PROBLEMS

PLANT APPLICATION PROBLEMS

The recent high number of casualties, the severe material damage, and the production losses due to fires, explosions, and other accidents have motivated all sectors of industry and responsible authorities to initiate scientific studies of fires, explosions, and other accidents. The ultimate goal of these investigations is to develop safety measures which will prevent or limit the effects of these accidents. This first problem set is therefore concerned with this topic. The principles and applications of fires, explosions, and other (plant-related) accidents are reviewed in this section.

PLANT APPLICATION 1

Flammability Limits

Introduction

The flammability limits (or explosion limits) is defined as the concentration range of a flammable gas/air mixture within which an ignition source can start a self-propagating reaction. The flammability of a gas mixture can be calculated by using Le Chatelier's Law, given the flammability of each of the gas components.

$$LFL = 1 / [(f_1/LFL_1) + (f_2/LFL_2) + \ldots\ldots\ldots + (f_n/LFL_n)]$$

$$UFL = 1 / [(f_1/UFL_1) + (f_2/UFL_2) + \ldots\ldots\ldots + (f_n/UFL_n)]$$

where: f_i = volume or mole fraction of each component
LFL = mixture lower flammability limit in volume or mole fraction
UFL = mixture upper flammability limit in volume or mole fraction
LFL_i = ith component lower flammability limit in volume or mole fraction
UFL_i = ith component upper flammability limit in volume or mole fraction.

Problem Statement and Data

Calculate the upper and lower flammability limits of a gas mixture which consists of 30 % methane, 50 % ethane, and 20 % pentane by volume. Flammability limits for a few selected compounds are given below.

Component	Lower Flammability Limit Vol %	Upper Flammability Limit Vol %
Ethane	3.5	15.1
Ethylene	2.7	34.0
Carbon monoxide	12.5	74.0
Methane	4.6	14.2
Methanol	6.4	37.0
Pentane	1.4	7.8
Propane	2.4	8.5
Toluene	1.2	7.0
Hydrogen	4.0	76.0

Solution

1. Using the equation given above, calculate the lower flammability limit of the mixture in percent.	Since the flammability data are given in percent, the volume percent of each component should be used.
2. Calculate the upper flammability limit of the mixture in percent.	Use the same equation given above.

Comment

The width of the flammability limits (the range between the lower and upper flammability limits) is a function of the following parameters:

- ignition energy,
- ignition pressure,
- ignition temperature,
- inert gas concentration, and
- relative humidity of the mixture.

The width of the flammability limits becomes wider when the ignition energy is higher, moving the UFL to a higher concentration. The higher the initial pressure at which the ignition source is activated, the wider the width of the flammability limits. The higher the temperature at the moment of ignition, the easier the reaction will propagate, making the width of the flammability limits wider. The flammability limits can also be changed significantly by changing the oxygen content or adding an inert gas to the gas/air mixture. The heat capacity of the inert or diluent gas plays a role since a diluent with a higher heat capacity acts as a better heat sink. For example, carbon dioxide is a better diluent than nitrogen because carbon dioxide has a higher heat capacity. The width of the flammability limits is wider for a drier (i.e., lower moisture content) mixture. Finally, the flash point of a flammable liquid is defined as the temperature at which the vapor pressure of the liquid is the same as the vapor pressure which corresponds to the lower flammability concentration.

PLANT APPLICATION 2

Ignition Delay Time

Introduction

The maximum spontaneous ignition temperature (SIT) or autoignition temperature (AIT) is defined as the temperature at which combustion occurs in bulk gas mixture when the temperature of a flammable gas/air mixture is uniformly raised. However, when the temperature of a flammable mixture is raised to or above the autoignition temperature, ignition is not instantaneous. There is a finite time delay before ignition takes place. The following equation can be used to correlate the time delay with the ignition temperature.

$$\ln t = k_1 (E/T) + k_2$$

where: t = time delay before ignition
k_1, k_2 = constants
E = apparent activation energy
T = absolute mixture temperature.

Problem Statement and Data

A flammable vapor flows through a 2-inch diameter insulated pipe at a flow rate of 4.5 acfm. A fire has heated a section of the pipe (4 feet long) to 150 °F, which is the above the ignition temperature of the vapor. The ignition delay time of the vapor is expressed by the equation shown below.

$$\ln t = (250/T) + 0.5$$

where: t = time delay before ignition, sec
T = absolute mixture temperature, °R.

Will ignition take place?

Solution

1. First, calculate the ignition delay time in seconds using the above equation.	Be sure to use the correct units.
2. Calculate the average residence time, t_r, of the vapor in the four feet section of the pipe.	The average residence time (t_r) can be calculated by dividing the volume (V) of the 4 feet section by the flow rate of vapor (Q).

3. Compare the residence time of the vapor in the 4 feet section of the pipe to the ignition delay time. Will ignition take place?	Ignition will not take place if the ignition delay time is greater than the average residence time of the vapor in the 4 feet section.

Yes ______
No ______

Comment

The autoignition temperature is strongly dependent on the nature of the contacting surfaces. When the surfaces are contaminated by dust, the autoignition temperature may be reduced by as much as 100 to 200 °C. There also is an ignition energy requirement for a fire to be ignited by a local source of ignition. For example, a flammable gas/air mixture can be ignited by a local ignition source only if the ignition source possesses an ignition energy greater than the minimum ignition energy. Thus, the ignition time delay correlations include the activation energy term. Ignition energy is a function of the mixture composition. The minimum ignition energy is usually observed at the stoichiometric composition of the combustible mixture.

PLANT APPLICATION 3

Kinetics

Introduction

Toxicology is the study of the effects of toxic materials on humans and animals. Important considerations in toxicology are: 1) classes of toxic substances, 2) routes of exposure, 3) dose-response relationship, and 4) factors that influence the toxicity. Classes of toxic substances include asphyxiants, irritants, allergic sensitizers, system poisons (e.g., neurotoxicants, hepatotoxicants, hemotoxicants, etc.), and carcinogens. Routes of exposure include inhalation, skin absorption, and ingestion. Dose-response relationship includes effective dose, toxic dose, and lethal dose. Factors which influence the toxicity include chemical composition, solubility of toxic agent in biological fluid, dose, concentration, duration and frequency of the exposure, age and physical conditions of the victim, and environmental factors such as temperature and humidity.

When a potentially toxic substance is introduced into the body, natural processes such as elimination (exhaling the substance as vapor) or metabolism occur to remove the substance as long as the body is not immediately overwhelmed by the toxic effect. This rate of elimination may be estimated by using first order kinetics as a first estimate. The first order kinetics model may be expressed by the following equation:

$$dC/dt = (k)(C)$$

where: dC/dt = rate of concentration change with time
C = concentration
t = time
k = first order kinetic constant.

The first order kinetic constant, k, is related to its half life by the following equation:

$$k = \ln(2)/t_{1/2}$$

where: $t_{1/2}$ = half life (time for half of substance to react or be eliminated).

Problem Statement and Data

It has been determined from laboratory testing that a human can tolerate a level of 9 mg of toxic agent Y per Kg of body weight and its half life is 3 hours in the body. Determine the maximum concentration of Y in air which a person with 65 Kg body weight can tolerate. Assume that the average breathing rate of a normal person is 45 l/min and all the toxic agent Y that is inhaled is adsorbed by the body.

Solution

1. First, determine the kinetic constant, k, from the half life data in hr^{-1}.	Use consistent units.
2. Since the rate (of reaction) is expressed in terms of the concentration, express the tolerable concentration of Y in the body as a function of the body volume.	Assume the body volume to be V_{body}. Remember that the tolerable level of Y is 9 mg/Kg and the body weight is 65 Kg. Also note that the concentration needs to be expressed as a function of V_{body} since the body density is not specified.
3. Determine the rate of concentration change or elimination rate, dC/dt in mg/volume-hr.	Since dC/dt = (k)(C) and C is expressed as a function of V_{body}, dC/dt also needs to be expressed as a function of V_{body}. See Basic Operation 12.
4. Calculate the maximum intake rate of Y required in mg/hr.	Since the body volume is 1.0 V_{body}, the intake rate can be calculated by multiplying the result of step 3 by 1.0.
5. Calculate the maximum concentration of Y in air that the body can tolerate in mg/l.	Divide the intake rate by the breathing rate. Use consistent units.

Comment

It should be noted that it is unusual that the elimination process can be expressed by first order kinetics. In reality, metabolic rates and reaction processes are not well known and the dose-response relationship must be estimated by more sophisticated methods. Median lethal dose (LD_{50}) is the dose which kills 50 percent of the animals in a test population and it is used to represent the dose fatal to an average individual. For example, LD_{50}s for ethanol, nicotine, and botulinus toxin are 10,000 mg/Kg, 1 mg/Kg, and 0.00001 mg/Kg, respectively.

PLANT APPLICATION 4

Fluid Flow

Introduction

When designing a local exhaust ventilation system for a process which generates dust particles, it is important to consider the minimum air velocity. The minimum air velocity is the velocity required to prevent settling of dust particles in the ducts. The minimum velocity is a function of dust particle size and particle density. Listed below are the minimum air velocities recommended for the transport of various types of particulate contaminants.

Type of Particulates	Examples	Recommended Velocity (ft/min)
Very fine light dust	Cotton lint, wood, flour	2000 - 2500
Dry dusts and powders	Fine rubber dust, cotton dust, light shavings	2500 - 3000
Average industrial dust, general foundry dust	Sawdust, grinding dust, limestone dust	3500 - 4000
Heavy dusts	Metal turnings, sand blast dust, lead dust	4000 - 4500
Heavy or moist dust (very heavy dust)	Lead dust with small chips, moist cement dust, quick lime dust	4500 and up

From Industrial Ventilation - A Manual of Recommended Practices, 19th Ed., ACGIH, Cincinnati, 1986.

For vapors, gases, smokes, and fumes, any economic air velocity is adequate. Typically, it is recommended to have an air cleaner before the blower or fan prior to discharge, and is definitely required prior to re-circulation.

Problem Statement and Data

An iron foundry has four work stations which are connected to a single duct. Each work station has a hood which transports 3000 acfm of air flow. The duct length is 400 feet and the pressure loss at the hood entrance is 0.5 inches of water. There also is a cyclone air cleaner which creates 3.5 inches of water pressure drop. Determine the diameter of the duct to ensure adequate transport of the dust. Also determine the power required for a combined blower/motor efficiency of 40 %.

Solution

1. Determine the minimum air velocity required for general foundry dust.	Use the high end of the range to be conservative.
2. Calculate the total air flow required in acfm.	There are four work stations.
3. Calculate required cross sectional area in ft^2.	See Basic Operation 5.
4. Calculate the duct diameter.	See Basic Operation 5.
5. In order to calculate power requirements, the pressure drop across the system needs to calculated first.	The pressure drop in a duct or pipe can be calculated by the following equation: $\Delta P_{duct} = 4\ f\ L\ V^2 \rho / 2\ g_c\ D$ where: ΔP_{duct} = pressure drop f = fanning friction factor, 0.003 for Re > 20,000 L = duct length V = gas velocity ρ = gas density D = duct diameter
a. Calculate the Reynolds number for the above duct.	See Basic Operation 6 for the Reynolds number calculation. Assume the viscosity of air to be 1.21×10^{-5} lb/ft-sec.
b. Calculate the pressure drop in the duct in lb_f/ft^2.	Make sure to use consistent units.

6. Calculate the total system pressure drop.	Be sure to use consistent units. See Basic Operation 3.
7. Calculate the power required in lb_f-ft/min and Hp.	The power required can be calculated by the following equation: $Hp = 3.03 \times 10^{-5} \Delta P \, Q_{air}/E$ where: E = combined fractional efficiency of blower and motor Hp = power, horsepower ΔP = pressure drop, lb_f/ft^2 Q_{air} = volumetric flow rate, acfm

Comment

There exists a phenomena called "drag effect" which actually reduces the pressure drop when particulates are present in the gaseous flow. The pressure drop reduction is said to occur due to the ball bearing effect of the particulates. The magnitude of pressure drop reduction is a function of particle size and particle characteristics (e.g., density). However, some researchers argue that it is an unsteady state phenomena which can not be relied on to occur consistently.

PLANT APPLICATION 5

Ventilation

Introduction

Ventilation is an important method of reducing the level of toxic air-borne contaminants in the process environment. Ventilation includes "general ventilation," and "local exhaust ventilation". General ventilation involves dilution of air and thus it is also called "dilution ventilation." Local exhaust ventilation is a method of removing contaminants before they enter the workplace air. Local ventilation is typically achieved by employing a hood which covers the specific area of contamination.

The Occupational Safety and Health Administration (OSHA) has set the permissible exposure level (PEL) of vinyl chloride (VC) at 1.0 part per million (ppm) as a maximum time weighted average (TWA) for an eight hour work day. The PEL was set at 1.0 ppm because vinyl chloride is a suspected carcinogen. If vinyl chloride escapes into the air, the concentration of vinyl chloride must be maintained at or below 1.0 ppm. The major source of VC escape into the workplace air in typical process conditions is fugitive emissions from pipe connections such as valves, flanges, and pump seals.

Problem Statement and Data

The vinyl chloride fugitive emission rate in a process was estimated to be 10 g/min by a series of bag tests conducted for the major pieces of connections (i.e., flanges and valves) and pump seals. Determine the flow rate of air necessary to maintain the PEL level of 1.0 ppm by dilution ventilation. Correct for incomplete mixing by employing a safety factor of 10. Also consider partially enclosing the process and using local exhaust ventilation. Assume that the process can be carried out in a hood with an opening of 30 inches wide by 25 inches high and the face velocity must be greater than 100 ft/min to ensure high capture efficiency. What will be the flow rate of air required for local exhaust ventilation? Which ventilation method seems better?

Solution

1. Convert the mass flow rate of the vinyl chloride to volumetric flow rate in cm^3/min and acfm.

Use the ideal gas law with R = 82.057 cm^3-atm/gmole-°K. The molecular weight of vinyl chloride is 78. See Basic Operation 4.

2. Calculate the air flow rate (in cfm) required to meet 1 ppm PEL.	1 ppm is equivalent to 1 X 10^{-6} mole or volume fraction. See Basic Operation 3.
3. Apply the safety factor to calculate the actual air flow rate for dilution ventilation.	Safety factors are often included in engineering calculations.
4. Now consider local exhaust ventilation by first calculating the face area of the hood in ft^2.	Area is given by the product of the width and height.
5. Calculate the air flow rate (in cfm) required for a face velocity of 100 ft/min.	The volumetric flow rate is obtained by multiplying the face area calculated in step 4 with the average throughput velocity (or face velocity). See Basic Operation 5.
6. Compare the flow rate of air required for dilution ventilation and local exhaust ventilation. Which method is better? Dilution ventilation ___ Local exhaust ventilation ___	Consider the cost of large blower(s) for the higher air flow rate.

Comment

Vinyl chloride is believed to be a human carcinogen which may result in liver damage upon prolonged exposure. Acute exposure may cause central nerve system depression. Typically, local exhaust ventilation is a preferred method of controlling toxic chemicals such as vinyl chloride since dilution ventilation may require multiple blowers. Most PVC plants are currently equipped with air monitoring probes located in different areas of the plant to alert personnel if more than 1 ppm level of vinyl chloride is recorded. Also, Federal vinyl chloride regulations require routine (daily) leak patrol of any equipment handling vinyl chloride to minimize fugitive emissions.

PLANT APPLICATION 6

Greenhouse Effect

Introduction

A potential major catastrophe facing mankind is that associated with the "greenhouse" effect. Carbon dioxide, as well as several other trace compounds in the atmosphere are critical in keeping the earth's surface warm enough for life to survive. In the absence of this insulating blanket, the earth's surface temperature would be approximately 30 °C lower - too frigid for any form of life to survive.

Short-wave radiation from the sun passes through CO_2 and warms the earth. The earth in turn emits this heat as infrared radiation of longer wavelengths that are absorbed by atmospheric CO_2. This retention of heat in the atmosphere, which further raises the earth's surface temperature, is called the "greenhouse" effect. The chief CO_2 source is fossil fuel combustion, which has been increasing every year and is likely to escalate in the future as the world's demand for energy grows. Thus, the rate at which this earth's bound carbon (i.e., fossil fuel) is transferred to the atmosphere by combustion and retained there is of great concern to scientists and engineers who study climate and the environmental impacts of climatic change.

A March 8, 1989, C & E News Science article titled "Deterioration of Global Environment Accelerates" provided a glimpse of catastrophes lying ahead if environmental change continues to "spiral out of control" - for example, the record drought and heat in North America (foreshadowing global warming and the greenhouse effect), more evidence of depleted atmospheric ozone, and disastrous flooding in Bangladesh. Worldwatch warns that the warming of Earth's climate - stemming from increasing levels of carbon dioxide and other "greenhouse gases" that hold heat in the lower atmosphere - would be "an environmental catastrophe on a new scale, with the potential to violently disrupt virtually every natural ecosystem and many of the structures and institutions that humanity has grown to depend on." The main sources of atmospheric CO_2, it notes, are burning of coal and other fossil fuels (adding an estimated 5.5 billion tons of carbon to the atmosphere in 1988) and large-scale destruction of tropical forests (adding 0.4 to 2.5 billion tons). Improved energy efficiency in transportation, electric appliances, lighting systems, and other areas is the most economical method, Worldwatch notes, with the largest and most immediate impact on carbon emissions and global warming. One step recommended is a global fuel efficiency standard for new cars of 50 miles a gallon by the year 2000.

Problem Statement and Data

In attempting to quantify the present and future risk associated with the "greenhouse" effect, the United States Environmental Protection Agency (USEPA) has hired Theodore-McGuinn Associates to estimate the reduction of these harful emissions to the atmosphere from automobile combustion through the use of the new gasoline additive, DurAlt FC, developed by Polar Molecular, a small technology-oriented company based in Saginaw, Michigan. EPA plans to use the results in not only their national inventory emission data bank but also in a revised meteorological study of the effect of these reductions on the "greenhouse" effect. In addition, EPA is considering mandating the use of the DurAlt FC additive in all gasoline powered vehicles. Because of the timeliness and the importance of the project, EPA has requested that both Dr. Theodore and Ms. Young McGuinn be assigned to project team. Specific information required includes the reduction of fuel usage, the mass reduction of hydrocarbon emissions to the atmosphere, the mass reduction of carbon dioxide to the atmosphere, and the consumer savings on an annual basis.

EPA has provided the following test data:

Current gasoline vehicle consumption rate = 7.1 X 10^6 barrels/day
Percent increase in gasoline economy with DurAlt FC = 4.5 %
Percent hydrocarbon emission reduction with DurAlt FC = 11 %

The following assumptions are applicable:

1. The chemical formula for gasoline is C_8H_{18}.
2. Combustion of gasoline in a standard engine is approximately 99 % complete.
3. One gallon of DurAlt FC is required to treat 1500 gallons of fuel at a cost of 1 cent/gallon of fuel.
4. The specific gravity of gasoline is 0.8.
5. The price of gasoline is 94 cents/gallon.

Solution

1. Determine the gasoline usage in gal/yr and lbmole/yr

Use approximate conversion factors. There are 42 (US) gal/barrel and 7.48 gal/ft^3. The molecular weight of the gasoline may be obtained from its chemical formula, C_8H_{18}. The specific gravity of the gasoline is specified in the **Problem Statement** section. Also see Basic Operation 1.

2. Calculate the fuel usage reduction in gal/yr with DurAlt FC additive.	The reduction on a percent basis is 4.5 %.
3. Calculate the volume of gasoline (in gal/yr) that is discharged to the atmosphere because of incomplete combustion.	The gasoline combustion efficiency is 99 %.
4. Calculate the mass of the gasoline that is discharged to the atmosphere (in lb/yr) because of incomplete combustion.	Use approximate conversion factors and note that the specific gravity of gasoline is specified.
5. Write the stoichiometric equation for the combustion of gasoline, C_8H_{18}, and oxygen, O_2.	Assume complete combustion to CO_2 and H_2O and be sure to balance the equation. Also see Basic Operation 7.
6. Using the result generated in step 2 and the reaction equation obtained in step 5, calculate the reduction of CO_2 generated in lbmole/yr and lb/yr.	Neglect the amount of gasoline that is not combusted.

7. Calculate the annual savings to the consumer through the use of DurAlt FC.	The fuel economy saving should be compared to the cost of the additive.
a. Calculate the savings due to fuel usage reduction through the use of DurAlt FC.	Refer to the result of step 2.
b. Calculate the cost of using DurAlt FC.	Refer to the result of step 1 and the cost of DurAlt FC per gallon of gasoline.
c. Calculate the annual savings.	Compare the results of 7a and 7b.

Comment

Although the EPA part of the problem has been hypothesized, the proposed scenario is not unrealistic. The reader should note that both Polar Molecular and DurAlt FC are real entities. DurAlt FC is currently marketed on a nonexclusive basis by health care and chemicals giant, Pfizer. Unlike most fuel additives which are simply single-purpose detergents or antiknock compounds, DurAlt FC is non-metallic and a true multipurpose combustion enhancer. By actually improving the efficiency of the engine's internal combustion process, DurAlt FC reduces hydrocarbon emissions, increases fuel economy and boosts performance while lowering the engine's octane requirement. Unfortunately, the product DurAlt FC has not been successfully commercialized by Polar Molecular at the time of the publication of this workbook.

PLANT APPLICATION 7

Accidental/Emergency Discharge into a Lake/Reservoir

Introduction

A major portion of our water-based recreational activities centers about the thousands of lakes, reservoirs, and other small, relatively quiescent bodies of water. In addition, these waters serve as a source of water for industrial and municipal use, including water released from reservoirs for agricultural uses, water quality control, and fisheries management. The ecosystems and quality of lakes, not only in our country but throughout the world, are of primary concern in water quality management.

Lakes and reservoirs vary from small ponds and dams to the magnificent and monumental large lakes of the world such as Lake Superior (one of the Great Lakes) and Lake Baikal in the Soviet Union (the deepest lake in the world, approximately one mile). The principal physical features of a lake are: length, depth, area (both of the water surface and of the drainage area), and volume. The relationship between the flow out of a lake or reservoir and the volume is also an important characteristic. The ratio of the volume to the flow represents the hydraulic retention time, that is, the time it would take to empty out the lake or reservoir if all inputs of water to the lake ceased.

It is often useful to describe water quality in lakes and reservoirs under the assumption that the body of water is completely mixed horizontally and vertically. This kind of assumption is similar to the one made in describing a continuously stirred tank reactor (CSTR). The completely mixed assumption can be partly justified on the basis of wind stresses on the water surface resulting in internal mixing. An assumption of this type should be recognized as a gross approximation to actual behavior since variations in concentrations of many substances will exist throughout the lake. However, this assumption permits many useful estimates to be made of the behavior of such systems since the relationships between lake inputs due to residual discharges or tributary inputs, flow through the lake, etc., and resulting concentration(s) are more easily treated analytically.

Thomann and Mueller ("Principles of Surface Water Quality Modelling and Control," Harper and Row, 1987) have provided simple, easy-to-use, equations that can be used to describe the concentrations of species in different bodies of water for (a large number of) various conditions. For the case of a steady continuous discharge of a pollutant species into a lake or reservoir undergoing an irreversible first order reaction, they have shown that the concentration of the pollutant can be described the following equation:

$$C = (m)\{1 - \exp[-((1/t_d) + k)t]\}/[Q(1 + kt_d)] \qquad (1)$$

where: C = concentration of pollutant at time t
m = mass flow rate of pollutant discharge
Q = net volume flow rate through lake or reservoir
t_d = lake retention time = V/Q
V = lake or reservoir volume
k = reaction velocity constant, $(\text{time})^{-1}$.

If the concentration is desired at a time θ following termination of the discharge, the concentration may be calculated using the following equation:

$$C = C_{eq} \exp(-[(1/t_d) + k]\,\theta) \qquad (2)$$

where: C_{eq} = equilibrium concentration achieved for the indefinite continuous discharge of pollutant.

Problem Statement and Data

A near core meltdown at a nuclear power plant brought about implementing an emergency response procedure. Part of the response plan resulted in the steady discharge of a radioactive effluent into a nearby reservoir. The mass flow rate of the discharge was 120,000 lb/hr with a radioactive waste concentration of 10^6 pico-Curies/l (PCi/l) over an eleven hour period. (One gram of radium undergoes 3.7×10^{10} nuclear disintegrations in 1 second. This number of disintegration is known as a **curie** (Ci) and it is the unit used in measuring nuclear activity). The reservoir volume and the net throughput volumetric flow rate are approximately (annual average) 3.6×10^8 ft^3 and 200 ft^3/sec, respectively. If the waste decays in a first order manner with a decay constant of 0.23 $(hr)^{-1}$, determine:

a. the equilibrium concentration associated with the steady waste discharge,
b. the maximum concentration, and
c. the time after termination of the waste discharge that the concentration will reach an acceptable level of 10 PCi/l.

Solution

1. Write the describing equation for the equilibrium concentration.	Set $t = \infty$ in Equation (1) given in the **Introduction** section of this problem.

2. Assign values to the terms in the equation given in step 1.	Assume the effluent to have the properties of water. Be dimensionally consistent. Note that $t_d = V/Q$.
3. Using the equation given in step 1, calculate the equilibrium concentration in units of PCi/ft^3 and PCi/l.	Substitute the values determined in step 2 into the equation obtained in step 1.
4. Calculate the maximum concentration that will result from the radioactive waste discharge in units of PCi/l.	Use equation (1) given in the **Introduction** section and note that the maximum radioactive waste discharge occurs at a time of 11 hours.
5. Calculate the time, θ , after the termination of the waste discharge that the concentration will reach an acceptable level.	Substitute the equilibrium concentration and the acceptable concentration into Equation (2) given in the **Introduction** section of this problem, and solve for θ .
6. Calculate the time from the start of the discharge that the concentration will reach the acceptable level.	The waste is discharged for 11 hours.
7. Discuss the limitations of Assume the effluent to have the properties of water. Be dimensionally consistent. Note that $t_d = V/Q$.	Refer to the assumptions made in the derivation of Equations (1) and (2).

Comment

Thomann and Mueller's work is an exceptably informative and well written text/reference book that is presented in clear, concise manner. A significant amount of information is provided for describing the fate of pollutant species in oceans, rivers, lakes, etc.

PLANT APPLICATION 8

Mass Transfer

Introduction

Respirators provide protection against inhaling harmful materials. Different types of respirators may be used depending on the level of protection desired. For example, supplied air respirators (e.g., a self-contained breathing apparatus) may be required in situations where the presence of highly toxic substances is known or suspected and/or in confined spaces where it is likely that toxic vapors may build up. On the other hand, a full-face or half-face air purifying respirator may be used in situations where measured air concentrations of identified substances will be reduced by the respirator below the substance's threshold limit value (TLV) and the concentration is within the service limit of the respirator (i.e., of the canister).

Air purifying respirators contain cartridges (or canisters) which contain an adsorbent, such as charcoal, to adsorb the toxic vapor and thus purify the breathing air. Different cartridges can be attached to the respirator depending on the nature of the contaminant. For example, a cartridge for particulates will contain a filter rather than charcoal. The bed of charcoal in the cartridge acts like a fixed bed adsorber and the performance of any charcoal cartridge may be evaluated by treating it as a fixed bed adsorber.

Problem Statement and Data

For a particular blend of carbon cartridge (for organic vapor), the adsorption potential for substance A can be expressed by the following equation:

$$\log_{10}(C) = -0.11\,[(T/V)\log_{10}(P_{v,A}/p)] + 2.2$$

where: C = amount of A adsorbed in charcoal, cm^3 liq/100 g charcoal

T = temperature, $^{\circ}K$

V = molar volume of A (as liquid) at the normal boiling point, 100 cm^3/gmole for substance A

$P_{v,A}$ = saturated vapor pressure of A

p = partial vapor pressure of A.

The saturated vapor pressure of substance A at 85 °C is 60 mmHg and the liquid density is 1.12 g/cm^3. The molecular weight of substance A is 110.

A respirator cartridge contains 80 g of the above blend of charcoal, and test have shown that the breakthrough will occur when 80 % of the charcoal is saturated. How long will this cartridge be effective if the ambient concentration of substance A is 700 ppm and the temperature is 85 °C? Assume that the breathing rate of a normal person is 45 l/min (or 45000 cm^3/min).

Solution

1. First, calculate the partial pressure of substance A in mm Hg.	See Basic Operation 3.
2. Determine the ratio of vapor pressures, $P_{v,A}/p$.	The saturated vapor pressure of A is 60 mm Hg.
3. Calculate the amount of A adsorbed per 100 g of charcoal.	Use the equation given the **Problem Statement**.
4. Calculate the mass of the substance A adsorbed in the cartridge (in g) at 80 % saturation (i.e., at breakthrough).	Remember that the cartridge contains 80 g of charcoal and the liquid density of A is 1.12 g/cm^3.
5. Next, calculate the volumetric flow rate of A inhaled through the cartridge from the vapor pressure and breathing rate.	Remember that the breathing rate is 45000 cm^3/min.

6. Calculate the intake mass flow rate of A.	Convert the volumetric flow rate calculated in step 5 to the mass flow rate using ideal gas law. See Basic Operation 4.
7. Calculate the time for breakthrough in minutes.	The time for breakthrough may be obtained from dividing the mass of A adsorbed at breakthrough by the intake mass flow rate calculated in step 6.

Comment

The typical economic concentration limit of organic vapor cartridges is approximately 1000 ppm. If the ambient concentration is above 1000 ppm, other methods of personal protection are recommended. It is also important to select the appropriate types of adsorbent since some toxic chemicals are not readily adsorbed by charcoal. For example, hydrogen cyanide is not well adsorbed by charcoal. Since the immediately dangerous to health and life (IDHL) level of hydrogen cyanide is 50 ppm and ordor threshold is greather than 50 ppm, by the time the worker smells the vapor, it will be too late to avoid death. Therefore, it is crucial to select a cartridge adsorbent that is specifically designed for hydrogen cyanide. Examples of such special cartridges are the cartridges for chlorine gas and pesticide vapors. Typically, cartridges are color coded so that they are easily distinguished (e.g., black for common organic vapors).

PLANT APPLICATION 9

Thermodynamics

Introduction

Knockout drums and seal drums are used in refineries and other chemical plants, usually to remove condensable vapors in process streams. They are operated at low pressures (0 to 5 psig) and may contain flammable mixtures of vapor and air. Although the chance of explosion is remote since there is usually no source of ignition, the American Petroleum Institute (API)recommends a design pressure of 50 psig. This design pressure is based on the peak explosion pressure of 7 to 8 times the operating pressure. In addition, a safety factor of 4 for this low pressure operation is recommended by the American Society of Mechanical Engineers (ASME). Therefore, a knockout drum with a design pressure of 50 psig should not rupture until the pressure is equal or greater than 200 psig.

The pressure rise due to the explosion in a knockout drum can be determined using basic thermodynamic principles. The internal energy change in the drum may be calculated by using the following equation:

$$\Delta U_{rxn} \ (\text{at } T_{in}) + \int_{T_{in}}^{T_{out}} \sum (n_i \ C_{v,i})_{out} \, dT = 0$$

where: ΔU_{rxn} = internal energy of reaction, cal/gmole
T_{in} = initial temperature, °K
T_{out} = final temperature, °K
n_i = number of moles for ith compound
$C_{v,i}$ = constant volume heat capacity for ith compound, cal/gmole-°K
i = component in flue or product gas.

This equation for a batch process is similar to the theoretical adiabatic flame temperature (TAFT) employed with flow incinerators. The internal energy of reaction is somewhat similar to and approximately given by the enthalpy of reaction (sometimes referred as the net heating value, NHV). The specific heat at constant volume conditions can be expressed by:

$$C_v = C_p - R$$

where: C_p = heat capacity at constant pressure, cal/gmole-°K
R = ideal gas law constant, cal/gmole-°K

The specific heat at constant pressure, in turn, can be expressed by the following equation:

$$C_p = a + b\,T + c\,T^2 + d\,T^3$$

where: a, b, c, d = constants
T = temperature, °K

Problem Statement and Data

Determine if the 50 psig design pressure suggested by API will contain an explosive mixture of air and n-pentane with an initial temperature of 25 °C and 5 psig initial pressure. Assume a stoichiometric concentration of pentane in air and the combustion reaction proceeds to completion. The internal energy of reaction of n-pentane at 25 °C is 777.46 kcal/gmole. The heat capacity constants (at constant pressure) are given below for the flue gas components.

	a	b	c	d
N_2	6.529	0.149×10^{-2}	-0.0227×10^{-5}	0
CO_2	5.316	1.429×10^{-2}	-0.8362×10^{-5}	1.784×10^{-9}
H_2O	6.970	0.345×10^{-2}	-0.0483×10^{-5}	0

Solution

1. First, write the combustion reaction equation for 1 mole of pentane with stoichiometric air.	See Basic Operation 7. Remember that air consists of 79 % nitrogen and 21 % oxygen.
2. Determine the number of moles initially and finally present, and the change in the number of moles.	Be sure to include nitrogen.
3. Express the constant volume heat capacity as a function of the constant pressure heat capacity.	See defining equation above.

4. Express the change in internal energy by integrating the internal energy change equation. Use the constant volume heat capacity and the number of moles.	Remember that the constant volume heat capacity is a function of T and integration should be done with respect to T. Set the integrated heat capacity as the right hand side of the equation and set the internal energy change as the left hand side side of the equation. Note that T_{in} = 298 °K.
5. Solve the equation obtained in step 5 for T_{out} by trial and error until the right hand side of the equation has the value of the internal energy of reaction at 25 ° C given previously.	Any suitable numerical method may be employed.
6. Calculate the final pressure in the vessel.	Use the ideal gas law (see Basic Operation 4). Be sure to include the effect of temperature and moles on the calculation.
7. Can the knockout drum withstand the explosion? Yes _______ No _______	Compare the final pressure to 200 psig (i.e. 50 times the safety factor of 4).

Comment

In a real application, the vessel pressure should never be very near the burst pressure. Typically, two thirds of the burst pressure is recommended as the maximum pressure which should be allowed. If the assumption that the reaction will proceed to completion does not hold, the above calculations should be performed first to determine the equilibrium concentrations for an adiabatic reaction.

PLANT APPLICATION 10

Hazard Operability Study

Introduction

A hazard operability study (HAZOP) is a very useful technique which may lead to a more reliable and safer process. Whether it is applied at preliminary design stages or to the detailed layout of an already existing plant, its benefits can be invaluable. It reduces the possibility of accidents for the process involved, improves on-stream availability of the process, can lead to a better understanding of the process and possible malfunctions, and provides training for the evaluation of any process. Finally, it is also a way of optimizing a process and providing a reliable and cost effective system.

Generally, HAZOP focuses on a major piece of equipment, although a lesser piece of equipment such as a pump or a valve may be chosen depending upon the nature of the materials being handled and the operating conditions. Once an intended operation is defined, a list of possible deviations from the intended operation is developed. The degrees of deviation from normal operation are conveyed by a set guide words, some of which are listed below.

Guide Words	Meaning	Examples
No or NOT	No part of the intention is achieved but nothing else happens.	No flow, no agitation, no reaction.
MORE/LESS	Quantitative increase(s) or decrease(s) to the intended activity.	More flow, higher pressure, lower temperature, less time.
AS WELL AS	All of the intention is achieved but some additional activity occurs.	Additional components contaminants, extra phase.
PART OF	Only part of the intention is achieved, part is not.	Component omitted, part of multiple destinations omitted.
REVERSE	The opposite of the intention occurs.	Reverse flow, reverse order of addition.
OTHER THAN	No part of the intention is achieved. Something different happens	Wrong component, start-up and shut-down problems, utility failure.

The purpose of these guide words is to develop the thought process and encourage discussion that is related to any potential deviations in the system. Upon recognizing a possible deviation, the possible causes and consequences can be determined.

Problem Statement and Data

Consider a small industrial boiler system generating low pressure saturated steam. The boiler drum receives preheated feed water that is required to maintain the water level in the drum between 30 and 40 % of its total height. There is a visual level indicator (LI) on the drum in addition to a level indicator controller (LIC) that is connected to a level indicator control valve (LICV) in the feedwater line. Natural gas fuel is fired below the boiler drum. The fuel line contains a pressure control valve (PCV) that is connected to a pressure controller (PC) located in the steam line in and leaving the drum.

Perform a HAZOP study on the system with the intention of providing the required amount of correctly treated feedwater to the boiler drum in order to maintain the prescribed water level.

Solution

1. Draw a line diagram of the system.	See Basic Operation 15.

2. Apply the first guide word NO to the system and list the deviation(s), cause(s), and consequence(s). Deviations, causes, and consequences:	Consider the cause of the loss of level in the drum and the possible explosion of the drum by flame impingement on the dry shell if the flame continues.
3. Apply the second guide word MORE to the system and list the deviation(s), cause(s), and consequence(s). Deviations, causes, and consequences:	Consider the cause of the possible excessive entrainment of steam.
4. Apply the guide word LESS to the system. Deviations, causes, and consequences:	Consider the level in the drum.
5. Apply the guide word AS WELL AS to the system. Deviations, causes, and consequences:	Consider the cause of fouling of boiler or corrosive steam.
6. Apply the guide word PART OF to the system. Deviations, causes, and consequences:	Consider the cause of fouling of boiler or corrosive steam.

7. Apply the guide word REVERSE to the system.	Consider the cause of the steam in the feedwater system.

Deviations, causes, and consequences:

8. Apply the guide word OTHER THAN to the system.	Consider the cause of the LICV failure.

Deviations, causes, and consequences:

Comment

The overall HAZOP method is summarized in the following steps:

1. Define objectives;
2. Define plant limits;
3. Appoint and train a team;
4. Obtain complete preparative work;
5. Conduct examination meetings;
    - select a manageable portion of the process;
    - review the flowsheet and operating instructions;
    - agree on how the process is intended to operate;
    - state and record the intention;
    - search for possible ways to deviate from the intention, utilizing the guide words;
    - determine possible causes for the deviation;
    - determine possible consequences of the deviation;
    - recommend action(s) to be taken;
6. Issue meeting reports; and
7. Follow up on recommendations.

After the serious hazards have been identified via a HAZOP study or some other type of qualitative approach, a quantitative examination should be performed. Hazard quantification or hazard analysis (HAZAN) involves the estimation of the expected frequencies or probabilities of events with adverse or potentially adverse consequences. It logically ties together historical occurrences, experience, and imagination. In order to analyze the sequence of events which lead to an accident or failure, event and fault trees are used to represent the possible failure sequences. Having identified the potential hazard, an analysis of the consequences can be initiated by selecting an appropriate model. This is discussed in two problems in the hazard and risk assessment section.