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STUDENT PROBLEMS

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# Safety, Health, and Loss Prevention in Chemical Processes - Volume 2

PROBLEMS FOR UNDERGRADUATE ENGINEERING CURRICULA

Prepared by the  
Undergraduate Education Subcommittee  
of the  
Center for Chemical Process Safety  
and

**Dr. Ronald J. Willey**  
*Northeastern University*  
**Dr. Daniel A. Crowl**  
*Michigan Technological University*  
**Dr. J. Reed Welker**  
*University of Arkansas*  
**Dr. Ron Darby**  
*Texas A&M University*

THE  
CENTER FOR CHEMICAL PROCESS SAFETY  
OF THE  
AMERICAN INSTITUTE OF CHEMICAL ENGINEERS  
3 Park Avenue, New York, NY 10016-5901

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*It is sincerely hoped that the information presented in this document will lead to an even more impressive record for the entire chemical industry; however, the American Institute of Chemical Engineers, its consultants, The Center for Chemical Process Safety (CCPS) Subcommittee members, their employers, their employers' officers and directors, Author's Universities, and their members of the faculty, and the Authors disclaim making or giving any warranties or representations, express or implied, including those with respect to fitness, intended purpose, use or merchantability and/or correctness or accuracy concerning the content of the information presented in this document. As between (1) American Institute of Chemical Engineers, its consultants, CCPS Subcommittee members, their employers, their employer's officers and directors, Author's Universities, members of their faculty, their assistants and consultants, and the Authors, and (2) the user of this document, the user accepts any legal liability or responsibility whatsoever for the consequence of its use or misuse.*

## ACKNOWLEDGEMENTS

The enclosed problem set is for the use in the education of undergraduate chemical engineering students. This SACHE product was prepared by Ronald J. Willey, Daniel A. Crowl, J. Reed Welker and Ron Darby with the direction and guidance of the Undergraduate Education Committee (UEC) of the Center for Chemical Process Safety (CCPS). This package was prepared for use by SACHE (Safety and Chemical Engineering Education) members. CCPS appreciates the work by the authors and the direction and guidance of the Undergraduate Education Committee.

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## PREFACE

This problem set represents a collection of problems written as SACHE products over the past 10 years. Problems are located in the document by area, and have a prefix letter to indicate the area covered (see the table below). Some problem sets have a few elementary problems for students new to the field. These are generally the first few problems in a particular set. More difficult and time consuming problems are the higher number problems in any particular set. The fluids problems are new contributions from Prof. Ron Darby. As in any major written work, there may be errors or suggestions for improvement. We would appreciate your feedback in this regard as we desire to improve this work for future users. Our purpose is to introduce students to the concept of process safety and to have students consider these aspects in their designs and problem solutions. Remember, “Engineers shall hold paramount the safety, health, and welfare of the public in the performance of their professional duties,” is the first canon in Professional Registration<sup>1</sup>.

Written on behalf of all authors, Ron Willey, [r.willey@neu.edu](mailto:r.willey@neu.edu), August 2001

Area of Chemical Engineering Education	Prefix Letter
Stoichiometry	S-
Thermodynamics	T-
Fluid Mechanics	F-
Kinetics	K-
Heat Transfer	HT-
Process Dynamics and Control	PD-
Computer Solutions	CA-
Mass Transfer	MT-

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<sup>1</sup> Michael R. Lindeburg, P.E., *Engineering-in-Training Reference Manual*, 8<sup>th</sup> ed., Professional Publications, Inc., Chapt 63.

## GLOSSARY

This glossary defines many of the terms used on Material Safety Data Sheets (MSDS). It also explains some of the significance of the terms related to safety, health, and loss prevention. The glossary can provide substantial assistance in understanding terms commonly used by safety and health professionals.

**ACUTE EFFECT** *An adverse effect on a human or animal body, with severe symptoms developing rapidly and coming quickly to a crisis. See also, "Chronic."*

**Importance:** How much and how long one is exposed to a chemical is the critical factor to how adverse the health effects will be.

**ACUTE TOXICITY** *The adverse (acute) effects resulting from a single dose or exposure to a substance.*

**Importance:** Ordinarily used to denote effects in experimental animals.

**ACGIH** *American Conference of Governmental Industrial Hygienists; an organization of professional personnel in governmental agencies or educational institutions engaged in occupational safety and health programs.*

**Importance:** ACGIH develops and publishes recommended occupational exposure limits (see TLV) for hundreds of chemical substances and physical agents.

**APPEARANCE AND ODOR** *The physical properties of a chemical, such as color and smell.*

**Importance:** Knowing what chemicals look and smell like allows an employee to recognize unsafe working conditions.

**ASPHYXIANT** *A vapor or gas which can cause unconsciousness or death by suffocation (lack of oxygen). Most simple asphyxiants are harmful to the*

*body only when they become so concentrated that they reduce oxygen in the air (normally about 21 percent) to dangerous levels (19.5 percent or lower).*

**Importance:** Asphyxiation is one of the principal potential hazards of working in confined spaces.

**BOILING POINT** *The temperature at which a liquid changes to a vapor state, at a given pressure; usually expressed in degrees Fahrenheit at sea level pressure (760 mmHg, or one atmosphere). For mixtures, the initial boiling point or the boiling range may be given.*

**Importance:** The lower the degree for the boiling point, the faster a liquid evaporates, increasing the amount of vapor present at room temperature for both health and fire exposures.

**"C," OR CEILING** *The letter "C" or the word "ceiling" on the TLV or PEL shows the highest airborne concentration of a specific chemical that is allowed in the workplace. This concentration should never be exceeded, even for short periods of time. See also, "PEL" and "TLV."*

**Importance:** Chemicals that react rapidly in the body, causing ill health effects carry this value.

**CARCINOGEN** *A cancer-causing material.*

**Importance:** If a substance is known to be cancer causing, a potential health hazard exists and special protection and precaution sections should be checked

on the MSDS.

**C.A.S. NUMBER** *Chemical Abstracts Service Number.*

**Importance:** C.A.S. Numbers are used on MSDS's to identify specific chemicals.

**cc** *Cubic centimeter; a volume measurement in the metric system, equal in capacity to 1 milliliter (ml). One quart is about 946 cubic centimeters.*

**CHEMICAL FAMILY** *A group of single elements or compounds with a common general name. Example: acetone, methyl ethyl ketone, and methyl isobutyl ketone are of the "ketone" family; acrolein, furfural, and acetaldehyde are of the "aldehyde" family.*

**Importance:** Elements or compounds within a chemical family generally have similar physical and chemical characteristics.

**CHEMTREC** *Chemical Transportation Emergency Center; a national center established by the Chemical Manufacturers Association in Washington, D.C. in 1970, to relay pertinent emergency information concerning specific chemicals.*

**Importance:** Chemtrec has an emergency 24 hour toll free telephone number (800-424-9300).

**CHRONIC EFFECT** *An adverse effect on a human or animal body, with symptoms which develop slowly over a long period of time. Also, see D "Acute."*

**Importance:** The length of time that a worker is exposed is the critical factor. Long periods of time pass, with repeated exposure to a chemical, before any ill effects are detected in a worker .

**CHRONIC TOXICITY** *Adverse (chronic) effects resulting from repeated doses of or exposures to a substance over a relatively prolonged period of time.*

**Importance:** Ordinarily used to denote effects in experimental animals.

**CO** *Carbon monoxide, a colorless, odorless, flammable and very toxic gas produced by the incomplete combustion of carbon; also a byproduct of many chemical processes.*

**CO<sub>2</sub>** *Carbon dioxide, a heavy, colorless gas, produced by the combustion and decomposition of organic substances and as a by-product of many chemical processes. CO<sub>2</sub> will not burn and is relatively non-toxic (although high concentrations, especially in confined spaces, can create hazardous oxygen-deficient environments.)*

**Importance:** CO and CO<sub>2</sub> are often listed on MSDS's as hazardous decomposition products.

**COMBUSTIBLE** *A term used to classify certain liquids that will burn, on the basis of flash points. Both the National Fire Protection Association (NFPA) and the Department of Transportation (DOT) define "combustible liquids" as having a flash point of 100 °F (37.8 °C) or higher. See also, "Flammable."*

**Importance:** Combustible liquid vapors do not ignite as easily as flammable liquids; however, combustible vapors can be ignited when heated, and must be handled with caution. Class 11 liquids have flash points at or above 100°F, but below 140°F. Class 111 liquids are subdivided into two subclasses:

Class IIIA: Those have flash points at or above 140°F but below 200°F.

Class IIIB: Those having flash points at or above 200°F.

**CONCENTRATION** *The relative amount of a substance when combined or mixed with other substances.*

*Examples: 2 ppm Xylene in air, or a 50 percent caustic solution.*

**Importance:** The effects of overexposure depend on the concentration or dose of a hazardous substance.

**CORROSIVE** *As defined by DOT, a corrosive material is a liquid or solid that causes visible destruction or irreversible changes in human tissue at the site of contact on-- in the case of leakage from its packaging—a liquid that has a severe corrosion rate on steel.*

**Importance:** A corrosive material requires different personal protective equipment to prevent adverse health effects.

**DECOMPOSITION** *Breakdown of a material or substance (by heat, chemical reaction, electrolysis, decay, or other processes) into parts or elements or simpler compounds.*

**Importance:** Decomposition products often present different hazards than the original material .

**DERMAL** *Used on or applied to the skin.*

**Importance:** Dermal exposure, as well as inhalation exposure, must be considered to prevent adverse health effects.

**DERMAL TOXICITY** *Adverse effects resulting from skin exposure to a substance. Also referred to as "Cutaneous toxicity."*

**Importance:** Ordinarily used to denote

effects in experimental animals.

**EMERGENCY AND FIRST AID PROCEDURES** *Actions that should be taken at the time of a chemical exposure before trained medical personnel arrive.*

**Importance:** These procedures may lessen the severity of an injury or save a person's life if done immediately following a chemical exposure .

**EPA** *U. S. Environmental Protection Agency: Federal agency with environmental protection regulatory and enforcement authority.*

**Importance:** EPA regulations must be met for the disposal of hazardous materials, as well as in spill situations.

**EVAPORATION RATE** *A number showing how fast a liquid will evaporate.*

**Importance:** The higher the evaporation rate, the greater the risk of vapors collecting in the workplace. The evaporation rate can be useful in evaluating the health and fire hazards of a material.

**FLAMMABILITY LIMITS** *The range of gas or vapor amounts in air that will burn or explode if a flame or other ignition source is present.*

**Importance:** The range represents an unsafe gas or vapor mixture with air that may ignite or explode. Generally, the wider the range the greater the fire potential. Also, see LEL, LFL, UEL, UFL.

**FLAMMABLE** *A Flammable Liquid is defined by NFPA and DOT as a liquid with a flash point below 100 °F (37.8 °C).*

**Importance:** Flammable liquids provide ignitable vapor at room temperatures and must be handled with caution.

Precautions such as bonding and grounding must be taken. Flammable liquids are: Class I liquids and may be subdivided as follows:

Class IA: Those having flash points below 73°F and having a boiling point below 100°F.

Class IB: Those having flash points below 73°F and having a boiling point at or above 100°F.

Class IC: Those having flash points at or above 73°F and below 100°F.

**FLASH POINT** The lowest temperature at which vapors above a liquid will ignite. There are several flash point test methods and flash points may vary for the same material depending on the method used. Consequently so the test method is indicated when the flash point is given (150° PMCC 200° TCC etc. ) A closed cup type test is used most frequently for regulatory purposes. Flash point test methods:

*Cleveland Open Cup (CC)*

*Pensky Martens Closed Cup (PMCC)  
Setaflash Closed Tester (SETA)*

*Tag Closed Cup (TCC)  
Tag Open Cup (TOC)*

**Importance:** The lower the flash point temperature of a liquid, the greater the chance of a fire hazard.

**Formula** The conventional scientific designation for a material (water is H<sub>2</sub>O sulfuric acid is H<sub>2</sub>SO<sub>4</sub> Sulfur dioxide is SO<sub>2</sub>. etc.)

**Importance:** Chemical formulas identify specific materials.

**GENERAL EXHAUST** *A system for exhausting air containing contaminants from a general work area.*

*see also "Local Exhaust."*

**Importance:** Adequate ventilation is necessary to prevent adverse health effects from exposures to hazardous materials and vapor accumulations that can be a fire hazard.

**g** *Gram; a metric unit of weight. One U.S. ounce is about 28.4 grains.*

**g/kg** *Grams per kilogram; an expression of dose used in oral and dermal toxicology testing to indicate the grams of substance dosed per kilogram of animal body weight. See also "kg."*

**Importance:** A measure of the toxicity of a substance.

**HAZARDOUS MATERIAL** *in a broad sense a hazardous material is any substance or mixture of substances having properties capable of producing adverse effects on the health or safety of a human being.*

**Importance:** Knowing what a hazardous material is and what materials are hazardous is important in preventing adverse health or safety effects.

**IDLH** *IDLH or Immediately dangerous to life or health means an atmospheric concentration of any toxic, corrosive or asphyxiant substance that poses an immediate threat to life or would cause irreversible or delayed adverse health effects or would interfere with an individual's ability to escape from a dangerous atmosphere.  
(<http://www.osha.gov/>)*

**Importance:** Exposure to concentrations greater than the IDLH for any length of time can mean serious injury including death. As a safety margin, the Standards Completion Program IDLH values were based on the effects that might occur as a consequence of a 30-minute exposure.



However, the 30-minute period was NOT meant to imply that workers should stay in the work environment any longer than necessary, in fact, EVERY EFFORT SHOULD BE MADE TO EXIT IMMEDIATELY! (Source: <http://www.cdc.gov/niosh/npg/pgintrod.html>)

**INCOMPATIBLE** *Materials which could cause dangerous reactions from direct contact with one another are described as incompatible.*

**Importance:** on a MSDS, incompatible materials are listed to prevent dangerous reactions in the handling and storage of the material.

**INGESTION** *The taking of a substance through the mouth.*

**Importance:** A route of exposure to a hazardous material.

**INGREDIENTS** *A listing of chemicals that are in a mixture.*

**Importance:** Knowing exactly what chemicals and how much of each is in a mixture helps you to understand the potential hazard a mixture presents.

**INHALATION** *The breathing in of a substance in the form of a gas vapor fume mist or dust.*

**Importance:** A route of exposure to a hazardous material.

**INHIBITOR** *A chemical which is added to another substance to prevent an unwanted chemical change from occurring.*

**Importance:** Inhibitors are sometimes listed on a MSDS, along with the expected time period before the inhibitor is used up and will no longer prevent unwanted chemical reactions.

**IRRITANT** *A substance which by contact in sufficient concentration for a sufficient period of time will cause an inflammatory response or reaction of the eye skin or respiratory system. The contact may be a single exposure or multiple exposures. Some primary irritants: chromic acid, nitric acid, sodium hydroxide, calcium chloride, amines, chlorinated hydrocarbons, ketones, alcohols.*

**Importance:** Knowing that a substance is an irritant allows you to be aware of the signs and symptoms of overexposure.

**kg** *Kilogram; a metric unit of weight about 2.2 U.S. pounds See also "g/kg" "g" and "mg."*

**L** *Liter; a metric unit of capacity. A U.S. quart is about 9/10 of a liter.*

**LC** *Lethal Concentration: A concentration of a substance being tested which will kill a test animal.*

**LC<sub>50</sub>** *Lethal Concentration 50; The concentration of a material in air which on the basis of laboratory tests is expected to kill 50 percent of a group of test animals when administered as a single exposure (usually 4 hours). The LC<sub>50</sub> is expressed as parts of material per million parts of air by volume (ppm) for gases and vapors or as micrograms of material per liter of air ( $\mu\text{g/L}$ ) or milligrams of material per cubic meter of air ( $\text{mg/m}^3$ ) for dusts and mists as well as for gases and vapors.*

**Importance:** Both are measures of the toxicity of a substance.

**LD** *Lethal Dose; A concentration of a substance being tested which will kill a test animal.*

**LD<sub>50</sub>** *Lethal Dose 50; A single dose of a material which on the basis of*

*laboratory tests is expected to kill 50% of a group of test animals. The LD<sub>50</sub> dose is usually expressed as milligrams or grams of material per kilogram of animal body weight (mg/kg or g/kg).*

**Importance:** Both are measures of the toxicity of a substance.

**LEL OR LFL** *Lower Explosive Limit or Lower Flammable Limit of a vapor or gas; the lowest concentration (lowest percentage of the substance in air) that will produce a flash of fire when an ignition source (heat, arc, or flame) is present. See also, "UEL."*

**Importance:** At concentrations lower than the LEL/LFL, the mixture is too "lean" to burn.

**LOCAL EXHAUST** *A system for capturing and exhausting contaminants from the air at the point where the contaminants are produced (welding, grinding, sanding, dispersion operations). See also, "General exhaust."*

**Importance:** Adequate ventilation is necessary to prevent adverse health effects from exposures to hazardous materials and prevent vapor accumulations that can be a fire hazard.

**MATERIAL IDENTIFICATION** *The name of a chemical. It may be a trade name, chemical name or any other name a chemical is known by. On a MSDS this section also includes the name, address, and emergency telephone number of the distributing chemical company.*

**Importance:** Proper identification of a chemical allows an employee to get additional health hazard and safety information.

**m<sup>3</sup>** *Cubic meter; a metric measure of volume, about 35.3 cubic feet or 1.3 cubic yards.*

**MELTING POINT** *The temperature at which a solid substance changes to a liquid state. For mixtures, the melting range may be given.*

**Importance:** The physical state of a substance is critical in assessing its hazard potential, route of exposure and method of control.

**mg** *Milligram; a metric unit of weight. There are 1,000 milligrams in 1 gram (g) of a substance.*

**mg/kg** *Milligrams per kilogram; an expression of toxicological dose. see also, "g/kg."*

**Importance:** A measure of the toxicity of a substance .

**mg/m<sup>3</sup>** *Milligrams per cubic meter; a unit of measuring concentrations of dusts, gases, or mists in air.*

**Importance:** The effects of overexposure depend on the concentration or dose of a hazardous substance .

**mL** *Milliliter; a metric unit of capacity, equal in volume to 1 cubic centimeter (cc) or about 1/16 of a cubic inch. There are 1,000 milliliters in 1 liter (L).*

**mm Hg** *Millimeters (mm) of Mercury (Hg); a unit of measurement for low pressures or partial vacuums .*

**Importance:** Vapor pressures are expressed in mm Hg.

**MUTAGEN** *A substance or agent capable of altering the genetic material in a living cell.*

**Importance:** if a substance is known to be a mutagen, a potential health hazard exists, and special protection and precaution sections should be checked on the MSDS.

**NIOSH** *National Institute for Occupational Safety and Health of the Public Health Service, U.S. Department of Health and Human Services (DHHS).*

**Importance:** Federal agency which—among other activities—tests and certifies respiratory protective devices, recommends occupational exposure limits for various substances and assists in occupational safety and health investigations and research.

**NO<sub>x</sub>** *Oxides of Nitrogen; undesirable air pollutants.*

**Importance:** Often listed on a MSDS as a hazardous decomposition product.

**OLFACTORY** *Relating to the sense of smell.*

**Importance:** The olfactory organ in the nasal cavity is the sensing element that detects odors and transmits information to the brain through the olfactory nerves. This sense of smell is a "built in" vapor detector.

**ORAL** *Used in or taken into the body through the mouth.*

**Importance:** A route of exposure to a hazardous material.

**ORAL TOXICITY** *Adverse effects resulting from taking a substance into the body via the mouth.*

**Importance:** Ordinarily used to denote effects in experimental animals.

**OSHA** *Occupational Safety and Health Administration of the U.S. Department of Labor.*

**Importance:** Federal agency with safety and health regulatory and enforcement authorities for most U.S. industry and business.

**OXIDIZING AGENT, OXIDIZER** *A chemical or substance which brings about an oxidation reaction. The agent may (1) provide the oxygen to the substance being oxidized (in which case the agent has to be oxygen, or contain oxygen), or (2) it may receive electrons being transferred from the substance undergoing oxidation. DOT defines an oxidizer or oxidizing material as a substance which yields oxygen readily to stimulate combustion (oxidation) of organic matter.*

**Importance:** if a substance is listed as an oxidizer on the MSDS, precautions must be taken in the handling and storage of the substance. Keep away from flammables and combustibles.

**PEL** *Permissible Exposure Limit; an exposure established by OSHA regulatory authority. May be a Time Weighted Average (TWA) limit or a maximum concentration exposure limit. See also, "Skin"*

**Importance:** if a PEL is exceeded, a potential health hazard exists, and corrective action is necessary.

**POISON, CLASS A** *A DOT term for extremely dangerous poisons, that is, poisonous gases or liquids of such nature that a very small amount of the gas, or vapor of the liquid, mixed with air is dangerous to life. Some examples: phosgene, cyanogen, hydrocyanic acid, nitrogen peroxide .*

**POISON, CLASS B** *A DOT term for liquid, solid, paste, or semisolid substances—other than Class A poisons or irritating materials—which are known (or presumed on the basis of animal tests) to be so toxic to man as to afford a hazard to health during transportation.*

**Importance:** if a substance is known to be a poison, health and safety hazards

exist and special protection and precaution sections should be checked on the MSDS.

**POLYMERIZATION** *A chemical reaction in which one or more small molecules combine to form larger molecules. A hazardous polymerization is such a reaction which takes place at a rate which releases large amounts of energy.*

**Importance:** if hazardous polymerization can occur with a given material, the MSDS usually will list conditions which could start the reaction and the time period before any contained the inhibitor is used up.

**ppm** *Parts per million: a unit for measuring the concentration of a gas or vapor in air—parts (by volume) of the gas or vapor in a million parts of air. Also used to indicate the concentration of a particular substance in a liquid or solid.*

**Importance:** The effects of overexposure depend on the concentration or dose of a hazardous substance.

**ppb** *Parts per billion; a unit for measuring the concentration of a gas or vapor in air—parts (by volume) of the gas or vapor in a billion parts of air. Usually used to express measurement of extremely low concentrations of unusually toxic gases or vapors. Also used to indicate the concentration of a particular substance in a liquid or solid.*

**Importance:** The effects of overexposure depend on the concentration or dose of a hazardous substance.

**REACTION** *A chemical transformation or change; the interaction of two or more substances to form new substances.*

**Importance:** Knowledge of reactions can prevent unsafe chemical changes.

**REACTIVITY** *A description of the tendency of a substance to undergo chemical reaction with itself or other materials with the release of energy. Undesirable effects—such as pressure buildup, temperature increase, formation of noxious, toxic, or corrosive by-product—may occur because of the reactivity of a substance to heating, burning, direct contact with other materials or other conditions in use or in storage.*

**Importance:** Knowledge of what conditions to avoid can prevent failsafe chemical reactions.

**REDUCING AGENT** *in a reduction reaction (which always occurs simultaneously with an oxidation reaction) the reducing agent is the chemical or substance which (1) combines with oxygen, (2) loses electrons in the reaction. See also, "Oxidizing Agent."*

**Importance:** if a material is listed as a reducing agent on the MSDS, precautions must be taken in the handling and storage of the substance. Keep separate from oxidizing agents.

**RESPIRATORY SYSTEM** *The breathing system; includes the lungs and air passages (trachea or "windpipe," larynx, mouth, and nose) to the air outside the body, plus the associated nervous and circulatory supply.*

**Importance:** Inhalation is the most common route of exposure in the occupational workplace.

**SENSITIZER** *A substance which on first exposure causes little or no reaction in man or test animals, but which on repeated exposure may cause a marked*

*response not necessarily limited to the contact site. Skin sensitization is the most common form of sensitization in the industrial setting, although respiratory sensitization to a few chemicals is also known to occur.*

**Importance:** Knowing that a substance is a sensitizer allows you to be aware of the signs and symptoms of overexposure.

**"SKIN"** *A notation, sometimes used with PEL or TLV exposure data; indicates that the stated substance may be absorbed by the skin, mucous membranes, and eyes—either by airborne or by direct contact—and that this additional exposure must be considered part of the total exposure to avoid exceeding the PEL or TLV for that substance.*

**Importance:** Even if workplace concentrations of a chemical do not exceed the TLV or PEL, the risk to health may be severe because breathing and skin contact are combined. Skin protection is advised.

**SKIN SENSITIZER** See Sensitizer.

**SKIN TOXICITY** See Dermal Toxicity.

**SOLUBILITY IN WATER** *A term expressing the percentage of a material (by weight) that will dissolve in water at ambient temperature.*

**Importance:** Solubility information can be useful in determining spill cleanup methods and fire-extinguishing agents and methods for a material.

**SO<sub>x</sub>** Oxides of Sulfur; undesirable air pollutants.

**Importance:** Often listed on a MSDS as a hazardous decomposition product.

## **SPECIAL PRECAUTIONS**

*Instructions that describe proper handling and storage procedures specific to that material.*

**Importance:** Following these procedures would prevent excessive employee exposure. These procedures tell you additional information needed to handle the material safely.

## **SPECIAL PROTECTION**

**INFORMATION** *A description of engineering precautions and personal protection that should be provided when working with a chemical in order to reduce an employee's exposure.*

**Importance:** Reducing the potential for exposure reduces the risk to health and safety.

**SPECIFIC GRAVITY** *The weight of a material compared to the weight of an equal volume of water; an expression of the density (or heaviness) of the material*  
*Example: if a volume of a material weighs 8 pounds, and an equal volume of water weighs 10 pounds, the material is said to have a specific gravity of 0.8*

$$8 \text{ lb} / 10 \text{ lb} = 0.8$$

**Importance:** Insoluble materials with specific gravity of less than 1.0 will float in (or on) water. Insoluble materials with specific gravity greater than 1.0 will sink (or go to the bottom) in water. Most flammable liquids have specific gravity less than 1.0 and, if not soluble, will float on water—an important consideration for fire suppression and spill clean-up.

## **SPILL OR LEAK PROCEDURES**

*Steps that should be taken if a chemical spill or leak occurs*

**Importance:** Proper removal of a chemical spill or leak from the work area eliminates the potential accumulation of

hazardous concentrations of the chemical, reduces the risk of creating an environmental pollution problem and conforms with local, state and federal regulations.

**STABILITY** *An expression of the ability of a material to remain unchanged*

**Importance:** For MSDS purposes, a material is stable if it remains in the same form under expected and reasonable conditions of storage or use. Conditions which may cause instability (dangerous change) are stated—for example, temperatures above 150°F, shock from dropping .

**STEL** *Short Term Exposure Limit; ACGIH terminology See also, “TLV-STEL.”*

**SYNONYM** *Another name or names by which a material is known Methyl alcohol, for example, is also known as methanol, or wood alcohol*

**Importance:** A MSDS will list common name(s) to help identify specific materials.

**TERATOGEN** *A substance or agent to which exposure of a pregnant female can result in mal-formations in the fetus*

**Importance:** if a substance is known to be a teratogen, a potential health hazard exists and special protection and precaution sections should be checked on a MSDS.

**TLV** *Threshold Limit Value; a term used by ACGIH to express the airborne concentration of a material to which nearly all persons can be exposed day after day without adverse effects ACGIH expresses TLV's in three ways:*

**TLV-TWA:** *The allowable Time Weighted Average concentration for a*

*normal 8-hour workday or 40-hour work week*

**TLV-STEL:** *The Short-Term Exposure Limit, or maximum concentration for a continuous 15 minute exposure period (maximum of four such periods per day with at least 60 minutes between exposure periods, and provided that the daily TLV-TWA is not exceeded)*

**TLV-C:** *The Ceiling exposure limit—the concentration that should not be exceeded even instantaneously*

*TLV's are reviewed and revised annually where necessary by the ACGIH*

**Importance:** if a TLV is exceeded, a potential health hazard exists and corrective action is necessary. Also see “Skin” relative to TLV's.

**TOXICITY** *The sum of adverse effects resulting from exposure to a material, generally by the mouth, skin, or respiratory tract*

**Importance:** Knowledge of the toxicity of a material helps prevent adverse health effects from exposure.

**TRADE NAME** *The trademark name or commercial trade name for a material*

**Importance:** A MSDS will list trade name(s) to help identify specific materials.

**TWA** *Time Weighted Average exposure; the airborne concentration of a material to which a person is exposed, averaged over the total exposure time—generally the total work-day (8 to 1/2 hours) See also, “TLV”*

**UEL OR UFL** *Upper Explosive Limit or Upper Flammable Limit of a vapor or gas; the highest concentration (highest percentage of the substance in air) that will produce a flash of fire when an*

*ignition source (heat, arc, or flame) is present*

and “Local Exhaust”

**Importance:** At higher concentrations, the mixture is too “rich” to burn. see also, “LEL.”

**UNSTABLE** *Tending toward decomposition or other unwanted chemical change during normal handling or storage*

**Importance:** A MSDS will list materials that are unstable and conditions to avoid to prevent decomposition or unwanted chemical changes.

**VAPOR DENSITY** *The weight of a vapor or gas compared to the weight of an equal volume of air; an expression of the density of the vapor or gas. Materials lighter than air have vapor densities less than 1.0 (example: acetylene, methane, hydrogen) Materials heavier than air (examples: propane, hydrogen sulfide, ethane, butane, chlorine, sulfur dioxide) have vapor densities greater than 1.0*

**Importance:** All vapors and gases will mix with air, but the lighter materials will tend to rise and dissipate (unless confined). Heavier vapors and gases are likely to concentrate in low places—along or under floors, in sumps, sewers and manholes, in trenches and ditches—and can travel great distances undetected where they may create fire or health hazards.

**VAPOR PRESSURE** The pressure exerted by a saturated vapor above its own liquid in a closed container

**Importance:** The higher the vapor pressure, the easier it is for a liquid to evaporate and fill the work area with vapors which can cause health or fire hazards.

**VENTILATION** See General Exhaust,

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## Safety Problems for a Course in Stoichiometry

Originally Prepared by Daniel A. Crawl  
Michigan Technological University, Houghton, MI

- S-1** The minimum ignition energy (MIE) is the minimum energy input required to initiate combustion in a flammable mixture. For flammable gases it is typically 0.1 mJ and for dusts it is typically 10 mJ, although substantial variation can be expected with specific materials.

The mass of a penny is typically 2.6 gms. How far must this penny be raised to contain potential energy equivalent to 0.1 mJ?

- S-2** Calculate the number of liters per year of liquid that can be transported through the following pipe sizes assuming a constant liquid velocity of 1 meter/sec.
- a) 3 cm ID
  - b) 5 cm ID
  - c) 25 cm ID
  - d) 50 cm ID

Comment on the magnitude of the result and the necessity for large pipe sizes in a chemical plant.

- S-3** Calculate the number of kg per year of ideal gas that can be transported through the following pipe sizes assuming a gas velocity of 3 meters/sec, a pressure of 689 kPa gauge, a temperature of 25°C, and a molecular weight of 44.
- a) 3 cm ID
  - b) 5 cm ID
  - c) 25 cm ID
  - d) 50 cm ID

Comment on the magnitude of the result and the necessity for large pipe sizes in a chemical plant.

- S-4** Large storage tanks are only capable of withstanding very low pressures or vacuums. Typically they are constructed to withstand no more than 20.3 cm of water gauge pressure and 6.3 cm of water gauge vacuum.
- A particular tank is 10-m in diameter.
- a) If an 80 kg person stands in the middle of the tank roof, what is the resulting pressure (in Pa) if the person's weight is distributed across the entire roof?
  - b) If the roof were flooded with 20.3 cm of water (equivalent to the maximum pressure), what is the total weight (in kg) of the water?

- S-5** A low pressure storage tank is padded with nitrogen. The purpose of the padding is to remove oxygen and to prevent a flammable atmosphere from forming in the tank due to the presence of a flammable liquid.
- A particular tank is padded with nitrogen to a total pressure of 0.03 psig. If the tank is at 55°F in the morning and is heated to 85°F in the afternoon, what will be the final pressure in the tank? If the maximum design pressure of the tank is 8 inches of water gauge, has the design pressure been exceeded?

**S-6** How much acetone liquid (in mls) is required to produce a vapor concentration of 200 ppm (parts per million) by volume in a room of dimensions 3 x 4 x 10 meters? The temperature is 25°C and the pressure is 1 atm. The following physical property data are available for acetone:

Molecular weight: 58  
Specific gravity: 0.781

**S-7** The lower flammability limit (LFL) for a gas is the minimum concentration of the gas, in air, below which there is too little fuel to support combustion. For propane the LFL is 2.1%.

- a) How many kg of propane are required to fill a room of dimensions 10 x 10 x 3 m if the final mixture is stoichiometric with air?
  - b) What is the volume percent concentration at the stoichiometric concentration?
  - c) How many kg of propane are required to fill the same room to a concentration equal to the LFL?
- For all cases assume a temperature of 25°C and a pressure of 1 atm.

**S-8** The flash point is the temperature below which a liquid is unable to produce enough vapor to support a combustion in air. For flammable materials mixed with a non-flammable material (such as water), the flash point of the mixture will occur at a temperature at which the partial pressure of the flammable component is equal to the saturation vapor pressure of the pure component at the flash point.

Acetone is used as a solvent in a laboratory. There is some concern about the fire hazards associated with acetone. One solution is to dilute the pure acetone with water, thus increasing the flash point and reducing the fire hazard.

Acetone has a reported flash point of 0°F. It's vapor pressure is represented by the Antoine equation:

$$\ln(P^{sat}) = 16.6513 - \frac{2940.46}{-35.93 + T}$$

Where

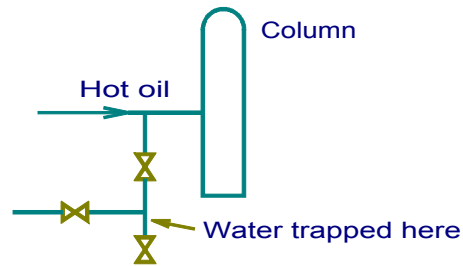
$P^{sat}$  is the saturation vapor pressure (mm Hg)  
 $T$  is the absolute temperature, K.

What mole fraction of water in an acetone-water solution is required to raise the flash point of the mixture to 50°F? to 100°F? Acetone is completely soluble in water.

**S-9** The liquid level in a tank 10 meters in height is determined by measuring the pressure at the bottom of the tank. The level gauge was calibrated to work with a liquid having a specific gravity of 0.9. If the usual liquid is replaced with a new liquid with a specific gravity of 0.8, will the tank be overfilled or underfilled? If the actual liquid level is 8 meters, what is the reading on the level gauge? Is it possible that the tank will overflow without the level gauge indicating the situation?

- S-10** The column shown below was used to strip low-volatile materials from a high temperature heat transfer fluid. During a maintenance procedure, water was trapped between the valves shown on the figure. During normal operation, the upper valve was opened and the hot oil came in contact with the cold water. The result was almost sudden vaporization of the water, followed by considerable damage to the column.

Consider liquid water at 25°C and 1 atm. How many times does the volume increase if the water is vaporized into vapor at 100°C and 1 atm?



- S-11** Inerting is a procedure by which oxygen is removed from a tank or process vessel using an inert gas, such as nitrogen.

One procedure for inerting pressure vessels is to pressurize the vessel with nitrogen and then vent the tank back to atmospheric pressure. The cycle is repeated until the oxygen concentration is lowered to satisfactory levels.

- a)** Show that, using a source of pure nitrogen, the oxygen concentration at the end of the  $j$ th pressurization cycle is given by

$$y_j = y_o \left( \frac{P_L}{P_H} \right)^j$$

Where

$y_j$  is the oxygen concentration at the end of the  $j$ th cycle.

$y_o$  is the initial oxygen concentration,

$P_L$  is the low pressure in the cycle,

$P_H$  is the high pressure in the cycle, and

- b)** Show that the total nitrogen used for the procedure is given by

$$\Delta n_{N_2} = j(P_H - P_L) \frac{V}{R_g T}$$

Where

$\Delta n_{N_2}$  is the total nitrogen used,

$V$  is the total vessel volume,

$R_g$  is the ideal gas constant, and

$T$  is the absolute temperature.

- c) A  $10 \text{ m}^3$  vessel contains air at 1 atm and  $25^\circ\text{C}$ . How many complete pressurization cycles with nitrogen are required to reduce the oxygen concentration to less than 1% by volume? Pure nitrogen is available at a pressure of 3.5 bars gauge. How many kg of nitrogen are used?

- S-12** The equations developed in problem S-11 apply to pressurization using a source of pure nitrogen. Show that for a source of nitrogen containing oxygen at a concentration of  $y_{\text{oxy}}$ , the concentration at the  $j$ th pressurization cycle is given by,

$$y_j = y_{j-1} \left( \frac{P_L}{P_H} \right) + y_{\text{oxy}} \left( 1 - \frac{P_L}{P_H} \right)$$

If the nitrogen supply in problem **S-11** contains 0.5% oxygen, how many cycles are now required?

## Safety Problems for a Course in Thermodynamics

Originally Prepared by J. Reed Welker  
University of Arkansas, Fayetteville AR

### T-1 Thermodynamics Principle: Adiabatic expansion of an ideal gas

#### Health and Safety Concept: Explosion Prevention

**Background:** There are a number of ways in which explosions may occur in a chemical plant or other places. One of those is simply that a tank containing a compressed gas may rupture. The rapidly expanding gas can damage property and injure or kill people. Codes and standards under which tanks are built have been very effective in promoting sound engineering practices, and such explosions are quite unusual. However, they can happen, and it is worthwhile to estimate how much damage might be done.

**Problem:** Compressed air is provided for the instrument air system in a chemical plant. The normal maximum pressure for the air delivery system is 150 psig, and a safety valve is placed on the air storage tank and set at 165 psig. The 1000-gallon storage tank has been in service for a long time, and there is some internal corrosion which has weakened the tank. One day the automatic pressure switch fails, and the tank pressure rises above the 150-psig set point. The safety valve fails to operate because of internal corrosion, and the tank explodes when the pressure reaches 214 psig. You may assume the gas to be ideal, and the specific heat of air is  $C_p = 0.25$  Btu/lb-°F. The expansion may be assumed to be adiabatic and reversible, and the temperature of the air in the tank when it fails is 120°F.

- a) Calculate the work done by the expanding gas.
- b) TNT generates about 2000 Btu/lb when it explodes. How many lb of TNT does the work of the air tank explosion equal?
- c) Is the assumption that the explosion of the tank is adiabatic reasonable?
- d) Is the assumption of reversibility reasonable?

### T-2 Thermodynamics Principle: Adiabatic expansion of high pressure liquid to gas

#### Health and Safety Concept: Explosion Prevention

**Background:** Kim-E and Reid discuss an interesting phenomenon in *Chemical Engineering at Supercritical Fluid Conditions*, Ann Arbor Science Publishers (1983). Carbon dioxide fire extinguishers exploded spontaneously because of stress-corrosion cracking that may have been caused by incomplete drying following hydrostatic testing. They provide detailed thermodynamic analysis of the problem, but we will be satisfied with a simpler analysis. Our goal will be to

make an estimate of the energy released following failure of a fire extinguisher. The energy release might then be used to estimate the damage, although we will not carry the analysis that far.

**Problem:** A carbon dioxide fire extinguisher contains 20 lb of  $\text{CO}_2$  stored at an ambient temperature of  $75^\circ\text{F}$ . Internal corrosion occurs, and one night, while there is no one in the building, the extinguisher explodes. How much work is done by the expanding gas? What is the TNT equivalent of the explosion if TNT does work at 2000 Btu/lb when it explodes? You may assume the expansion is adiabatic and reversible, but the  $\text{CO}_2$  is not an ideal gas. The *Chemical Engineers' Handbook*, 5th ed, gives thermodynamic data for carbon dioxide. You may assume that the  $\text{CO}_2$  in the fire extinguisher is all liquid. Note that carbon dioxide does not form a liquid when reduced to atmospheric pressure, but instead forms solid and vapor phases. Does the assumption of reversibility seem reasonable?

**T-3 Thermodynamic Principle:** Adiabatic expansion of high pressure liquid to gas

**Health and Safety Concept:** Explosion Prevention

**Background:** A number of commercially-important gases are shipped and stored under high pressures. Some gases liquefy because the pressure is high enough to be the vapor pressure of the material at the storage pressure. Under such conditions, there will be two phases in the storage tank: a liquid phase and a vapor phase. The two phases will be very nearly in equilibrium because the storage conditions preclude large temperature gradients in the tanks. If a storage tank containing liquid under a high pressure fails, the liquid will no longer be at its vapor pressure. Instead, the pressure will be reduced and the liquid will vaporize very rapidly, usually within milliseconds of pressure reduction. As the liquid vaporizes, there is a very large volume increase. The large volume of vapor thus formed will expand rapidly, with explosive force. The phase change and expansion are so rapid that the entire process is essentially adiabatic. The blast damage can be substantial.

**Problem:** A tank containing  $100\text{ m}^3$  of liquid propane is overheated during a fire and ruptures. The pressure in the tank at the time of rupture is 20 bar gauge. The resulting explosion is called a BLEVE (for Boiling Liquid Expanding Vapor Explosion). Determine the amount of work done when the tank explodes. What is the equivalent explosion work in terms of kg of TNT if one kg of TNT does 1120 kcal of work in exploding? Data for this problem can be found in the *Chemical Engineers' Handbook*. The amount of vapor in the tank at the time the tank ruptures is small enough to be neglected.

**T-4 Thermodynamics Principle:** Adiabatic expansion of high pressure liquid to gas

**Health and Safety Concept:** Explosion prevention

**Background:** A number of commercially-important gases are shipped and stored under high pressures. Some gases liquefy because the pressure is high enough to be the vapor pressure of the material at the storage pressure. Under such conditions, there will be two phases in the storage tank: a liquid phase and a vapor phase. The two phases will be very nearly in equilibrium because the storage conditions preclude large temperature gradients in the tanks. If a storage tank containing liquid under a high pressure fails, the liquid will no longer be at its vapor pressure. Instead, the pressure will be reduced and the liquid will vaporize very rapidly, usually within milliseconds of pressure reduction. As the liquid vaporizes, there is a very large volume increase. The large volume of vapor thus formed will expand rapidly, with explosive force. The phase change and expansion are so rapid that the entire process is essentially adiabatic. The blast damage can be substantial. The potential for such an explosion is not only present for what we normally think of as hazardous materials. It also occurs for such mundane materials as water. The danger also occurs under conditions where no chemical processing occurs, so we must extend our vigilance to all situations where danger might exist.

**Problem:** The thermostat on a 40-gal water heater fails and the water is heated to a much higher temperature than normal. The relief valve also fails to operate and the water tank ruptures. The tank ruptures when the water reaches 300°F and you may assume the process of expansion following the tank rupture to be adiabatic and reversible. What is the TNT equivalent of the explosion if TNT does 2000 Btu/lb of work when it explodes? (Most home water heaters are 40 gal or larger.)

In January, 1982, a water heater in the cafeteria of a school in Spencer, Oklahoma, exploded following a failure of the thermostat and the relief valve. Seven people were killed and 33 were injured. All were in the room next to the room where the water heater was located. It was estimated that the water heater failed at a pressure of 87 psi.

**T-5 Thermodynamic Principle:** Expansion of a confined liquid

**Health and Safety Concept:** Release Prevention

**Background:** We normally think of liquids as being quite incompressible. In fact, liquids are at least slightly compressible, particularly when the system temperature is near the critical point. Liquids also have larger changes in density (or specific volume) when the temperature changes than when the pressure changes. As an example, you might have seen gasoline leaking from an overfilled fuel tank on a car that had been filled with gasoline from a cool underground tank. When the fuel warmed after the tank was filled, the tank began to leak. In the transportation and storage of chemicals in industry, considerable effort is taken to prevent overfilling of tanks. Liquids are always stored with an ullage space at the tank top to allow for liquid expansion. The amount of ullage space can be

estimated from thermodynamic data for the liquid and an estimate of the temperature range over which the liquid will be stored.

**Problem:** A common problem encountered in the transport of liquefied gases is that the transporting tank may be overfilled. Assume that liquid propylene is taken from ambient pressure storage in a refrigerated tank. It is initially saturated at 15.0 psia, just slightly above ambient pressure. The propylene is transferred to a tank truck. The tank on the truck has a total volume of 8000 gal. The total quantity of propylene transferred to the truck tank is 7800 gal. As the propylene begins to warm, it will expand. At what temperature will the tank be completely filled with liquid? Might filling the tank with 7800 gal lead to a safety problem? If so, what is the maximum amount (in gal) that may be safely loaded if the temperature of the liquid may reach 100°F on a hot summer day? Thermodynamic data may be found in the *Chemical Engineers' Handbook*.

**T-6 Thermodynamics Principle:** Flow work for expansion of an ideal gas

**Health and Safety Concept:** Ignition prevention

**Background:** Many of the common chemicals used in industrial processes are flammable. When they are stored or transported, there is always a chance that they may be spilled. If a flammable material is spilled, a flammable mixture of fuel and vapor will usually be formed. Once the mixture is formed, the only way to prevent its ignition is to keep it from contacting an ignition source. For that reason, great care is taken to eliminate sources of ignition in the vicinity where flammable materials are stored. National fire codes are quite strict in specifying storage conditions and handling conditions for liquids that might ignite. One method for reducing ignition sources is to keep electrical equipment that might generate sparks or arcs away from the area where flammable materials are used.

**Problem:** It is necessary to transfer carbon disulfide from drums to a storage tank in a chemical processing unit. Carbon disulfide is very easily ignited: its lower flammable limit (LFL) is 1.3 percent in air, and its ignition temperature is about 100°C. Thus, ordinary electrically-driven portable pumps cannot be used because they might ignite the carbon disulfide. An air-driven pump is available. It generates 0.25 horsepower by expanding air through a flow engine. The air comes from the plant air system, and is at 125 psig and 80°F when it enters the engine. Assuming that the engine operates adiabatically and reversibly, how many standard cubic feet of air must flow through the engine every minute to generate the 0.25 horsepower? The air behaves ideally and has a heat capacity  $C_p = 0.25$  cal/gram-K.



**T-7 Thermodynamics Principle:** Adiabatic flash of a superheated liquid

**Health and Safety Concept:** Relief venting of superheated liquid

**Background:** A number of chemicals are transported and stored as liquids under high pressure. If these chemicals cannot be kept confined under a pressure equal to or higher than their vapor pressure, they will flash, becoming part liquid and part vapor. If the chemical is released to the atmosphere, two potential problems occur. The chemical may be either flammable or toxic. In either case, the chemical must be prevented from being released to the atmosphere. One way of preventing the release is to provide tanks that can hold the chemical if it must be taken from the normal storage or disposal system. A relief valve is usually provided to prevent overpressure, and the relief valve cannot simply allow the chemical to go to the atmosphere. The chemical flowing through the relief valve is discharged into a tank at atmospheric pressure. If the chemical was at a high pressure before going through the relief valve, it will partially flash to become a vapor-liquid mixture. The vapor will occupy a large volume and might be flared for disposal. The liquid will be stored temporarily until it can be recovered and put back into the process or disposed of safely.

**Problem:** Butadiene is used in a chemical processing plant as an intermediate processing material. It is pumped through the plant as a liquid at ambient temperature of 80°F and a pressure high enough to keep it in the liquid phase. If there is a process shutdown, the butadiene, which comes from another part of the plant more than a mile away, cannot be shut off quickly. The butadiene is therefore shunted through a relief system to an atmospheric pressure holding tank, where it flashes partly to vapor as it enters the tank. The pumping rate is 2 m<sup>3</sup>/min and the design will provide shutdown within 5 minutes. How large a tank will be required to contain *all* the butadiene? How large will the tank have to be if the vapor is vented from the tank through a flare? The catch tank will initially be filled with nitrogen, and you may assume for convenience that the nitrogen is displaced by plug flow as the butadiene enters. Thermodynamic data can be found in the *Chemical Engineers' Handbook*.

**T-8 Thermodynamics Principle:** Energy balance with kinetic and potential energy

**Health and Safety Concept:** Stopping mechanical equipment safely

**Background:** Safety does not always apply only to the chemical plants where people work. People also have to travel to their jobs. Thermodynamic analyses do not always apply only to problems in the chemical plant. They also apply to ordinary problems at home and during activities at other places. One of the most common causes of accidental death is automobile accidents. Well-designed brakes are an important part of the automobile. Under heavy usage, the brakes may overheat and fail. An estimation of the temperature of the brake components is helpful in brake design.

**Problem:** Most chemical engineering problems involving the energy balance neglect the kinetic and potential energy terms, but those terms are not always negligible. In addition, the energy balance can be used to solve a number of other kinds of problems. For example, a car has disk brakes. The disks are steel, weigh about 15 lb, and have a heat capacity of about 0.11 Btu/lb-°F. The brake pads are a composite material. There are two pads per wheel, and the pads weigh about one pound each and have a heat capacity of about 0.2 Btu/lb-°F. If the driver makes a panic stop from 55 mi/hr and the car weighs 3600 lb, estimate the maximum temperature that might be reached by the brake disks and pads. The brake disks and pads are initially at 75 °F.

**T-9 Thermodynamics Principle:** Expansion of a confined liquid

**Health and Safety Concept:** Release Prevention

**Background:** The density (or specific volume) of a liquid does not change very much when the pressure on the liquid is changed. Neither does the density change much when small temperature changes occur. However, if the liquid is confined, a small rise in temperature will cause a *very* large change in pressure. If the liquid is confined in a pipe, and if there is no vapor space in the pipe, the pressure can easily become so large that the pipe will crack or burst. There is not much data in the literature on the density of compressed liquids because the effect is small enough to neglect for most purposes. However, pressure and temperature effects must sometimes be estimated for liquids. One of the ways we can estimate the effect a higher temperature will have on a confined liquid is to calculate the pressure required to keep the density of the liquid constant when the temperature is increased. We can make the estimate using an equation of state if an equation of state can be found that represents the liquid PVT behavior.

**Problem:** Benzene is transported in a Schedule 40 pipe. Benzene has a freezing temperature of 5.5 °C, so if the temperature becomes too low, the benzene may freeze in the pipe. Normally, the benzene flowing through the pipe is hot enough that even on the coldest day, it will not freeze. Even if the benzene freezes, the pipe will not burst, because (unlike water) benzene contracts when it freezes. During a particularly cold spell, the benzene pipe is shut in and the benzene freezes in the line, which is several hundred feet long. A while later, a malfunctioning steam trap allows a large quantity of water to spill, forming a pool of hot water which is trapped in the containment trench under the benzene pipeline. The hot water warms the benzene in the pipe, and the pipe bursts. You point out that the ends of the pipe were still frozen when the pipe ruptured, and that the relief valve was connected at the portion of the pipe where the benzene was frozen, so it could not be expected to operate. You also postulate that the pipe was full of liquid, and that the warming will cause the liquid to tend to expand. Your boss asks you to estimate how high the temperature must have gone to cause the pipe to rupture. You cannot find data for the effect of temperature on the density of liquid benzene, so

you decide to make the best estimate you can in a short time using the Peng-Robinson equation of state. For this problem, you are to calculate the pressure exerted by liquid benzene if its volume remains constant at the specific volume at 5.5 °C and the liquid temperature increases. Make the calculations for a temperature range of 5.5 °C to 20 °C and plot the results. Is the pressure rise high enough to cause the pipe to rupture? Compare the results of your plot with any data you can find in the literature. (A pipe rupture followed by a spill of several hundred barrels of benzene actually occurred under circumstances similar to those described here during the winter of 1995-96.)

**T-10 Thermodynamics Principle:** Properties of a real gas

**Health and Safety Concept:** Personal emergency equipment

**Background:** Many of the chemicals used in commerce and trade are toxic. (Actually, many newspaper writers and television newscasters believe that the word “chemical” should always be preceded by an adjective like “hazardous,” “toxic,” or “poisonous.” If they are correct, we do a marvelous job of protecting society from such effects.) If toxic chemicals are processed in a chemical plant, it is possible that spills and leaks may occur. While our goal is to prevent all releases, if they happen, we must protect workers from the toxic effects of the chemicals. One method of protection is to provide a self-contained breathing apparatus (SCBA) that will provide enough air for the worker to either control the spill or to escape from the spill area. Common SCBA equipment is designed for storing air under pressures of about 2200 psi or 4500 psi, and the air supply may be sufficient for 30 minutes or 60 minutes. At such high pressures, air does not behave like an ideal gas.

**Problem:** Determine the volume required for a portable personal emergency air system if the delivery rate of air must be 40 liters/minute and the maximum pressure in the supply tank can be either 2215 psia or 4500 psia. Find the volume for both 30 minutes and 60 minutes supply at both pressures. Assume the tank temperature to be about 80 °F.

**T-11 Thermodynamics Principle:** Adiabatic expansion of high pressure liquid to gas

**Health and Safety Concept:** Explosion Prevention

**Background:** A number of commercially-important gases are shipped and stored under high pressures. Some gases liquefy because the pressure is high enough to be the vapor pressure of the material at the storage pressure. Under such conditions, there will be two phases in the storage tank: a liquid phase and a vapor phase. The two phases will be very nearly in equilibrium because the storage conditions preclude large temperature gradients in the tanks. If a storage tank containing liquid under a high pressure fails, the liquid will no longer be at its vapor pressure. Instead, the pressure will be reduced and the liquid will vaporize very rapidly, usually within milliseconds of pressure reduction. As the liquid vaporizes, there is a very large volume increase. The large volume of vapor thus

formed will expand rapidly, with explosive force. The phase change and expansion are so rapid that the entire process is essentially adiabatic. The blast damage can be substantial. The potential for such an explosion is not only present for what we normally think of as hazardous materials. It also occurs for such mundane materials as water. The danger also occurs under conditions where no chemical processing occurs, so we must extend our vigilance to all situations where danger might exist.

**Problem:** Aluminum soft drink cans are recycled because recycling is cheaper than making new aluminum. (It also makes good ecological sense because aluminum cans degrade the environment if they are discarded.) The cans are recycled by melting them. Occasionally, one of the cans will contain some water when it enters the recycling furnace. The water can be superheated in the can. At some point the water will exceed the superheat limit and flash to steam (and residual liquid water). Assume for this problem that the can has not been opened and that the water heats to its saturation temperature at the can pressure limit. An aluminum soft drink can is designed for an internal pressure of 90 psig. If the can ruptures, estimate the energy released as the high temperature liquid inside (which you may assume to be pure water) flashes to steam and hot water.

## T-12 Thermodynamics Principle: Heat of combustion

**Health and Safety Concept:** Fire and explosion prevention

**Background:** Almost anyone knows that explosives can do a lot of damage if used carelessly or under the wrong conditions. However, even most engineers do not understand just how little energy is involved in most explosions. For example, a human requires about 2000 kcal/day of energy to live at a moderate work level, and people who do hard physical work all day may require twice that or more. In terms of Btu, 2000 kcal is about 8000 Btu. The energy released when one pound of TNT detonates is about 2000 Btu. Thus, every day an average human expends the energy equivalent of about 4 lb of TNT. Now 4 lb of TNT can do some substantial damage when it detonates. However, if the energy is dissipated slowly, the work done is much more benign. We also do not think of the amount of energy required for use in our daily lives. A common home furnace may generate 50,000 Btu/hr of heat just to keep a house warm, and what seems like an enormous amount of energy is used for transportation. If the energy is used improperly, a substantial risk can result. We can estimate the energy available from common fuels quite easily based on their heat of combustion.

**Problem:** Gasoline has a heat of combustion of about 120,000 Btu/gal. The exact value depends on the blend of chemicals in the gasoline and whether the products of combustion are gases or liquids. One pound of TNT will produce about 2000 Btu of work when it detonates. Assuming that all the heat of combustion in the gasoline is converted to work, how many gallons of gasoline are required to equal the work in one pound of TNT? What is the equivalent number of pounds of TNT in the energy released when all the gasoline in an automobile tank is burned? Assume the tank

contains 16 gallons of gasoline.

**T-13 Thermodynamics Principle:** Gas-liquid equilibrium

**Health and Safety Concept:** Fire and explosion prevention

**Background:** Many common industrial chemicals are flammable. If they are used in a process, they must be kept under strict control to prevent fires. Since almost any combustible material may also support an explosion under the proper conditions, it is also necessary to keep strict control to prevent explosions. One method of preventing fires and explosions is to exclude oxidizers from mixing with flammable materials. Fuel, an oxidizer, and an ignition source are all required to be together at the same time to start a fire or to initiate an explosion. Nitrogen is an inert gas that is readily available and reasonably inexpensive, so it is frequently used as an inerting agent. If used in continuous processes, the nitrogen is frequently separated from the flammable chemical and recycled.

**Problem:** Nitrogen is used to dry propane from a solid in a processing plant. Nitrogen is used because the propane-nitrogen mixture is not flammable. However, the propane-nitrogen mixture cannot be discharged to the atmosphere because it would be unsafe and because it would be expensive. The nitrogen coming from the drying equipment contains 27 mole percent propane at 100°F and 1.0 atm. In order to separate the propane from the nitrogen, the mixture is compressed and the propane is contacted with n-decane. The decane absorbs some of the propane from the nitrogen. The absorber operates at 200 psia and 80°F. You may assume that the concentration of propane in the decane leaving the absorber is 95 percent of its equilibrium concentration (in terms of mole fraction). The decane-propane mixture is then taken to a flash drum where the pressure is reduced to 1.0 atm and the temperature is controlled at 60°F. Some of the decane-propane mixture flashes to vapor. The remainder is recycled back to the absorber. You may assume that the nitrogen is insoluble in the decane and that the liquid and gas mixtures are ideal. Raoult's law may thus be used for the solution. Determine:

- a) The mole fraction of propane in the liquid mixture leaving the absorber.
- b) The concentrations of both the liquid and vapor streams leaving the flash drum.

The vapor pressures of propane and decane may be obtained from the following equations, which are taken from *The Properties of Gases and Liquids* by Reid, Prausnitz, and Sherwood (1977).

$$\ln(P_p^V) = 15.7260 - \frac{1872.46}{T - 25.16}$$

*and*

$$\ln(P_D^V) = 16.0114 - \frac{3456.80}{T - 78.67}$$

The vapor pressures are in mm Hg and the temperatures are in Kelvins. The solution of the problem requires some extrapolation of the vapor pressures beyond the range of best accuracy for the equations, but allows the problem to be worked easily.

- c) Describe how you would work this problem if you could not assume ideal behavior.

#### T-14 Thermodynamics Principle: Adiabatic heat of reaction

**Health and Safety Concept:** Disposal of hazardous materials

**Background:** Hazardous materials must be disposed of responsibly if they cannot be recycled or separated and used. The materials may be disposed of by chemical reactions, and the reaction used for most organic chemicals is combustion. In order to assure that the organic material is completely destroyed, it must be reacted at temperatures high enough to assure complete combustion. The products of complete combustion, which are usually water and carbon dioxide, may be safely discharged to the atmosphere. Note that if the organic material contains sulfur or nitrogen, the product gases may have to be scrubbed to remove the acid gases formed during combustion. Even if there is no nitrogen in the organic molecule, some nitrogen oxides will likely be formed during combustion. Most of the nitrogen in the organic molecule will be changed to molecular nitrogen during combustion.

**Problem:** We have a mixture of acetone, water, and some trace organic materials. We must dispose of the mixture, and one method of doing so is to burn it. The temperature of the combustion products must be above 1000°C in order for the trace organic compounds, which are highly toxic, to be destroyed. The mixture is 78 percent by weight acetone, and the balance may be considered to be water. The other organics are too small in concentration to be important. You may assume that the combustion reaction goes to completion. The liquid mixture is initially at 25°C. Will combustion of the

mixture using 25 percent excess air provide the 1000°C temperature required? You may assume that the heat capacities are constant (unless your instructor advises you otherwise), and the following values apply:

<u>Material</u>	<u>Heat capacity, J/gmole K</u>
Water, liquid	75
Acetone, liquid	129
Water, gas	38
Oxygen, gas	37
Nitrogen, gas	32
Carbon dioxide, gas	74

Heat of vaporization, J/gmole

Water	41,000
Acetone	32,000

The heat of combustion of acetone can be calculated from heats of formation.

**T-15 Thermodynamics Principle:** Adiabatic decomposition of a gas

**Health and Safety Concept:** Explosion prevention

**Background:** Many industrial gases are transported in cylinders under high pressure. In a few cases, the gas has a positive heat of formation. A chemical that has a positive heat of formation is naturally unstable, because it can undergo an exothermic reaction without the addition of any other chemical. Such chemicals can be stable until they are subjected to high temperatures or to shock. They then react (through decomposition) very rapidly. The rapid decomposition may result in a deflagration or a detonation, damaging plant facilities and endangering workers.

**Problem:** Acetylene is a very unstable gas that has a high positive heat of formation. Because the heat of formation is positive, if the acetylene decomposes, a large release of energy will occur. Assume that you have acetylene contained by a pressure vessel at 25°C and 100 psia pressure. If the acetylene decomposes, both the temperature and the pressure will increase. Estimate the temperature and pressure of the products if the reaction occurs inside the storage vessel. Since the initial pressure is relatively low and the final temperature high, you may assume that all gases behave ideally. However, the heat capacities of the acetylene, carbon, and hydrogen are not constant. Heat capacities and heats of formation for these materials may be found in the *Chemical Engineers' Handbook*. The reaction will be rapid enough that you may assume it to be adiabatic.

**T-16 Thermodynamics Principle:** Dew point calculation

**Health and Safety Concept:** Safe handling of gas mixtures

**Background:** Most industrial processes use mixtures of chemicals, whether there is a reacting mixture or a product mixture that must be separated. When a vapor mixture is being processed, it must be kept in mind that the vapor might condense, and that the dew point temperature depends on both the pressure and the composition of the mixture. (Stated in another way, the dew point pressure depends on both the system temperature and the composition.) The Gibbs Phase Rule can be applied to such a condition, and it shows that if the composition is known, only the temperature or pressure may be specified independently. Thus, if we are to handle vapor mixtures in a single phase, we must be careful not to use process conditions where two phases will form. We usually try to avoid processing streams that contain both liquid and vapor.

**Problem:** In the natural gas industry, peak demands for winter gas supply are sometimes met by mixing propane and air together to produce a mixture that has the same heat of combustion as natural gas. Assume that such blending has taken place and that the propane-air mixture has been blended with natural gas and is being distributed through a pipeline to the customers. Severe safety problems can occur if the propane condenses out of the propane-air-natural gas mixture. Assume the blending process has resulted in a mixture that is 70 mole percent methane, 7 mole percent ethane, 11 mole percent propane, and the balance air. Then assume the gas temperature can fall to - 20 °F in some parts of the pipeline. Determine the highest pressure that the gas may be allowed to reach before liquid begins to condense from the mixture. Also determine the concentration of each of the components in the liquid mixture that forms.

**T-17 Thermodynamics Principle:** Adiabatic flash of multi-component liquid

**Health and Safety Concept:** Relief venting of superheated liquids

**Background:** There are many instances in chemical processes when multi component liquid mixtures are processed at temperatures above their atmospheric pressure bubble point. The pressure under which processing takes place must then be kept above the bubble point pressure of the mixture in order to prevent the mixture from vaporizing. If process pressures become too high, the liquid mixture will be vented through a relief valve to a lower pressure, usually atmospheric pressure. When the pressure is reduced, part of the liquid will flash to vapor and part will remain as a liquid. Proper design of relief systems requires that the vapor and liquid thus formed be disposed of without being discharged to the air or water at the plant. One way of safely disposing of the vapor is to send it to a flare stack, but it must be separated from the liquid first. The liquid, which has a much lower volume, can be contained in the flash tank for later disposal or recovery.

**Problem:** Determine the fraction of vapor and the composition of the vapor



and liquid phases when a feed mixture that originally contained 30 mole percent n-hexane, 20 mole percent cyclohexane, 30 mole percent 2,2,4-trimethylpentane, and 20 mole percent n-decane is brought to 100 °C and 1.0 atm. The vapor pressure equations for these hydrocarbons may be given by the Antoine equation,

$$\text{LOG}(P^{\text{vap}}) = A - \frac{B}{t + C}$$

Where  $P^{\text{vap}}$  is in mm Hg,  $t$  is in °C, and LOG denotes base 10 logarithm. The following constants are given in *Lange's Handbook*, 13th ed:

<u>Component</u>	<u>A</u>	<u>B</u>	<u>C</u>
n-Hexane	6.87601	1171.17	224.41
n-Decane	6.94365	1495.17	193.86
2,2,4-Trimethylpentane	6.81189	1257.84	220.74
Cyclohexane	6.84130	1201.53	222.65

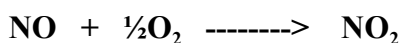
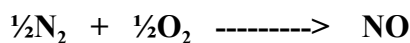
These hydrocarbons may be assumed to form ideal solutions.

#### **T-18 Thermodynamics Principle:** Chemical reaction equilibrium

##### **Health and Safety Concept:** Toxicology

**Background:** Many chemicals are quite toxic. They can cause short term effects such as acute poisoning or long term effects such as cancer. Some chemicals have both effects. In order to keep such chemicals from endangering workers, the Occupational Safety and Health Administration has promulgated rules that specify safe exposure levels for workers. One of those safe exposure levels is the Permissible Exposure Limit, or PEL. The PEL is a concentration of chemical in the air to which a worker can be exposed for 40 hours per week throughout his lifetime without either short-term or long-term ill effects. The PEL is primarily defined for lifelong exposure, and is set at a low enough level to preclude any health effect. Mixtures of chemicals may also occur, and methods have been formulated to estimate the maximum concentrations that are allowable for workers where mixed chemical exposure are found. The intended result is to protect workers, but a side effect is to protect the public as well.

**Problem:** Nitrogen and oxygen may react according to the following stoichiometry:



Both of the oxides of nitrogen are quite toxic. The OSHA PEL for NO is

25 ppm and the PEL for NO<sub>2</sub> is 3 ppm. Obviously, in any process where air is heated to a high enough temperature, some of the oxides may form. The problem is complicated by the fact that the reaction forming NO is endothermic but the reaction in which NO is further oxidized to NO<sub>2</sub> is exothermic. Thus, the equilibrium concentrations of the two are driven in opposite directions: conditions favoring formation of one do not favor the formation of the other. (Other reactions, which we will not consider in this problem, may also occur, so the results may differ substantially from the results we get here. We simplify the problem to make it easier to solve. We will ignore formation of other oxides of nitrogen.)

Assume that the oxides are formed from air, and that a catalyst is available that will cause the reactions to come to equilibrium at all the temperatures we consider. (In practice, we try to use such catalysts to reduce pollution from automobile exhausts.) Calculate the equilibrium concentrations of NO and NO<sub>2</sub> at temperatures from 200 °C to 2000 °C.

If the sum

$$\sum \left[ \frac{y_I}{PEL_i} \right] > 1$$

then the PEL for the mixture will be exceeded. Will the PEL for the mixture be exceeded over the temperature range in question? If so, over what temperature range will the PEL not be exceeded?

#### **T-19 Thermodynamics Principle:** Vapor-liquid equilibrium

**Health and Safety Concept:** Fire and explosion prevention

**Background:** Many flammable chemicals are stored as liquids in tanks that are vented to the atmosphere. If air can flow freely into and out of the tank, the vapor-air mixture above the liquid level can contain sufficient vapor to be flammable. If ignited, an explosion and fire will result. If the chemical has a sufficiently high vapor pressure at the storage temperature, the vapor-air mixture will be too rich to burn. If the vapor pressure is low enough, the vapor-air mixture will be too lean to burn. The term “too rich” means that the concentration of fuel in the vapor space is higher than the upper flammable limit (UFL). “Too lean” means the concentration of fuel is less than the lower flammable limit (LFL). Flammability limits are usually measured for the fuel vapor (or gas) in air at ambient conditions of about 25 °C and 1.0 atm. The limits can change when the temperature or pressure change substantially, but most concern is taken for ambient conditions, because most accidental spills occur at ambient conditions.

**Problem:** The lower flammable limit (LFL) of methanol is 6.0 percent in air

and the upper flammable limit (UFL) is 36 percent in air. If methanol is stored in a tank that is vented to the atmosphere, over what temperature range will the equilibrium vapor-air mixture above the methanol surface be flammable? The vapor pressure of methanol is given in *Lange's Handbook*, 13th ed, as

$$\text{LOG} (P^{\text{vap}}) = 7.89750 - \frac{1474.08}{t + 229.13}$$

Where t is in °C and LOG denotes a base 10 logarithm. The vapor pressures are in mm Hg.

**T-20 Thermodynamics Principle:** Heat of mixing

**Health and Safety Concept:** Explosion prevention

**Background:** Most students of chemistry have been told that concentrated acids are to be diluted by pouring the concentrated acid slowly into water. The reason for pouring the acid into the water is that the mixing process is highly exothermic and substantial temperature increases may occur. If the more dense acid is poured into the water, it tends to sink to the bottom and the water solution can absorb much of the energy generated during mixing. Even if the acid and water are carefully mixed, the temperature may still rise enough to cause dangerous conditions if the mixing is too fast and no cooling of the mixture is possible.

**Problem:** The mixing of two chemicals can result in a quite large increase in temperature of the mixture over the temperatures of the constituents. If the temperature increases enough, the liquid will boil explosively, which can have serious safety consequences. Assume that you are going to mix 500 lb of water at 80 °F and 500 lb of sulfuric acid, also at 80 °F. What will the final temperature of the mixture be? Will the mixture be above the boiling point? Data for this problem can be found in the *Chemical Engineers' Handbook*.

**T-21 Thermodynamics Principle:** Freezing points of mixtures

**Health and Safety Concept:** Safe handling of fluids

**Background:** Most chemical operations try to process materials in a single phase. Two phases are more difficult to transfer during processing and two phases may cause equipment to malfunction or to wear out prematurely. In mixtures of hydrocarbons, it is sometimes difficult to determine which component will begin to freeze first. If small amounts of a soluble material is added to a solvent, the freezing point of the solvent will decrease, even if the solute is a solid. As more solute is added, a point will be reached at which one or the other of the materials will no longer remain liquid. We can consider this to be a solubility limit if the solute is a solid at the system temperature, or as a freezing point depressant if both solute and solvent are below their normal freezing point. If both solute and

solvent are initially liquids, the temperature at which solids will exist in equilibrium with the liquid mixture depends on the liquid concentrations and other liquid properties. We sometimes exploit this phenomenon of freezing point depression.

**Problem:** A mixture of cyclohexane and n-octane is to be prepared for use as a low temperature heat transfer fluid. If the mixture freezes in the transfer piping or the cooler tubes, the piping or tubes will become plugged and an overpressure will result. Although relief valves will be provided, they may also be plugged, or they may discharge flammable materials to the environment, an event that must be avoided. Determine the lowest temperature that can be reached by mixtures of cyclohexane and n-octane (the eutectic point). Do that by calculating the entire melting point curve for cyclohexane-n-octane mixtures. In order to make your calculations easier, the following information is available, and the mixtures may be assumed to behave according to regular solution theory.

	<u>Cyclohexane</u>	<u>n-Octane</u>
Solubility parameter, $\delta$ (cal/cm <sup>3</sup> ) <sup>1/2</sup>	8.2	7.5
Liquid volume, $\underline{V}^L$ (cm <sup>3</sup> /gmole)	109	164
$\Delta h^f$ (J/gmole)	3080	20740
Normal melting point (K)	279.7	216.3
$C_{p,s}$ solid (J/gmole-K)	146	236
$C_{p,l}$ liquid (J/gmole-K)	150	241

## T-22 Thermodynamics Principle: Vapor-liquid equilibrium

**Health and Safety concept:** Flash point and LFL

**Background:** The lower flammable limit (LFL) is the lowest concentration of a flammable material in air that can be ignited. The upper flammable limit (UFL) is the highest concentration that can be ignited. Any concentration between the LFL and the UFL can be ignited if an ignition source is present. Both LFL and UFL are usually measured for concentrations of flammable chemicals in air. The LFL and UFL values depend on the temperature of the system, and to a lesser extent, the pressure. Flammability limits are usually measured at ambient conditions, about 25 °C and atmospheric pressure. The flash point temperature of a liquid is the lowest temperature at which the liquid surface can be ignited. The flash point is normally measured at atmospheric pressure. The flash point and LFL are related, because the flash point is a near-equilibrium measurement. The vapor concentration just above the liquid surface must be the LFL concentration in order for ignition to occur. Thus, it should be possible to predict the flash point for chemical mixtures by predicting the temperature at which the vapor concentration in air above the mixture will equal the LFL concentration. If the liquid is a non-ideal mixture, an equation of state or activity coefficient model will be required to estimate vapor-liquid concentrations. The solubility of air (oxygen and nitrogen) in the liquid fuel is normally neglected in the calculation because gas solubility is low.

**Problem:** The vapor pressure of ethanol can be estimated from the Antoine equation

$$\text{LOG}(P^{\text{vap}}) = 8.32109 - \frac{1718.10}{t + 237.52}$$

Where  $P^{\text{vap}}$  is in mm Hg,  $t$  is in °C, and LOG means base 10 logarithm. (The data are from *Lange's Handbook*, 13th ed.) Estimate the flash point of a mixture of 500 ml of ethanol and 500 ml water. The lower flammable limit of ethanol (LFL) is 3.3 percent and ethanol has a flash point of 55 °F. Mixtures of ethanol and water are not ideal. Your instructor may ask you to calculate activity coefficients by a particular method. If not, make the best estimate you can.

**T-23 Thermodynamics Principle:** Osmotic pressure

**Health and Safety Concept:** Concentration of toxic chemical

**Background:** If a solution contains one chemical that can diffuse through a membrane and one chemical that cannot diffuse through the membrane the two chemicals can be separated. (Usually, for real membranes, both chemicals will diffuse through the membrane, but one will diffuse faster and provide different equilibrium concentrations on either side of the membrane.) This process of diffusion through a membrane is called osmosis, and one method for separating two materials is to provide a membrane through which only one of the materials can diffuse. Then, by raising the pressure on one side of the membrane, the material that will diffuse through can be purified. The process is frequently used to remove salts and other dissolved chemicals from water. It is also used for separating other chemicals from mixtures.

**Problem:** A solution contains water and tert-butyl alcohol. The alcohol is toxic and the solution cannot be disposed of safely except at high cost. We estimate we can use the alcohol or burn the solution if the concentration is raised to 90 mass percent alcohol. The solution initially contains 10 mass percent tert-butyl alcohol and we wish to concentrate it to 90 mass percent alcohol. We have found a semi-permeable membrane that will allow water to pass through, but tert-butyl alcohol cannot pass through. We have decided to try to separate the water by reverse osmosis. Estimate the pressure required to separate the water at the beginning concentration (10 mass percent) and the final concentration (90 mass percent). The reverse osmosis will be carried out at 30 °C. These solutions are not ideal. Does reverse osmosis look like a viable method for separating tert-butyl alcohol and water?

## T-24 Thermodynamics Principle: Vapor-liquid equilibrium

**Health and Safety Concept:** Flash points and LFL for mixtures

**Background:** The lower flammable limit (LFL) is the lowest concentration of a flammable material in air that can be ignited. The upper flammable limit (UFL) is the highest concentration that can be ignited. Any concentration between the LFL and the UFL can be ignited if an ignition source is present. Both LFL and UFL are usually measured for concentrations of flammable chemicals in air. The LFL and UFL values depend on the temperature of the system, and to a lesser extent, the pressure. Flammability limits are usually measured at ambient conditions, about 25 °C and atmospheric pressure. The flash point temperature of a liquid is the lowest temperature at which the liquid surface can be ignited. The flash point is normally measured at atmospheric pressure. The flash point and LFL are related, because the flash point is a near-equilibrium measurement. The vapor concentration just above the liquid surface must be the LFL concentration in order for ignition to occur. Thus, it should be possible to predict the flash point for chemical mixtures by predicting the temperature at which the vapor concentration in air above the mixture will equal the LFL concentration. If the liquid is a non-ideal mixture, an equation of state or activity coefficient model will be required to estimate vapor-liquid concentrations. The solubility of air (oxygen and nitrogen) in the liquid fuel is normally neglected in the calculation because gas solubility is low.

**Problem:** You must estimate the flash point of a mixture of tert-butyl alcohol and water that has 80 percent by weight tert-butyl alcohol. The *Chemical Engineers' Handbook* contains data for the binary system and shows that an azeotrope occurs at 760 mm Hg and 79.91 °C with a mole fraction of water of 0.3541. The flash point of pure tert-butyl alcohol is found to be 52 °F. Using only this information (and molecular weights and vapor pressures of the pure materials), estimate the flash point of the solution.

## T-25 Thermodynamics Principle: Freezing point depression

**Health and Safety concept:** Toxicology

**Background:** Many chemicals are toxic and must not be allowed to enter the air or water. Considerable research has led to the estimation of the concentrations of chemicals that can be tolerated by humans. The Permissible Exposure Limit (PEL) is the concentration that workers can be legally exposed to for an eight-hour period five days per week throughout their lifetime. The PEL is a time-weighted average, so the instantaneous concentration may be higher than the PEL. The Short Term Exposure Limit (STEL) is the concentration permitted by law for exposures up to 15 minutes as many as four times per day, as long as there is a period of one hour between exposures and the PEL is not exceeded. The ceiling concentration must never be exceeded. These concentrations are estimated based on tests made with animals and extrapolated to humans. They are also lower than any concentration known to cause health effects, either acute or chronic. Thus, they should provide for a safe work place. In some cases, chemicals must be separated in the plant in order to obtain pure materials. Here

we look at a method of obtaining very pure chemicals by freezing. If a toxic material can be removed from solution by freezing, not only will the water (in this case) in which it is dissolved contain less of the chemical, but the chemical that is frozen will be very pure until the eutectic point is reached.

**Problem:** We wish to separate a solution of phenol (which is both toxic and flammable) and water by freezing, and in order to study the process to determine its feasibility, we need a freezing point curve for all possible mixtures of the two chemicals. Estimate the freezing points of mixtures and plot a curve showing the freezing point of the mixture as a function of the mole fraction of phenol. The solutions are not ideal. Heat capacities of phenol will be difficult to find, but organic materials have heat capacities that are similar for liquids and solids, so you may assume the liquid and solid heat capacities of phenol are equal. To simplify the problem, you may assume the same for water. The following data may be used:

Heat of fusion of water = 1436 cal/gmole  
Heat of fusion of phenol = 2372 cal/gmole  
Normal melting point of water = 0.0 °C  
Normal melting point of phenol = 40.92 °C

The van Laar constants for estimating the activity coefficients are

$$\alpha = 3.22 \quad (\text{LN } \gamma_{\text{Phenol}} @ x_p = 0)$$
$$\beta = 0.83 \quad (\text{LN } \gamma_{\text{Water}} @ x_w = 0)$$

## T-26 Thermodynamics Principle: Vapor-liquid equilibrium

**Health and Safety Concept:** Flammability limits

**Background:** Liquids do not burn in the liquid phase. Rather, when a liquid pool is ignited, the burning occurs in the vapor just above the liquid surface. In order for ignition to occur, the fuel concentration in the vapor phase must be higher than the lower flammable limit (LFL). The LFL is defined as the lowest concentration of vapor (or gas) in air that can be ignited. The LFL is normally measured at ambient conditions, about 25 °C and 1.0 atm, and will change as the temperature and pressure change. However, the rate of change is not large for small changes in temperature and pressure, and most of the cases of primary interest are near ambient conditions. The liquid from the free surface of a liquid pool will evaporate into the atmosphere. If the pool temperature is high enough, the vapor concentration in the air immediately above the pool surface will reach the LFL, and a flame will flash across the surface if an ignition source is provided. The lowest temperature that will result in the flash across the surface is the flash point of the liquid. The LFL and flash point are related because at the flash point, the concentration in the air above the pool must be equal to the LFL. The Upper Flammable Limit (UFL) is the highest concentration of fuel in air that can be ignited. There is no concept analogous to the flash point for the UFL.

**Problem:** Ethanol and isopropanol are to be stored in atmospheric pressure tanks. Determine over what liquid temperature range the three

chemicals will form flammable vapor mixtures if the liquids are in a tank open to the atmosphere and the air above the liquid surface is saturated with vapor. Do you think it would be wise to provide an inert atmosphere over the surface of these liquids if they are stored under ambient temperature conditions?

**T-27 Thermodynamics Principle:** Ideal gas law

**Health and Safety Concept:** Inerting and purging

**Background:** Many flammable and toxic materials are stored in tanks. If a flammable material is stored in a tank, the usual practice is to reduce the oxygen concentration in the tank before the flammable material is put into the tank. This practice assures there will be no ignition as the tank is filled. Purging is normally done using nitrogen because nitrogen is the cheapest inert gas available and it is readily available. The nitrogen may be added either by flowing it through the tank, by alternately pressurizing the tank and then reducing the pressure, or by alternately vacuuming the tank to sub-atmospheric pressure and then filling it to a pressure near atmospheric pressure. Of course, the tank must have been designed and tested to make certain it can withstand the highest pressure used during purging or the lowest vacuum used during purging. The last step in purging is always to test the atmosphere in the tank to make certain the composition of the gas inside is at the limit required by the process of purging.

**Problem:** A 10,000-gallon tank must be purged before putting it into service. It contains air, and the oxygen concentration in the air is to be reduced to 1.0 mole percent by either flow-through purging or pressure purging. In flow-through purging, nitrogen is continuously supplied to the tank at 1.0 atm pressure and you may assume the tank contents to be perfectly mixed. For pressure purging, the tank is filled with nitrogen to a pressure of 3 atm gauge, the nitrogen and air in the tank are allowed to mix, and the gas in the tank is then vented to the atmosphere. Determine the volume of nitrogen required in both cases.

**T-28 Thermodynamics Principle:** Heat of combustion for gas mixtures

**Health and Safety Concept:** Acceptable heating value for fuel gas

**Background:** Most heaters and burners are designed for a specific fuel heating value, and the heating value must be within a reasonably narrow range for safe operation of the burner. For example, a gas burner designed for operation on natural gas could not be fueled with propane without modification because the heating value of propane is too high, and damage would result. While modifications can be made to most burner systems relatively easily, to fail to make the modifications when changing fuel could cause serious safety problems.

**Problem:** A natural gas mixture contains 85 percent methane, 11 percent ethane, and 4 percent propane. If the gross heating value of



natural gas exceeds 1050 Btu/SCF, there can be safety problems with burners because the burners are designed to operate with gas having a heating value of about 1000 Btu/SCF and a higher heating value can cause incomplete combustion and abnormally high temperatures at the burner. Air can be added to the natural gas to reduce the heating value of the fuel gas. How much air, in SCF, must be added to 100 SCF of the original fuel gas to reduce its heating value to 1000 Btu/SCF? What will the composition of the gas be after air is mixed with it? In the natural gas industry, a standard cubic foot is measured at 60 °F and 14.7 psia.

**T-29 Thermodynamics Principle:** Chemical reaction equilibrium

**Health and Safety Concept:** Tank failure

**Background:** All chemical processing plants have storage tanks of some kind. The tanks may be small and designed to hold only a few gallons of chemical, or they may be huge, holding millions of gallons of chemical. Most of the tanks commonly used in the process industries are steel because steel is strong and relatively inexpensive. It can be used successfully for a broad range of chemicals. However, steel can rust if it is exposed to the atmosphere under the right conditions. While the rate at which rusting occurs is difficult to estimate, the eventual result can be predicted. If the vessel is exposed to a continuous supply of oxygen, it will eventually rust to the point that there is no steel left. If the amount of oxygen is limited, the chemical reaction will be limited by the availability of oxygen or by chemical equilibrium in the oxidation reaction.

**Problem:** A low pressure steel tank is delivered to a construction site. The construction foreman sees the open fill and discharge connections on the tank and fears that the alternate heating/cooling cycles during the day and night will cause moisture to condense on the inside of the tank, promoting rust formation (he is right in his analysis). He decides to close off the fill and discharge lines to keep air from entering the tank. He reasons that if no air enters, rust cannot form. However, if oxygen is trapped inside the tank when it is closed, the oxygen can react with the steel. Assume the reaction is:



Estimate the oxygen concentration and the pressure in the tank when the reaction comes to equilibrium. Has the construction foreman made a good decision?

**T-30 Thermodynamics Principle:** Heat of reaction

**Health and Safety Concept:** Explosions

**Background:** There are a number of chemical reactions whose origin is not accurately known, but about which we may speculate. For example, the manufacture of soap is a technology that is so old that we are uncertain where it

originated. The manufacture of gunpowder is another technology that does not have a proven origin. We surmise that in both cases the technology was discovered accidentally, because there was no methodology for the people who discovered the technology to know what the end product would be worth. While the end result of either soap manufacture or gunpowder manufacture is the product of accidental discovery, both have had astounding effects on modern life.

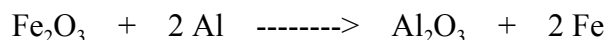
**Problem:** According to Greener (*History of Firearms, 1936*) gunpowder was probably discovered by the ancient Chinese around 954 AD. The soil in the area of China where the discovery was made had very high concentrations of potassium nitrate, which became mixed with charcoal from incomplete combustion of wood. Assume that such a mixture was formed that contained 1.0 kg of carbon, 1.0 kg of potassium nitrate, and 3.0 kg of soil, which is inert. Assume this mixture was thrown into a fire. Estimate the amount of energy released by the reaction of charcoal and potassium nitrate.

**T-31 Thermodynamics Principle:** Adiabatic reaction temperature

**Health and Safety Concept:** High temperature reactions

**Background:** Some chemical reactions are highly exothermic and can produce very high temperatures. While we usually think of high temperatures being produced by burning fuels with air or oxygen as the oxidizing agent, there are reactions that require neither oxygen nor air to be present in the gas phase during the reaction. The following reaction is an example of one of them.

**Problem:** Assume a reaction occurs as follows:



The reaction is entirely in the solid phase. Although the heat capacities of the chemicals vary with temperature, in order to make the problem easier to solve, you may assume the heat capacities to be constant and given as follows:

$\text{Al}_2\text{O}_3$	25 cal/gmole-K
$\text{Fe}_2\text{O}_3$	29 cal/gmole-K
Al	8 cal/gmole-K
Fe	10 cal/gmole-K

Determine the adiabatic reaction temperature for the reaction assuming the reactants are present in stoichiometric proportions at the start of the reaction. The initial temperature is 25 °C.

**T-32 Thermodynamics Principle:** Heat of reaction

**Health and Safety Concept:** Dust explosions

**Background:** The *Northwest Arkansas Times*, in an article published July 22,

1996 describes an explosion at the Western Sugar Company in Scottsbluff, Nebraska. The blast followed a bolt of lightning according to one witness. “The explosion leveled seven of eight silos at the plant and scattered plywood and sugar up to a mile away ...” It’s apparent that a dust explosion can cause substantial damage. In the sugar explosion, one person was still missing and 15 others were injured. The explosion occurred on Saturday when only 31 people were in the plant. About 150 people normally work there.

**Problem:** Estimate the energy generated by the explosion of sugar in a storage silo 20 ft in diameter and 50 ft high. In order to make the estimate, assume that the silo is empty except for a mixture of sugar dust (powdered sugar) and air, and that the dust concentration is at the lower flammable limit. How many pounds of TNT is the blast equal to if TNT has a heat of combustion of 2000 Btu/lb?

**T-33 Thermodynamics Principle:** Chemical reaction equilibrium

**Health and Safety Concept:** Personal safety

**Background:** Freeze-dried foods sometimes contain a small packet of iron oxide. The purpose of the iron oxide is to react with oxygen that might be in the packet to keep the oxygen concentration low. Food preservation is improved because there will be no deterioration due to oxidation of the organic components in the food. In addition, no aerobic bacteria can grow in the food if there is not oxygen present. The iron oxide is not toxic in the small amounts present in the packet, and the packet is made of material that will not allow the iron oxide to mix with the food.

**Problem:** Determine the approximate oxygen concentration in a freeze-dried food packet if there is a small packet of ferrous oxide (FeO) present. The ferrous oxide will oxidize to become ferric oxide (Fe<sub>2</sub>O<sub>3</sub>) in the presence of oxygen.

## Safety Problems for a Course in Fluid Mechanics

Originally Prepared by Ron Darby  
Texas A&M University, College Station, Texas

### Dimensional Analysis

- F-1** An ethylene storage tank in your plant explodes. The distance ( $R$ ) that the blast wave travels from the blast site depends upon the energy released in the blast ( $E$ ), the density of the air ( $\rho$ ), and time ( $\theta$ ). Use dimensional analysis to determine:
- The dimensionless group(s) that can be used to describe the relationship between the variables in this problem.
  - The ratio of the velocity of the blast wave at a distance of 2000 feet from the blast site to the velocity at a distance of 500 feet from the site.
  - The pressure difference across the blast wave ( $\Delta P$ ) also depends upon the blast energy ( $E$ ), the air density ( $\rho$ ), and time ( $\theta$ ). Use this information to determine the ratio of the blast pressure at a distance of 500 ft from the blast site to that at a distance of 2000 ft from the site.

### Source Problems

- F-2** A flammable liquid is draining from a cylindrical vessel through a tube in the bottom of the vessel, as illustrated in the figure, F-2. The liquid has a specific gravity of 1.2 and a viscosity of 2 cP. The entrance loss coefficient from the tank to the tube is 0.4, and the system has the following dimensions:  
 $D = 2$  in.,  $d = 3$  mm,  $L = 20$  cm,  $h = 5$  cm,  $e = 0.0004$  in.
- What is the volumetric flow rate of the liquid in  $\text{cm}^3/\text{s}$ ?
  - What would the answer to (a) be if the entrance loss is neglected?
  - Repeat part (a) for a value of  $h = 75$  cm.

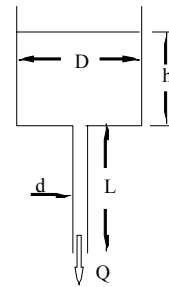


Figure. F-2

- F-3** A toxic oil with a viscosity of 25 cP and SG of 0.78 is contained in a large open tank. A vertical pipe, made of commercial steel, with a 1 in. ID and a length of 6 ft, is attached to the bottom of the tank. You find out that the oil is draining through the pipe at a rate of 30 gpm.
- How deep should the oil in the tank be for it to drain at this rate?
  - If a globe valve is installed in the pipe, how deep must the oil be to drain at the same rate, with the valve wide open?
- F-4** A storage tank contains ethylene glycol at 1 atm and  $20^\circ\text{C}$  ( $\rho = 1110$   $\text{kg}/\text{m}^3$ ,  $\mu = 0.0199$   $\text{Pa}\cdot\text{s}$ ). The tank is 2 m in diameter and has a horizontal 1 in. (2.54 cm) inside diameter pipe attached to the side of the tank near the bottom. The liquid level is 3 m above the pipe entrance. If the pipe breaks off right at the tank, what is the initial flow rate of the ethylene glycol and how long will it take for the ethylene glycol to drain from the tank?

- F-5** The pipe connected to the tank in Problem 4 has a gate valve in the line located 3 m from the tank. If the pipe breaks off downstream of the valve, what will the maximum flow rate be?
- F-6** A storage tank containing ethylene at a pressure of 200 psig and a temperature of 70°F springs a leak. If the hole through which the gas is leaking is 1/2 in. in diameter, what is the leakage rate of the ethylene, in SCFM?
- F-7** A storage tank contains ethylene at 200 psig and 70°F. If a 1 in. line that is 6 ft long and has a globe valve on the end is attached to the tank, what would be the rate of leakage of the ethylene (in SCFM) if
- The valve is fully open?
  - The line breaks off right at the tank?
- F-8** The ethylene storage tank in Problem F-7 has a 1/2 in. diameter horizontal pipe attached to the tank. If the pipe breaks off at a point 200 ft from the tank, and there are 4 standard 90° elbows and one globe valve between the tank and the break, what is the flow rate through the line in SCFM?
- F-9** A 2 in. Sch. 40 pipeline is connected to a storage tank containing ethylene at 100 psig and 80° F.
- If the pipe breaks at a distance of 50 ft from the tank, determine the rate at which the ethylene will leak out of the pipe (in lb<sub>m</sub>/s). There is one globe valve in the line between the tank and the break.
  - If the pipe breaks off right at the tank, what would the leak rate be?
- F-10** Oxygen is to be fed to a reactor at a constant rate of 10 lb<sub>m</sub>/s from a storage tank in which the pressure is constant at 100 psig and the temperature is 70°F. The pressure in the reactor fluctuates between 2 and 10 psig, so you want to insert a choke in the line to maintain the flow rate constant. If the choke is a 2 ft length of tubing, what should the diameter of the tubing be?

### Reaction Forces

- F-11** Water at 68°F is flowing through a 45° pipe bend at a rate of 2000 gpm. The inlet to the bend is 3 in. ID and the outlet is 4 in. ID. The pressure at the inlet is 100 psig and the pressure drop in the bend is equal to half of what it would be in a 3 in. 90° elbow. Calculate the net force (magnitude and direction) that the water exerts on the pipe bend.
- F-12** A high pressure gas cylinder contains nitrogen at a pressure ( $P_1$ ) of 2500 psig at 60°F. A valve with a 1/2 in. inlet and outlet is attached to the top of the cylinder, and a horizontal 1/2 in. tubing line is attached to the valve outlet. With the valve open, the tube breaks off at the valve exit and the nitrogen escapes. Determine the net force that is exerted on the valve. The loss coefficient for the valve can be assumed to be 0.6.

**F-13** Figure F-13 illustrates the flow in the nozzle of a relief valve attached to a large pressure vessel. The fluid is water at 150°F, and in both cases the pressure in the vessel is  $P_1 = 100$  psig and  $P_2$  is atmospheric when the valve opens. In case A, the fluid impacts on the disk and is diverted parallel to the disk (90° from the axis of the nozzle), and in case B the fluid leaves the disk at an angle of 45° downward from the plane of the disk. The diameter of the nozzle is 2 inches and the clearance between the end of the nozzle and the disk is 1/2 inch in both cases. If the loss coefficient for the valve/disk system is 0.25 based on the velocity in the nozzle, determine:

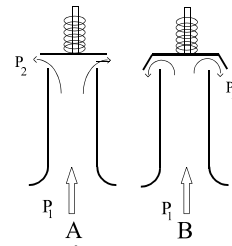


Fig. F-13

- a) the flow rate in gpm, and
- b) the net force acting on the disk, for both case A and case B. (Gravity forces can be neglected).

**F-14** A relief valve is mounted on the top of a large vessel containing hot water. The inlet diameter to the valve is 4 in., and the outlet diameter is 6 in. The valve is set to open when the pressure in the vessel reaches 100 psig, which happens when the water is at 200° F. The liquid flows through the open valve and exits to the atmosphere on the side of the valve, 90° from the entering direction. The loss coefficient for the valve has a value of 5, based on the exit velocity from the valve.

- a) Determine the net force (magnitude and direction) acting on the valve.
- b) You want to attach a cable to the valve to brace it such that the tensile force in the cable balances the net force on the valve. Show exactly where you would attach the cable at both ends.

**F-15.** An emergency relief valve is installed on a reactor, as illustrated in the Figure, F-15, to relieve excess pressure in case of a runaway reaction. The lines upstream and downstream of the valve are 6 in. sch 40 pipe. The valve is designed to open when the tank pressure reaches 100 psig, and the vent exhausts to the atmosphere at 90° to the direction entering the valve. The fluid can be assumed to be incompressible, with an SG of 0.95, a viscosity of 3.5 cP, and a specific heat of 0.5 BTU/lb<sub>m</sub> °F. If the sum of the loss coefficients for the valve and the vent line is 6.5, determine:

- a) The mass flow rate of the fluid through the valve in lb<sub>m</sub>/s and the value of the Reynolds number in the pipe when the valve opens, and;
- b) The rise in temperature of the fluid from the tank to the vent exit, if the heat transferred through the walls of the system is negligible, and;
- c) The force exerted on the valve supports by the fluid flowing through the system. If you could install only one support cable to balance this force, show where you would put it.

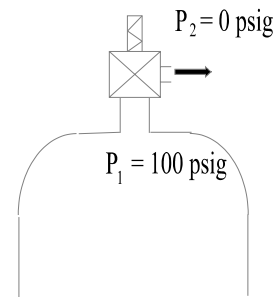


Fig. F-15

- F-16** A relief valve is installed on a pressure vessel as shown in Fig. F-15. The entrance to the valve is 4.5 in. diameter and the exit (which discharges to the atmosphere in the horizontal direction,  $90^\circ$  from the entrance) is 5 in. diameter. The loss coefficient for the valve is 4.5 based on the velocity at the valve inlet. The fluid in the tank is a liquid, with a density of 0.8 g/cc.. If the valve opens when the pressure at the valve reaches 100 psig, determine:
- a)** The mass flow rate through the valve, in ( $\text{lb}_m/\text{s}$ ), and;
  - b)** The net force (magnitude and direction) exerted on the valve.
  - c)** Determine the location (orientation) of a cable which is to be attached to the valve to balance this force (note that a cable can only support a tensile force).

## Safety Problems for a Course in Kinetics

Originally Prepared by Ronald J. Willey  
Northeastern University, Boston, MA

### K-1 Acetaminophen Metabolic Removal

**Kinetics Principles Involved:** 1st Order Reaction - Metabolic removal of acetaminophen

**Level:** Beginning, Undergraduate Kinetics Course

**Health and Safety Concept:** Toxicology and Industrial Hygiene

**Background:** Mechanism for metabolization of acetaminophen (from reference<sup>2</sup>)  
The removal of agents ingested in the body are often modeled by first order kinetics. Surprisingly, acetaminophen (Tylenol™) is toxic if a very high dose is taken (Mechanism is described below). Emergency room personnel use a nomogram that shows critical concentrations of acetaminophen plasma level as a function of time after ingestion on a semi-log plot. The resultant nomogram is consulted for the determination of a patient's risk and what action is subsequently required. If the level-time condition falls below the critical line, the body can detoxify the toxic agent. If it is above, emergency treatments are required, such as the administration of N-Acetylcysteine (NAC). The critical plasma level decays by a ~ 1st rate thus a first order rate constant can be found. Students receive an introduction to first order kinetic systems by plotting concentration-time data on semi-log paper and then finding the rate constant. Acetaminophen is metabolized primarily by sulfation and glucuronidation of para hydroxyl group. Neither unchanged acetaminophen nor its glucuronide and sulfate conjugates are toxic. Thus acetaminophen is a remarkably safe drug when used at usual therapeutic doses. However, a small fraction of an administered dose of acetaminophen is converted to a reactive metabolite which is toxic. This toxic reactive metabolite is detoxified in a second reaction with glutathione and is excreted in the urine as cysteine and mercapturic acid metabolites.

#### Acetaminophen Metabolic Removal

Acetaminophen plasma level,  $\mu\text{g/ml}$ , as a function of time for the line which separates "no risk" (concentration below the critical concentration) and "possible risk" (concentration above the critical concentration) is given below:

Time after ingestion, hr	Critical Plasma Level $\mu\text{g/ml}$
4	135
8	66
12	33
16	16
20	8
24	4

<sup>2</sup> Haddad, L.M. and Winchester, J.F., *Clinical Management of Poisoning and Drug Overdose*, W.B. Sanders Company, Philadelphia, 1983, pp. 562-575.



- Prepare a nomogram by plotting the above data on semi-log graph paper. Label the "No Risk" region and the "Possible Risk" region.
- Determine the pseudo first order rate constant.
- N-Acetylcysteine (NAC) can be administered orally to counteract the toxic risk due to the high concentration of acetaminophen. If a 70 kg person's blood level contains 50  $\mu\text{g/ml}$  after 12 hr of acetaminophen, how much NAC should be administered? Administration of 1200 mg/kg of NAC has been documented at 100% survival.
- Data are missing for plasma levels at time equal 0. Explain why or why not a valid measurement can be made at time equal 0.

## K-2 Influence of Temperature on the Rate of a Reaction

**Kinetics Principle Involved:** Arrhenius Equation

**Level:** Beginning, Undergraduate Kinetics Course

**Health and Safety Concept:** Temperature Control & Stability, Runaway Reactions

**Background:** Many chemical industrial losses are due to "runaway" reactions and the associated rapid increase in temperature. This problem helps the student grasp the influence of temperature on a reaction. They gain an appreciation of the expression "The reaction rate doubles for every 10°C increase in temperature."

### Influence of Temperature on the Rate of a Reaction

The specific rate constant,  $k$ , of a reaction depends on temperature. The dependency on  $k$  upon temperature is modelled after the Arrhenius Equation.

$$k = Ae^{-E_a/RT}$$

Where:

A is the frequency or pre-exponential factor

$E_a$  is the activation energy for the reaction in interest, J/mol

T is the absolute temperature, K

R is the gas constant 8.314 J/mol K

and the rate of reaction is equal to  $k(T) \cdot f$  (conc. of the species present)

- A common cited "rule" of thumb is that the rate of reaction "k" doubles for every 10°C. What activation energy "E<sub>a</sub>" does this correspond to at 50°C, 100°C, 200°C, and 500°C respectively?
- Another "rule" of thumb cites that a "catalyst" lowers the activation energy for a catalyzed reaction compared to a non-catalyzed reaction by a factor of 2 to 4. If the activation energy found at 500°C is decreased by a factor of 4, what is the incremental increase in temperature needed to double the rate of reaction?

- c) Your kinetics text book has values for activation energy for example reactions. Compare one of these examples to the values found in parts a & b. What do you conclude?
- d) Briefly explain what physically can happen in a reactor for an exothermic reaction in which the temperature begins to rise. Assume that the reactants are plentiful enough to keep concentrations constant and that reactor cooling is achieved by a water cooled coil.

### K-3. Combustion in a Closed Vessel

**Kinetics Principle:** Intrinsic rate estimation based on macroscopic data

**Level:** Undergraduate Kinetics Introductory

**Health and Safety Concept:** Explosion and flammability test units. Autoignition temperature.

**Background:** Lower and upper flammability limits of mixtures of fuels and air are determined in fixed volume vessels. Another flammability property of combustibles is the auto-ignition temperature - the lowest temperature in which a stoichiometric mixture of fuel and air will automatically combust without an outside source of energy (a spark). This problem presents sample experimental information which might result from an auto-ignition experiment with methane and air. Students are required to use some of their thermodynamics background (no calculations are involved). The pressure increases because of temperature not because of a change in the number of moles. Some students may confuse the problem with combustion inside a compressed piston chamber.

#### Combustion in a Closed Vessel

Consider the combustion of methane in a constant volume vessel. Initially 0.01 moles of methane and the stoichiometric amount of oxygen as air are added to a 2.5 liter adiabatic "bomb" (a well insulated vessel which can withstand very high pressures). Slowly, the temperature is increased. At 538°C, the pressure suddenly increases at an average rate of 20 bar/s for a period of 250 milliseconds then the pressure slowly tails off.

- a) Why does the pressure increase suddenly?
- b) Estimate the average intrinsic rate of methane combustion.
- c) What is the significance of 538°C?

### K-4. Oxidation and Corrosion

**Kinetics Principle Involved:** Integration of rate equations. Analysis of rate data to determine which rate equation applies to the data.

**Level:** Undergraduate Kinetics Course near discussion of rate equations/models

**Health and Safety Concept:** Corrosion and models to describe

**Background:** All materials, to some degree, are susceptible to deterioration by their environment. One form of environmental degradation is corrosion of which several types can occur: oxidation, aqueous corrosion, galvanic corrosion, and gaseous reduction. In oxidation, oxygen in the atmosphere reacts with metals. Left long enough the metal will eventually convert to an oxide. In some instances the oxide layer forms an excellent barrier (like  $\text{Al}_2\text{O}_3$  on aluminum) in other cases the oxide weakens the structure. Direct attack oxidation is modelled by two approaches: linear growth and ionic diffusion. Students are given these two differential equations and asked to solve. Then data are provided for an application.

Reference: Shackelford (1990), p. 605-612.

Oxidation and Corrosion

In general metal and alloys form stable oxide compounds under exposure to air at elevated temperatures. Gold is a notable exception. In some cases the oxidation forms a stable surface barrier in others the metal is continually attacked until fracture occurs. Corrosion by direct oxidation is described by one of two rate equations.

One rate of growth model for an oxide film for a porous coating is the linear model described by the following differential equation:

$$dy/dt = c_1 \quad (1)$$

Where:

y is the thickness of the oxide layer

t is the time

$c_1$  is a constant with units of L/ $\theta$

Another model is the parabolic growth rate law which models rate of growth of an oxide film limited by ionic diffusion of  $\text{O}^{2-}$  through an oxide layer.

$$dy/dt = c_3 1/y \quad (2)$$

- a) Solve both of these differential equations subject to  $y=y_0$  at the time equal 0.
- b) An oxidation experimental was performed on a Ni film. From the data given below determine which oxidation model applies and estimate the constants of integration for the proper model.

Oxidation study of Ni at 600°C

t, h	oxide layer thickness, nm
0.0	100
0.5	158
1.0	198
1.5	235
2.0	263
2.5	293
3.0	314
3.5	340
4.0	361

- c) (Graduate Level) Show the derivation of Eqn. 2 starting with Fick's 1<sup>st</sup> law of diffusion.

### K-5. Ethylene Glycol Production from Ethylene Oxide

**Kinetics Principle Involved:** 1st Order Reaction, batch reactor

**Health and Safety Concept:** Handling of Ethylene Oxide, MSDS sheets.

**Background:** Ethylene glycol from ethylene oxide is a major chemical reaction. It provides a text book example for 1st order reactions. However, the properties of ethylene oxide make it a chemical to be handled with great care as this problem is intended for students to find out. This problem is very similar to example done in Professor Fogler's text (1992) p.110-112. This problem can supplement Professor Fogler's example taking in account the handling of ethylene oxide.

Reference: Fogler, H.S., "Elements of Chemical Reaction Engineering," 2nd Ed., Prentice Hall, Englewood Cliffs, New Jersey, 1992.

Merck Index

Ethylene Glycol Production from Ethylene Oxide

Consider the production of ethylene glycol from a 1 M (molar) solution of ethylene oxide in a 10 liter batch reactor at 55°C in a pilot plant setting.

- a) Write the stoichiometric reaction equation. Assume that the reaction is first order in ethylene oxide concentration and that it is nearly irreversible. The first order rate constant is  $0.3 \text{ min}^{-1}$ .
- b) Why can the assumption be made that the reaction is first order in ethylene oxide concentration only?
- c) How many minutes should a technician wait to achieve 99.95% conversion of the ethylene oxide?
- d) The technician reports to you that the pilot plant has run out of 1 M solution of ethylene oxide and that a batch needs to be made up. What important precaution(s) must be taken in handling ethylene oxide? (Hint: Find an MSDS sheet on ethylene oxide. What is its normal boiling point?)

### K-6. Dust Explosion Testing

**Kinetics Principle Involved:** Rate laws and stoichiometry

**Level:** Undergraduate kinetics course

**Health and Safety Concept:** Test units for dust explosions

**Background:** Dust explosions can be extremely violent and damaging. For example, common household cornstarch can explode with energy equal to the release of energy by an explosion created in a similar amount of methane-air mixture. Deflagration venting is required to keep losses to a minimum. The nature of a dust explosion is evaluated in a fixed volume sphere in which a deflagration index is determined based pressure/time data after an explosion is set. Depending on the value of  $K_{st}$  the dust is classified into one of three classes (St-1, St-2, or St-3). Dust Explosion Testing

Dust explosion testing is completed in a fixed volume sphere of about 20 liters in volume. Approximately 1 gram/liter of dust is dispersed with air into the sphere for about 3 seconds followed by the discharge of a spark. In the right conditions, an explosion occurs.

Consider a test on corn starch purchased from a local grocery store  $[(C_6H_{10}O_5)]_n$

- Write a balanced stoichiometric equation for the combustion of corn starch.
- If the test vessel is 20 liters and air is added at 1 atmosphere, how many grams of corn starch is required based on a stoichiometric reaction?
- The deflagration index is defined as: (see Crowl & Louvar 2002, p.259-260)

$$K_{st} = \left( \frac{dP}{dT} \right)_{\max} V^{1/3}$$

The following data were acquired in a dust explosion apparatus. What is the deflagration index based on this test?

Vessel Size: 20 liters

<u>Time, ms</u>	<u>Pressure, bar (abs)</u>
0	1.0
10	1.1
15	1.2
20	2.0
25	4.2
30	8.2
35	8.2
40	8.1
45	8.0
50	7.8

- Why does the pressure increase during this explosion?
- Discussion question: Why is excess starch required in the test?

## K-7. Sequential Reactions: Halogenation of Benzene to Chlorobenzenes

**Kinetics Principle Involved:** First Order Complex Reactions in a batch reactor

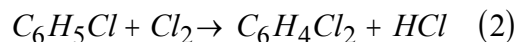
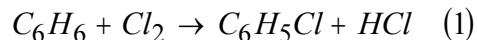
**Level:** Undergraduate kinetics course mid course

**Health and Safety Concept:** Handling and care of benzene and chlorinated benzenes. Use of MSDS sheets in experimental planning.

**Background:** Prof. J. M. Smith used the chlorination of benzene as an example of sequential reactions in his text book (Example 2-9). This problem uses these reactions to demonstrate a simple reactor optimization problem. The safety concept involved is the looking up hazards associated with the handling of benzene, chlorine, HCl, and chlorinated benzene. The use of MSDS sheets facilitates finding safety (as well as property) information about these chemicals. Students should be made aware about MSDS sheets as soon as possible in their training. MSDS sheets can save a lot of potential problems if consulted before the actual work begins.

Sequential Reactions: Halogenation of Benzene to Chlorobenzene

Consider the reactions for the production of chlorobenzene and 1,4 dichlorobenzene.



at 55° C

$$k_1 = 82.0 \text{ m}^3 \text{ kmol}^{-1} \text{ h}^{-1}$$

$$k_2 = 6.0 \text{ m}^3 \text{ kmol}^{-1} \text{ h}^{-1}$$

Numerous safety precautions must be taken with these reactions.

- Review the MSDS sheets on all reactants and products. What major precautions must be made by operators performing these reactions?
- If the reactions are conducted at 55°C and atmospheric pressure, what are the phases of each reactant and product?
- Write the rate equations for each reaction.
- Plot the concentrations of  $C_6H_6$ ,  $C_6H_5Cl$  and  $C_6H_4Cl_2$  as function of time for a period of 30 mins for a reaction performed in a batch reactor for  $C_6H_6 = 11.2 \text{ kmol/m}^3$  at  $t=0$ . Assume that all chlorine gas added is absorbed by the liquid phase and that its concentration is constant at  $0.089 \text{ kmol/m}^3$ . At what time does the maximum concentration of  $C_6H_5Cl$  occur?

## K-8. Production of Acrylonitrile

**Kinetics Principle Involved:** Production of Acrylonitrile

**Level:** Undergraduate

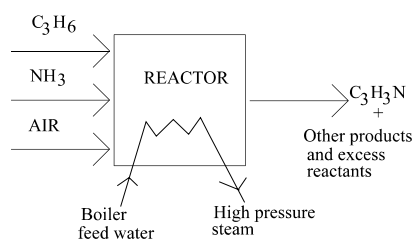
**Health and Safety Concept:** HAZOPS analysis of a kinetic process

**Background:** Hazard and Operability studies (HAZOP) is one of a number of methods used to identify hazards in a chemical process facility.<sup>3</sup> A full HAZOP is completed by a committee, so you may elect to extend this problem to a term project and split the class up into groups of four. If you elect this approach *Kirk-Othmer Encyclopedia of Chemical Technology*, 4<sup>th</sup> ed., Vol.1, 1991, p. 352-369, is an excellent starting point to learn about the acrylonitrile process, HAZOP procedure manuals are available as well. One good reference is the *Cyanamid Hazard Evaluation Manual* which is available by request from the Corporate Loss Preventions Office of the American Cyanamid Company, 1 Cyanamid Plaza, Wayne, NJ 07470 or from SACHE.

This particular problem focuses on only one "node" (the reactor) and asks students to apply six guide words to process parameters. If this is a group project the problem can incorporate more of the process, more guide words, and more process parameters.

### Production of Acrylonitrile

Acrylonitrile is an important monomer in the polymer industry, consider the simplified process flow sheet shown below:



HAZOPS (Hazardous and Operability Study) are one of several methods to analyze a process for hazards. The overall process is usually done in teams; however, to demonstrate the method consider the following simple problem. The HAZOPS method is applied to process vessels and lines (nodes). Using guide words of "no/not/none", "more/higher/greater", "less/lower", "other/than", and "sooner/faster"<sup>1</sup> process parameters such as "temperature" and "reaction" can be evaluated as to what is a possible cause and possible consequence. For example "temperature - higher" might be caused by loss of boiler feed-water and the consequences might be a reactor vessel wall failure. Relief valves and auxiliary cooling water are possible actions to cover such a case.

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<sup>3</sup> *Guidelines for Hazard Evaluation Procedures*, American Institute of Chemical Engineers, New York, 1985.

You are to make up a HAZOP status sheet for the reactor vessel for two process parameters of temperature and reaction using the five words given above. The columns can be labeled as:

Equipment	Process Parameter	Deviation (Guide word)	Possible Causes	Possible Consequences	Action Required
Reactor vessel	Temperature	Higher (etc.)	Loss of cooling water (etc.)	Reactor wall fails	Auxiliary cooling water pump

### K-9. Polymerization - Loss of Cooling Water

**Kinetics Principle Involved:** Non-isothermal batch reactor

**Level:** Undergraduate kinetic course - mid to late course

**Health and Safety Concept:** Runaway reactors, the necessity of proper relief valve sizing.

**Background:** On April 30, 1953 a reactor exploded at the American Polymer Corp. Plant located in Peabody, MA. It was the greatest disaster ever experienced by that city. One person was killed and 30 people suffered injuries. Property damage was \$1,000,000 (1953 \$) and one building was leveled. The accident resulted when a 600 gallon reactor vessel which containing vinyl acetate and acetone blew up. Although documentation is missing as to why, the reactor over-pressurized and blew up. One possible reason is the loss of cooling (or adiabatic reactor) which results in the contents expanding due to vaporization and density changes.

Polymerization - Loss of cooling water

Consider a 2.27 m<sup>3</sup> batch reactor charged with 20% vinyl acetate and 80% acetone by mass. At 60°C the desired polymer, polyvinyl acetate, is achieved in 1h with 1 kg of a peroxide based initiator. 90.0% of the vinyl acetate reacts within this period. The cooling water jacket is designed to handle this heat load and maintains a constant temperature of 60°C.

- Assume that the reactor is first order in vinyl acetate concentration. Estimate the first order rate constant for the above conditions.
- Assume that  $\Delta H$  for the overall reaction is  $\sim -90,000$  kJ/kmol, the activation energy is  $\sim 40,000$  kJ/kmol, and  $C_p \sim 2.6$  kJ/kg°C. If the cooling water jacket is lost (i.e. no cooling), estimate the change in temperature and conversion as a function of time treating the reactor as an adiabatic reactor.
- What can happen in part b if the relief system is substantially undersized?



## K-10. Identification of Initiation, Propagation, and Termination in an Accident

**Kinetics Principles Involved:** Vapor cloud explosion-flame speed

**Level:** Undergraduate (mid-course)

**Health and Safety Concept:** Description of the accident process.

**Background:** Accidents, like polymerization, follow a three step process. In fact the same terminology is used. In this problem students read about an accident scenario and are requested to identify the initiation step, the propagation steps and the termination step. Further, students are introduced to the term, VCE, vapor cloud explosion, one of the most feared of explosions.

Identification of initiation, propagation, and termination in an accident

A vapor cloud explosion (VCE) is the most feared of explosions. Many lives have been lost and considerable destruction has occurred. Consider the following events:

At a propane storage tank farm a valve began to leak. A vapor cloud of propane traveled across a distance of 200 m. The cloud reached an ignition source at a building located off site. A large fire ball was ignited and flashed back to the tank farm. Many fires resulted and subsequently many fire balls called BLEVES occurred. Finally, the fuel is consumed and the fires ceased. Over 500 lives were lost and \$100,000,000 in damage resulted from this accident (for photographs see SACHE Slide Lecture: Seminar on Tank Failures by Willey, 1993). Crowl and Louvar, 2002, identify that most accidents follow a three step sequence. In fact the same terminology is used in polymerization reactions; however, the definitions are different.

- Initiation: the event that starts the accident.
- Propagation: the event or events that maintain or expand the accident.
- Termination: the event or events that stop the accident or diminish it in

size.

- a) Identify the initiation of this accident.
- b) Identify the propagation of this accident.
- c) Identify the termination of this accident.
- d) Estimate the time for the flame front to flash back 200 m back to the tank farm if the flame speed of propane is approximately 3 m/sec. Actual flame speeds are extremely dependent on prevalent winds, and obstacles such as buildings. Flame speeds up to sonic (~300 m/s) or higher are possible under certain conditions.

## K-11. Compliance with OSHA List of Hazardous Chemicals

**Kinetics Principle Involved:** Comparison of two reaction pathways to the same product

**Level:** Undergraduate

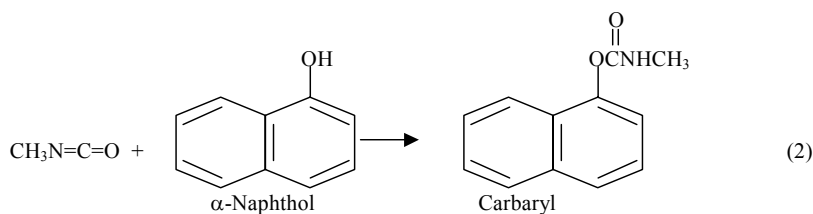
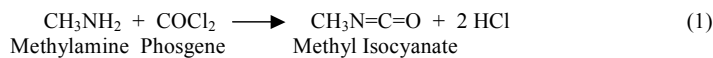
**Health and Safety Concept:** Reviewing OSHA list of hazardous chemicals. Consideration of alternative reaction pathways

**Background:** Process safety management programs as required by OSHA can appear to be very complicated and labor intensive. Laura J. Gimpelson, Calabrian Corporation; Houston, Texas presented a paper at the 1992 Process Plant Safety Symposium entitled "Process Safety at a Small Chemical Company Survival of the Smart Worker," (p. 19 Vol. 1 of the Proceedings). In this work she describes an approach to focus on what's critical. Problem 11 introduces students to the OSHA list of hazardous chemicals and requires a library search. The second part of the question is an essay type and requires further library reading. Reactions used in the example are related to the Bhopal, India disaster.

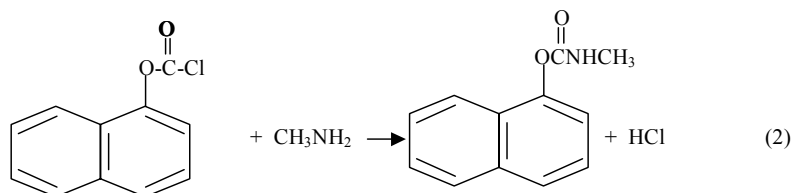
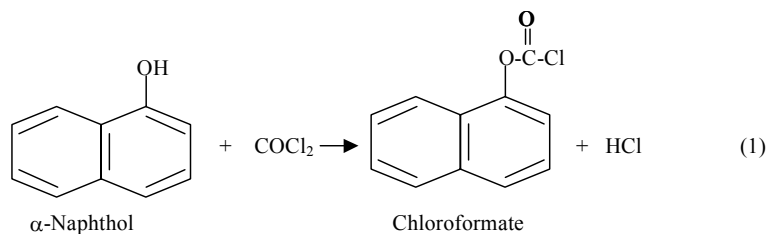
### Compliance with OSHA List of Hazardous Chemicals

Compare two methods to manufacture carbaryl given below:

Methyl Isocyanate Route:



Nonmethyl Isocyanate Route:



- a) You are the manager of environmental health and safety for a small chemical company. It has been proposed that the company produce carbaryl. Which chemicals above are on OSHA's List of Hazardous Chemicals in OSHA's Process Safety Management Standards 29 CFR 1910.119?
- b) Several of these chemicals are extremely toxic. In fact, one chemical was responsible for many of the civilian casualties that occurred in Bhopal, India, December 3, 1984. Review the article in "Chemical and Engineering News, February 11, 1985, p.30 and discuss which method you would propose to make carbaryl and why.

### K-12. Accident Investigation of a Backyard Barbecue Explosion

**Kinetics Principles Involved:** Estimation of a rate of a chemical reaction and modelling

**Level:** Undergraduate

**Health and Safety Concept:** Accident Investigations

**Background:** After an explosion it is desirable to perform investigations into both the causes and consequences of the event.<sup>4</sup> Documentation is required about damage near the explosion center, damage to all acceptor buildings and structures, documentation of debris and missile sizes, shapes, weights and distances thrown along. A survey of the explosion site can be used by investigators to draw conclusions about the explosion. In this problem the student is on a team investigating a recent explosion.

#### Accident Investigation of a Backyard Barbecue Explosion

You are assigned with a structural engineer to investigate an explosion of a backyard barbecue in Dedham, Mass. Upon arrival at the site you find a broken garage window (one pane of a 6 pane garage door) which was closest to the barbecue at a distance of 20 m. The structural engineer tells you that glass breaks at overpressures of 1 kPa (0.15 psig). You know that the following scaling law applies:

$$(\text{overpressure, kPa}) = 160 \left( \frac{r}{m_{TNT}^{1/3}} \right)^{-1.2}$$

Where:

**r** is the radius from the center of explosion, m  
**m<sub>TNT</sub>** is the mass equivalent of TNT, in kg.

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<sup>4</sup> Inspiration for this problem came from a paper by Whitney, M.G.; Barker, D.D. and Spivey, K.H., *Explosion Accident Consequences Investigation Methodology*, 1992 Proceedings of the Process Plant Safety Symposium, AIChE, New York, Vol. 1, p.206-218.

this equation is valid for pressures < 10 kPa

Note: The equivalent energy of TNT is 4,600 kJ/kg.  
You also know that propane explosions are only about 2% efficient (only about 2% of the total energy available is given off as explosive energy).

- a) Estimate how many kg of propane exploded in the backyard.
- b) Estimate the time length of the explosion if ignition was in the center of a spherical vapor cloud with propane concentration approximately at its stoichiometric concentration. Assume that the flame speed is 3 m/s.

### K-13. VSP Data and Analysis

**Kinetics Principle Involved:** Exothermic reaction runaway

**Level:** Undergraduate - Mid course

**Health and Safety Concept:** Relief valve sizing

**Background:** Vent sizing is an important consideration in reactor sizing. In the mid 1980's an experimental method was developed to determine the proper vent sizing for two phase flow during a runaway reaction. An example of a two phase discharge is the opening of a well-shaken champagne bottle. The cross sectional area required for relief for two phase relief is several times greater than the single phase relief of either gas or liquid. Data to determine vent sizing for two phase relief are obtained from an experimental apparatus called the VSP or Vent Sizing Package. The VSP tracks temperature and pressure as a function of time while the contents inside are slowly heated. At some temperature the contents begin to react rapidly exothermically and a rapid temperature and pressure rise occurs (i.e. a simulation of a runaway reactor). Students are given some VSP data to analyze and an equation to estimate the proper vent size for a 15m<sup>3</sup> batch reactor.

#### VSP Data and Analysis

VSP (Vent Sizing Package) data are used to determine vent sizes for reactors which might have a runaway reaction. A runaway reaction is characterized by an exothermic reaction whose rate increases rapidly because the heat removal is too low. Consider the results for a VSP experiment conducted on a 38.531% methanol 61.47% acetic anhydride mixture by weight. Methanol is the excess reactant.

- a) What is the reaction that will take place and is it exothermic?
- b) Prepare the following graphs from the attached data:

Temp.	vs	time
Pressure	vs	time
ln dp/dt	vs	-1000/T
ln dT/dt	vs	-1000/T

- c) At what time into the run does the reaction begin to "take off"? At what temperature did this auto-acceleration occur?
- d) The heat released per unit mass,  $q$ , due to an exothermic reaction runaway is estimated from VSP data by the following equation:

$$q = \frac{1}{2} C_v \left[ \left( \frac{dT}{dt} \right)_s + \left( \frac{dT}{dt} \right)_M \right]$$

Where the subscript, S, is the temperature rise at the relief valve set pressure and  $(dT/dt)_M$  is the rate of temperature increase at the maximum over pressure of the valve. A relief valve which opens at 50 psi gauge and has 20% over pressure (60 psi gauge max) is being sized for a reactor for the reaction data above. If  $C_v$  is 2,100 J/kg K, what is the value of  $q$  for the relief valve design equation given above?

- e) The relief valve area design equation is as follows (Details of the derivation are elsewhere<sup>5</sup>):

$$A = \frac{m_o q}{G_T \left[ \sqrt{\frac{V}{m_o} T_s \frac{dP}{dT}} + \sqrt{C_v \Delta T} \right]^2}$$

Where:

- A is the area of the relief valve  
 $m_o$  is the initial mass in the reactor vessel  
 $G_T$  is the mass flux  
 $V$  is the reactor volume  
 $T_s$  the temperature at which the relief valve begins to open  
 $dP/dT$  the rise in pressure at the point when the relief valve begins to open  
 $\Delta T$  the temperature rise observed due to overpressure.

Determine the area for a relief valve described in part d holding 9500 kg of reactants based on the data given in the VSP data. Assume that  $G_T = 3000 \text{ kg/m}^2\text{s}$  and that  $V=15\text{m}^3$ .

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<sup>5</sup> Leung, J.C., "Simplified Vent Sizing," AIChE Journal, **32(10)**, 1986, p. 1623.

VSP Data<sup>6</sup>

Time, min	T, °C	-1000/T, K <sup>-1</sup>	dT/dt, °C/mi	dP/dt, psi/mn	P, psia
0	20.02	-3.411	0.402	-1.152	14.26
43.138	39.01	-3.203	0.438	0.137	16.73
57.659	48.49	-3.109	1.002	0.294	18.99
64.169	57.52	-3.024	2.046	0.791	21.90
66.171	62.29	-2.981	2.903	1.370	24.06
67.674	67.26	-2.938	3.943	2.095	26.49
68.574	71.26	-2.904	4.896	2.784	28.48
69.272	75.30	-2.870	6.192	3.784	31.10
69.558	77.30	-2.853	7.005	4.545	32.23
70.258	83.35	-2.805	9.927	7.219	36.41
70.603	87.37	-2.774	12.463	9.890	39.63
70.885	91.41	-2.743	15.395	12.866	42.61
71.452	103.47	-2.655	26.983	26.448	53.52
71.724	112.91	-2.590	42.782	51.906	65.05
71.841	118.60	-2.553	52.095	67.093	71.09
71.888	121.19	-2.536	57.378	80.556	75.19
71.915	122.85	-2.525	60.792	87.907	77.27
71.940	124.50	-2.515	63.722	94.106	79.38
72.007	129.27	-2.485	75.010	136.347	87.51
72.100	137.01	-2.438	95.777	218.927	105.46
72.203	148.13	-2.374	117.48	313.074	131.18
72.313	161.90	-2.299	125.837	439.771	173.72
72.409	173.10	-2.241	97.51	384.490	192.12
72.501	179.66	-2.208	41.622	176.50	246.02
72.664	182.98	-2.192	3.365	31.219	261.05
72.808	183.18	-2.192	2.001	20.38	270.29
75.063	187.69	-2.170	1.729	12.354	300.24
85.229	205.16	-2.091	1.163	9.083	444.48
93.748	197.06	-2.127	-2.666	-16.013	389.31
101.847	176.84	-2.222	-2.243	-11.066	275.64

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<sup>6</sup> Data provided by G. Boicourt, BASF Corporation, Wyandotte, MI.

## K-14. Explosions and Runaway Reactors - Heat Transfer Considerations - An Introduction.

**Kinetics Principles Involved:** Non-isothermal reactors

**Level:** Undergraduate mid-course

**Health and Safety Concept:** The importance of temperature control and heat removal in exothermic reactions.

**Background:** Taffanel and LeFloch<sup>7</sup> first published rate of heat generation and removal curves as a function of temperature in 1913. Students are provided with five equations for heat generation and removal (four kinetic and heat transfer) and are asked to analyze what can happen at various instantaneous temperatures.

Explosions and Runaway Reactors-Heat Transfer Considerations-An Introduction

- a) Given below are four heat generation equations for zero order reactions and one heat removal equation. Plot these equations on a graph showing the rate of heat generated/removed versus temperature from 70 to 110°C. Scale the heat rate axis from -20 to 100 kW. The heat generation equations are:

$$\begin{aligned}Q_{\text{gen1}} &= 1 \times 10^{13} * \exp(-10,000/T) \\Q_{\text{gen2}} &= 1 \times 10^{13} * \exp(-9,700/T) \\Q_{\text{gen3}} &= 8.954 \times 10^{16} * \exp(-12,827/T) \\Q_{\text{gen4}} &= 8.954 \times 10^{16} * \exp(-12,700/T)\end{aligned}$$

and the heat removal equation assuming that heat transfer is proportional to  $t - t_{\text{surroundings}}$ :

$$Q_{\text{rem}} = 2.5 (t - 75^\circ\text{C}) \text{ kW}$$

Where:

T is temperature in K  
t is temperature in °C  
Q is in kW

- b) For the heat generation curve 1. If the initial temperature is 70°C what happens to the temperature? If the initial temperature is 95°C what happens?
- c) For the heat generation curve 2. If the initial temperature is 70°C what happens? 95°C? 108°C?
- d) Identify the steady state temperatures for each curve and determine if they are stable or unstable operating points.

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<sup>7</sup> Taffanel, J. & LeFloch, G., Comptes Rendus Ac. Sc. 1913, 156, 1544. (From Medard, L. Accidental Explosions Vol. 1: Ellis Horwood, Chichester, West Sussex, PO 19 1EB, England).

- e) Note that  $Q_{\text{gen}3}$  curve is tangent to the  $Q_{\text{rem}}$  curve at one temperature implying

$$Q_{\text{rem}} = Q_{\text{gen}3}$$

and

$$dQ_{\text{rem}}/dT = dQ_{\text{gen}3}/dT$$

Taffnel and LeFloch<sup>8</sup> specified this borderline case as a condition for an explosion. Explain by comparing this curve to  $Q_{\text{gen}4}$  and  $Q_{\text{gen}2}$ .

### K-15. Hot Spot Along a Tubular Reactor

**Kinetics Principles Involved:** Non isothermal tubular flow reactors

**Level:** Undergraduate near introduction to non isothermal tubular flow reactors

**Health and Safety Concept:** Tubular flow reactors with exothermic reactions. Possibility of creep deformation.

**Background:** Exothermic reactions occurring within tubular flow reactors are common industrial processes. This problem is an introductory problem for demonstration of heat and mass transfer concepts in a non-isothermal tubular reactor. Decomposition of ethylene oxide is chosen as the reaction system because of its known hazards.

The following equations can be given to students if you wish to provide additional help:



$$-\Delta H = 134,600 \text{ kJ/kmol}$$

$$C_{\text{EO}} = C_{\text{EOo}} [(1 - x_{\text{EO}})/(1 + x_{\text{EO}})]$$

Where:  $x_{\text{EO}}$  is the conversion of EO (ethylene oxide)

$$C_{\text{EOo}} = P_{\text{EO}}/RT = P_t/RT \quad \text{Inlet concentration is estimated by the ideal gas law.}$$

by the mass balance:

$$r dV = F_t dx$$

$$dV = \pi (d^2/4) dz$$

$$r = kC_{\text{EO}} = k(T) C_{\text{EOo}} [(1 - x_{\text{EO}})/(1 + x_{\text{EO}})]$$

$$k(T) = 1.5 \times 10^{13} \exp(-218,000/RT)$$

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<sup>8</sup> Taffnel, J. and LeFloch, G. Comptes Rendus Ac. Sc. 1913, 156, 1544.



$$F_t = 38 \times 10^{-9} \text{ kmol/s}$$

so  $dx/dz = (\pi d^2 r)/(4 F_t)$

and by the energy balance:

$$dT/dz = (\pi d^2 r - \Delta H)/(4 F_t C_p)$$

Where:  $C_p = (1-x) \cdot C_{pEO} + x \cdot C_{pCO} + x \cdot C_{pCH_4}$

### Hot Spot Along a Tubular Reactor

Ethylene oxide (EO) is thermodynamically unstable. Under certain conditions it decomposes to carbon monoxide and methane. Assume that the vapor phase decomposition kinetics are first order and the rate constant is <sup>9</sup>:

$$k, \text{ s}^{-1} = 1.5 \times 10^{13} \exp(-218,000/RT)$$

Where:

R is 8.314 kJ/kmol K

T is temperature in K

- Determine the temperature and conversion profile as a function of length for an adiabatic tubular reactor of 1 m in length and 0.5 cm in ID for  $38 \times 10^{-9}$  kmol/s of EO entering the reactor at 705 K and 1 bar pressure. Assume that the total pressure is constant and that Cp's for EO, CH<sub>4</sub> and CO are 72.7, 40.0 and 29.0 kJ/kmol K respectively.
- Repeat for an entering temperature of 715 K. What do you observe different for a 10 K increase in temperature?
- Plot rate vs. distance on an expanded x axis scale (use intervals of about 0.05 micron) at the point where rate "takes off" in part b.
- If the reactor tube material is constructed from stainless steel 304, what can happen in case b

### K-16. Batch Reactor With An Overcharge of Catalyst

**Kinetics Principle Involved:** Non isothermal batch reactor

**Level:** First year graduate

**Health and Safety Concept:** Runaway reactors. Proper relief system sizing

**Background:** This problem is an extension of Problem 9 that was related to a polymer reactor explosion. One possible initiator event cited was that 10 times the normal catalyst charge was added to the batch. This question asks students to

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<sup>9</sup> Mueller, K.H., Walters, J.D., J. Am. Chem. Soc. 73, 1458 (1951)

examine the consequence of such an action. The question is designed to be discussed in class because many fundamental engineering issues are involved.

#### Batch Reactor With an Overcharge of Initiator

Consider a 2 m<sup>3</sup> batch reactor normally charged with 1677 kg of material (335 kg monomer bP 73°C MW=86.1, and 1342 kg of an organic solvent, bP 56.5°C and 1 kg of initiator). The polymerization reaction is exothermic with a  $-\Delta H$  of 1,000 kJ/kg<sub>mono</sub>. The 1<sup>st</sup> order rate constant as a function of temp. is  $k = 1,700 \exp(-4800/T) \text{ s}^{-1}(\text{kg}_{\text{init.}}/\text{m}^3)^{-1/2}$ . Heat transfer is automated to keep the reactor temperature constant at 60°C. At maximum cooling water flow, the overall transfer coefficient is 1.2 kW/m<sup>2</sup>°C for a coil area of 8.4 m<sup>2</sup>. The cooling water temperature is 30°C. Assume that  $c_p = 2.6 \text{ kJ/kg}^\circ\text{C}$ .

- If the initiator charge is 10 kg instead of 1 kg, how does this influence the overall kinetic equations used to model the reactor?
- What happens in terms of heat transfer if 10 times the normal charge of catalyst is used?
- As the reaction proceeds the viscosity of the solution thickens, what will this do to overall heat transfer?
- Assume that the overall heat transfer is constant, prepare conversion and temperature curves as a function of time for the case for when 10 kg of catalyst is charged into the reactor. What can possibly happen?

#### K-17. Startup of An Acetylene Hydrogenation Reactor

**Kinetics Principles Involved:** Catalytic reactor improper start up

**Level:** Graduate first year

**Health and Safety Concept:** Considerations which must be made during the start up.

**Background:** The production of ethylene is a major chemical process. One by-product is acetylene which has to be totally removed before further downstream processing. The method of removal is selective hydrogenation via passing the product gases across a supported noble metal catalyst bed.

An undocumented loss occurred when an acetylene hydrogenation reactor was started up with hydrogen in place of nitrogen. Students are asked to review the ethylene process and determine what can happen under a circumstance where hydrogen is used in place of an inert.

#### Start up of an Acetylene Hydrogenation Reactor

Review the process to make ethylene. Consider the reactor used to hydrogenate the by-product acetylene.

- One day the process started up with this reactor filled with hydrogen. What do you foresee may be the consequences of this action? Support

your answer with some sample calculations for a typical  $C_2H_2$  hydrogenation reactor used in an ethylene production plant. (In actuality, an undocumented loss of  $\$6 \times 10^6$  of a supported noble metal catalyst occurred by sintering)

- b) Given the above facts and findings, suggest the correct start up procedure to get this reactor back on line.

### K-18. Modeling Differential Scanning Calorimetry

**Kinetics Principle Involved:** Non isothermal reactions, adiabatic reactor modelling

**Level:** Undergraduate - directly after introduction of non isothermal reactors

**Health and Safety Concept:** Methods to evaluate reactivity

**Background:** Hofelich and Thomas<sup>10</sup> analyzed an industrial rule of thumb that "if the operating temperature of a process is  $100^\circ C$  below the nearest detectable exotherm observed in a DSC experiment the operation will not experience this thermal event." In their analysis they modeled a DSC with a simple first order exothermic reaction. Students are asked to develop and to show a solution to this model.

#### Modeling Differential Scanning Calorimetry

Differential scanning calorimetry (DSC) is a popular tool used to evaluate the potential thermal hazard with exothermic reaction liquids. Sample sizes are quite small (1 to 10 mg) and experimental time is relatively short (1 hr). DSC is a process which measures the heat generated as the reactants placed inside a cell are heated at the constant rate of 10 K/min starting at  $25^\circ C$ .

- a) Consider a DSC with 10 mg of a reactant ( $\Delta H_{rxn} = -80$  kJ/mol, M.W.=150,  $\rho = 0.91$  kg/l) which reacts in a first order fashion with the rate constant as shown below:

$$k = A \exp(-E_a/RT)$$

Plot the heat generation rate, J/min, as a function of temperature as the material under goes heating from  $25^\circ C$  to  $250^\circ C$  for the following values of A and  $E_a$ .

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<sup>10</sup> Hofelich, T.C. and Thomas, R.C. "The Use/Misuse of the 100 Degree Rule in the Interpretation of Thermal Hazard Tests," Proceedings of the Inter. Syms. on Runaway Reactions (1989, Cambridge, MA, CCPS, AIChE, New York, New York).

<b>A, min<sup>-1</sup></b>	<b>Ea</b>
3.8 x 10 <sup>4</sup>	40 kJ/mol
2.2 x 10 <sup>7</sup>	60 kJ/mol
1.3 x 10 <sup>10</sup>	80 kJ/mol
5 x 10 <sup>15</sup>	120 kJ/mol
2 x 10 <sup>21</sup>	160 kJ/mol

- b) Which condition is most severe and why?
- c) What main safety device(s) is required on a reactor used with exothermic reactions and why?

### K-19. Production of Nitroglycerin - Comparison of Reactor Sizing

**Kinetics Principle:** Comparison of batch to continuous tubular reactors

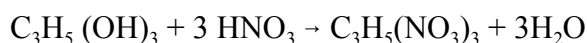
**Level:** Undergraduate - during reactor design

**Health and Safety Concept:** Reduction of inventory leads to an overall safer plant.

**Background:** Trevor Kletz advocates "intensification" (reduction of the amount handling and inventory) as a method of improving plant design for safety.<sup>11</sup> Students are asked to compare two reactor designs used to prepare nitroglycerin and to determine the associated risk with each. The continuous method reduced the required reactor volume by a factor of 1,000. This primarily was because mass transfer was increased significantly in the continuous reactor design. I suggest that students be told to read the reference given in the problem to assist in understanding.

#### Production of Nitroglycerin - Comparison of Reactor Sizing

Reducing the amount of a hazardous material can increase safety and reduce cost.<sup>12</sup> One place where intensification can be applied is switching from large batch reactors to smaller continuous reactors. Consider the production of nitroglycerin (NG) made from a mixture of glycerin, nitric and sulfuric acids. The reaction is:



The reaction is exothermic and temperature must be watched closely (operators of batch reactors sat on one-legged stools as to not to fall asleep). The reaction in a 1 ton batch reactor was diffusion limited taking 120 minutes for completion.

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<sup>11</sup> Kletz, T., *Plant Design for Safety - A User Friendly Approach*, Hemisphere Pub. Co., New York, 1991. p. 21-28.

<sup>12</sup> Ibid.

- a) What is the TNT equivalent in kg of a reactor holding 1 metric ton of products? (The equivalent energy of TNT is 4,681 kJ/kg.)
- b) Over-pressure from an explosion can be estimated by the equation:

$$P, \text{ kPa} = (r)^{-2.48} (m_{\text{TNT}})^{0.827} \times 1,000$$

for  $r/m_{\text{TNT}}^{1/3}$  between 1.0 to 4.0 m/kg<sup>1/3</sup>  
 where r is in m and m is the mass equivalent of TNT in kg

If the batch reactor exploded, at which radius would the over-pressure be 70 kPa (all buildings inside the radius would probably be destroyed)?

- c) Perform the same calculation as in parts a and b for a continuous nitration reactor which contain at most 1 kg of reaction products.
- d) What are the major reactor design differences between the batch reactor and the continuous reactor? What fundamental change improved the rate for the continuous reactor?

## K-20. The Chemical Kinetics of Explosions

**Kinetics Principle:** First order. Simplified background into explosions

**Level:** Undergraduate around first order reactions

**Health and Safety Concept:** Explosions and fundamental understanding of these.

**Background:** This problem provides some background on the chemical kinetics of explosions by asking students to develop mechanisms and resultant rate equations for a few simple chain reactions. Louis Medard's<sup>13</sup> book about explosions and Smith's section 2-8 serve as the reference for this problem.

### The Chemical Kinetics of Explosions

Explosions are the result of a chain of elementary reactions occurring primarily in the gas phase. Each successive reaction requires a chemical entity (molecule or radical) from a preceding reaction.

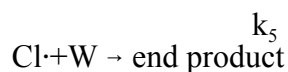
- a) Write down the elementary steps for the formation of HCl starting with Cl<sub>2</sub> activated by light in a Cl<sub>2</sub> + H<sub>2</sub> mixture.
- Label the chain carriers. Label the initiation step, the propagation step(s) and the termination step(s).
- b) Sometimes, as in oxidation of hydrogen, two chain carriers can result from a collision of one chain carrier and one molecule. Write down an example reaction demonstrating chain-branching. What is important in this

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<sup>13</sup> Medard, Louis A., *Accidental Explosions Vol. I Physical and Chemical Properties*, 1989, Ellis Horwood Limited, Chichester, West Sussex, England.

mechanism regarding explosions?

- c) If the terminator step in part a) was:



show derivation of the rate equation:

$$-\frac{d C_{\text{Cl}_2}}{dt} = +k C_{\text{H}_2} C_{\text{Cl}_2}$$

Use the stationary state hypothesis:

- d) Can the stationary state hypothesis be used in part b)?

### K-21. Application of Frank-Kamenetskii Relation For Safe Storage of Ammonium Nitrate Based Fertilizers

**Kinetics Principle:** Auto decomposition of materials when the radius or temperature exceeds a critical value

**Level:** Undergraduate

**Health and Safety Concept:** Safe storage of materials which can self decompose.

**Background:** In 1939, Frank-Kamenetskii<sup>14</sup> considered the following problem<sup>15</sup>. A gas undergoing an exothermic reaction obeying the Arrhenius equation is placed in a spherical container whose wall is maintained at a fixed temperature  $T_0$ . The gas loses heat by conduction. The wall of the vessel offers little resistance to heat transfer. The analysis results in a dimensionless parameter which (depending upon geometry of the storage vessel) predicts a critical  $T_0$  given a characteristic radius or a critical radius given  $T_0$  where the object will self heat and eventually explode. Although originally developed for gases the equation can be used to estimate storage conditions for ammonium nitrite and ammonium nitrate based fertilizers. Explosions with ammonium nitrate, although rare, can be catastrophic. An explosion purposely set to break up solid  $\text{NH}_4\text{NO}_3$  went out of control and caused the death of 500 people, injured 1900 and destroyed Oppau, Germany. Texas City (1947) and Brest, France (1947) had similar explosions.

Application of Frank-Kamenetskii Relation for Safe Storage of Ammonium Nitrate Based Fertilizers

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<sup>14</sup> Frank-Kamenetskii, D.A. Acta Physicochimica, U.S.S.R., 1939, 10, 365; Zhur.Fiz. Khim., 1939, 13, 738.

<sup>15</sup> Medard, L.A., Accidental Explosions, Vol. 1, Ellis Horwood Ltd., Chichester, England, 1989, 48.

Frank-Kamenetskii<sup>16</sup> developed the following dimensionless parameter which can estimate if a gas stored in a constant volume container undergoing exothermic reaction will self heat and thus possibly explode.

$$\delta = \frac{Ea (-\Delta U_{rxn}) M r_{eq}^2 A \exp\left(\frac{-Ea}{RT_o}\right)}{R k T_o^2}$$

Where:

- $\delta$  - dimensionless parameter
- Ea - activation energy
- $\Delta U_{rxn}$  - heat of reaction at constant volume
- r - the equivalent radius of storage volume as a sphere
- A - the Arrhenius equation frequency factor, 1/s
- k - the thermal conductivity
- $T_o$  - the constant temperature around the outside of the storage vessel
- M - molar volume
- R - universal gas content

If  $\delta$  exceeds 3.32, the material inside the spherical storage container will self heat and may eventually explode. Thus, for  $\delta = 3.32$  given a radius one finds a critical storage temperature or given a storage temperature a critical radius can be found. This equation can also apply to systems storing liquids or solids.

- a) A laboratory reports the following critical temperatures for ammonium nitrate based fertilizers for the following cube sizes:

cube size, cm	decomposition temperature, K	
	1	2
2	438	463
4	423	448
8	408	431
16	397	420

Determine the activation energy for the decomposition reactions of fertilizer 1 and 2.

- b) The maximum storage temperature of these two fertilizers is 100°C. If fertilizer bags are available at L x 2L x 0.5L, what maximum value of L

<sup>16</sup> Frank-Kamenetskii, D.A., Acta Physicochimica, U.S.S.R., 1939, 10, 365; Zhur. Fiz. Khim. 1939, 13, 738.

would safely allow the fertilizer to be stored based on the above tests?

## **K-22. Combustibility Testing of Dusts-Burning Rate Tests**

**Kinetics Principle:** Modelling of complex reactions with external diffusion resistance

**Level:** Undergraduate late course or graduate if computations are desired.

**Health and Safety Concept:** Flammability of dusts of characterization of solids.

**Background:** One characterization test of the flammability of solids is the test of combustibility of the material at room temperature. This problem is from a German reference; however, the ASTM has similar tests.

A simple burning test is actually a complex kinetic problem to analyze. The test consists of the ignition of one end of a triangular pile of powder compacted together placed under a low velocity flowing air stream. The time to burn 20 cm (or not to burn at all) helps characterize the dust combustibility characteristic.

Combustibility is related to dust explosions although the relation is general at most.

Dust explosions have been known for approximately 200 years<sup>17</sup>. Six story mill buildings have been destroyed by dust explosions originating in grain storage silos. The ignition of just a teaspoon of corn starch always leaves a memorable impression on the observer of the severity of a dust explosion.

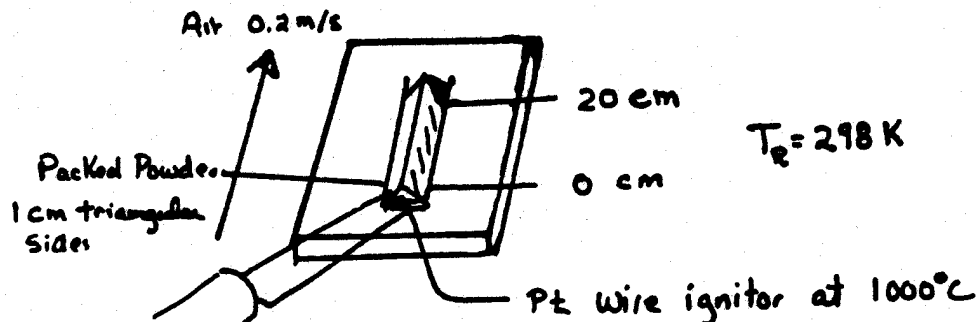
### Combustibility Testing of Dusts-Burning Rate Tests

A characterization test of solid powders and solids in general is combustibility. Consider the burning rate test of a packed powder shown below: Burning rate gives an indication of how fast a fire spreads after ignition. The test consists of measuring the time to burn 20 cm. If the time takes less than 90 seconds the material is classified as easily ignitable.

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<sup>17</sup> Bartknect, W., *Dust Explosions, Course, Prevention, Protection*, Springer-Vellag, New York, 1989, pp.1-33.





- Would the presence of an air flow influence the burning rate for:
  - NaCl?
  - Cellulose fiber?
  - Black gun powder?
- A hydrocarbon based material has a 70 sec. burn rate. What general equations are required to estimate an intrinsic rate constant (do not solve)?
- (Graduate level) Estimate the intrinsic rate constant for the condition shown in Fig. 1.

### K-23. Purification of Process Condensate - Carbon Steel Corrosion

**Kinetics Principle Involved:** Reaction mechanisms leading to rate equation

**Level:** Undergraduate

**Health and Safety Concept:** Corrosion

**Background:** J. Madsen reports on process condensate purification in ammonia plants<sup>18</sup>. During the 1970's the requirements for reducing the pollution of the environment increased<sup>1</sup>. Major efforts have been made to reuse the stripper process condensate as make-up water to the cooling tower circuit, the demineralization unit, and for saturation of natural gas<sup>1</sup>. Contamination of the process condensate can occur by entrainment of CO<sub>2</sub> into the water downstream of the CO<sub>2</sub> separation in the overhead system of a CO<sub>2</sub> regeneration.

Increasing amounts of iron corrosion products had entered the HPC system via the water balance feed line<sup>1</sup>. The corrosion products eventually blocked CO<sub>2</sub> flash vessel packing, thus "overboarding" the system with CO<sub>2</sub>. Madsen analyzed this situation through a corrosion mechanism. Students are given the mechanism and asked to examine a rate equation and provide some analysis. They may need

<sup>18</sup> Madsen, J., *Process Condensate Purification in Ammonia Plants and Related Facilities Safety*, Vol. 31, AIChE, New York, New York, 1991, 227.

their undergraduate chemistry book to look up the definitions of pH and dissociation constants.

### Purification of Process Condensate-Carbon Steel Corrosion

Emphasis in processing today centers on recycling and energy integration. One problem with process water recycling is the potential to build up corrosive agents within the water. Corrosion of carbon steel is dependent on temperature, pH and turbulence (lack of). For example a stripper on the top of CO<sub>2</sub> regenerator in an ammonia synthesis plant results in substantial contact between CO<sub>2</sub> and water. At saturation, the pH can be about 3.9 when little NH<sub>3</sub> is present. At this condition the following reaction occurs at the surface of carbon steel which chemically exists as Fe CO<sub>3</sub>.



The following equilibrium equations approximate the system:



- a) Show that the following expressions may be derived from the equilibrium relationships 2 and 3.

$$\log \left( \frac{[\text{HCO}_3^-]}{[\text{CO}_2]_{aq}} \right) = \text{pH} - \text{p}K_2$$

$$\log \left( \frac{[\text{CO}_3^{--}]}{[\text{HCO}_3^-]} \right) = \text{pH} - \text{p}K_3$$

Where K<sub>2</sub> and K<sub>3</sub> are the first and second dissociation constants for the dissociation of carbonic acid.

- b) At 40°C, K<sub>1</sub> = 4.94 x 10<sup>-7</sup> mol/l and K<sub>2</sub> = 6.05 10<sup>-11</sup> mol/l, generate a curve showing the equilibrium conversion of CO<sub>2(aq)</sub> and HCO as a function of pH.
- c) The rate of Eqn. A can be expressed as r=k[H<sup>+</sup>][FeCO<sub>3</sub>]. Assume that [FeCO<sub>3</sub>] is approximately constant and compare the rate at pH 8 versus pH 5. What do you conclude about the importance of pH in corrosion?

### K-24. Using Kinetics to Evaluate Reactivity Hazards

**Kinetics Principle Involved:** Decomposition reactions, Adiabatic runaway

**Level:** Undergraduate-advance standing, first year graduate

**Health and Safety Concept:** Reactivity ratings method to estimate.

**Background:** Several rating systems exist to determine relative reactivity of materials towards decomposition, polymerization, or other self reactivity. The NFPA system [0 (non reactive) to 4 (readily capable of detonation or explosive decomposition)] is the most common and students need to be exposed to this system. However, how can one assign a chemical a reactivity rating with only a few specifics known like activation energy, adiabatic temperature after decomposition and the frequency factor? E.S. DeHaven<sup>19</sup> develops the "L system" which correlates quite well with the NFPA assignment. His correlation follows a theoretical basis quite nicely. The question requires students to derive his relation starting from a first order reaction.

A hint you may offer (depending on the students' level) the following approximation:

$$(T - T_i) = (T_d - T_i) (x)$$

Where:

T is the temperature at conversion, x  
T<sub>i</sub> is the initial temperature  
T<sub>d</sub> is the adiabatic temperature reached at full conversion  
x is the conversion of the reactant to its decomposition products

Using Kinetics to Evaluate Reactivity Hazards (continued)

Several methods to evaluate reactivity hazards of substances have been proposed over the years. One system proposed by E.S. DeHaven<sup>20</sup> uses kinetic data to evaluate the hazard potential of materials due to self reactivity. The results correlated well with the NFPA reactivity assignment.

- a) Starting with  $-dc/dt = kc$  and where  $k = A \exp(-E_a/RT)$  and assuming that the temperature rise in an adiabatic system is proportional to the disappearance of the reactant show that:

$$T_{qm} = \frac{E_a}{2R} \left[ \sqrt{\frac{4RT_d}{E_a} + 1} - 1 \right]$$

by determining  $dT/dt$  in terms of temperature, then finding  $d^2T/dt^2$  and setting it equal to zero. (Notation is defined below) and show that:

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<sup>19</sup> E.S. DeHaven, "Using Kinetics to Evaluate Reactivity Hazards," in Loss Prevention, Vol. 12. AIChE, New York, 1979, 41.

<sup>20</sup> E.S. DeHaven, "Using Kinetics to Evaluate Reactivity Hazards," in Loss Prevention, Vol. 12, AIChE, New York, 1979, 41.

$$(dT/dt)_{\max} = A (T_d - T_{qm}) \exp (-Ea/RT_{qm})$$

Notation:

c	Concentration, kmol/m <sup>3</sup>
t	Time, s
k	First order rate constant, s <sup>-1</sup>
A	Frequency factor, s <sup>-1</sup>
Ea	Energy of activation, kJ/mol
T	Temperature, K
R	Gas constant 0.008134 k J/mol K
T <sub>qm</sub>	Temperature at maximum temperature rise, (dT/dt) <sub>max</sub>
T <sub>d</sub>	The adiabatic temperature after full decomposition or self polymerization
(dT/dt) <sub>max</sub>	Maximum rate of temperature rise

Mr. DeHaven then defines the "L system" which is defined base 10 logarithm of (dT/dt)<sub>max</sub> and assigned the following NFPA reactivity index.

L	NFPA reactivity index assigned
<-1	0 materials normally stable. Not reactive with water.
-1<L<2	1 materials normally stable but can be unstable at elevated T and P
2<L<6	2 materials are unstable but do not detonate
6<L<8	3 materials capable of detonation or explosive decomposition requires strong initiation
>8	4 materials can readily decompose or explode at normal T and P

b) Determine L and the NFPA ratings for the following chemicals.

	Td, K	Ea	A, sec <sup>-1</sup>
propane	626	264.8	8.175 x 10 <sup>14</sup>
ethylene	1005	157.7	6.49 x 10 <sup>12</sup>
acetylene	2898	168.5	1.55 x 10 <sup>12</sup>
tert-butyl hydroperoxide	(919 + 100) <sup>21</sup>	158.2	1.023 x 10 <sup>16</sup>

## K-25. Detonation - An Introduction

**Kinetics Principle:** Flame speeds in closed pipes

<sup>21</sup> For peroxides use T<sub>d</sub> + 100 see D.R. Strull in "Linking Thermodynamics and Kinetics to Predict Real Chemical Hazards," in Loss Prevention, Vol. 7, AIChE, New York, 1973, 67. Data shown in part b) are from a table in this paper.

**Level:** Undergraduate - late kinetics course when a different type of problem is needed.

**Health and Safety Concept:** Destructiveness of detonations and methods of prevention.

**Background:** Detonations occur when exothermic reactions take place in closed environments like pipes. The theory behind transition from a deflagation to a detonation is quite complex; however, students should understand that two possibilities exist and the difference can be substantial.

Detonation - an introduction

- a) What is a deflagation in a gas mixture?
- b) What is a detonation in a gas mixture?

Detonations occur in closed environments like a pipe when a reactant(s) decomposes or reacts exothermically. An equation to estimate detonation velocity was developed by the Chapman-Jouquet Theory<sup>22</sup>:

$$v = \sqrt{2(\delta^2 - 1) (-\Delta U)}$$

Where:

- v is the flame speed in m/s
- $\delta$  ratio of the specific heat capacities at constant pressure to constant volume ( $c_p/c_v$ )  $\sim 1.32$
- $\Delta U$  is the change in internal energy (J/kg)

- c) Estimate the detonation velocity for a stoichiometric mixture of:

- 1.  $C_3H_8 + Air$
- 2.  $C_2H_2$  decomposition to C and  $H_2$

$$T_1 = 298 \text{ K}$$

- d) What safety devices can be used to stop detonations?

## K-26. Limitation of Effects by Changing Reaction Conditions

**Kinetics Principle Involved:** Reactor design for sequential exothermic reactions

**Level:** Undergraduate - reactor design

**Health and Safety Concept:** Limitation of effects of failures by changing

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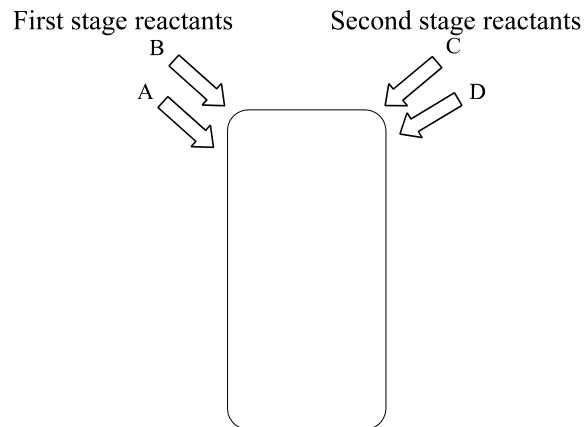
<sup>22</sup> Reviewed in Medard, L.E., *Accidental Explosions, Vol. 1, Physical and Chemical Properties*, Ellis Horwood Ltd., Chichester, England, 1989.

reaction conditions.

**Background:** Trevor Kletz writes that plants can be made safer by reducing inventory of hazardous materials, using safer materials instead and using hazardous materials in a less hazardous form<sup>23</sup>. Another chapter discussed ways of limiting effects of failures by change in reaction conditions. Students are asked to consider the example Dr. Kletz used to demonstrate "limitation".

#### Limitation of Effects by Changing Reaction Conditions

Shown below is a batch reactor used to make a co-polymer. If by mistake the first stage reactants (A and B) were added during the second stage reaction period or the second stage reactants (C and D) were added during the first stage reaction period a runaway would occur. Discuss an alternative reactor design which could avoid or minimize the potential runaways.



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<sup>23</sup> Kletz, T., *Plant Design for Safety - A User Friendly Approach*, Hemisphere Publishing Corporation, New York, 1991, p. 73.

## K-27. Use and Abuse of Low Temperature Shift Catalyst

**Kinetics Principle:** Operation of catalytic reactors

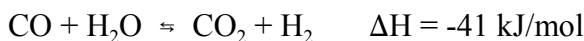
**Level:** Undergraduate - late in a kinetics or reactor design class

**Health and Safety Principle:** Catalyst stability in reactor operation

**Background:** Kitchen et. al.<sup>24</sup> presented a paper on low temperature shift catalysts used in ammonia synthesis plants. LTS catalysts can encounter extreme and unusual conditions. The catalyst must endure these extremes to keep the plant operating economically. Students are given an example to better understand shift reactors.

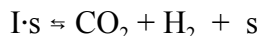
### Use and Abuse of Low Temperature Shift Catalyst

The water-gas shift reaction is used in ammonia synthesis gas plants as a source to maximize hydrogen production. The reaction is:

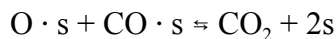
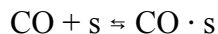
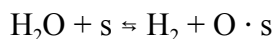


- a) Explain how and why two separate reactors are used in ammonia synthesis plants?
- b) Two mechanisms have been proposed for the reaction.

Mechanism I. Associative on a single site



Mechanism II. Regenerative on two sites



Where:

s - site

I·s - surface intermediate

Describe experiments which could distinguish which mechanism applies.

- c) What are possible catalyst poisons for the low temperature shift (LTS) catalyst bed?
- d) Fresh LTS catalyst is in an oxidized state. Before use, it must be "reduced" by flowing H<sub>2</sub> across the catalyst bed after the LTS catalyst charge has been placed inside the LTS reactor. What major concerns must

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<sup>24</sup> Kitchen, D., Henson, W.G.S., Madsen, J.K., "Use and Abuse of Low-Temperature Shift Catalyst," Ammonia Plant Safety, Vol. 30, AIChE, 1990, 105.

be considered for the reduction process?

### K-28. Conversion of Stack Gas SO<sub>2</sub> to Elemental Sulfur

**Kinetics Principle Involved:** Reactor design from an empirical rate equation

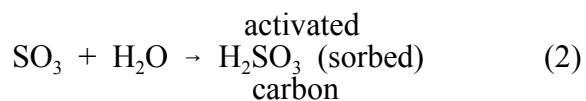
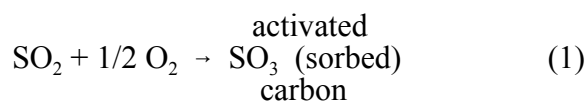
**Level:** Undergraduate, advanced or graduate

**Health and Safety Concept:** Pollution Control Methods

**Background:** Brown et. al.<sup>25</sup> described and modelled a process to remove SO<sub>2</sub> from stack gases using an activated carbon multistage bed. The activated carbon removes the SO<sub>2</sub> in the first stage then it passes through to a sulfur generator followed by a sulfur stripper followed by a hydrogen sulfide generator. Their work showed a rate equation which students are asked to examine.

Conversion of Stack Gas SO<sub>2</sub> to Elemental Sulfur

Brown et. al.<sup>26</sup> Studied the conversion of stack gas SO<sub>2</sub> to elemental sulfur by an activated carbon process. The rate of absorption involved two steps:



The activated carbon with H<sub>2</sub>SO<sub>3</sub> was then regenerated through a multibed process.

- a) You are assigned to study the rate of reaction 1) and 2) in flue gas constituents. What are the major variables which must be studied?

Their work came up with the following kinetic expression:

rate of H<sub>2</sub>SO<sub>3</sub> sorbed kg/kg carbon

$$dx_v/dt = 1.59 \times 10^{-4} \exp(+3066.67/T) y_{\text{SO}_2}^{0.4} y_{\text{O}_2}^{0.63} y_{\text{H}_2\text{O}}^{0.73} (1-x_v/0.38)$$

NO conc > 100 ppm

Where:

$x_v$	carbon loading of sulfuric acid, kg H <sub>2</sub> SO <sub>4</sub> /kg C
$t$	time, min
$y_i$	volume fraction of species i
$T$	temperature, K

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<sup>25</sup> Brown, G.N., Torrence, S.L., Repik, A.J. Stryker, J.L., Ball, F.J., "Conversion of Stack Gas SO<sub>2</sub> to Elemental Sulfur by An Activated Carbon Process," in "Recent Advances in Air Pollution Control," R.W. Coughlin, R.D. Siegel, and C. Rai Eds. AIChE Symposium Series #137, Vol. 70, 1974.

<sup>26</sup> Ibid.



- b)** What type of kinetic expression is this?
- c)** Does the effect of temperature shown seem reasonable?
- d)** What does the term,  $-x_v/0.38$ , represent?
- e)**<sup>27</sup> Consider an inlet gas stream of 1 m<sup>3</sup>/h (STP, for a pilot plant) composed of 2,000 ppm SO<sub>2</sub>, 150 ppm NO, 13% H<sub>2</sub>O, and 3% O<sub>2</sub> at 366 K and an entering flow of solid of activated carbon which flows countercurrently. If the inlet  $x_v = 0$  and outlet  $x_v = 0.01$ , how much activated carbon is required per time and what residence time is required to achieve 95% conversion of SO<sub>2</sub>.
- f)** (For class discussion) If your calculations in part **b)** showed a fairly high steam load (something greater than 50 kW has to be considered unreasonable), what would you do? Here are some choices:
- 1) Don't bother telling anyone, after all it is a job, and you are doing what you are told.
  - 2) Tell your supervisor, and wait. Supervisor comes back with the following reply. "It's a State job. They won't accept any changes."
  - 3) Tell the purchasing agent. He replies. "It's a State job, we bid low and any way that we can save money is a must"
  - 4) Write a letter to the steam plant superintendent with copies to your supervisor and the purchasing agent after exhausting 2 & 3.
  - 5) Don't tell anyone and quit!

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<sup>27</sup> Graduate level

## Safety Problems for a Course in Heat Transfer

Originally Prepared by Ronald J. Willey  
Northeastern University, Boston, MA

### HT-1. Comparison of Properties and Their Influence on Heat Transfer

**Heat Transfer Principle:** Convection

**Level:** Undergraduate Chemical Engineering (Introduction to Heat transfer Ch.1 Holman)

**Health and Safety Concept:** Proper heat exchanger sizing reduces chances of runaways.

**Background:** Properties of fluids play an important role in heat transfer and the resultant exchanger length required to accomplish a given amount of heat transfer. Occasionally, vessels and heat transfer elements designed for one application have been proposed to be used for another application without consideration of viscosity and density changes. The most severe case is a vessel used for an exothermic reaction of a very viscous medium in which the heat transfer coils are undersized because they were initially sized for a lower viscosity medium. The result can be a “runaway” reaction. This problem compares the properties of three materials and the influence that properties have on the Reynolds number, the Prandtl number, and Nusselt number and the resultant heat transfer coefficient.

**Questions:**

10 kg/min of water, air, or glycerin need to be heated from 5 to 15°C in a 2.5 cm diameter tube.

- a) The average temperature is defined as  $T_{ave} = (T_{b1} + T_{b2})/2$  for materials flowing through pipes where  $T_{b1}$  and  $T_{b2}$  are the respective inlet and outlet temperatures of the fluid. Compare the ratios of the properties density, viscosity, kinematic viscosity, heat capacity, thermal conductivity, and thermal diffusivity for air and glycerin to water at  $T_f$ .
- b) The Reynold’s number for a fluid flowing inside a tube as defined on a mass flow rate basis is:

$$Re = 4 * m / \pi d \mu$$

Where:

Re = Reynolds Number

m = Mass flow rate

d = Characteristic length (Diameter)

$\mu$  = Viscosity

and the Prandtl number is defined as:

$$Pr = \nu/\alpha = \mu c_p/k$$

Where:

$\nu$  = Kinematic Viscosity

$\alpha = k/\rho c_p$

$\mu$  = Viscosity

$c_p$  = Heat Capacity

$k$  = Thermal Conductivity

Compare the Reynold's number and Prandtl number of air and glycerin as ratioed to water for each of these materials flowing at 10 kg/min at  $T_{ave}$  through a 2.5 cm tube.

- c) You will learn a number of correlations for heat transfer. A rather simple one is the Dittus Boelter relation for heating of a fluid when the flow regime is turbulent. The Nusselt number (Nu) is given as follows:

$$Nu = h D/k = 0.023 Re^{0.8} Pr^{0.4}$$

When the flow regime is laminar and the pipe is extremely long with a constant wall temperature, the Nusselt number is found to be a constant:

$$Nu = 3.66$$

The amount of heat transfer for a pipe is described by Newton's Law of Cooling.

$$q = h A (T_w - T_{ave}) = h \pi D L (T_w - T_{ave})$$

Where:

$q$  = Rate of heat transfer

$h$  = heat transfer coefficient

$A$  = Area available for heat transfer

$\pi$  = pi

$D$  = Diameter of Pipe

$L$  = Length of pipe

$T_w$  = Wall (Pipe) temperature

$T_{ave}$  = Average ambient temperature

$Re$  = Reynolds number

$Pr$  = Prandtl number

Assume that  $(T_w - T_{ave}) = 50^\circ C$ , compare the Nu,  $q$  required, and finally the length required to heat each fluid from  $5^\circ C$  to  $15^\circ C$ . What properties influence the length most for air and glycerin compared to water?

## HT-2. Insulation of a Hot Pipe

**Heat Transfer Principle:** Steady-state conduction of heat through piping/insulation walls

**Level:** Undergraduate Chemical Engineering (Introduction to Conduction Ch. 2 Holman)

**Health and Safety Concept:** Insulating hot pipes eliminates occurrence of burns

**Background:** Many companies define unsafe surface temperatures of hot objects at  $T_{\text{SURFACE}} > 60^{\circ}\text{C}$  up to a height of 8' above the floor. Burns may result upon contact of surfaces above  $60^{\circ}\text{C}$ . When an outer wall temperature of a pipe is above this temperature, insulation is required<sup>28</sup>.

**Questions:**

- a) Given the following wall temperatures, calculate the minimum thickness of fiberglass insulation required to lower contact temperature to a safe temperature ( $60^{\circ}\text{C}$  and below). Use fiberglass insulation with a thermal conductivity of  $0.035 \text{ W/m}^2\text{ }^{\circ}\text{C}$ . The pipe is 2-inch Schedule 40. Assume an ambient temperature of  $T = 20^{\circ}\text{C}$ , and a convection heat-transfer coefficient of  $3.0 \text{ W/m}^2\text{ }^{\circ}\text{C}$ .  
 $T_{\text{wall}} = 100^{\circ}\text{C}; 200^{\circ}\text{C}; 300^{\circ}\text{C}; 400^{\circ}\text{C}; 500^{\circ}\text{C}$ .
- b) Determine the pipe wall temperature for an insulated pipe which has 0.5 inches of fiberglass insulation and an outside surface temperature of  $60^{\circ}\text{C}$ .
- c) Commercial organically based heat transfer fluids are often used in high temperature applications. Discuss what can happen if these fluids “leak” into the insulation surrounding the pipe. (Reference: *Spontaneous Insulation Fires*, Dr. L. Britton, AIChE Loss Prevention Symposium, 1990.)

### HT-3. Influence of Thermal Conductivity

**Heat Transfer Principles:** Conduction

**Level:** Undergraduate Chemical Engineering (Holman Ch 2)

**Health and Safety Concept:** Properties of Materials-Flash Point

**Background:** Material properties play an important role in heat transfer. For example, thermal conductivities of organic solutions are lower than aqueous based solutions. As a result, organic materials do not “shed” heat as easily as aqueous solutions and thus can reach higher localized temperatures when subjected to equivalent heat fluxes. Other important properties of organics are the flash point and the related fire point. The flash point of a flammable or combustible liquid is the lowest temperature at which a brief flash fire may occur when an ignition source is present. If the flash point is below  $100^{\circ}\text{F}$ , the material is classified as a flammable and local fire codes must be consulted on proper storage of these materials. If the flash point is above  $100^{\circ}\text{F}$ , the material is classified as a combustible and less stringent storage precautions exist. The fire point is the lowest temperature at which a full scale-self sustaining fire can result if air and an ignition source are available. The fire point is always a few degrees (and not too many!) above the flash point. (It may be necessary to review OSHA Standard 1910-106 Combustible and Flammable Liquids for specific handling requirements).

**Questions:**

- a) Consider a 2 m diameter tank, which is well insulated resulting in negligible heat loss, holding 5 m (in height) water. Heat transfer via

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<sup>28</sup> The author acknowledges the assistance of Mark Bellisario in the formulation of this problem.

- radiation is providing a constant heat flux to the top of  $6 \text{ W/m}^2$ . At the bottom of the tank is a heat sink which keeps the bottom of the tank at a constant temperature of  $20^\circ\text{C}$ . Estimate the top surface temperature.
- b) Repeat part a) for the tank holding 5 m of ethylene glycol.
  - c) What is the flash point of ethylene glycol, and therefore, what is its classification?
  - d) In consideration of the answers in part a), b) and c), what are some of the concerns one might have about subjecting the ethylene glycol to this type of heat flux?

#### HT-4. Determination of the Evaporation Rate of Liquid Nitrogen from a Cryogenic Container

**Heat Transfer Principle:** Introduction to steady-state conduction - one dimension

**Level:** Undergraduate (Introduction to conduction - Holman, Chapter 2)

**Health and Safety Concept:** Sizing of relief valves

**Background:** Liquid nitrogen is stored in cryogenic tanks that are well insulated to prevent boil off. The question below is used to estimate the relief valve size required because of heat transfer by conduction through the insulated jacket<sup>29</sup>.

##### Questions:

- a) Determine the inside diameter of the following cryogenic storage tank. The total volume of the cylindrical tank for liquid is 240 liters and an inner height of 1 meter. The wall of the tank consists of three layers of material. The inner and outer layer of the wall is 1.5 mm 304 stainless steel. The central layer of the wall consists of an evacuated space with insulation at a thickness of 22 mm.
- b) Determine the heat flow through the wall of the tank and the evaporation rate. Assume the liquid nitrogen is stored at 23 psig and  $-188^\circ\text{C}$  and that the ambient temperature is  $24^\circ\text{C}$ . The thermal conductivity of 304 stainless steel and the insulation can be assumed constant at values of  $120 \text{ W/m}^\circ\text{C}$  and  $0.72 \text{ mW/m}^\circ\text{C}$ , respectively. The latent heat of vaporization of nitrogen is  $5.577 \text{ kJ/gmol}$ . Neglect the heat transferred through the ends of the cylindrical tank, convection, and radiation effects.
- c) Consider that over a period of time, the evacuated space in tank wall filled with air at atmospheric pressure. Determine the heat flow (W) through the wall and the evaporation rate (kg/h) under these new conditions. Assume that the thermal conductivity of the layer of insulation with air will be equal to the thermal conductivity of air.
- d) Determine the diameter required for a relief valve to properly fit the tank using the following equation<sup>30</sup>. Size the relief valve using the maximum possible evaporation rate of the liquid nitrogen. Assume a discharge

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<sup>29</sup> The author acknowledges the assistance of William Menaker in the formulation of this problem.

<sup>30</sup> Crowl, D. A. & Louvar, J. F. *Chemical Process Safety: Fundamentals with Applications*. 2<sup>nd</sup> ed. Prentice Hall, Englewood Cliffs, New Jersey, 2002, p 390. Eqn. 9-6.

coefficient of 1.0 and the ratio of heat capacities of 1.4.

$$A = \frac{Q_m}{C_o P} \sqrt{\frac{T}{M} \left[ \frac{g_c \gamma}{R_c} \left( \frac{2}{\gamma + 1} \right)^{(\gamma+1)/(\gamma-1)} \right]}$$

Where:

- A = area of discharge
- $Q_m$  = evaporation rate
- $C_o$  = discharge coefficient
- P = absolute upstream pressure
- $\gamma$  = ratio of heat capacities
- $g_c$  = gravitational constant
- M = molecular weight
- $R_c$  = ideal gas constant
- T = absolute temperature of discharge

#### HT-5. Determination of Evaporation Rate of Propane

**Heat Transfer Principle:** Introduction to Heat Transfer (Conduction, Convection & Radiation)

**Level:** Undergraduate (Holman Ch 1 & 2)

**Health and Safety Concept:** Prevention of BLEVES

**Background:** BLEVES<sup>31</sup>, Boiling Liquid Expanding Vapor Explosions, are one of the most serious explosions anyone can imagine. BLEVES refers to the mechanism when a vessel containing a liquid above its atmospheric boiling point ruptures and the flashing liquid develops a blast wave. It does not require the liquid to be a flammable; however, several serious BLEVES have involved liquefied petroleum gas (LPG) - a flammable. A mechanism for a BLEVE of a LPG containing tank can begin by an external flame striking the wall of a tank filled with LPG that is stored at ambient pressure and its resultant vapor pressure (60 to 200 psig). Initially, little happens, except the relief of LPG through the relief valve on the tank due to boiling off of the liquid within the tank. However, when the level of the liquid inside the tank drops below the flame impingement point, the tank wall weakens from direct flame impingement and fails. At this point, the tank opens up like a zipper. An enormous cloud of vaporized LPG quickly forms above the tank. This mixture, with oxygen in the air, is simultaneously ignited by the fire and a tremendous explosion. In 1983 over 500 people were killed when a series of BLEVES occurred near Mexico City. Prevention of BLEVES have advanced to the point where they seldom occur. Part of the prevention is to stop flame impingement or to keep the tank wall wet during the fire. In the shipment of LPG by rail, shelf couplers and head shields

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<sup>31</sup> The author acknowledges the assistance of William Menaker and Professor Reed Welker in the formulation of this problem

are now required by Federal rules and the tank cars must be insulated to keep the walls in the vapor space cooler during fire exposure.

**Question:**

LPG is stored in a cylindrical carbon steel tank with hemispherical ends and is equipped with a relief valve that opens at 260 psig (a boiling temperature of about  $T=54^{\circ}\text{C}$ ). The tank is 10 m long and 3 m in diameter and is initially at 90 % full. Heat from an impinging flame is transferred to the wall surface by two mechanisms: radiation and convection. Then, heat is transfer though the tank wall to the boiling liquid by conduction. Assume that a flame ( $T=1,100^{\circ}\text{C}$ ) is striking an area of  $20\text{ m}^2$  along the tank wall up to a point 1 m high on the side. For radiational heat transfer, use a view factor of 0.3 and an emissivity function of 1.0 (really absorptivity in this case). For convective heat transfer, use a convective heat-transfer coefficient of  $20\text{ W/m}^2\text{ }^{\circ}\text{C}$ . For conductive heat transfer through the wall assume that the tank wall has a thickness is  $\frac{1}{2}$ " and a thermal conductivity of  $43\text{ W/m}^{\circ}\text{C}$ . Estimate how long it takes for LPG to boil off from 90% full to a height of 1 m assuming that the liquid inside the tank is at its constant boiling temperature of  $54^{\circ}\text{C}$ . The time is approximately the time available for firemen to put out the flame and evacuate the surrounding area before a BLEVE occurs. Use a heat of vaporization for LPG at  $380.6\text{ kJ/kg}$  and the liquid density at  $532\text{ kg/m}^3$ .

**HT-6. Determination of the Temperature at the Tip of a Fin**

**Heat Transfer Principle:** Introduction to steady-state conduction - one dimension

**Level:** Undergraduate (Introduction to conduction through fins - Holman, Chapter 2)

**Health and Safety Concept:** High temperature surfaces can be unsafe

**Background:** Hot surfaces can burn human skin. A rule of thumb is that any surface above  $140^{\circ}\text{F}$  ( $60^{\circ}\text{C}$ ) can cause a burn on a person. Consider the following finned tube heater that might be considered for use in a home<sup>32</sup>.

**Questions:**

A house is heated with forced steam through a longitudinal fin-tube heat exchanger. Saturated steam is at pressure of 25 psia and is forced through a 50 ft copper pipe (OD = 1 inch, ID = 0.8 inch). There are a total of 8 aluminum fins with a longitudinal length of 50 feet, a height from the base of the pipe of 2 inches, and a thickness of  $\frac{1}{16}$  inch. The ambient temperature is  $70^{\circ}\text{F}$  and the mass of condensate measures at 100 lb/hr. Assume that all heat transferred through the copper pipe wall is transferred through the fins only.

- a) Find the heat flow through the copper pipe wall.
- b) Calculate the outside wall temperature of the copper pipe.
- c) Calculate the heat transfer coefficient,  $h$ , from the aluminum fin to the air.
- d) Find the temperature at the tip of each fin.
- e) Is the tip temperature safe for children to come into contact with? If the

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<sup>32</sup> The author acknowledges the assistance of William Menaker in the formulation of this problem

answer is no, what could be done to prevent contact by children?

### HT-7. A Pipe Too Long

**Heat Transfer Principle:** The Conduction Shape Factor

**Level:** Undergraduate Chemical Engineering (S.S. Conduction Ch. 3 Holman)

**Health and Safety Concept:** Ethics and Communication

**Background:** NIMBY “Not in my back yard” lead to a decision to build a steam generation plant 1 mile away from the center of a large university. After the plant was built (at several million dollars of investment) it was discovered that the steam main could not deliver the steam.

#### Questions:

- a) Estimate the heat lost for a 12” steam main carrying 600 psig steam a distance of 1 mile. Assume that the steam main is buried 4 feet below ground level. Use a ground surface temperature of 0°C (the location is in a northern state) . Treat the system as an isothermal cylinder buried in a semi-infinite medium. Use a thermal conductivity for the ground of 0.8 W/m°C. Also estimate the heat lost as kg/h of steam load.
- b) The contract issued by the State Agency specifies that the steam main shall have 6” of fiberglass insulation. No other details are provided. Your purchasing agent has found 6” insulation with a thermal conductivity of 0.2 W/m°C for a very low cost. Estimate the heat lost for the insulated steam main in part a) and the equivalent steam load.
- c) (For class discussion) If your calculations in part **b)** showed a fairly high steam load (something greater than 50 kW has to be considered unreasonable), what would you do? Here are some choices:
  - 1) Don’t bother telling anyone, after all it is a job, and you are doing what you are told.
  - 2) Tell your supervisor, and wait. Supervisor comes back with the following reply. “It’s a State job. They won’t accept any changes.”
  - 3) Tell the purchasing agent. He replies. “It’s a State job, we bid low and any way that we can save money is a must”
  - 4) Write a letter to the steam plant superintendent with copies to your supervisor and the purchasing agent after exhausting 2 & 3.
  - 5) Don’t tell anyone and quit!

### HT-8. Those Rags Have Got to Be Moved!

**Heat Transfer Principle:** The Conduction Shape Factor

**Level:** Undergraduate Chemical Engineering (S.S. Conduction Ch. 3 Holman)

**Health and Safety Concept:** Auto-ignition temperature

**Background:** Plumbers often use rags which accumulate oil and hydrocarbons over time. On rare occasions, these rags are left on a floor near a furnace or a



heat source. Over time these rags can begin to heat because of heat transfer by radiation and convection. If the material in the rags is combustible, the temperature could reach the auto-ignition temperature and the rags will then catch on fire. For more general article on the prevention of fires for thermal fluid systems, see J. Oetinger's article in *CEP*, Vol 98 (1), pp 46-48, 2002.

**Questions:**

- a) Determine the auto-ignition temperature for hexane<sup>33</sup>.
- b) An incinerator used in the combustion of trash and for the production of steam has an internal wall temperature of 301°C and an external wall temperature of 300°C. The walls are carbon steel and 1/2" in thickness. The incinerator dimensions are 10' wide, 20' long, and 12' high. Estimate the total amount of heat lost through the walls.
- c) A workman leaves a pile of rags soaked in a high boiling point oil with an auto-ignition temperature similar to hexane (approximately 1 kg of oil and rags in a spherical shape with a diameter of 8" and with an initial temperature of 20°C) 12" away from the wall of the furnace. Let the effective thermal conductivity of the air between the rags and the furnace be 0.05 W/m °C. The effective heat capacity of the rags is 2,400 J/kg °C. Using the maximum heat flux to the rags from the furnace wall and assuming no evaporation, estimate the time that the janitors have before these rags may self ignite.

### HT-9. Cooling of a French Fry

**Heat Transfer Principle:** Unsteady-State Conduction in a Multidimensional System

**Level:** Undergraduate (Intermediate Conduction- Ch. 4 Holman)

**Health and Safety Concept:** Allowing hot food to cool off prevents mouth injuries in the food industry.

**Background:** Many popular foods are prepared in very hot environments. When these foods are served, they need to be cooled down to a safe contact temperature to prevent mouth injuries. Most restaurants require the center temperature of served food to be no more than 50°C. When foods come out of preparation at 100°C and higher, cooling down to a safe temperature sometimes takes longer than expected<sup>34</sup>.

**Question:**

A french fry (1 cm x 1 cm x 6 cm) has just come out of its frying oil at a temperature of 100°C. It is immediately exposed to the ambient conditions of  $T_{amb} = 20^\circ\text{C}$  with a convection heat transfer coefficient of 10 W/m<sup>2</sup>°C. Using the Heisler charts for a multidimensional object, determine the time required for the french fry to cool down to a safe center temperature of 40°C. Assume that the

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<sup>33</sup> This is a property of the material and is usually available on MSDS sheets or within an index like the Merck Index

<sup>34</sup> The author acknowledges the assistance of Mark Bellisario in the formulation of this problem

french fry has properties of water.

### **HT-10 Determination of the Cooling Time for a Potato Puff**

**Heat Transfer Principle:** Unsteady-state conduction

**Level:** Undergraduate Chemical Engineering (Conduction Holman, Chapter 4)

**Health and Safety Concept:** Prevention of contact with hot surfaces

**Background:** Contact with hot surfaces can be a painful experience. This problem uses the unsteady state “cooling” of a spherical object to demonstrate the time one must wait before serving up the hot food<sup>35</sup>.

**Question:**

How long of a cooling time is required for a spherical potato puff before it is ready to be served for dinner? The potato puff is deep fried at 325°F and is removed with a bulk temperature of 212°F. The ambient surroundings is 70°F. Assume a thermal conductivity is half of water at the same temperature and a heat capacity and molecular weight equal to water. The heat transfer coefficient of 6 W/m<sup>2</sup> °C and the specific gravity is assumed equal to 0.6. The diameter of the potato puff is 2.5 cm. The maximum safe serving temperature of the potato puff is 130°F.

### **HT-11 Chip Frying and HAZOPS**

**Heat Transfer Principle:** Convection/Conduction Heat Transfer

**Level:** Undergraduate Chemical Engineering (Ch 4 Holman with Numerical methods)

**Health and Safety Concept:** Hazards and Operability studies (HAZOPS)

**Background:** This problem is intended as a class project of one to two weeks duration. It can be done in groups or individually. The HAZOPS portion will require some outside resources. An outside resource that I used was the Cyanamid Hazard Evaluation Manual which is available from Corporate Loss Prevention Office of the American Cyanamid Company, 1 Cyanamid Plaza, Wayne, NJ 07470 (Additional references: Center for Chemical Process Safety book which Guidelines for Hazard Evaluation Procedures).

**Questions:**

- a) Fitra Chips Inc. is using a continuous fryer to cook 1.3 mm thick, 5 cm diameter potato chips. The process consists of the reticulation of oil through a heat exchanger to a continuous fryer which is a long open channel. Sliced potatoes are added at the beginning of the fryer channel and are removed at the end as cooked potato chips. The process is quite complex and the prediction of outlet chip temperature, moisture content, oil content, and brownness involve an understanding of both heat and

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<sup>35</sup> The author acknowledges the assistance of William Menaker in the formulation of this problem

mass transfer. Simplified equations are (assuming steady state cooking)<sup>36</sup>:  
 Temperature of the oil bath as a function of position:

$$v \frac{\partial T_o}{\partial x} = -(h_t a_o / c_{po} \rho_o) * (T_o - T_c) - (a_l D h_{fg} / c_{po} r_o) * N_m$$

Temperature of a chip in the oil bath as a function of position (the chip is treated as a lumped-heat-capacity system see Holman p 141).

$$v \frac{\partial T_c}{\partial x} = +(h_t a_c / c_{pc} \rho_c) * (T_o - T_c)$$

Percent moisture content within a chip as a function of time in the fryer.

0 < t < 25 seconds, M = 0.8 (chip is 80% moisture)

at t > 25 seconds, M = 19.65/t + 0.014

Notation:

$a_c$	interfacial surface area passing a point per unit time of the chip divided by the volumetric flow rate of the chips, $m^{-1} s^{-1}$ .
$a_l$	1/(volume element of oil) in which evaporation is occurring, $m^{-3}$ .
$a_o$	interfacial surface area passing a point per unit time of the chip divided by the volumetric flow rate of the oil, $m^{-1} s^{-1}$ .
$c_{pc}$	heat capacity of the chips, J/kg s.
$c_{po}$	heat capacity of the oil, J/kg s.
$h_t$	heat transfer coefficient., $W/m^2 \text{ } ^\circ C$ .
$h_{fg}$	heat of vaporization of water, J/kg.
D	diameter of the chip, cm
M	mass fraction of water in the chip, dimensionless $0 < M \leq 1.0$ .
$N_m$	rate of evaporation within a volume element, $a_l$ , kg/s
$T_c$	lumped temperature of the chip, $^\circ C$
$T_o$	temperature of the oil, $^\circ C$ as it enters the fryer.
t	time, s.
v	velocity of the material through the fryer, m/s
x	the linear position down the fryer, m.
$\rho_c$	density of the chips, $kg/m^3$ .
$\rho_o$	density of the oil, $kg/m^3$ .

Assuming that the fryer is 1 m wide, 18 meter long and an oil depth of 0.1 meter, determine and plot oil and chip temperatures as function of position within the fryer for an oil feed rate of 0.3, 0.6, and 1.2  $m^3/min$  and a potato feed rate of 200, 400, and 800 kg/hr. The oil enters at a temperature of 175 $^\circ C$  and the sliced potatoes enter at a temperature of 25 $^\circ C$ . The oil has a density of 805  $kg/m^3$  and a  $c_p$  of 2,483 J/kg C. Assume that the potatoes have properties similar to water. Use a heat transfer coefficient of 10  $W/m^2 \text{ } ^\circ C$ .

**b)** HAZOPS (Hazardous and Operability Study) is one of several methods to analyze a process for hazards. The overall process is usually done in

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<sup>36</sup> These equations are simplification of equations presented by Feng, W., Shouche, S., and Nikolaou, M. "Modeling and Predictive Control of a Continuous Fryer," Poster Session, AIChE Annual Meeting Nov 12-17, Miami Beach, Florida, 1995.

teams; however, to demonstrate the method consider the following. The HAZOPS method is applied to process vessels and lines (nodes). Using guide words of “no/not/none”, “more/higher/greater”, “less/lower”, “other than”, and “sooner/faster” process parameters such as “temperature” and “reaction” can be evaluated as to what is the possible cause and possible consequence. For example examination of “temperature higher” within the fryer may be caused by the oil heat exchanger operating at too high of a temperature. Possible consequences might be burnt chips. Installing a temperature controller on the heat exchanger would reduce the likely hood of over heating the chips.

You are to make up a HAZOPS status sheet for the fryer using the process parameters of entering oil temperature and oil flow rate using the five words above. The columns can be labeled as:

Equipment	Process Parameter	Deviation (Guide Word)	Possible Causes	Possible Consequences	Action Required
Fryer	Temperature	Higher	Heater Out of Control	Burnt Chips	Temperature controller on heat exchanger

## HT-12 Cooling of a Thick Shake

**Heat Transfer Principle:** Convection by laminar flow across a flat plate

**Level:** Undergraduate (Introduction to principles of convection Ch. 5 Holman)

**Health and Safety Concept:** Influence of viscosity on heat transfer - Viscous materials require more area for equivalent heat transfer.

**Background:** Viscous materials influence heat transfer significantly. This example demonstrates the increase in area required for equivalent heat removal when viscosity is increased 10,000 fold.

**Questions:** You are an engineer specifying a cooling plate for thick shakes. Shakes are prepared at 82°C, and it is proposed to pre-cool to 78 °C by passing the material across a 0.1 m wide flat plate with a surface temperature of 4°C. Mass flow rate is estimated at 0.1 kg/s and fluid thickness is 1 cm high.

- Given this information, determine the length of a plate required to cool the material as if it was a stream of water.
- Assume that the viscosity of the thick shake is 10,000 times greater than the viscosity of water for any given temperature and that all other shake properties are equal to those of water for any given temperature. Calculate the length of plate required to cool the shake from 82°C to 78°C using the same flow rates and cooling plate temperature used in the calculations for water.
- What factors influenced the answer in part **b)** compared to part **a)**?

## HT-13 Tricky Flame Arresters

**Heat Transfer Principle:** Forced Convection

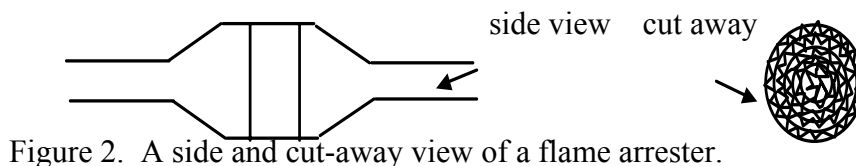
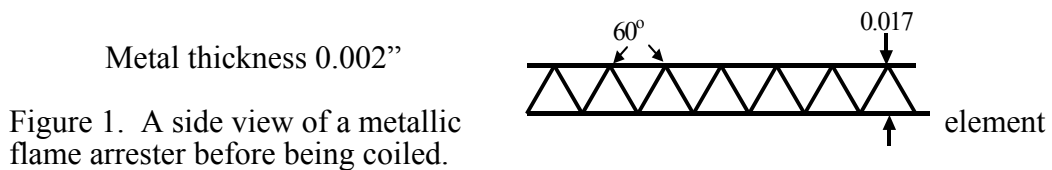
**Level:** Undergraduate Chemical Engineering (Forced Convection Ch. 6 Holman)

**Health and Safety Concept:** Flame arresters are important process safety equipment

**Background:** Flame arresters are installed in many process lines and within vents for large hydrocarbon storage tanks. One type of an arrester is a thin wall metal arrester composed of a crimp metal between two metals forming a corrugation similar to corrugated cardboard. This corrugated sheet is then rolled up to form the core of the flame arrester. An excellent review is available in Ref 1<sup>37</sup>.

### Questions:

- A flame velocity within a pipe can vary tremendously from a deflagration (a reaction or flame front moving at a speed below the speed of sound) to a detonation (a reaction or flame front moving faster than the speed of sound). Consider a flame front approaching a triangular cell shaped flame arrester as drawn in Figure 1 at the speed of 100 m/s (a deflagration) and a temperature of 1,100°C. Someone suggested that this device quenches the flame by lowering the gas temperature below the autoignition point of the gases (say 300°C in this problem). If the average wall temperature of the metal is 200°C during the quenching process, how long does the flame arrester have to be? Assume the properties of air for the combustion gas mixture.
- The actual quench mechanism is related to the combustion reaction. Review your chemistry textbook under elementary combustion reactions and supply an answer as to what is the flame arrester's real quench mechanism.



<sup>37</sup> Howard, W. B. "Flame Arresters and Flashback Preventers", Plant Operation Progress, Vol 1, No 4, p 203, Oct 1982.

## HT-14 When Can You Put That Iron Away?

**Heat Transfer Principle:** Free Convection

**Level:** Undergraduate Chemical Engineering (Free Convection Ch 7 Holman)

**Health and Safety Concept:** Hot surface temperatures can burn

**Background:** Hot surfaces can burn human skin or cause fires. A rule of thumb is that any surface above  $60^{\circ}\text{C}$  can be unsafe. Consider the following simple everyday example below<sup>38</sup>.

**Question:**

Your first job interview is about to occur and you have decided to iron some clothes the night before. You pull out an iron which has a  $\frac{1}{4}$ " stainless steel polished plate to serve as the ironing surface. When sitting vertical, the surface can be roughly modeled as a vertical rectangular plate of 4" wide and 8" high. After you have ironed your clothes you now desire to put the iron away. The surface temperature at the time of unplugging is  $110^{\circ}\text{C}$  and the iron is left in the vertical position. How long should you wait before you put the iron into the closet? Your room temperature is  $20^{\circ}\text{C}$ .

## HT-15 How Hot Is That Electric Fry Pan ?

**Heat Transfer Principle:** Free Convection

**Level:** Undergraduate Chemical Engineering (Free Convection Ch 7 Holman)

**Health and Safety Concept:** Hot surface temperatures can burn

**Background:** Hot surfaces can burn human skin. A rule of thumb is that any surface above  $60^{\circ}\text{C}$  can burn a person's finger when touched.

**Questions:**

- a) It's Thanksgiving morning and you are home for the holidays. Your mother pulls out a 1350 W electric fry pan and begins to cook pancakes. You have just had a lecture on free convection from horizontal surfaces, and therefore; offer to estimate the pan's real surface temperature. If 5% of the rated energy leaves the 10" by 10" top surface by free convection, estimate the surface temperature of the electric fry pan. The surrounding air temperature may be taken as  $20^{\circ}\text{C}$ .
- b) The pan has an edge that is 1" high and  $\frac{1}{8}$ " thick. The surface temperature is set at  $204.4^{\circ}\text{C}$  ( $400^{\circ}\text{F}$ ). Using a film temperature of  $112^{\circ}\text{C}$ , estimate the film coefficient for heat transfer from the vertical edge.
- c) Is it safe to touch the top edge? Estimate the temperature at the upper edge by treating the edge like a fin. Assume that the pan is made of aluminum.

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<sup>38</sup> The author acknowledges Ms. Michelle Hoey for the suggestion of this problem

## HT-16 Snow in July

**Heat Transfer Principles:** Conduction, Convection, and Radiation

**Level:** Undergraduate Chemical Engineering (Holman Ch 1, Ch 8)

**Health and Safety Concept:** Runaway Reactions and Resultant Releases

**Background**<sup>39</sup>: There was once a town...where all life seemed to live in harmony with its surroundings...Then a strange blight crept over the area. Mysterious maladies swept the flocks of chickens; the cattle and sheep sickened and died... The farmers spoke of much illness in their families. In the town, the doctors had become more and more puzzled by new kinds of sickness... In the gutters, under the eaves, and between the shingles of the roofs a white granular powder still showed a few patches; some weeks before it had fallen like snow upon the roofs and the lawns, the fields and streams.  
*THIS TOWN DOES NOT ACTUALLY EXIST... I KNOW OF NO COMMUNITY THAT HAS EXPERIENCED ALL THE MISFORTUNES I DESCRIBE. Yet every one of these disasters has actually happened somewhere, and many real communities have already suffered a substantial number of them.*

Adapted by John Fuller<sup>40</sup> from Rachel Carson The Silent Spring. Fawcett Publications, Inc. Greenwich, Conn., 1962

On Saturday, July 10, 1976, this prophecy was filled. A community did suffer all of the misfortunes Rachel Carson wrote about in Chapter 1 in her 1962 book the Silent Spring. This community was Seveso, Italy.

The story begins with a reactor vessel 2.3 m in diameter and 3.4 m high where 2,3,5-trichlorophenol(TCP) was being synthesized from 1,2,4,5-tetrachlorobenzene in NaOH, ethylene glycol, and xylene. Heating was done by coils surrounding the vessel using superheated, 12 bar, steam (saturation temperature of about 188°C) as the heating medium. Most of the processing was done at 170°C. On the day of the accident, as the reaction step finished, the crew decided to leave for the weekend before finishing the final processing step- the addition of quench water. Six hours later the reactor system over pressurized and a release of NaTCP, NaOH, and approximately 2 kg of 2,3,7,8 tetrachlorodibenzopara-dioxin (an extreme toxin) left the reactor. The relief system worked exactly as designed by preventing the explosion of the reactor; however, the relief went directly into the environment above roof. It was then dispersed by a wind across the country side where children playfully thought it was snowing. Eventually, this “snow”, which did not melt, altered the life style of several hundred of Seveso residents forcing them to give up their homes and move to another location and overall altered the way chemicals are processed in Europe via the initiation of a European directive on the handling of toxic

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<sup>39</sup> A set of slides about this accident are available as a SACHE product. See “Seminar on Seveso Release Accident Case History,” prepared by Ronald J. Willey, AIChE 1994.

<sup>40</sup> Fuller, John G. *The Poison that Fell from the Sky*, Random House, Inc. New York, 1977.

chemicals.

In search of the cause of the accident, examination of heat transfer played an important role. An “auto initiation” temperature of 220°C (a temperature where the materials could self-react exothermally creating other products) was known. However, the reactor was left at 170°C when it was shut down. So how did it heat? The answer was in the superheated steam. Its entering temperature was 300°C. Heat transfer to the upper surface of the liquid occurred by both conduction/convection and radiation. This problem takes a simplified look at both heat transfer mechanisms.

**Questions:**

- a) Compare the ratio of enthalpy available in steam as it cools from 300°C to its saturation temperature with the amount of enthalpy available as the steam condenses. What conclusion might one make here?
- b) The reactor vessel was only 1/3 full. Thus, the upper walls of the reactor vessel were near 300°C when the reactor was shutdown. If the reactor walls were 300°C at a location of 0.1 m above the rim of the liquid/wall interface and the wall temperature at the rim was near 170°C, estimate the heat flow inside the wall by conduction through the stainless steel from the 0.1 m location above the rim to the rim. Assume that the reactor vessel was made of stainless steel and had a thickness of 1.25 cm”. (Ans. 1914 W)
- c) Next assume that the temperature at the rim interface was 300°C and that the bulk fluid temperature was 170°C. Estimate the required film coefficient for all of the heat flow from part **b)** to travel from the reactor wall into the reactor fluid within the first 1 cm of liquid height below the surface. What is the temperature rise per hour for the liquid ( $c_p=2740$  J/kg C, density =1050 kg/m<sup>3</sup>) for this liquid volume under these conditions? Based on the magnitude of the heat transfer coefficient and the rate of temperature rise does heat transfer by conduction explain the rise in temperature beyond 220°C in six hours?
- d) Another explanation for localized heating was heat transfer by radiation from upper reactor walls to the fluid surface. If the radiation shape factor from the liquid surface (at 170°C) to the upper reactor walls (at 300°C) was 0.2 and the emissivities of the wall and the liquid were 0.8 and 0.9 respectively, estimate the rate of heat transfer by radiation to the surface of the liquid. Determine the heating rate, °C/hr, assuming that the rate of energy accumulated is equal to the energy received at the surface by radiation and that only the first cm of liquid is heated by this energy input. Is this also a possible explanation for the temperature rise that occurred after the reactor was shut down?
- e) The experience of others is often the best wisdom. What would you do differently related to the release system for this reactor?

### HT-17 Liquid Nitrogen Spills

**Heat Transfer Principle:** Boiling Heat Transfer

**Level:** Undergraduate Chemical Engineering (Radiation & Boiling Heat Transfer Ch. 8 & 9 Holman)



**Health and Safety Concept:** Minimum oxygen content in environments must exceed 18%

**Background:** Spills of cryogenics, liquid nitrogen and natural gas, show some very interesting phenomena.<sup>41,42</sup> Initially, the liquid never wets the surface because of the Leidenfrost phenomenon, a thin film of gas exists between the liquid and the surface. Because of this film of gas, little flow resistance is observed and the material spread quickly and moves rapidly to the lowest point in the room (often to sewer trenches). During this period heat transfer is entirely by radiation from the room to the exposed upper surface area of the cryogenic. Gradually, the surface underneath the cryogenic cools and wetting takes place. The evaporation rate is then accelerated several orders of magnitude. Secondly, if the oxygen concentration falls below 19.5% in an environment, people can faint. Concentrations below 13% can be deadly. An equation, often used for sweep through purging estimations, can also be used to estimate the time available to evacuate a room or area when a spill occurs<sup>43</sup>.

$$Q \cdot t = V \cdot \ln [(C_1 - C_0)/(C_2 - C_0)]$$

Where:

- Q: is flow rate of entering species at concentration  $C_0$ ,
- V: is the volume of the room or vessel being purged
- $C_1$ : is the initial concentration of species in the area, any consistent set of concentration units can be used
- $C_2$ : is the final concentration of species
- $C_0$ : is concentration of species in the entering stream.
- t is the time to reach  $C_2$ .

**Questions:**

- a) A liquid nitrogen tank fails inside a room. The nitrogen forms a pool with an exposed surface area of 5.0 m<sup>2</sup>. Calculate the rate of evaporation assuming radiation heating dominates. The surrounding room conditions are at a temperature of 25°C and at atmospheric pressure. Use a  $\Delta H_{\text{vapN}_2} = 5.577$  kJ/mol, and an  $\epsilon = 0.8$ .
- b) Using a 20 m by 25 m by 7 m room, how long would it take for oxygen levels to drop by 20%, assuming that no make up air enters the room and that there is a constant evaporation rate due to radiation heating from the surrounding room?
- c) Once the temperature difference between the contact floor and pool of nitrogen drops to a certain value nucleate boiling will dominate.

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<sup>41</sup> This can be seen in an easy classroom demonstration. Pour a small amount of liquid nitrogen into a control volume. Initially, the nitrogen will “dance around” (film boiling) with the slightest movement. Later as the surface cools, N<sub>2</sub> evaporates much more quickly, and the class will hear a “sizzling” indicating the transition to nucleate boiling.

<sup>42</sup> The author acknowledges the assistance of Richard Hennessy in the formulation of this problem.

<sup>43</sup> Crowl, D.A., and Louvar, J.F., *Chemical Process Safety: Fundamentals with Applications*, 2<sup>nd</sup> ed. Prentice Hall Englewood Cliffs, NJ, 2002, p 300.

Assuming a surface contact area of 10 m<sup>2</sup>, and using Figure 9-8 in Holman<sup>44</sup>, estimate the evaporation rate of nitrogen for a temperature difference of 20 C.

- d) Repeat part b) for nucleate boiling.

## HT-18 A Leaky Refrigerator System

**Heat Transfer Principle:** Condensation

**Level:** Undergraduate Chemical Engineering (Condensation Ch 9 Holman)

**Health and Safety Concept:** Estimation of a continuous release

**Background:** Many accidents result in spills or releases of undesirable process materials. For example, a small hole can develop within a refrigerant heat exchanger. Estimation of the rate of release is of importance in dispersion estimations (see Problem 12) of the release into the surroundings.

### Questions:

- a) An old refrigeration system is using Freon (dichloro-difluoromethane). The condenser consists of a 10 by 10 array of 10 mm-diameter tubes with a wall temperature of 32°C and a length of 4 m. Estimate the condensation rate of this unit using a Freon vapor temperature at 38°C and a  $h_{fg}$  of 130 kJ/kg.
- b) A 1/4" hole opens up on the shell side of the condenser and Freon gas is released. Estimate the release rate using the following equation<sup>45</sup>.

$$(Q_m)_{\text{choked}} = C_o A P_o \sqrt{\frac{g_c M \gamma}{R_c T} \left( \frac{2}{\gamma + 1} \right)^{(\gamma+1)/(\gamma-1)}}$$

For this problem let:

$C_o$	= 1.00
$\gamma$	= 1.32
$P_o$	= 0.9 MPa
$M$	is the molecular weight
$R$	is the Universal Gas Constant
$A$	is the cross sectional area of the opening

<sup>44</sup> Holman, J.P. , *Heat Transfer*, 7<sup>th</sup> edition, McGraw-Hill, New York, 1990, p 523.

<sup>45</sup> Crowl, D.A. and Louvar, J.F. *Chemical Process Safety: Fundamentals with Applications*, 2<sup>nd</sup> ed. Prentice-Hall, Englewood Cliffs, New Jersey, 2002. p-133, Eqn. 4-50.

## HT-19 An Ammonia Release

**Heat Transfer Principle:** Condensation

**Level:** Undergraduate Chemical Engineering (Condensation Ch. 9 Holman)

**Health and Safety Concept:** Toxic release and dispersion models

**Background:** Major equipment can occasionally fail catastrophically with a resultant “puff” of toxic material released into the surroundings. Emergency response requires an estimation of the release quantity and the concentration as a function of distance and time. Given below is an equation to estimate the concentration of a “puff” release (a sudden single release of a quantity of material) in the down wind direction as a function of time<sup>46</sup>.

### Questions:

- a) A skating rink is using an ammonia refrigeration system. The condenser on the system is an horizontal unit using a 20 by 20 array of 8 mm tubes 5 m long. Ammonia is condensed on the shell side of the exchanger. The ammonia temperature is 30°C and the tube wall temperature is 28°C,  $h_{fg}$  for ammonia is 1145 kJ/kg at 30°C. Estimate the condensation rate for this unit.
- b) The condenser fails catastrophically and 100 kg of ammonia is released as a puff. Determine the down wind distance where the maximum center point ammonia concentration is below the OSHA permissible exposure level of 18 mg/m<sup>3</sup> (assume that the surrounding temperature is 25°C and thus this is equivalent to 25 ppm by volume). Assume that the wind is blowing at a rate of 3 m/s. How many minutes will it take the center point of the puff to reach this location<sup>47</sup>?

$$\langle C \rangle = \frac{Q}{0.026x^{2.55}} \exp \left\{ -\frac{1}{2} \left( \frac{(x - ut)}{0.10x^{0.92}} \right)^2 \right\}$$

Where:

- $\langle C \rangle$  is the concentration in the wind direction  
Q is the total release amount in kg  
x is the distance directly downwind from the release in m  
u is the wind velocity in m/s  
t is the time in s

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<sup>46</sup> Crowl, D.A. and Louvar, J.F. Chemical Process Safety: Fundamentals with Applications, 2nd ed. Prentice-Hall, Englewood Cliffs, New Jersey, 2002. p-190

<sup>47</sup> This equation is a simplification of Eqn. 5-38 on p-190 in Crowl and Louvar using the substitution of the equations given for sigma as a function of x. It is for a ground level release and cannot be used for an elevated release. Dispersion is quite complex and depends upon the local weather and time of day. See Section 5-2 Crowl and Louvar for more details.

## HT-20 Hot Water Heaters Can Go Bust

**Heat Transfer Principle:** Boiling Heat Transfer

**Level:** Undergraduate Chemical Engineering (Ch. 9 Holman)

**Health and Safety Concept:** Relief valve sizing

**Background:** Home electric hot water heaters are a common device found in many homes and commercial areas. A typical hot water heater is 30 to 40 gallons and consists of a resistant heater element.

### Questions:

- A 40 gallon electric hot water heater is rated at 10 kW and has a 1/4" by 6 foot long horizontal cylindrical resistant heater element. Estimate the temperature excess if the resistant heater element is 70% efficient. Assume that the water supply pressure is 50 psig.
- If peak heat transfer coefficient in the nucleate boiling regime occurred at a temperature excess of 90°F, estimate the peak energy flux and power through the heater element.
- How can a current/power overload be prevented from reaching the heater element?
- Hot water heaters are equipped with thermostats and relief valves. If the thermostat failed "unsafe" (i.e. the thermostat misreads an actual high temperature as a low temperature) the temperature within the hot water heater could reach the boiling point and pressurize. Relief valves are attached to relieve any excess pressure build up and thus reduce the risk of an explosion. An equation to estimate the cross sectional area of a relief valve under 2 phase flow conditions is given below<sup>48</sup>:

$$G_T = \frac{Q_m}{A} = 0.9\psi \frac{\Delta H_v}{v_{fg}} \sqrt{\frac{g_c}{C_p T_s}}$$

$$A = \frac{Q_m v_{fg}}{G_T \Delta H_v}$$

Where:

- |        |  |
|--------|--|
| $G_T$  | is the mass flux through the relief            |
| $Q_m$  | is the mass flow rate through the relief valve |
| $A$    | is the area of the relief valve                |
| $\psi$ | correction factor, use 1.0 for this problem    |

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<sup>48</sup> Crowl, D.A. and Louvar, J.F. Chemical Process Safety: Fundamentals with Applications, 2<sup>nd</sup> Edition, Prentice-Hall, Englewood Cliffs, New Jersey, 2002. p-397, Eqn. 9-15 and p-412 Eqn. 9-35.

$\Delta H_v$	is the heat of vaporization
$v_{fg}$ phase	is the specific volume difference between the vapor and the liquid
$C_p$	the heat capacity of the fluid at constant pressure
$T_s$	the absolute saturation temperature at the relief set pressure
$Q$	is the constant heat input
$m_0$ with	is the mass in the vessel (assume that the hot water heater is full with saturated liquid)
$V$	the volume of the vessel
$g_c$	-gravitational constant

If the hot water heater is fitted with a 60 psig relief valve, estimate the relief valve diameter for a 40 gallon hot water tank for an heat input of 10 kW.

## HT-21 Insulation of a Heat Exchanger

**Heat Transfer Principle:** Introduction to Heat Exchanger Concepts

**Level:** Undergraduate Chemical Engineering (Introduction to Heat Exchangers - Ch 10 Holman)

**Health and Safety Concept:** Insulating hot pipes eliminates occurrence of burns

**Background:** Many companies define unsafe surface temperatures of hot objects at  $T_{\text{SURFACE}} > 60^\circ\text{C}$ . Thus, burns may result upon contact of surfaces above  $60^\circ\text{C}$ . When an outer wall temperature of a pipe is above this temperature, insulation is required. Heat exchangers often contain fluids above this critical temperature. Since a temperature gradient exists in each of the fluids in the pipe, insulation should be based on the hottest temperature of the outer fluid<sup>49</sup>.

### Questions:

- A  $20\text{ m}^2$  counter-current double pipe heat exchanger is used to remove heat from a hot oil stream. The oil stream is flowing at  $260\text{ kg/min}$  and enters the inner pipe of the exchanger at  $140^\circ\text{C}$ .  $100\text{ kg/min}$  of water is used as the coolant and enters the exchanger at  $25^\circ\text{C}$ . Calculate the water and oil exit temperature. The overall heat transfer coefficient for the oil-water system is  $300\text{ W/m}^2\text{ }^\circ\text{C}$  and assume  $C_{p,\text{oil}} = 2.4\text{ kJ/kg }^\circ\text{C}$ .
- Calculate the thickness of fiberglass insulation (with  $k = 0.035\text{ W/m}^2\text{ }^\circ\text{C}$ ) required to lower the outer pipe contact temperature to  $60^\circ\text{C}$ . The outer pipe is 3-inch Schedule 40. Assume that the pipe's outer wall temperature is equal to the outlet water temperature calculated in part a). Ambient conditions are  $T = 20^\circ\text{C}$ , with an ambient air convection heat transfer coefficient of  $6.0\text{ W/m}^2\text{ }^\circ\text{C}$ .
- If the inlet water temperature increased to  $55^\circ\text{C}$ , what potential difficulties can be encountered?

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<sup>49</sup> The author acknowledges the assistance of Mark Bellisario in the formulation of this problem

## HT-22 Heat of Dilution

**Heat Transfer Principle:** Convection

**Level:** Undergraduate Chemical Engineering (Holman Ch.6; McCabe Ch.12,13,16)

**Health and Safety Concept:** Acid dilution produces heat and materials of construction.

**Background:** Acid dilution<sup>50</sup> is a common process in industry due to the various applications of acids at various concentrations. Surprisingly, a large amount of heat can be released in the process. If the heat generated from the dilution is not removed there could be potential for hot surfaces or even spills. Cooling coils can be used in situations like this to remove the heat generated<sup>51</sup>.

### Questions:

- a) Given the following information for the dilution of sulfuric acid from 100% to a 50% solution in a CSTR, calculate the length of a coolant coil necessary to fully accommodate the heat generated:

$-\Delta H_{\text{dilution}} \text{H}_2\text{SO}_4$ 100% to 50%:	300 kJ/kg <sub>mixture</sub>
Process feed rate:	2.0 kg <sub>acid</sub> /min
Process temperature:	25°C (isothermal)
Inlet and outlet coolant H <sub>2</sub> O temperature:	10°C in, 20°C out
Average velocity of fluid over tube:	1.5 m/s
Viscosity of 50% acid solution	5 cps
Density of 50% acid solution	1,311 kg/m <sup>3</sup>

Assume that all other properties of the acid solution are similar to water.

Coolant coil: 1/2" BWG 20;  $k_c=34.6 \text{ W/m C}$

- b) If the process was adiabatic, what would be the approximate outlet stream temperature?
- c) What material(s) would you recommend that the cooling coil be constructed of?

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<sup>50</sup> This is an easy classroom demonstration. With great care, add 5ml of H<sub>2</sub>SO<sub>4</sub> to 5 ml of water held in a test tube (always add acid to water, never water to acid). Let students touch the test tube surface, they should feel a very hot surface. As concentrated sulfuric acid can cause severe skin burns, students must be equipped with chemical splash goggles.

<sup>51</sup> The author acknowledges the assistance of Richard Hennessy in the formulation of this problem. The original suggestion was provided by Mr. David Erickson, Office of Radiation, Michigan State University, East Lansing, MI.

## HT-23 HTHTM - HIGH TEMPERATURE HEAT TRANSFER MEDIUMS

**Heat Transfer Principle:** Shell and Tube Heat Exchanger Design

**Level:** Undergraduate Chemical Engineering (Ch. 10 Holman, Ch. 15 McCabe et al.)

**Health and Safety Concept:** Fire Point

**Background:** Heat exchangers where the heat transfer has to be done at temperatures well above the boiling point of water use commercial heat transfer fluids. These fluids are organic based blends and thus can burn if exposed to oxygen (or an oxidizer) and an ignition source (the three parts of the fire triangle consist of fuel : oxygen : ignition, the ignition source is considered always available). The fire point is the lowest temperature at which a vapor above a liquid will continue to burn once ignited<sup>52</sup>.

### Questions:

- a) Using the Internet or any other source, determine the fire point for DOWTHERM A. Also estimate the thermal conductivity, specific heat, viscosity, and density at the average “use temperature” (405°F) for DOWTHERM A.
- b) A 1-2 passes shell (15”ID) and tube heat exchanger with 108 tubes (carbon steel tube with a 1” square pitch) 3/4”OD, 16 BWG, 12’ long is available. Baffles are spaced 6 inches apart and are 25% baffles. It is desired to heat 12,000 kg/h of engine oil from 40 to 160°C on the tube side using a 28,000 kg/h DOWTHERM A. This hot stream is available at 420°F. Will this exchanger work? If yes, what is the “fouling” factor.
- c) A leak develops on the shell side of a shell and tube heat exchanger similar to the application specified in part b). What problems might result, and what precautions could be taken to minimize the potential of these problems from occurring?

## HT-24 Titanium/carbon Steel Heat Exchangers

**Heat Transfer Principle:** Shell and Tube Heat Exchanger Design

**Level:** Undergraduate Chemical Engineering (Ch. 10 Holman, Ch. 15 McCabe et al.)

**Health and Safety Concept:** Ignition of pure metals

**Background:** Heat exchangers used in corrosive environments require special materials to prevent corrosion. One metal used in extreme environments (sea water or acid services) is titanium. Often the corrosive agent is placed on the tube side (tubes are constructed of titanium) and the other less corrosive heat transfer medium is placed on the shell side. These exchangers are expensive and have a great deal of value to scrap dealers when retired from service. Scrap dealers,

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<sup>52</sup> Crowl, D.A. and Louvar, J.F. *Chemical Process Safety: Fundamentals with Applications*, 2nd ed., Prentice-Hall, Englewood Cliffs, New Jersey, 2002. p-227.

however, don't realize how hazardous the valuable titanium can be. One or two scrap dealers have lost their scrap yard because of this lack of knowledge<sup>53</sup>.

**Questions:**

- a) A 2-4 shell (inside diameter of 4" with a baffle pitch of 4" and  $f_b=0.1000$ ) and tube (48-3/8"OD 22 BWG titanium tubes, tube pitch of 0.45 inches) heat exchanger is being designed as a sea water/fresh water heat exchanger. Typical flow rate and temperature data has been specified as follows: 25 gpm of sea water entering at 10°C on the tube side, 30 gpm of fresh water entering on the shell side at 80°C and exiting at 40°C. What should the tube length be in the new exchanger to meet this heat transfer demand?
- b) Finely divided titanium burns in air at 700°C. Larger pieces ignite at higher temperatures. Once the ignition is initiated, there is no stopping it. The  $TiO_2$  that is formed dissolves in the molten Ti ( $T>1660^\circ C$ ) and the surface is even more reactive as more Ti is exposed. Further, exothermic reactions result when iron is present by the formation of iron/titanium alloys and by the reduction of iron oxide by titanium to metallic iron and titanium oxide. Scrap dealers often use oxyacetylene torches to cut open steel units. Look up (or calculate) the adiabatic flame temperature of a pure oxygen/ acetylene mixture (oxygen to acetylene at its stoichiometric ratio for full combustion). Can you foresee any problems using this method to cut open a titanium/carbon steel heat exchanger?
- c) What "management systems" should be in place to prevent accidents like this before the exchanger goes to the scrap yard?

## HT-25 A Swimming Pool Heater

**Heat Transfer Principle:** Heat Exchanger Design

**Level:** Undergraduate Chemical Engineering (Ch 10 Holman, Ch 15 McCabe et al.)

**Health and Safety Concept:** Corrosion and Consequences, Fail Safe

**Background:** Corrosion is the single most seen failure in heat exchangers. An interesting example is the following case. It was noted for some time that a steam/condensate return heating system required no condensate make up during normal operation. Eventually, the boiler at the power plant creating the steam suffered a tube failure. Elemental analysis on the tube wall surface detected higher levels of chlorine deposits. The cause was another heat exchanger located at the university swimming pool.

**Questions:**

- a) A 300,000 gallon swimming pool requires a total of 3 turnovers per day on a continuous basis. The water is circulated through a filtering system, a chlorinating treatment system, and a heater. A 1-1 shell and tube heat exchanger is used as the heater. It is composed of an 12" ID shell with

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<sup>53</sup> This problem is base on an article by Pines, B.A., "Analysis of Titanium/Carbon Steel Heat Exchanger Fires," POP Vol 11 No 2 April 1992, p 113.



140-5/8" BWG 20 steel tubes on a 13/16" square pitch. The tube side heats 40 psig water recirculated from the pool from 75 to 83°F. The shell side uses 10 psi steam as the heating agent. Determine the length of the exchanger required to meet these conditions.

- b) Explain the root cause for the power plant boiler tube fail?  
 c) The steam supply to the heat exchanger is on control system consisting of a sensor (the outlet temperature of the pool water from the heater), a controller, and a control element (a air operated control valve). If the power was interrupted to the controller, how should the control valve fail?

## HT-26 Fluid Agitation

**Heat Transfer Principle:** Convection Heat Transfer

**Level:** Undergraduate Chemical Engineering (Ch 15 McCabe et al. p 451)

**Health and Safety Concept:** Runaway Reactions

**Background:** Fluid agitation in an agitated vessel with a coil for heat removal is an important unit process and provides necessary heat transfer to prevent runaway reactions. This question compares the rate of heat removal to the rate of heat generated by an exothermic reaction. McCabe, Smith, and Harriot<sup>54</sup> present an equation to estimate the heat transfer coefficient for a set of helical cooling coils with a turbine agitator inside a tank. The equation is:

$$\frac{h_c D_c}{k} = 0.17 * \left( \frac{D_a^2 n \rho}{\mu} \right)^{0.67} \left( \frac{c_p \mu}{k} \right)^{0.37} \left( \frac{D_a}{D_t} \right)^{0.1} \left( \frac{D_c}{D_t} \right)^{0.5} \left( \frac{\mu}{\mu_w} \right)^{0.24}$$

Where:

- $D_a$  is the diameter of the agitator blade
  - $D_c$  is the diameter of the cooling coil
  - $D_t$  is the diameter of the tank
  - $h_c$  is the heat transfer film coefficient for the coil outside surface.
  - $k$  is the thermal conductivity of the fluid within the reactor
  - $n$  is the revolutions of the agitator per second
  - $\mu$  is the viscosity of the fluid
- other notation are the standard symbols.

The net heat generated by a zero order reaction can be approximated by the rate constant (as estimated by the Arrhenius equation) times the heat of formation times the volume of the reactor:

$$Q_{gen} = -\Delta H_{rxn} * A_0 \exp(-E/RT) * V$$

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<sup>54</sup> McCabe, W.L., Smith, J.C., and Harriot, P. *Unit Operations of Chemical Engineering*, 5th ed. McGraw-Hill, 1993, p-451.

Where:

- $Q_{\text{gen}}$  Is the heat released (or required) by the reaction mixture  
 $A_0$  pre-exponential constant, units of  $\text{kmol/s m}^3$  for a zero order reaction  
 $E$  Activation energy,  $\text{kJ/kmol K}$   
 $-\Delta H_{\text{rxn}}$  is the Heat of reaction,  $\text{kJ/kmol}$   
 $R$  is the Universal gas constant =  $8.314 \text{ kJ/kmol K}$   
 $T$  is the absolute temperature in  $\text{K}$   
 $V$  is the volume of the reactor

**Questions:**

- a) Plot  $Q$  generated as a function of temperature from  $20$  to  $70^\circ\text{C}$  for a reaction with a  $-\Delta H_{\text{rxn}}$  of  $240,000 \text{ kJ/kmol}$  (an exothermic reaction), an  $A_0$  of  $4.2 \times 10^7 \text{ kmol/s m}^3$ , and an  $E$  of  $80,000 \text{ kJ/kmol}$  for a reaction carried out in a  $6 \text{ m}^3$  reactor.
- b) The vessel is  $2 \text{ m}$  in diameter and is equipped with an turbine agitator of  $0.5 \text{ m}$  in diameter. The process fluid has a bulk viscosity of  $100 \text{ cps}$ , a viscosity at the coil wall of  $150 \text{ cps}$ , a density of  $950 \text{ kg/m}^3$ , a heat capacity of  $2400 \text{ J/kg }^\circ\text{C}$ , and a thermal conductivity of  $0.26 \text{ W/m }^\circ\text{C}$ . Plot the outside film coefficient as a function of rpm of the agitator between  $50$  to  $300 \text{ rpm}$ 's. The cooling coil has a diameter of  $3 \text{ cm}$ .
- c) Assume that the coil's inside wall film coefficient is  $3,000 \text{ W/m}^2\text{C}$ , and that the agitator design speed is  $100 \text{ rpm}$ , what is the over all heat transfer coefficient base on outside coil area? The wall thickness of the coil is  $2 \text{ mm}$  and provides negligible resistance to heat transfer.
- d) It is desired to run the reaction at  $50^\circ\text{C}$ . What coil length will meet this need? Assume that all other conditions are as given in part c) and that  $10 \text{ gpm}$  cooling water is available at  $25^\circ\text{C}$ .
- e) Plot the rate of heat removal as function of batch temperature for this cooling coil from  $20^\circ\text{C}$  to  $70^\circ\text{C}$ . Assume that the water temperature is constant within the coil at  $25^\circ\text{C}$ . Plot on the same chart as that used in part a).
- f) If the temperature of the batch for condition d) was perturbed to  $55^\circ\text{C}$  what would happen?
- g) Is there another "safe temperature" to run this reaction at? Explain.

**HT-27 A Baffled Tank**

**Heat Transfer Principle:** Convection Heat Transfer in Agitated Tanks

**Level:** Undergraduate Chemical Engineering (Ch. 15 McCabe et al.)

**Health and Safety Concept:** Over Heating because of Fluid Agitation

**Background:** Many liquid mixtures are stored in holding tanks before processing. Often these tanks contain agitators and have a cooling jacket placed around the side of the tank in order to remove excess heat due to agitation or to keep the mixture at the required temperature. If inadequate cooling exists, the material being stirred can reach a critical temperature where self sustaining exothermic reactions could occur. This temperature can be called the "auto

initiation” temperature. At this temperature the heat released by reaction is not removed fast enough and the materials continue to heat even faster. A runaway reaction can result with rapid temperature and pressure rises if the tank is a closed system.

**Questions:**

- a) McCabe et al.<sup>55</sup> give an equation for the film coefficient on the liquid side of a tank with a material under agitation. Estimate the film coefficient between the liquid and the wall for a 5 ft high, 5 ft diameter tank equipped with a 24” agitator operating at a speed of 120 rpm. The tank contains a fluid with a bulk viscosity of 20,000 cps, a wall viscosity of 30,000 cps, a specific gravity of 1.26, a heat capacity of 2,400 J/kg/C and a thermal conductivity of 0.290 W/m C.
- b) Where on the jacket should the water enter and exit?
- c) The tank is constructed of 1/8” carbon steel and the jacket gap is 1/2”. If 20°C cooling water is entering the tank cooling jacket at 5 gpm, estimate the overall heat transfer coefficient for this system.
- d) Figure 9.12 in McCabe<sup>56</sup> gives the Power Number as a function of Reynolds Number of a six blade turbine. Estimate the power that is being delivered to the fluid.
- e) To what temperature will the material reach with this power input?
- f) What instrument(s) allows one to estimate “auto initiation” temperature of a mixture?
- g) What precautions should be made to make sure that the material does not exceed its “auto initiation” temperature?

## HT-28 Introduction to Heat Transfer in Agitated Vessels

**Heat Transfer Principle:** Convection Heat Transfer in Agitated Vessels

**Level:** Undergraduate Chemical Engineering (Ch 15 McCabe et al. p 451)

**Health and Safety Concept:** Awareness of Processing in Agitated Vessels

**Background:** Heating by a steam jacketed tank is an important unit operation. Often the material being heated is under agitation. Two factors can be overlooked by operating personnel. One deals with the loss of heat transfer capability as the material within the vessel becomes more viscous. The other is the use of superheated steam which has a temperature above the saturation point. Conditions are safe at the saturation point but not so safe at the higher superheated temperature. Serious accidents have resulted such as runaway reactions (the release at Seveso, Italy is an example- see Problem 24), or desired products are further converted to other unwanted materials. The example below deals with starch cooking. Runaway reactions are not a concerning here; however, the ultimate product of an enzymatic reaction is undesirable. McCabe,

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<sup>55</sup> McCabe, W.L., Smith, J.C., and Harriott, P., *Unit Operations of Chemical Engineering*, 5th Edition, McGraw-Hill New York, 1993, p-451.

<sup>56</sup> Ibid. p-250.

Smith, and Harriot<sup>57</sup> present an equation to estimate the heat transfer coefficient for heat transfer to or from a jacket of a baffled tank using a standard turbine agitator<sup>58</sup>.

$$\frac{h_j D_t}{k} = 0.76 * \left( \frac{D_a^2 n \rho}{\mu} \right)^{2/3} \left( \frac{c_p \mu}{k} \right)^{1/3} \left( \frac{\mu}{\mu_w} \right)^{0.24}$$

Where:

- $D_a$  is the diameter of the agitator blade
  - $D_t$  is the diameter of the tank
  - $h_j$  is the heat transfer film coefficient at the jacket surface inside the tank.
  - $k$  is the thermal conductivity of the fluid within the reactor
  - $n$  is the revolutions of the agitator per second
- other notation are the standard symbols.

### Questions:

- a) Consider a tank used to prepare a paste by the enzymatic conversion of cooked starch. Initially the solution inside the tank has properties very close to that of water at 25°C. The heating medium is saturated steam at 1.0 barg. Assume that the tank is 1.8 m diameter and has a turbine agitator 0.75 m in diameter rotating at the speed of 30 rpm. Determine the jacket film coefficient under these conditions. Assume that the jacket wall temperature is very close to that of steam.
- b) Estimate the initial total rate of heat transfer if the liquid level is 1.5 m inside the tank and estimate the initial rate of temperature rise (°C/min) for the batch. Assume that most of the resistance to heat transfer is within the jacket film coefficient.
- c) As the starch solution heats, it reaches a “strike temperature” where it becomes extremely viscous. Assume that the viscosity at the strike temperature is 50,000 cps. Estimate the heat transfer coefficient at the jacket wall under this condition.
- d) Estimate the rate of heat transfer for the starch cook if the strike temperature is 73°C and estimate the rate of temperature rise (°C/min) of the batch at the conditions given by part c).
- e) As the starch continues to cook, the viscosity is reduced. Why?
- f) Consider that the agitator is shut off and the steam is left on. What could happen over a long time?

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<sup>57</sup> Ibid, p-451.

<sup>58</sup> Many correlations exist in the literature for other type of agitators and related equipment. See Perry’s Chemical Engineers’ Handbook, 6th Edition, p 10-19 for examples.

## HT-29 Double the Trouble

**Heat Transfer Principles:** Multiple Effect Evaporation

**Level:** Undergraduate Chemical Engineering (McCabe et al. Ch 16)

**Health and Safety Concept:** Leaks and Spills

**Background:** The concentration of NaOH-water solutions is a process used in pulp mills. The process is typically carried out in a multiple effect evaporator system. Up to seven multiple effects can be used. This means many pumps, pipes, and vessels where leaks and spills can occur. When the mechanical seal, (or packed gland), on a pump shaft becomes worn or defective leaks can occur. Initially the flow may be relatively minor, however, if the seal fails totally there can be a major release. Piping systems are a major source of releases, these can range from pinholes leaks, typically due to corrosion and leaking gaskets, to catastrophic failures caused by events such as gasket blow out, valve failures, failed expansion joints, or other failures. How to react in each situation is the topic for this problem.

### Questions:

- A double effect evaporator system is to be fed with 20,000 kg/h of 5% NaOH solution at a temperature of 80°C. The concentrated liquor from the system is to be 40% NaOH. Saturated steam at 300 kPa absolute is available and the vacuum on the second effect is set at 20 kPa. The system is a feed forward type. The overall heat transfer coefficient for the first effect is 4,000 W/m<sup>2</sup>°C and for the second effect is 6,000 W/m<sup>2</sup> C. Calculate the area required in each effect, the steam requirement, the capacity, and the economy for this system.
- You are placed in charge of the double effect evaporator system for the concentration of NaOH. One morning the waste water superintendent is calling around the plant and reaches your desk. He has noticed a distinct increase in pH of the waste water stream before it reaches a pH buffering system over the past 24 hours. List what might be the cause in your department?
- You require a new pump on one of the units. What type of specifications would you make to insure no shaft leaks?
- A 1" pipe line develops a 1/4" hole because of corrosion. Supply pressure to the line is 30 psig. What is the rate of discharge for a 5% NaOH solution using the following equation from Crowl and Louvar?<sup>59</sup>

$$Q_m = AC_o \sqrt{2 \rho g_c P_g}$$

Where:

$Q_m$  is the rate of discharge, kg/s  
 $A$  is the area of the hole, m<sup>2</sup>

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<sup>59</sup> Crowl, D.A., Louvar, J.F., *Chemical Process Safety: Fundamentals with Applications*, 2<sup>nd</sup> ed., Prentice-Hall 2002 p-117.

$C_o$  is the discharge coefficient, assume a value of 1.0  
 $\rho$  is the density,  $\text{kg/m}^3$   
 $g_c$  is  $1 \text{ kg m / N s}^2$   
 $P_g$  is the pressure in the pipe at the discharge,  $\text{N/m}^2$

- e) If a leak like the one given in part **d**) did occur, what specific actions would you do to clean up the spill that developed?

### HT-30 Where Do You Place the Condenser ?

**Heat Transfer Principle:** Sizing of Exchangers with Change of Phase and Sub-cooling

**Level:** Advance Undergraduate Chemical Engineering (Holman Ch.10; McCabe Ch.15)

**Health and Safety Concept:** Dealing with Short Life Radioactive Isotopes.

**Background:** A boiling water reactor had a condensate sampling line which was designed to let short living  $^{16}\text{N}_2$  decay several half lives (half life of 7 seconds).<sup>60</sup> The sample line was designed to produce 1 liter per minute of condensate at  $60^\circ\text{C}$  and allow for a residence time of three minutes. After completion, the residual radiation measured at the end of the sample line indicated a radiation level much higher than expected.<sup>61</sup>

#### Questions:

- a) Using a sample rate of 1 liter per minute of condensate, determine the length of a shell and tube heat exchanger required to condense the steam and bring the condensate exit temperature down to  $60^\circ\text{C}$ . Use a fouling factors of  $0.00015 \text{ m}^2 \text{ }^\circ\text{C/W}$  for the coolant water side and  $0.0002 \text{ m}^2 \text{ }^\circ\text{C/W}$  for the steam/condensate side.

Temperature of coolant $\text{H}_2\text{O}$ to condenser:	$25^\circ\text{C}$
Temperature of coolant $\text{H}_2\text{O}$ from condenser:	$30^\circ\text{C}$
Steam Pressure:	70 bar absolute
Steam is on the tube side and $h_i$ in the <u>condensing region</u> is estimated at	$10,000 \text{ W/m}^2\text{C}$
Number of Tubes	108
Tube dimensions	3/8" BWG 18 (SS)
Shell	6" Schedule 80 pipe

- b) Determine the length of a 3/4" Schedule 40 pipe necessary to allow a three minute retention time of the cooled condensate.
- c) As mentioned above, after the sampling system was installed the residual radiation measured at the end of the sample line indicated a radiation level much higher than expected. What was incorrect?

<sup>60</sup> This problem was suggested by Ernst Schori, Consultant, RD 1 Box 235, Canaan, NH 03741.

<sup>61</sup> The author acknowledges the assistance of Richard Hennessy in the formulation of this problem.

## Safety Problems for a Course in Process Dynamics and Control

Originally Prepared by Daniel Crowl  
Michigan Technological University, Houghton, MI

**PD-1** A large storage tank is filled manually by an operator. The operator first opens a valve on a supply line and carefully watches the level on a level indicator until the tank is filled (a while later). Once the filling is completed, the operator closes the valve to stop the filling.

Once a year the operator was distracted and the tank overfilled. To prevent this an alarm was installed on the level gauge to alert the operator to a high level condition. With the installation of the alarm, the tank now overfilled twice per year. Can you explain?

**PD-2** "Fail safe" is a concept used to specify the position of process instrumentation in the event of power, air pressure, or other utility failures. For instance, the valve supplying cooling water to a chemical reactor would fail in the open position ("fail open") in the event of a power failure. This would provide maximum cooling to the reactor and prevent dangerous high temperatures in the vessel.

Specify the proper fail-safe positions for the valves in the following equipment. Specify either fail open or fail close:

- a) A flammable solvent is heated by steam in a heat exchanger. The valve controls the flow of steam to the exchanger.
- b) A valve controls the flow rate of reactant to a reactor vessel. The reaction is exothermic.
- c) A valve controls the flow rate of reactant to a reactor vessel. The reaction is endothermic.
- d) A valve controls the flow of natural gas to a utility furnace in a power station.
- e) A remotely-operated valve is connected to a drain on a storage tank.
- f) A remotely-operated valve is used to fill a tank from a supply line.
- g) A valve controls combustion air to a furnace.
- h) A valve controls the pressure in a steam header.

**PD-3** Interlocks are used to insure that operations in a chemical plant are performed in the proper sequence. Interlocks can be mechanical or electronic. In many cases they can be as simple as a lock and key.

Specify the simplest mechanical interlock capable of achieving the following functions:

- a) A valve cannot be closed until a furnace is shut down.
- b) Two valves cannot both be closed at the same time.
- c) A valve must be closed before a pump is started.
- d) Feed to a reactor cannot be started until the reactor vessel stirring motor is activated.

**PD-4** A process operator is given the following instructions: "Charge 10-lb of catalyst into batch reactor A at 3 hours into the cycle." Determine at least 15 ways in which the operator might fail to perform the instructions correctly.

**PD-5** A storage tank is vented to the atmosphere. If a hole develops in the tank the liquid level,  $h_L$ , is given by the following differential equation:

$$\frac{dh_L}{dt} = -\frac{C_o A}{A_t} \sqrt{2gh_L}$$

Where:

$h_L$  is the liquid level height above the leak,  
 $C_o$  is the constant discharge coefficient = 0.61,  
 $A$  is the cross-sectional area of the leak,  
 $A_t$  is the cross-sectional area of the tank, and  
 $g$  is the acceleration due to gravity.

- Integrate the above equation to determine an expression for the liquid level height as a function of time. Assume an initial liquid level above the leak of  $h_L^o$ . Can you use Laplace transforms to solve the problem?
- What is the "driving force" that pushes the water out of the hole in the tank?
- If the cross-sectional area of the tank is increased, does the liquid level change faster, slower, or the same?
- If the liquid level is increased, does the liquid level change faster, slower, or the same?
- A cylindrical tank 10-feet high and 20-feet in diameter is used to store water. The liquid level in the tank is initially at 7 feet. If a one-inch puncture occurs two-feet off the bottom of the tank, how long will it take for the water to drain down to the leak? What is the total amount of liquid (in gallons) discharged?
- Linearize the above differential equation and use Laplace transforms to determine an expression for the liquid level as a function of time. Why is the expression different from the expression obtained in part a?
- What would be the significance of the leak if the liquid were flammable? toxic?

**PD-6** Surge tanks are used to hold intermediate inventory between process units in a chemical plant. The motivation is to prevent interruptions or changes in production in one unit from propagating to the other unit. That is, the second unit can continue to operate at its normal rate using the stored inventory in the surge tank until the first unit is brought back into normal operation. Likewise, the first unit can continue to operate if the second unit is interrupted, with intermediate product accumulating in the surge tank.

Consider a surge tank used to store an intermediate liquid product between two process units. Assume that the liquid is pumped out of the surge tank at a constant rate to the second process:

- Should the tank be low and flat or tall and skinny? What is your selection basis for this decision?
- How would you determine the required volume of the tank? Have you



- also considered the possibility of overflowing the tank?
- c) How would the results of part b change if the liquid were toxic or flammable?

**PD-7** Your family has a gas-operated barbecue unit which everyone enjoys during the summer. The unit operates from a 20-lb propane tank. The problem with these units is that it is difficult to determine how much propane remains.

You certainly do not wish to accidentally run out of propane during the biggest holiday weekend of the summer, when all the relatives are visiting! One solution is to buy a spare tank which you can use when the first runs out. However, doubling the supply of propane more than doubles the risk of an accident leading to a fire or explosion. Name at least two other methods to reduce the likelihood of running out of propane without increasing the supply.

**PD-8** For all chemical processes, the instrumentation must be capable of tracking changes in the process, even when the changes occur quite rapidly. For a particular process, temperature changes as fast as  $10^{\circ}\text{C}/\text{minute}$  must be followed. What time constant thermocouple should you select for this operation?

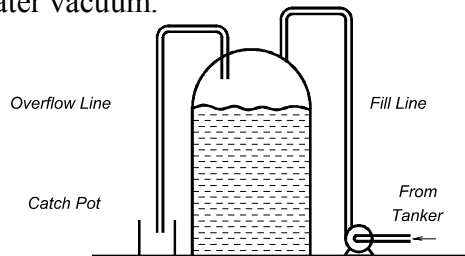
**PD-9** A surge tank is used between two processes. The tank is 10-feet high and 20-feet in diameter.

- a) The liquid level is initially at 5 feet. If the input flow is 200 gpm and the output flow is 0, how long will it take to overflow?
- b) The liquid level is initially at 5 feet. If the input flow is 200 gpm and the output flow is 199 gpm, how long will it take to overflow?

**PD-10** Thermocouples in chemical plants are usually found in sheaths. These sheaths protect the thermocouple and also allow the thermocouple to be removed and replaced without shutting down the process. One chemical plant had some thermocouples which did not have sheaths, although they looked like the sheathed type. This led to an accidental release of toxic and flammable material. Can you explain why?

**PD-11** Liquid levels in storage tanks are frequently determined by measuring the pressure at the bottom of the tank. In one such tank the material stored in the tank was changed and an overflow resulted. Why?

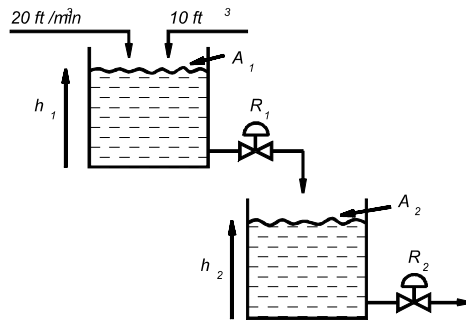
**PD-12** The tank shown below has an overflow line to prevent overflowing the tank. During a routine filling operation, the operator was told to stop filling when liquid began to overflow into the catch-pot. When this occurred the operator stopped the input flow and the tank was subsequently sucked in due to vacuum. How did this occur? This tank (like most storage tanks) is only capable of withstanding a few inches of water vacuum.



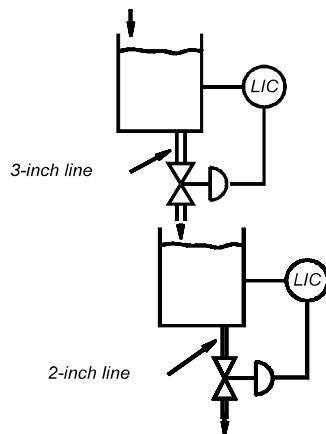
**PD-13** The two-tank system shown below is operating at steady state. The output volumetric flow for each tank is given by  $q = h/R$  where  $h$  is the liquid height and  $R$  is a resistance value.

At time  $t = 0$ ,  $10 \text{ ft}^3$  of water are quickly added to the first tank. Determine the maximum deviation in level (feet) in both tanks from the ultimate steady-state values and the time at which each maximum occurs. Determine the maximum quantity of material which can be added quickly to the first tank which does not result in an overflow of either tank.

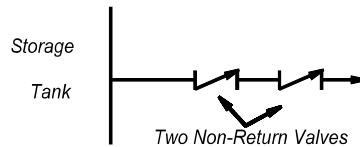
Data:  $A_1 = A_2 = 10 \text{ ft}^2$   
 $R_1 = 0.1 \text{ ft/CFM}$   
 $R_2 = 0.35 \text{ ft/CFM}$   
 Tank heights = 10 ft



**PD-14** The figure below shows two tanks in series, both with independent level controllers. This configuration will result in the lower tank inevitably overflowing. Can you explain why?



**PD-15** Non-return valves are used to prevent materials from flowing backward in a process line. The figure below shows two non-return valves installed in a process line to prevent back-flow of a liquid. The process originally had a single non-return valve, but the corrosive liquid disabled the valve after only a few months of operation. To solve the problem two valves were installed as shown. This modification did not improve the reliability of the system. Why? Can you suggest a better arrangement?



**PD-16** A cover plate on a pump housing is held in place by eight bolts. A pipe fitter is instructed to repair the pump. The fitter removes all eight bolts only to find the cover plate stuck on the housing. A screwdriver is appropriated to pry off the cover. The cover flies off suddenly and toxic liquid sprays throughout the work area.

Clearly the pump unit should have been isolated, drained and cleaned prior to repair. There is, however, a better procedure for removing the cover plate. What is this procedure?

**PD-17** Pumps can be shut-in by closing valves on the inlet and outlet sides of the pump. This can lead to a rapid increase in the temperature of the liquid shut inside the pump.

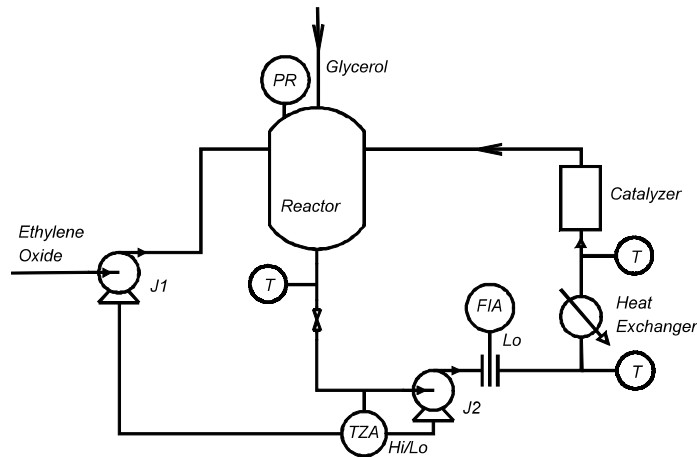
A pump contains 4 kg of water. If the pump is rated at 1-HP, what is the maximum temperature increase expected in the water in °C/hour? Assume a constant heat capacity for the water of 1 kcal/kg°C. What will happen if the pump continues to operate?

**PD-18** An operator was told to control the temperature of a reactor at 60°C. He set the set point of the temperature controller at 60. The scale actually indicated 0 - 100 percent of a temperature range of 0 - 200°C. This caused a runaway reaction which over-pressured the vessel. Liquid was discharged and injured the operator. What was the setpoint temperature the operator actually set?

**PD-19** The figure below shows a batch reaction system. A batch of glycerol is placed in the reactor and circulated through a heat exchanger which acts as both a heater and a cooler. Initially it is used as a heater and when the temperature reaches 115°C, addition of ethylene oxide is started. The reaction is exothermic and the exchanger is now used as a cooler.

a) If the temperature of the glycerol is below 115°C, the ethylene oxide will not react fast enough. Likewise, if the temperature is above 125°C the

- reaction will proceed dangerously fast. What interlock is present on the system to insure that the temperature is within the proper range?
- What alarms are present to indicate a low flow condition in the recirculating loop?
  - How is the pressure within the reactor monitored?
  - An explosion occurred within this unit while instrument FIA was out of order. All other instruments were functional. What happened? How could the process be redesigned to prevent this problem?



**PD-20** Pneumatic process equipment operates in the range of 3 to 15 psig. Thus, for example, a signal of 3 psig might represent 0 psig in the process and 15 psig might represent 1,200 psig in the process.

A pneumatic pressure gauge was designed to operate in the range of 3-15 psig, corresponding to the pneumatic signal sent from the plant. However, the scale printed on the gauge read 0 to 1,200 psig, corresponding to the actual process pressures. This gauge was accidentally over-pressured, resulting in an accident. What happened?

**PD-21** A light in the control room of a chemical plant indicated whether a valve was closed or not. In reality it only indicated the status of the signal being sent to the valve. The valve did not close when it should have and the plant exploded. Why? How would you prevent this problem?

**PD-22** Exothermic chemical reactions are frequently dangerous because of the potential for a "runaway reaction." Cooling coils are provided in batch reactors to remove the energy of reaction. In the event of a cooling water failure, the reactor

temperature rises, resulting in a higher reaction rate and higher energy generation. The result is a runaway. During a runaway the temperature can rise very fast, resulting in dangerous pressures within the reactor and a possible explosion.

Loss of cooling can be detected by measuring the temperature within the reactor and sounding an alarm. Frequently, by the time the alarm sounds, it is too late. Design a better instrumentation and alarm configuration to detect loss of cooling more directly. Draw the instrumentation diagram.

**PD-23** A flammable liquid is to be stored in a large storage vessel. Two vessels are available. One vessel is called a "weak seam roof" tank with the weakest part of the vessel being the welded seam between the roof and the vertical wall of the tank. The other vessel is a domed roof tank with the weakest part being the seam along the bottom of the tank. Which tank is the best choice for storing this material?

**PD-24** Water will flash into vapor almost explosively if heated under certain conditions.

- a) What is the ratio in volume between water vapor at 298 K and liquid water at 298 K?
- b) Hot oil is rapidly pumped into a storage tank. Unfortunately, the tank contains some water which flashes rapidly into vapor and ruptures the tank. If the tank is 10 m in diameter and 5 m high, how many kg of water at 298 K are required to produce enough water vapor to pressurize the tank at 298 K and 8" water gauge pressure, the design pressure of the storage tank?

**PD-25** A storage tank has a diameter of 20 ft and a height of 10 ft. The output volumetric flow from this tank is given by:

$$q_{\text{out}} = (2 \text{ ft}^3/\text{min}) h$$

Where:

h is the height of liquid in the tank.

At a particular time the tank is at steady state with an input flow of 10 ft<sup>3</sup>/min.

- a) What is the steady state liquid height in the tank?
- b) If the input flow is ramped up at the rate of 0.1 ft<sup>3</sup>/min, how many minutes will it take for the tank to overflow?

**PD-26** A gas detector is used to determine the concentration of flammable gas in a gas stream. Normally the gas concentration is 1% by volume, well below the alarm limit of 4% and the lower flammability limit of 5%. If the gas concentration is above the lower flammability limit it is flammable.

A particular gas detector demonstrates first-order behavior with a time constant of 5 seconds. At a particular time the gas stream is flowing at 1 m<sup>3</sup>/sec through a duct of 1 m<sup>2</sup> cross section. If the gas concentration suddenly increases from 1% to 7% by volume, how many m<sup>3</sup> of flammable gas pass the sensor before the alarm is sounded? Is it possible for a plug of flammable gas to pass the detector without an alarm ever being sounded?

**PD-27** A semi-batch reactor is a batch reactor in which the rate of reaction is controlled

by the flow of reactant into the reactor.

Consider a semi-batch reactor with a single input flow of pure reactant. A single, irreversible, liquid phase reaction converts the reactant to liquid product.

Let

$M$  = total mass of material in the reactor,

$\dot{m}$  = mass flow rate of pure reactant into the vessel,

$x$  = mass fraction of reactant within the reactor,

$t$  = time in minutes.

- a) Derive an ordinary differential equation describing the total mass,  $M$ , within the reactor as a function of time. If the reactor is initially empty, and the inlet mass flow rate is a constant 10 lb/min, solve the equation to determine how long it will take to fill the vessel to the 500 lb level.
- b) At  $t = 20$  minutes, the mass fraction of reactant in the reactor is 0.05. The mass flow rate of pure reactant remains a constant 10 lb/min. At this time, due to an error in operation, the temperature of the reacting liquid has dropped below the temperature required for reaction. Thus, the consumption of reactant via reaction is negligible. Derive a differential equation for the mass fraction of unreacted reactant in the vessel. Combine this with the differential equation obtained in part a to obtain

$$\frac{dx}{dt} = \frac{1 - x}{t}$$

Integrate the equation, using the initial condition given, to determine the time at which the reactant mass fraction reaches a level of 0.15. At this concentration a dangerous situation is encountered. If the temperature is restored, the high mass fraction will result in a runaway reaction with possible explosion of the reaction vessel.

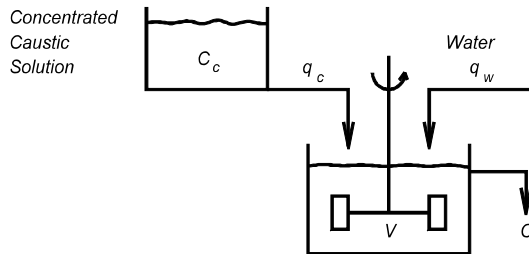
**PD-28** Careful numbering of process equipment is important to avoid confusion. On one unit, the equipment was numbered J1001 upwards. When the original allocation of numbers ran out the new equipment was numbered JA1001 upwards. An operator was verbally told to prepare pump JA1001 for repair. Unfortunately, he prepared pump J1001 instead, causing an upset in the plant. What happened?

**PD-29** The system pictured below is used to dilute a concentrated caustic solution. It is started up with pure water in the mix tank. The following variables are defined:

$q_c$	volumetric flow of caustic,
$q_w$	volumetric flow of water,
$V$	tank volume,
$C_c$	concentration (mass/volume) of caustic in caustic tank,
$C$	concentration (mass/volume) of caustic exiting mix tank.

- a) Derive a mathematical model to describe the concentration of caustic,  $C$ , in the mix tank effluent. You may assume that the caustic solution has approximately the same density as the water and that the volume in the tank is constant.

- b) Usually the final mix concentration is much less than the concentrated caustic solution. Simplify the model for conditions which give rise to  $C_c \gg C$ . When will this occur?
- c) Assuming the conditions of part b), derive a transfer function between the outlet concentration and the volumetric flow of caustic. What is the time constant for this system?
- d) Use the model developed to consider the effect of various failure modes in the process. Consider the effect of a failure (or stop) in flow  $q_c$ , and separately,  $q_w$ .



**PD-30** Controllers can be used to stabilize processes which are normally unstable. Consider the unstable process represented by the transfer function

$$G = \frac{K}{(\tau_1 s + 1)(\tau_2 s - 1)}$$

- a) Why is this process unstable?
- b) We wish to control this process by a feedback controller with only proportional mode. Is it possible to stabilize the system with this control scheme and, if so, what values of the controller gain,  $K_c$  will achieve the stability?
- c) What will happen to the process if the controller fails? What precautions might you consider for this situation?

**PD-31** A process stream carries a fluid at a normal flow rate of 20 CFM. However, due to pumping, this flow can vary from 18 to 22 CFM over a period of 1 minute. It is desired to use a small storage tank to reduce the fluctuations. Determine the minimum tank area and height required to

- a) reduce the flow fluctuations in half, and
- b) prevent overflow of the tank during normal flow conditions. The output volumetric flow from the tank is represented by  $Rh$  where  $h$  is the fluid height in the tank. For the system under consideration the value of  $R$  is 5 CFM/ft.

Comment on precautions you might consider if the fluid were toxic and/or flammable.

Comment on precautions you might consider to prevent overflow during abnormal conditions.

**PD-32 a)** Show that for any pump the maximum liquid discharge velocity is given by

$$u = \sqrt[3]{-\frac{2g_c W_s}{\rho A}}$$

Where:

$u$  is the maximum liquid discharge velocity,  
 $W_s$  is the pump shaft work,  
 $\rho$  is the density of the liquid, and  
 $A$  is the pump outlet discharge area.

- b)** What assumptions are inherent in the above equation?  
**c)** A 1 kw pump discharges water through a 50-mm ID pump outlet. What is the maximum velocity of liquid from this pump? What is the maximum discharge rate in kg/s?



**Safety Problems Requiring a Computer for Solution**  
Originally Prepared by Daniel Crowl  
Michigan Technological University, Houghton, MI

**CA-1 Liquid Discharge through a Hole**

Calculate the discharge rate of a liquid through a 10-mm hole, if the tank head space is pressurized to 0.1 barg. Assume a 2-m liquid head above the hole.

Data: Liquid density =  $490 \text{ kg/m}^3$

**CA-2 Liquid Trajectory from a Hole**

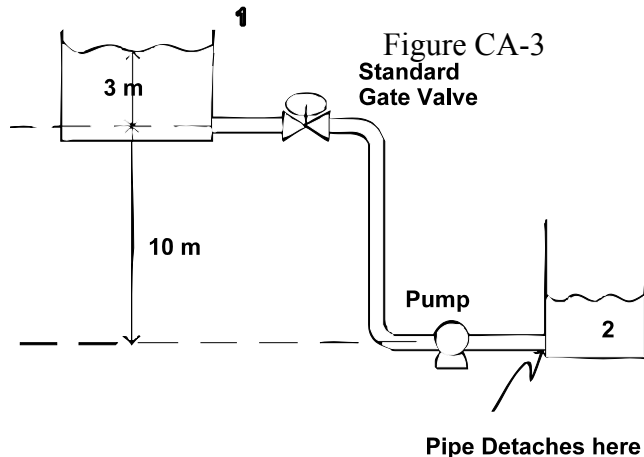
Consider again CA-1. A stream of liquid discharging from a hole in a tank will stream out of the tank and impact the ground at some distance away from the tank. In some cases the liquid stream could shoot over any diking designed to contain the liquid.

- a) If the hole is 3 m above the ground, how far will the stream of liquid shoot away from the tank?
- b) At what point on the tank will the maximum discharge distance occur? What is this distance?

**CA-3 Liquid Discharge through a Piping System**

Figure CA-3 shows a transfer system between two tanks. The system is used to transfer a hazardous liquid. The pipe is commercial steel pipe with an internal diameter of 100-mm with a total length of 10 m. The piping system contains two standard, flanged 90° elbows and a standard, full-line gate valve. A 3-kw pump with an efficiency of 70% assists with the liquid transfer. The maximum fluid height in the supply tank is 3 m, and the elevation change between the two tanks is as shown in Figure CA-3.

Data: Fluid density ( $\rho$ ) =  $1600 \text{ kg/m}^3$   
Fluid viscosity ( $\mu$ ) =  $1.8 \times 10^{-3} \text{ kg/m s}$



#### CA-4 Gas Discharge through a Hole

Calculate the discharge rate of propane through a 10 mm hole at the conditions of 25°C and 4 barg (5.01 bar abs).

Data: Propane heat capacity ratio = 1.15 (Crane, 1986)  
Propane vapor pressure at 25°C = 8.3 barg

#### CA-5 Gas Discharge through a Piping System

Calculate the mass flow rate of nitrogen through a 10 m length of 5 mm diameter commercial steel pipe. Assume a scenario of pipe shear at the end of the pipe. The nitrogen is supplied from a source at a pressure of 20 bar gauge and a temperature of 298 K. The piping system includes four 90° elbows (standard, threaded) and two full line gate valves. Calculate the discharge rate by two methods 1) using the orifice discharge equation, CPQRA Equation (2.1.17) or Crowl and Louvar (2002) Equation (4-50), and assuming a hole size equal to the pipe diameter, and 2) using a complete adiabatic flow model. For nitrogen,  $k = 1.4$ .

#### CA-6 Two-Phase Flashing Flow through a Pipe

Propane is stored in a vessel at its vapor pressure of 95 bar gauge and a temperature of 298 K. Determine the discharge mass flux if the propane is discharged through a pipe to atmospheric pressure. Assume a discharge coefficient of 0.85 and a critical pipe length of 10 cm. Determine the mass flux for the following pipe lengths:

- a) 0 cm
- b) 5 cm
- c) 10 cm
- d) 15 cm

Data:

Heat of vaporization:	$3.33 \times 10^5$ J/kg
Volume change on vaporization:	$0.048$ m <sup>3</sup> /kg
Heat capacity:	2230 J/kg K
Liquid density:	490 kg/m <sup>3</sup>

#### CA-7 Gas Discharge due to External Fire

Calculate the gas relief through a relief valve for an uninsulated propane tank with 5 m<sup>2</sup> surface area that is exposed to an external pool fire.

Data:	
Surface area	5 m <sup>2</sup> = 53.8 ft <sup>2</sup>
Environment factor $F$	1.0

Latent heat of vaporization $h_{fg}$	333 kJ/kg (Perry and Green, 1984)
1 Btu/hr	$2.93 \times 10^{-4}$ kJ/s

### CA-8 Isenthalpic Flash Fraction

Calculate the flash fraction of liquid propane flashed from 10 barg and 25°C to atmospheric pressure.

Data:	
Heat capacity, $C_p$	2.45 kJ/kg K (average 231-298°K)
Ambient temperature, $T$	298 K (25°C)
Normal boiling point, $T_b$	231K (-42°C)
Heat of vaporization, $h_{fg}$	429 kJ/kg at -42°C (Perry and Green, 1984)

### CA-9 Boiling Pool Vaporization

Calculate the vaporization rate due to heating from the ground at 10 s after an instantaneous spill of 1000 m<sup>3</sup> of LNG on a concrete dike of 40 m radius.

Data:	
Thermal diffusivity of soil, $\alpha_s$	$4.16 \times 10^{-7}$ m <sup>2</sup> /s
Thermal conductivity of soil, $k_s$	0.92 W/m K
Temperature of liquid pool, $T$	109 K (-164°C)
Temperature of soil, $T_g$	293 K (20°C)
Heat of vaporization of pool, $L$	498 kJ/kg at -164°C (Shaw and Briscoe, 1978)

### CA-10 Evaporating Pool

Estimate the evaporation rate for a 100 m<sup>2</sup> pool of liquid hexane at a temperature of 298 K.

Data:	
$M$	86
$P^{sat}$	151 mm Hg

### CA-11 Pool Evaporation using Kawamura and MacKay (1987) Direct Evaporation Model

Determine the evaporation rate from a 10 m diameter pool of pentane at an ambient temperature of 296 K. The pool is on wet sand and the solar energy input rate is 642 J/m<sup>2</sup>s.

Data:	
Ambient temperature:	296 K
Wind speed at 10 meters:	4.9 m/s
Physical properties of pentane:	
Molecular weight:	72
Heat of vaporization:	27 kJ/mol

Vapor pressure at ambient temp.:	0.652 bar abs
Physical properties of air:	
Diffusivity:	$7.1 \times 10^{-6} \text{ m}^2/\text{s}$
Kinematic viscosity:	$1.5 \times 10^{-5} \text{ m}^2/\text{s}$
Heat transfer properties:	
Heat transfer coefficient for pentane:	$43.1 \text{ J/m}^2 \text{ s } ^\circ\text{C}$
Heat transfer coefficient for ground:	$45.3 \text{ J/m}^2 \text{ s } ^\circ\text{C}$

### CA-12 Plume Release #1

Determine the concentration in ppm 500 m downwind from a 0.1 kg/s ground release of a gas. The gas has a molecular weight of 30. Assume a temperature of 298 K, a pressure of 1 atm, F stability with a 2 m/s wind speed. The release occurs in a rural area.

### CA-13 Plume Release #2

What continuous release of gas (molecular weight of 30) is required to result in a concentration of 0.5 ppm at 300 m directly downwind on the ground? Also estimate the total area affected. Assume that the release occurs at ground level and that the atmospheric conditions are worst case.

### CA-14: Puff Release

A gas with a molecular weight of 30 is used in a particular process. A source model study indicates that for a particular accident outcome 1.0 kg of gas will be released instantaneously. The release will occur at ground level. The plant fence line is 500 m away from the release. Determine,

- a) The time required after the release for the center of the puff to reach the plant fence line. Assume a wind speed of 2 m/s.
- b) The maximum concentration of the gas reached outside the fence line.
- c) Determine the distance the cloud must travel downwind to disperse the cloud to a maximum concentration of 0.5 ppm. Use the stability conditions of part b).
- d) Determine the width of the cloud, assuming a 0.5 ppm boundary, at a point 5 km directly downwind on the ground. Use the stability conditions of part b).

### CA-15 Plume with Isopleths

Develop a spreadsheet program to determine the location of an isopleth for a plume. The spreadsheet should have specific cells for inputs for:

- \* release rate (gm/sec)
- \* release height (m)
- \* spatial increment (m)
- \* wind speed (m/s)

- \* molecular weight
- \* temperature (K)
- \* pressure (atm)
- \* isopleth concentration (ppm)

The spreadsheet output should include, at each point downwind:

- \* both y and z dispersion coefficients (m)
- \* downwind centerline concentrations (ppm)
- \* isopleth locations (m)

The spreadsheet should also have cells providing the downwind distance, the total area of the plume, and the maximum width of the plume, all based on the isopleth value.

Use the following case for computations, and assume worst case stability conditions:

Release rate:	50 gm/sec
Release height:	0 m
Molecular weight:	30
Temperature:	298 K
Pressure:	1 atm
Isopleth conc:	10 ppm

### CA-16 Puff with Isopleths

Develop a spreadsheet program to draw isopleths for a puff. The isopleths must be drawn at a user specified time after the release. The spreadsheet should have specific inputs for:

- \* total quantity released (kg)
- \* time after release (s)
- \* distance downwind for center of puff (m)
- \* release height (m)
- \* spatial increment (m)
- \* wind speed (m/s)
- \* molecular weight
- \* temperature (K)
- \* pressure (atm)
- \* isopleth concentration (ppm)

The spreadsheet output should include, at each point downwind:

- \* downwind location, or location with respect to puff center.
- \* both y and z dispersion coefficients (m)
- \* downwind centerline concentrations (ppm)
- \* isopleth locations (m)

Use the following case for your computations:

Release mass:	50 kg
Release height:	0 m

Molecular weight: 30  
 Temperature: 298 K  
 Pressure: 1 atm  
 Isoleth conc: 1.0 ppm  
 Weather stability: F  
 Wind speed: 2 m/s

- a) At what time does the puff reach its maximum width?
- b) At what time and at what distance downwind does the puff dissipate?

### CA-17 Britter and McQuaid Dense Gas Dispersion

Britter and McQuaid (1988) report on the Burro LNG dispersion tests. Compute the distance downwind from the following LNG release to obtain a concentration equal to the lower flammability limit (LFL) of 5% vapor concentration by volume. Assume ambient conditions of 298 K and 1 atm. The following data are available:

Spill rate of liquid:	0.23 m <sup>3</sup> /s
Spill duration (Rd):	174 s
Wind speed at 10 m above ground (u):	10.9 m/s
LNG density:	425.6 kg/m <sup>3</sup>
LNG vapor density at boiling point of -162°C:	1.76 kg/m <sup>3</sup>

### CA-18 Blast Wave Parameters

A 10-kg mass of TNT explodes on the ground. Determine the over-pressure, arrival time, duration time, and impulse 10 m away from the blast.

### CA-19 TNT Equivalency

Using the TNT equivalency model, calculate the distance to 5 psi over-pressure (equivalent to heavy building damage) of an VCE of 10 short tons of propane.

Data:	
Mass:	10 tons = 20,000 lb
Lower heat of combustion (propane)( $E_c$ ):	19,929 Btu/lb (46.350 kJ/kg)
Assumed explosion efficiency ( $\eta$ ):	0.05
Assumed $E_{c,TNT}$ :	2,000 Btu/lb

### CA-20 TNO and Baker-Strehlow Methods for Vapor Cloud Explosions

(Baker, et. al, 1994) Consider the explosion of a propane/air vapor cloud confined beneath a storage tank. The tank is supported 1 meter off the ground by concrete piles. The concentration of vapor in the cloud is assumed to be at stoichiometric concentrations. Assume a cloud volume of 2094 m<sup>3</sup>, confined below the tank, representing the volume underneath the tank. Determine the over-pressure as a function of distance from the blast using:

- a) the TNO multi-energy method

- b) the Baker - Strehlow method

### CA-21 Energy of Explosion for a Compressed Gas

A 1 m<sup>3</sup> vessel at 25°C ruptures at a vessel burst pressure of 500 bar abs. The vessel ruptures into ambient air at a pressure of 1.01 bar and 25°C. Determine the energy of explosion and equivalent mass of TNT using the following methods:

- Brode's equation for a constant volume expansion, CPQRA Equation (2.2.11) or Lees (1996) Equation (17.4.29).
- Brown's equation for an isothermal expansion, CPQRA Equation (2.2.12), or AIChE/CCPS (1989) Equation (2.2.3).
- Crowl's equation for thermodynamic availability, CPQRA Equation (2.2.13), or Lees (1996) Equation (17.4.43).

### CA-22 Prugh's Method for Over-pressure from a Ruptured Sphere

A 6 ft<sup>3</sup> sphere containing high pressure air at 77°F ruptures at 8000 psia. Calculate the side-on over-pressure at a distance of 60 ft from the rupture. Assume an ambient pressure of 1 atm and temperature of 77°F.

Additional data for air:

Heat capacity ratio, $\gamma$	1.4
Molecular weight of air	29

### CA-23 Baker's Method for Over-pressure from a Ruptured Vessel

Rework CA-22 using Baker's method (AIChE/CCPS, 1994).

### CA-24 Velocity of Fragments from a Vessel Rupture

A 100-kg cylindrical vessel is 0.2 m in diameter and 2 m long. Determine the initial fragment velocities if the vessel ruptures into two fragments. The fragments represent 3/4 and 1/4 of the total vessel mass, respectively. The vessel is filled with helium at a temperature of 300 K, and the burst pressure of the vessel is 20.1 MPa.

For helium,

Heat capacity ratio, $\gamma$ :	1.67
Molecular weight:	4

### CA-25 Range of a Fragment in Air

A 100 kg end of a bullet tank blows off and is rocketed away at an initial velocity of 25 m/s. If the end is 2-m in diameter, estimate the range for this fragment. Assume ambient air at 1 atm and 25°C.

### CA-26 BLEVE Thermal Flux

Calculate the size and duration, and thermal flux at 200 m distance from a

BLEVE of an isolated 100,000 kg (200 m<sup>3</sup>) tank of propane at 20°C, 8.2 bar abs (68°F, 120 psia). Atmospheric humidity corresponds to a water partial pressure of 2810 N/m<sup>2</sup> (0.4 psi). Assume a heat of combustion of 46,350 kJ/kg.

### CA-27 Blast Fragments from a BLEVE

A sphere containing 293,000 gallons of propane (approximately 60% of its capacity) is subjected to a fire surrounding the sphere. There is a torch-like flame impinging on the wall above the liquid level in the tank. A BLEVE occurs and the tank ruptures. It is estimated that the tank fails at approximately 350 psig. Estimate the energy release of the failure, the number of fragments to be expected, and the approximate maximum range of the fragments. The inside diameter of the sphere is 50-ft, its wall thickness is 3/4-inch, and the shell is made of steel with a density of 487 lb<sub>m</sub>/ft<sup>3</sup>. Assume an ambient temperature of 77°F and a pressure of 1 atm.

### CA-28 Over-pressure from a Combustion in a Vessel

A 1 m<sup>3</sup> vessel rated at 1 barg contains a stoichiometric quantity of acetylene (C<sub>2</sub>H<sub>2</sub>) and air at atmospheric pressure and 25°C. Estimate the energy released upon combustion and calculate the distance at which a shock wave over-pressure of 21 kPa can be obtained. Assume an energy of combustion for acetylene of 301 kcal/gm-mole.

### CA-29 Radiation from a Burning Pool

A high molecular weight hydrocarbon liquid escapes from a pipe leak at a volumetric rate of 0.1 m<sup>3</sup>/s. A circular dike with a 25 m diameter contains the leak. If the liquid catches on fire, estimate the thermal flux at a receiver 50 m away from the edge of the diked area. Assume a windless day with 50% relative humidity. Estimate the thermal flux using the point source and the solid plume radiation models.

Additional Data:

Heat of combustion of the liquid:	43,700 kJ/kg
Heat of vaporization of the liquid:	300 kJ/kg
Boiling point of the liquid:	363 K
Ambient temperature:	298 K
Liquid density:	730 kg/m <sup>3</sup>
Heat capacity of liquid (constant):	2.5 kJ/kg-K

### CA-30 Radiant Flux from a Jet Fire

A 25-mm hole occurs in a large pipeline resulting in a leak of pure methane gas and a flame. The methane is at a pressure of 100 bar gauge. The leak occurs 2-m off the ground. Determine the radiant heat flux at a point on the ground 15 m from the resulting flame. The ambient temperature is 298 K and the humidity is 50% RH.

Additional Data:

Heat capacity ratio, <i>k</i> , for methane:	1.32
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Heat of combustion for methane: 50,000 kJ/kg  
 Flame temperature for methane: 2,200 K

**CA-31 Dose-Response Correlation via Probits**

Eisenberg (1975) reports the following data on the effect of explosion peak overpressures on eardrum rupture in humans:

Percentage Affected	Peak Overpressure (N/m <sup>2</sup> )
1	16,500
10	19,300
50	43,500
90	84,300

Determine the probit correlation for this exposure.

**CA-32 Percent Fatalities from a Fixed Concentration-Time Relationship**

Determine the likely percentage of fatalities from a 20-min exposure to 400 ppm of chlorine.

**CA-33 Fatalities Due to a Moving Puff**

A fixed mass of toxic gas has been released almost instantaneously from a process unit. The release occurs at night with calm and clear conditions. If the gas obeys the probit equation for fatalities

$$Y = -17.1 + 1.69 \ln(\Sigma C^{2.75} T)$$

Where *C* has units of ppm and *T* has units of minutes.

- a) Prepare a spreadsheet to determine the percent fatalities at a fixed location 2000-m downwind as a result of the passing puff. Vary the total release quantity and plot the percent fatalities vs. the total release quantity.
- b) Change the concentration exponent from *n* = 2.75 to *n* = 2.50 in the probit equation and determine the percent fatalities for a 5-kg release. How does this compare to the previous result?

Additional data:

Molecular weight of gas: 30  
 Temperature: 298 K  
 Pressure: 1 atm  
 Release height: Ground level  
 Wind speed: 2 m/s

## Safety Problems for a Course in Mass Transfer

Originally Prepared by Ronald J. Willey  
Northeastern University, Boston, MA

### MT-1 Molecular diffusion of gases

**Mass Transfer Principle:** Diffusion

**Level:** Undergraduate Chemical Engineering (introduction to mass transfer Ch.6 Geankoplis)

**Health and Safety Concept:** Flammability limits.

**Background:** Flammability limits of a flammable in air are often quoted by LFL (lower flammability limit) and UFL (upper flammability limit). Potential for a fire exists any time a fuel such as a hydrocarbon vapor is within this range. The concentration of a pure hydrocarbon just above its liquid source is directly related to its vapor pressure. This gaseous mixture may or may not be in the flammability limits. Diffusion plays a role on what distance from the liquid source is the mixture still in the flammable range. Under the proper conditions, a flammable mixture can reach an ignition source and a fire will ensue.

**Questions:**

A vertical 10 mm ID test tube 150 mm in length holds liquid methanol (to a level of 10 mm from the bottom) at a temperature of 300 K. The total surrounding air pressure is atmospheric. Assume that the diffusion coefficient for methanol in air is  $0.135 \text{ cm}^2/\text{s}$ .

- a) Estimate the evaporation rate, kg/s, assuming molecular diffusion as the only mass transfer mechanism.
- b) If the lower flammability limit, LFL, of methanol is 6% in air, determine the distance from the top of the test tube where the mixture is flammable. Assume that the level is being maintained at 10 mm..
- c) What is the UFL of methanol in air?
- d) Estimate the time for the level to drop to 5 mm.

### MT-2 Estimation of a Binary Diffusion Coefficient for Benzene

**Mass Transfer Principle:** Binary Diffusion Coefficient for a Gas Mixture

**Level:** Undergraduate Chemical Engineering (Introduction to Mass Transfer Ch.6 Geankoplis)

**Health and Safety Concept:** MSDS's

**Background:** The MSDS (Material Safety Data Sheet) is available for all chemicals that you will encounter. The MSDS sheet presents several important pieces of information such as: **Identification:** This section contains the name, the chemical formula, CAS number, and synonyms.

**Product and Component Data:** This section provides mixture compositions

**Physical Data:** includes physical property data such as appearance, boiling point,

specific gravity, and vapor pressure data at various temperatures (very helpful when you can not find the data any where else).

**Fire and Explosion Hazard Data:** provides information about the flash point (FP), the fire point, the lower flammability limit (LFL) sometimes referred to as the lower explosion limit, the upper flammability limit (UFL) sometimes referred to as the upper explosion limit, and the autoignition temperature (AIT).

**Reactivity Data:** contains details about stability, and incompatibilities involved with storage and contact with various atmospheres and other materials.

**Toxicity and Health Hazard Data:** provides information about the lethal dose ( $LD_{50}$ ), the threshold limit value (TLV), and the OSHA permissible exposure limits (PEL).

**Ventilation and Personal Protection:** contains information about skin and eye protection when handling and when working around the chemical.

**Special Storage and Handling Protection** provides details about how to store the chemical. Spill, Leak, and Disposal Procedures provides the action to take in the event of a spill.

#### Questions:

- a) Estimate the diffusion coefficient for the system air/benzene at 25°C by the method of Fuller et al.<sup>62</sup> Compare this value to the experimental value of  $9.62 \times 10^{-6} \text{ m}^2/\text{s}$  ref. <sup>63</sup>.
- b) Obtain a copy of the MSDS sheet for benzene. What is the major environmental, health, or safety issue with personnel handling benzene?

### MT-3 That Rotten Egg Smell

**Mass Transfer Principles:** Diffusion

**Level:** Undergraduate Chemical Engineering (Introduction to Mass Transfer Ch.6 Geankoplis)

**Health and Safety Concept:** Threshold Limits Values and  $LC_{50}$  (TLV)

**Background:**  $H_2S$  is a common foul odor and can be sensed from leaking gas lines and other sources. It is perceptible in air in a dilution of 0.002 mg/l (approximately 2 ppb).  $H_2S$  is a neurotoxin and after a period of time in its presence, the smell can no longer be detected. To characterize safe levels of exposures, threshold limit value-time weighted average - TLV-TWA (ACGIH) and permissible exposure levels - PELs (OSHA) are used. Further to characterize lethal situations a value called the  $LC_{50}$ , lethal concentration, is used where the subscript 50 represents 50% of the population will die if exposed. Often  $LC_{50}$  are for mammals like rats

#### Questions:

- a) Estimate the diffusion coefficient for  $H_2S$  in stagnant air at 300 K and 1

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<sup>62</sup> E.N. Fuller, P.D. Schettler, and J.C. Giddings, *Ind. Eng. Chem.*, **58**, 19 (1966).

<sup>63</sup> C.Y. Lee, and C.R. Wilke, *Ind. Eng. Chem.*, **46**, 2381 (1954).

- atm.
- b) What are the TLV-TWA and PEL for H<sub>2</sub>S.
  - c) Provide an LC<sub>50</sub> (with species identified) for H<sub>2</sub>S.

#### MT-4 Ammonia Water Solutions

**Mass Transfer Principle:** Liquid-liquid diffusion

**Level:** Undergraduate (Introduction to Mass Transfer Ch.6 Geankoplis)

**Health and Safety Concept:** Volatilization of hazardous chemicals

**Background:** Ammonia-water solutions are common in the chemical process industry. One of the hazards in dealing with ammonia-water is the volatilization of ammonia into the surroundings if the solution is not properly contained in sealed containers.

**Questions:**

- a) Estimate the diffusion coefficient at 15°C and 30°C for NH<sub>3</sub> in water using the Wilke-Chang equation. Compare the 15°C value to the literature value of  $1.77 \times 10^{-9} \text{ m}^2/\text{s}$ .
- b) What can happen if one inhales ammonia?
- c) Should ammonia water solutions be used in a waste water neutralization application? Discuss the pros and the cons.

#### MT-5 How Harmful Is Chlorine?

**Mass Transfer Principle:** Unsteady-State Diffusion in a Semiinfinite Slab

**Level:** Undergraduate (Unsteady State Mass Transfer Ch.7 Geankoplis)

**Health and Safety Concept:** References about hazardous chemicals

**Background:** “Chlorine in low concentrations isn’t very harmful,” was a statement made by a local New Hampshire newscaster when reporting on a small explosion that happened in New Hampshire where chlorine had combined with other wastes. In the paper industry, lives have been lost due to chlorine leaks. A great desk reference for quick information about the hazards associated with chemicals is the *Merck Index*. Another desk reference is N. Irving Sax, *Dangerous Properties of Industrial Materials*: 6<sup>th</sup> Edition New York: Van Nostrand Reinhold Company, 1984.

**Questions:**

- a) Imagine a very thick slab containing  $1 \times 10^{-4} \text{ kg mol/m}^3$  of chlorine gas in motionless air (assume that a porous material prevents convection but allows diffusion). Suddenly the front face of this semiinfinite slab is removed and the chlorine/air mixture is exposed into an external air stream with a convective coefficient  $k_c = 1.5 \times 10^{-4} \text{ m/s}$ . Assuming that the equilibrium distribution coefficient,  $K = 1.0$ , and that  $D_{AB}$  within the slab is  $1 \times 10^{-5} \text{ m}^2/\text{s}$ , calculate the concentration (in  $\text{mg/m}^3$ ) of Cl<sub>2</sub> at the

- exposed front face after  $t = 5, 50,$  and  $500$  seconds at  $x=0$  m.
- b) Go to your library and obtain the information reported in either the Merck Index or Sax about Chlorine. Why is chlorine hazardous?
  - c) How low of a concentration isn't very harmful? What is the TLV-TWA 8 hrs (in  $\text{mg}/\text{m}^3$ ) for Chlorine gas? Compare the value to gasoline, carbon monoxide, and benzene.

### MT-6 What's in a Laboratory Glove?

**Mass Transfer Principle:** Unsteady State Diffusion

**Level:** Undergraduate Chemical Engineering (Unsteady State Mass Transfer Ch.7 Geankoplis)

**Health and Safety Concept:** Compatibility of Materials and Industrial Hygiene

**Background:** Chemically resistant gloves should be worn whenever the potential for contact with corrosive or toxic substances and substances of unknown toxicity exist. Gloves should be selected on the basis of the materials being handled, the particular hazard involved, and their suitability for the operation being conducted. Before each use, gloves should be checked for integrity. Gloves should be washed prior to removal whenever possible to prevent skin contamination. Non-disposable gloves should be replaced periodically, depending on frequency of use and their resistance to the substances handled.<sup>64</sup>

**Questions:**

- a) Consider that someone is using latex gloves with  $2 \text{ M H}_2\text{SO}_4$ . If the diffusion coefficient for  $\text{H}_2\text{SO}_4$  solutions through the glove is estimated at  $3 \times 10^{-12} \text{ m}^2/\text{s}$ , how long could they hold their finger in a  $2\text{M}$  solution of  $\text{H}_2\text{SO}_4$  before the concentration on the opposing side of the  $4 \text{ mil}$  ( $4/1000$  of an inch) thick glove reaches  $1/100$  of the surface concentration at the exposed surface of the glove? Assume a value of  $10$  for the equilibrium distribution coefficient.
- b) Look up the compatibility rating of a latex gloves. What chemicals should be avoided when using latex gloves?

### MT-7 You Overfill Your Gasoline Tank

**Mass Transfer Principle:** Convective Mass Transfer

**Level:** Undergraduate Chemical Engineering (Convective Mass Transfer Ch.7 Geankoplis)

**Health and Safety Concept:** Industrial Hygiene (TLV)

**Background:** The handling of gasoline is a routine occurrence. Yet spills can happen from time to time and vaporization occurs. Under certain conditions the

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<sup>64</sup> Northeastern University Chemical Hygiene Plan see <http://www.dac.neu.edu/oehs/lchpdoc.htm> 1998.

gasoline vaporized exceeds the TLV of 300 ppm.<sup>65</sup>

**Questions:**

- a) A spill of gasoline occurs such that a pool 0.6 meters in diameter is formed in an area that has a ventilation rate of 85 m<sup>3</sup>/min. If the air velocity is 2 m/s, what is the steady state concentration (in ppm) of gasoline fumes in the enclosed area? Use a diffusivity of gasoline in air of 1 X 10<sup>-5</sup> m<sup>2</sup>/s and assume that the temperature is 25°C and pressure is 1 atm. The vapor pressure of gasoline (MW=94) at 25°C is 31,700 Pa. A correlation to estimate the convective mass transfer coefficient is as follows:<sup>66</sup>

$$j_D = (k_c / \nu) * (N_{Sc})^{2/3} = 0.037 N_{ReL}^{-0.2}$$

Here, the characteristic length to use in the Reynolds number is the diameter of the gasoline pool. Assume that the fluid properties are similar to air.

- b) At what velocity would the concentration equal the TLV?  
c) Discuss methods to control spills of flammables.

**MT-8 Release of Volatile Solvents in Non-enclosed Exposures**

**Mass Transfer Principle:** Convective Mass Transfer

**Level:** Undergraduate Chemical Engineering (Convective Mass Transfer Ch.7 Geankoplis)

**Health and Safety Concept:** Industrial Hygiene (TLV)

**Background:** Occasionally estimation of concentrations for volatilization of hazardous chemicals in non-enclosed exposures is required to determine if a person is being exposed to concentrations above the threshold limit value (TLV) or if a flammable mixture exists.<sup>67</sup> Equations to perform such estimations are presented below.<sup>68</sup>

$$Q_M = \frac{M k_c A P^{Sat}}{R_g T_L} \quad \text{and} \quad C_{ppm} = \frac{k_c A P^{Sat}}{k_{mix} Q_v P} \times 10^6$$

Where:

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<sup>65</sup> This MT-is a contribution from Prof. Ron Darby of Texas A&M University.

<sup>66</sup> Perry's Chemical Engineers' Handbook, 7<sup>th</sup> Ed., R.H. Perry and D.W. Green Editors McGraw Hill, New York, 1997 p-5-59.

<sup>67</sup> This MT-is a contribution from Prof. Ron Darby of Texas A&M University.

<sup>68</sup> D.A. Crowl and J.F. Louvar, *Chemical Process Safety: Fundamentals with Applications*, 2<sup>nd</sup> ed., Prentice Hall Englewood Cliffs, NJ, 2002, p 89.

A	is the surface area of the liquid from which the volatile is releasing
C <sub>ppm</sub>	is the concentration of the volatile in ppm
k <sub>c</sub>	is the convective mass transfer coefficient
k <sub>mix</sub>	is the nonideal mixing factor
M	is the molecular weight of the volatile vaporizing
P <sup>sat</sup>	is the vapor pressure of the volatile
P	is the overall pressure
Q <sub>M</sub>	is the evolution rate of the material (mass per time)
Q <sub>v</sub>	is the ventilation rate
R <sub>g</sub>	is the gas constant
T <sub>L</sub>	is the temperature at the liquid surface (K)

### Questions:

- a) The effective ventilation rate for outside exposures has been estimated at 85 m<sup>3</sup>/min.<sup>69</sup> A worker is standing near an open drum (D=0.6 m) of toluene at 25°C. Estimate the concentration for a non ideal mixing factor of 0.1 to 0.5. The prevailing wind speed is 8 km/h. A correlation to estimate the convective mass transfer coefficient is as follows:<sup>70</sup>

$$j_D = (k_c / v) * (N_{Sc})^{2/3} = 0.037 N_{ReL}^{-0.2}$$

Here, the characteristic length to use in the Reynolds number is the diameter of the drum. Assume that the fluid properties are similar to air.

- b) How does this level compare to the TLV of toluene?  
 c) What other hazards exist with an open drum of toluene?

## MT-9 Mass Transfer along a Pipe

**Mass Transfer Principle:** Mass transfer in laminar flow

**Level:** Undergraduate (Convective Mass Transfer Chapt. 7 Geankoplis)

**Health and Safety Concept:** Estimation of release rates

**Background:** Source models are used to estimate release rates for pipes, hoses, flanges, or tanks that may accidentally rupture or leak. They provide useful information for the evaluation of consequences of an unexpected leak such as exposure (TLV estimation), fire (LFL estimation), or explosion potential (LEL estimation). If the potential leaks are too severe, alternatives can be investigated

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<sup>69</sup> R. C. Matthiessen, "Estimating Chemical Exposure Levels in the Workplace," *Chemical Engineering Progress*, April, 1986, p. 30.

<sup>70</sup> Perry's Chemical Engineers' Handbook, 7<sup>th</sup> Ed., R.H. Perry and D.W. Green Editors McGraw Hill, New York, 1997 p-5-59.

at the design stage to mitigate or to eliminate such leaks. Crowl and Louvar<sup>71</sup> provide a number of source models for flow of liquids and vapors through a hole and pipes. An example for estimation for flow of a liquid through a hole is presented in this problem.

**Questions:**

- a) Pure water at 26.1°C is flowing at a velocity of 0.03 m/s inside a stainless steel tube of 6.35 mm inside diameter.<sup>72</sup> Ten centimeters of this tube is coated inside with benzoic acid. Estimate the outlet concentration of benzoic acid. The solubility of benzoic acid in water is 0.02948 kg mol/m<sup>3</sup>. The diffusivity of benzoic acid in water is 1.245 X 10<sup>-9</sup> m<sup>2</sup>/s.
- b) A 2mm diameter hole suddenly appears in the tubing. If the water pressure inside the tube is 100 kPa gauge, what is the release rate, kg/s, of the water-benzoic acid mixture into the environment? An equation to estimate release rate of liquids through a hole is given below.<sup>73</sup>

$$Q_m = AC_o\sqrt{2\rho P_g}$$

Where:

- $Q_m$  is the release rate in kg/s  
 $A$  is the area of the hole, m<sup>2</sup>  
 $C_o$  is the orifice coefficient (use 0.61 unless otherwise known).  
 $\rho$  is the density, kg/m<sup>3</sup>  
 $P_g$  is the gauge pressure in the pipe, Pa

## MT-10 Ultra Low Metering of a Gas

**Mass Transfer Principle:** Knudsen Diffusion

**Level:** Undergraduate (Chapt. 7 Geankoplis)

**Health and Safety Concept:** Estimation of release rates for a broken gas line.

**Background:** Source models are used to estimate release rates for pipes, hoses, flanges, or tanks that may accidentally rupture or leak. They provide useful information for the evaluation of consequences of an unexpected leak such as exposure (TLV estimation), fire (LFL estimation), or explosion potential (LEL estimation). If the potential leaks are too severe, alternatives can be investigated at the design stage to mitigate or to eliminate such leaks. Crowl and Louvar<sup>74</sup>

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<sup>71</sup> D.A. Crowl and J.F. Louvar, *Chemical Process Safety: Fundamentals with Applications*, 2<sup>nd</sup> ed., Prentice Hall Englewood Cliffs, NJ, 2002, pp 109-170.

<sup>72</sup> This MT-statement is very similar to those found in Geankoplis Example and MT-7.3-2.

<sup>73</sup> D.A.Crowl and J.F. Louvar, pp 154.

<sup>74</sup> D.A. Crowl and J.F. Louvar, *Chemical Process Safety: Fundamentals with Applications*, 2<sup>nd</sup> ed., Prentice Hall Englewood Cliffs, NJ, 2002, pp 109-170.



provide a number of source models for flow of liquids and vapors through a hole and pipes. An example for estimation for isothermal flow of a gas through a pipe is presented in this problem.

**Questions:**

- a) A process operating in high vacuum requires an extremely low flow of hydrogen for calibration purposes. Imagine that a 10mm long, 100 angstrom capillary is available. If the hydrogen pressure on the upstream side of the capillary is 150 Pa and the temperature is 300 K, estimate the flow of hydrogen (kg/s) through this novel metering system.
- b) The hydrogen for the above process is being furnished through 1/8" OD laboratory lines (wall thickness 0.021"). The line break 5 meters from the pressure regulator (set at 40 Psig). Estimate the flow of hydrogen into the room in kg/s and m<sup>3</sup>/min. The following equation from Crowl and Louvar can be used under the condition of isothermal choked flow.<sup>75</sup> Assume that this condition exists in this case with  $P_{choked} = 101325$  Pa (atmospheric pressure).
- c) What safety device could be added to the hydrogen laboratory supply line

$$Q_m \text{ (kg / s)} = AP_{choked} \sqrt{\frac{MW}{RT}}$$

to prevent a fire from reaching the regulator and supply tank?

**MT-11 A Puff**

**Mass Transfer Principle:** Dispersion of material

**Level:** Undergraduate Chemical Engineering

**Health and Safety Concept:** Toxic Release and Dispersion Models (Chapt 5. Crowl and Louvar)

**Background:** Sudden releases of toxic and hazardous chemicals can occur by the relieving of a process vessel, or by the rupturing of a pipe, a tank, a train car, or a tank truck. Several empirical models are used to model the dispersion of such releases as they travel along prevailing winds through local terrain. The major division for dispersion models are "puff models" a near instantaneous release of material, and "plume models" a continuous release from a stationary source. Sophisticated software now exists to model dispersions based on the many variables that exist at any potential source. However, quick estimations can be made by Pasquill-Gifford Models.<sup>76</sup> One such model is for a puff release at ground level.

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<sup>75</sup> Adapted from D.A.Crowl and J.F. Louvar, pp 138.

<sup>76</sup> D.A. Crowl and J.F. Louvar, *Chemical Process Safety: Fundamentals with Applications*, 2<sup>nd</sup> ed., Prentice Hall Englewood Cliffs, NJ, 2002, pp 186-195.

$$C = \frac{Q_m}{\sqrt{2\pi^{3/2}}\sigma_x\sigma_y\sigma_z} \exp\left\{-\frac{1}{2}\left[\left(\frac{x-ut}{\sigma_x}\right)^2 + \frac{y^2}{\sigma_y^2} + \frac{z^2}{\sigma_z^2}\right]\right\}$$

Where:

- C is the conc, kg/m<sup>3</sup> or kg mol/m<sup>3</sup>  
 Q<sub>m</sub> is the total release in kg or kg mol  
 x is the x direction orientated in the wind direction, m  
 u is the wind speed, m/s  
 σ<sub>i</sub> is dispersion coefficient, m. For stability Class C: σ<sub>x</sub>=σ<sub>y</sub>=0.10x<sup>0.92</sup>, σ<sub>z</sub>=0.34x<sup>0.71</sup> (x in m)  
 y is the distance from the center line of the wind vector, m  
 z is the height from ground level, m  
 t is the time, s

### Questions:

- Consider a sudden release of NH<sub>3</sub> from a cooling system holding 200 kg of NH<sub>3</sub>. If the local wind is blowing at 3 m/s, and day light gives a stability similar to stability class C, plot the maximum concentration of the puff as a function of x distance for a distance from 0.1 km to 1.0 km.
- If the TLV of ammonia is 25 mg/m<sup>3</sup>, at what distance from the release does the center concentration drop below the TLV?
- Sometimes the best action in an event like this is to advise people to close their doors and windows and stay inside until the cloud passes. How long must people stay inside based on the answer found in part b?

## MT-12 A Plume

**Mass Transfer Principle:** Dispersion of material

**Level:** Undergraduate Chemical Engineering

**Health and Safety Concept:** Toxic Release and Dispersion Models (Chapt 5. Crowl and Louvar)

**Background:** Sudden releases of toxic and hazardous chemicals can occur by the relieving of a process vessel, or by the rupturing of a pipe, a tank, a train car, or a tank truck. Several empirical models are used to model the dispersion of such releases as they travel along prevailing winds through local terrain. The major division for dispersion models are “puff models” a near instantaneous release of material, and “plume models” a continuous release from a stationary source. Sophisticated software now exists to model dispersions based on the many variables that exist at any potential source. However, quick estimations can be made by Pasquill-Gifford Models.<sup>77</sup> One such model for a plume release from a stack of height, H<sub>r</sub> is: .

<sup>77</sup> D.A. Crowl and J.F. Louvar, *Chemical Process Safety: Fundamentals with Applications*, 2<sup>nd</sup> ed., Prentice Hall Englewood Cliffs, NJ, 2002, pp 186-195.

$$C = \frac{Q_m}{2\pi\sigma_y\sigma_z u} \exp\left[-\frac{1}{2}\left(\frac{y^2}{\sigma_y^2}\right)\right] X \exp\left[-\frac{1}{2}\left(\frac{z-H_r}{\sigma_z}\right)^2\right] + \exp\left[-\frac{1}{2}\left(\frac{z+H_r}{\sigma_z}\right)^2\right]$$

Where:

- C is the conc, kg/m<sup>3</sup> or kg mol/m<sup>3</sup>  
 Q<sub>m</sub> is the release rate in kg/s or kg mol/s  
 x is the x direction orientated in the wind direction, m  
 u is the wind speed, m/s  
 σ<sub>i</sub> is dispersion coefficient, m. For stability Class C: σ<sub>x</sub>=σ<sub>y</sub> = 0.11x(1 + 0.0001x)<sup>-1/2</sup>, σ<sub>z</sub>=0.08x(1 + 0.0002x)<sup>-1/2</sup> (x in m)  
 y is the distance from the center line of the wind vector, m  
 z is the height from ground level, m  
 H<sub>r</sub> is the height of the stack from the ground, m (in this MT-assume that the plume does not rise further above the top of the stack)

**Questions:**

- A power plant is emitting 50 kg/h per of NO from a stack 40 m in height. Estimate the NO concentration in ppb 500 m downwind from the power plant. Prevailing wind that day is 3 m/s and the stability class is C.
- Repeat the calculation in part a) for a position 100 meters off the downwind centerline 500 m downwind at ground level. How does this value compare to part a)?
- What are some of the long-term exposure problems when children are exposed to low concentrations of nitric oxide?
- List three approaches used to control nitric oxide emissions from stationary sources.

**MT-13 A Chlorine Leak**

**Mass Transfer Principle:** Forced Convection

**Level:** Undergraduate Chemical Engineering

**Health and Safety Concept:** Modeling Gas Dispersions

**Background:** Sudden releases of toxic and hazardous chemicals can occur by the relieving of a process vessel, or by the rupturing of a pipe, a tank, a train car, or a tank truck. Several empirical models are used to model the dispersion of such releases as they travel along prevailing winds through local terrain. The major division for dispersion models are “puff models” a near instantaneous release of material, and “plume models” a continuous release from a stationary source. Sophisticated software now exists to model dispersions based on the many variables that exist at any potential source. However, quick estimations can be made by Pasquill-Gifford Models.<sup>78</sup> One such model is for a puff release at

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<sup>78</sup> D.A. Crowl and J.F. Louvar, *Chemical Process Safety: Fundamentals with Applications*, 2<sup>nd</sup> ed. Prentice Hall Englewood Cliffs, NJ, 2002, pp 186-195.

ground level.

$$C = \frac{Q_m}{\sqrt{2\pi}^{3/2} \sigma_x \sigma_y \sigma_z} \exp \left\{ -\frac{1}{2} \left[ \left( \frac{x-ut}{\sigma_x} \right)^2 + \frac{y^2}{\sigma_y^2} + \frac{z^2}{\sigma_z^2} \right] \right\}$$

Where:

C	is the conc, kg or kg mol/m <sup>3</sup>
Q <sub>m</sub>	is the total release in kg or kg mol
x	is the x direction orientated in the wind direction, m
u	is the wind speed, m/s
σ <sub>i</sub>	is dispersion coefficient, m. For stability Class C: σ <sub>x</sub> =σ <sub>y</sub> = 0.10x <sup>0.92</sup> , σ <sub>z</sub> =0.34x <sup>0.71</sup> (x in m)
y	is the distance from the center line of the wind vector, m
z	is the height from ground level, m
t	is the time, s

### Questions:

- Consider a sudden release of chlorine from a tank truck that has tipped over on an off-ramp from a major highway. The truck was carrying 5,000 kg of chlorine which all vaporized and formed a puff. The wind speed this particular day is 2 m/s and is blowing in such a direction that a small town is located 2,000 m directly downwind from the release. Plot the concentration, mg/m<sup>3</sup>, due to chlorine at the center of this town as a function of time starting with time=0 when the truck tips over until time=60 minutes. Assume stability class C.
- If the TLV of chlorine is 1.5 mg/m<sup>3</sup>, does the concentration of chlorine in the center of the town ever exceed this amount?
- How long do the officials have to warn people?
- At what distance down stream does the maximum concentration stay below the TLV-TWA for chlorine during the whole passage of the puff?
- How long must people remain in their home?

### MT-14 Mercury in a Sink Drain

**Mass Transfer Principle:** Diffusion versus surface reaction rate controlling

**Level:** Undergraduate Chemical Engineering (Convective Diffusion Ch 7 Geankoplis)

**Health and Safety Concept:** Inherently safer processes and reportable quantities

**Background:** Mercury is a very toxic substance. Yet, it has many practical applications including thermometers, pressure measurement, and diffusion pumps, not to mention batteries. Many universities and high schools have had mercury in the laboratories, primarily as thermometers and manometers. This was especially prevalent before the 1970's. Over the years, mercury at one time or another has reached sink drains within these laboratories. The Massachusetts Water Resources Authority (MWRA) currently imposes an effective discharge

limitation for mercury of 1.0 part per billion (ppb) from its regulated sources, including hospitals and institutions.<sup>79</sup> The rate of Hg dissolution into water is governed by many factors (pH, external chemicals within the water like chlorine); however, let's assume that it is proportional to dissolved oxygen and the intrinsic surface reaction rate between mercury and that dissolved oxygen in water is given by the following rate equation:<sup>80</sup>  $\text{rate Hg (kg/m}^2 \text{ sec)} = 1.2 \cdot 10^{-5} \cdot [\text{dissolved oxygen kg/m}^3]$

Another concept covered in this MT-is reportable quantities. If an accidental release or spill occurs of a hazardous substance above a reportable quantity, it must be reported to appropriate authorities. These may include local emergency planning committees (LEPC), state emergency response commissions, or governmental agencies such as the EPA under the Superfund law (CERCLA).

#### Questions:

- What is the diffusion coefficient for dissolved oxygen in water at 20°C?
- If the maximum solubility of oxygen in water is 9.1 mg/l at 20°C and the average coverage of the mercury by the water in a 2.5 cm diameter trap is 10 cm (the upper surface of the water is exposed to air and may be assumed to be saturated), is the dissolution of Hg into the waste water a surface reaction or a diffusion controlled process? Assume that 10 ml Hg is exposed to the water as a hemisphere in the lower part of the trap.
- Assuming that the rate of dissolution of Hg is reaction controlled, and that this particular sink empties into a laboratory flow system that flows at an average of 20 l/min, is this laboratory waste water in compliance with the MWRA standards?
- Inherently safer practice implies finding alternatives that are safer. List some of the alternatives to mercury thermometers, manometers, and Hg diffusion pumps.
- What is the EPA reportable quantity for an accidental spill of mercury?

### MT-15 Flash Distillation

**Mass Transfer Principle:** Binary distillation

**Level:** Undergraduate Chemical Engineering (Ch 11 Geankoplis)

**Health and Safety Concept:** FP, LFL, UFL, AIT of materials

**Background:** Distillation is a very common process often carried out with flammables. Several terms are used to characterize flammables:  
Flash Point (FP): The lowest temperature in which the pure liquid can be ignited. The flame is not self sustaining.  
Lower Flammability Limit (LFL): Lower vapor composition (in mole percent) in air in which a fire or combustion can occur.  
Upper Flammability Limit (UFL): Upper vapor composition (in mole percent) in

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<sup>79</sup> <http://www.masco.org/mercury/>

<sup>80</sup> This equation has been created by the author for demonstration purposes only.

air in which a fire or combustion event can occur).

Auto-ignition Temperature (AIT): Temperature at which material will self ignite (generally in air environments).

**Questions:**

- a) A continuous flash distillation process is being used to split a 100 kg mol/h of a 70/30 (by mol%) benzene/ toluene stream into a more concentrated benzene stream. What are the predicted concentrations and flow rates out of this flash unit, if it is run at atmospheric pressure and the feed is 50 % vaporized (by mol%) before entering the unit?
- b) What are the FP, LFL, UFL, and AIT for benzene and toluene respectively?
- c) When the unit starts up, what precautions should be taken to minimize a fire?

**MT-16 Flash Point Estimation of Mixtures**

**Mass Transfer Principles:** Distillation

**Level:** Undergraduate Chemical Engineering (Ch 11, Geankoplis)

**Health and Safety Concept:** Flash Point

**Background:** The NFPA guidelines are often used to determine the amount of flammables that can be stored in laboratories.<sup>81</sup> Flammable liquids are divided into three classes with Class I the most flammable and having three subcategories (A,B,C). The classification uses flash points and vapor pressures to determine the Class and Subclass. Quantities that can be stored within confined laboratory space are then restricted for the more flammable liquids as judged by the flash point. If the room has sprinklers, more flammable material can be stored. Pure ethanol has a flash point of 55°F and is classified as a Class 1 flammable (flash point below 100°F). Its quantity of storage quantity is thus restricted. However, ethanol diluted with water will have a higher flash point and fall in a higher class and thus more material can be stored. Flash point for water-miscible flammables can be estimated using vapor pressure of the pure component and Raoult's law.

**Questions:**

- a) Construct the vapor-liquid equilibrium diagram for ethanol water (1 atm).
- b) Using the McCabe Thiele Method, determine the number of ideal stages needed for 90 wt% overhead and a 0.5 wt% bottom (ethanol) at total reflux.
- c) The feed for this unit is 15 wt% ethanol. Estimate its flash point in °F. See the reference below for a similar example with methanol-water.<sup>82</sup>
- d) Note that the ethanol-water system is less ideal than the methanol-water system. For extra credit, qualitatively discuss what is the effect of this

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<sup>81</sup> NFPA 45: "Fire Protection for Laboratories Using Chemicals," NFPA Quincy Ma, 1982.

<sup>82</sup> D.A. Crowl and J.F. Louvar, *Chemical Process Safety: Fundamentals with Applications*, 2<sup>nd</sup> ed. Prentice Hall Englewood Cliffs, NJ, 2002, p 232.

non-ideal behavior. A process simulator may be used to assist in this answer.

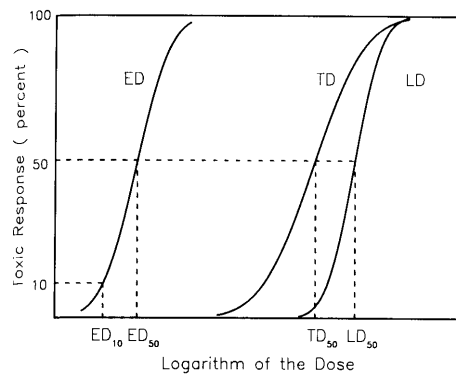
## MT-17 Ammonia Absorption Tower

**Mass Transfer Principle:** Mass Transfer Coefficients for Packed Towers

**Level:** Undergraduate Chemical Engineering (Chapt.10 Geankoplis)

**Health and Safety Concept:** Probit method of estimating risk

**Background:** Many methods exist for representing a response-dose curve which typically appears as shown below (reference Crowl and Louvar Figure 2-8, p35.)<sup>83</sup>:



Where:

- ED is the effective dose where a person begins to see an effect (eyes water etc.).
- TD is the toxic dose where long term illness may occur.
- LD is the lethal dose where death will occur.
- 50 is the point where 50% of the population will be effected.

A method to model this data is the Probit Method<sup>84</sup> in which the percentages are transformed to a Probit variable (Y). A condensed table of percentages transformed to Probits is as follows:

Percentage (%)	1	10	20	30	40	50	60	70	80	90	99
Probit, (Y)	2.67	3.72	4.16	4.48	4.75	5.00	5.25	5.52	5.84	6.29	7.33

Then linear models are developed of the form:

$$Y = k_1 + k_2 \ln V$$

Where  $k_1$  and  $k_2$  are constants determined from experience that match the

<sup>83</sup>Ibid, p 48.

<sup>84</sup>Ibid p 49.

causative variable  $V$  in consistent units. For example, the probit model can estimate the number of people that would die if a group of people are exposed to a 1,000 ppm of ammonia in air for 2 minutes. In this case, the causative variable is  $C^{2.75}t$  where  $C$  is the concentration in ppm and  $t$  is time in minutes. For deaths due to ammonia exposure,  $k_1 = -30.57$  and  $k_2 = 1.385$ .  $k_1$  and  $k_2$  will vary depending on the causative variable under examination (glass breakage, ear drum rupture, death due to exposure in chlorine plumes etc). In the example above, we can calculate  $Y$  and then estimate if any deaths will occur:  
 $Y = -30.57 + 1.385 \ln ( 1,000 \text{ ppm}^{2.75} * 2 \text{ min} )$  where  $V = C^{2.75}t$  and  $Y = -3.3$ .  
 In this example the probit is below zero. Thus, the conclusion made is that no one will die from this event. If  $Y = 5.00$ , then from Table 1, 50% of those exposed would die.

**Questions:**

- a) An ammonia absorption tower composed of 9.5 mm (3/8") Raschig Rings has been proposed. The mass velocity of water will be set at 2.0 kg/s m<sup>2</sup> and the ammonia stream entering (25 ppm of ammonia) will be set at a mass velocity of 0.5 kg/s m<sup>2</sup>. Temperature of operation will be 30°C. Predict  $H_G$ ,  $H_L$ , and  $K_y a$  for this tower.
- b) Imagine that one day the tower went out of service and personnel nearby are exposed to 1,000 ppm of ammonia in air. How much time in minutes would be available before 1 person in 100 dies?

**MT-18 SO<sub>2</sub> Absorption Tower and Gas Relief System**

**Mass Transfer Principle:** Gas-Liquid Separation Process

**Level:** Undergraduate Chemical Engineering (Ch 10 Geankoplis)

**Health and Safety Concept:** Sizing of Rupture Disk for Gas Service (Chapt. 9 Crowl & Louvar)

**Background:** Relief systems are required on many process units. Generally a relief system consists of a spring-operated relief valve or a rupture disk and piping that transports the relief flow to a safe point of disposal such as a roof top, a knock-out drum, or a secondary trap. Elementary equations for relief sizing for numerous scenarios are available in Crowl and Louvar<sup>85</sup>. One example is the sizing of a gas relief when the upstream pressure is high enough that choked flow occurs. The governing equation is:

$$(Q_m)_{\text{choked}} = C_o A P_o \sqrt{\frac{g_c M \gamma}{R_G T} \left( \frac{2}{\gamma + 1} \right)^{(\gamma + 1)/(\gamma - 1)}}$$

Where:

$Q_m$  is the discharge flow rate through the rupture disk,

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<sup>85</sup> Crowl, D.A. and Louvar, J.F. *Chemical Process Safety: Fundamentals with Applications*, 2<sup>nd</sup> ed. Prentice-Hall, Englewood Cliffs, New Jersey, 2002, Chapt 9.



	mass/time
$C_o$	is the orifice coefficient, use 1.0 for gases
$A$	is the area of the rupture disk
$P_o$	is the upstream pressure (upstream pressure must exceed the downstream pressure by 1.89 times for air to achieve critical flow through the opening).
$\gamma$	is the ratio of the heat capacities = 1.40 for air
$M$	is the molecular weight
$T$	is the temperature
$R_G$	is the universal Gas Constant

**Questions:**

- A tray tower is to be designed for the absorption of  $\text{SO}_2$  from an air stream using pure water at 293 K (68 F). The entering gas contains 1,000 ppm  $\text{SO}_2$  and the exiting concentration of must be below 10 ppm. The normal operating pressure will be 101.3 kPa. The air flow rate is set at 100 kg/hr and the entering water is set at 2 times the minimum water required to carry out the absorption process. Assuming that the actual trays are 50% efficient, how many trays are needed? Equilibrium data for  $\text{SO}_2$ - water system can be found in Geankoplis A.3-19 p 885.
- If the surrounding pressure around the column is atmospheric (101.3 kPa), at what minimum pressure within the column would critical flow begin to occur?
- Using the pressure found in part **b)** and the design flow rate of air in part a), what diameter rupture disk would be needed for this process unit?

**MT-19 Ethanol-water Distillation and LOC**

**Mass Transfer Principle:** Distillation

**Level:** Undergraduate Chemical Engineering (Ch. 11 Geankoplis)

**Health and Safety Concept:** Inerting of process vessels to prevent fires (Ch. 7 Crowl and Louvar)

**Background:** Start up of process equipment is always risky. If flammables are involved, care must be taken to avoid flammable/air mixtures that can ignite. One method used is “sweep-through” purging of an inert such as nitrogen through the process unit before the addition of the flammable<sup>86</sup>. The purging is continued until the outlet oxygen concentration is a fraction below the limiting oxygen concentration (LOC) for ignition. The volumetric quantity of inert required to reduce the oxygen concentration for sweep-through purging can be estimated by the following equation:

$$Q_v t = V \ln \left( \frac{C_1 - C_0}{C_2 - C_0} \right)$$

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<sup>86</sup> Crowl, D.A. and Louvar, J.F. Chemical Process Safety: Fundamentals with Applications, 2<sup>nd</sup> ed. Prentice-Hall, Englewood Cliffs, New Jersey, 2002, p 300.

Where:

$Q_v$  Flow rate of the inert

$t$  Time

$V$  Volume of system to be purged

$C_1$  Concentration of oxygen in the unit before purging

$C_2$  Concentration of oxygen in the unit after purging, for time  $t$ .

$C_0$  Initial oxygen concentration in the inert stream.

LOC can be estimated by the following equation<sup>87</sup>:

$$\text{LOC (\%O}_2\text{)} = \text{LFL} * (\text{Moles of O}_2\text{/Moles of Fuel})$$

Where LFL is the lower flammability limit and the (Moles of O<sub>2</sub>/Moles of Fuel) is the ratio of stoichiometric coefficients for oxygen to fuel in the combustion reaction of oxygen plus fuel to CO<sub>2</sub> and H<sub>2</sub>O.

### Questions:

- a) A distillation column is to be designed to separate a 15 wt% ethanol-water mixture to 90 wt% top fraction and 0.5 wt% bottom fraction ethanol. The reflux will be set at 2 times the minimum. The feed will enter at its boiling point as a saturated liquid, and the column will operate at atmospheric pressure. How many ideal trays are needed for this separation?
- b) What is the minimum oxygen concentration for ethanol vapor?
- c) If the volume of the proposed distillation column is 2 m<sup>3</sup>, estimate the time to purge the column to ¼ LOC concentration found in part b) with a 0.1 m<sup>3</sup>/min flow of N<sub>2</sub>.

## MT-20 Outlet Compositions for an Existing Distillation Column

**Mass Transfer Principle:** Binary Distillation

**Level:** Undergraduate Chemical Engineering (Ch. 11 Geankoplis)

**Health and Safety Concept:** Relief Vent Lines Piped to Flares and Flare Sizing (Crowl & Louvar Ch. 8)

**Background:** Major refineries and chemical plants tie process vent lines and relief vent lines from various processing units to flares. The function of flares is to prevent releases of organic chemicals or toxic gases directly to the environment. Instead these materials are combusted to inert products such as CO<sub>2</sub> and water. A design criteria<sup>88</sup> for flares is that the heat intensity at the base of the flare not exceed 1,500 BTU/hr ft<sup>2</sup>. The effects of thermal radiation are detailed in the following table (also from the same reference):

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<sup>87</sup> Ibid, p 238.

<sup>88</sup> Crowl, D.A. and Louvar, J.F. *Chemical Process Safety: Fundamentals with Applications*, 2<sup>nd</sup> ed., Prentice-Hall, Englewood Cliffs, New Jersey, 2002, p-375-376.

<u>Heat Intensity</u> Btu/hr ft <sup>2</sup>	<u>Heat Intensity</u> W/m <sup>2</sup>	<u>Effect</u>
2,000	6,300	Blisters in 20 seconds
5,300	17,000	Blisters in 5 seconds
3,000 to 4,000	9,450 to 12,600	Vegetation and wood are ignited
350	1,100	Solar Radiation

Soen H. Tan in Hydrocarbon Processing, Jan 1967 derived the following equation to estimate the safe height of flare towers to protect personnel who stay beyond a certain distance from the flare.

$$H_t = -60 d_t + 0.5 \sqrt{(120 d_t)^2 - \left( \frac{4 \pi q_f X_t^2 - 960 Q_m \sqrt{M}}{\pi q_f} \right)}$$

Where:

- H<sub>t</sub> is the flare height (ft).
- d<sub>t</sub> is the diameter of the flare stack (ft)
- q<sub>f</sub> is the heat intensity (Btu/hr/ft<sup>2</sup>)
- X<sub>t</sub> is the distance from the stack at grade (ft)
- Q<sub>m</sub> is the vapor rate (lb/hr)
- M is the molecular wt.

**Questions:**

- a) A distillation tower with 10 trays is available for separation. The plant has a need to separate a saturated vapor stream of 5,000 kg mol/hr of 60 mol% benzene and 40 mol% toluene into a benzene-rich stream and a toluene-rich streams. Using tray number 5 (from the top) as the feed tray, a reflux ratio of 4.0, and a Murphree tray efficiency of 50%, determine the outlet compositions for this tower.
- b) Determine the height required of a 4' foot diameter flare tower that can handle the feed stream in part a) given a heat intensity of 1,500 BTU/hr ft<sup>2</sup> at a radius 400 ft from the base of the flare.

**MT-21 Liquid-liquid Extraction and Static Electricity**

**Mass Transfer Principle:** Stage Operations: Liquid-Liquid extraction

**Level:** Undergraduate Chemical Engineering (Ch. 12 Geankoplis)

**Health and Safety Concept:** Static Electricity (Ch. 7.2 Crowl and Louvar)

**Background:** Spark-ignition hazards must be considered whenever static charge may accumulate in an environment that contains a flammable gas, liquid or dust<sup>89</sup>. Electrostatic charge can occur through contact electrification, charge

<sup>89</sup> Perry's Chemical Engineers' Handbook, 7<sup>th</sup> Edition, R.H. Perry and D.W.Green Editors, McGraw Hill, 1997, p 26-70.

induction, and spraying. Contact electrification occurs when a contact is followed by separation between solid-solid, liquid-solid, or liquid-liquid surfaces. A typical example is the discharging of an organic liquid through a nozzle into a tank. At the point of separation, electrons or ions flow from the nozzle to the liquid (or visa versa), creating a charge accumulation in the liquid flowing into the tank. Under certain circumstances, the charge build-up can be high enough to create a spark and a fire may follow. Grounding and bonding of conductive process equipment is a common mitigation method. As a rule of thumb, the minimum conditions for a spark discharge are  $J > 0.1$  mJ and  $V > 350$  volts. If both of these conditions exist, a spark may occur.

Crowl and Louvar present several equations and methods to estimate static electricity concerns<sup>90</sup>. For exemplary purposes, the following equations are taken from Crowl and Louvar (1<sup>st</sup> Edition):

The charge accumulated in filling a tank is:

$$Q = I_s \tau + (Q_o - I_s \tau) e^{-t/\tau}$$

And the maximum spark energy can be calculated by the following equation:

$$J = 0.5CV^2 = 0.5Q^2 / C$$

Where:

Q	is the charge in coulombs.
$I_s$	is the streaming current in amps (see Crowl and Louvar Eqn. 7-12 and 7-14).
$\tau$	is the relaxation time (see Crowl and Louvar Eqn. 7-16).
t	is the time from the initial addition of material into the tank.
J	is the total stored energy in joules.
V	is the potential difference in volts.
C	is the capacitance of the charged system in farads (see Crowl and Louvar Eqn. 7-25).

When V exceeds 350 volts and J exceeds 0.1 mJ where flammables are present, a spark may occur and the condition is considered dangerous<sup>91</sup>.

### Questions:

- a) A liquid-liquid extraction column is being designed for the separation by liquid-liquid extraction of isopropanol from a hexane mixture by pure water. The equilibrium data for this system are<sup>92</sup>:

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<sup>90</sup> Crowl, D.A. and Louvar, J.F. *Chemical Process Safety: Fundamentals with Applications*, Prentice-Hall, Englewood Cliffs, New Jersey, 1990, pp 200-227

<sup>91</sup> Ibid, p. 201.

<sup>92</sup> Warning: although data are based from an actual experimental system; this data should not be used for comparison or design purposes.

Light Phase (mass %)			Heavy Phase (mass %)		
IPA	Hex.	Water	IPA	Hex.	Water
0.012	0.988	-	0.081	-	0.919
0.025	0.975	-	0.105	-	0.895
0.065	0.935	-	0.148	0.001	0.851
0.161	0.839	-	0.252	0.002	0.746
0.273	0.727	-	0.358	0.01	0.632
0.36	0.61	0.03	0.432	0.05	0.518
0.44	0.46	0.1	0.461	0.15	0.389
0.5	0.3	0.2	0.334	0.3	0.2

The entering hexane stream contains 0.15 mass fraction of IPA and no water. The entering water stream is free of hexane and IPA. The desired outlet stream is 0.01% IPA in hexane. If 1.5 times the minimum water is used, and stage efficiency is 10%, how many stages are required for this separation?

- b)** The tank containing the hexane stream holds 10,000 liters. Before the process begins, the tank is filled at a rate of 100 liters per minute through a 5 cm nozzle. Compute  $Q$ ,  $V$ , and  $J$  for the tank just after filling if the relaxation time is  $1 \times 10^5$  seconds,  $I_s$  is  $1.5 \times 10^{-13}$  amps, and the capacitance is  $3 \times 10^{-10}$  farad. Is there a potential for a spark discharge?
- c)** What safety precautions should be taken when transferring flammable materials in regard to minimizing fires due to static electricity?
- d)** (Extra Credit) Compare the values given for relaxation time,  $I_s$ , and  $C$  for part **b)** using the equations given in Crowl and Louvar. Treat the hexane stream as pure hexane.

## MT-22 Reverse Osmosis and Liquid Relief Sizing

**Mass Transfer Principle:** Membrane Separation Processes

**Level:** Undergraduate Chemical Engineering (Geankoplis, Ch13)

**Health and Safety Concept:** Relief Sizing (Crowl and Louvar Ch. 9).

**Background:** Relief valves are required for any line following a positive displacement pump. This prevents line rupture or pump damage should the line ever be blocked in by a closed valve downstream of the pump. Relief valves are specified by the set pressure i.e., the pressure where the relief valve begins to open. The set pressure is equal to the maximum allowable working pressure (MAWP) or to 10% above the normal operating pressure (which must be below the MAWP). As the pressure continues to increase beyond the set pressure (called over-pressure), the relief valve opens more to a point where full relief occurs (maximum over-pressure). For liquid flow, spring relief valve sizing can be determined by the following equation<sup>93</sup>:

<sup>93</sup> Crowl, D.A. and Louvar, J.F. *Chemical Process Safety: Fundamentals with Applications*, 2<sup>nd</sup> ed., Prentice-Hall, Englewood Cliffs, New Jersey, 2002. p 385.

$$A = \left[ \frac{\text{in}^2 (\text{psi})^{1/2}}{38.0 \text{gpm}} \right] \frac{Q_v}{C_o K_v K_p K_b} \sqrt{\frac{(\rho / \rho_{ref})}{1.25 P_s - P_b}}$$

Where:

A is the computed relief area (in<sup>2</sup>)

( $\rho/\rho_{ref}$ ) is the spec. gravity rel. to water

$Q_v$  is the volumetric flow through the relief (gpm)  $P_s$  is the set pressure, psi

$C_o$  is the discharge coefficient  $P_b$  is the gauge back pressure, psi

$K_v$  is the viscosity correction (Fig 9-2 Ref 32.)

$K_p$  is the over-pressure correction (Fig. 9.3 Ref 32.)

$K_b$  is the back-pressure correction (Fig.9-4 Ref 32.)

This equation assumes a maximum over pressure from set pressure of 25% (1.25  $P_s$ ).  $K_p$  corrects for maximum over pressures different from 25%.

### Questions:

- A reverse-osmosis membrane unit is to be used at 25°C for a NaCl feed solution containing 1.0 kg NaCl/m<sup>3</sup>. Preliminary experiments of the membrane with a 10 cm<sup>2</sup> area showed for a feed solution containing 10 kg/m<sup>3</sup> of NaCl that the exit concentration across the membrane was 0.3 kg NaCl/m<sup>3</sup> with a measured flow rate of 2 X 10<sup>-8</sup> m<sup>3</sup>/s. This test was done at DP of 5 MPa. Feed flow rate was several orders of magnitude above the product flow rate. Determine the solvent permeability (kg solvent/s m<sup>2</sup>), and the solute permeability constant (m/s) for this membrane.
- The proposed unit in part a) will be operated in the field at a DP of 3 MPa. Calculate the water flux, solute flux and the solute rejection, R, for operation of this unit.
- The RO unit will operate at a pressure of 3 MPa gauge using a positive displacement pump with a capacity of 5 gpm. What should the set pressure be for a spring operated relief valve based on the information given in the background? Assume that the MAWP for the pump, piping, and unit is 4 MPa g.
- Using the set pressure found in part c), what is the diameter of a spring operated relief valve if  $C_o = 0.61$ ,  $K_v = 1.0$ ,  $K_p = 0.6$ , and  $K_b = 1.0$  and the back pressure is 10 psi?

## MT-23 Cross Circulation Dryers and Explosion Venting

**Mass Transfer Principle:** Drying of Process Materials

**Level:** Undergraduate Chemical Engineering (Ch. 9 Geankoplis)

**Health and Safety Concept:** Deflagation Venting for Equipment Handling Dusts (Ch. 9 Crowl & Louvar)

**Background:** The potential for dust explosions is present during milling and processing of small particle solids. Occasionally, the first small explosion leads

to a second stronger explosion because the surrounding dust is displaced into the environment during the first explosion. Control of dust explosions is handled several ways including explosion suppression and proper venting of explosions. Vent areas for low pressure structures (pressures below 1.5 psig, 10 kPa gauge) can be estimated by the following equation<sup>94</sup>:

$$A = \frac{C_{vent} A_s}{\sqrt{P}}$$

Where  $C_{vent}$  is a function of the dust explosion class, St. The higher the St rating, the more over-pressure that will occur upon an explosion<sup>95</sup>.

St Class	$C_{vent}$ (kPa <sup>1/2</sup> )	Example
St-1 dusts	0.26	Grain Dust
St-2 dusts	0.30	Organic Pigment
St-3 dusts	0.51	Fine Metal Dust

And

- $A_s$  is the internal surface area of the process vessel or the building being vented.  
 $P$  is the maximum over-pressure that can be withstood by the weakest structural element.

#### Questions:

- a) An organic-based material is processed in a through-circulation dryer as a 20 mm bed of 2-mm-diameter particles. The initial moisture content is 0.75 kg H<sub>2</sub>O/kg organic and the equilibrium moisture content is 0.02 kg H<sub>2</sub>O/kg organic. The inlet air (0.5 m/s) has a humidity of 0.03 kg H<sub>2</sub>O/kg dry air and a temperature of 120°C. If the total critical moisture content is 0.4 kg H<sub>2</sub>O/kg organic, calculate the time for the particles to dry to 0.1 kg H<sub>2</sub>O/kg organic. Take the bulk density of the bed to be 800 kg/m<sup>3</sup> and the solid density to be 1,600 kg/m<sup>3</sup>.
- b) If the dryer in part a) is 2 m long, 1 m high, and 1 m wide, estimate the proper vent size if the maximum over-pressure is 10 kPa gauge and the material is an St-2 explosive class dust.

### MT-24 Crystallization and Redundant Backup

**Mass Transfer Principle:** Crystallization

**Level:** Undergraduate Chemical Engineering (Ch. 12 Geankoplis)

**Health and Safety Concept:** Risk Assessment (Ch. 11 Crowl and Louvar)

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<sup>94</sup> Crowl, D.A. and Louvar, J.F. *Chemical Process Safety: Fundamentals with Applications*, 2<sup>nd</sup> ed., Prentice-Hall, Englewood Cliffs, New Jersey, 2002. p 407.

<sup>95</sup> See NFPA 68, "Venting of Deflagrations," NFPA, Quincy Ma for more details.

**Background:** Risk assessment includes scenario identification and consequence analysis<sup>96</sup>. Frequently, equipment reliability and combined reliabilities of redundant instrumentation is analyzed. The more a reliable a system is, the less chance of an unexpected failure. Reliabilities are often modeled by the Poisson distribution:

Reliability  $R(t) = e^{-mt}$  where  $m$  is the failure rate (faults per year) and time is in years. The failure probabilities,  $F$ , is equal to  $1-R$ . When two independent systems are involved, the reliability of the net process becomes:

$$R = 1 - \prod_{i=1}^n (1 - R_i) = 1 - \prod_{i=1}^n F_i$$

Redundant backup of key instruments can decrease failure probability significantly. It is not unusual to see two methods of measuring temperature or pressure on process equipment. On key equipment, even the most elementary of instruments may be used. For example the author has seen low pressure (vacuum) for an industrial turbine measured by an absolute pressure transducer and a mercury manometer.

**Questions:**

- a) A batch of 1,000 kg of NaCl is dissolved in sufficient water to make a saturated solution at 100°C. How much water is required for the initial saturated solution?
- b) The solution is cooled to 0°C. What weight of crystals will be obtained if no evaporation occurs?
- c) If 5% of the original water evaporated, what weight of crystals will be obtained?
- d) Compute the reliability and failure rate during a 1 year period for temperature measurement by the following instruments:  
A thermocouple  $m = 0.52$  faults per year  
An RTD,  $m = 0.32$  faults per year  
A bimetallic thermometer  $m = 0.027$  faults per year
- e) It is proposed to measure temperature on a crystallizer with a thermocouple and an RTD. What is the net reliability over a period of one year for temperature measurement by these two instruments?

**MT-25 Adsorption Modeling and Hazards Identification**

**Mass Transfer Principle:** Adsorption Isotherms

**Level:** Undergraduate Chemical Engineering (Ch 12 Geankoplis)

**Health and Safety Concept:** Hazards Identification (Ch 10 Crowl and Louvar)

**Background:** Hazard identification is an important step in the review of any

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<sup>96</sup> Crowl, D.A. and Louvar, J.F. *Chemical Process Safety: Fundamentals with Applications*, 2<sup>nd</sup> ed. Prentice-Hall, Englewood Cliffs, New Jersey, 2002. p 474.



process. There are several methods that can be followed including process hazards checklist, what-if analysis, Dow Fire and Explosion Index, hazard and operability studies, and informal safety reviews. A typical process safety checklist consists of a list of questions under the general categories of general layout, building, process piping, equipment venting, instrumentation and electrical safety equipment, and raw materials. An example is given in Fig. 10-2 of Crowl and Louvar<sup>97</sup>.

### Questions:

A wastewater solution having a volume of 5 m<sup>3</sup> contains 0.5 kg/m<sup>3</sup> of a hazardous chemical (HC). This solution is mixed thoroughly in a batch process with 5 kg of a silica aerogel adsorbent until equilibrium is reached. Equilibrium isotherm data for this system is as follows:

- a) Fit the data to Langmuir and Freundlich isotherms. Which model fits the data best?

c, kg/m <sup>3</sup> HC	0.005	0.1	0.3	0.5	1
q, (kg HC/kg Silica)	0.01	0.081	0.17	0.25	0.4

- b) Calculate the final equilibrium value and % HC removed in the above process.
- c) The MSDS for the HC in the above process has a high vapor pressure and a TLC of 1.0 ppm. The HC is non explosive but can react violently in the presence of reducing agents. The batch process has not undergone any major revision in 5 years when the process PI&D's were last updated. Review the 18 items given under "Process" in Figure 10-2 of Crowl and Louvar<sup>98</sup>. Determine which of the 18 "Does not Apply" or "Further study required" and briefly explain why for each.

## MT-26 Mixing Time and Fluid Agitation

**Mass Transfer Principle:** Mixing Time

**Level:** Undergraduate Chemical Engineering (Ch 3 Geankoplis)

**Health and Safety Concept:** Runaway Reactions and Relief Sizing (Ch 9 Crowl and Louvar)

**Background:** A major area of research in the 1980's was the development of methods to determine relief areas for systems where two phase flow can occur. Often, two phase flow will occur in relief systems attached to reactors where "runaway" reaction(s) over-pressurizes the unit. Runaway reactions are exothermic reactions that "auto-accelerate" when the rate of heat removed is less than the rate of heat generated. The temperature in the unit continues to rise at an accelerating rate until the reactants are nearly consumed or the reactor blows. Reactor agitation is important in terms of mixing and heat transfer. Loss of

<sup>97</sup> Crowl, D.A. and Louvar, J.F. *Chemical Process Safety: Fundamentals with Applications*, 2<sup>nd</sup> ed., Prentice-Hall, Englewood Cliffs, New Jersey, 2002. p 433-436.

<sup>98</sup> Ibid, p 433-437.

agitation has several times resulted in a runaway reaction and a subsequent explosion.

Equations to estimate relief areas for two phase flow are based on data acquired from the DIERS Vent Sizing Packages (VSP)<sup>99</sup>.

$$q = \frac{1}{2} C_v \left[ \left( \frac{dT}{dt} \right)_s + \left( \frac{dT}{dt} \right)_m \right]$$

$$G_T = \frac{Q_m}{A} = 0.9\psi \frac{\Delta H_V}{v_{fg}} \sqrt{\frac{g_c}{C_p T_s}}$$

$$A = \frac{m_o q}{G_T \left[ \sqrt{\frac{V}{m_o} \frac{\Delta H_V}{v_{fg}}} + \sqrt{C_p \Delta T} \right]^2}$$

Notation:

q	exothermic heat release per unit mass
$C_v$	liquid heat capacity at constant volume
$dT/dt_s$	heating rate at set pressure of relief
$dT/dt_m$	heating rate at max pressure of relief
$G_T$	mass flux through the relief
$Q_m$	is the release rate, mass/time
$\psi$	correction factor for 2 phase flashing flow
$\Delta H_V$	heat of vaporization of the fluid
$v_{fg}$	change in specific volume
$C_p$	liquid heat capacity at constant pressure
$T_s$	temperature of fluid at set pressure, absolute (K)
A	required area for the relief system
$m_o$	mass of fluid within reactor before relief
V	volume of liquid initially in the vessel
$\Delta T$	Temperature rise above set pressure

### Questions:

- a) A 6 m<sup>3</sup> reactor is used to make a polymer by mixing two monomers. The diameter of the reactor is 2 m and is filled to a height of 1 m with a mixture of monomers A and B that has a solution viscosity of 15,000 cps. If the density of the monomer mixture is 750 kg/m<sup>3</sup> and the agitator (a 0.5 m pitched blade turbine operating at 50 rpm) is placed at the center of the mixture, estimate the mixing time for this mixture.

<sup>99</sup> Crowl, D.A. and Louvar, J.F. *Chemical Process Safety: Fundamentals with Applications*, 2<sup>nd</sup> ed, Prentice-Hall, Englewood Cliffs, New Jersey, 2002. p 399, p 398.

- b) VSP data from this system determined  $dT/dt_s = 0.5$  K/s and  $dT/dt_m = 0.65$  K/s at a set temperature of  $200^\circ\text{C}$ . Determine the relief diameter required for this reactor if  $v_{fg}=0.08$  m<sup>3</sup>/kg,  $C_p=2.5$  kJ/kg K,  $\psi=0.77$ ,  $\Delta T=10$  K, and  $\Delta H_v=300$  kJ/kg.

### MT-27 Dense Gas Dispersion Models.

**Mass Transfer Principle:** Dense Gas Dispersion into the Atmosphere

**Level:** Graduate Chemical Engineering (will require reading Louvar and Louvar to complete the problem)

**Health and Safety Concept:** Consequence Analysis (Ch. 6 Louvar and Louvar)

**Background:** Release of chemicals into the environment can have important consequences. An extreme example is the disaster at Bhopal<sup>100</sup>. Both OSHA PSM (Process Safety Management) and EPA RMP (Risk Management Plan) programs require consequence analysis based on the release of a hazardous chemical. Generally, this information goes into emergency response plans that are coordinated with in-plant and outside parties who respond to emergencies. Software is available to predict the dispersion of hazardous chemicals released into the environment, and many predictive improvements have been made over the years. One improvement in dispersion modeling is the factoring in of gas buoyancy when the gas is heavier than air. When the release first occurs, this gas or vapor may have an effective density that forces it to travel along ground level for some distance before dispersing into the air currents above. Resultant concentrations will be higher than that predicted by Puff or Plume models. Thus in this situation, dense gas dispersion models are used in the consequence analysis. For the questions below, the student should consult Louvar and Louvar<sup>101</sup> for the relevant equations.

#### Questions:

- a) Using the Puff Model, predict the maximum ground level concentrations in the wind direction of a release of 40,000 kg of MIC (MW=57), exiting a stack 20 m high at points 500, 1000 and 2000 m away from the source. The release occurs on a very calm evening with ambient temperature of  $25^\circ\text{C}$  and a wind speed of 2 m/s.
- b) Using the same background information as in part a), compute the ground level concentration of MIC using Dense Gas Dispersion Models as presented in Reference 101.

### MT-28 Hazardous Waste Generation, Extraction, and Disposal

**Mass Transfer Principle:** Liquid-Liquid Extraction

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<sup>100</sup> Willey, R.J. "The Bhopal Disaster," ISBN 0-8169-0766-8 SACHE-AIChE, New York, New York, 1999.

<sup>101</sup> Louvar, J.F., Louvar, B.D., Health and Environmental Risk Analysis: Fundamentals with Applications, Prentice Hall, Upper Saddle River, NJ, 1998.

**Level:** Undergraduate or Graduate

**Health and Safety Concept:** Toxicology/Environmental

**Background:** Most chemical manufacturing operations involve the generation, use, and disposal of substances that are hazardous because of their toxicity or flammability. In many cases, the hazardous substance is a chemical that is widely used and not considered dangerous. For example, common salt is used in many processes without causing any particular problems with toxicity. However, if salt is contained in water that is discharged to streams, it may cause irreversible damage to the environment, including both plant and animal life. Thus, while salt is not a particularly hazardous material to handle and to use in processing, it must be kept out of the water that is discharged from a plant. Other substances may be much more toxic, of course, and they must be kept from the environment as well.

The nature of the substances and their effects on the environment are sometimes known quite well, but sometimes it is only known that they have a toxic effect. Sometimes the toxic effects are inferred for one materials through comparison with another similar material. For example, if we know that high concentrations of sodium chloride are toxic to certain plants in the ecosystem, we can infer that high concentrations of potassium chloride will also be toxic to the same plants. (Of course, we must keep in mind that the same substances may be required for life. Sodium and potassium salts are necessary for proper cell growth and reproduction, and potassium deficiencies in particular are encountered in nature. We frequently add potassium salts in the form of fertilizers to enhance plant growth.)

We cannot add large quantities of most substances to the ecosystem without damage. Thus, the kind and amount of materials present in water streams discharged from a plant must be closely monitored to make certain that the discharged water will be within the quality standards specified by the Environmental Protection Agency. The standards for the purity of discharged water depend on the substances in the water and the potential damage to the environment. Specific concentrations can be obtained from the Environmental Protection Agency.

The specific method used to remove hazardous substances from water depends on the nature of the hazardous substance and the concentrations involved. Several different methods can be used. The following MT-illustrates one method that might be used.<sup>102</sup>

**Question:** The water used in a chemical processing plant contains a mixture of organic acids. The acids are not particularly toxic to the environment in small concentrations, but the concentration in the process water stream is 0.5 percent by weight leaving the process, and that concentration is too high for discharge. The acids cannot be used in the plant for any other purpose, and there is insufficient acid for their recovery, purification, and sale. The acids are soluble in hydrocarbons, and it is decided to extract the acids from the water streams by countercurrent liquid-liquid extraction, then use the hydrocarbon as a fuel for one of the plant process heaters. There is no chlorine, nitrogen, or sulfur in the acids, so when they are burned with the fuel, they will not contribute any additional

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<sup>102</sup> This problem is a contribution from Dr. Reed Welker, University of Arkansas.

pollution to the air. The hydrocarbon used for the extraction is the fuel oil for process heaters. Equilibrium data for the acid-water-oil system are given in the table below. Determine how much oil will be required to reduce the concentration of acid from the 0.5 mass percent in the feed to 0.05 mass percent, which has been found to be acceptable for discharge. The oil rate used in the process will be 1.5 times the minimum, and the water to be treated will enter the extraction system at a rate of 3500 gallons per day. The oil has a specific gravity of 0.88. Assume the process is to be performed in a countercurrent liquid-liquid extractor having an overall efficiency of 20 percent. How many stages will be required for the extractor?

Mass percent in water layer			Mass percent in oil layer		
Acid	Water	Oil	Acid	Water	Oil
0.05	99.90	0.04	0.10	0.05	99.85
0.10	99.85	0.05	0.20	0.08	99.76
0.20	99.73	0.07	0.40	0.12	99.48
0.30	99.60	0.10	0.60	0.17	99.23
0.40	99.46	0.14	0.80	0.23	98.97
0.50	99.31	0.19	1.00	0.30	98.70

### MT-29 Benzene Absorption

**Mass Transfer Principles:** Equilibrium Stage Operation

**Level:** Undergraduate or Graduate

**Health and Safety Concepts:** Toxicology and Flammability

**Background:** When hazardous materials are required for chemical processing, they must be very carefully controlled to keep them from entering the environment. Hazardous materials always have one of two general properties: they are flammable or toxic. Frequently, a hazardous material is both flammable and toxic, and the toxic concentrations are usually much lower than the flammable concentrations. Toxicity may further be divided into two other general groups, one including materials that are acutely toxic and whose effects show up within a short time of exposure. Other materials have more insidious effects: their damage to health becomes known only after long exposure. A single material may exhibit both acute and chronic toxicity, depending on concentrations and effects.<sup>103</sup>

It is sometimes very hard to show that a material exhibits long term health effects. Two good examples are the artificial sweeteners saccharin and cyclamates. Saccharin is generally accepted to be carcinogenic; however, it is still used in a variety of foods and cosmetics because there is no completely acceptable alternative. Some years ago, cyclamates were widely used as artificial sweeteners; however, some evidence seemed to show that cyclamates were carcinogens, and they were banned for use in the United States. More recent data

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<sup>103</sup> This problem is a contribution from Dr. Reed Welker, University of Arkansas.

(spring of 1989) indicates that cyclamates are not the carcinogens they were once thought to be, and they may again be allowed to be used for artificial sweeteners.

It is usually much easier to determine a material's flammability characteristics because no living organism needs to be tested to find the properties. For example, the lower flammable limit (LFL) is the lowest concentration at which a vapor or gas will ignite in air. Although the LFL depends on the system temperature and to some lesser extent pressure, the most obvious need is for data at ordinary ambient conditions. Thus, defining LFL's at one atmosphere and room temperature provides sufficient data to use for estimating danger of ignition. Such properties as the amount of energy released during combustion are also easily measured. An ignition temperature is more difficult to define and measure. For many materials, an ignition temperature measured as the temperature at which a stoichiometric mixture of flammable vapor and air begins a self-sustaining exothermic reaction has been determined. It is called the auto-ignition temperature (AIT) and serves as an approximate limit for determining when ignition will occur.

In order for a fire or deflagration to occur, there must be a fuel, an oxidizer, and an ignition source such as a spark or a temperature high enough for ignition. The ignition temperature is low enough for some materials that they will ignite at ambient temperature or below when mixed. Such materials are said to be hypergolic. Even materials that ignite only at temperatures several hundred degrees above ambient are ignited by small amounts of energy, frequently less than one millijoule. Most vapor-air mixtures can be ignited by the spark from a static discharge, for example. Because of the ease of ignition and the rapid combustion reaction that ensues, substantial rules and standards have been written to define conditions for use of flammable materials. The standards of the NATIONAL FIRE PROTECTION ASSOCIATION are available in most libraries. They form the basis for many laws governing use of flammable materials.

Whether a material is toxic or flammable or both, it must be kept well confined if it is to be used in commerce. The basic process design must account for such materials and assure they are either used during the processes or destroyed so they will not harm workers or the environment. Where it is possible, recovery and recycling of chemicals is the best way of keeping them under control. If a material is recycled, it will never be discharged to become a potential pollutant.

**Questions:** Benzene is used in a process as a solvent for a solid product, and it is dried from the solid at the end of the process. Since benzene is quite flammable (its LFL is 1.3 percent) and toxic (its permissible exposure limit is 10 parts per million), nitrogen is recycled as a carrier gas during drying. Neither the nitrogen nor the benzene is ever to be released from the process. In order to recycle both the benzene (as a liquid solvent) and the nitrogen (as a carrier in the drying process), the benzene in the nitrogen is stripped out in a tray absorber. The benzene entering the absorber is at a concentration of 7.4 mole percent in nitrogen. It must be reduced to a concentration of 0.4 mole percent in nitrogen, after which the nitrogen stream will be heated and recycled to dry the product. The benzene will be absorbed in an oil having a molecular weight of 200. The oil enters the absorber at a rate of 0.5 moles of oil per mole of pure nitrogen entering the absorber. Raoult's law can be assumed to apply, and the absorber is designed to operate at 50°C (because the nitrogen-benzene stream entering is hot) and 1.0 atm. The vapor pressure of the oil is negligible, and the nitrogen can be assumed

to be insoluble in the oil. Determine the mole fraction of benzene in the liquid leaving the absorption tower and the number of ideal trays required for the process.

### **MT-30 A Methanol Spill - a Method to Control Fires**

**Mass Transfer Principle:** Flash Distillation

**Level:** Undergraduate and Graduate

**Health and Safety Concept:** Fire Protection

**Background:** Many common industrial materials will burn if they are ignited. In order for ignition to occur, three criteria must be met. There must be fuel present, there must be an oxidizer present, and there must be an ignition source. The fuel is normally a gas or vapor, but it can also be a solid. Solids are particularly dangerous if they are in small particles, or dusts. Almost all organic materials will burn, frequently explosively, if they are finely divided enough. Liquid fuels normally will have to be vaporized before they will burn, unless they are in the form of fine droplets or mists. When we see a liquid pool burning, for example, the fuel has first been vaporized and the vapor is burning. Gases can burn directly once they are mixed with the oxidizer<sup>104</sup>.

The usual oxidizer for accidental fires is the oxygen in the air. Since oxygen is nearly always available, fire prevention usually requires that the fuel is kept in containment of some kind, so that if the fuel is a gas, it will not be able to mix with air, and if the fuel is a liquid, it will not vaporize and then mix with the air. There is a minimum concentration of fuel in air that is required for ignition. It is called the lower flammable limit (LFL), and it is measured at atmospheric pressure and ambient temperature. The LFL depends on temperature, and the temperature effects can be estimated. However, unless the temperature range is large, the effect is not usually important. Pressure has only minor effects on the LFL unless the pressure change is substantial.

If a liquid is spilled, it will begin to vaporize. If the liquid is warm enough, the equilibrium concentration of vapor above the liquid surface will be at or greater than the LFL and it will be possible to ignite the liquid. Once a liquid pool is ignited, it will normally continue to burn because sufficient energy will be transferred from the flame back to the pool to vaporize additional fuel. The concentration of fuel in the vapor phase will reach the LFL at a temperature that is called the flash point. The flash point temperature is constant for any given pure fuel, but if the fuel is a mixture, the flash point will be a function of the composition of the fuel. There is also a minimum oxygen concentration (MOC) that must be available for ignition to occur. Ignition is frequently prevented by displacing the oxygen in the air above a liquid using nitrogen or carbon dioxide, for example. Some fuels are soluble in water, and it is theoretically possible to extinguish a fire burning in those fuels by diluting them with water. The reason that the fire can thus be extinguished is that the mixture of water and fuel will provide a lower vapor phase concentration of fuel than would a pool of pure fuel.

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<sup>104</sup> This MT-is a contribution from Dr. Reed Welker, University of Arkansas.

It is sometimes not possible or not desirable to extinguish a fire. In such a case, the fire would simply be allowed to burn out. Or, put another way, the fire would be extinguished when it ran out of fuel.

In the following problem we will explore some ways of looking at fires and their extinguishment by adding water or by allowing the fuel to be exhausted.

**Questions:** Methanol is a common industrial chemical. It is flammable, having a flash point of 52 °F and an LFL of 6.7 percent. (The LFL is measured as a mole percent of fuel in air). Methanol may be stored in large tanks, and the tanks will likely have a diked space around them to keep methanol from spreading in the event of a spill. Assume that methanol has spilled into such a diked area, and that it has ignited. We wish to extinguish the fire by mixing water with the methanol. If 5,000 gal of methanol has spilled, how much water must be mixed with it in order to extinguish the fire? Does this sound like a reasonable way to extinguish the fire?

Now assume that we have a mixture that originally contains 20 mole percent methanol and 80 mole percent water. If we start with 5000 gal of the solution, how much will remain when the fire goes out?

This problem can be tricky, so some help will be provided. First, the fire will go out when the concentration of methanol in air above the fuel surface falls below the LFL, subject to the constraint that the MOC is available. You can estimate the concentration by using the relationship

$$y_m = \gamma_m x_m P_m^{sat} / P \quad (1)$$

Where:

$y_m$  mole fraction methanol in the vapor phase  
 $x_m$  mole fraction methanol in the liquid phase  
 $\gamma_m$  liquid phase activity coefficient  
 $P_m^{sat}$  vapor pressure of methanol  
 $P$  system pressure

The system temperature will be the bubble point temperature, which means that for a binary system of water and methanol in equilibrium with air

$$x_m \gamma_m P_m^{sat} + x_w \gamma_w P_w^{sat} + P y_{O_2} + P y_{N_2} = P \quad (2)$$

Where:

$y_{O_2}$  mole fraction of oxygen  
 $y_{N_2}$  mole fraction of nitrogen  
 $w$  subscript for the water component  
 $m$  subscript for the methanol component

and:

$x_w$   $1 - x_m$

(3)



The temperature can be found by choosing a temperature (by trial and error) that will satisfy Equation 2. Vapor pressure data can be obtained from a number of sources. The following Antoine-type equations are good enough for our present purposes.

$$\ln(P^v/P_c) = A - B/(T + C) \quad (4)$$

Where the following constants are used:

	WATER	METHANOL
P <sub>c</sub> , psia	3206.7	1153.6
A	6.53247	7.513334
B	7173.79	6468.101
C	389.4747	396.2652

The temperature in Equation 4 is in °F. The MOC for methanol-air mixtures is 10 mole percent.

The activity coefficients can be found by an equation such as the van Laar equation or the Wilson equation, and the constants for those equations can be determined by fitting the equations to experimental vapor-liquid equilibrium data such as found in the sixth edition of PERRY'S CHEMICAL ENGINEERS' HANDBOOK.

The second part of the problem requires that a differential distillation problem must be solved. The Rayleigh method is appropriate for the problem because there is effectively one stage in the distillation process.

### MT-31 Pressure Relief for Distillation Columns

**Mass Transfer Principle:** Flash Distillation

**Level:** Undergraduate and Graduate

**Health and Safety Concept:** Pressure Relief (Ch. 9 Crowl and Louvar)

**Background:** Pressure relief devices are used in industry to remove excess energy in the case of a process upset or fire. Typical devices include pressure relief valves or rupture disks. Pressure relief valves have the advantage of closing when the pressure drops, but are more expensive than a rupture disk. Disks are more common on batch process. The exit from the pressure relief device typically goes into a header that in turn is connected to either a scrubber or flare preventing the discharge of toxic or flammable chemicals into the atmosphere. The relief device size (cross sectional area or diameter) is based upon removing the energy from the worst credible scenario. The rate of discharge is usually based upon the sonic velocity and the required energy removal rate.<sup>105</sup>

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<sup>105</sup> This problem is contributed by Prof. Chuck Sheppard, University of Tulsa, Tulsa, OK.

**Questions:**

Benzene and toluene are to be separated using distillation. The column operates slightly above atmospheric pressure. Therefore, the overhead and bottoms temperatures are around 177 and 232°F respectively. The reboiler transfers energy from 15 psig steam (~250°F). The column is equipped with a pressure relief device to remove excess energy in the case of a process upset or fire.

Consider the two cases below:

- a) If the condenser coolant is lost and a tube in the reboiler breaks, what would be the maximum pressure at the top? What determines the rate at which vapor must be removed from the column? What is the maximum cross-sectional area for flow?
- b) If the condenser coolant is lost, what is the maximum temperature that can be reached in the base of the distillation column (assuming infinite area)? If the column only contained benzene, what would be the maximum pressure at the top? Make a sketch of the reboiler duty and process temperature with time. Hint: show the steam temperature and what happens to the energy transfer rate as the driving force goes to zero.

**MT-32 Humidification for Control of Static Electricity**

**Mass Transfer Principle:** Humidification

**Level:** Undergraduate and Graduate

**Health and Safety Concept:** Static Electricity (Ch. 7 Crowl and Louvar)

**Background:** When one walks across a carpet in the winter and touches a grounded object a spark is discharged. The strength of this spark is enough to ignite a flammable atmosphere. This occurs in the winter because of the low humidity, when the humidity is high the water molecules in the air drain off the electrons gathered from the carpet. Thus maintaining water content can be an important safety consideration when there is rubbing of surfaces (e.g., flow or other transport systems)<sup>106</sup>.

**Questions:**

Nylon fibers are being moved from one machine to another over rollers. The process area is approximately 10'x10'x30'. The air is replaced by outside air 5 times per hour. The outside air is 40°F with a relative humidity of 50%. It is planned to increase the humidity via mist from nozzles to 50% at the inside temperature of 70°F Answer the questions below:

- a) Where would you locate the spray nozzles?
- b) How much air in ft<sup>3</sup> and pounds are supplied per hour?
- c) How much water do you supply an hour?
- d) What is the furnace heat load assuming no other energy losses? Where else would you lose energy; would these be significant?

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<sup>106</sup> This Problem is contributed by Prof. Chuck Sheppard, University of Tulsa, Tulsa, OK