

SAFETY

in the Chemical Laboratory

Edited by NORMAN V. STEERE,
140 Melbourne Ave., S.E.
Minneapolis, Minn. 55414

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Safe Practice in the Chemistry Laboratory— a Safety Manual—Part I

Conrad Schuerch, Ph.D., Chairman, Department of Chemistry,
State University College of Environmental Science and
Forestry, Syracuse, New York, 13210

INTRODUCTION

The chemist has a professional, moral and legal responsibility to be thoroughly familiar with the rules of safety as applied to chemical operations and to follow them at all times. Rules of safety cannot be completely codified, however, especially for a research laboratory, and it is therefore necessary for the chemist to work defensively at all times, to consider each operation for its intrinsic dangers, and to build into each experimental setup methods of control, security and escape. This is your responsibility in the laboratory and your health, eyesight, and life can depend first on your forethought, and second on your calm at time of danger. So can the lives of your associates. Serious accidents happen rarely but they are almost always due to carelessness and are preventable.

The most serious immediate dangers in a chemistry laboratory are usually due to explosions, fires and runaway reactions. Dangers that usually become apparent over somewhat longer periods are due to contamination by toxic materials, poisoning, and asphyxiation. Be alert to possibilities for all these hazards and avoid them.

HAZARDOUS PROPERTIES OF CHEMICALS

Flammability of Liquids

Fire is the principal cause of serious laboratory accidents and usually involves organic solvents. Nearly all organic solvents are flammable, and some are extremely so because of their high vapor pressure at room temperature. Furthermore, it should be remembered that all organic vapors or gases (except a few with

one or two carbons like methane, ethane and carbon monoxide) are heavier than air and pour and flow along a surface like liquids. Open flames or other heat sources quite distant from a source of vapors can thus cause a flashback and fire or explosion.

In discussing flammability, a few definitions are needed: The *flash point* of a liquid is the temperature at which it gives off sufficient vapor to form an ignitable mixture with the air near the surface of the liquid or within the vessel used. If the flash point of a solvent is below room temperature (25°) it is termed a class I solvent and is most dangerous. Examples of common class I solvents are ether, benzene, acetone, petroleum ether and ethyl acetate.

The *auto-ignition temperature* of a solvent is the minimum temperature required to initiate or cause self-sustained combustion independently of applied heat. For example, carbon disulfide has an auto-ignition temperature of 100°C and therefore the vapors can take fire on contact with an ordinary low pressure steam line. The auto-ignition temperature of ether is 180°C and serious fires have been caused by evaporation of ether on a hot plate.

Explosive Characteristics

Explosions usually result from extremely rapid exothermic reactions of mixtures of compounds. As heat is evolved, reaction rate increases and often large volumes of expanding gases are produced in fractions of a second. Many reactions can take place explosively but oxidations are among the most common sources of accidents.

Conrad Schuerch, Ph.D., received his B.S. degree from the Massachusetts Institute of Technology in 1940 and his Ph.D. in Organic Chemistry there in 1947. He was Sessional Lecturer at McGill University 1947-48 and Harold Hibbert Memorial Fellow there 1948-49. Since 1949 he has been with the Department of Forest Chemistry, State University College of Forestry at Syracuse University, where he is Professor and Chairman.

Dr. Schuerch was recipient of the John Simon Guggenheim Memorial Fellowship at Imperial College, London, 1959-60, and in 1972 received the Anselme Payen Award of the Division of Cellulose, Wood and Fiber Chemistry of the American Chemical Society. He is a member of TAPPI, London Chemical Society, and the American Chemical Society.

Therefore intimate mixtures of oxidizing and oxidizable substances are especially hazardous as are individual compounds containing oxidizing and oxidizable groups. For examples, impurities in ammonium nitrate—a common commercial chemical—have initiated devastating explosions that have wiped out city blocks. Trinitrotoluene and nitro-cellulose are used for blasting and for propellant charges. The vapor of carbon disulfide in concentrations of 1-50% by volume in air can explode on ignition. The corresponding explosion range for acetylene is 2-80% and even ammonia gas will ignite in concentrations of 15-28% in air.

Explosions can also result from reactions initiated by the cleavage of weak bonds in sensitive compounds. If the reactive intermediates generated induce the formation of larger numbers of intermediates (usually free radicals) a branching sequence develops that rapidly causes a detonation. Such explosions can be initiated by heat or mechanical shock and substances like lead azide react in this manner and can be used as detonators in cartridges. They deserve respect.

An especially treacherous source of explosions are peroxides formed by auto-oxidation of common solvents. Solvents that are especially susceptible to the formation of peroxides or hydroperoxides are some aromatics with benzylic hydrogens (for example, cumene) and most especially a number of ethers: ethyl ether, isopropyl ether and dioxane. Typically, ether from a half-filled bottle that has been left in a laboratory for a few months will be used in an extraction procedure. On concen-

Editor's Note

There is always need for a laboratory to have certain established safe practices, and for an inexpensive and specific means of communicating the safe practices to the continual flow of new people working in the laboratory. This column reprints in full a concise pamphlet prepared for use in the Department of Chemistry in the College of Environmental Science and Forestry at Syracuse University. The pamphlet, which was mimeographed on eight pages of standard-sized letter paper, seems to us an excellent example of effective communication in print.

Dr. Schuerch reports that their safety manual is handed out to all new graduate students, postdoctoral research workers, technicians, and to seniors beginning research projects.

Requests for reprints or answers to specific questions should be addressed to the author.

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trating the ether to isolate the product, the peroxide will also be concentrated and on overheating near the end of the evaporation will detonate and blow glass splinters in all directions. Ethers should, therefore, never be left for long periods in a half-filled container or in the light.

Do not subject potentially explosive substances to friction. For example, do not store in screw cap or ground glass-stoppered containers, and keep the mixtures away from stopcocks and stirrer packing glands. Many compounds containing high proportions of oxidizable and oxidizing groups are best stored wet.

Functional groups which contribute to explosive properties by either one or the other mechanism (rapid combustion or detonation) include the azide (N_3), diazo ($-\text{N}=\text{N}-$), diazonium ($-\text{N}_2^+, \text{X}^-$), nitro ($-\text{NO}_2$), nitroso ($-\text{NO}$), nitrite ($-\text{ONO}$), nitrate ($-\text{ONO}_2$), fulminate ($-\text{ONC}$), peroxide ($-\text{O}-\text{O}-$), peracid ($-\text{CO}_3\text{H}$), hydroperoxide ($-\text{O}-\text{O}-\text{H}$),

ozonide (O_3), N-haloamine ($-\text{N} \begin{smallmatrix} \text{Cl} \\ \text{X} \end{smallmatrix}$),

amine oxide ($\equiv\text{NO}$), hypohalites ($-\text{OX}$), chlorates (ClO_3), perchlorates (ClO_4) and acetylides of heavy metals ($-\text{C}\equiv\text{CM}$).

Spontaneous Ignition

A number of substances and mixtures will take fire spontaneously in air, and are

termed pyrophoric. They include Raney nickel, palladium and methyl alcohol, platinum oxide and alcohol vapors or hydrogen, powdered potassium, finely divided sodium or sodium alkyls, zinc and magnesium alkyls and dry Grignard reagents, phosphine, and iron carbonyl. They must be handled with extreme caution.

Toxicity

Many common chemicals have extremely dangerous immediate toxic effects. These include corrosive reagents such as mineral acids, caustic alkali solutions, bromine, and boron trifluoride, and vesicants and lachrymators, the effects of which are immediately obvious. There are also a number of compounds that are more treacherous and dangerous because their effects are not immediately recognized but can produce longer range systemic damage including nerve, kidney and liver injury, cancer, etcetera. Sometimes the only observable warning is relatively minor discomfort as from headaches or dizziness. Because of the frequency of use, a number of solvents with high toxicity should be treated with especial care. Among them are carbon tetrachloride, tetrahydrofuran, tetrachloroethane, chloroform, butanol and especially benzene. Some organic liquids will attack or penetrate the unbroken skin. Among these are aniline, nitrobenzene, phenylhydrazine, nitrobenzene, methyl sulfate, diazomethane, mustard gas types ($-\text{S}-$

$\text{CH}_2-\text{CH}_2\text{Cl}$) and nitrogen mustards ($\text{>N}-\text{CH}_2-\text{CH}_2-\text{Cl}$). Dimethyl sulfide penetrates the unbroken skin and enters the circulatory system extremely rapidly and can carry with it dissolved materials which would normally not pass the skin barrier. Allowing dimethyl sulfide solutions to touch the body is therefore hazardous.

In general, *all chemicals* that touch the skin should be washed off immediately and thoroughly with large amounts of tepid water. Washing should be continued long after the chemical appears to be removed, especially if the chemical has low water solubility. (Skin is lipophilic and extraction is slow.)

Do not smell a chemical directly. Fan a small amount of air from the surface of the neck of the vessel toward your face and sniff cautiously.

Mercury spills can be dangerous since a low concentration of mercury vapor can cause serious toxic reactions. The mercury should be cleaned up as carefully as possible and returned to the stockroom for reclaiming. The contaminated area should be powdered with flowers of sulfur to convert residual traces to the sulfide. The following day the sulfur may be swept up.

Many gases, vapors and dusts are extremely toxic and work with them should always be carried out under an effectively operating hood. Some require exceptional precautions and should be destroyed chemically rather than vented into the ventila-

tion system. Special attention should be given to carbon monoxide, cyanides, volatile organometallic compounds (As, Hg, Pb), nickel carbonyl, and alkaloid dusts.

Especially reactive substances are frequently very toxic. A partial list would be diazomethane, ketene, ethylene oxide, ethyleneimine, phosgene, hydrazoic acid, diisopropyl fluorophosphate and tetraethyl pyrophosphate. They should only be used in a hood. Radioactive substances involve exceptional dangers which are beyond the scope of this review.

Other Hazards

In addition to the chemicals used, a number of other safety hazards exist in the laboratory. The proper use of glassware under vacuum can prevent serious cuts caused by implosion. Glass vacuum dewars should always be wrapped with electrical tape to prevent flying when they implode. Almost all energy sources involve some hazard: electricity and electrical wiring, heating elements, flames and torches, lasers, and ultraviolet light. Liquid N₂ or air should never be confined in a closed system. High pressure vessels usually require separate explosion-proof rooms. Whenever special equipment is used, special precautions should be carefully noted and obeyed!

(To be concluded in December)

Editor's Note

The Editor is sorry that the following biographical sketch of Lowell A. Muse was inadvertently omitted from the September 1972 issue of the Journal of Chemical Education.

Mr. Muse received a Bachelor of Arts degree in chemistry from Florence State College, Florence, Alabama, in 1951. After two years of active duty in the Navy, he was employed as an analytical chemist by the Tennessee Valley Authority at Muscle Shoals, Alabama. In 1956, Mr. Muse joined the staff of the Oak Ridge Institute of Nuclear Studies, Oak Ridge, Tennessee as supervisor of the radioisotope training laboratory.

From 1961 to 1964, he was radiation safety officer for American Nuclear Corporation, Oak Ridge, Tennessee. From 1964 to 1969, Mr. Muse was employed by Oak Ridge Associated Universities; assisting in training programs in the use of radioactive materials, including the Atoms-In-Action program in South and Central America. Since 1969, Mr. Muse has been with the University of Georgia as Radiation and Laboratory Safety Officer. His present address is: Radiation and Laboratory Safety Officer, Safety Services Department, Public Safety Division, Barrow Hall Annex, University of Georgia, Athens, Georgia 30601.

Short Course:
Fundamentals of Fire and Explosion Hazards Evaluation

BARBIZON-PLAZA HOTEL, NEW YORK, NEW YORK
MONDAY AND TUESDAY, NOVEMBER 27-28, 1972

This course is designed to provide the student with a basic understanding of the chemical and physical principles employed in fire and explosion hazards evaluation. Emphasis has been placed on materials and the reactions they can undergo, the effects of such reactions on the surroundings and the experimental assessment of the risk involved in various process conditions. The objective of the course is to create an awareness of the technology available to the chemical engineer and an appreciation of the value of its application to design and operation of process facilities.

The course has been divided into four parts, corresponding to a two-day, four-session format. The level of the material presented requires the ability to apply basic principles of chemistry and physics, but no advanced training is required.

LECTURER

Lecturer for this AIChE Today Series will be Dr. Chester Grelecki, President and Chief Scientist, Hazards Research Corp., Denville, N.J. For the past fifteen years, Dr. Grelecki has been engaged in the study of combustion, explosion and detonation phenomena. He is the author of 15 papers in the scientific literature dealing with the kinetics of propellant reactions, propellant chemistry and safety in handling explosive compositions.

REGISTRATION

Requests to register for this course should be directed to the American Institute of Chemical Engineers, 345 East 47th

St., New York, N.Y., 10017. Telephone (212)752-6800. Registration will be limited and the fee will be \$140.

SCHEDULE

● First Day—9:00 A.M.—5:00 P.M.

Damage Potential of Explosions

1. Classifying Hazardous Reactions
2. Estimating Energy of Explosions
3. Estimation of Blast Effects
4. Characterization of Shock Waves
5. Examples of Shock Wave Characteristics
6. Interaction of Blast Waves with Environment
7. Blast-Resistant Structures

Detonation in Condensed Phases

1. Classification of Materials
2. Factors Affecting Detonability of Materials
3. Sensitivity of Materials
4. Explosive Output of Materials
5. Detonation Velocity and Critical Diameter
6. Avoidance of Detonable Mixtures

● Second Day—9:00 A.M.—5:00 P.M.

Gas Phase Explosions

1. Characteristics of Flames
2. Ignition—Flash Point and Flame Point
3. Ignition, Spontaneous
4. The Concept of Concentration Limits
5. Countermeasures in Vapor Explosions

Dust Explosions, Thermal Explosions, Deflagrations

1. Dust Explosions: I. Static Electricity
2. Dust Explosions: II. Ignition Sensitivity of Clouds
3. Dust Explosions: III. Explosion Severity
4. Dust Explosions: IV. Venting Requirements

5. Thermal Explosions: I. Theoretical Concepts
6. Thermal Explosions: II. Experimental Measurements
7. Thermal Explosions: III. Application to Reactor Design
8. Deflagrations: I. General Concepts
9. Deflagrations: II. Experimental Measurements
10. Deflagrations: III. Application to Reactor Design

Safety . . .

