been to develop or/and apply predictive models (many developed in other fields) that describe how physical mechanisms cause (and can be used to control) the exposures of workers to organic vapors, hazardous particulate aerosols, and dermally toxic chemicals, with the expectation that such tools will improve the overall practice and knowledge base of industrial hygiene.



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List of Abbreviations

List of abbreviations, acronyms, subscripts and superscripts, notations, and symbols used in this book (and an example of the equation where the abbreviation is used)

GENERAL ABBREVIATIONS AND ACRONYMS (SEE ALSO THE SEPARATE LISTS OF SUBSCRIPTS, SUPERSSCRIPTS, AND GREEK SYMBOLS TO FOLLOW)

A	Area, e.g., surface area or face area (except for A in the Antoine equation)
ACH	Air changes per hour (Equation 20.15)
AHDD	Annual heating degree day (<i>ca.</i> Equation 17.9)
a.k.a.	Also known as
C	Airborne concentration in mg/m^3 (never as ppm)
CMD	Count median diameter (Equations 3.3–3.6)
D	A large diameter (as in a duct Chapter 12)
d	A small diameter (as in a particle Chapter 3)
D	Diffusivity (Equation 5.2 and Equation 5.5)
EDR	Environmental dilution ratio (Equations 5.16 and 5.17)
F	Force (as in Equations 2.3 and 3.7)
FanSP	Fan static pressure (Equations 16.4 and 16.5)
FanTP	Fan total pressure (Equations 16.1 and 16.2)
G	Contaminant generation rate (G_{moles} in Equation 5.3; G_{mass} in Chapter 19)
H_i	Henry's law coefficient for the i th component in a mixture (Equation 6.13)
$h_{\text{something}}$	Head loss due to some named thing within ventilation (Section 14.I.4)
K_{hood}	DallaValle hood factor in ventilation (Equation 13.6)
K_{mix}	Design mixing factor in ventilation, short for $K_{\text{room mixing}}$ (Equation 19.2)
LEV	Local exhaust ventilation
LFL	Lower flammable limit (same as LEL)
LOD	Limit of detection (Table 11.1)
MMAD	Mass median aerodynamic diameter (Equation 3.17).
MMD	Mass median diameter (Equation 3.6)
MW	Molecular weight of a chemical or compound
n	Any number or a specific number, e.g., number of moles
N_{Reynolds}	Reynolds number (Equation 12.3)
NIOSH	National Institute for Occupational Safety and Health, a U.S. government research agency
NTP	Normal temperature and pressure (see Chapter 2.I)
OEL	Generic occupational exposure limit, such as a TLV [®] , PEL, etc.
OSHA	Occupational Safety and Health Administration, a U.S. government enforcement agency
P	Pressure (molecular, static, or ambient atmospheric pressure)
P_{partial}	Partial pressure of a chemical within an airborne mixture (Equation 2.12)
P_{vapor}	Vapor pressure of a liquid chemical when by itself (Equation 2.8)
$P_{\text{vapor},i}$	P_{vapor} of chemical " i " within a liquid mixture (Equation 6.7)
ppm	Parts of a chemical per million parts of air (ppm_{liq} refers to ppm of a liquid)
Q	Volumetric flow rate (e.g., ft^3/min or m^3/s)
$\mathcal{R}$	Universal gas constant (Equation 2.16)
Rel.Y_i	Relative Y_i of vapors from a liquid mixture (Equation 6.19)
Rel.Haz	Fraction of the total VHR within an airborne mixture (Equation 6.21)

SP	$P_{\text{inside a duct}} - P_{\text{outside the duct}}$ (Equations 11.14–11.16)
STP	Standard temperature [0°C] and pressure [760 mmHg] (see Chapter 2.I)
<i>T</i>	Temperature
<i>t</i>	Time
TP	Total Pressure _{inside the LEV} – the ambient $P_{\text{outside the LEV}}$ (Equation 11.28)
TUC	Time of useful consciousness (Table 4.4)
TWA	Time-weighted average (Chapter 4 and Equation 20.1)
<i>V</i>	Velocity, such as air or particle velocity
VHI	Common logarithm of a VHR (Equations 5.12 and 8.11)
VHR	Vapor hazard ratio = $P_{\text{vapor}}/\text{TLV}^{\circ}$ or other OEL (Equations 5.20 and 8.4)
Vol	Volume as in air or room volume (also used as Vol% within a liquid)
VP	Velocity pressure (Equation 11.21)
<i>X</i>	Usually a generic unknown (except a particular distance in Equation 13.2)
X_i	Molar fraction of “ <i>i</i> ” in a liquid mixture (Equation 2.5 and Equation 6.3)
Y_i	Molar fraction of “ <i>i</i> ” in air (Equation 2.6 and Equation 6.15)
<i>Z</i>	Vertical distance (Figure 13.30)

ABBREVIATED SUBSCRIPTS AND SUPERSCRIPTS

aero	Aerodynamic (Equation 3.13)
BZ	Breathing zone (Equation 5.17–5.21)
<i>i</i>	The <i>i</i> th component within a group or mixture
liq.	In a liquid state, cf. airborne; replaces “ <i>l</i> ” in 1st edition
moles	Moles or based on moles, cf. based on mass
<i>n</i>	The last (or <i>n</i> th) member of a series (see also “ <i>i</i> ” above)
net	After adjusting for buoyancy (Equation 3.7)
<i>o</i>	The initial or starting point (Equation 19.8)
wt	Weight basis, cf. mass (only in Equation 11.3); replaces “ <i>w</i> ” in 1st edition
∞ subscripted	Steady-state or after a long time (Equations 5.17 and 19.14)
∞ superscripted	At an infinitely large dilution or very small concentration (Chapter 6)

GREEK SYMBOLS (WITH ITS *ENGLISH* PRONUNCIATION)

Δ (Delta)	A change or the difference between two conditions
γ (gamma)	Activity coefficient (Equation 6.8)
κ (kappa)	A generic empirical proportionality constant (e.g., $\kappa_{\text{mass tx}}$ in Equation 5.2)
η (eta)	Dynamic or absolute viscosity [g/cm/s] (Equation 3.9)
ν (nu)	Kinematic viscosity [cm ² /s] (Equation 5.2)
ρ (rho)	Density (ρ [g/L] for gases and vapors; $\rho_{\text{liq.}}$ [g/mL]; ρ_{particle} [g/cm ³]; ρ_{wt} [lb/ft ³])
τ (tau)	Characteristic time or the time of one room air change (Equation 19.13)

ABBREVIATED LATIN PHRASES

<i>ca.</i>	<i>Circa</i> meaning approximately or roughly
<i>cf.</i>	<i>Confer</i> meaning compared with or compared to
<i>e.g.</i>	<i>Exempli gratia</i> meaning for example
<i>i.e.</i>	<i>Id est</i> meaning that is or in other words
<i>viz.</i>	<i>Videlicet</i> meaning namely (used before a list)

RESPIRATOR ACRONYMS (CHAPTER 22)

APF	<i>Assigned protection factor.</i> The level of respiratory protection that a respirator or class of respirators is expected to provide to employees who have been properly fitted and trained.
APR	<i>Air-purifying respirator.</i> A respirator with an air-purifying filter, cartridge, or canister that removes specific air contaminants by passing ambient air through the air-purifying element.
ASR	<i>Atmosphere-supplying respirator.</i> A respirator that supplies the wearer with breathing air from a source independent of the wearer's ambient atmosphere; includes SARs and SCBAs.
EPF	<i>Effective protection factor.</i> The respiratory protection measured on an individual wearing a properly selected, fit-tested, and functioning respirator that is worn for only some fraction of the wearer's total exposure time at work; cf. WPF.
ESLI	<i>End of service life indicator.</i> A system that warns the respirator user that the chemical adsorbent is approaching saturation or will no longer be effective.
HEPA	<i>High efficiency particulate aerosol</i> filters remove at least 99.97% monodisperse particles that are 0.3 µm in diameter; synonymous with N100, R100, and P100 particulate filters certified by NIOSH under 42 CFR 84.
IDLH	<i>Immediately dangerous to life or health.</i> An atmosphere that poses an immediate threat to life, would cause irreversible adverse health effects, or would impair an individual's ability to escape from a dangerous atmosphere.
MUC	<i>Maximum use concentration.</i> The maximum atmospheric concentration of a hazardous substance from which an employee can be expected to be protected when wearing a respirator.
PAPR	<i>Powered air-purifying respirator.</i> An air-purifying respirator that uses a blower to force the ambient air through air-purifying elements and into the inlet covering.
PLHCP	<i>Physician or other licensed healthcare professional.</i> An OSHA term for an individual whose legally permitted scope of practice (i.e., license, registration, or certification) allows him or her to provide some or all of the healthcare services required by OSHA's respirator standard (29 CFR 1910.134).
PPF	<i>Program protection factor.</i> The measured protection provided by a respirator as used within a specific respirator program; see also SWPF and WPF.
QLFT	<i>Qualitative fit test.</i> A pass-or-fail fit test to assess the adequacy of a particular respirator's fit that relies on the individual's response to the test agent.
QNFF	<i>Quantitative fit factor.</i> The particular fit factor resulting from a QNFT.
QNFT	<i>Quantitative fit test.</i> A numerical assessment of the protection or fit measured on a given individual while wearing a particular respirator.
SAR	<i>Supplied air respirator</i> , a.k.a. an airline respirator. An atmosphere-supplying respirator for which the source of breathing air is not carried by or worn on the user.
SCBA	<i>Self-contained breathing apparatus.</i> An atmosphere-supplying respirator for which the breathing air source is carried by or worn on the user.
SWPF	<i>Simulated workplace protection factor.</i> The respiratory protection measured on an individual who is performing a series of physical activities while wearing a properly selected, fit-tested, and functioning respirator in a controlled setting.
WPF	<i>Workplace protection factor.</i> The respiratory protection measured on an individual only while they are wearing a properly selected, fit-tested, and functioning respirator (cf., a EPF) as part of a comprehensive respirator program during their performance of normal work tasks (cf., a SWPF).



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List of Conversion Factors

To convert a value in its initial units on the left to the desired units on the right (except for temperature), *multiply* by its “equivalence.” For example, $10\text{ cm}^2 \times 0.155 = 1.55\text{ in.}^2$.

To convert a value in its initial units on the right to the desired unit on the left (except for temperature), *divide* by its “equivalence.” For example, $1\text{ in.}^2/0.155 = 6.45\text{ cm}^2$.

Area	
1 centimeter ²	= 0.15500 inch ²
1 inch ²	= 6.4516 centimeter ²
1 meter ²	= 10.7639 feet ²
	= 1.19599 yard ²
1 hectare = (100 m) ²	= 2.471 acres
1 acre	= 43,560 feet ²
1 mile ²	= 640 acres
Density	
1 gram/cm ³	= 62.428 lb/ft ³
	= 8.344 lb/gallon
1 grain/ft ³	= 2,288.35 mg/m ³
Energy	
1 Btu	= 0.2520 kcal
1 Joule	= 0.2390 calorie
	= 9.478×10^{-4} British thermal unit
1 kWh	= 3,412 Btu
1 kcal = 1 Cal	= 3.9683 Btu
1 Therm	= 10^5 Btu
1 barrel of oil equivalent	= 5.8×10^6 Btu
1 lb bituminous Coal	= $12,500 \pm 2,500$ Btu
1 ft ³ natural gas	= $1,040 \pm 30$ Btu
Flow	
1 ft ³ /min	= 28.317 L/min
1 m ³ /min	= 35.3147 ft ³ /min
1 m ³ /s	= 2,118.9 ft ³ /min
1 gallons/min	= 3.7854 L/min
1 ampere	= 1 Coulomb/s
Length	
1 centimeter	= 0.3937 inch
1 inch	= 2.5400 centimeters
1 foot	= 0.3048 meter
1 meter	= 3.2884 feet
	= 1.09361 yard
1 kilometer	= 0.6214 mile (statute)
1 statute mile	= 5280 feet
1 nautical mile	= 6076.1 feet

(Continued)

Mass and Force

1 grain	= 1/7,000 pound
1 gram	= 0.035274 ounce
1 kilogram	= 2.2046 pound (lb)
1 ounce	= 28.350 grams
1 pound	= 453.59 grams
1 Newton	= 0.22481 pound (lb)
1 ton (a.k.a. "short ton")	= 2,000 pounds
1 metric ton ("long ton")	= 1,000 kilograms

Power

1 kWatt	= 1.3410 horsepower
1 horsepower	= 6,356.0 "wg $\times$ ft ³ /min = 33,000 ft $\times$ lb/min
1 ton of refrigeration	= 12,000 Btu/h

Pressure

1 atmosphere	= 1.01325 bar = 101,513 Pascal [Pa] = 760.001 mmHg = 14.696 pounds per inch ² [psi] = 407.60 inch H ₂ O at 21°C
1 Pascal [Pa]	= 1 Newton/m ² = 0.00750 mmHg = 0.004023 inch H ₂ O at 21°C
1 inch water gauge at 21°C	= 248.6 Pascal [Pa]

Temperature (These Conversions are not Simple Proportions)

°C	= $5 \times (°F - 32) / 9$
°F	= $(9 \times °C / 5) + 32$
°K	= °C + 273.15 $\approx$ °C + 273
°R	= °F + 459.67 $\approx$ °F + 460

Velocity

1 meter/min	= 3.281 ft/min
1 meter/s	= 196.85 ft/min
1 mile/hour	= 88 ft/min

Volume

1 cm ³	= 0.06102 inch ³
1 foot ³	= 28.317 liters
1 gallon	= 0.1337 foot ³
1 liter	= 0.035315 foot ³ = 0.2642 gallon
1 m ³	= 35.3147 feet ³
1 ounce	= 29.57 mL
1 barrel	= 42 gallons

1 An Introduction to Industrial Hygiene Chemical Hazard Control

This chapter starts with an introduction to both the professional practice of industrial hygiene [IH] and the organization of this book. The chapter then elaborates sequentially on how all airborne exposures can be placed within a handful of scenarios defined in terms of the spatial distance between the source of the airborne agent and the person being exposed, how the book follows the IH paradigm that prioritizes reducing exposures first by controlling preferentially the source, then by modifying the pathway, and least desirably by personal protection of the receiver. The last section of the chapter explains this book's use of learning goals and special notations intended to focus one's reading of a broad range of topics into the nuggets that must be thoroughly understood and the few that are memorable.

I AN OVERVIEW OF INDUSTRIAL HYGIENE

Readers will come to see that this author likes to start chapters with definitions. This seems like a good way to get everyone on the same page (meant more figuratively than literally). The formal definition of industrial hygiene [IH] not only provides a guide to how the profession is usually taught, learned, and practiced but in this context also provides insight into the structure of this book. While this definition may appear at first glance to be just words, to the experienced hygienist each of these phrases has a significant meaning that will be discussed in detail below.

Industrial hygiene is both the *science and art* devoted to the *Anticipation, Recognition, Evaluation, and Control* of those *environmental* factors or stresses arising in or from the workplace which cause *sickness, impaired health, significant discomfort or inefficiency among workers or among citizens* of the community.

Certainly, "science" differs from the "art" of any human venture. The need to use both is crucial in an applied science such as IH. The student who can excel in the science classroom or during an examination may not necessarily be creative in applying these concepts, effective at conveying new ideas or at convincing others to change, or comfortable working in an advisory capacity as any industrial hygienist must. On the other hand, someone who is good at selling ideas but does not have the scientific knowledge to make valid (let alone cost-effective) decisions will not succeed as an industrial hygienist either. The best hygienists are good at both the science and the art. (Someone who is or who wants to be good at only one thing may be trying to enter the wrong profession.) Good industrial hygienists have a wide range of both technical and interpersonal skills. It is partly this diversity that makes IH an interesting profession.

The next phrase of the definition that says the profession is devoted to four functions implies that the practice of IH is best viewed as progressing from one of the following functions to the next:

- Anticipation: the prospective recognition of hazardous conditions based on chemistry, physics, engineering, and toxicology
- Recognition: both the detection and identification of hazards or their adverse effects through chemistry, physics, and epidemiology

Evaluation: the quantitative measurement of exposure to environmental hazards and the qualitative interpretation of those hazards

Control: conception, education, design, and implementation of beneficial interventions carried out that reduce, minimize, or eliminate hazardous conditions

IH is typically taught in this same sequence of functions. A course centered on this book would fall squarely into the control function. This list of functions makes IH sound nicely organized if not compartmentalized, but, in fact, a practicing hygienist's day may easily be fragmented into some of each of these functions; and while working at one function, the IH practitioner needs to use or be cognizant of all the other functions and keep that framework of multiple functions clearly in the back of their mind. To leave any of these functions completely alone is to court professional failure.

The range of stressors with which IH deals is wide, which also contributes to job satisfaction. Hygienists often group stressors into the categories such as those listed below. Although some might argue that the last category is not really an environmental factor, most would agree that psychological factors at work can be stressors. This book focuses on the control of chemical hazards and predominantly upon airborne chemical hazards, although many of the principles presented also apply to airborne biological hazards.

Chemical: gases, vapors, dusts, fumes, mists, solvents

Physical: barometric pressure, temperature, noise, vibration, nonionizing, and ionizing radiation

Biological: bacteria, fungi, parasites, and their toxins (although toxins are also chemicals)

Ergonomic: the interaction of machine design and operational practices with our human anatomy

Mechanical: primarily safety (injury, fatality, property damage)

Psychological: peer pressure, job security and satisfaction, education, and motivation

The IH profession's focus on *factors and stressors arising in* versus *from the workplace* has varied over the years. In its origin, IH was a branch of public health that was rooted in the workplace. However, what starts within the boundaries of the workplace often crosses the fence-line to enter the surrounding community. Thus, the practice of IH has historically oscillated between a narrow focus on employees within the plant to a wider interest in air and water emissions, solid waste, and physical hazards that leave the workplace. The reference within the definition to two settings and later to two groups of people reflects IH's broad responsibilities rather than a narrow focus.

People in both settings can respond to health hazards in a variety of ways, from fatalities (not explicitly in the definition) to *sickness, impaired health, significant discomfort or inefficiency*, or even outrage. It is interesting to speculate why fatalities on the high end of the response spectrum were left out of the definition of IH. Outrage, expressed as either a personal or community response to a hazard, is a dimension with which the IH profession has only recently become aware. The level of subjective outrage is often irrespective of either the quantitative health hazard or the spectrum of response listed above, but as Peter Sandman advocates, it is just as measurable and often just as important to the mission or goal of a company or agency as is the objective health hazard.¹⁻³ This wide spectrum of adverse health effects is also important to keep in mind when trying to set priorities among multiple health hazards, and is a key factor underlying the adage that "not all exposure limits are created equal."

Not all IH work is quantitative. While the roots of IH are based on science, very little day-to-day IH work is quantitative. This apparent dichotomy is reflected in a quotation attributed to Albert Einstein: "Not everything that counts can be counted. And not everything that can be counted counts." Not only is much of IH an art, the science of IH has limits to its knowledge.

Take exposure limits for example (Chapter 4): each exposure limit is our best quantitative indicator of a chemical's toxicity at the time it was adopted. However, most exposure limits have changed at least once owing to new knowledge or interpretations. In fact, we are forced to use judgment in each of the four functions of IH: to anticipate the effects of new chemicals, to recognize a widening spectrum of adverse health responses, to evaluate current exposures and the links between historic exposures and reported health effects, and to control exposures in the diverse settings in which people work.

Industrial hygienists do not go around personally controlling workplace hazards, at least not often. The practice of IH is a management function that involves multiple tasks and activities from quantitative exposure assessment to human and public relations, the supervision of technical staffs, financial planning and accountability, and documentation (*that means lots and lots of writing*). Management skills are talked about in some classes but are difficult to learn in the classroom. They build on character but rely on experience. The ability of industrial hygienists to extend their knowledge and apply judgment and management skills, rather than just plugging data into a formula, is another personal reward of practicing the profession.

Yet another personal reward is the satisfaction of doing something in one's own life that can make a positive difference to someone else's life. For industrial hygienists, that other someone else is ostensibly the employees, but good preventive health decisions also benefit the employers who might not otherwise make good choices for themselves and the community who might not otherwise have any advocate within the workplace. While the functions of anticipation, recognition, and evaluation are essential to IH and are necessary precursors to control, it is only by controlling a hazard that anyone can actually make a positive change. It is only after a control has been implemented that exposures and the risks of adverse health effects are reduced, and we can say that we have made a positive difference.

Some IH jobs such as consulting or OSHA enforcement focus on recognition or evaluation but rarely provide the opportunity to implement feasible and cost-effective solutions in a specific workplace that affects individual employees. IH researchers usually only see their findings implemented years later via new policies, methods, or technologies. It is primarily the purview of the plant hygienist working as part of a management team who can routinely see the beneficial impact of their work and knowledge. Yet no matter what role we play within the profession, if we all keep our eye on the eventual objective of control, we can all claim a portion of the satisfaction in the accomplishments of the profession.

II THE SPATIAL SPECTRUM OF EXPOSURE SCENARIOS

Much of the early part of this book focuses on the physical mechanisms that determine how people are exposed to airborne chemical hazards at work; later chapters illustrate how these same mechanisms can be used to reduce employee exposure. Exposure starts with a "source" or origin of a chemical contaminant. The effect of most factors that determine the rate at which a given source can emit gases, vapors, or/and aerosols is predictable, at least qualitatively if not quantitatively. Chapter 2 introduces the reader to (or perhaps reminds them of) the physical principles that govern the behavior of gases and vapors. Chapter 3 discusses the physical principles that govern the behavior of aerosols. Chapter 4 weaves the differences between gaseous hazards and aerosol hazards into a discussion of the standards and guidelines upon which decisions to control hazards are based. Chapters 5 and 6 elaborate on the role of vapor pressure in determining the rate at which vapors are generated, in contrast to aerosols that have no vapor pressure and whose rate of generation depends almost entirely upon processes that are external to and independent of the kind of aerosol being generated.

Once an airborne hazard is generated by whatever mechanism, the pathway of the contaminant from source to a person can be described by a perhaps surprisingly narrow range of exposure

scenarios. Chapter 5 elaborates upon the thesis that virtually every occupational airborne chemical exposure can be categorized into one of the following four scenarios.^a

1. *People working within about an arm's length from the source, where its plume just begins to form but does not have much time to dissipate.* A plume is a highly concentrated stream of air such as smoke from a fire (although gaseous plumes are usually neither hot nor visible). Turbulence within the wake of a person standing upwind of the source can cause part of the contaminant to migrate upwind (and away from the plume) the short distance into their breathing zone. Control of exposures in this near-field will focus on substitution with another chemical whose vapors need less dilution and on local exhaust ventilation [LEV] to gather the plume into a hood before it can reach other nearby breathing zones.
2. *People working within the plume after it leaves the source by convection and begins to dissipate by turbulent diffusion.* In this scenario, the plume is not locally exhausted, nor is it yet constrained by walls that can cause it to circulate within the workroom. Control of exposure from within a *free-field* plume (where unlike omnidirectional noise, the chemical concentration within a plume decreases slowly in the direction of the air current or wind) is mainly limited to avoiding the path of the plume (a seemingly simple step if it were visible) or again substituting the chemical in use with a less hazardous chemical, as above.
3. *People working where the plume is not completely exhausted and the chemicals can recirculate within the airspace.* The concentration of airborne chemicals that accumulate within a room is often somewhat uniform (like a *reverberant field* of noise). The concentration will rise until the rate that the contaminant is generated equals the rate at which it is removed by general room air ventilation. Such general or dilution ventilation can control some airborne hazards, but it is usually not the most cost-efficient way to control them.
4. *People working in a room or air space with a source of airborne chemical but little or no ventilation.* Without ventilation, airborne hazards will accumulate even further. An aerosol can accumulate with virtually no upper limit, but a vapor's concentration will eventually be limited either by the amount of liquid available to evaporate or by the liquid's vapor pressure (P_{vapor} will be explained in Chapter 2). Work in such unventilated or/and confined spaces is the *worst-case* scenario.

Once the contaminant becomes an airborne plume, convection (the flow of air) is the primary mechanism causing the plume to move, and turbulent diffusion is the primary mechanism causing the plume to dissipate. Together, convection and turbulence largely control employee exposures in scenarios 1 and 2 above. Thermal buoyancy and sedimentation (*e.g.*, particle falling velocities) are secondary mechanisms that can be important in these scenarios but are more often important in scenario 3. Chapter 2 discusses buoyancy. Chapter 3 discusses aerosols. Chapter 5 discusses evaporation, elaborates on the above four exposure scenarios, and presents methods to anticipate exposure concentrations within these scenarios. Chapters 8 and 9 focus on how the principles introduced within the previous chapters can be used to reduce the rate at which contaminants are generated at their source or to keep employees out of the plume. Most of the subsequent chapters focus on either removing the plume from the room (via *LEV* in scenarios 1 and 2, explained in Chapters 10 through 18) or diluting the accumulation within the room (via *general ventilation* in scenario 3, explained in Chapters 19 and 20). The final two chapters (Chapters 21 and 22) discuss how to control personal exposures via limiting employee time of exposure or providing respirators and other forms of personal protective equipment [PPE]. In contrast to learning about other occupational health hazards such as heat, noise, pressure, and radiation that are physically and pathologically unrelated, the

^a The concepts pertaining to the terms *near-field*, *free-field*, and *reverberant field* as used in the study of noise also pertain to the first three of these four chemical exposure scenarios. The last chemical exposure scenario of vapor equilibrium has no equivalence in noise because sound cannot accumulate (it dissipates literally at the speed of sound).

topics within this book are closely linked and build upon themselves. Thus, the reader will reencounter the principles of Chapters 2 and 3 many more times later within this book.

III THE IH PARADIGM OF CONTROL PRIORITIES

This book is also structured around a long-standing and well-justified paradigm for how industrial hygienists would prefer to control occupational hazards. A paradigm (paʻədī nī) is an example or solution often referred to for guidance as a pattern or model. Rarely do standards or guidelines specify the exact form by which a hazard in the workplace must be controlled. Thus, the professional is generally free to recommend the best way to control each hazard at each workplace. Over time, IH practitioners have developed a philosophic hierarchy of preferred controls referred to as “the industrial hygiene control paradigm.” The IH control paradigm has been stated in different ways at different times, but the basic concepts embodied in Table 1.1 are always the same. In its essence, the paradigm states that the best way to control a hazard is as physically close to its source (its point of origin) as feasible.

The traditional statement: “Engineering controls are preferred over administrative controls are preferred over personal protection.”

The modern statement: “Source controls are preferred over pathway controls are preferred over receiver controls.”

Controlling the *source* means to change the origin or intervene in the process that creates the hazard. Proactive intervention means to recognize potential hazards during the design phase of a process or factory (before it is built). Making changes on paper (or in a digital plan), especially to the source of the hazard, is always less expensive than changing an existing hazard. The following “...tions” (from Table 1.1) are all source controls:

1. Substitution—use a less hazardous chemical(s) or process.
2. Source Modifications—change the process operating conditions or layout.

Controlling the *pathway* for airborne hazards generally means to intervene in how the contaminant moves through the air from the source to someone’s breathing zone, although the pathway can also lead to the skin (for dermal hazards) and rarely to the mouth (for ingestion hazards).

3. Work Practices—change the way employees conduct their work including improved housekeeping.
4. Automation—use robotics or computer-aided manufacturing [CAM].

TABLE 1.1

The Role of the IH Control Paradigm on the Structure of This Book

Traditional Preferences	Modern Preferences	Specific Control	Chapter
Engineering controls	Source controls	1. Substitution	8
		2. Source modifications	9
	Pathway controls	3. Work practices	9
		4. Automation	9
		5. Separation	9
		6. Isolation	9
		7. Ventilation	10–20
Administrative controls	Receiver controls	8. Administration	21
Personal protection controls		9. PPE	21–22

5. Separation—place the source or employee in different locations.
6. Isolation—enclose major identifiable sources or the employee.
7. Ventilation—basically moving air, but more specifically using either “general ventilation” to dilute airborne hazards or “local exhaust ventilation” to extract airborne chemicals near their source via a hood, ducting, a fan, etc.

Controlling the *receiver* means to reduce the dose reaching employees through administrative control and PPE.

8. Administration—adjusting schedules to reduce either the number of people exposed, their duration of exposure, or the timing of required tasks that affect multiple people’s exposure (some IHs include “work practices” and training within administration).
9. PPE—includes clothing, gloves, and respirators that intervene at the last possible moment in the chemical’s trip from the source to the absorptive barriers of the body.

The modern statement of the control paradigm groups both administration and personal protection as a *receiver control* because they both require the active participation of the exposed employee. While employee participation has some advantages and should be considered a part of any control strategy, reliance upon their consistent cooperation is the least predictable of the three levels of control.

As can be seen in Table 1.1, the source and non-ventilation pathway controls are the most highly preferred options, *if* they can be implemented. The first five technical chapters (Chapters 2 through 6) present the scientific principles underlying the mechanisms that generate and transport an airborne contaminant from the source into the occupied workplace. Chapters 8 and 9 explain how these mechanisms can be manipulated to reduce exposures. Further applications of these non-ventilation controls will evolve as a practicing hygienist develops a broader understanding of manufacturing processes in their industry and adds knowledge of the proprietary technologies and the production hardware and conditions within their specific workplace. Since access to such applied knowledge is much more easily gleaned on the job than from a textbook or classroom, it comprises only a small proportion of this book.

Given the strikingly different exposure scenarios introduced above, it should not be surprising that there is no single way to control all chemical exposures or even any given chemical exposure. One control may be more costly to install or to operate in one setting but not in another setting. Cultural, educational, and social differences among settings can have as much influence on the success of a given control as the technical issues. Cost-effectiveness also depends upon the technologic and market issues affecting the *temporal horizon* to which the use of the control can be foreseen (see Chapter 7). A good industrial hygienist will develop a wide arsenal of tools from which to choose the best control in any situation. Even within a chosen control, the hygienist must still choose the parameters that will affect its eventual effectiveness and work within the management policies that will affect its acceptance. The point is that IH is based on science, but the details of control are an acquired art.

IV THE APPROACH AND PHILOSOPHY OF THIS BOOK

It is the perennial goal of educators in general (and this author in particular) to try “to put old heads on young bodies.” Since learning builds on prior experience, the learning process followed by this book tries to build on prior academic training rather than expecting the student to have had much prior hands-on experience within the workplace. Thus, this book tries to bridge the gap between the basic physical science principles and mechanisms that underlie the generation and dispersion of airborne chemicals and the wealth of chemical hazard control recommendations, techniques, and tools accumulated by previous generations of IH practitioners. This book assumes that the reader is academically trained in science and math, but has seen only a small number of manufacturing or other work settings with chemical hazards and is inexperienced in the selection, design, implementation,

or management of chemical exposure control systems. Thus, most of the technical chapters start with definitions or/and principles from physical chemistry and Newtonian physics that the student should be able to recall with appropriate prompting.

The emphasis will be on learning the *why* as much as the *what*: the logic being that if you understand why something happens or why two variables are related, you will be better able to understand the formula and how to use that relationship rather than just seeing a formula as a sequence of letters or symbols.

While much of ventilation has its origins in engineering, no engineering background is expected from the reader. As a result, this book may be a student's first introduction to two classic engineering tools: empirical equations^b and force, mass, and energy balances.^c These tools will not be taught as methods in and of themselves, but they will be used repeatedly throughout the text.

The book has many equations, but the author has tried diligently to avoid using vague notation that is endemic to engineering texts. The resulting frequent use of long subscripts makes some equations look longer than they might otherwise appear, but the longer, more explicit notation will hopefully be more meaningful. Keep in mind that a short list of abbreviations and symbols is included near the front of this book.^d

As a textbook, some derivations of equations are included to help lead at least some readers to transition from what they hopefully already know (or at least knew at one (perhaps brief) time in another class) to an end point that is useful within IH. Such derivations are denoted by being enclosed within a lightly shaded background. Industrial hygienists do not derive such equations in practice. If you feel yourself getting bogged down in a derivation, try going straight to the end point and then maybe look back at the derivation only as needed to explain its terms.

V LEARNING GOALS AND SPECIAL NOTATIONS

Each chapter within this book is broken into sections labeled by a roman numeral and a title. Virtually every section is further broken into untitled subsections labeled by an Arabic number. And a few subsections have sub-subsections labeled by lowercase letters. This notation allows easy cross-referencing by chapter, section, and subsection. For instance, Section 6.III.2 refers to Chapter 6 Section III subsection 2; any cross-referenced section without a chapter refers to the section within the current chapter being read.

This book contains more information than a student needs to learn at one time. The excess will hopefully provide a professional resource after graduation. To guide the student toward the most immediate or fundamental pieces of information, each of the chapters is preceded by specific *learning goals*. Each *learning goal* is preceded by one of the symbols listed within Table 1.2. The two box symbols should correspond to the *box notation* enclosing that material within the text. The third symbol highlights important concepts that do not necessarily have a specific focal point within the

^b Empirical equations are based on a theory or principle but include one or more “empirical” coefficients or powers found via regression or other statistical technique that allows the equation to better match the experimental data. The following two examples are from future chapters: Equation 3.9a uses an “empirical” C_{slip} factor to allow Stoke's law to predict the falling velocity of very small particles, and Equation 5.2 predicts solvent vapor generation rates in which several variables are raised to “empirical” powers:

$$V_{\text{falling}} = C_{\text{slip}} \rho_{\text{net}} d^2 g / 18\eta \quad 3.9a$$

$$G_{\text{moles}} = \kappa_{\text{mass tx}} [\text{Width}][\text{Length}]^{0.5} \frac{V^{0.6} D^{0.67}}{V^{0.17}} (P_{\text{vapor}} - \text{ambient } P_{\text{partial}}) \quad 5.2$$

^c Mass or energy balances yield equations based on the principle that what goes into a system plus what is generated within that system equals what comes out of that system plus what is destroyed or accumulates within the system. This concept of balances can be applied to everything from biology to air or water, to pollutants, and to personal finances.

^d A few exceptions to “explicit notations” are made where the author uses a notation already widely accepted within the profession to avoid later confusion that might result from a reader trying to adapt from a clearer notation to that professional de facto standard notation.

TABLE 1.2
An Explanation of the Symbols Used within Each Chapter's Learning Goals

Symbol	Implied Meaning
☐	Something that appears in this book within a solid box means that it is important to <i>know</i> thoroughly. The reader should be able to use what is in the box without having to look it up. The author considers information enclosed in a solid box to be either central to IH or/and to its underlying the science. Where the item is an equation, learn it as a concept not just as a formula. ^a
☐	Dashed boxes are used in this book to highlight useful tools or information that the reader may want to find again later (or need to find again quickly) but is not expected or intended to be memorized. The student should still <i>know how</i> or <i>be able</i> to use the enclosed information with the book open at that page. During an examination, it is not the time to try to use an equation for the first time.
	The <i>take a note</i> symbol is used where a learning goal summarizes concepts that may not have a single focus that could or should be boxed in either of the above ways. To paraphrase Einstein very loosely, not everything that counts can be boxed.
✓	Rather than an explicit learning goal, this notation is used within the text to highlight a rule-of-thumb, a summary, or a trend that is intended to give the student a practical (field-usable) perspective on a topic. Think of a rule-of-thumb as one way “to put an old head on a young body.”

^a The author has enclosed a total of 29 equations within a solid box. The first group of 13 equations not related to ventilation is compiled on pp. 243–244 (Section 9.VIII). The second group of 16 equations related to ventilation is compiled on pp. 284–285 (Section 11.VI). You might want to tab these pages for future reference; a trimmed and labeled Postit® is a convenient and inexpensive aid to speed access.

text. Your instructor may modify these learning goals. Trying to read only the portions of text that pertain to these learning goals runs the risk of failing to see their context.

Each learning goal also incorporates a *key phrase* loosely adapted from Bloom et al.'s “cognitive domains.”³⁴ The idea behind these key phrases is that one does not need to know everything at the same level. Table 1.3 elaborates on the level of learning implied by each *key phrase* that this author thinks should be sought by the student at this time in their education.

TABLE 1.3
An Explanation or Elaboration of Each Key Phrase Used within This Book

Phrase	Implied Meaning
“Know ...”	Knowing means more than just memorizing the words or symbols in a box. Knowing includes also understanding the concept and how it might be used in IH practice. This is especially true for boxed equations; they are more than just letters and numbers, and should be viewed as a shorthand method of expressing a concept.
“Be able to ...”	Ability is a small step short of <i>to know</i> as defined above. One goal of <i>be able</i> is to be able to translate an IH problem as presented into terms from which the right equation or principle can be applied. Being able to apply concepts to real-world problems lends itself to open-book questions.
“Know how ...”	Know how to use the information for an IH purpose; usually said of a figure, graph, or equation that definitely does not have to be memorized.
“Understand ...”	Be able to discuss, evaluate, or interpret the concept. Often related to problems where a non-quantitative or qualitative answer is expected; <i>e.g.</i> , what are the factors that determine an outcome? Or, in what direction would the outcome change for a given change in one of its underlying factors?
“Be familiar with ...” or “Be aware of ...”	Recognize the listed term or concept if it is presented; be able to fit it into or separate it from a list; or at the very most, be able to discuss the term or topic in a short essay question.

The topic of ventilation within Chapters 10 through 20 of this book heavily references the ACGIH *Industrial Ventilation, A Manual of Recommended Practice for Design* (often referred to here as the *Industrial Ventilation Manual* or occasionally just *the Vent Manual*).⁵ While the *Industrial Ventilation Manual* is a valuable working tool, but it is not a textbook,^e and IH students do not need to know everything within it. Thus, this book is selective in its coverage of the *Manual's* ventilation topics. At the same time, this book also goes well beyond the *Manual* on the topics of non-ventilation and receiver controls. Taken as a whole, this book provides a unique, comprehensive tool to learn the challenging yet rewarding role that IH can play in controlling chemical health hazards at work. The engineering student or specialist who wishes to go beyond the level of ventilation design expected of most competent industrial hygienists may be better served by other texts written by and for engineers such as Heinsohn,⁶ Burton,⁷ Goodfellow and Tähti,⁸ or Burgess et al.⁹

Admittedly, not every industrial hygienist works very much with ventilation. Few probably design a full ventilation system on their own. However, almost all hygienists will encounter ventilation and will work with people who are in charge of ventilation at their facilities. For better or for worse, students rarely know whether or not ventilation will be a major responsibility within their individual future careers. Numerous past graduates, who as a student thought ventilation was a waste of time, in fact, got their first job because of that particular knowledge. Others unexpectedly found themselves in charge of monitoring and improving ventilation systems at their facility. This book is intended for you, the IH student, and your future, in the expectation that with knowledge the best time of your life is yet to come.

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^e This author would categorize it somewhere between an engineering textbook and a working reference book.



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2 The Behavior of Gases and Vapors

The learning goals of this chapter:

- ☐ Understand Dalton's law; know that $P_{\text{partial},i} = Y_i \times P$. (Of course, know what Y_i is.)
- ☐ Know how to convert between airborne molar fraction [Y_i], ppm, and mg/m^3 .
- ☐ Be able to calculate a vapor pressure if given an Antoine equation.
- ☐ Know how to approximate the change in vapor pressure from a change in its liquid temperature.
-  Understand why partial pressure is an expression of concentration.
- ☐ Know how to calculate a vapor's equilibrium ppm from its vapor pressure at NTP.
-  Understand the effect of atmospheric pressure on a saturated vapor's ppm and mg/m^3 concentrations.
-  Understand the circumstances that determine whether ppm or mg/m^3 will change or remain constant.
- ☐ Know how to calculate the density of any gaseous material at NTP if given its molecular weight [MW].
-  Understand how vapor density can affect the vertical movement of a plume.

This chapter presents virtually all the definitions and physical laws that describe the behavior of gases and vapors within the environment. While Dalton's law about the effects of pressure and temperature on gas volume and density should be a review for anyone who's had college-level chemistry or/and physics, the effect of liquid temperature (and Antoine's equation) is likely to be new. These principles are then used to explore the effects of temperature and pressure on airborne concentrations in industrial hygiene [IH] units of ppm and mg/m^3 and on plume density that will be used later in Chapters 5, 8, 13, 16, and 20.

I GAS AND VAPOR DEFINITIONS

This section is all about definitions. It starts with practical differences among the meanings of "normal" and between absolute and relative units of temperature and pressure (two intrinsic properties of all gases and vapors), and works its way to a definition of vapor pressure (a term that is very important within industrial hygiene) and to the distinction between gases and vapors (the latter is only important in getting from a liquid state to a gaseous state; once they are airborne, gas molecules and vapor molecules behave in identical ways).

1. *Temperature* is a measure of the amount of kinetic energy contained within molecules. Although the Fahrenheit scale (1724) preceded the Celsius scale (1742) by a few years (and the latter was initially proposed upside down), degrees Celsius has become the preferred unit. And whereas a "standard temperature" of 0°C (32°F) is convenient to create inside a laboratory when chemical properties are measured, that standard temperature is too cold for human comfort or for safe work without the appropriate clothing. Most environmental and occupational health data refers to "normal temperature" that is in the range of human comfort and habitation without special clothing. Unfortunately, not everyone uses quite the same definition of "normal" temperature.

- a. A temperature of 25°C or 77°F is common in environmental chemistry and was assumed to be normal by the people who popularized the common molar volume of 24.45 L. This is a larger volume than the 22.4 L that one mole of an ideal gas occupies at standard temperature and pressure [STP] like you perhaps learned in chemistry because gases expand as they are heated. While 24.45 is one of three “memorable numbers” frequently used in IH,^a the temperature to which it corresponds may be a bit warmer than most indoor settings or even many outdoor settings (of course, the latter varies by geographic region, season, and time of day).
- b. A temperature of 21°C or 70°F was assumed to be normal within the *Industrial Ventilation Manual*.¹ This value is perhaps more typical of controlled indoor environments, homes, or institutional buildings and is a nice round Fahrenheit value. (70°F actually corresponds to 21.1°C, but the difference of 0.1°C is inconsequential in daily practice.)
- c. A temperature of 20°C or 68°F was assumed to be normal by NIOSH in publications such as their *Pocket Guide to Chemical Hazards*.² It is also the minimum temperature specified by the *International Building Code* that a space-heating system should be able to maintain (IBC Section 1203).³ This value may be a bit cooler than room temperatures during the summer season, but it is a nice round metric value (being another, along with 25°C, exact integer conversion between °C and °F). A molar volume of 24.04 L at this temperature is not common within the IH literature.

The above lack of a universally agreed upon “normal temperature” in occupational health is awkward. While a 5°C or 9°F range of normal temperatures generally has a small impact on most practical (real world) problems,^b any academic problem should state or be defined at a specific temperature. By default (or should a temperature be left unstated), this book will follow two of the common practices mentioned above, meaning it will assume that “normal” is 25°C or 77°F when discussing chemistry but 21°C or 70°F when discussing ventilation.

Temperatures expressed in degrees either Celsius or Fahrenheit could be said to be (but are rarely called) “relative temperatures.” Their zero values correspond to the freezing temperatures of water and of a 50:50 salt-to-water mixture, respectively. Each of these relative temperature scales also has a corresponding “absolute temperature” scale in which each degree is the same size as in their respective relative scales, but the zero value is based on the theoretical absence of all molecular kinetic energy. The chemistry student will, no doubt, be familiar with the Kelvin scale (given by Equation 2.1), while the engineering student may have also been introduced to the Rankine scale (given by Equation 2.2).

$$\text{Kelvin: } ^\circ\text{K} = ^\circ\text{C} + 273.15 = (5/9)^\circ\text{R} \approx ^\circ\text{C} + 273 \quad (2.1)$$

$$\text{Rankine: } ^\circ\text{R} = ^\circ\text{F} + 459.67 = (9/5)^\circ\text{K} \approx ^\circ\text{F} + 460 \quad (2.2)$$

Some IH students may remember the use of absolute temperature in degrees Rankine from studying radiant heat stress.⁴ All four of these temperature scales will be used herein from time to time.

2. *Pressure [P]* is the force [*F*] per unit of surface area [*A*], as stated in Equation 2.3a. In turn, the force exerted on a surface is the product of the pressure on that surface multiplied times its surface or cross-sectional area, as stated in Equation 2.3b.

^a “Memorable numbers” means what this author, many instructors, and professional closed-book exams expect a certified industrial hygienists should know by memory. They include 24.45 L and 760 mmHg from this chapter and 4005 used frequently within ventilation (to be covered in Chapters 10–20, but first introduced within Chapter 11).

^b To jump ahead in knowledge, because a chemical’s vapor pressure approximately doubles every 12°C, a range of 5°C would correspond to a 40% difference in evaporation rate and vapor concentration. A difference of this magnitude is measurable but is unlikely to be decisive when making predictions without having exposure data.

$$\text{Pressure} = P = \frac{F}{A} = \frac{\text{Force}}{\text{Area}} \quad (2.3a)$$

$$\text{Force} = F = P \times A = \text{Pressure} \times \text{Area} \quad (2.3b)$$

Pressure can exist within solids as either tension (pulling), compression (pushing), shear (a force like friction parallel to a surface), or torsion (twisting). Pressure within a fluid (*viz.*, a gas, vapor, or liquid) can only be compression or shear. The random motion of a fluid's molecules striking a surface in which it is in contact will create a pressure perpendicular to that surface. The normal atmospheric air pressure listed in Table 2.1 is created by the inertia of about 8×10^{23} molecules impacting each square centimeter of surface every second. Air pressure is a part of meteorology, aerodynamics, pneumatics, and ventilation. We will see later within this chapter that the pressure of each individual gas and vapor within the atmosphere is related to its airborne concentration (as in the oxygen that we need to survive or the airborne chemical hazards that industrial hygienists need to control). We will see in later chapters that the friction produced by air flowing over a surface will produce a shear force resulting in drag (Chapter 3) or pressure loss in ventilation (Chapters 11 and 14).

- a. Unlike the variations among normal temperature, a single, widely accepted value exists for “normal pressure,” as listed in Table 2.1.^{5,6} Like temperature, pressures can also be measured or/and expressed in either absolute or relative terms. The units in Table 2.1 are all *absolute pressure*. An absolute pressure is measured above the zero that exists in a complete vacuum. Because absolute pressure gauges must contain a vacuum as an internal reference, accurate absolute pressure gauges are more expensive and larger than relative pressure gauges. A mercury-filled barometer is a primary absolute pressure gauge. The units marked on the face of a commercially manufactured absolute pressure gauge generally include an “a” suffix, such as “psia” meaning pounds per square inch absolute (*i.e.*, the pressure above the zero of a vacuum). Because thermodynamic properties and chemical reaction rates are dependent upon the absolute pressure and temperature of the reactants, most pressure gauges on chemical reactors are in units like psia. The human body also responds to, or performs in relation to absolute pressure (Chapter 4), and physical relationships such as Dalton's law and the Universal Gas law (later in this chapter) use absolute pressure.
- b. While a value for *normal pressure* has been agreed upon, the actual atmospheric pressure at sea level commonly varies from this value on the order of ± 1 inch or ± 25 mmHg

TABLE 2.1
One “Normal” Atmosphere in Various Units of Pressure

	English Units	Metric Units
Force per unit area	14.696 $\approx$ 14.7 psi (where psi is pounds per square inch)	101,325 Pa ^a (1 Pascal = 1 N/m ²)
Barometric pressure ^b	29.921 in. Hg (mercury)	760.001 mmHg
Ventilation pressure ^c	407.60 in. of water at 70°F	1,035.3 cm of water at 21°C

^a A “bar” is a pressure term used in meteorology meaning 10^6 dynes/cm², 10^5 N/m², 10^5 Pa, or 0.986923 atm. Thus, one normal atmosphere is also 1.01325 bar.

^b As used in meteorology, a barometer measures air pressure by the height that it can push liquid mercury up into a vacuum-filled glass tube.

^c No one measures atmospheric pressure with a water-filled barometer; however, water-filled manometers are used to measure the small differences in pressure encountered in ventilation. The basis for the 407.60 “wg” shown here is documented in an appendix to Chapter 11.

in conjunction with changes in the weather. Atmospheric pressure also decreases with altitude above sea level. Equation 2.4 is helpful to anticipate the atmospheric pressures when above sea level.^c The first two versions of Equation 2.4 work well if you know the specific barometric pressure at sea level; the last four versions assume normal temperature and pressure [NTP] at sea level and use the more intuitive power of 2 (like a half-life).

$$P_{\text{at altitude}} = P_{\text{at sea level}} \times e^{(-\text{altitude in feet}/26,640)} = P_{\text{at sea level}} \times e^{(-\text{altitude in meters}/8,100)} \quad (2.4a)$$

When conditions at sea level are NTP ...

$$P_{\text{at altitude}} [\text{mmHg}] = 760 \times 2^{(-\text{altitude in feet}/18,465)} = 760 \times 2^{(-\text{altitude in meters}/5,615)} \quad (2.4b)$$

$$P_{\text{at altitude}} [\text{atmospheres}] = 2^{(-\text{altitude in feet}/18,465)} = 2^{(-\text{altitude in meters}/5,615)} \quad (2.4c)$$

These equations will be used with Dalton's law (related to partial pressure) in Section III and with the Ideal Gas law (related to vapor density) in Section V. Changes in air density due to altitude affect rotameters used in air sampling, anemometers used in ventilation, direct reading gas or vapor meters, some noise meter calibrators, and human respiration.

But beware! The barometric pressure in weather reports is almost never what one would measure at that location. The pressures in weather and aviation reports are adjusted to what the pressure would be at sea level at the reporting location using something like Equation 2.4. Thus, such reported barometric pressures are not real except at sea level.

- c. Relative pressures are measured in comparison to the ambient atmospheric pressure. A positive pressure relative to the ambient atmosphere is commonly called a "gauge pressure." A relative pressure meter will usually (but not always) indicate its units of measurement with an appended "g" such as "psig."^d Equation 2.5 may be used where one needs to convert between absolute and relative pressures. For example, psia = psig + 14.7 psi at NTP.

$$P_{\text{gauge}} = P_{\text{absolute}} - [\text{The ambient atmosphere in the units of } P] \quad (2.5a)$$

$$P_{\text{absolute}} = P_{\text{gauge}} + [\text{The ambient atmosphere in the units of } P] \quad (2.5b)$$

Gauge pressures are particularly important in safety and in ventilation. The outward stress on a pipe or pressure vessel is determined by gauge pressure because one ambient atmosphere is always on the outside of the vessel pushing in. Air will move in response to differences in static pressure. The small pressure differences applicable to ventilation are conveniently expressed by the difference in the height of two columns of water in a manometer (to be covered in Section II of Chapter 12). The abbreviation "wg" is used in the American ventilation literature to mean inches of water gauge. Neither relative pressure nor pressure differences have a normal value (*cf.* the normal absolute atmospheric pressures in Table 2.1).

- ✓ 3. It may not be obvious from the above definitions but is important to remember that one can use either relative or absolute values when dealing with differences (*e.g.*, $\Delta T = T_2 - T_1$ or

^c The coefficients in these equations are 2.6% higher than those in the first edition of this book to reduce the maximum predictive errors below 14,000 ft (4267 m) from 2.6% 1.1% to less than $\pm 0.4\%$; however, all of these exponential equations can severely overestimate barometric pressures above 18,000 ft. A more accurate equation $(1 - (\text{ft}/145,675))^{5.256}$ can predict atmospheric pressures with predictive errors of less than $\pm 0.1\%$ below 16,000 ft and $\pm 0.3\%$ up to 35,000 ft.⁶

^d A pressure that is less than the ambient atmosphere is commonly called a vacuum pressure. A "Torr" is a nonstandard unit of vacuum pressure meaning 1/760 of a standard atmosphere or minutely smaller (by 10^{-7} mmHg) than 1 mmHg.

$\Delta P = P_2 - P_1$); you will obtain the same answer. However, when dealing with ratios (*e.g.*, T_2/T_1 or P_2/P_1), one must always use absolute values or else you will obtain the wrong answer. Choose wisely.

4. *Partial pressure* is the absolute pressure exerted by the molecules of one gas or vapor that exists in combination with other gases or vapors that comprise the total pressure. Thus, the term “partial” can be taken literally to mean one particular part of the total pressure. Rather than abbreviating partial pressure as simply P_i where the subscript i refers to the generic i th component within a mixture, this book will use either the slightly more expressive $P_{\text{partial},i}$ or where appropriate the subscript will be a named chemical, *e.g.*, P_{oxygen} . In either case, P_{partial} is commonly expressed in units of either mmHg or atmospheres. However, the reader will soon be shown via Dalton’s law, that a partial pressure is equivalent to an airborne chemical concentration expressed in traditional IH units of mg/m^3 or ppm.
5. *Molar fraction* is the relative portion of the molecules of one named chemical compared to all of the molecules within a mixture as a whole. Unlike partial pressure, molar fraction has no units, so you do not even need to recall that a mole is Avogadro’s number (6.02×10^{23}) of molecules. Molar fractions can be expressed as either a percentage (obtained by multiplying a decimal fraction by 100) or parts per million (multiply a decimal fraction by 10^6). This same concept can be applied to either liquids or gases and vapors, but for a variety of reasons, two different abbreviations are used.
 - a. By convention, the symbol X_i always denotes the molar fraction in a liquid. Use Equation 2.6 to calculate the molar fraction in a liquid mixture.

$$X_i = \frac{\text{Number of } i \text{ molecules within a liquid mixture}}{\text{Number of all molecules within a liquid mixture}} \quad (2.6)$$

Because liquid mixtures are commonly expressed as either a weight or volume fraction rather than as a molar fraction, these other liquid fractions will usually need to be converted into molar fractions as will be explained within Section 6.II.

- b. Similarly, the symbol Y_i always denotes the molar fraction in a vapor or gas. Use Equation 2.7 to calculate the molar fraction in a gaseous mixture.

$$Y_i = \frac{\text{Number of } i \text{ molecules within an airborne mixture}}{\text{Number of all molecules within an airborne mixture}} \quad (2.7)$$

Because a mole of any two gases or vapors at the same T and P would comprise the same volume, the Y_i molar fraction is also a volume-to-volume ratio. And Dalton’s law (to be discussed in Section III) states that the Y_i molar fraction is also a pressure-to-pressure ratio. We will see in Chapter 6 how physical and chemical conditions within a liquid mixture can affect the proportions within its airborne vapors. In fact, it may help you to remember how to keep the X_i and Y_i notations distinct if you take a glance now at the X – Y diagrams in Figure 6.4 and think of the airborne Y_i as the dependent variable on the Y or vertical axis that varies with the independent liquid X_i variable on the X or horizontal axis.

6. A “closed room” is simply an unventilated room; in other words, a room without either natural ventilation (no open doors or windows) or mechanical ventilation (no fan or/and air ducts).^e On the other hand, a “closed room” is not airtight; it leaks. In fact, to construct an airtight room, chamber, or vessel requires special materials and construction methods. Gaps in doors, windows, and even pores in common wall materials allow the air pressure inside any closed room to always stay at the same pressure as the ambient pressure outside

^e Ventilated rooms will be discussed in Chapters 11 and 20.

the room. Thus, if gas or vapor is released from a chemical source inside a closed room (such as by evaporation), the added airborne molecules will force some of the airborne molecules already inside the room to seep outside so that the total pressure inside the room stays equal to the atmospheric pressure outside the room. Similarly, if the air temperature inside the room increases (or decreases), the air density will change, and some air will escape from the room (or enter into it) to keep the pressure inside the room equal to the atmospheric pressure outside the room.

7. *Vapor pressure* [P_{vapor}] is the partial pressure exerted by the airborne molecules of a compound that is in equilibrium with its liquid. To be in equilibrium means that the concentration does not change; thus, the rate at which molecules are leaving the liquid (evaporating) must be equal to the rate at which airborne molecules are being reabsorbed back into the liquid. The reabsorption rate depends upon the frequency at which that chemical's airborne molecules strike each unit surface area of the liquid surface. That frequency depends upon the absolute T (in effect, the molecules' speed) and the molecules' molar concentration (mol/m^3) but not upon the ambient P . In fact, it is the moles/ m^3 and T that determine each chemical's partial pressure.
 - a. Vapor pressure has been abbreviated as P_0 , P^0 , P_V , P_{VP} , P_{sat} , or even VP in chemistry and engineering texts, such as those to be listed in Table 2.2. The more literal abbreviation P_{vapor} will be used herein to help the reader to differentiate vapor pressure more easily from the VP abbreviation used for velocity pressure.^f
 - b. Vapor pressure is a direct indicator of a chemical's volatility. All materials have a vapor pressure. A chemical with a high vapor pressure is highly volatile, meaning it will evaporate rapidly. A chemical with a low vapor pressure is less volatile. High-molecular-weight liquids (and even solids) have a very low vapor pressure ($\ll 1$ mmHg) that can still be important if the material is sufficiently toxic (e.g., liquid mercury).
 - c. Any given chemical's vapor pressure will increase as its liquid temperature increases, as will be discussed within Section II of this chapter. When a liquid reaches the temperature at which its vapor pressure equals or exceeds the ambient atmospheric pressure, its vapor molar fraction [Y_i] will equal one and it will appear to boil. The *normal boiling point* [bp] listed on a chemical's safety data sheet [SDS] or a similar tabulation is the temperature at which its vapor pressure equals 760 mmHg.
 - d. P_{vapor} is the maximum concentration at which a chemical can exist as a vapor at a specified temperature. When a chemical's airborne concentration is at its vapor pressure, its vapor is said to be *saturated*. Thus, the term "saturated vapor" refers to a vapor that is in equilibrium with its liquid. The only way that an airborne chemical can be more concentrated than its vapor pressure is if it were present as an aerosol. In fact, when a saturated vapor concentration is cooled, the vapor will start to condense into either a visible fog (what some might call steam or what an IH should call a mist) or a fume (minute solid particles).
 - e. For the vapors throughout a closed room to come into equilibrium with its liquid, at least enough liquid must initially be present to generate all the vapor molecules needed to fill the entire enclosed airspace up to its vapor pressure concentration. The criterion for "enough liquid" will be discussed in Section VII of Chapter 5.
 - f. And P_{vapor} is also an important predictor of the airborne concentration in ventilated workplaces or in a plume whether indoors or outdoors. Because a vapor is always considered to be in equilibrium right at its air-liquid interface, P_{vapor} is the idealized concentration that always exists right at any liquid's surface. Unless the whole room

^f The abbreviation VP to denote *velocity pressure* is heavily used within IH and the ventilation literature. VP is introduced herein in Chapter 10, is formally defined in Chapter 11, and is used extensively when sizing ducts in Chapter 14, selecting a fan in Chapter 16, and assessing their performance in Chapter 18.

is in equilibrium, that vapor concentration is rapidly diluted before its plume reaches people. Because the dominant mechanism that dilutes vapor plumes is generally independent of the kind of vapor within the plume, a vapor's concentration anywhere within a room is a potentially predictable fraction of its vapor pressure concentration at its source.

8. The term *gas* has two related meanings. In one context, a gas is the airborne state of a chemical whose *vapor pressure* is less than one atmosphere, which simultaneously means whose normal boiling point is less than normal room temperature. The term *gas* can also apply to a chemical entity that is so volatile that all of a liquid at NTP would evaporate; in fact, it would evaporate so fast that it would appear to boil. Such a chemical can only be stored either at normal temperature under a pressure of more than one atmosphere (e.g., inside a gas storage cylinder) or at normal pressure as a liquid cooled to a temperature below its boiling point (and kept in a well-insulated container such as a Dewar). Temperatures below -90°C (-130°F) are called *cryogenic*.⁸
9. A *vapor* is the airborne state of a chemical whose *vapor pressure* is less than one atmosphere. Simultaneously, a vapor is also the airborne state of a chemical whose *boiling point* is above *normal room temperature*. If an abundance of a liquid whose *vapor pressure* is less than one atmosphere or whose *boiling point* is above *normal room temperature* existed inside a closed room at normal temperature, it would not completely evaporate but rather would reach an equilibrium with its liquid (to be in equilibrium means that the airborne concentration does not change over time). By this definition, the molar fraction of a vapor that is in equilibrium with its liquid source must be less than one (otherwise, it would be a gas).

A chemical engineering model to be introduced within Chapter 5 hypothesizes that the vapor molecules immediately above an actively evaporating liquid are in equilibrium with that liquid. Such vapors get diluted as soon as they leave that surface. Because each airborne molecule of a vapor or gas acts independently from each other, once they are airborne, gases and vapors will behave in identical ways.

10. Industrial hygienists commonly express *airborne concentrations* as either ppm or mg/m^3 . IH students are likely to be already acquainted with the conversion from ppm to C in mg/m^3 and back again, as stated in Equation 2.8a and b, respectively.⁷ This conversion offers a classic example of how to understand an equation conceptually, actually two examples!
 - a. One way to view Equation 2.8a is that airborne ppm is a ratio of either volume-to-volume, mole-to-mole, or pressure-to-pressure but has no relationship to mass. On the contrary, units of C in mg/m^3 clearly includes the mass of the chemical being described. In order to convert from mg/m^3 to ppm, one must conceptually remove the mass component in C_i by dividing it by the chemical's molecular weight [MW]. The 24.45 (any gas or vapor's molar volume in liters at an NTP of 25°C) can be viewed as just the memorable proportionality constant that is always on the other side of the ratio from MW_i .

$$\boxed{\text{ppm}_i = C_i \left(\text{mg}/\text{m}^3 \right) \frac{24.45}{\text{MW}_i}} \quad \text{at NTP (25}^{\circ}\text{C and 760 mmHg)} \quad (2.8a)$$

To make the inverse conversion as shown by Equation 2.8b, one must conceptually insert mass into the dimensionless ppm by multiplying it by the MW_i , with 24.45 still on the other side of the ratio.

$$C_i \left(\text{mg/m}^3 \right) = \text{ppm}_i \frac{\text{MW}_i}{24.45} \text{ at } 25^\circ\text{C and } 760 \text{ mmHg} \quad (2.8b)$$

- b. Another way to view these equations conceptually is by noticing that $\text{MW}/24.45$ is the density or concentration in grams per liter of the chemical if it were present as a pure gas or vapor.[§] From that perspective, the mass concentration is just the fraction of that pure g/L concentration denoted by its ppm converted into a molar fraction. (It is nice but not essential to know how the 10^6 grams, and liters conveniently get canceled out while converting units.)

Understanding a concept embodied within an equation like this allows one to be able to reconstruct and use it without having to memorize it as just a series of letters and numbers. Equation 2.8c is added here just to put this more generalizable form that is applicable at other temperatures and pressures on the same page (even though the basis for this equation would not be covered until Section IV).

$$\text{ppm} = C \left[\text{mg/m}^3 \right] \times \frac{24.45}{\text{MW}} \times \frac{760 \times (^\circ\text{C} + 273)}{P \left[\text{mmHg} \right] \times 298} \quad (2.8c)$$

II VAPOR PRESSURE CHANGES WITH LIQUID TEMPERATURE

The temperature of a solvent is often assumed equal to that of the environment, although it can vary independently of the nearby ambient temperature. A solvent can be heated if it is in contact with some external source of heat (*e.g.*, a drying oven); but without external heat, a solvent will cool slightly below the ambient temperature due to the loss of its *heat of evaporation* (see subsection VI.4). This section explains the effect of liquid temperature on vapor pressure.

1. As stated within subsection I.1, temperature is a result (and an indication) of the kinetic energy of individual molecules. The more kinetic energy that a molecule has, the more likely it is to leave the surface of a liquid and become airborne. The greater the tendency for molecules to become airborne, the greater will be their equilibrium vapor concentration. Thus, heating a liquid will increase its vapor pressure, and cooling a liquid will decrease its vapor pressure. Conversely, a single vapor pressure (*e.g.*, gleaned from a chemical's SDS) is only applicable at a single temperature; and to be useful, the reference temperature for that vapor pressure must be known. Because not everyone uses the same normal temperature, a P_{vapor} value without a known reference temperature can be misleading by $\pm 50\%$.
2. The variation of vapor pressure with its liquid temperature is nonlinear. Specifically, P_{vapor} changes more rapidly than the change in liquid temperature. An early method to predict the change in vapor pressure due to temperature was the Clausius–Clapeyron equation, given below as Equation 2.9.⁹ Its development *circa* 1840 was a major early success of statistical thermodynamics. It turns out to be a good predictor of P_{vapor} for metals (see subsection II.5) but not very accurate for organic solvents. If you ever do have to use the Clapeyron equation, remember that the temperature in the denominator must always be in degrees absolute.

$$\log \left[P_{\text{vapor}} \right] = A - \frac{B}{(T_{\text{absolute}})} \quad \text{the Clapeyron equation} \quad (2.9)$$

[§] Think about it! The MW in grams of a chemical is one mole. And one mole will occupy 24.45 L at NTP.

3. In 1888, L.C. Antoine proposed adding a third empirical coefficient to the Clapeyron equation (the concept of empirical equations was introduced in Chapter 1). The Antoine equation gives reasonably accurate predictions of P_{vapor} as a function of liquid temperature for organic solvents (usually within $\pm 1\%$). A generic form of the Antoine equation is shown in a dotted box^h as Equation 2.10a, but be aware that Antoine equations come in several mathematically equivalent variations.

$$\boxed{\log[P_{\text{vapor}}] = A - \frac{B}{(C + T)}} \quad \text{the generic Antoine equation} \quad (2.10a)$$

Such variations include use of the natural logarithm ($\ln[P_{\text{vapor}}]$) instead of the common logarithm ($\log[P_{\text{vapor}}]$), expressing T as $^{\circ}\text{C}$ instead of $^{\circ}\text{K}$, or placing a plus sign before the fraction instead of a minus sign. The “Instructions for Using the Vapor Pressure Table” in Appendix B of Perkins’ textbook provides five examples of these variations.⁷ However, most of these variations are easy to use as long as the user notes and uses the right form pertinent to the particular set of data. Each resource for Antoine coefficients listed in Table 2.2 clearly states the form of the equation they use.

The references listed in Table 2.2 generally present the Antoine coefficients for each chemical with a temperature range over which they are purported to be accurate. Sometimes the temperature range is either outside the temperatures normally of interest to IH (especially if the pressure–temperature data was generated for use in industrial distillation, refining, or chemical reaction processes) or not provided at all (*e.g.*, denoted as “NA” in Perkins’ IH text⁷). While extrapolation beyond those limits will result in degraded accuracy, the result may still be acceptable for IH purposes, but the limitation should be noted in any of your written documentation. A search across multiple sources (particularly Dreisbach^{10–12}) may yield a set of coefficients that covers or better approximates your temperature range of interest. Of the resources in Table 2.2, Howard and Meylan’s handbook¹⁶ probably has the most extensive chemical coverage of single point P_{vapor} data at 25°C , plus it has molecular

TABLE 2.2
Some Published Resources for Vapor Pressure Data Listed in Chronological Order

Single Temperature	Antoine Coefficient	Publication Citation
✓	✓	Dreisbach, R.R.: <i>Physical Properties of Chemical Compounds</i> (1955–1961) ^{10–12}
	✓	Boublik, Fried, and Hala: <i>The Vapor Pressures of Pure Substances</i> (1973) ¹³
	✓	Hirata, Ohe, and Nagahama: <i>Computer Aided Data Book of Vapor Pressures</i> (1976) ¹⁴
	✓	Reid, Prausnitz, and Sherwood: <i>The Properties of Gases and Liquids</i> (1987) ⁸
	✓	Yaws: <i>Handbook of Vapor Pressure</i> (1994) ¹⁵
✓	✓	Perkins: <i>Modern Industrial Hygiene</i> (1997) ⁷
✓		Howard and Meylan: <i>Handbook of Physical Properties of Organic Materials</i> (1997) ¹⁶
✓		<i>CRC Handbook of Chemistry and Physics</i> (2004) ⁵

^h Recall from Chapter 1 that this author uses a dotted box to indicate something (an equation in this case) that a student should know how to use (and certainly what it can do) but does not need to memorize.

structure diagrams and Henry's constants (the latter will be discussed in Chapter 6).ⁱ

While it may at first seem daunting to realize that values of P_{vapor} at normal temperature vary widely among chemicals,^j the rate at which vapor pressures change with temperature is relatively similar among chemicals. Antoine coefficients from Reid, Prausnitz, and Sherwood (1987)⁸ were used to find the following useful rule-of-thumb.

This rule-of-thumb can predict the increase in P_{vapor} with a 95% variability of $\pm 70\%$. Predictions within $\pm 70\%$ can sometimes be useful within IH, but basic mathematics causes that precision to decrease when extrapolating further, *e.g.*, at two doublings, the precision of estimating P_{vapor} 24°C above normal becomes ± 1.7 squared = $\pm 3\times$.

As a rule-of-thumb, P_{vapor} for organic solvents will approximately double from that at NTP for an increase in liquid temperature of approximately 12°C or 21°F.

Example 2.1

Find the vapor pressure at 12°C intervals above and below 25°C (*viz.*, at 13 and 37°C) using the following Antoine coefficients for the common log of vapor pressure of toluene in mmHg that are accurate within $\pm 0.3\%$ between 0 and 50°C.¹³

$$A = 6.93325 \quad B = 1,335.533 \quad C = 218.8$$

The P_{vapor} values in the right column of data shown below are the antilog of the $\log[P_{\text{vapor}}]$ values shown in the left column of data.

$$\log[P_{\text{vapor}}] = A - \frac{B}{(C + T)} \quad P_{\text{vapor}} = 10^{\log P_{\text{vapor}}}$$

$$\log[P_{\text{vapor}}] \text{ at } 13^\circ\text{C} = 6.93325 - \frac{1,335.533}{(218.8 + 13)} = 1.1717 \quad P_{\text{vapor}} = \text{at } 13^\circ\text{C} = 10^{1.1717} = 14.8 \text{ mmHg}$$

$$\log[P_{\text{vapor}}] \text{ at } 25^\circ\text{C} = 6.93325 - \frac{1,335.533}{(218.8 + 25)} = 1.4542 \quad P_{\text{vapor}} = \text{at } 25^\circ\text{C} = 10^{1.4542} = 28.5 \text{ mmHg}$$

$$\log[P_{\text{vapor}}] \text{ at } 37^\circ\text{C} = 6.93325 - \frac{1,335.533}{(218.8 + 37)} = 1.7122 \quad P_{\text{vapor}} = \text{at } 37^\circ\text{C} = 10^{1.7122} = 51.6 \text{ mmHg}$$

The above temperatures and vapor pressures for toluene can be found in Figure 2.1 along with the curves for its two adjacent homologous partners of aromatic solvents and water. Each curve in Figure 2.1 constitutes what is sometimes called a “saturation line.” Notice how similar the vapor pressure of water is to the vapor pressure of toluene within this temperature range. In the examples above, the P_{vapor} of toluene increases by ratios of 1.93 and 1.81 each time the liquid temperature increases by 12°C. These ratios are close to the rule-of-thumb factor of $2\times$ per 12°C pointed out above. The pattern of the ratio of toluene's vapor pressure decreasing from $1.93\times$ over the 12°C below 25°C to an increase of $1.81\times$ for the 12°C above 25°C reflects the subtle pattern predicted by

ⁱ Two good online resources include the NIH Toxnet database ChemIDplus at chem.nlm.nih.gov/chemidplus/ for single-point P_{vapor} values and the NIST Chemistry WebBook Standard Reference database at webbook.nist.gov/chemistry/ for Antoine parameters.

^j For instance, the values for P_{vapor} listed in Appendices A and B of this book span eight orders of magnitude.

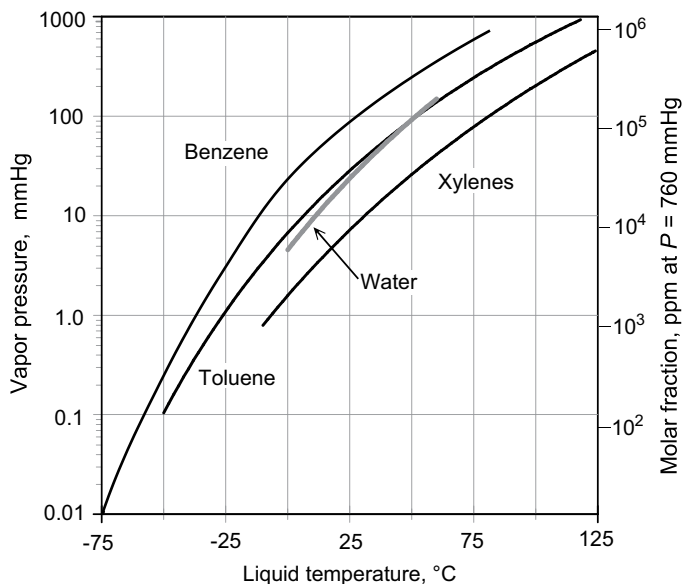


FIGURE 2.1 Antoine results for four selected solvents.

the mathematical form of the Antoine equation that is visible in Figure 2.1. This gradual flattening of the $\log[P_{\text{vapor}}]$ curve indicates that extrapolating the $2\times$ per 12°C increase in P_{vapor} above its single listed temperature will tend to overestimate the actual vapor pressure and its associated exposure hazard (this pattern will be repeated in Example 2.8).

In contrast (but probably of less practical importance), the antilog of Equation 2.10a (shown below as Equation 2.10b) indicates that the absolute rate at which vapor pressure increases with temperature (*i.e.*, mmHg per degree) actually increases with temperature. This latter pattern is not visible on the semi-log plot shown in Figure 2.1, but can be seen by the shape of the saturation line on any psychrometric chart used for heat stress analysis and comfort ventilation, which is in fact a linear plot of the vapor pressure of water versus temperature (“100% relative humidity” in Figures 17.5 and 20.5 is an example of such a saturation line).

$$P_{\text{vapor}} = 10^{A-(B/(C+T))} \text{ or } = e^{A-(B/(C+T))} \quad (2.10b)$$

4. The vapor pressure of metals also varies with temperature. Molecules of molten metal evaporate just like those of a solvent, but (with the exception of mercury) when hot metal vapors cool they condense into fumes rather than liquid mists. The hotter the metal, the more fumes are formed. Predictive coefficients for metals that follow the somewhat simpler Clapeyron equation are available in such references as the *CRC Handbook of Chemistry and Physics*.⁵
5. A chemical’s normal boiling point (bp, defined in subsection I.7) is a common but often imprecise surrogate for its vapor pressure at normal temperature.^k However, extrapolating from a boiling point to a lower working temperature is fraught with the same type of error as predicting the number of doublings in P_{vapor} when heating above 25°C .

Figure 2.2 plots the vapor pressure at 25°C versus its boiling temperature for over 400 chemicals. The agreement looks quite good for those chemicals whose boiling point is close to the 20°C – 25°C normal temperature range. However, the further that a chemical’s

^k Two examples of this kind of use will be given in subsections 4.IV.3.c and 4.VIII.3.b.

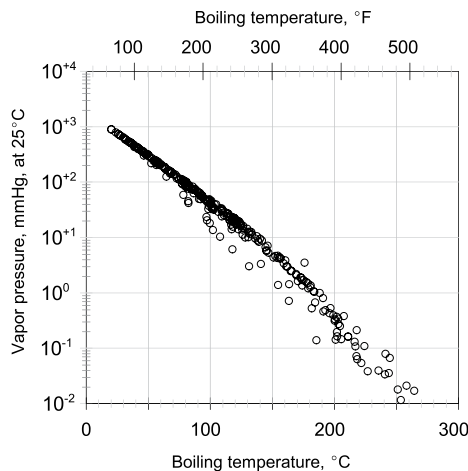


FIGURE 2.2 Plot of vapor pressure at 25°C as a function of boiling temperature at 760 mmHg.

boiling point is above this normal temperature range, the greater will be the effect of deviations from the above doubling of P_{vapor} per 12°C rule-of-thumb. The result is a spreading of the data toward the right side of Figure 2.2. The magnitude of the potential errors that can result from trying to predict a chemical's P_{vapor} from its boiling temperature must be interpreted in comparison to the logarithmic scale on the Y-axis. Thus, boiling temperatures much above 100°C or 200°F (375°K) can only predict a chemical's vapor pressure at normal temperature within about an order of magnitude (a range of 10×).

If you work in a mountainous region or the aviation industry, it can also be important to remember that a chemical will physically appear to boil whenever the ambient atmospheric pressure is reduced to equal a chemical's vapor pressure at that ambient temperature. Thus, a chemical's apparent boiling temperature will be reduced at higher altitudes (see Example 2.5). However, reducing the ambient pressure does not increase a chemical's vapor pressure or cause a liquid to evaporate more rapidly than at sea level.¹ While knowing at what altitude a chemical will appear to boil is rarely useful to an IH, Equations 2.4 and 2.10 could be combined to make that prediction.

6. The case study reported by Franklin et al. (2000) presents a classic example of not anticipating the effect of temperature on vapor pressure, exposure levels, and employee hazard.¹⁷ They treated seven painters who suffered rather severe respiratory (dyspnea and asthma) and dermal (rash) symptoms from exposure to vapors from a polyurethane paint with a hexamethylene diisocyanate [HDI] hardener. Normally the vapor pressure of HDI is less than 0.05 mmHg (depending upon the concentration of its *biuret* form). However, these particular employees were instructed to start painting a boiler before it had been given adequate time to cool. HDI's vapor pressure at over 300°F was close to boiling, and exposures would have been approximately 10,000× greater than normal. Even without the temperature being "too hot to handle," you should now be able to anticipate and avoid such acute hazards.

¹ As will be stated in Equation 5.2, the rate of evaporation is proportional to vapor pressure and molecular gas-phase diffusivity to the 0.67 power (and other variables). Diffusivity increases inversely with ambient pressure, but the atmospheric pressure will only decrease by about 50% at altitudes in which humans normally venture. A liquid's evaporation rate will increase substantially when it boils. The reason food takes longer to cook at high altitudes is because the water within it boils at a lower temperature.

III IH USES OF DALTON'S LAW

1. In 1801, John Dalton reported his findings that the total pressure of a mixture of gases equals the sum of its partial pressures. His “law” is stated mathematically in Equation 2.11. Recall that partial pressure is abbreviated as P_{partial} while the total pressure is usually abbreviated as just P without a subscript. When Dalton's law is applied to IH, the sum equals the ambient P which may or may not be the normal 760 mmHg due to either the altitude (as per Equation 2.4) or the weather.^m

$$P[\text{Total pressure}] = P_{\text{ambient}} = \text{Sum of } P_{\text{partial}} = \sum P_{\text{partial}} = \sum_{i=1}^{i=n} (Y_i \times P_{\text{ambient}}) \quad (2.11)$$

Hygienists commonly use the following corollary to Dalton's law: “The partial pressure of each component of gas or vapor in a mixture is proportional to its molar fraction in that gaseous mixture,” as stated mathematically in Equation 2.12.

$$P_{\text{partial}} = Y_i \times P_{\text{ambient}} \quad (2.12a)$$

or

$$Y_i = \frac{P_{\text{partial}}}{P_{\text{ambient}}} \quad (2.12b)$$

These relationships are valid because each molecule at anywhere near normal pressure is largely independent of all the other molecules surrounding it. Statistical thermodynamics has since shown that the pressure that gaseous molecules exert on a surface depends upon the density of molecules and their kinetic energy, and the kinetic energy of molecules depends upon their absolute temperature. Thus, each kind of gaseous molecule creates its own partial pressure in proportion to its molar fraction within the total mixture of airborne molecules.

2. One can combine the above definitions of partial pressure, molar fraction, and vapor pressure with Dalton's law to show that the various expressions of concentration shown in the following list are in fact equivalent. Physicists would probably be most comfortable with the first or second terms (recall that the second term is just a special case of the first); chemists might relate easily to the second and third terms; and industrial hygienists tend to use the fourth and fifth terms.

Term or Expression	Symbol	Units
Partial pressure	P_{partial}	mmHg
Vapor pressure	P_{vapor}	mmHg
Gaseous molar fraction	Y_i	unitless fraction = P_{partial}/P
Gaseous parts per million	ppm _i	parts per million = $Y_i \times 10^6$
Mass per volume concentration	C_i	mg/m ³

Dalton's law (Equation 2.12) relates the first two terms to the third. The third and fourth terms are related by their previous definitions stated mathematically in Equation 2.13a. In fact, by looking back at Equation 2.8a (appended to Equation 2.13a here to form Equation 2.13b), one can see that all these terms are equivalent. By this point, these terms should at

^m The reader is reminded of the list of symbols provided in the front pages of this book as a potentially useful resource.

least start to be understood as physical concepts, not just as symbols in an abstract equation. The same principle that underlies Dalton's law (the independent nature of airborne molecules) underlies each of these equations.

$$\frac{P_{\text{partial},i}}{P} \times 10^6 = Y_i \times 10^6 = \text{ppm}_i \quad (2.13a)$$

$$\boxed{\frac{P_{\text{partial},i}}{P} \times 10^6 = Y_i \times 10^6 = \text{ppm}_i = C_i \frac{24.45}{\text{MW}_i} \text{ at NTP}} \quad (2.13b)$$

3. Dalton's law can also be used to find the concentration of a saturated vapor. Its most direct application is to use the pressure ratio from Equation 2.13a to find the ppm of a chemical that is in equilibrium with its vapor pressure. Equation 2.14a will yield the correct answer at any ambient pressure, while Equation 2.14b applies only at normal atmospheric pressure. Despite this limitation, Equation 2.14b will be used frequently.

$$\text{ppm}_{\text{equilibrium}} = \frac{P_{\text{vapor}} \times 10^6}{P_{\text{ambient}}} \quad (2.14a)$$

$$\boxed{\text{ppm}_{\text{equilibrium}} \text{ at NTP} = \frac{P_{\text{vapor}} \text{ mmHg} \times 10^6}{760 \text{ mmHg}}} \quad (2.14b)$$

It is *important* to notice that the dependence of the saturated ppm on ambient pressure stated within Equation 2.14a *is not* applicable to absolute concentration as stated within Equation 2.15.

$$C_{\text{equilibrium}} \left[\text{mg}/\text{m}^3 \right] = \frac{P_{\text{vapor}} [\text{mmHg}] \times \text{MW} \times 10^6}{24.45 \times 760 [\text{mmHg}]} = 53.82 \text{ MW} \times P_{\text{vapor}} \quad (2.15)$$

 As the physics of P_{vapor} was explained in subsection I.7, a certain absolute airborne concentration $[\text{mg}/\text{m}^3]$ of each chemical's molecules must be present to create its vapor pressure, independent of all the other molecules that comprise the total atmospheric pressure. In contrast, the ratio of vapor molecules to air molecules given by Equation 2.14a will change whenever the density of the ambient air molecules changes, due say to altitude or the weather, independent of the chemical's vapor pressure. Thus, while the result derived from Equation 2.14a will depend upon the ambient pressure, the array of constant physical parameters in Equation 2.15 will yield the same answer at any ambient pressure.

4. Practicing hygienists can use the concepts of partial pressure and especially of vapor pressure often. The following examples use these concepts to demonstrate how to convert between vapor pressure and concentration. The first example is of much more practical value to an IH than the second.

Example 2.2

What will be the equilibrium vapor concentration of n-hexane in a closed room at normal temperature and sea level pressure? In this example, the subscript i = hexane = C_6H_{14} . Its vapor pressure is 151 mmHg at 25°C (as found for instance in the Vapor Hazard Ratio table attached to this book as Appendix A). Specifying that the room is closed (meaning "unventilated but not sealed") is necessary to assure that, as the evaporating vapor molecules add to the air molecules already existing within the room, as many excess molecules can leak out of the room as necessary to keep the total P inside the room at the same normal one atmosphere as the 760 mmHg air outside the

room. The $C_{\text{equilibrium}}$ for hexane could have been found using Equation 2.15 but is shown here in three steps as a demonstration.

$$Y_{\text{hexane}} = \frac{P_{\text{partial}}}{P} = \frac{P_{\text{vapor}}}{760} = \frac{151}{760} = 0.1987 \quad (\text{a unitless fraction}) \quad (\text{using Equation 2.12b})$$

$$\text{ppm}_{\text{hexane}} = Y_i \times 10^6 = 198,700 \text{ ppm} \quad (\text{a fraction with units}) \quad (\text{using Equation 2.13a})$$

$$C_{\text{hexane}} = \text{ppm}_{\text{hexane}} \times \frac{\text{MW}_{\text{hexane}}}{24.45} = 198,000 \times \frac{86.2}{24.45} \approx 700,000 \text{ mg/m}^3 \quad (\text{using Equation 2.8b})$$

This equilibrium concentration is 3,975 times higher than the TLV[®] exposure limit for hexane.

Example 2.3

Industrial hygienists do not have much need to go from ppm all the way to mmHg, but physiologists tend to report airborne concentrations as partial pressures. Thus, if you wanted to talk to a physiologist about the effect of carbon dioxide at its TLV[®], you might want to find its partial pressure in mmHg at 5,000 ppm at sea level. Here, the subscript i equals CO₂, and the same equations can be used in approximately the reverse order.

$$Y_{\text{CO}_2} = \frac{\text{ppm}_{\text{CO}_2}}{10^6} = \frac{5,000}{10^6} = 0.005 \quad (\text{a unitless fraction}) \quad (\text{using Equation 2.13a})$$

$$P_{\text{CO}_2} = Y_i \times P = 0.005 \times 760 = 3.8 \text{ mmHg} \quad (\text{using Equation 2.12a})$$

The next two examples involve two conditions at which vapor pressure equals the ambient atmospheric pressure. Both conditions are extreme and of more academic than practical interest, but they can test your understanding of the concepts of partial pressure and vapor pressure that underlie Equations 2.12 and 2.15, respectively.

Example 2.4

What will eventually happen when a solvent continues to be heated until its vapor pressure equals the ambient pressure? When P_{vapor} rises to equal the ambient pressure, Y_i will equal one and the liquid will appear to boil. A liquid's temperature when this happens at normal P is called its "boiling temperature" or its "boiling point." Fortunately for employee health, organic solvents are rarely boiled.

Example 2.5

What will happen to a solvent when the total ambient pressure is reduced until it equals P_{vapor} ? The most common instance in which ambient pressure is reduced is as one goes up in altitude. Recall that P_{vapor} is unaffected by the ambient P , but at the point that the ambient P is decreased enough to equal the liquid's P_{vapor} , Y_i will again equal one and the liquid will appear to boil even at a normal room temperature. Water at normal body temperature would appear to boil at an altitude of approximately 62,800 ft; recall that blood is mostly water. Fortunately (again), *no one* works unprotected at such altitudes.

IV IH USES OF THE IDEAL GAS LAW

1. The Ideal Gas law is commonly expressed as Equation 2.16. While the Ideal Gas law may not be the most accurate predictor of how gas pressure, volume, and temperature are related (compared for instance to the van der Waals equation of state), it is adequately accurate for dilute gases such as air and for virtually all IH purposes.

$$\text{The ideal gas law: } P \times \text{Vol} = n_{\text{moles}} \times R \times T \quad (2.16)$$

where

P = absolute pressure of the gas (usually total pressure although the law can also be used to predict the behavior of individual components using their partial pressures).

Vol = volume of air (e.g., L, m³, or ft³).ⁿ The symbol “Vol” is used herein to avoid confusion with the common use of “V” in IH and ventilation to mean velocity.

n_{moles} = number of moles of a gas or vapor (n_{moles} = mass in grams/MW).

R = the universal gas constant in units that match those used for P , Vol , and T such as 0.082 atm $\times$ L/ $^{\circ}$ K $\times$ mol or 0.730 atm $\times$ ft³/ $^{\circ}$ R $\times$ mol. Luckily, a hygienist does not need to memorize any value for R .

T = absolute temperature in either $^{\circ}$ K = $^{\circ}$ C + 273 or degrees Rankine $^{\circ}$ R = $^{\circ}$ F + 460.

2. Despite its underlying importance, Equation 2.16 is not boxed herein because IHs rarely use that form of the Ideal Gas law and almost never have to use one of the above values of R . Because $P \times \text{Vol}/T$ for a given parcel of air or other gas always equals the constants $n_{\text{moles}} \times R$, the value of $P \times \text{Vol}/T$ in any one condition (subscripted as condition “1”) must equal the same ratio in any other condition (subscripted as condition “2”). Thus, IHs find that expressing the Ideal Gas law on some form of Equation 2.17 is much more useful.^o

$$\frac{P_{1,\text{absolute}} \text{Vol}_1}{T_{1,\text{absolute}}} = \frac{P_{2,\text{absolute}} \text{Vol}_2}{T_{2,\text{absolute}}} \quad (2.17)$$

IHs are generally interested in the effect of changes in P or/and T on volume. For instance, the ambient pressure at work changes from normal with altitude and weather but is predictable or/and easily measurable.^p Similarly, T in the workplace can be affected by a nearby heat source, solar heating, or/and a seasonal pattern, but it too is easy to measure and is generally within the somewhat narrow range of human tolerance.¹⁸

In contrast, gas volume is an explicit interest to IHs in two situations and an implicit interest in two others. IH students may have encountered Equation 2.18a, used explicitly to find or predict the air volume while air sampling (usually covered within another course). Equation 2.19b will be used in Chapter 11 to find or predict the change in the air volume while it moves through an exhaust ventilation system (specifically in Equation 11.6). An inflatable balloon is often used by academics to demonstrate changes in volume, but is not a common IH problem (however, it will be discussed in Section 2.V).

$$\boxed{\text{Vol}_2 = \text{Vol}_1 = \left(\frac{P_{1,\text{absolute}}}{P_{2,\text{absolute}}} \right) \times \left(\frac{T_{2,\text{absolute}}}{T_{1,\text{absolute}}} \right)} \quad (2.18a)$$

$$\frac{\text{Vol}_2}{\text{Vol}_1} = \left(\frac{P_{1,\text{absolute}}}{P_{2,\text{absolute}}} \right) \times \left(\frac{T_{2,\text{absolute}}}{T_{1,\text{absolute}}} \right) \quad (2.18b)$$

ⁿ At NTP, the value for $\text{Vol}/n_{\text{moles}}$ in Equation 2.16 is actually the familiar 24.45 L/mol. Technically, as Perkins (1997) points out,⁷ the molar volume is less than that by up to 5% for solvents with a MW of 75–100 and less by up to 10% for solvents with a MW over 150, but just 24.45 works fine for most IH calculations.

^o The word “absolute” is included within the subscripts of Equation 2.17 and other equations in this section derived from it as a reminder to avoid using $^{\circ}$ C, $^{\circ}$ F, or a gauge pressure in such ratios (see subsection I.3).

^p Pressure can comprises its own health hazard if working in low pressure at high altitude where supplemental oxygen may be required (see Section 4.IV) or working at high pressure (e.g., under water or in caissons) where a range of administrative controls are required.⁶

The next two sections of this chapter will involve gas volume implicitly to solve IH problems using the Ideal Gas law. Volume does not actually appear in the equations used to solve problems in either case, but its role within the Ideal Gas law is implicit. First, the effect of temperature and pressure on the concentration of a generic contaminant will be discussed within Section 2.V, but notice in Equation 2.19 that volume is in the denominator.

$$\text{Contaminant concentration} = C \left(\text{mg/m}^3 \right) = \frac{\text{Mass (mg)}}{\text{Volume (m}^3\text{)}} \quad (2.19)$$

Then, the effect of temperature on air density will be discussed within Section 2.VI. Density is simply mass divided by volume, such as shown in Equation 2.20, but again, notice that volume is in the denominator.

$$\text{Gas density} = \rho \text{ (g/L)} = \frac{\text{Mass (g)}}{\text{Volume (L)}} \quad (2.20)$$

As a result, both gas C and gas ρ will vary inversely with volume!

3. *Evaporation* comprises an important exception to the Ideal Gas law. Clearly, the Antoine equation (discussed in Section II) shows that the effect of liquid temperature on vapor pressure does not follow the Ideal Gas law. Additionally, evaporation involves a change of state from a liquid to a vapor. The Ideal Gas law does not encompass the dramatic increase in molar volume that occurs during evaporation. Consider that a mole of an evaporating liquid with a density near 1 g/mL starts as a volume equal to its MW in mL; thus, its liquid volume in L is its MW/10³. In comparison, the volume of that mole as a theoretically pure vapor at NTP is about 24.45 L.^q Using methyl-ethylbenzene (MW = 120, $\rho_{\text{liq}} = 0.87$) as a specific example, the ratio of its theoretical molar volume as a vapor (24 L) to its molar volume as a liquid ($120 \text{ g} \times 0.87 \text{ g/mL} / 10^3 \text{ mL/L} = 0.104 \text{ L}$) would be about 240:1. The volume change that occurs during evaporation is discussed in more detail within Section 5.VII.

V THE EFFECTS OF T AND P ON AIRBORNE CONCENTRATION

By now you should know that the airborne concentration of a contaminant can be expressed as either a molar concentration (ppm_i), a mass concentration (C_i as mg/m^3), or a partial pressure (P_{partial} as mmHg). This section discusses how altitude, the Antoine equation, Dalton's law, and the Ideal Gas law all work together in sometimes challenging ways to determine how ppm_i and C_i each do or do not change in response to a change in either T and/or P . The appropriate application of these principles depends upon how the contaminated air is constrained. The source of the gaseous contaminant in each of the four settings listed in Table 2.3 is not important.^r The dynamics operating within each setting will first be described qualitatively with depictions, then mathematically, followed by quantitative examples.

1. The quintessential *rigid, inelastic, airtight enclosure* is a sealed, storage tank for a gas or volatile liquid (no fan, pump, or pipe by which more mass could be added or removed; not even a pressure release valve). Common academic examples include a basketball and an automobile tire that are assumed to be rigid. In this setting, any change in external pressure will have no effect on conditions inside the enclosure. Because neither the mass nor the

^q "Theoretically pure" means the vapor comprises 100% of its molar volume, i.e., $Y_i = 1$, even though by definition, saturated vapors are always less than pure and the $\text{ppm}_{\text{equilibrium}}$ in Equation 2.14 is always $\leq 10^6$.

^r It is important to note that the effects of evaporation of a volatile liquid are absent from all these settings. However, liquid evaporation will be discussed in subsection V.5 and appear in Example 2.8.

TABLE 2.3
Four Settings in Which a Change in Pressure or Temperature Can Change the Concentration of a Contaminant

	Boundary is Rigid and Inelastic with a Constant Volume	Boundary is Flexible or Elastic with a Variable Volume
A sealed enclosure with airtight walls	<i>e.g.</i> , a sealed chamber or unvented tank; see subsection V.1 $P_{\text{inside}} \propto 1/T_{\text{inside}}$ Both <i>C</i> and ppm are constant	<i>e.g.</i> , a balloon or air duct; see subsection V.2. $P_{\text{inside}} \propto e^{-\text{altitude}}$ Only ppm is constant.
An enclosure with leaky walls or a parcel of air with no walls at all	<i>e.g.</i> , a “closed room” or small building; see subsection V.3 $P_{\text{inside}} = P_{\text{ambient}}$ but is independent of <i>T</i> ppm is constant when heating but <i>C</i> is constant when cooling	<i>e.g.</i> , a plume; subsection V.4 refers to Section 5.II $P \propto e^{-\text{altitude}}$ Neither <i>C</i> nor ppm is constant

volume inside the enclosure can change, the only thing that can cause a change inside the enclosure is its internal temperature.

The cube on the left in Figure 2.3 depicts such an enclosure containing 16 moles of contaminated air (OK, 16×24.45 L would be way smaller than a room, but the principle can be scaled up to thousands of moles). If you bother to count, there are initially 12 moles of air (depicted by dots) and four moles of a contaminant (depicted by stars) for a molar fraction of 25%, per Equation 2.7. The cube on the right depicts this same enclosure after it has been heated by 25% of its absolute temperature. At the higher temperature, each molecule has more energy (the dots and stars should look larger), but because no molecules can escape, neither the mass of contaminant per unit of volume nor the ratio of contaminant-to-air can change. The only variable left to change is the pressure. In fact, it is the potential for a sufficient increase in pressure to rupture such a tank and create a safety hazard that makes this setting of interest. Normally, this process is reversible and can return to its same initial state as the temperature drops.

Thus, whether a sealed, fixed enclosure is heated or cooled, its volume and thus both the ppm_i and the C_i are constant (*i.e.*, $\text{ppm}_2 = \text{ppm}_1$ and $C_2 = C_1$), but *P* changes in accordance with Equation 2.21. One important detail to remember in this setting is that the units of pressure inside a storage tank (and especially semirigid inflatable objects like a basketball and car tire) are commonly expressed “relative” to the ambient pressure (*e.g.*, psig); therefore, some manipulations using Equation 2.5 may be required.

$$P_2 = P_1 \times \frac{T_{2,\text{absolute}}}{T_{1,\text{absolute}}}$$

(2.21)

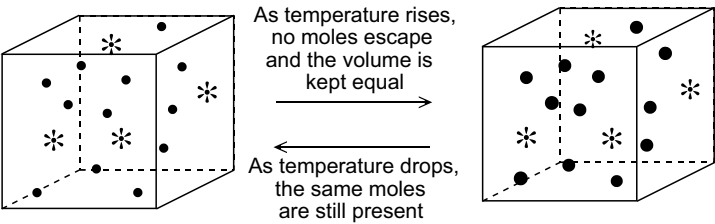


FIGURE 2.3 Depicting the effect of heating or cooling contaminated air inside a rigid, airtight enclosure that leaves both the ppm and *C* (mg/m³) unchanged.

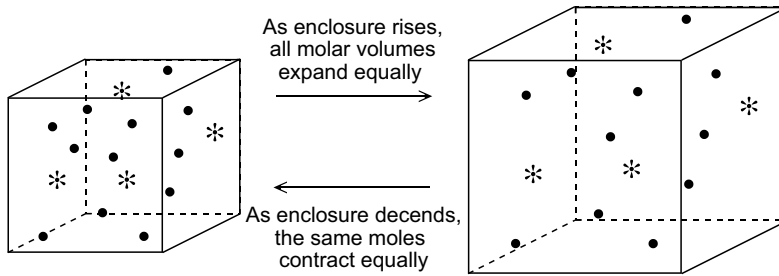


FIGURE 2.4 Depicting the effect of expanding or reducing the volume occupied by contaminated air inside a flexible or inflatable but airtight enclosure that leaves only the ppm unchanged.

- Figure 2.4 depicts a flexible or highly elastic, airtight enclosure. Air inside a ventilation duct is free to expand and contract in such a manner (covered within Section 16.VIII). A good academic example of this setting is a high-altitude research balloon made of polyethylene (flexible, fairly impermeable, but inelastic) that expands by unfolding (*e.g.*, see www.ravenaerostar.com). A common classroom demonstration would be a highly elastic party balloon.^s

Table 2.3 shows that conditions inside a balloon are a function of both altitude and temperature. Altitude affects pressure in accordance with Equation 2.4. The volume of a flexible or highly elastic balloon will respond (expand or contract) almost instantly to match its internal pressure to the ambient external pressure. The temperature inside such a balloon may also match the ambient temperature, except for solar heat loads in daylight and radiant cooling at night.

The initial cube on the left in Figure 2.4 (again) starts with 16 moles of gas. The cube on the right of Figure 2.4 depicts the resulting expansion of its boundary with temperature, at which point the same number of moles (and mass) occupy a larger volume (*e.g.*, m³). Normally, this process is reversible and can return to its same initial state when the altitude drops and the ambient pressure increases.

Because no molecules can cross an airtight wall, the ratio of molecules within a sealed, flexible enclosure is unchanged, and $\text{ppm}_2 = \text{ppm}_1$. However, its volume follows the Ideal Gas law given by Equation 2.22. And because C changes inversely proportional to volume, C will change in accordance with Equation 2.23.

$$\text{Vol}_2 = \text{Vol}_1 \frac{P_{1,\text{absolute}}}{P_{2,\text{absolute}}} \times \frac{T_{2,\text{absolute}}}{T_{1,\text{absolute}}} \quad (2.22)$$

$$C_2 = C_1 \times \frac{P_{\text{ambient},2}}{P_{\text{ambient},1}} \times \frac{T_{1,\text{absolute}}}{T_{2,\text{absolute}}} \quad (2.23)$$

- Another useful setting is that of an *enclosure with rigid but leaky walls*, such as the classic “closed room” defined in subsection 2.I.6. Because the walls leak, the pressure inside a closed room will virtually equal the pressure outside [P_{ambient}]. Anything that starts to change the pressure inside the room relative to the ambient pressure outside will cause some molecules to be pushed through openings or leaks in walls to re-equalize that pressure. For practical purposes, P_{ambient} can be assumed to be constant if the enclosure is too

^s A party balloon is fairly elastic as it starts to inflate, but gets less flexible as it inflates, and eventually approximates a rigid enclosure just before it pops.

big to be lifted in altitude and changes in the local barometric pressure (*ca.* $\pm 0.1\%$) are much smaller than the daily temperature fluctuations (commonly $\pm 3\%$ to $\pm 20\%$).

Figure 2.5a depicts such an enclosure initially with (again) 4 of the 16 moles being a gaseous contaminant. Heating such a room or building by 25% is slightly above a normal daily temperature swing, but such a change makes it easy to depict driving off 25% of all the molecules in proportion to their initial molar fractions. The result is the enclosure on the right in which 3 out of the 12 moles remaining inside are the contaminant (still at 250,000 ppm), but their mass concentration is now only three contaminant moles per unit of volume.

Restating the above events mathematically, whenever a closed room or other rigid enclosure with contaminated air is subjected to an increase in T (or to a decrease in P), the ratio of contaminant to air molecules within that enclosure will stay constant and the ppm of the contaminant is unaffected ($\text{ppm}_2 = \text{ppm}_1$). However, the volume occupied by the molecules within that space will expand (per Equation 2.22), some contaminant will escape, and the mass (and the C in mg/m^3) of the molecules remaining will decrease in accordance with Equation 2.24.[†]

$$C_2 = C_1 \frac{T_{1,\text{absolute}}}{T_{2,\text{absolute}}} \quad (2.24)$$

At first glance, the process might seem reversible upon cooling (and it might be in *very* special circumstances). However, think about what happens to the molecules of contaminant that escape when such a one-room building or enclosure is heated?

In the real world, such previously emitted molecules are blown or drift away, and when that room is later cooled, pure (uncontaminated) air would enter. While being

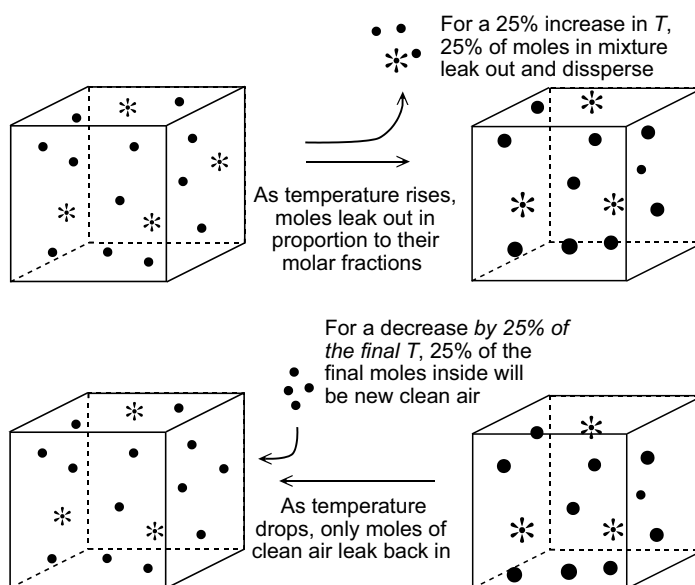


FIGURE 2.5 (a) Depicting the effect of increasing the temperature of contaminated air inside a “closed room,” resulting in the same contaminant ppm but a reduced C . (b) Depicting the effect of decreasing the temperature of contaminated air inside a “closed room,” resulting in the same contaminant C but a reduced ppm.

[†] If the effect of P were not disregarded, Equation 2.24 would be mathematically identical to Equation 2.23.

cooled, the amount of contaminant and the resulting C (mg/m^3) concentration would be unchanged ($C_2 = C_1$), but the ppm concentration would decrease as predicted by Equation 2.25 due to more moles of air entering the cooled enclosure. The (perhaps interesting but usually not practical) net result of repeatedly heating and cooling a room with contaminated air is to eventually drive virtually all of the contaminant out of the room (see Example 2.9).

$$\text{ppm}_2 = \text{ppm}_1 \quad (2.25)$$

4. The best (and perhaps only) example of the fourth setting is a plume of vapor. The boundaries of such an ephemeral parcel of air can expand if they are initially cold or contract if they are hot, but they also leak as the plume disperses. Plumes will be discussed within the next two sections of this chapter and in various ways later in much of Chapter 5 and in Sections 8.VI, 9.IV, 13.VIII, and 20.III.
5. As previously stated, the effects on concentration caused by evaporation and changes in vapor pressure comprise an exception to the above settings. While the Antoine equation and Dalton's law could be used to predict the independent effect of vapor pressure, the answer gets complicated because the liquid temperature can change independent of the air's T and because temperature changes often involve temporal dynamics. The simple answer is that any change in P_{vapor} will affect the equilibrium concentrations (both the $\text{ppm}_{\text{equilibrium}}$ and the $C_{\text{equilibrium}}$) right at the source, as stated in Equations 2.14 and 2.15, respectively. Because the amount of dilution caused by the turbulent mixing typically within most work environments is independent of the vapor being diluted and largely also of the air's T and P , all of the subsequently diluted concentrations within the resulting plume will change in direct proportion to a change in P_{vapor} .

Example 2.6

Suppose that an employer built an airtight chemical storage facility that was 20 ft long, 8 ft wide, with an 8 ft ceiling (6 m by 2.4 m by 2.4 m), about the size of a standard intermodal container (being airtight was a misguided attempt to prevent emissions). The location was in a high desert at an altitude of 5,250 feet (1,600 m) where daily room temperatures in the summer could range from a low of 60 to a high of 120°F (15°C–49°C). By how much could the pressure inside the enclosure change from morning to afternoon?

This building clearly falls into the rigid, airtight enclosure setting listed in Table 2.3. The obvious difference in temperature ratios that result from using °F versus using °C should be a clue or a reminder to not use either one of these relative temperatures in a ratio! To answer this question, either Equation 2.1 or 2.2 can be incorporated into Equation 2.21, where condition 1 is ambient at altitude at low temperature and condition 2 is inside the heated enclosure.

$$P_2 = P_1 \times \frac{T_{2,\text{absolute}}}{T_{1,\text{absolute}}} \quad (\text{repeat of Equation 2.21})$$

$$\frac{P_2}{P_1} = \frac{^{\circ}\text{C}_2 + 273}{^{\circ}\text{C}_1 + 273} = \frac{49 + 273}{15 + 273} = \frac{322}{288} = 1.118 \quad (\text{using Equations 2.1 and 2.21})$$

$$\frac{P_2}{P_1} = \frac{^{\circ}\text{F}_2 + 460}{^{\circ}\text{F}_1 + 460} = \frac{120 + 460}{59 + 460} = \frac{580}{519} = 1.118 \quad (\text{using Equations 2.2 and 2.21})$$

Notice that as a ratio, we did not need to know what the ambient pressure was. A ratio of 1.12 means that the pressure inside the building could increase by as much as 12% due to the temperature fluctuations.

Example 2.7

What force would that excess pressure put on a door measuring 3' × 6' 8" (20 ft² = 1.86 m²)?

Although there are many ways to answer this question, eventually some form of Equations 2.3, 2.4, 2.5, and 2.21 and an equivalence from Table 2.1 will be used.

$$P_1 \text{ at altitude} = 2^{(-\text{ft}/18,465)} \quad (\text{repeat of Equation 2.4})$$

$$P_1 \text{ at altitude} = 2^{(-5,280/18,465)} = 0.820 \text{ atm} \quad (\text{using Equation 2.4})$$

$$P_{2 \text{ inside}} = 0.820 \text{ atm.} \times 1.118 = 0.917 \text{ atm.} \quad (\text{using Equation 2.21})$$

$$P_{\text{relative}} = P_{\text{absolute}} - P_{\text{ambient}} \quad (\text{repeat of Equation 2.5a})$$

$$P_{\text{difference}} = 0.917_{\text{inside}} - 0.820 = 0.097 \text{ atm.} \quad (\text{using Equation 2.5a})$$

$$\text{Force} = P_{\text{relative}} \times \text{Area} \quad (\text{repeat of Equation 2.3b})$$

$$\text{Force}_{\text{on door}} = (0.097 \times 14.7 \text{ psi}) \times \left(21 \text{ ft}^2 \times 144 \frac{\text{in.}^2}{\text{ft}^2} \right) \quad (\text{using Equation 2.3b})$$

$$\text{Force}_{\text{on door}} = (1.42 \text{ psi}) \times 3,024 \text{ in.}^2 = 4,294 \text{ lb} \quad (\text{using Equation 2.3b})$$

Example 2.8

Suppose that on one of those hot days, a container of n-hexane were to spring a leak and add its vapor pressure to the enclosure. What would be the total pressure and force on that door?

To answer this question, one would need to add the vapor pressure of hexane at 120°F or 49°C. Conveniently, 49°C is $2 \times 12^\circ\text{C} = 24^\circ\text{C}$ above 25. Thus, one option is to estimate P_{hexane} to be $4 \times$ its 151 mmHg at 25°C as listed in Appendix A which would be about 600 mmHg. The more accurate option would be to use the Antoine equation.⁸

$$\ln[P_{\text{vapor}}] = A - \frac{B}{(^{\circ}\text{K} + C)} \quad (\text{repeat of generic Equation 2.10a})$$

$$\ln[P_{\text{hexane}}] = 15.8366 - \frac{2,697.55}{(298^\circ\text{K} - 48.78)} \quad (\text{use of Equation 2.10a})$$

$$P_{\text{hexane}} = \exp^{\ln[P_{\text{vapor}}]} = e^{5.969} = 391 \text{ mmHg} \quad (\text{use of Equation 2.10b})$$

In this example, the rule-of-thumb overestimates the more accurate option by $600/391 = 1.53$ by 53%. As in Example 2.6, this 391 mmHg / 760 equals 0.514 atmosphere, which $\times 14.7$ is equal to 7.56 psi just from the vapor. Applying a total internal pressure of 1.42 psi from the heat + 7.56 psi from the vapor = 8.98 psi to the 3,024 in.² door, means the total force on the door is a whopping 27,155 lbs.

Example 2.9

Not surprisingly, soon after the above event, the door and a few other parts of the enclosure started to leak, *i.e.*, they were no longer airtight. The spilled hexane eventually evaporated and dissipated as the enclosure would cool each night, suck in fresh air, and start another heating

cycle the next day. What fraction of the remaining vapors would be removed during each heating-cooling cycle?

This building is now a “closed room.” There are again multiple ways to answer this question. To use a previous result, assume that the vapor concentration on the last day of evaporation was at the $\text{ppm}_{\text{equilibrium}}$ corresponding to the P_{vapor} found in Example 2.8.

$$\text{ppm}_{\text{equilibrium}} = \frac{P_{\text{vapor}} \times 10^6}{P_{\text{ambient}}} \quad (\text{repeat of Equation 2.14a})$$

$$\text{ppm}_{1 \text{ end of day}} = \frac{391 \text{ mmHg} \times 10^6}{0.816 \times 760 \text{ mmHg}} = 630,480 \text{ ppm} \quad (\text{using Equation 2.14a})$$

The ppm after fresh air has entered the enclosure while it cooled throughout the night can now be determined via Equation 2.25.

$$\text{ppm}_2 = \text{ppm}_1 \quad (\text{repeat of Equation 2.25})$$

$$\text{ppm}_{2 \text{ at start of day}} = \text{ppm}_{1 \text{ end of day}} \times \frac{T_{2 \text{ at start}}}{T_{1 \text{ at end}}} \quad (\text{using Equation 2.25})$$

$$\text{ppm}_{2 \text{ at start of day}} = 630,480 \times \frac{288}{322} = 563,910 \text{ ppm} \quad (\text{using Equation 2.25})$$

The decrease to 563,910 ppm from 630,480 ppm yields a ratio of 0.8944 of the vapor that remains, meaning that 10.56% of the contaminant is removed in one diurnal heating-cooling cycle.^u This same fraction will be removed during each repeating cycle. The following equations can be used to show that in this case, 50% of the vapors will be removed in just over 6 days, but it will take 84 days (almost 3 months) for enough vapors to be removed for the air to reach the 50 ppm TLV[®] for n-hexane.

$$[\text{Fraction remaining}_1] = 1 - [\text{Fraction removed}_1] \quad (2.26a)$$

$$[\text{Fraction remaining}_n] = [\text{Fraction remaining}_1]^n \quad (2.26b)$$

$$n = \frac{\log [\text{Fraction remaining}_n]}{\log [\text{Fraction remaining}_1]} \quad (2.26c)$$

where

Fraction remaining₁ = The fraction still inside the enclosure after one cycle (which also equals 1 minus the fraction removed).

Fraction remaining_n = The fraction remaining after “n” number of cycles.

VI THE EFFECTS OF T AND MW ON PLUME DENSITY

Airborne contaminants will generally move with the air in which they are suspended. However, any difference between the density of a plume and the density of the ambient air surrounding that plume creates a vertical force called buoyancy. Buoyancy will give a plume a vertical velocity.^v The ultimate path of the plume will depend on the ratio of its vertical velocity to the air’s ambient

^u The ratio 0.8944 is the reciprocal of the 1.118 ratio found in Example 2.6 because these examples use the same temperature ratio in heating and cooling. A more typical diurnal temperature excursion would exchange only 1%–3% of the air.

^v The effect of buoyancy acting on an entire parcel of air (such as on a plume) is like convection versus its effect on individual molecules which is like that of molecular diffusion to be described in Section 5.II.

horizontal velocity. This section will show that buoyancy can be caused by a difference between the two parcels' temperatures and/or their MWs.

1. As previously stated in Equation 2.20, density is simply mass divided by volume. Because the typical units of gas or vapor density (g/L) differ from those for most solids and liquids (g/mL) by two to three orders of magnitude, this book will differentiate these two densities by always using just plain ρ when referring to a gas or vapor density in g/L versus ρ_{liq} when referring to the density of liquids in g/mL or ρ_{particle} when referring to solids. Thus, any ρ notation without one of those subscripts can be assumed to be the gaseous density in g/L.

A simple and memorable way to quantify a gas' density is to recall that the mass of one mole of a gas (*i.e.*, its MW in grams) occupies one molar volume (*i.e.*, 24.45 L at NTP). Thus, the density of any gaseous material of known MW at NTP can be found by using Equation 2.27. This solid-boxed equation should be learned, but again, it is best learned conceptually as a tool rather than just as a couple of mathematical symbols.

$$\frac{\text{The mass of one mole}}{\text{The volume of one mole}} = \boxed{\text{Pure gas } \rho_{\text{at NTP}} = \frac{\text{MW}_{\text{known}}}{24.45}} \quad (2.27)$$

2. Changes in density can be found by yet another form of the Ideal Gas law. Equation 2.28a (based on Equation 2.18) can be used to find or predict a new density (mass per unit of volume), while Equation 2.28b can be used to find the relative change in the density of a given parcel of air. But *please* notice how the ratios of pressure in Equation 2.28 are inverted compared to those in Equation 2.18 because for density, volume is in the denominator.

$$\rho_2 = \rho_1 \left(\frac{P_{2,\text{absolute}}}{P_{1,\text{absolute}}} \right) \times \left(\frac{T_{1,\text{absolute}}}{T_{2,\text{absolute}}} \right) \quad (2.28a)$$

and

$$\boxed{\frac{\rho_2}{\rho_1} = \left(\frac{P_{2,\text{absolute}}}{P_{1,\text{absolute}}} \right) \times \left(\frac{T_{1,\text{absolute}}}{T_{2,\text{absolute}}} \right)} \quad (2.28b)$$

Equation 2.29 combines the above variant of the Ideal Gas equation with Equation 2.27 for ρ at NTP to yield the gas density in the more general case where conditions are not normal. Units of P in mmHg or inches of mercury could be substituted for atmospheres as long as they are used in both the numerator and the denominator.

$$\rho = \frac{\text{MW}_{\text{known}} \times P [\text{atm}] \times 298}{24.45 \times 1 \text{ atm} \times (^\circ\text{C} + 273)} = \frac{\text{MW}_{\text{known}} \times P [\text{atm}] \times 537}{24.45 \times 1 \text{ atm} \times (^\circ\text{F} + 460)} \quad (2.29)$$

3. An inconvenience will be encountered when one attempts to use Equation 2.29 to determine the MW of a mixture of air and a gas or vapor contaminant. In principle, the MW of any mixture [$\text{MW}_{\text{mixture}}$] can be found by adding the mass contributed by each component that makes up the mixture, again using Dalton's law. Equation 2.30 represents an important principle but is inconvenient to use if the number of components is large.



$$MW_{\text{mixture}} = \frac{\sum(Y_i \times MW_i)}{\sum(Y)} \approx \frac{\sum(Y_i \times MW_i)}{1 \text{ (or 100 if } Y_i \text{ is in \%)}} \quad (2.30)$$

Example 2.10

Use Equation 2.30 to find the MW of a mixture whose molar percentages ($Y_i \times 100$) are 78% nitrogen (MW = 28) and 21% oxygen (MW = 32). Do you recognize this mixture? It's air.

$$MW_{\text{mixture}} = \frac{(0.78 \times 28) + (0.21 \times 32)}{0.78 + 0.21} = \frac{28.56}{0.99} = 28.85 \text{ g/mol} \quad (\text{using Equation 2.30})$$

In IH practice, the MW of a hazardous mixture is rarely known (and as you will read, not commonly calculated). However, pure air is one obviously common mixture of gases that is well studied and whose MW is known. The major components of standard dry air shown in Table 2.4 are applicable to all altitudes in which humans can live or work without special respirators (and even well into the range in which we can survive only with a respirator). This table also shows how Equation 2.30 can be used to calculate the MW of standard dry air [MW_{air}]. Notice that 28.966 is slightly larger (by 0.1 g) than the approximation found in Example 2.10 due to rounding errors. However, because the normal range of humidity ($MW_{\text{water}} = 18$) can reduce the MW of air by only 0.1–0.2 g, the approximation is really quite acceptable.

On the other hand, all of us should be interested to know that data (shown in Figure 2.6) recorded since 1958 at the Mauna Loa Observatory, Hawaii (elevation 11,140 ft = 3397 m) indicate that carbon dioxide is accumulating within the earth's atmosphere at a rate that is now more than 2 ppm per year. CO_2 has risen 25% in the last 50 years and is now consistently above 400 ppm! Although the cumulative effect of this increase in carbon dioxide on the MW of air could be seen from Equation 2.30 to be more negligible than the effect of water, its effect on climate change (e.g., global warming and sea level rise) could be substantial.^w

TABLE 2.4
Chemical Composition of Standard Dry Air⁶ Modified to Reflect Current CO_2 Levels¹⁹

Chemical Component	Molecular Weight MW_i	Y_i (%)	$Y_i \times MW_i$
Nitrogen (N_2)	28.0134	78.0771	21.8721
Oxygen (O_2)	31.9988	20.9458	6.7024
Argon (A)	39.9480	0.9339	0.37308
Carbon dioxide (CO_2)	44.0098	0.0405	0.01782
Neon (Ne)	20.179	0.00182	0.00037
Helium (He)	4.0026	0.00052	0.00002
Methane (CH_4)	16.0425	0.00018	0.00003
Krypton (Kr)	83.80	0.00011	0.00010
Hydrogen (H_2)	2.0158	0.00005	0.00000
Sum of molar fractions = $\sum(Y_i)$ =		100.0000	
Molecular weight via Equation 2.30 =			28.966

^w The Intergovernmental Panel on Climate Change (IPCC) has published a series of five authoritative and detailed Assessment Reports over the last 27 years that are available at www.ipcc.ch/report/ar5.

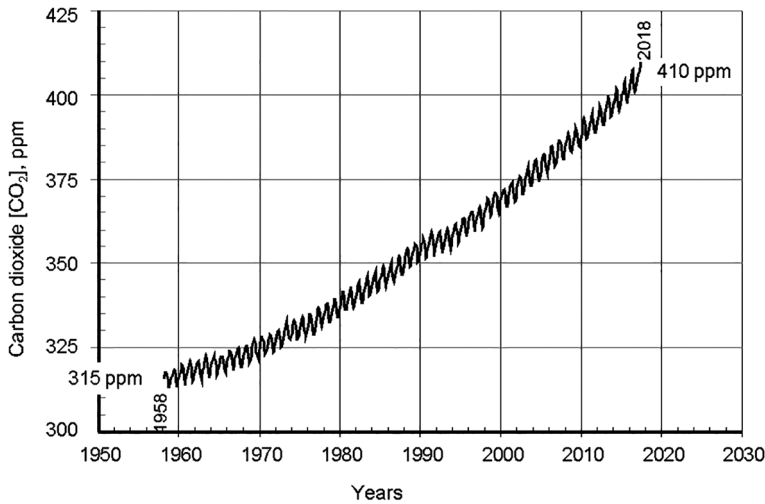


FIGURE 2.6 Monthly average carbon dioxide data from Keeling et al. show a consistent seasonal cycle with peaks in May and lows in September or October.¹⁹

Example 2.11

What is the normal density of air? Recall that Equation 2.27 can be used to find the density of any pure gas of known MW at NTP. Although the MW of a mixture is rarely known, the results of Table 2.4 for pure air create one of those rare times.

$$\rho_{\text{air at NTP}} = \frac{\text{MW}_{\text{air}}}{24.45} = \frac{28.964}{24.45} = 1.1846 \text{ g/L or about } 1.2 \text{ g/L} \quad (\text{using Equation 2.27})$$

- Knowing the density of pure air at NTP is a good academic question, but an IH is more likely to ask how does the density of a contaminated plume at another MW, and perhaps at another temperature, compare to the density of pure air at NTP?

From Equation 2.29, one can see that pressure, temperature, and MW can all affect gas density. However, for the purposes of calculating a plume's density, it is safe to assume that the entire room or any vicinity near an outdoor source is at the same ambient air pressure. For instance, we will see in the ventilation chapters how a difference in air pressure as small as 0.01 in. of water pressure (out of a total of approximately 407 in. of water in 1 atm) can cause an air velocity of up to 400 fpm (2 m/s or 4.5 m/h). Since the velocity of room air is usually much slower than that, we can conclude that the ratio of pressures within a room, workplace, or plume will be less than $0.01/407 = 3 \times 10^{-5}$.

After eliminating pressure as a variable, the only practical reason that the density of a plume could be different from the density of the ambient air is because either the plume's MW or its temperature differs significantly from the ambient air's. Rather than just any two MW and temperature conditions (the generic condition 1 versus condition 2 shown in Equation 2.31a), Industrial hygienists are most commonly interested in the ratio between a contaminated and/or a hot plume and pure air at normal (25°C) temperature, as shown within Equation 2.31b. Notice that when looking at the ratio of densities in Equation 2.31, the values of the ambient P and 24.45 L/mol in Equation 2.29 drop out.

$$\frac{\rho_2}{\rho_1} = \frac{\text{MW}_2 \times (^{\circ}\text{C}_1 + 273)}{\text{MW}_1 \times (^{\circ}\text{C}_2 + 273)} = \frac{\text{MW}_2 \times (^{\circ}\text{F}_1 + 460)}{\text{MW}_1 \times (^{\circ}\text{F}_2 + 460)} \quad (2.31a)$$

$$\frac{\rho_{\text{plume MW at } T}}{\rho_{\text{air at } 25^{\circ}\text{C}}} = \frac{\text{MW}_{\text{plume}} \times 298}{28.964 \times (^{\circ}\text{C}_{\text{plume}} + 273)} = \frac{\text{MW}_{\text{plume}} \times 537}{28.964 \times (^{\circ}\text{F}_{\text{plume}} + 460)} \quad (2.31b)$$

Figure 2.7 was created by vertically aligning the effect of either temperature or MW on a plume's density relative to the density of normal room air at 25°C determined using Equation 2.31b. For instance, a plume with an MW of 58 is aligned directly above a plume at -191°F; in both cases, their plume will have twice the density of pure air at 25°C. Alternatively, Equation 2.32 (derived directly from Equation 2.31b) can be used to find the MW of a plume that would behave the same as a plume of air at a given temperature. Of the two variables, temperature is considerably easier to measure, its effect on a plume is more intuitive for most people to envision, and in this author's experience is more likely to differ from ambient air by a greater ratio than will their MWs.

$$\text{Equivalent } \frac{\text{MW}_{\text{plume}}}{\text{MW}_{\text{air}}} = \frac{298}{(^{\circ}\text{C}_{\text{plume}} + 273)} = \frac{537}{(^{\circ}\text{F}_{\text{plume}} + 460)} \quad (2.32)$$

- Hot processes are very common in industry. While plumes (even hot plumes) are not always visible, almost everyone has seen smoke rise from a fire. Smoke will rise because it is hotter and less dense than the surrounding air. Any plume (whether visible or not) that is less dense than the surrounding air will tend to rise in the same manner as smoke. An equation will be presented in Chapter 13 to predict the velocity of a hot plume as a function of its temperature. Indoors, if a hot plume is not initially captured and removed via local exhaust ventilation, it will continue to rise, cool, and slightly expand until it encounters either a ceiling or a thermal inversion layer,^x where it will spread horizontally and perhaps circulate back into the workspace where the contaminant is likely to become hazardous to health until it slowly escapes from the room via general ventilation (to be covered in Chapters 5, 19, and 20).

Cold plumes are rare in the workplace, but they do occur. A vapor plume will often be slightly cooler than room temperature because the process of evaporation is endothermic.

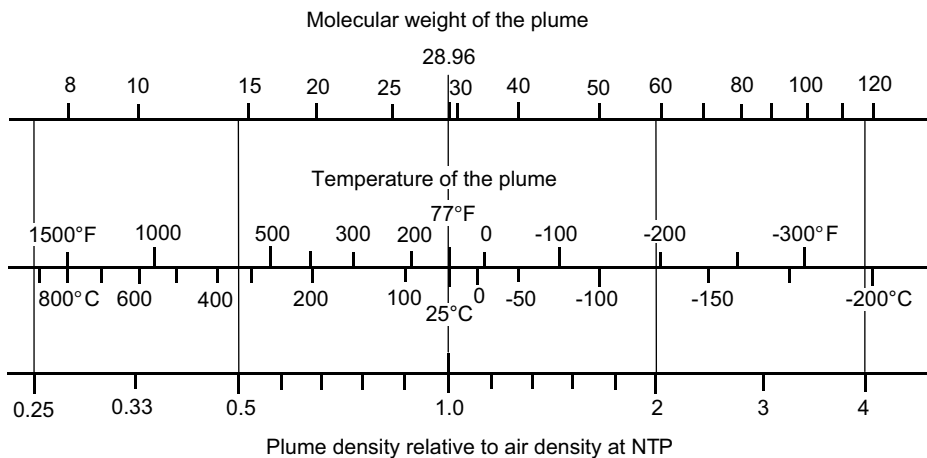


FIGURE 2.7 The independent effects of a plume's MW (the ratio of $\text{MW}_{\text{plume}}/28.966$ on the top scale) and its temperature (the ratio of $T_{\text{plume}}/25^{\circ}$ in the middle scale) on its density ($\rho_{\text{plume}}/1.1846 \text{ g/L}$ on the bottom scale) determined via Equation 2.31b.

^x Normally temperature decreases with elevation; an inversion means that the temperature of the air above is warmer than the temperature below the altitude of the inversion level.

The heat of evaporation must be absorbed from the ambient environment and thus can cool both the liquid source and its vapor plume. Examples of this cooling include the effect on one's body due to the evaporation of perspiration and the cooling of air passing through an evaporative cooler. The more volatile a chemical is, the more rapidly it will cool. Evaporation can cool a highly volatile solvent such as ethyl ether ($P_{\text{vapor}} = 537 \text{ mmHg}$), methylene chloride ($P_{\text{vapor}} = 435 \text{ mmHg}$), carbon disulfide ($P_{\text{vapor}} = 358 \text{ mmHg}$), or 1,2-dichloroethylene ($P_{\text{vapor}} = 331 \text{ mmHg}$) 40°F (20°C) below room temperature, but evaporation will cool most solvents by less than 20°F (10°C), and most plumes' temperature is likely to be cooled by less than 10°F (5°C) below ambient temperature. As you should expect, a high density would impart a downward velocity to a plume. The same effect would occur whether the plume were colder than the surrounding air or were contaminated by a vapor whose MW was greater than the MW of air.

The following examples of air densities at three non-normal temperatures are intended to help the reader to visualize the effect of a plume's density on its behavior implied by Equation 2.31b. Along the way (and in the future), Equation 2.33 is very handy for converting any small ratio into a percent difference.

$$\boxed{\% \text{ Difference} = 100 \times [\text{Ratio} - 1]} = 100 \times \left[\frac{\text{Numerator} - \text{Denominator}}{\text{Denominator}} \right] \quad (2.33)$$

Example 2.12

Compare the density of steam at the temperature of boiling water to that of air.

$$\frac{\rho_{\text{plume at } 100^\circ\text{C}}}{\rho_{\text{air at } 25^\circ\text{C}}} = \frac{\text{MW}_{\text{plume}} \times 298}{\text{MW}_{\text{air}} \times 100 + 273} = \frac{298}{373} = 0.799 \quad (\text{using Equation 2.31b})$$

Using Equation 2.33 shows that $100 \times (0.799 - 1) = -20\%$, meaning that a ratio of 0.799 is 20% less dense than normal air. You may observe how steam from a boiling pan on a stove tends to rise but can easily be blown sideways (or even downward if you happen to have a stove-top exhaust hood popularized by Jenn-Air).

Example 2.13

Compare the density of a fog that can sometimes be seen in a highly humid setting drifting down the outside of a glass of ice-cold water to the density of air. Assume the fog is at 0°C .

$$\frac{\rho_{\text{plume at } 0^\circ\text{C}}}{\rho_{\text{air at } 25^\circ\text{C}}} = \frac{\text{MW}_{\text{plume}} \times 298}{\text{MW}_{\text{air}} \times 0 + 273} = \frac{298}{373} = 1.091 \quad (\text{using Equation 2.31b})$$

This time using Equation 2.33 shows that the air surrounding the glass is $100 \times (1.091 - 1) = 9\%$ more dense than normal air. This cold plume's density is less different from air than was steam (albeit more dense rather than less dense).

Example 2.14

Compare the density of an easily visible fog that will form when dry ice is placed into water to the density of air. Assume this fog is at the -103°C or -153°F sublimation temperature of CO_2 .

$$\frac{\rho_{\text{plume at } -103^\circ\text{C}}}{\rho_{\text{air at } 25^\circ\text{C}}} = \frac{\text{MW}_{\text{plume}} \times 298}{\text{MW}_{\text{air}} \times -103 + 273} = \frac{298}{195} = 1.528 \quad (\text{using Equation 2.31b})$$

Again, using Equation 2.33 shows that this plume is $100 \times (1.528 - 1) = 53\%$ more dense than normal air. Recall how dry ice fog will flow down onto a table or, if formed as a stage effect, will flow down-stage into the audience or orchestra pit. This density difference is significant.

VII DENSE VAPORS

While any version of Equation 2.31 works fine and well for either a pure chemical or a mixture at a known MW, vapors cannot (by definition) be present at 100% purity and the MW of a vapor–air mixture is not easily known.^y One could use Equation 2.30 and the process shown in Table 2.4 to find the mixture's MW [MW_{mixture}], but that is way too long to be practical. The following series of steps lead to simpler ways.

1. The following steps begin by treating standard air as one component and a toxic vapor as the other component of a mixture, and then use Dalton's and the Ideal Gas laws to derive Equation 2.34a.

$$\rho_{\text{mixture}} = \sum_{i=1}^{i=n} (Y_i \rho_{\text{pure } i}) + (Y_{\text{air}} \rho_{\text{air}}) \quad (2.34a)$$

where

Y_i = the molar fraction of each contaminant.

$\rho_{\text{pure } i}$ = the density of each gaseous contaminant i calculated as if it were a pure gas using Equation 2.27 at NTP (even though a pure vapor is, by definition, not possible).

Y_{air} = the remaining fraction of the atmosphere that is not the contaminant (*i.e.*, $1 - \sum Y_i$ as shown in Equation 2.34b).

$\rho_{\text{air}} = 1.1846 \text{ g/L}$ at NTP determined using Equation 2.27.

Equation 2.34b uses the further simplification that whatever is not air is the contaminant that an IH typically wants to measure or predict.

$$\rho_{\text{mixture}} = \sum_{i=1}^{i=n} (Y_i \rho_{\text{pure } i}) + \left(\left(1 - \sum_{i=1}^{i=n} Y_i \right) \rho_{\text{air}} \right) \quad (2.34b)$$

Similar to the cancelations that occurred to yield Equation 2.31, the molar volume (whether at NTP or any other T and P) in both the $\rho_{\text{pure } i}$ and ρ_{air} values will cancel out of Equation 2.34b, yielding Equation 2.35.

$$\frac{\rho_{\text{mixture}}}{\rho_{\text{air}}} = \frac{\sum_{i=1}^{i=n} Y_i MW_i}{MW_{\text{air}}} + \left(1 - \sum_{i=1}^{i=n} Y_i \right) \quad (2.35)$$

^y By definition, a chemical's P_{vapor} is its maximum vapor concentration at a given temperature, and must be less than one atmosphere (otherwise it would be a gas). Because P_{vapor} for a vapor must be less than one atmosphere, its Y_i must always be less than unity. The rest of that total atmosphere is air. Therefore, a vapor plume will always be a mixture of the vapor and air.

The prediction gets even simpler if the mixture has only one vapor component, in which case the generic i becomes that one vapor, and the summations are not needed. Some quantitative results of using Equation 2.36 can be seen within Examples 2.16 and 2.17.

$$\boxed{\frac{\rho_{\text{one vapor}}}{\rho_{\text{air}}} = 1 + \left(Y_{\text{vapor}} \times \left[\frac{\text{MW}_{\text{vapor}}}{\text{MW}_{\text{air}}} - 1 \right] \right)} \quad \text{for any one vapor} \quad (2.36)$$

But wait, there's more. Because any volatile chemical's maximum Y_{vapor} is limited to its saturated vapor pressure P_{vapor}/P , Equation 2.36 can be simplified once more.^z Equation 2.37 shows that the maximum $\rho_{\text{vapor}}/\rho_{\text{air}}$ depends not only upon the chemical's MW, but also upon its vapor pressure.^{aa} Equation 2.37 is the simplest way to answer the question, "How much more dense than air can a vapor of 'dimethyl-chicken wire' possibly be?"

$$\boxed{\frac{\rho_{\text{sat. vapor}}}{\rho_{\text{air}}} = 1 + \left(\frac{P_{\text{vapor}}}{\text{ambient } P} \times \left[\frac{\text{MW}_{\text{vapor}}}{\text{MW}_{\text{air}}} - 1 \right] \right)} \quad \text{for one vapor at saturation} \quad (2.37)$$

Example 2.15

How much more dense than air can benzene vapor at NTP possibly be? One can tell by comparing the $\text{MW}_{\text{benzene}} = 78$ with the $\text{MW}_{\text{air}} = 28.97$ that the density of a hypothetically pure benzene vapor would be $78/28.97 = 2.7 \times$ more dense than air. However, the only way a pure vapor can form at NTP is if the chemical's P_{vapor} were 760 mmHg. Benzene's vapor pressure is only 95 mmHg, and its maximum Y_{benzene} at NTP = $95/760 = 0.0125$.

$$\text{Maximum } \frac{\rho_{\text{sat. vapor}}}{\rho_{\text{air}}} = 1 + \left(\frac{95}{760} \times \left[\frac{78}{28.964} - 1 \right] \right) = 1.211 \quad (\text{using Equation 2.37})$$

Equation 2.37 followed by Equation 2.33 shows that benzene's saturated vapor is only 21% more dense than air. It may be noteworthy that at saturation, benzene vapor is as much more dense than air as the steam from boiling water found in Example 2.12 is less dense than air. A method to be covered much later (Section 13.VIII) predicts that a plume 20% less dense than air is capable of causing an upward plume velocity of about 20 fpm; however, flow downward is often impeded if not prevented by a horizontal surface below the source (e.g., a surface supporting the liquid's container, the floor, or the ground).

Example 2.16

What is the mixture density for 1.2% benzene vapor compared to clean room air? This 1.2% happens to be the lowest concentration at which a benzene vapor will burn (a.k.a. its "LFL"). Here, Equation 2.36 is appropriate because Y_i is not a saturated vapor.

$$\frac{\rho_{\text{one vapor}}}{\rho_{\text{air}}} = 1 + 0.012 \times \left(\frac{78}{28.964} - 1 \right) = 1.020 \quad (\text{using Equation 2.36})$$

^z If that limitation is not obvious by now, please go back and review Equations 2.13 and 2.14.

^{aa} Some authoritative documents aver that an isothermal vapor's density with respect to air depends only on its MW and disregards its P_{vapor} .^{20,21} This further simplification would only apply to gases where $Y_{\text{equilibrium}}$ can equal one, in which case $\rho_{\text{vapor}}/\rho_{\text{air}}$ in Equation 2.37 will reduce to just the ratio of $\text{MW}_{\text{vapor}}/\text{MW}_{\text{air}}$.

- ✓ A ratio of 1.02 means that this barely flammable vapor is only 2% more dense than air. It turns out that the lowest vapor concentration at which most combustible vapors can be ignited and burn (their LFL) is around 1%–2%. For benzene, this 1.2% is almost a tenfold decrease below its 12.5% equilibrium vapor concentration. In other words, after the benzene vapors leaving the liquid are diluted over tenfold, they are no longer at a flammable concentration. At that point, its plume density is only 2% more than the density of the surrounding air. The density of such a barely flammable concentration can cause a downward plume velocity of only 5–10 fpm which is less than most random room air currents. Thus, once the saturated benzene vapor is no longer combustible, the plume is no longer significantly more dense than the air around it. Or stated in a more generalized rule-of-thumb, *most vapors below their LFL are only approximately 2% to 4% heavier than air and will generally move with the air around it.*

Example 2.17

What is the mixture density for 1,000 ppm benzene vapor compared to clean room air?

The specified $Y_{\text{benzene}} = 1,000 \text{ ppm}/1,000,000 \text{ ppm} = 0.001$ (using Equation 2.13)

$$\frac{\rho_{\text{one vapor}}}{\rho_{\text{air}}} = 1 + 0.001 \times \left(\frac{78}{28.964} - 1 \right) = 1.00169 \quad (\text{again using Equation 2.36})$$

Percent difference = $100 \times (1.0017 - 1) = 0.17\%$ heavier than air (using Equation 2.33)

- ✓ Almost all gas and vapor exposure limits are less than 1,000 ppm and most are less than 10 ppm (you could glance ahead to Figure 4.3). Thus, as another rule-of-thumb, occupationally hazardous vapors are less than 0.1% heavier than air. The nearly neutral buoyancy of vapors at less than 1,000 ppm means that virtually no vertical forces act on a plume diluted to a concentration in the range of occupational health exposure limits, and such contaminants will follow the air in which they are diluted.

2. Only a limited range of chemicals in a limited range of conditions can create a vapor whose plume is appreciably greater than air. The data in Figure 2.8 were generated using Equation 2.37 for 346 organic chemicals that have a TLV[®] and whose P_{vapor} at 25°C is less than 760 mmHg (*i.e.*, chemicals that form a vapor rather than a gas) but more than 0.001 mmHg (*i.e.*, have a saturated $Y_{\text{vapor}} > 1 \text{ ppm}$). Each open circle marks the ratio of the density of that chemical's saturated vapor relative to the density of air at 25°C, *i.e.*, each chemical vapor's maximum density at NTP. None of the ratios for these chemicals exceeds four. The straight line is the density ratio of true gases; 40 real gases with TLV[®] would fall along that line and have density ratios of up to 7.2 but are not included within this figure.^{ab}

A few lessons can be drawn from these figures. First, the density of most of these vapors is much less than the density that the National Fire Protection Association [NFPA] and others attribute solely to the ratio of the vapor's MW to air (*e.g.*, MW/29 in NFPA 325¹⁹). The tendency for vapor pressures to decrease as MWs increase keeps the density of saturated vapors from continuing to increase with MW. Figure 2.8 shows that the highest vapor densities occur for chemicals with a MW in the region of 100 to 200 g/mol. Lighter chemicals even at a high molar fraction do not add much weight to the mixture, and heavier chemicals do not have enough P_{vapor} to exist at a high enough vapor molar fraction to add much weight.

^{ab} The organic gases with the highest density ratios are all halogens: difluorodibromomethane at 7.2, dichlorotetrafluoroethane at 5.9, chloropentafluoroethane at 5.3, hexafluoropropylene at 5.2, and trifluorobromomethane at 5.1.

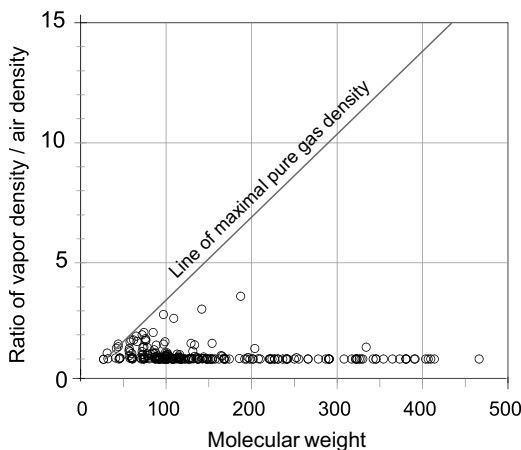


FIGURE 2.8 The ratio of the density of 346 saturated vapors relative to that of clean air, highlighting their divergence from hypothetical “pure” vapors.

Second, the range of the density of most vapors is not very broad. Only 3–4% of the vapor densities of all the organic chemicals in Figure 2.8 are more than twice as dense as air. The density of 80% of the vapors in Figure 2.8 is within 20% of the density of air, and more than 45% are within 1%.

Recall that the density due to a vapor’s MW can be equated to that due to a lower temperature via Equation 2.32. For instance, a plume that is 20% more dense than normal air due to heavy vapors will behave just like a plume that is approximately -20°C or -5°F (found by starting at 1.2 on the bottom scale in Figure 2.7, then going straight up to the temperatures on the middle scale). A density ratio of 1.2 can have a measurable effect as shown in Figure 2.9, like the fog produced when dry ice is put in hot water.

A third lesson is depicted in Figure 2.10. The initial density of a saturated vapor right at a liquid source will decrease rapidly as the plume is diluted (*e.g.*, Figure 2.9 shows a 100-fold dilution within just a few inches^{ac}). The densities in Figure 2.10 are those of the same chemicals that are shown in Figure 2.8 but diluted by a factor of 10. Virtually none of these minimally diluted vapor densities exceeds that of clean air by more than 20%. Even the density of a heavy gas (that could initially be present at a *Y* of 100%) will rapidly

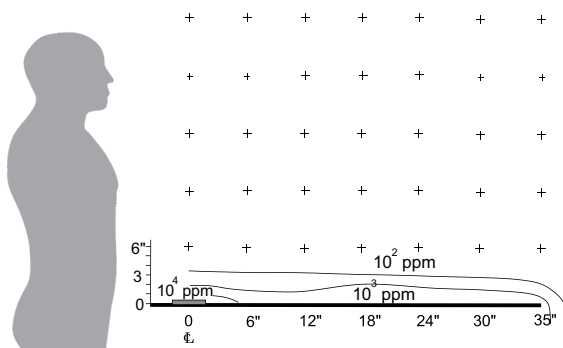


FIGURE 2.9 Benzene vapor emanating from a petri dish on a 6 × 6 foot table in still air as measured by Gumaer²¹ to which the person and 6 in. grid marks were added.

^{ac} Figure 5.11 will show that a plume undergoes the same rapid rate of dilution in a ventilated setting.

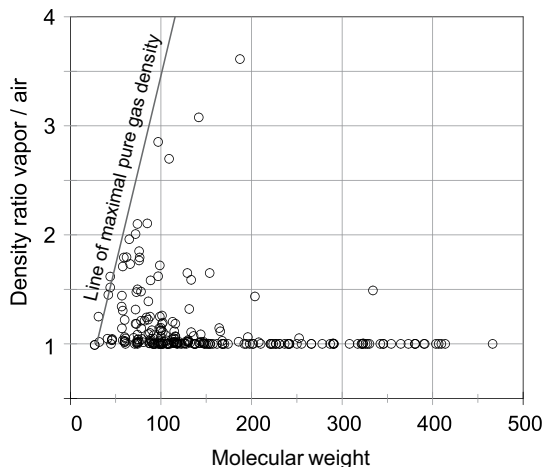


FIGURE 2.10 The ratio of the density of the same vapors as in Figure 2.8 but diluted tenfold compared to the density of clean air.

approach that of air when it is diluted by as little as 10 $\times$ (as represented by the dashed line within Figure 2.10).^{ad}

A few other points of comparison are offered. The vapors of solvents at their typical lower typical flammability limits [LFL] of 1%–2% are roughly 1%–5% more dense than clean air (see Example 2.16). The vapors of a chemical whose flash point is above room temperature cannot even reach their LFL concentration at room temperature; therefore, those vapors are even closer to air’s density. And vapors at concentrations below 1000ppm (a Y_{vapor} of 0.001 is the highest TLV[®] except for CO₂) are less than 1% more dense than air, not enough to flow to and collect near the floor in rooms with occupants, machinery, or/and ventilation that each typically cause general air currents in excess of 40 to 50 fpm. Looking ahead at data to be presented in Chapter 5, air currents will rapidly dilute any saturated vapor pressure concentration by at least 1,000-fold within about one arm’s length from its liquid origin or source. Turbulence caused by someone standing upwind of a source will easily dilute the saturated vapor pressure concentration at the liquid surface by at least 10⁴ by the time the vapors reach their breathing zone.

3. So when are dense vapors important? A dense vapor from a liquid already on the floor or ground (*e.g.*, from a liquid leak or spill) needs an external mechanism to generate some turbulence and begin the dilution process. Examples of common dilution mechanisms include ventilation, human activity, wind, or even thermal air currents. Without an external mechanism (such as in a closed, unventilated, and unoccupied room or outdoors on a still night), a dense vapor that is generated on the floor or ground can accumulate vertically within a walled-space and spread horizontally as if flowing by gravity. If outdoors, the flow would be downhill almost like a liquid; if indoors, the flow could go down a vent or a stairway. In these scenarios enough vapor could accumulate to create an acute inhalation hazard, a conflagration hazard if the vapor is flammable and there is an ignition source, or an oxygen deficiency by displacing air (see Chapter 4).

^{ad} An interesting relationship of limited utility (a.k.a. “trivia”) allows one to calculate the new density ratio of a diluted vapor from its previously known density ratio via $1 + (([\text{density ratio}] - 1)/[\text{dilution factor}])$. For instance, if a mixture with an initial density ratio of 5 is diluted tenfold, its new density ratio will be $1 + ((5 - 1)/10) = 1.4$. Moreover, if one were to rescale the vertical axis in Figure 2.10 to be a maximum of this same 1.4 instead of 5, those data points would be spread vertically to look identical to those in Figure 2.8 and the dashed line would appear where its solid line is now.

However, if the liquid evaporates somewhere above the ground, the requisite falling motion of an initially dense plume (as is just visible in Figure 2.9) would start the dilution process and change the density from that depicted in Figure 2.8 toward that depicted in Figure 2.10. Once diluted, a molecule's weight will not cause it to separate from the air or to accumulate near the ground. In other words, if an initially dense vapor does not start out on or near "the bottom," it will not stay dense long enough to get there on its own.

Thus, it may be inappropriate to place an exhaust hood near the floor in a production facility but appropriate for an exhaust hood to be near the floor in a solvent or paint storage room. Several sections within the *International Mechanical Code* (part of most local building code requirements in the United States) specify that the inlet to a local exhaust ventilation system for flammable vapors and gases shall be located not more than 18 in. (46 cm) above the floor.²² Although this building code may be a local legal requirement, the recommendation is probably not beneficial when mechanical ventilation or human activity is mixing the air within a room. The flow and dispersion of dense plumes have not been well studied except in the case of liquefied natural gas [LNG] storage facilities; while the MW of natural gas (mostly methane) is less than air, the cold temperature of LNG (112°K = -161°C) makes its vapors very dense.²³ Several publications are now available for the more technically inclined reader to explore dense vapor dispersion models.²⁴⁻²⁷

4. An academically interesting but probably relatively rare situation in practice (except for vapor degreasers to be discussed in Section VIII.6 of Chapter 4) occurs when an initially cool solvent is heated. Heat would tend to drive the vapor pressure up as predicted by the Antoine equation (Equation 2.10) making the plume more dense, but a hotter plume would tend to make the plume less dense as predicted by the $T_{\text{room}}/T_{\text{plume}}$ ratio in Equation 2.28b due to the Ideal Gas law. Which change would predominate?

The data shown in Figure 2.11 were derived using Equation 2.31b assuming that the plume temperature is equal to the vapor temperature. Each chemical in Figure 2.11 seems to follow the same pattern. As a cool solvent gets hotter, its vapors initially become slightly less dense. Eventually (when P_{vapor} reaches 5%–10% of 760 mmHg), the exponential influence of temperature on vapor pressure (as characterized by the Antoine equation) and the contribution of the vapors to the MW of the mixture will overcome the linear influence of absolute temperature on an ideal gas causing the plume density to increase. However, even at the boiling point where Y_i reaches 1 (the upper end of each line in Figure 2.11 except ethyl ether), the plume's density will stay slightly below that predicted by the ratio of MWs alone due to the buoyant effect of its high temperature.

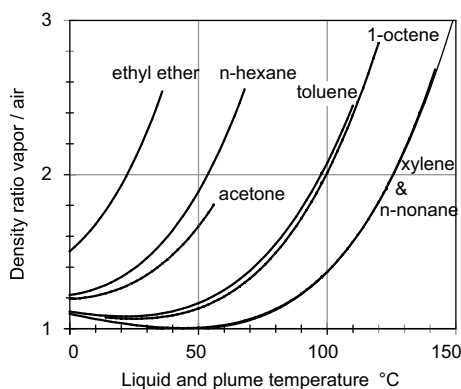


FIGURE 2.11 The effect on saturated plume density caused by heating organic solvents.

The actual behavior of any particular heated vapor plume is difficult to predict because the mechanisms that control molecular and turbulent dispersion turn out to be related to (but are somewhat different from) those mechanisms that control thermal cooling. A large, hot plume may cool rapidly enough to create a supersaturated vapor, condense, and form a visible mist (or what would appear to be steam if the solvent were water). Eventually, such a plume will be diluted below its saturation concentration, and the mist (steam) will reevaporate and disappear. Thus, the behavior of a vapor plume can be determined as much by its temperature as by its MW. Should you want to track an invisible plume, try using a smoke tube to make it visible (described in Section I of Chapter 12) or a real-time, direct-reading detector. The path may surprise you.

PRACTICE PROBLEMS

1. Envision someone having to enter a series of railroad tank cars in order to remove residual (unevaporated) octane on a normal (25°C) day near sea level. What would be the ppm vapor concentration inside the tank car? The P_{vapor} and TLV® data for many chemicals is in the Vapor Hazard Ratio tables in Appendix A of your book.

ans. = 18,553 ppm (which is about 62× its TLV® exposure limit)

2. Suppose that the tank cars with residual octane were not cleaned until late in the afternoon when the temperature had climbed to 37°C (12°C above normal) or 98.6°F. What would you expect to be the octane concentration at that point based on a rule-of-thumb of how vapor pressures for organic chemicals change with temperature?

ans. = 37,105 ppm

3. Use the following parameters for the Antoine equation to find a more accurate prediction of the vapor pressure of octane at 37°C (note that this formula yields a P_{vapor} for octane at 25°C of 13.9 mmHg).

$\ln [P_{\text{vapor}}] = A - (B/(\text{°K} + C))$	A =	B =	C =	Valid Range (°C)
<i>n</i> -Octane	15.9426	3,120.29	-63.63	24–135

ans. = this P_{vapor} should be 5%–6% lower than the approximate results in Problem 2

4. Use Dalton's law to find the partial pressure of oxygen in mmHg at sea level on a 25°C normal day, knowing that it comprises 20.948% of clean air. (The TLV uses mmHg oxygen to define an oxygen deficiency.)

ans. = 159 mmHg

5. Assume that the pressure in your car tires is 35 psig in the morning when the tire is at 50°F or 10°C. Inflation pressure is always measured as a gauge pressure.
 - a. What is the absolute pressure inside the tire in the morning?
 - b. What is the absolute tire pressure while driving at highway speeds on a summer afternoon when the tire temperature is 150°F or 65.5°C? (A tire is usually not more than approximately 50°F above ambient.)
 - c. What would a tire pressure gauge read when the tire temperature is 150°F or 65.5°C?

ans. = 44.7 psig

6. Assume that your refrigerator is set at 37°F or 2.8°C, and that when you open the door to look for a snack, enough cold air is replaced by room air to raise the temperature inside to 57°F or 14°C. The moment you close the refrigerator, the air inside starts to cool, and the cooling causes the pressure inside the refrigerator to start to decrease.

- a. If the atmospheric pressure were normal, what is the minimum pressure that could occur inside the closed refrigerator when the air again reaches 37°F or 2.8°C if there were no leaks?

ans. = 0.9613 atm or 14.127 psia

- b. At that point, what is the pressure difference between the ambient pressure and the pressure inside the closed refrigerator? (*Can you hear the air leaking into your refrigerator or freezer at home when you close the door? Try to open your freezer just a few seconds after you close it.*)

ans. = 0.569 psig

- c. If the refrigerator door were 30 in. wide by 48 in. tall, what force would the above pressure difference create on the door tending to hold it closed? (*It is a good thing that its door seals leak!*)

ans. = 819 lb

7. How would the density of a hypothetically pure ($Y = 100\%$) vapor of xylenes (a mix of iso-, meta-, or para-xylene) compare to normal air density? For xylenes (CAS# 1330-20-7), MW = 106.16, and P_{vapor} at NTP = 8 mmHg.

ans. 3.667 times the density of air

8. How would the density of xylenes' vapor at its saturated vapor pressure at 25°C compare to normal air density?

ans. 1.028 times the density of air or 2.8% more dense than air

9. Use Figure 2.7 or Equation 2.37 to estimate the temperature of air that would have the same density as each of the above plumes due to their MW.

ans. equivalent temperatures of -192°C and 17°C

10. On which if any of these plumes is buoyancy likely to have a significant effect in a workplace? And, would that vertical trajectory (if any) be upward or downward?

ans. significantly downward only if hypothetically pure

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3 The Behavior of Aerosols

The learning goals for this chapter:

-  Be able to classify a given aerosol as a fume, mist, dust, or fiber.
-  Understand the mechanisms of impaction and sedimentation and how they affect aerosol behavior in the environment and within the respiratory tract.
-  Be familiar with the mechanism of centrifugation as used in aerosol samplers and air cleaners.
-  Understand the difference between a normal and log-normal distribution and which distribution applies to aerosols.
- ☐ Know how to use $d_{\text{aero}} = d_{\text{Stokes}} \sqrt{\rho}$ to convert between a Stokes diameter and an aerodynamic diameter.
-  Know where and how to access particle size data and how to find or calculate a particle's falling velocity.
-  Be able to use a figure or table to determine the percent inhalable, thoracic, or respirable fraction for a given particle aerodynamic diameter.

This chapter delays starting with definitions until after covering some basic but perhaps not obvious differences between aerosols and the vapors covered in Chapter 2. The chapter then progresses to discuss the statistical mathematics of aerosol particle size distributions, the physics of small particle motion, the difference and uses of the terms Stokes diameter and aerodynamic diameter, and concludes by tying all of these concepts into the way aerosols are categorized and treated as an airborne hazard based on their particle diameter.

I HOW AEROSOLS DIFFER FROM GASES AND VAPORS

Rather than starting with definitions of aerosols, this section first contrasts aerosols with the molecules that comprise gases and vapors. Aerosols are unlike vapors in at least three aspects: they lack an intrinsic property (such as vapor pressure) to become airborne, individual aerosol particles are much larger than the air molecules in which they are suspended, and an aerosol's behavior depends strongly on its size (diameter).

1. Because powders, dusts, and solid materials have no intrinsic ability (such as vapor pressure) that would cause them to become airborne spontaneously, the generation of most aerosols relies on some external mechanism.^a Grinding, crushing, or dropping can both break up a solid material and propel small particles into the air. Scraping, shaking, or blowing can aerosolize an already existing powder.^b Spraying or splashing can aerosolize both a relatively nonvolatile liquid and any solid suspended within the liquid. Because solid materials lack an intrinsic source-generating property, source control of aerosols is limited to either modifying the external mechanism to reduce the number of fine particles being generated (such as slowing a speed or reducing a force) or reducing the intrinsic susceptibility of a given dust, powder, or fiber to become aerosolized (as by wetting or

^a The exception is the vapors from high temperature, molten metals, and high-molecular-weight organic materials that cool and condense to form fumes or smoke.

^b The development of a predictive index for the “dustiness” of a powder has generated some recent interest.^{1–3}