INTRODUCTION

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HISTORY OF INDUSTRIAL HYGIENE

Industrial hygiene is the science of protecting man's health through the control of the work environment. Man and his environment are indivisible. They react upon each other in the form of a "give-and-take" relationship. Frequently it is assumed that man moves through his environment and molds it to his desires; however, it may be more productive to think of the environment and man as moving through and changing each other simultaneously.

Historically, there was very little concern for protecting the health of the worker prior to 1900. Man's life, at the dawn of civilization, was a struggle for existence, and the mere job of survival was an occupational disease. As stratification of social classes progressed, slaves performed the common labor; and this continued until relatively recent times. The propensity of man towards war provided a fluid and steady slave supply. So disdainful was the idea of manual labor, that at one period in their culture Egyptians were prohibited by law from performing it. With this attitude of society in regard to the working man, it is no wonder there were no efforts made to control the working environment and to provide a healthful, comfortable place in which to work.

As early as the fourth century, B. C., lead toxicity in the mining industry was recognized and recorded by Hippocrates, although no concern was demonstrated for the subsequent protection of the worker. Approximately 500 years later, Pliny the Elder, a Roman scholar, made reference to the dangers inherent in dealing with zinc and sulfur, and described a bladder-derived protective mask to be used by laborers subjected to large amounts of dust or lead fumes. For the most part, however, the Romans were much more concerned with engineering and military achievements than with any type of occupational medicine.

In the second century, Galen, a Greek physician who resided in Rome, wrote voluminous theories on anatomy and pathology. Dogmatic in his writing, Galen recognized the dangers of acid mists to copper miners, but he gave no impetus to the solution of the problem.

The advent of feudalism in the Middle Ages did little to improve work standards; possibly the sole advancement of the age was the provision of assistance to ill members and their families by the feudal "guilds." Observation and experimentation flourished in the great universities of the 12th and 13th centuries, but the study of occupational diseases was virtually ignored.

Further achievements in the field of industrial hygiene were sadly lacking until the publication,

in 1473, of Ulrich Ellenbog's pamphlet on occupational diseases and his notable hygiene instruction. Hazards associated with the mining industry were effectively described in 1556 by Georgius Agricola, a German scholar. His "De Re Metallica" was translated into English in 1912 by Herbert and Lou Henry Hoover. Agricola's 12-sectioned treatment included suggestions for mine ventilation and protective masks for miners, a discussion of mining accidents and descriptions of what we refer to today as "trench foot" (effects on the extremities due to lengthy exposure to the cold water of damp mines) and silicosis (a disease of the lungs caused by inhalation of silica or quartz dust).

As late as the 16th century industrial hygiene was fraught with mysticism. For example, it was believed that demons inhabited the mines and could be controlled by fasting and prayer. Typical of the Renaissance was the alchemist, Paracelsus. For five years this Swiss doctor's son worked in a smelting plant and subsequently published his observations on the hazards of that industry. The book was laden with erroneous conclusions, such as the attribution of miners' "lung sickness" to a vapor comprised of mercury, sulfur and salt; nevertheless, his warnings about the toxicity of certain metals and outline of mercury poisoning were quite advanced.

Generally accepted as the first inclusive treatise on occupational diseases was "De Morbis Artificum" by Bernardo Ramazzini, an Italian physician. Published in 1700, this book described silicosis in pathological terms, unrefined as they were, as observed by autopsies on miners' bodies. Ramazzini outlined "cautions" which he felt would alleviate many industrial hazards, but these were for the most part ignored for centuries. "De Morbis," however, had a gargantuan effect on the future of public hygiene. The question asked by Ramazzini, which was later to be included in almost every physician's case history of a patient, was "Of what trade are you?"

The 18th century saw many notable physicians scratching the surface of the industrial hygiene problem. Sir George Baker correctly attributed "Devonshire Colic" to lead in the cider industry and was instrumental in its removal. Percival Pott, in recognizing soot as one of the causes of scrotal cancer, was a major force in the passage of the "Chimney-Sweepers Act of 1788." Both a political and medical influence, Charles Thackrah wrote a 200-page treatise dealing with occupational medicine. A farsighted scientist, Thackrah asserted that "Each master . . . has in great measure the health and happiness of his workpeople

in his power . . . let benevolence be directed to the prevention, rather than to the relief of the evils." Thomas Beddoes and Sir Humphry Davy collaborated in describing occupations which were prone to cause "phthisis" (tuberculosis). Davy also aided in the development of the miner's safety lamp.

In spite of these numerous advances, the 18th century developed few *true* safeguards for workers. It was not until the English Factory Acts of 1833 were passed that government first showed its interest in the health of the working man. These are considered the first effective legislative acts in the field of industry and required that some concern be given to the working population. However, this concern was in practice directed more toward providing compensation for accidents than controlling the causes of these accidents. Various European nations followed England's lead and developed Workmen's Compensation Acts. These laws stimulated the adoption of increased factory safety precautions and inauguration of medical service in industrial plants. A sense of "community responsibility" was evolving, epitomized by the interest of newspapers and magazines in the control of the environment. For example, the London Illustrated News, one of the most popular publications of the 19th century, affixed the blame in a mine explosion to negligence in proper gas-testing methods. The same article made a point of the fact that no safety lamps had been provided. In 1878, the last of the English "factory acts" centralized the inspection of factories by creating a post for this purpose in London.

The United States had an early 20th century champion of the cause of social responsibility for workers' health and welfare in the person of Alice Hamilton, a physician. She presented substantiated evidence of a relationship between illness and exposure to toxins; she went further by proposing concrete solutions to the problems. This was the start of an "Occupational Medicine Renaissance." Public awareness was becoming acute and legislation was being passed. In 1908 the federal government passed a compensation act for certain civil employees, and in 1911 the first state compensation laws were passed; by 1948 all the states had passed such legislation.

These Workmen's Compensation Laws were important factors in the development of industrial hygiene in the United States, as it became more profitable to control the environment than to pay for the compensation.

The U. S. Public Health Service has been a world leader in evaluating diseases of the working man and development of controls, as well as fostering an interest in occupational diseases by various state agencies, universities, management and unions. The U. S. Public Health Service and the U. S. Bureau of Mines were the first federal agencies to conduct exploratory studies in the mining and steel industries, and these were undertaken as early as 1910. The first state industrial hygiene programs were established in 1913 in the New York Department of Labor and by the Ohio Department of Health (see Chapter 49).

One of the earliest attempts made to link the industrial environment with a specific disease was the exploration of the high incidence of tuberculosis among garment workers. Given needed authority in 1912 by Presidential action, the Public Health Service embarked upon investigations in many industries and backed up their findings with concrete, workable solutions.

By 1933 federal employee health service was offered by the Tennessee Valley Authority, followed by the Army, Navy, Air Force and Atomic Energy Commission less than ten years later. The great depression of the 1930's had gone far to convince the federal government of a real need for intervention in the economy and welfare of American life. On an even larger scale, the creation of international bodies, such as the International Labor Organization and the World Health Organization, has given the world common goals for which to strive. Through studies and consulting services these organizations share the magnitude of the problem. They realize that technical advances necessarily have disadvantages as well as advantages, particularly in the field of industrial hygiene. For example, as the development of atomic energy progresses, a radiation hazard exists which was heretofore unknown.

RECENT DEVELOPMENTS

Today we view occupational medicine in an entirely new light. A tenet of our modern society is that every worker has the right to the fulfillment of his spiritual and material needs, while at the same time enjoying freedom from fear of trauma and disease. Our emphasis has shifted from correctional to preventive industrial hygiene, and occupational medicine has now become an integral part of medical education. The rapid advancement in automation provides a tremendous challenge in the field of environmental control.

Although the United States has moved more rapidly than any other nation in the world in ferreting out diseases of the work force and developing control measures, the ever increasing desire of our society for an acceleration in elimination of diseases caused by the environment, and specifically the work environment, has demanded a far greater effort than what has been shown in the past. Congress has reacted to these social demands by passing three major pieces of legislation:

1. The Metal and Nonmetallic Mine Safety Act of 1966. Health and safety standards for metal and nonmetallic mines are spelled out in this Act. A Review Board (The Federal Metal and Nonmetallic Mine Safety Board of Review) is created, consisting of five members, appointed by the President, with the advice and consent of the Senate. Groundwork is laid for the creation of advisory committees to assist the Secretary of the Interior; these committees are expected to include an equal number of persons qualified by experience and affiliation to present the viewpoint of operators of such mines, and of persons similarly qualified to present the viewpoint of workers in these mines, as well as one or more representatives of mine inspection or

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safety agencies of the state. The Act also provides for mandatory reporting (at least annually) of all accidents, injuries and occupational diseases of the mines; and expanded programs are developed for the education of personnel in the recognition, avoidance and prevention of accidents or unsafe or unhealthful working conditions. Finally, this Act promotes sound and effective coordination between federal and state governments in mine inspection procedures. Major deficiencies of this Act included the fact that no health representatives were provided on Advisory Committees, nor was there a provision for research in mine safety or miner health.

2. The Federal Coal Mine Health and Safety Act of 1969. This Act attempts to attain the highest degree of health protection for the miner. It delineates mandatory health standards and provides for the creation of an Advisory Committee to study mine problems. Additional authority is given, through this Act, to the federal government to withdraw miners from any mine which is found to be in danger, and prohibits re-entry into any such mine. The Act itself reads, to "provide, to the greatest extent possible, that the working conditions in each underground coal mine are sufficiently free of respirable dust concentrations in the mine atmosphere to permit each miner the opportunity to work underground during the period of his entire adult working life without incurring any disability from pneumoconiosis or any other occupation-related disease during or at the end of such period." This is accomplished by the control of dust standards and respiratory equipment; the development of rules for roof support, proper ventilation, grounding of trailing cables, distribution of underground high-voltage and a provision for mandatory medical examinations for the miners at fixed intervals.

3. Occupational Safety and Health Act of 1970. The declared Congressional purpose of the Occupational Safety and Health Act of 1970 is to "assure so far as possible every working man and woman in the nation safe and healthful working conditions and to preserve our human resources." Under its terms, the federal government is authorized to develop and set mandatory occupational safety and health standards applicable to any business affecting interstate commerce. The responsibility for promulgating and enforcing occupational safety and health standards rests with the Department of Labor; the Department of Health, Education and Welfare is responsible for conducting research on which new standards can be based and for implementing education and training programs for producing an adequate supply of manpower to carry out the purposes of the Act.

The latter's responsibilities are carried out by the National Institute for Occupational Safety and Health. Among the functions which may be carried out by the Institute is the one which calls for prescribing of regulations requiring employers to measure, record and make reports on the exposure of employees to potentially toxic substances or harmful physical agents which might endanger their safety and health. Employers required to do so may receive full financial or other assistance for the purpose of defraying any additional expense to be incurred. Also authorized are programs for medical examinations and tests as may be necessary to determine, for the purposes of research, the incidence of occupational illness and the susceptibility of employees to such illnesses. These examinations may also be at government expense. Another HEW function is annual publication of a list of all known toxic substances and the concentration at which toxicity is known to occur. There will also be published industrywide studies on chronic or low-level exposure to a broad variety of industrial materials, processes and stresses on the potential for illness, disease or loss of functional capacity in aging adults; also authorized at the written request of any employer or authorized representatives of employees, is determination by HEW as to whether any substance normally found in the place of employment has potentially toxic effects. Such determinations shall be submitted to both the employer and the affected employee as soon as possible. Information obtained by the Department of Health, Education and Welfare and the Department of Labor under the research provisions of the Act is to be disseminated to employers, employees and organizations thereof.

Space does not permit a detailed discussion of each of these pieces of legislation, but they are required reading for any student interested in industrial hygiene.

SCOPE & FUNCTION OF INDUSTRIAL HYGIENE

Definition of the Profession

Industrial hygiene is both a science and an art. It encompasses the total realm of control, including recognition and evaluation of those factors of environment emanating from the place of work which may cause illness, lack of well being or discomfort either among workers or among the community as a whole.

Definition of the Professional

The industrial hygienist is a competent, qualified individual educated in engineering, chemistry, physics, medicine or a related biological science. His abilities may encompass three major areas: (1) recognition of the interrelation of environment and industry; (2) evaluation of the impair-

ment of health and well-being by work and the work operations; and (3) the formulation of recommendations for alleviation of such problems.

Scope

The scope of industrial hygiene is threefold. It begins with the recognition of health problems created within the industrial atmosphere. Some of the more frequently encountered causes of these problems are: chemical causes (liquid, dust, fume, mist, vapor or gas); physical energy (electromagnetic and ionizing radiations); noise, vibration and exceedingly great temperature and pressure extremes; biological (in the form of insects, mites, molds, yeasts, fungi, bacteria and viruses) and ergonomic (monotony, repetitive motion, anxiety and fatigue, etc.). These stresses must all be evaluated in terms of their danger to life and health as well as their influence on the natural bodily functions.

The second heading encompassed within the scope of industrial hygiene is that of *evaluation*. The "work atmosphere" must be evaluated in terms of long-range as well as short-range effects on health. This can be accomplished by a compilation of knowledge, experience and quantitative data.

Finally, industrial hygiene includes the *development* of *corrective measures* in order to eliminate existing problems. Many times these control procedures will include: a reduction of the number of persons exposed to a problem; the replacement of harmful or toxic materials with less dangerous ones; changing of work processes to eliminate or minimize worker exposure; adoption of new ventilation procedures; increasing distance and time between exposures to radiation; introduction of water in order to reduce dust emissions in such fields as mining; "good housekeeping," including clean toilet facilities and adequate methods of disposing of wastes; and the provision of proper protective working attire.

Function

A unique field, industrial hygiene employs the chemist, physicist, engineer, mathematician and physician in order to adequately fulfill the responsibilities inherent in the profession, which include:

1. Examination of the industrial environment;
2. Interpretation of the gathered data from studies made in the industrial environment;
3. Preparation of control measures and proper implementation of these control measures;
4. Creation of regulatory standards for work conditions;
5. Presentation of competent, meaningful testimony, when called upon to do so by boards, commissions, agencies, courts or investigative bodies;
6. Preparation of adequate warnings and precautions where dangers exist;
7. Education of the working community in the field of industrial hygiene; and
8. Conduct of epidemiologic studies to uncover the presence of occupation-related illness.

WHERE ARE THE NEEDS?

There are approximately 4,000 industrial hygienists in the United States. These dedicated scientists often undergo periods of deep frustration as they attempt to coordinate facts and arrive at workable solutions. The realization that time is of the essence in dealing with potential health hazards makes the industrial hygienist keenly aware of his great responsibilities. An alert response by an astute industrial hygienist could save the lives and health of many workers. A true statesman, the good industrial hygienist learns to temper his findings and conclusions with patience; for he knows that oftentimes employers will not be receptive to the tremendous cash outlays necessary to implement a good industrial hygiene program.

Currently, industrial hygienists are employed by industry, federal, state and local governments, universities, insurance companies and unions. Many large industries have staffs of ten or more people. Other industries, depending upon their organization, will have only one industrial hygienist at the corporate office and trained technicians in each of the company's plants. Small industries (less than 5000 employees) unless they have highly specialized problems, have not found the need to employ a full-time industrial hygienist. These companies either use the services available to them from government agencies or retain industrial hygiene consultants.

A number of excellent universities offer a Master's degree in industrial hygiene. Harvard, the first university to confer this degree, started their program in *1918*. Since they pioneered such a program 55 years ago, there are at least eight more universities offering graduate programs in industrial hygiene leading to a Master's or Doctorate degree. Their names, as well as information on grants and scholarships can be obtained from the National Institute of Occupational Safety and Health, Rockville, Maryland. With the advent of new federal laws protecting the health of the worker, the need for professional industrial hygienists and technicians will increase dramatically in the 1970's. Those companies which currently do not have need for an industrial hygienist will hire at least one as a result of the recently enacted legislation. Companies which had a small staff will find it to their advantage to increase their capabilities and provide more comprehensive service than they did in the past.

There are only two or three cities in the United States which currently have comprehensive industrial hygiene programs. Other cities will find that protecting the health of the worker is a solid investment and consequently will develop programs. There are not more than ten states in the United States providing comprehensive industrial hygiene programs. Just as with industries, the states will need a large number of industrial hygienists in the 1970's to fulfill the requirements of the Occupational Safety and Health Act. Additional funding by the federal government will spur the development of such programs. Unions have begun to realize the benefits of employing a full-time

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professional industrial hygienist on their staffs. Presently at least three industrial hygienists are employed by unions. This trend will continue with increased awareness of the union officials of the benefits accruing to the workers through sound industrial hygiene programs.

CONTENTS AND OBJECTIVES OF THE SYLLABUS

The chapters which follow are written by persons of outstanding reputation in the particular field covered by his (her) chapter. A group of distinguished professionals has been selected from various types of industries, from universities, consulting groups and government, from the east to the west coast, all having the desire of providing a manuscript sufficiently comprehensive that it will encompass the entire environmental field, including subjects not commonly considered part of industrial hygiene; i.e., water pollution, safety and solid waste.

Our objectives have been:

1. To compile into one source the diversity of expertise needed to attain competency in the recognition, evaluation and prescription of methods of control of environmental problems.

2. For the use of persons having a basic science degree who are entering the field of industrial hygiene and environmental control, provide a manual which will furnish them with the broad scope of knowledge required for an intelligent approach to the diversity of problems encountered in this field.

3. To make available a tool which may be used as a text in training courses or in universities to introduce graduate students to the field of industrial hygiene and environmental health.

4. To introduce persons having a specialty in one of the facets of industrial hygiene or environmental health to all *other* facets of this profession.

It is our aim to reach the beginners in the profession, whether in government, industry, research or universities; the graduate students entering the profession from cognate fields and persons having a specialty who need a "refresher" in the related fields.

The world in which we live is so complex, we believe that any individual truly interested in one facet of the environment should be, at the least, somewhat knowledgeable in the various categories of environmental control methods.

THE SIGNIFICANCE OF THE OCCUPATIONAL ENVIRONMENT AS A PART OF THE TOTAL ECOLOGICAL SYSTEM

Don D. Irish, Ph.D.

OCCUPATIONAL AREA IS PART OF THE WHOLE

The occupational ecological system is a significant part of the total ecological system. Since it can be measured, we can exert some control over it and make contributions to the health and well-being of the people in the occupational ecological system. These contributions can favorably affect the impact of the total system on our population since a worker may spend one-fourth of his time in the occupational area, and workers are a significant part of the total population.

The purpose of this chapter is to examine the relation of the occupational environment to the total ecological system, to observe the significance of this relationship to the work of the industrial hygienist, and to recognize the favorable effect that his work in the occupational environment could have on the total system.

Nonoccupational exposure is an exceedingly complex and variable factor. Recognition of such exposure is necessary to an understanding of the overall environmental impact on man. The man who drove to work in heavy traffic or walked down a busy street received much greater exposure to carbon monoxide from automobile exhaust than he would have in an acceptable work area. Similarly, a worker who smokes one pack or more of cigarettes per day will be exposed to many times the amount of carbon monoxide that he would be exposed to in an acceptable work environment. This smoker would also be exposed to many times the amount of particulate matter from his smoking than he would contact in an acceptable work area.

There are many other nonoccupational exposures but these examples serve to illustrate two obvious areas of excessive exposure in the nonoccupational area. Such exposures cannot be ignored by those responsible for the health and well-being of people even if their responsibility is primarily in the occupational area.

OCCUPATIONAL INTERACTION WITH NONOCCUPATIONAL

In considering the occupational area one must recognize the interaction with the nonoccupational area and the significance of this interaction to the health and well-being of the individual.

We learned a long time ago that a man who drinks a lot of alcoholic beverages is much more susceptible to injury from exposure to carbon tetrachloride; also, that a man with excessive exposure to silica dust is more susceptible to tuberculosis. Such possible interactions should be kept in mind.

The following illustration demonstrates a different kind of interaction. We were studying the blood bromide concentration of men exposed to low concentrations of methyl bromide in their work. The environmental exposure in their operating area was carefully measured. The exposure was well within acceptable limits. Clinical studies verified this fact. It was valuable to establish a relationship between exposure and blood bromide at exposures within acceptable limits, as this would be useful in the future as a clinical check on the workmen.

One day a workman from this group was found to have a blood bromide concentration sufficiently high to be of concern if it had come from exposure to methyl bromide. Investigation revealed that he had been taking inorganic bromide medication which accounted for the high blood bromide.

Workmen may be brought to the clinic for regular preventive checkups. Biochemical measurements on these workmen may be exceedingly valuable to verify acceptable exposure, also to catch any indication of fluctuations in operating conditions and allow correction before significant exposure can occur. This is a very useful system, but we must be sure we have all the facts before we conclude what caused any observable biochemical changes.

THE INDIVIDUAL AS PART OF THE ECOLOGICAL SYSTEM

Ecology is defined in Webster's dictionary (1971) as "The science of the totality or pattern of relations between organisms and their environment." I prefer to call ecology the science of the interaction of *everything* with *everything else*. The ecological system is the system within which these interactions take place.

The ecological system is not exactly synonymous with the environment. My environment includes everything around me. The ecological system *includes* me. The individual person is a highly significant factor in the control of the environment in the interest of the health and well-being of the person.

A freight elevator was installed with all the usual safety devices. It was approved by state inspectors. A switch on the door made it necessary to close the door before the hand switch would operate the elevator. A tall lanky lad found that he could get his toe to operate the switch closed by the elevator door, and with contortion he could

still reach the operating switch. It would have been easier to close the front door, but it was a challenge. He was that rarity, a man with the reach to do it. No one knows how many times he operated the elevator this way, but one day he left his other foot over the edge of the elevator and seriously injured that foot when the elevator passed the next floor. Yes, fools can be very ingenious in overcoming "foolproof" engineering.

Misoperational problems are not limited to mechanical injury. There was the individual who liked a window wide open. Under certain wind conditions the air from the window blew across the face of a hood so as to allow volatile chemicals to escape from the face of the hood into the work area around the hood.

There was also the man who liked to "sniff" perchloroethylene. He arranged his work so that he could be "high" on perchloroethylene a large part of his work day.

The individual is a significant part of the occupational ecological system. His understanding and cooperation are essential to attaining a healthful work environment. We hope this understanding will carry over to some degree to the nonoccupational ecological system.

PEOPLE IN THE ENVIRONMENT

An important factor in the environment of an individual is "people." People in both the occupational and the nonoccupational environments are of significance to the health and well-being of that individual.

One day the psychologist in our personnel department asked me if we were having any complaints of noise from a certain operation. I told him we were, but we could find no justification for the complaints based on noise measurements made in the area. He commented, "You won't; the workers just don't like the foreman."

In another instance we found it desirable to coordinate a careful study of the environment with a concurrent clinical study of the workmen in the area. One group of older, experienced workmen refused to cooperate. They liked the foreman and their work and were afraid we might make some changes. With friendly understanding, the purpose was explained and they were reassured. You are always dealing with people in the occupational environment.

Another illustration introduces a different problem. Joe came into the clinic with a mashed thumb. The physician tried to get an understanding of the reason for the accident. He asked, "What happened, Joe?" "Oh, I got my thumb in between a couple of drums." "You have a good record, Joe, why did this occur?" "I was thinkin'." "What were you thinking about, Joe?" "Oh, I was thinkin' about my wife's sister." Knowing that health or financial problems in the family may worry people, the physician asked, "What's wrong with your wife's sister?" Joe answered with ecstatic fervor, "Doc, there just *ain't nothin' wrong* with my wife's sister."

We should recognize that people in the *nonoccupational* environment may have an effect which may result in misoperation. Such misopera-tion can lead to exposure to chemical substances, physical energies, or mechanical injury. This can occur either on or off the job.

The problem of people in the environment is not measured by any analytical instrument, though the instrument may measure a misoperation caused by people. The problem of people is not controlled by preventive engineering alone, though it can help. Effective operation requires a good understanding of people and the ability to get their understanding and cooperation. This is an obligation of the industrial hygienist, the physician and other persons responsible for control of the environment in the interest of the health and well-being of the workmen.

CHEMICALS, ENERGIES AND ORGANISMS

The usual considerations in the occupational environment are more measurable than people. Chemical substances are a concern of the industrial hygienist. Physical energies include: ionizing radiation, a concern of the health physicist; heat, light and noise, a concern of the industrial hygienist; and mechanical injury, a concern of the safety engineer. Then there are biological organisms (other than man) which are a concern of the sanitary engineer.

These are part of the environment both on and off the job. These can be controlled in the occupational environment by good engineering and good operating procedures attained with the understanding and cooperation of the employees. Yes, people are also very important here.

We observed that men from a specific operation were reporting to the clinic with mild complaints which seemed similar to complaints that would be expected from an over-exposure to a solvent used in the operation. Careful analysis by the industrial hygienist, in many locations and at many different times, did not show enough solvent in the air to cause the trouble. A continuous recording analytical instrument was devised in the research laboratory and installed in the operating area. Through its use we found that when either the supervisor or the industrial hygienist was not around, the operator was inclined to leave a leak or spill to be cleaned up by the next shift operator. The men named this instrument the "Squealer" as it was telling us of their misoperation. They began to work with an eye on the recorder. They realized that when the "Squealer" did not squeal they felt better. They changed the name of the instrument to the "Stink clock." The supervisor told us he saved the price of the instrument by reduced solvent loss, and that the overall operation by the men greatly improved. We had their understanding and their cooperation. They realized that we were interested in their health and well-being.

During regular preventive observation of the men in the clinic, lack of adverse effects may show that exposures to chemical substances in the environment have not been excessive. It should not be taken to mean that excessive exposures are impossible or unlikely under other circumstances of use.

For example, a supplier assured his customer that there was no hazard from skin contact asso-

ciated with a particular material because there had been frequent skin contacts with the material in their own operations with no adverse effects. They neglected to indicate how they handled the material, or that contacts were always followed by immediate decontamination of the skin. In use by the customer, the material was spilled on a man's skin. He was several miles out in the "bush" in northern Canada in the winter with the temperature below zero Fahrenheit, and with no water available for decontamination. The man died from poisoning due to skin absorption of the material. Simple experiments on animals in the toxicological laboratory showed that the material was very toxic when absorbed through the skin. When a supplier indicates that no problems have been encountered in handling a particular material, ask how they handle it. Ask them what toxicological information they have on the material.

In controlling the occupational environment in the interest of health and well-being, established acceptable exposure limits for a healthful environment are very useful. These acceptable exposures are expressed as "acceptable concentrations" by the American National Standards Institute and as "threshold limit values" by the American Conference of Governmental Hygienists (such standards are discussed in detail in Chapter 8). These limits are not exacting scientific thresholds of response. They are the judgments of people with knowledge and experience. The intelligent use of these limits depends on the understanding and judgment of the man who must control the occupational environment.

We must recognize that the industrial hygienist usually deals with a variable exposure. Enough analyses are needed to clearly define the probable fluctuations and to establish a significant time weighted average. Maximum concentrations must be determined as well as duration and frequency of peaks of exposure. The summation of this information to define the exposure situation requires the good judgment of a knowledgeable industrial hygienist. The application of the established acceptable limits for a healthful environment also requires the good judgment of a knowledgeable industrial hygienist. Acceptable limits cannot be used effectively as just a routine check point.

Those people responsible for suggesting acceptable limits or for using acceptable limits are part of the ecological system — the industrial hygienist, the physician, the toxicologist and all the other environmental control people. The effectiveness of their operation can have a very significant effect on the occupational ecological system.

When an injury does occur, clinical observation of the victim can provide very valuable information and should be reported in the literature. As was discussed in the previous section, the exposure can be variable. Most important, be sure you know all of the chemical substances or physical energies to which the victim was exposed and, hopefully, quantitation of exposure.

During the early development of 2,4 dichlorophenoxy acetic acid (2,4 D), careful toxicological studies were made on animals in the toxicological laboratory. It was concluded that the material at the high dilution used in the field as a weedkiller was not a significant hazard. After years of use there was a report of a death in Canada from 2,4 D. The man drank a glass full of the diluted solution from the spray tank with suicidal intent. The physician who observed the man in the clinic and the manager of the contract spray company where the solution had been mixed, both confirmed that it was, in fact, 2,4 D. Calculating from the toxicological information, I did not think this was possible. An agricultural scientist was going to visit the area where this death occurred so I asked him to investigate. He asked the foreman of the spray crew, "What did you use as a weedkiller before you used 2,4 D?" "Oh, we used sodium arsenite." "Then you stopped using sodium arsenite?" "No, we just added 2,4 D to the sodium arsenite."

The man who died had drunk enough sodium arsenite to have killed ten people. When you draw a conclusion from that first clinical case, be sure you know all of the materials to which the victim was exposed. This serves as a reminder that people are involved, people between you and the actual circumstances of the incident.

As previously stated valuable information on the nature and amount of exposure can be obtained by biochemical measurements on a person suspected of exposure. This depends on the absorption, transport, metabolism and excretion of the material. Blood, urine or exhaled air analysis can give valuable clues to the nature of certain of the materials to which the person was exposed. The analysis used depends on the way the body handles the material in question. Many volatile organic materials are exhaled in the breath. Infrared analysis can give an indication of the nature of the material and some indication of the amount of exposure.

To illustrate, a man came into the clinic and reported that he had been exposed to a certain volatile solvent. Infrared analysis of his exhaled air showed that he had not been exposed to the solvent he indicated but to a very different solvent. Had the clinic proceeded on the basis of his report of exposure, the handling of the case would have been in error. Some biochemical measurements can be very useful when wisely used.

COMPLEXITY OF THE WHOLE

The ecological picture as a whole is too complex to understand or to control when considered in its entirety (both occupational and nonoccupational). Yet, those who are responsible for the health and well-being of people in the system must keep the total picture in mind.

That total picture includes the chemical substances, physical energies and biological organisms in the occupational area which we can measure and over which we can have some control. As previously discussed, the exposures can be variable. Levels of concentration alone are not enough. One must know the frequency and duration of exposures. There is no simple mathematical procedure which will give a specific numerical answer. One can determine the time weighted average and the maximum concentration, duration and fre-

quency of peak concentrations. These are meaningful if one has sufficient analytical data which represent the actual exposure conditions. These exposure conditions can then be related to the acceptable limits proposed by various organizations. This comparison gives some understanding of the significance of possible exposures in the area studied. In addition, however, one must keep in mind the complexity of the whole. The final decision requires judgment of the whole based on available knowledge and experience.

Comparable factors are in the nonoccupational area where we have little control. Hopefully, we may have some effect by carry-over of experience from the occupational area. In both the occupational and nonoccupational area the individual is an important factor. The people in the environment of the individual both on and off the job have a significant effect.

OBTAINING UNDERSTANDING AND COOPERATION

Obtaining the understanding and cooperation of people in the environment of concern is critical to effective control of that environment. This statement has been made several times in this chapter. It was a significant factor in many of the illustrations used. This is such an important part of effective control that it justifies summation here for emphasis. Without understanding and cooperation all the most careful measurements and careful engineering of an operation may be ineffective. We repeat — fools are most ingenious in overcoming "foolproof" engineering.

It is simple to state "Get their understanding and cooperation." *Getting* it is not always that simple. How does one get it? The method will vary with the industrial hygienist and with the people in the operation of concern. The following methods are suggested as having been successful under many circumstances. What you will do depends on your judgment of the particular circumstances with which you are concerned at a particular time and the people with whom you are concerned.

Previous mention was made of the value of a careful environmental survey and concurrent clinical study of the men involved as a preventive control. Before such a study is made, it is valuable to get all the men in the operation together. A regular safety meeting can be used; it should include all the people — supervisors as well as laborers. Explain what is intended and why. Invite questions from the group. Answers and explanations should be in simple, direct language which they can understand.

During the survey of the environment, the workers' interest and understanding may be helpful. You can obtain a lot of information on the operation from the individual workmen. When the survey is complete, it should be reported to the whole group. Tell them basically what was found, in language they can understand. Indicate what should be done, if anything, to assure a good work environment. When they understand that you have a sincere interest in the workers' health and well-being, it increases their cooperation in effectively controlling the operation.

When you are checking the environment of an operation, talk with the individual workmen. Ask them for information and suggestions. Including them in control efforts will result in more effective cooperation. Take every opportunity to inform all the people who may be concerned with your area of operation. Discussion at safety meetings is useful in getting information to a group. Also look for a chance for discussion with individuals, — all individuals — executives, supervisors, engineers, operators, janitors.

You should also be concerned with the design of a new production unit. Your cooperation with the engineers in design and construction can aid in giving consideration to control of the evironment. Inclusion of good environmental control principles in the design and in the construction of a new production unit is essential. It can save a lot of reconstruction later. It also can make the control of the environment in the interest of health and well-being a much more effective operation.

When talking with groups at a safety meeting or with individual workmen, take every opportunity to discuss also the application of their understanding of healthful working conditions to their off-the-job activities. Through the understanding and cooperation of the employees, we may also have a significantly favorable effect on the nonoccupational ecological system as well as the occupational; hopefully, some of the "understanding" will be carried over by the workmen to their off-the-job activities.

PRACTICAL CONTROL

Yes, the total picture is complex, yet there are a lot of practical things that can be done. We can measure the chemical substances, physical energies and biological organisms in the occupational environment. We can control them through good engineering and good operation. We can and must obtain the understanding and cooperation of the employee in order that our environmental control may be effective. We can compare our findings with the acceptable limits suggested by various groups. With an understanding of the basis of these limits and the significance of our findings, we can judge the effectiveness of our control. We must recognize the possible impact of both occupational and nonoccupational factors.

The most effective use of our present knowledge should be made. We need to make an effort to increase that knowledge through toxicological, environmental and clinical research. We should recognize the complexity of the whole ecological system. This complexity should not discourage us from the effective application of the good practical knowledge which is available. With the practical application of all the factors discussed and the understanding and cooperation of the workers, our efforts can have a very favorable effect on health and well-being.

REVIEW OF MATHEMATICS

Janet L. Patteeuw

INTRODUCTION

The mathematics required in the practice of industrial hygiene is that usually included in mathematics courses which precede the calculus and includes an introduction to statistics. It assumes, as a minimum, a previous acquaintance with elementary algebra and plane geometry at the high school level.

COMPUTATION

Laws of Exponents

Exponents provide a shorthand method of writing the product of several like factors. If b is any number and n is a positive integer, the product of n of the quantities b is denoted by b^n. Symbolically,

$$b \cdot b \cdots b = b^n,$$

where n is the exponent, b is the base, and b^n is read "b to the nth power." This definition can be extended to include exponents other than positive integers. If n and m are positive integers, the following properties hold:

$$b^0 = 1 \quad \text{if } b \neq 0$$

$$b^{-n} = \frac{1}{b^n}$$

$$b^{n/m} = \sqrt[m]{b^n} = \left(\sqrt[m]{b}\right)^n.$$

The theorems on exponents follow easily from the preceding definitions:

(1) $b^m \cdot b^n = b^{m+n}$

(2) $\dfrac{b^m}{b^n} = b^{m-n}$

(3) $(b^m)^n = b^{m \cdot n}$

(4) $(ab)^n = a^n \cdot b^n$

(5) $\left(\dfrac{a}{b}\right)^n = \dfrac{a^n}{b^n}.$

Scientific Notation

Very large and very small numbers can be expressed and calculated efficiently by means of scientific notation, a method which depends primarily on the use of exponents.

A number is said to be expressed in scientific notation when it is written as the product of an integral power of 10 and a rational number between 1 and 10. For example,

$$253 = 2.53 \times 10^2$$

$$0.0253 = 2.53 \times \frac{1}{100} = 2.53 \times \frac{1}{10^2} = 2.53 \times 10^{-2}.$$

The procedure illustrated by these examples may be stated as follows:

(1) Place the decimal point to the right of the first non-zero digit, thus obtaining a number between 1 and 10.

(2) Multiply this number by a power of 10 whose exponent is equal to the number of places the decimal point was moved. The exponent is positive if the decimal point was moved to the left and negative if it was moved to the right.

By use of the laws of exponents and scientific notation, computations involving very large or very small numbers are simplified. For example,

$$\frac{378,000,000,000 \times 0.000004}{2000}$$

$$= \frac{3.78 \times 10^{11} \times 4 \times 10^{-6}}{2 \times 10^3}$$

$$= \frac{3.78 \times 4 \times 10^{11-6}}{2 \times 10^3}$$

$$= 3.78 \times 2 \times 10^{11-6-3}$$

$$= 7.56 \times 10^2$$

$$= 756.$$

Significant Digits

Measurements, in contrast to discrete counts, often result in what are called approximate numbers. For example, the dimensions of a table are reported as 29.6" by 50.2". This implies that the measurement is accurate to the nearest tenth of an inch and that the table is less than 50.25" and more than 50.15" in length. Similarly, using symbolic notation,

$$29.55'' < \text{width} < 29.65''.$$

Thus the area of the table is not $29.6 \times 50.2 = 1485.92$ square inches. Instead the exact area is between $29.55 \times 50.15 = 1481.9325$ square inches and $29.65 \times 50.25 = 1489.9125$ square inches; it is clearly nonsense to report the area as 1485.92 with six non-zero digits when even the fourth digit is in doubt. It thus becomes important to indicate the digits which are "significant."

In making measurements the number of significant digits that can be recorded is determined by the precision of the instruments used. It is possible to indicate the accuracy of a measurement by actually giving the tolerance or possible error. For example, the length of the table could have been recorded as 50.21 ± 0.02 inches, indicating that the actual length lies between 50.19 and 50.23 inches.

Another method of indicating accuracy is to express all measurements in scientific notation. The digits in the rational number are then called significant digits. For example, 124.6 can be written as 1.246×10^2 where 1, 2, 4 and 6 are the significant digits. This method clarifies measurements such as 24,000 by indicating whether they

are accurate to the nearest thousand, hundred or ten units.

Summarizing the preceding, the significant digits in a number are:

    (1) Non-zero digits
    (2) All zeros which are not used to place the decimal, i.e., zeros only if they are:
        (a) between non-zero digits
        (b) at the right of non-zero digits and are, in some way, indicated as significant
        (c) at the right of non-zero digits which occur after a decimal point.

For example,

Number	Significant Digits
$24{,}000 = 2.4 \times 10^4$	2, 4
$24{,}000 = 2.400 \times 10^4$	2, 4, 0, 0
$1087 = 1.087 \times 10^3$	1, 0, 8, 7
$0.0015 = 1.5 \times 10^{-3}$	1, 5
$0.0003 = 3 \times 10^{-4}$	3

Computational Accuracy

In any computation involving sums and differences, the number with the least number of digits following the decimal point determines the number of decimal places to be used in the answer. For example,

$$\begin{array}{r} 2883 \\ 43.46 \\ 0.1376 \\ \hline 2926.5976 \end{array} \text{ should be } 2927.$$

Since 2883 has no digits following the decimal place the answer must be expressed as 2927.

With products or quotients the accuracy of the result depends on the number of significant digits in the component measurements. Thus the number of significant digits to be retained in the result is the least number of significant digits in any of the factors. For example,

$$8.216 \times 3.71 = 30.48136 \text{ should be } 30.5.$$

Since 3.71 has only three significant digits, only three should be retained in the result.

Note that in the use of a formula involving absolute constants, these constants may be assumed to have as many significant digits as desired; in other words, they may be ignored in any determination of the number of significant digits to be retained in the result of the computation.

Rounding

In performing computations, it is recommended that rounding be accomplished after the calculation has been performed in order to incur the least possible error. The rules of rounding state that in rounding off a digit:

    (1) Add 1 if the succeeding digit is more than 5
    (2) Leave it unchanged if the succeeding digit is less than 5
    (3) If the succeeding digit is exactly 5 round off the number so that the final digit is even.

In each of the following examples the number is rounded to three digits:

    (1) 45273 is rounded to 45300
    (2) 45243 is rounded to 45200
    (3) 45250 is rounded to 45200
    (4) 45350 is rounded to 45400
    (5) 45250.03 is rounded to 45300.

Logarithms

Lengthy computations can often be greatly simplified by the use of logarithms. The formal definition states that if b is any positive number different from 1, and $b^y = x$, then the exponent y is called the logarithm of x to the base b. In symbols, $y = \log_b x$. For example, $\log_3 9 = 2$ since $3^2 = 9$.

It is important to note that a logarithm is an exponent. Since this is true the same properties that hold for exponents also hold for logarithms. They can be restated in the following manner:

    (1) $\log_b (x \cdot y) = \log_b x + \log_b y$

    (2) $\log_b \left(\dfrac{x}{y}\right) = \log_b x - \log_b y$

    (3) $\log_b (x^n) = n \log_b x.$

Common Logarithms. Logarithms which use 10 as a base are called common or Briggsian logarithms. Usually these are written simply as log x, without any base indicated, meaning $\log_{10} x$.

In order to find the common logarithm of a number note first that $\log 1 = 0$ and $\log 10 = 1$ since $10^0 = 1$ and $10^1 = 10$. Thus the logarithm of any number between 1 and 10 will be a value between 0 and 1. The values have been calculated and are available in tabular form. A portion of such a table is shown below.

Table 3-1

N	0	1	2	3	4	5	6	7	8	9
50	6990	6998	7007	7016	7024	7033	7042	7050	7059	7067
51	7076	7084	7093	7101	7110	7118	7126	7135	7143	7152
52	7160	7168	7177	7185	7193	7202	7210	7218	7226	7235
53	7243	7251	7259	7267	7275	7284	7292	7300	7308	7316
54	7324	7332	7340	7348	7356	7364	7372	7380	7388	7396

Note that the decimal points are omitted in such a table. Hence

$$\log 5.34 = 0.7275.$$

In order to find common logarithms of numbers larger than 10 or less than 1, the method of scientific notation is used. The logarithm of such a number can be written as the sum of an integer,

called the characteristic, and a positive decimal fraction between 0 and 1, called the mantissa. For example,

$$534 = 5.34 \times 10^2 = 10^{0.7275} \times 10^2 = 10^{2.7275}.$$
$$\text{Thus } \log 534 = 2.7275.$$

More simply, in finding the logarithm of a number written in scientific notation, the characteristic is

the exponent of the power of 10 and the mantissa is the entry in the table corresponding to the first part. For example,

$$\log 52 = 1.7160.$$

This same rule applies to numbers less than 1, although the result can be written in many different ways. For example,

$$0.00534 = 5.34 \times 10^{-3}$$
$$\log 0.00534 = -3 + 0.7275$$
$$= 10 - 3 + 0.7275 - 10$$
$$= 7.7275 - 10$$
$$= \bar{3}.7275$$
$$= -2.2725.$$

The final form, -2.2725, is the most inconvenient since it does not contain a characteristic and mantissa.

When the logarithm of a number is known, it is a simple process of using the tables and working backwards in order to find the original value, called the antilogarithm.

Natural Logarithms. The natural or Napierian system of logarithms employs as its base the irrational number e whose decimal expansion is 2.71828 . . . . Natural logarithms are usually denoted by $\ln x$ or $\log_e x$.

Tables also exist for the natural logarithms of numbers between 1 and 10. To obtain the natural logarithms of other numbers the number must again be written in scientific notation. Then the properties of logarithms are applied. For example,

$$642 = 6.42 \times 10^2$$
$$\ln 642 = \ln 6.42 + 2 \ln 10$$
$$= 1.85942 + 2(2.30259)$$
$$= 6.46460.$$

Note that the number to the left of the decimal point in a natural logarithm does not indicate the location of the decimal point in the antilogarithm. *Logarithmic Conversions.* In order to change logarithms with a base b into logarithms with any other base a it is only necessary to multiply by the constant factor $\log_a b$. That is, $\log_a x = \log_b x \cdot \log_a b$.

Specifically, for conversions between natural and common logarithms,

$$\log x = 0.4343 \cdot \ln x$$
$$\ln x = 2.3026 \cdot \log x.$$

Computation with Logarithms. Simplification in computation is obtained by the use of the three basic properties of logarithms stated above. Consider, for example, the heat stress equation

$$E_{max} = (10.3)\ (V)^{0.4}\ (42 - VP_a).$$

This computation can be greatly simplified by writing it in the form

$$\log E_{max} = \log 10.3 + 0.4 \log V + \log (42 - VP_a).$$

GRAPHING

A graph is a pictorial representation of the relationship between two or more quantities. By this means a union is formed between the two elementary streams of mathematical knowledge — algebra and geometry.

Cartesian (Rectangular) Coordinate System

The most common two-dimensional graph makes use of linear scales for each of the quantities

being considered. Two perpendicular lines and a unit of length are chosen. Customarily the horizontal line is called the x-axis and the vertical line the y-axis. By this means a one-to-one correspondence can be established between the points in a plane and all ordered pairs of real numbers. This is demonstrated in Figure 3-1.
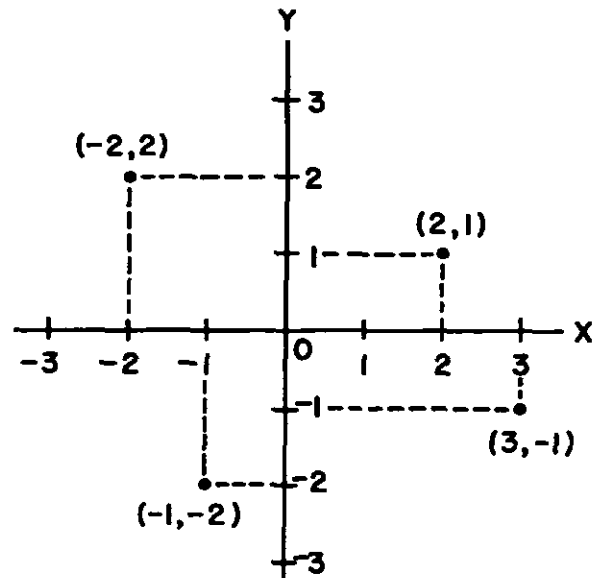

Figure 3-1

Linear Functions

An equation in which none of the variables is raised to a power is called a linear or first-degree equation. The graph of such a function is always a straight line. A linear equation often appears in what is known as slope-intercept form: $y = mx + b$, where x is the independent variable; y is the dependent variable; b is the y-intercept, the value for y when $x = 0$; and m is the slope, the change in y divided by the change in x.

As an example consider the graph of the equation $y = \dfrac{-3}{2}x + 2$ shown in Figure 3-2.

Since the y-intercept is 2, the line passes through the point (0, 2). Since the slope is $-3/2$, the line falls three units vertically for every two units that it runs horizontally.

Second and Higher Degree Equations

There are many forms of second and higher degree equations, but few will be encountered in industrial hygiene. One exception may be the parabola which has the general form $y = Ax^2 + Bx + C$. As an example, consider the equation $y = 4x - \dfrac{x^2}{2}$. The simplest method of graphing such a function is to form a table of values that satisfy the equation.

Table 3-2

y	-1	0	1	2	3	4	5	6	7	8
x	-4.5	0	3.5	6	7.5	8	7.5	6	3.5	0

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(0,2)
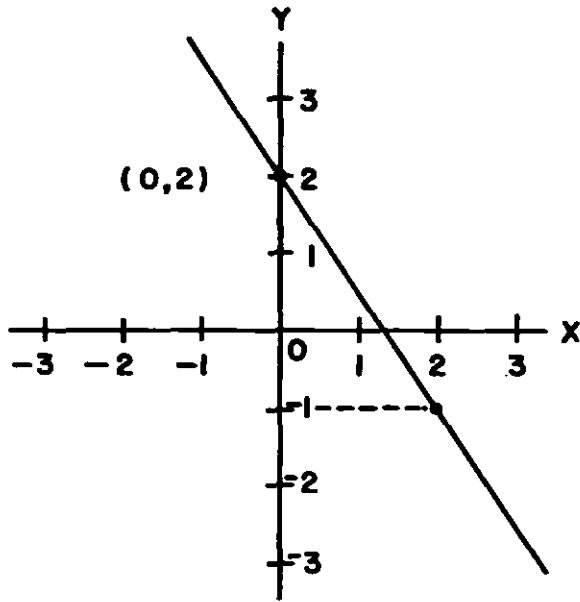
Figure 3-2

The graph of this function is illustrated in Figure 3-3.

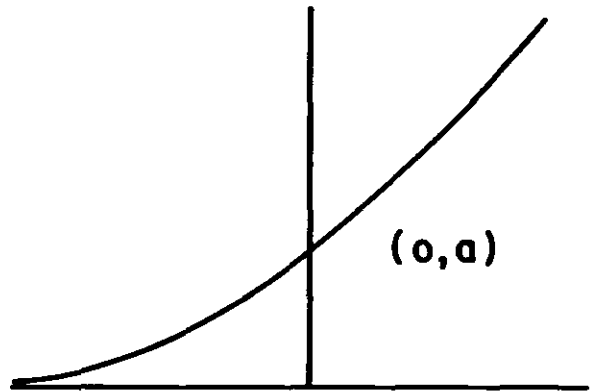Figure 3-4

If the logarithm of both sides of the equation $y = a(c^{bx})$ is taken the result is $\log y = \log a + bx \cdot \log c$. If x and log y are taken as the variables, this equation has the slope-intercept form of the equation of a straight line, $y = mx + b$. This equation may then be plotted as a straight line on semilogarithmic paper, which has a linear scale on the horizontal axis and a logarithmic scale on the vertical one. As shown in Figure 3-5, the y-intercept becomes log a while the slope is b log c.

Figure 3-3

Exponential Functions

An exponential function is any function in which a constant is raised to a variable power and has the general form $y = a(c^{bx})$. A number of ventilation, dilution and noise level equations are of this type. Should such a function be graphed on rectangular coordinate paper when, for example, c > 1 and b is positive, the result is a curve of the type shown in Figure 3-4.
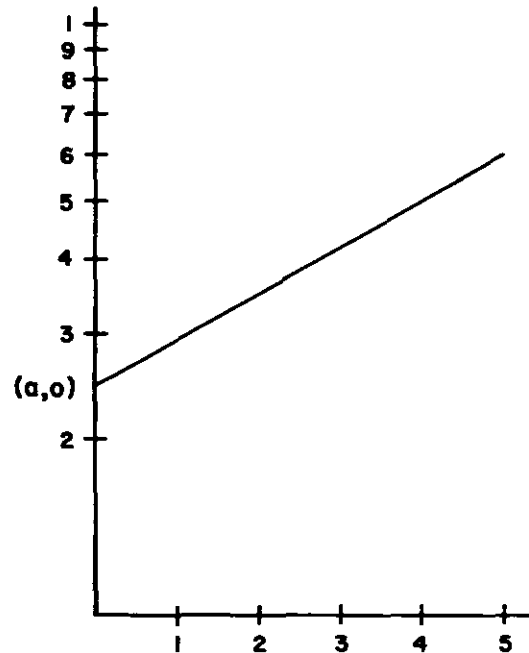

(a,0)

Figure 3-5

Power Functions

A power function has the general form $y = ax^b$. Graphing such a function on rectangular coordinate paper often requires the finding of a

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great number of points. However, if the logarithm of both sides of the equation is taken the result is log y = log a + b log x. If log x and log y are the independent and dependent variables respectively, the form of this equation is again the slope-intercept form of a straight line, y = mx + b. This equation may then be plotted on logarithmic paper, which has a logarithmic scale on both axes. The plot will be a straight line with slope b and y-intercept log a as shown in Figure 3-6.
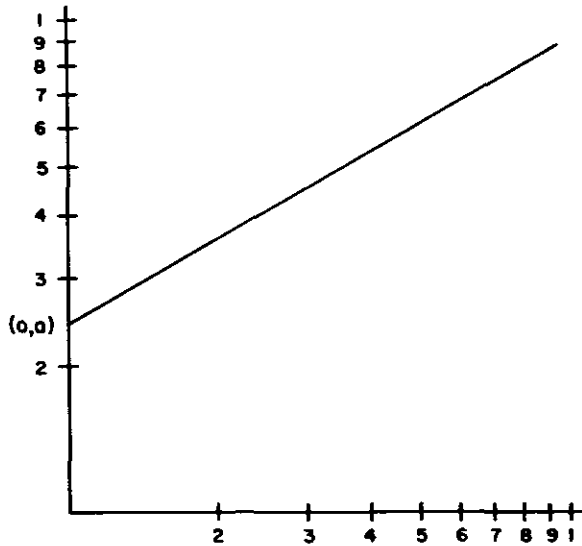

Figure 3-6

STATISTICS

Frequency Distributions

In any study of statistics the main concern, either in fact or in theory, is with sets of numerical data. The entire set is usually called the population while some subset of it which is being considered is called a sample. One of the first steps in analyzing a population is to arrange the members of the sample in an array, thus exhibiting the frequency distribution of the population.

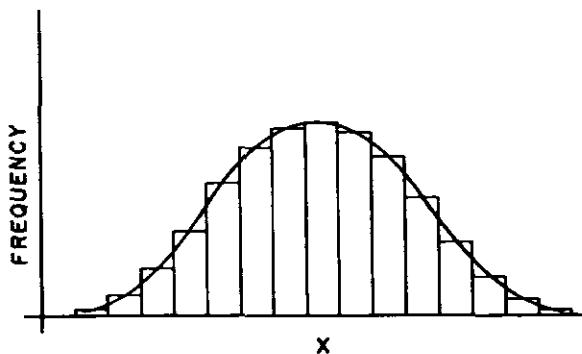The frequency distribution that occurs most often in both industry and nature is the normal

Figure 3-7

distribution. This distribution can be represented by a bell-shaped curve; that is, a symmetrical curve with most of the values falling somewhere near the middle of the range of values, as shown in Figure 3-7.

Many other distributions have also been characterized. In fact, studies of the distribution of measurements of particulate air pollutants and particle sizes indicate that a suitable frequency function is that of the log-normal distribution. In this distribution, the logarithms of the actual measurements are approximately normally distributed. A special type of logarithmic paper, called log-probability paper, is used to plot this distribution.

Measures of Central Tendency

In addition to the general information provided by a frequency distribution, there are quantitative characterizations of a population called parameters. The first of these is a measure of central tendency, a number about which the data tend to concentrate.

If the distribution of a set of numbers is approximately normal, three measures of central tendency are frequently used. The most important of these is the arithmetic mean, the sum of all the values divided by the number of values. Symbolically,

$$\bar{x} = \frac{x_1 + x_2 + \cdots + x_n}{n} = \frac{\sum_{i=1}^{n} x_i}{n}.$$

If one or more of the values appears more than once, the calculation may be simplified by multiplying each of the values by the number of times it appears. Then

$$\bar{x} = \frac{\sum_{i=1}^{n} (x_i \cdot f_i)}{N},$$

where f_i is the frequency with which x_i appears and N is the total number of values being considered. This is the method used to calculate a time-weighted average, such as that used in referring to threshold limit values.

The second common measure is the median, the middle observation when the numbers are arranged in order of magnitude. If there are an odd number of values, the median is uniquely defined; if there are an even number, the average of the two middle values is used. For example, the median of the numbers

7, 11, 21, 24, 31, 92 is $\frac{21+24}{2}$ or 22.5.

Another measure of central tendency is the mode, the number in a collection which occurs most frequently, if such a number exists. This value is often not uniquely defined, or, if it is, may not be representative of the sample.

If the frequency distribution is approximately log-normal rather than normal, the most appropriate measure of central tendency is the geometric mean. This is defined as the nth root of the product of the n values. Symbolically,

$$\bar{x}_g = \sqrt[n]{x_1 \cdot x_2 \cdots x_n}.$$

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This calculation can be greatly simplified by the use of logarithms.

Since $\bar{x}_g = (x_1 \cdot x_2 \cdots x_n)^{\frac{1}{n}}$,

$$\log \bar{x}_g = \frac{1}{n}(\log x_1 + \log x_2 + \cdots + \log x_n)$$

$$= \frac{1}{n}\left(\sum_{i=1}^{n} \log x_i\right)$$

and $\bar{x}_g = \text{antilog}\left[\frac{1}{n}\left(\sum_{i=1}^{n} \log x_i\right)\right]$.

Again, if some of the values should appear more than once, as in a particle size distribution, the formula becomes

$$\bar{x}_g = \text{antilog}\left[\frac{1}{N}\left(\sum_{i=1}^{n} f_i \cdot \log x_i\right)\right].$$

This computation may be carried out by the use of either common or natural logarithms.

Measures of Dispersion

A second numerical characterization of a population is provided by a measure of dispersion, a number describing how the values of the collection deviate from some central value.

If the distribution is approximately normal, the appropriate measure of dispersion is the standard deviation. The difference between any value in a set of data and the mean is called the deviation from the mean. If these deviations are squared, summed, and divided by $n-1$, the resulting number is the variance of the distribution. The positive square root of the variance is the standard deviation. Symbolically,

$$s = \sqrt{\frac{\sum_{i=1}^{n}(x_i - \bar{x})^2}{n-1}}.$$

To simplify calculations, this may also be written as,

$$s = \sqrt{\frac{n\sum_{i=1}^{n} x_i^2 - \left(\sum_{i=1}^{n} x_i\right)^2}{n(n-1)}}.$$

Again, if some of the values should appear more than once, this frequency of appearance, f_i, is introduced into the equation. In that case

$$s = \sqrt{\frac{\sum_{i=1}^{n}(x_i - \bar{x})^2 f_i}{N-1}}.$$

As a computational aid the standard deviation may also be written as

$$s = \sqrt{\frac{N\sum_{i=1}^{n} f_i x_i^2 - \left(\sum_{i=1}^{n} f_i x_i\right)^2}{N(N-1)}}.$$

The significance of the standard deviation lies in the fact that if a distribution is approximately normal, 68.3% of the observations will lie within one standard deviation of the mean, 95.4% will lie within two standard deviations of the mean, and 99.7% will lie within three standard deviations of the mean. A graphic presentation of this is shown in Figure 3-8.
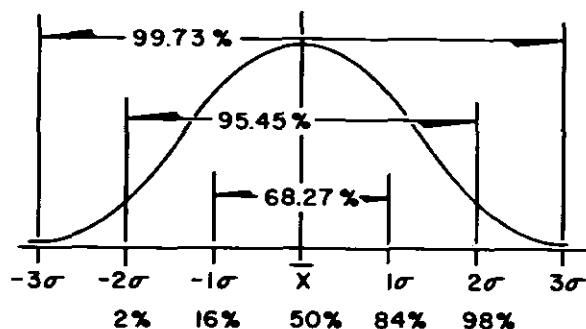

Figure 3-8

When the distribution is approximately lognormal, the standard geometric deviation is the appropriate measure of dispersion. The equation for this measure is

$$s_g = \text{antilog}\sqrt{\frac{n\sum_{i=1}^{n} \log^2 x_i - \left(\sum_{i=1}^{n} \log x_i\right)^2}{n(n-1)}}.$$

Again, when some of the values appear more than once the frequency, f_i, is introduced. Then,

$$s_g = \text{antilog}\sqrt{\frac{N\sum_{i=1}^{n} f_i \log^2 x_i - \left(\sum_{i=1}^{n} f_i \log x_i\right)^2}{N(N-1)}}.$$

The significance of the standard geometric deviation is analogous to that of the standard deviation if we recall that in a log-normal distribution the logarithms of the values are approximately normally distributed. Thus, 68.3% of the values lie between $\bar{x}_g/s_g$ and $\bar{x}_g \cdot s_g$, 95.4% lie between $\bar{x}_g/2s_g$ and $\bar{x}_g \cdot 2s_g$, and 99.7% lie between $\bar{x}_g/3s_g$ and $\bar{x}_g \cdot 3s_g$. It should be noted that these are the principles which govern the use of log-probability graph paper.

Testing Hypotheses

Frequently an investigator has in mind a particular hypothesis or assumption about the population being sampled. This usually consists of assigning a specific value to one or more of the parameters of the population, such an assignment depending on past experience. Then a test must be devised whereby the hypothesis is either accepted or rejected once the sample has been taken. The determination of this test depends on certain characteristics of the population which will not be discussed here. A good statistical reference such as those cited at the end of this chapter will provide a detailed method for selection of a test statistic. It should be understood, though, that the failure to reject a hypothesis does not imply that it is true; it simply means that the information is such that we are not in a position to reject the hypothesis.

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Curve Fitting

In addition to characterizing a population, the methods of statistics are often used in making predictions. This involves the consideration of relationships between two or more variables. Such a study usually begins with the plotting of the points on a rectangular coordinate system, giving a visual image of the relationship between the variables. In the case where the values of y are fairly well approximated by a linear function of x, linear correlation is said to exist. A measure of the closeness of this correlation is given by the linear correlation coefficient

$$r = \frac{\sum\limits_{i=1}^{n} (x_i - \bar{x}) \cdot (y_i - \bar{y})}{\sqrt{\sum\limits_{i=1}^{n} (x_i - \bar{x})^2 \cdot \sum\limits_{i=1}^{n} (y_i - \bar{y})^2}}.$$

If this value is close to 0, there is little linear relationship between the variables; while if it is near +1 or −1, the linear relationship may be greater. However, the extent of such a relationship depends strongly on the sample size. Also, there may be a high degree of correlation that is not of the linear type and thus not indicated by the linear correlation coefficient.

When a relationship is seen to exist between two variables, it is often desirable to approximate the function in order to predict the value of one variable from the other. This is often accomplished simply by joining the data points by a curve that appears to best approximate the relationship, as shown in Figure 3-9.
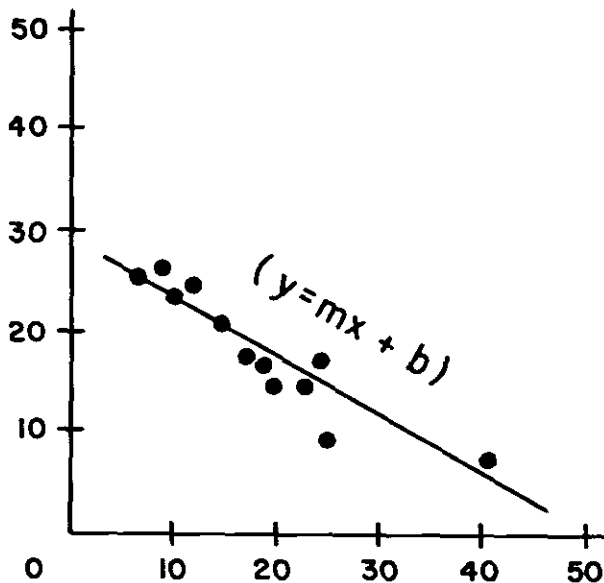

Figure 3-9

An equation of this curve can then be found by substituting points on the curve into the general equation of the curve and solving the resulting

equations simultaneously. A more precise method of determining the equation is given by the method of least squares, a procedure which minimizes the error committed in fitting a curve of a definite type to a set of data. A detailed description of this method can be found in most of the references cited at the end of this chapter.

Dimensional Analysis

Expressions of concentrations of atmospheric contaminants in industrial hygiene are usually corrected to 25°C and 760 mm Hg pressure, but the actual conditions are frequently not sufficiently removed from this standard to require temperature and pressure corrections. When calculating concentrations, recall that one gram-mole is the amount of material in grams equal to the molecular weight of the material. Also, at standard temperature and pressure (0°C and 760 mm Hg), one gram-mole of any compound in the gaseous state occupies 22.4 liters.

Terms Peculiar to Industrial Hygiene

The concentration of gases and vapors is usually expressed as parts per million parts of air, ppm, on a volumetric basis.

$$ppm = \frac{parts}{10^6 \text{ parts (air)}}$$

$$= \frac{micro\text{-}liter}{liter \text{ (air)}}$$

$$= \frac{cubic \text{ meters}}{10^6 \text{ cubic meters (air)}}$$

$$= \frac{cubic \text{ feet}}{10^6 \text{ cubic feet (air)}}$$

This is similar to the concept of percent,

$$\% = \frac{parts}{100 \text{ parts}}.$$

The concentration of fumes, mists, dusts, and of gases and vapors on occasion, is expressed as milligrams of material per cubic meter of air, mg M³.

Examples

(1) Given the concentration of a contaminant in ppm, convert to mg M³.

$$\text{Since } 1 \text{ ppm} = \frac{1 \text{ liter}}{10^6 \text{ liters}}$$

$$\text{Concentration} = \left(\frac{1 \text{ liter}}{10^6 \text{ liters}}\right) \times \left(\frac{1 \text{ gram-mole}}{22.4 \text{ liters}}\right)$$

$$\times \left(\frac{MW \text{ Grams}}{\text{gram-mole}}\right) \times \left(\frac{10^3 \text{ liters}}{M^3}\right)$$

$$= \frac{grams}{10^3 M^3}$$

$$= \frac{mg}{M^3}.$$

At 25°C and 760 mm Hg, one gram-mole of a perfect gas or vapor occupies 24.45 liters. Therefore, under these conditions,

$$\frac{mg}{M^3} = ppm \times \frac{Molecular \text{ Weight}}{24.45}.$$

(2) Derive an equation for the preparation of

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a known concentration of a volatile liquid given the following:

V_T = Chamber volume in liters
MW = Molecular weight of a substance
T = Absolute temperature

P = Pressure in mm Hg
ρ = Density in grams per milliliter
v = Volume of material to be used in milliliters
C = Concentration in ppm

$$C \text{ (ppm)} = \frac{(v \text{ ml}) \, \rho \, \dfrac{gm}{ml} \, \dfrac{22.4 \text{ liters}}{gm\text{-}mole} \, \dfrac{gm\text{-}mole}{MW \text{ gms}} \, \dfrac{T}{273} \, \dfrac{760}{P}}{V_T \text{ Liters}} \times 10^6 \frac{\text{parts}}{10^6 \text{ parts}}$$

$$= \frac{(v) \, (\rho) \, \dfrac{22.4}{MW} \, \dfrac{T}{273} \, \dfrac{760}{P}}{V_T} \times 10^6.$$

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REVIEW OF CHEMISTRY

Fred I. Grunder

INTRODUCTION

Chemistry is that branch of the physical sciences which plays an extremely important role in the characterization and quantitative measurement of the toxic substances of interest in the field of occupational health. A proper understanding of the several phases of chemistry permits the occupational health specialist to use this tool effectively in solving the environmental problems in this field. A proper understanding of inorganic chemistry is required for the appreciation of the properties of the mineral and inorganic chemical substances which are of concern to the health and well-being of the worker exposed to these materials as airborne particulates, fumes, or mists in the workplace. A basic grasp of organic chemistry is important because of the great variety of toxic organic solvent vapors and particulate compounds encountered in industrial operations. Analytical chemistry is a major tool used in occupational studies in the evaluation of chemical hazards, including the levels of airborne contaminants in the working environment and the concentrations of toxic substances, intermediates, and metabolites in the human or animal body tissues and fluids.

GENERAL INORGANIC CHEMISTRY

It can be observed readily that the world is composed of a tremendous variety of material substances. Superficial inspection reveals many of these to be composed of two or more identifiable components. Often more deliberate study will show the components to be made up of still other distinguishable substances. If the examination process is continued with ever-increasing sophistication, there will come a point where further subdivision will no longer be possible. The materials which cannot be divided into simpler chemical entities are called *elements*. The smallest unit which can be recognized as a particular element is known as an *atom*. Each atom of an element is chemically identical to every other atom of the same element, while uniquely different from those of other elements. There are presently 105 known elements, from which the material of the universe is made.

Atoms are composed principally of positively-charged *protons*, negatively-charged *electrons* and uncharged *neutrons*. The protons are situated at the center of the atom along with uncharged neutrons in the *nucleus*. The electrons are oriented at some distance from the nucleus and impart size and electrical balance to the atom. Each atom has the same number of protons as electrons to maintain electrical neutrality. The number of protons in the nucleus is the *atomic number* which uniquely defines the elemental identity of the atom. The number of protons combined with the number of neutrons approximates the *atomic weight*. The atomic weight of an atom is proportional to its true, physical mass. Hence, 12.0 grams of carbon (atomic weight = 12) contain 6.023×10^{23} carbon atoms. The mass in grams of any element which is equal to that element's atomic weight is called one gram-molecular weight, or one *mole*, which always contains 6.023×10^{23} (Avogadro's Number) atoms of that element. Each of the elements has a name and a symbol assigned to it. For example, the eleventh element (atomic number 11) is called sodium which has the chemical symbol Na.

Elements combine with one or more other elements in definite ratios to form *compounds*. The smallest unit of a compound is called a *molecule*. Molecules are held together by the sharing of pairs of electrons between the atoms to form chemical bonds. Bonds are classified according to the extent of the sharing involved. A *covalent* bond is one in which the pair of electrons is shared equally by two atoms. An example of a covalent bond is the hydrogen molecule in which the two identical atoms share the lone electron pair. If the atoms involved are not from the same chemical element, the chances of equal sharing are diminished. In extreme cases, the bond is known as *ionic*. Sodium chloride (NaCl) is a good example of an ionic bond, the sodium existing essentially as the positively-charged ion and the chlorine as the negative chloride ion. Sharing of more than one electron pair leads to double and triple bonding. The nitrogen molecule is an example of a higher-order bond. In this case, the two atoms share three pairs of electrons to form a triple bond.

The chemical symbol for a compound is merely a composite of its constituent atoms along with numerical indications of the ratios of the combining elements to one another. For instance, the symbol for water, H_2O, represents a molecule which contains two atoms of hydrogen and one of oxygen. The *molecular weight* of a compound is equal to the sum of the atomic weights of all the atoms making up the molecule of that compound. Similarly to the case for individual atoms, the mass in grams of any compound which is equal to that compound's molecular weight is called one mole which contains 6.023×10^{23} molecules of that compound.

Often it is convenient and useful to express a molecular symbol or *formula* as more than just an accounting of the atoms present. It is known, for example, that certain groupings of atoms appear regularly in chemistry. They are called

"groups" or "functional groups" or "radicals" and they are treated as separate elemental forms when writing the formula. In organic chemistry the methyl (CH_3-) and ethyl (C_2H_5-) groups are common functional substituents in class compounds. Confusion is avoided in organic chemistry by using constitutional or structural formulas. For example, the formula for ethyl alcohol, is written as CH_3CH_2OH or C_2H_5OH rather than C_2H_6O (a molecular formula) to emphasize the constitutional arrangement of the atoms within the molecule and to distinguish it from methyl ether (CH_3OCH_3) which has the same molecular formula.

Chemistry uses the element symbols to abbreviate complex descriptions of chemical reactions. For instance, if a reaction is initiated between hydrogen and oxygen in a mixture, water will be produced. The whole reaction can be written as the symbolic expression:

$$2H_2 + O_2 \rightarrow 2H_2O.$$
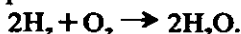
The exact way in which a chemical reaction is written expresses certain essential aspects of the reaction. This equation identifies the reactants as hydrogen and oxygen and shows that they combine in a ratio of two molecules of H_2 to one of O_2 to yield two molecules of H_2O. A complete description of the above reaction would include a description of the pertinent reaction conditions. It is significant that the equation is balanced with respect to both the numbers and the kinds of atoms in the reactants and the products. In correct chemical equations, atoms cannot be created, destroyed, or transmuted. In organic chemistry (see discussion of bonds in section on Organic Chemistry) where the structure of molecule is especially important reactants and products are written structurally:
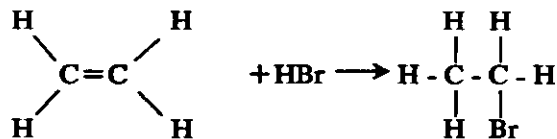
Chemical reactions occur because the final products are energetically more stable than the initial reactants under the conditions of the reaction. The difference in energy between reactants and products can commonly be observed as heat liberated, as in the burning of wood. Consideration of the amounts of liberated heat of reaction is important in thermodynamics where this is shown quantitatively as part of the chemical equation:

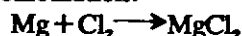$$CaO + CO_2 \longrightarrow CaCO_3 + 42.5 \text{ kcal/mole.}$$

The value of 42.5 kcal/mole is the amount of energy released as heat in the reaction. It is given the symbol ΔH and is defined as the *heat of reaction*. In tabular form, positive values for heats of reaction represent *endothermic* reactions which absorb heat from the surroundings. The reaction of CaO and CO_2 releases heat energy, indicating that it is *exothermic* and that the heat of reaction is negative ($\Delta H = -42.5$ kcal/mole). It appears positive in the preceding equation because it is a positive product of the reaction. Another expression for the same reaction is:

$$CaO + CO_2 \longrightarrow CaCO_3,$$
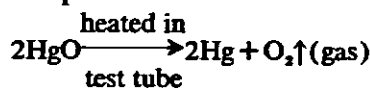$$\Delta H_{reac} = -42.5 \text{ kcal/mole.}$$
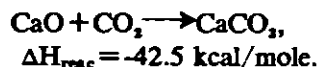
Basically, chemists are concerned with four types of chemical reactions, i.e. combination, decomposition, displacement, and double decomposition. Examples of these are as follows:
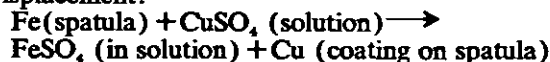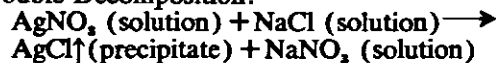
Combination:
$$Mg + Cl_2 \longrightarrow MgCl_2$$

Decomposition:
$$2HgO \xrightarrow[\text{test tube}]{\text{heated in}} 2Hg + O_2 \uparrow (gas)$$

Displacement:
$$Fe(\text{spatula}) + CuSO_4 (\text{solution}) \longrightarrow$$
$$FeSO_4 (\text{in solution}) + Cu (\text{coating on spatula})$$

Double Decomposition:
$$AgNO_3 (\text{solution}) + NaCl (\text{solution}) \longrightarrow$$
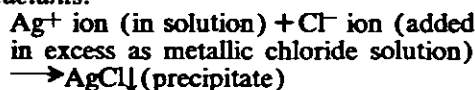$$AgCl \uparrow (\text{precipitate}) + NaNO_3 (\text{solution})$$

Chemical reactions go to completion when one of these four conditions is met:

1) *Increasing the concentration of one of the reactants:*

Ag^+ ion (in solution) + Cl^- ion (added in excess as metallic chloride solution) $\longrightarrow AgCl \downarrow$ (precipitate)

Silver chloride has a very low solubility product which means that the product $(Ag^+) \times (Cl^-)$ cannot exceed its value of 1.56×10^{-10} moles per liter*;

*One gram mole is the number of grams equal to the molecular weight of a substance.

2) *Removing one of the products as a gas:*

$$CaCO_3 \overset{\Delta}{\rightleftharpoons} CaO + CO_2 \uparrow$$
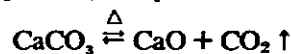
The escape of the gaseous product, carbon dioxide, allows quicklime to be formed from limestone in a kiln.

3) *Removing one of the products as a precipitate:*

$$Pb (C_2H_3O_2)_2 + H_2S (\text{gas}) \longrightarrow PbS \downarrow + 2CH_3COOH$$

When hydrogen sulfide is passed into a weakly acid solution of a soluble lead salt, the lead is converted completely to highly insoluble lead sulfide.

4) *Removing one of the products as a slightly ionized substance:*

$$NaOH + NH_4Cl \rightleftharpoons NaCl + NH_4OH$$
$$\text{and } NH_4OH \rightleftharpoons NH_3 + H_2O$$

The addition of sodium hydroxide to ammonium chloride produces slightly ionized ammonium hydroxide which dissociates into ammonia and water. As a result the reaction shifts almost entirely to the right.

In the examples of chemical reactions given above there are two additional basic classifications: first, reactions involving an electron transfer and a resulting change in the oxidation state of a substance and, secondly, reactions where there is no oxidation-reduction process. Thus, in the burning of magnesium in chlorine gas, magnesium is oxidized from the elemental to the divalent (+2)

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state while chlorine is reduced from the elemental to the negative (-1) state whereas in the double decomposition reactions there is no oxidation-reduction process occurring, but only an exchange of elements whose reactions go to completion for the reasons stated previously. The following discussion treats further the matter of oxidation-reduction, an extremely important aspect of analytical chemistry processes.

In the water molecule, H_2O, the hydrogen atoms are essentially ionized by the oxygen's strong affinity for electrons. The resulting charge and oxidation state for hydrogen is then $+1$ and that for oxygen is -2. In the elemental form (H_2 & O_2) hydrogen and oxygen display no net charge and they have an oxidation state of 0. The reaction of hydrogen and oxygen to form water however, involves a transfer of electrons. The hydrogen atoms' loss of their electrons to the oxygen atom is called *oxidation*; the gain of these electrons by the oxygen is called *reduction*. Reactions of this type are called oxidation-reduction reactions or *redox* reactions. In any redox reaction, the total number of electrons lost by an oxidized species must exactly equal the number of electrons gained by the reduced species. This relationship enables redox reactions to be used in quantitative analysis. The amount of a substance in a redox reaction which will give up or receive one mole of electrons (6.023×10^{23} electrons) is called an *equivalent*.

Naturally occurring materials, irrespective of their elemental make-up, assume three different descriptions or states: *solids, gases* and *liquids.* Solids have a definite shape and volume and are held together by strong inter-molecular and inter-atomic forces. For many substances, the forces are strong enough to maintain the atoms in definite, ordered arrays called *crystals.* Solids having little or no crystalline character are called *amorphous.*

Gases, on the other hand, have weaker attractive forces between individual molecules. As a result, gases diffuse rapidly and assume the shape of their container; their volumes are easily affected by changes in temperature and pressure. Because true gases (the fixed gases) are relatively free of interactions between individual molecules, the behavior of a gas is dependent on only a few general laws based upon the properties of volume, pressure, and temperature. Under normal conditions, for instance, the pressure exerted by a gas multiplied by its volume is a constant at a fixed temperature and a given number of molecules:

$$PV = constant.$$

A temperature rise will produce a corresponding increase in pressure at constant volume and fixed number of molecules. A temperature rise will also produce a corresponding increase in volume at constant pressure and number of molecules:

$$T_2/T_1 = P_2/P_1 \text{ or } T_2/T_1 = V_2/V_1$$

where T_1 = absolute temperature (degrees Kelvin or Rankin) of a gas whose volume is V_1 and T_2 = absolute temperature of a gas whose volume is V_2.

At constant temperature and pressure, equal volumes of gases contain equal numbers of molecules regardless of the nature of the gas. A volume of 22.4 liters will contain one mole or 6.02×10^{23} molecules (or atoms of a monatomic gas) at sea-level pressure and $0°C$ or $32°F$. An equation for relating the four properties of gases (P, V, number of moles, T) which is applicable over a fairly wide range of conditions is called the *ideal gas law*;

$PV = nRT$, where P = pressure

$\quad$ V = volume

$\quad$ n = number of moles

$\quad$ T = temperature in degrees absolute

$\quad$ R = gas constant (determined by the units used for the other four).

When dealing with gases, it is customary to express volumes in terms of standard conditions of temperature and pressure. Thus, if data are obtained at conditions other than standard it is necessary to correct the volumes. For this purpose, an adaptation of the ideal gas law is used:

$$V_s = (P/P_s)(T_s/T) V$$

where V_s = volume at standard temperature and pressure

$\quad$ P_s = standard pressure

$\quad$ T_s = standard temperature in degrees absolute

$\quad$ V = volume observed

$\quad$ P = pressure observed

$\quad$ T = temperature observed in degrees absolute

The molecules of the liquid state of matter are separated by relatively small distances such that the attractive forces between molecules tend to hold the molecules within a definite volume at a fixed temperature. The repulsive forces between molecules also exert a sufficiently strong influence, however, that volume changes caused by increases in pressure may be neglected.

One of the most useful properties of liquids is their ability to *dissolve* gases, other liquids, and solids. Solvents are covalent compounds in which the molecules are much closer together than a gas; therefore, the intermolecular forces are relatively strong. When the molecules of a certain covalent solute are physically and chemically similar to those of a liquid solvent, the intermolecular forces of each are of the same magnitude and the solute and solvent will usually mix readily with each other.

The amounts of dissolved solutes are commonly expressed in terms of *concentrations* in solvents. The *molarity* of a solution is the number of moles of solute per liter of solution, designated by "M". The *molality* is the number of moles of solute per 1000 grams of solvent, designated by "m". The *normality,* "N", of a solute is the number of gram-equivalent weights of solute per liter of solution. The expression "parts per million" represents one part by weight of solute per one million parts by weight of solvent in liquid systems. One "ppm" is equivalent to one microgram

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per milliliter or to one milligram per liter of solution.

In aqueous solutions the concepts of acidity and basicity are important. For most purposes an acid can be described as a hydrogen ion (proton) donor. Hydrochloric acid is an excellent example of a strong acid. Similarly, a base is described as a hydrogen ion acceptor. Sodium hydroxide is an example of a strong base. For aprotic compounds which have no ionizable hydrogen, an acid can be defined as a substance (such as aluminum chloride) which accepts an electron pair from a base, and any substance, (such as NH_3) that can behave as an electron pair donor is a base.

In aqueous systems, the acidity or basicity of a solution is measured by pH which is defined as the negative logarithm of the hydrogen ion concentration (expressed in moles per liter). It ranges from 1 to 14, pH 14 being extremely basic (the hydroxide ion, OH^-, greatly predominating), pH 1 being extremely acidic (the hydrogen ion, H^+, greatly predominating), and pH 7 being neutral (the hydrogen ion and hydroxide ion concentrations equal). icͻb'

The basic concepts of general chemistry presented in this section are designed to provide the non-chemist members of the industrial hygiene profession with a general understanding of the principles of chemistry as they relate to the application of analytical chemistry to occupational health. The reference texts cited at the end of this chapter should be consulted periodically, as the needs of work situations require, to obtain the more detailed information on the aspects of individual problem areas.

ORGANIC CHEMISTRY

Organic chemistry is the study of carbon compounds, excluding the limited number of those inorganic substances which contain carbon such as carbon monoxide, carbon dioxide, carbonates and metal carbonyls. The common elements found in the thousands of organic compounds include carbon, hydrogen, oxygen, nitrogen, phosphorus, sulfur, chlorine, bromine, and iodine, in the order of their relative occurrence. Organic chemistry is involved in most activities of modern life. The basic principles of organic chemistry are applied to the study of drugs, rubber, clothing, plastics, explosives, fuels, paints, solvents and numerous other essential commodities.

The carbon atom forms four covalent bonds. These bonds may be to other carbon atoms, to hydrogen, oxygen, one of the halogens (chlorine, bromine, iodine, fluorine), nitrogen, sulfur or to other atoms. The bonds may involve single electron-pairs which form single bonds, two electron-pairs giving double bonds ($>C=C<$), or three electron-pairs forming triple bonds ($-C\equiv C-$).

More than one million organic compounds are known. Their existence is due to the unique capacity of carbon atoms to join together forming chains or rings. Compounds formed from hydrogen and carbon only are called *hydrocarbons*. The aliphatic series of saturated hydrocarbons provides the simplest example of this property.

methane

ethane

propane

$C_{60}H_{122}$ hexacontane
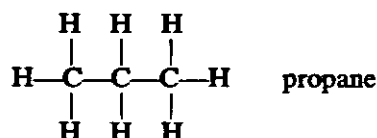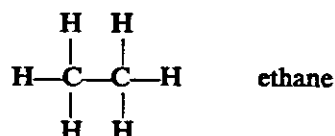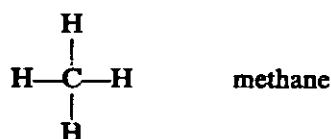
Homologous series of compounds are named according to the number of carbon atoms in the longest chain. The standard (International Union of Pure and Applied Chemistry) rules for naming carbon compounds are summarized below:

1) The longest continuous chain of carbon atoms is named as the parent compound.

2) The carbon atoms in this chain are given numbers starting at one end, and substitute groups are given numbers corresponding to their position on the chain. The direction of the numbering is chosen to give the smallest sum for the numbers of the side chain constituents:

$$CH_3\text{-}CH_2\text{-}CH\text{-}CH\text{-}CH_3$$

is named 2-methyl-3-ethyl pentane
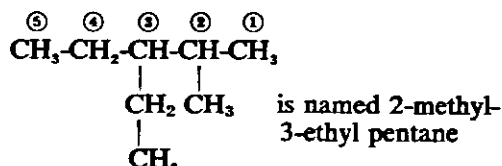
3) If the same group appears more than once, the prefix di-, tri-, or tetra- is used to indicate how many groups there are:

or 2,4-dimethyl-3-ethyl pentane
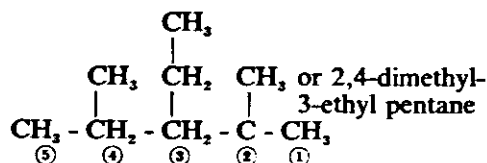
4) With two identical side chain groups at one position, numbers are given for each:

or 2,2-dimethyl pentane
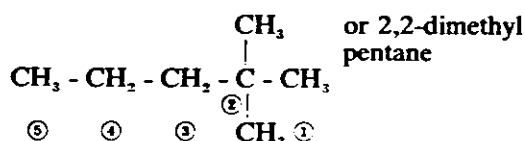
5) If several different substituent groups are present, they are assigned according to the alphabetical arrangement of substituents or in order of increasing size of the side chain.

Branched chains often have names of their own.

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Thus, $\begin{matrix} CH_3 \\ CH_3 \end{matrix}\!\!>\!CH-$ is an isopropyl group. For example,

$\begin{matrix} CH_3 \\ CH_3 \end{matrix}\!\!>\!CHOH$ is called isopropanol

$\begin{matrix} CH_3 \\ CH_3 \end{matrix}\!\!>\!CHCH_2CH_3$ is called isopentane.

The field of organic chemistry is generally divided into two broad classes of organic compounds, aliphatic compounds and aromatic compounds.

Aliphatic Hydrocarbons

The saturated hydrocarbons, which contain only single bonds, are also known as alkanes or paraffinic hydrocarbons. The general formula for these compounds is C_nH_{2n+2} where n is an integer. They are less reactive than the unsaturated hydrocarbons and are insoluble in water, sodium hydroxide and sulfuric acid. They do, however, undergo reaction under certain vigorous conditions. When treated with either chlorine or bromine and light or a catalyst, a halogen atom can substitute for a hydrogen atom:
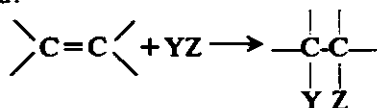
$$-\overset{|}{\underset{|}{C}}\!-\!H + Cl_2 \xrightarrow{\text{light}} -\overset{|}{\underset{|}{C}}\!-\!Cl + HCl$$
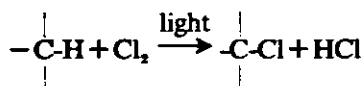
They can be heated from 400° to 600°C to promote thermal decomposition, a process called cracking, and yield simpler alkanes, alkenes and hydrogen.

Alkenes are unsaturated, olefinic hydrocarbons. They contain at least one carbon-carbon double bond. The suffix -ene is substituted for -ane in naming them. The parent hydrocarbon chain is chosen as the longest chain containing the double bond. The position of the double bond is designated by the number of the first carbon atom involved in the double bond. Thus, $CH_3CH = CHCH_3$ is 2-butene, and $CH_2 = CHCH_2CH_3$ is 1-butene. The double bond is given the lowest number, so the compound $CH_3\text{-}\overset{}{\underset{|}{C}H}\text{-}CH = CH\text{-}CH_3$
$\overset{|}{CH_3}$

is 4-methyl-2-pentene rather than 2-methyl-3-pentene.

Characteristic reactions of this group occur at the carbon-carbon double bond. The most characteristic reaction of the alkenes is the addition reaction. Generalized, this reaction can be represented:

$$\begin{matrix} \\ \end{matrix}\!\!>\!C = C\!<\!\!\begin{matrix} \\ \end{matrix} + YZ \longrightarrow -\overset{|}{\underset{|}{C}}\!-\!\overset{|}{\underset{|}{C}}\!-$$
$$Y\ \ Z$$

Many substitution groups can be represented by Y and Z (examples are H_2, HX, X_2, H_2SO_4, H_2O and others where — X is used to indicate a halogen such as chlorine or bromine).

The paraffin-base oils contain mainly saturated open-chain hydrocarbons, whereas asphalt-base oils contain appreciable amounts of naphthenes such as cyclopentane, cyclohexane and their alkyl derivatives. The major fractions separated from crude petroleum are shown in the following table:

TABLE 4-1

Major Fractions in Crude Petroleum

Fraction	Boiling Point Range, °C	Composition (Approximate)
Gas	<20	C_1-C_4
Petroleum Ether	20-60	C_5-C_6
Ligroin (Light Naphtha)	60-100	C_6-C_7
Natural Gasoline	40-205	C_5-C_9 + Cycloalkanes
Kerosene	175-325	C_9-C_{16} + Aromatics
Fuel Oil	300-375	C_{15}-C_{20}
Lubricating Oil	>300	C_{20}-C_{25}
Asphalt or Petroleum Coke	>300	>C_{25}

Aromatic Hydrocarbons

Benzene is the simplest of the aromatic compounds; it has the formula C_6H_6 and its structure is:

$$HC \overset{H\quad H}{\underset{H\quad H}{\overset{\diagup C - C \diagdown}{\underset{\diagdown C = C \diagup}{}}}} CH,$$
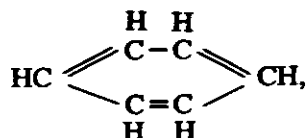
although experimental evidence indicates that all the carbon-carbon bonds are equivalent.

The correct structure is often shown as:

Where the circle indicates that the multiple bonding is shared equally among all six carbon atoms.

Benzene readily undergoes substitution reactions, such as halogenation:

$$C_6H_6 + X_2 \xrightarrow{\text{(Fe catalyst)}} C_6H_5X + HX \ (X = Cl, Br)$$

Benzene is very stable and resists addition reactions which would destroy the ring system.

In naming monosubstituted derivatives of benzene, the substituent's name is prefixed to "benzene." Thus:

is chlorobenzene   is nitrobenzene

Some aromatic compounds are better known by such common names as:

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toluene

phenol

aniline

benzoic
acid

For aromatic derivatives containing two ring substituents, the position on the ring is designated by the use of the terms ortho (o), meta (m), and para (p) as exemplified by:

o-dibromobenzene

m-dibromobenzene

p-dibromo-
benzene

When the substitution groups are different, they are named successively and the compound name is terminated with "benzene." If one of the substitution groups provides a compound which has a commonly accepted name (e.g., toluene or phenol) any further derivative is named after the last-named compound:

p-bromoiodo-
benzene

p-nitro-
toluene

o-bromo-
phenol

If more than two substitution groups are attached to the ring, numbers (starting with the parent group) are assigned to each carbon atom to indicate the position of each substituent:

2, 4, 6-trinitrotoluene (TNT)

Halogen Derivatives of the Hydrocarbons

Halogenated hydrocarbons are obtained from the substitution reaction of hydrocarbons with HX or X_2 under varied conditions. Generalized, the reaction with halogens is represented:

$$R \cdot H + X_2 \longrightarrow R \cdot X + HX$$
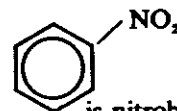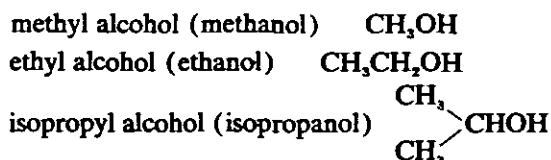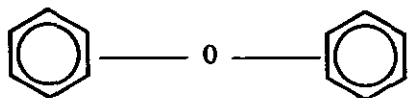
where R is an alkyl group and X is a halogen, such as chlorine or bromine.

One or more halogen atoms may be attached to a chain or ring structure; each additional atom changes the physical and chemical properties of the preceding compound in a series. For example, the successive derivatives of methane are:

$$CH_4 + Cl_2 \xrightarrow{HCl} CH_3Cl$$

CH_3Cl	used as a local anesthetic for minor surgical operations — a gas
$+Cl_2$ (HCl)	
CH_2Cl_2	commercially used as a solvent and in quick-drying paints and varnishes
$+Cl_2$ (HCl)	
$CHCl_3$	(chloroform) — a commercial solvent and anesthetic
$+Cl_2$ (HCl)	
CCl_4	(carbon tetrachloride) — very toxic; an important solvent.

Typical aromatic halogen derivatives, such as the chlorobenzenes, are obtained by the substitution reaction of the halogens with the aromatic hydrocarbon. The halogen derivatives of benzene are called aryl halides which are generally less reactive than the alkyl halides. Halogenation may proceed with the complete substitution of hydrogens attached to the ring carbons.

Oxygen Derivatives of the Hydrocarbons

An oxygenated carbon compound is one containing oxygen in a functional group attached to a chain or ring carbon. The *alcohols* have the general formula ROH, where R is an alkyl group. If the hydroxyl group (-OH) is attached directly to an aromatic ring, it is referred to as phenol, cresol, xylenol, or naphthol. Alcohols are often prepared by conversion of an alkene by adding sulfuric acid to the double bond and hydrolysis of the resulting alkylsulfuric acid:

$$CH_2 = CH_2 \xrightarrow{H_2SO_4} CH_3CH_2OSO_2OH \xrightarrow{H_2O}$$

$$CH_3CH_2OH \quad \text{ethyl alcohol.}$$

The characteristic reactions of alcohols involve either the replacement of the OH hydrogen or of the entire hydroxyl group.

$$ROH + HX \longrightarrow RH + H_2O \quad X = Cl \; Br, \; I$$

$$ROH + M \longrightarrow RO^-M^+ + 1/2 \; H_2$$

M = metal such as Na, Mg, Al

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Some of the common alcohols are:

methyl alcohol (methanol) CH_3OH

ethyl alcohol (ethanol) CH_3CH_2OH

isopropyl alcohol (isopropanol) $\begin{array}{c} CH_3 \\ > CHOH \\ CH_3 \end{array}$

Ethers have the general formula R-O-R'. Their names are derived from those of "R" groups followed by the word "ether." Thus, $CH_3OC_2H_5$ is methyl ethyl ether and

is diphenyl ether.

Diethyl ether is the most common member of this class of compounds. It is used as a solvent and an anesthetic. Ethers are often prepared by dehydration of alcohols:

$$2\ ROH \xrightarrow[\text{heat}]{H_2SO_4} R\text{-}O\text{-}R' + H_2O$$
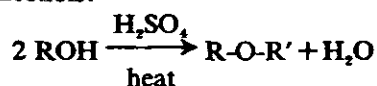
Ethers, as compared with alcohols are fairly inert.

Aldehydes and *ketones* are carbonyl compounds having one and two alkyl groups respectively joined to the carbonyl function:
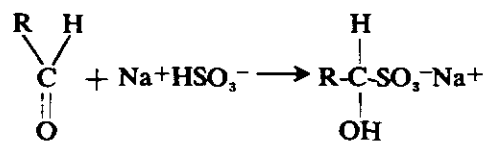

aldehyde   ketone
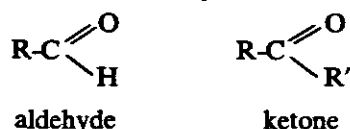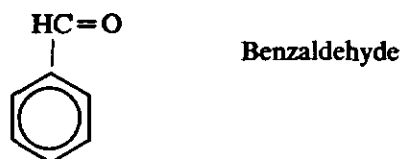
(R and R' may be either aromatic or aliphatic)

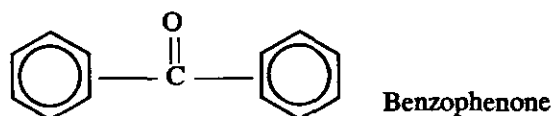These compounds can be prepared by oxidation of alcohols:
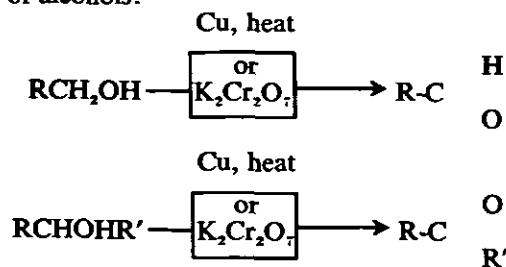
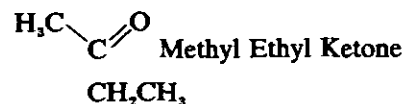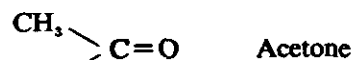The carbonyl group $(-\overset{\overset{\displaystyle O}{\|}}{C}-)$ is primarily responsible for the characteristic reactions of these compounds which can be oxidized to carboxylic acids or reduced to alcohols. They also undergo addition reactions involving the carbon-oxygen bond such as the analytically important one with sodium bisulfite:


Some common aldehydes are:

HCHO   Formaldehyde

CH_3CHO Acetaldehyde

$CH_2 = CHCHO$ Acrolein

             Benzaldehyde

A few common ketones are:

$\begin{array}{c} CH_3 \\ > C=O \\ H_3C \end{array}$ Acetone

$\begin{array}{c} H_3C \\ \quad C \overset{O}{\diagup} \\ CH_2CH_3 \end{array}$ Methyl Ethyl Ketone

          Benzophenone

Carboxylic acids contain a carboxyl group $(-C\overset{\displaystyle O}{\underset{\displaystyle OH}{\diagup}})$ and are acidic in nature. The general formula for monocarboxyl acids is RCOOH where R may be aromatic or aliphatic. These acids can be obtained by the oxidation of primary alcohols, aldehydes or alkyl benzenes.
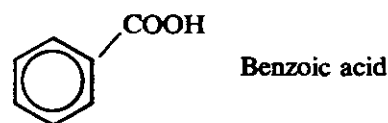
$$RCH_2OH \xrightarrow{KMnO_4} RCOOH$$
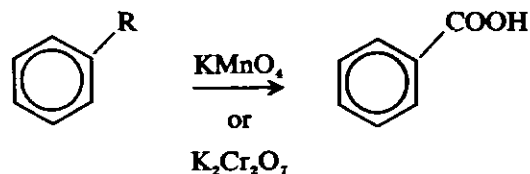
In the reactions that occur, the hydroxyl is usually the reacted group. A typical reaction is one of the type:

$$R\text{-}C\overset{\displaystyle O}{\underset{\displaystyle OH}{\diagup}} + Z \longrightarrow R\text{-}C\overset{\displaystyle O}{\underset{\displaystyle Z}{\diagup}}$$
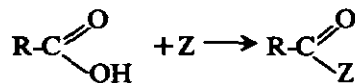
where Z may be Cl, OR', NH_2, etc.

Some of the common acids are:

HCOOH   Formic acid

CH_3COOH Acetic acid

         Benzoic acid

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Isomers are defined as compounds having the same molecular formula but a different structure. There are essentially two major types of isomerism: structural isomerism and optical isomerism. Examples of structural isomers include the pentanes, all of which have the empirical formula C_5H_{12} but different physical and chemical properties:

$$CH_3-CH_2-CH_2-CH_2-CH_3$$
n-pentane

iso-pentane   neopentane
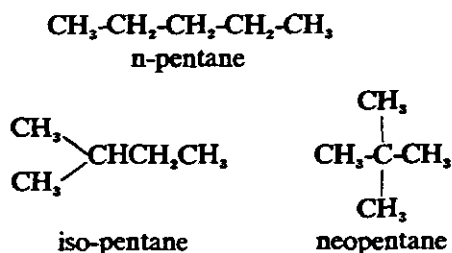
A more striking example of structural isomerism is the compound C_2H_6O. This can be the molecular formula for methyl ether CH_3OCH_3, or ethyl alcohol CH_3CH_2OH, two compounds showing marked differences in physical and chemical properties.

Optical isomers involve a central atom to which a number of different groups are attached. Two optical isomers are molecules which are identical except for the spatial orientation of the groups attached to the central, asymmetric atom. They are mirror-images of one another. The most readily observed difference between the two is the difference in the rotation of the plane of polarization if a beam of plane-polarized light is allowed to pass through a solution of the compound. This type of isomerism is useful in identifying certain biochemical reaction products.

ANALYTICAL CHEMISTRY

The analytical methods used in industrial hygiene may be divided into classical chemical methods and instrumental methods. Such a distinction is based more on the historical development of analytical chemistry than on any clear differences between the two methods, as both the strictly chemical and the instrumental methods usually are completed with a physical measurement, such as spectrophotometry. It is possible to further separate the classical chemical methods as volumetric or gravimetric.

Classical Chemical Methods of Analysis

A *volumetric analysis* is one which is completed by measuring the volume of a liquid reagent of known concentration required to react completely with a substance whose concentration is being determined. The chemical reaction must be such that the amount of the known reactant can be related exactly to the amount of the analysis substance present. A reaction, to be useful for volumetric analysis, must be rapid, complete and have a sharp endpoint. Two basic types of reactions may be considered as representative of volumetric analyses.

Acidimetry and *alkalinity* reactions involve the neutralization of acids and bases. A titrimetric procedure is used to determine the amount of a standard solution of a reagent (i.e., one of precisely-known concentration) required to react

completely with a specific chemical substance in a prepared solution of a sample.

Titrations dependent upon neutralization reactions must be complete at a definite endpoint based on an abrupt change in pH which occurs at the equivalence point. An example of a neutralization reaction in an aqueous system is the following:

$$NaOH + HCl \longrightarrow NaCl + H_2O$$
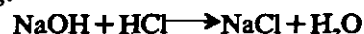
When the hydrogen ion (H^+) and hydroxide ion (OH^-) concentrations are equal, the solution is said to be neutral (pH 7.0 aqueous solution). However, the actual pH at the equivalence point of an acid-base titration is not necessarily equal to 7.0, since it depends on the degree of ionization and hydrolysis of the products of the reaction.

The majority of titrimetric procedures use an indicator to determine the endpoint accurately. An indicator is generally a complex organic compound having a weakly acidic or basic character capable of a sharp transformation in color over a definite, but narrow, pH range. Several factors play a role in determining the pH interval over which a given indicator exhibits a color change:

1) Temperature,
2) Electrolyte concentration (total ionic strength),
3) Effect or organic solvent systems.

Two sources of error that may occur when determining the end-point of a titration using visual indicators are:

1) The indicator does not change color at or near the hydrogen ion concentration that prevails at the equivalence point;
2) Very weak acids (or bases) cannot be titrated with satisfactory results.

The first of these sources of error can easily be corrected by using a blank. The second, however, cannot be remedied because of the difficulty in deciding exactly where the color change occurs.

The other type of chemical reaction suitable for titrimetry is called *oxidation-reduction* or *"redox."* The ions of a large number of elements can exist in different oxidation states. Suitable oxidizing or reducing agents can cause a redox reaction with such ions. Many of these reactions satisfy the requirements of volumetric analysis.

One of the most widely used oxidizing agents is potassium permanganate ($KMnO_4$). It has an intense purple color which can serve as its own indicator for the endpoint. The reagent will oxidize metallic ions from low to high oxidation states and negative ions such as chloride to chlorine at the zero or ground state. Its use in some reactions is restricted due to the multiplicity of possible reactions that may occur in the presence of more than one oxidizable substance.

Potassium dichromate ($K_2Cr_2O_7$) is another important oxidant. It is not as powerful as potassium permanganate and some of its reactions proceed slowly. However, the solid reagent can be obtained in high purity and stable, reliable solutions may be prepared conveniently. Dichromate solutions are most useful for titrations carried out in 1 to 2 normal acid or alkaline solutions.

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A substance which is useful both as an oxidizing and as a reducing agent is iodine, generally used in the form of the triiodide ion, I_3^-, which is formed by the reaction of iodine, I_2, with the iodide ion I^-. The indirect or iodometric methods involve the treatment of a solution with an excess of iodine and then measuring the amount of iodine used. Starch is an indicator for iodimetry and iodometry. Iodometry is used regularly for the determination of aldehydes and hydrogen sulfide collected in sampling reagents of sodium bisulfite or ammoniacal cadmium sulfate, respectively.

Gravimetric analyses constitute another important group of analytical methods for determining substances quantitatively. A gravimetric method is one in which the analysis is completed by making a weight determination. A gravimetric procedure requires that the analytical substance must be separated quantitatively from other chemical entities in the sample. Numerous techniques are available for this separation. These include precipitation, solvent extraction, volatilization, complexation and electrochemical separations.

Precipitation methods are the most common gravimetric procedures. However, all precipitates are not suitable for gravimetric analysis. The precipitate must have a sufficiently low solubility to insure that the solubility losses do not affect the results of the analysis seriously. Further, it must be possible to isolate the precipitate quantitatively from the liquid by simple, rapid filtration and to free it readily of contaminants by a simple treatment. The exact chemical composition of the precipitate must be definite to allow calculation of the component of interest. Ideally, the precipitate should not be hygroscopic and should have a large molecular weight relative to the analytical constituent contained therein.

Solid-liquid solvent extractions involve both simple removal of impurities by dissolving them from the desired precipitate and the reaction of the solvent with a component to make it either soluble or insoluble. Soxhlet extractions are good examples of the latter technique. Organic solvents find considerable application to this type of extraction.

Liquid-liquid extractions make use of two mutually immiscible liquids to redistribute the desired solute on the basis of differences in solubility. The extraction of a metallic salt from an acid solution into an organic solvent is one example.

Solid-gas extractions are used to remove a desired gas from a mixture of gases. Adsorption of volatile organic compounds from the air by activated carbon is an example of solid-gas extraction.

Another useful technique in gravimetric analysis involves the use of *volatilization* methods. Simple examples include the determination of water by loss on ignition and the decomposition, evolution and subsequent weighing of carbon dioxide. Volatilization methods can be classified either as evaporation and/or sublimation or as distillation and aeration procedures. The drying of a sample to remove water and the separation of aluminum chloride are accomplished by evaporation and sublimation techniques, respectively.

In the case of liquid mixtures of organic substances, the individual components may be separated effectively by distillation at atmospheric pressure or under vacuum. The determination of carbonate by the generation and removal of carbon dioxide followed by subsequent weighing is an example of a gravimetric aeration technique.

Elemental substances may be separated from other substances and metallic constituents deposited quantitatively by electro-chemical separations. In electrolytic methods, a pure deposit that adheres firmly to the electrode is required. Temperature, the presence of complexes and the evolution of hydrogen affect the quality of a deposit. Deposits obtained from complex ions in solution tend to be dense and adherent. Heating and stirring the solution during electrolysis speeds up deposition as a result of higher current densities. When the material has been completely deposited, it may be dried and weighed.

Instrumental Methods of Analysis

The final measurement in an analytical determination has been greatly facilitated in recent years by the use of highly sophisticated instrumentation. The industrial hygienist should never lose sight, however, of the preparatory work necessary before the final measurement can be made. Instrumentation is available for the qualitative and quantitative analysis of both inorganic and organic compounds.

The basic feature of *ultraviolet and visible spectrophotometry* is the selective absorption by aqueous and other solutions of definite wavelengths of light in the ultraviolet and visible regions of the electromagnetic spectrum. The fundamental law governing ultraviolet-visible absorption photometry is Beer's Law which relates the absorption of light linearly to concentration:

$$A = kC$$

"A" is the absorbance of the solution, "C" is the concentration and "k" is a constant whose value depends upon the wavelength of the radiation, the nature of the absorbing system, and the optical path length or cell thickness. Absorption data for spectra are usually recorded in terms of absorption versus wavelength. Wavelengths used for analysis are those at which the substance absorbs strongly. Ultraviolet and visible spectrophotometry is used in occupational health laboratories for the determination of inorganic substances and numerous organic contaminants of air, urinary metabolites and such blood components as carboxyhemoglobin and circulating heavy metals.

Infrared spectrophotometry makes analytical use of the molecular vibrations and rotations in chemical substances exposed to radiation from the infrared region of the spectrum. The atoms within a molecule vibrate and rotate at definite frequencies which are characteristic of that molecule. A sample placed in a beam of radiation in a dispersive infrared spectrophotometer absorbs energy at certain definite frequencies characteristic of the molecular components in the sample cell and will transmit the other frequencies. The absorption (or transmittance) within a specific frequency

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range may be correlated with the specific motions of the functional chemical groups of a molecule to identify their presence or absence.

No two compounds with different molecular structures can have identical infrared spectra. Hence, the infrared absorption spectrum is a characteristic physical property (it is often termed a "fingerprint") of a compound, and it is a powerful tool in both qualitative and quantitative analyses, particularly for organic compounds as well as for certain inorganic structures, notably CO, SiO, and NO bonds. Quantitative analysis may be performed on a sample by selection of a specific absorption band whose response varies directly with the concentration of a given chemical species.

X-ray diffraction and fluorescent methods are based upon physical properties related to the atomic numbers of the constituent atoms in chemical compounds and not on any chemical properties of these substances.

When monochromatic x radiation strikes a crystalline material, the planes of the atoms in the material diffract the x ray beam at angles which depend upon the interplanar spacings in the crystal lattice. An appropriate x-ray spectrometer is used to scan and measure the wavelength and intensity of the diffracted rays. The resulting *x-ray diffraction* pattern is characteristic of the components of a sample, and crystalline materials, such as quartz (a form of free silica) or asbestos can be identified readily in mixtures of compounds. The sample patterns are compared with those of standards to identify and measure quantitatively the crystalline components of a sample.

X ray fluorescence is produced by an element which is irradiated by an intense beam of x rays. This fluorescence is observed as secondary x rays whose wavelengths are characteristic of that element. An x-ray spectrometer can be used to disperse the emitted secondary x rays and elements identified in the resulting spectrogram. Analytical curves are prepared from standard series of the pure compounds and the elemental constituents determined quantitatively. Errors of less than five percent are common with this method. The sensitivity (limit of detection) will vary from a few parts per million by weight to one percent depending on the element and the matrix material.

Emission spectroscopy and *atomic absorption spectrophotometry* are complementary techniques for the determination of atoms, ions, and a few molecular substances. The region of the electromagnetic spectrum involved includes the near infrared, the visible and the ultraviolet. The methods for analysis make practical use of this radiation for both qualitative and quantitative determinations.

Flame emission and emission spectrographic techniques are based upon the excitation of atomic and ionic species to higher energy levels from which states they emit characteristic wavelengths of light as they return to their individual ground states. In flame emission, the sample solution is aspirated into a flame and certain wavelengths are monitored to detect characteristic emissions. An emission spectrograph uses electrical energy to excite the atomic (or molecular) species in a solid or liquid sample. The complete emission spectrum is dispersed with a diffraction grating or a prism. The spectra are detected by phototubes or are recorded on a photographic emulsion supported on a plate or film. The recorded spectrograms are examined in a comparator-densitometer using qualitative and quantitative standards of reference. Flame emission spectroscopy is also used for quantitative analysis since the amount of light emitted at a characteristic wavelength is proportional to the concentration of element.

Atomic absorption spectrophotometry makes use of the property that the atomic vapors of an element will absorb that element's characteristic radiation in proportion to its concentration in a flame. The sample is aspirated in solution form into a flame as in flame emission spectroscopy. The operating principle is based upon the decrease in the intensity of a monochromatic beam of light from a hollow cathode lamp or other source consisting of the same elemental substance. Atomic absorption is used mostly for quantitative analyses and, as with flame emission and arc and spark emission spectroscopy, it is valuable for the determination of metallic and metal-like elements in any type of sample which can be solubilized.

The term *gas* or *vapor phase chromatography* includes all chromatographic separation techniques using a gas as the mobile phase. Gas-liquid chromatography (GLC) makes use of a liquid distributed over the surface of a solid support as the stationary phase in the form of a column and a gas (helium, argon, nitrogen or hydrogen) as the mobile phase. The injected sample is vaporized and transported onto the column with one of the common carrier gases. The stationary phase adsorbs the sample components but not the carrier gas. Different compounds in the sample are retained to varied degrees by the stationary phase; hence, they pass through the column at different rates. The mobile carrier gas phase, which flows continually through the column, carries the different sample components through the column to appear in turn at a detecting device used in establishing the retention times of the individual compounds and in providing a signal for amplification to a recorder or integrator for a quantitative analysis. The output is recorded as a series of peaks on a strip chart recorder or fed to an electronic integrator for direct readout. The elution time is a function of the component, the particular stationary phase and the column temperature.

When the separate sample components have been identified, standardization of the GLC method is performed with a series of gas or vapor standards under identical chromatographic conditions. Measurement of peak areas, preferably by electronic integrators, provides the basis of quantitative analysis. This instrumental technique is extremely useful for the determination of organic contaminants in ambient and industrial atmospheres.

A wide variety of *electrochemical methods* depend on the phenomena that occur within an electrochemical cell. One electrochemical method that is used for specific analyses is polarography or voltametry in which the current passing through

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a solution is measured as a function of the applied voltage. Essentially every element and many organic functional groups may be responsive to polarographic analysis. The polarographic behavior of any substance is unique for a given set of experimental conditions. If an unknown substance can undergo either cathodic reduction or anodic oxidation, qualitative and quantitative analysis is possible. Polarographic recordings, called polarograms, are obtained by measuring the current and the applied voltage between a special type of polarized microelectrode and a non-polarized reference cell. Typical applications of polarography include the analysis of samples for lead, cadmium, zinc or mercaptans.

A second electrochemical technique useful in many applications is based upon the use of ion-selective electrodes. These electrodes are used for the measurement of several cations (positive ions) and anions (negative ions) in solution including K^+, Na^+, Ag^+, H_3O^+, Cl^-, F^- and NO_3^-.

Three types of electrodes in common use are glass, liquid and solid state membrane electrodes. Glass membrane electrodes depend on the presence of certain compounds in glass to render them useful for the determination of certain ions. One of the properties of the glass electrode is its highly selective response to hydrogen ions when used as a pH electrode. Other glass membrane electrodes are available for the determination of ions such as sodium, potassium and calcium. Liquid membrane electrodes respond to a potential established across the interface between the solution to be analyzed and an immiscible liquid that bonds selectively with the specific ion. This type of electrode has been developed for the perchlorate and nitrate ions. Solid state membrane electrodes have the opposite property of glass (i.e., useful for measuring anions); have been developed recently and their operation depends upon the principle of selective precipitation. Thus, the fluoride ion electrode consists of a single crystal membrane of lanthanum fluoride supported between a reference solution and the sample solution. Specific ion electrodes are so closely related to pH electrodes that they tend to be affected by acidity or basicity changes; however, these effects can be overcome by buffering an unknown sample to a pH near the neutral point. The sensitivity of these electrodes depends upon each particular type.

Only a few of the analytical methods available to occupational health have been discussed. Subsequent chapters will elaborate on analytical principles and techniques in greater detail, particularly with regard to applications in occupational health. In addition, the list of recommended texts for additional reading should be consulted regularly.

Suggested Further Reading

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