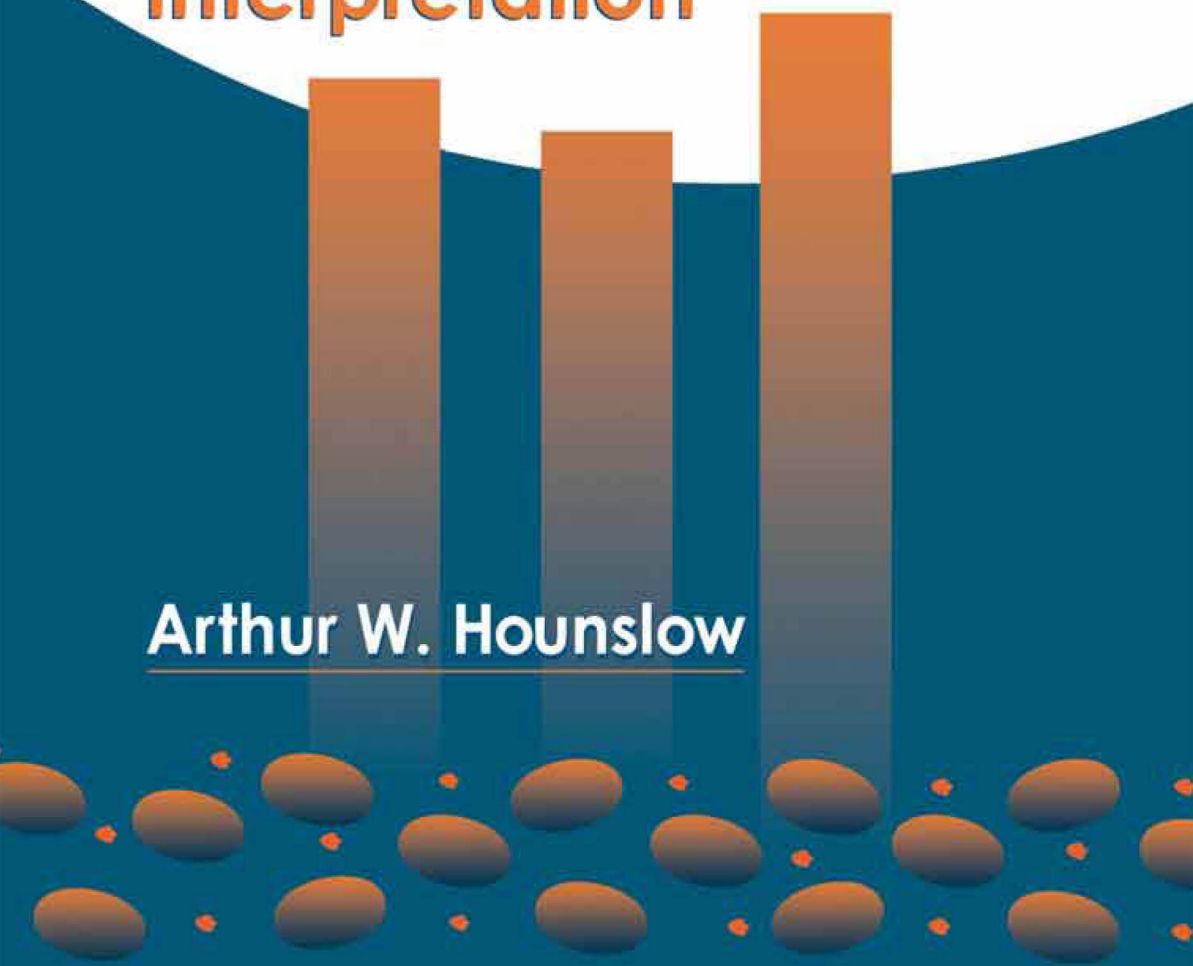
WATER QUALITY DATA

Analysis and Interpretation



Arthur W. Hounslow

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PREFACE

The purpose of this text is to help bridge the gap between "standard" geology and geochemistry and the present job requirements of hydrogeologists in their evaluation of various water-pollution scenarios.

Many geologists enter the field of geology because they enjoy geology, are not too good at math, and dislike chemistry. Through their course of study, they soon become aware that water has many facets depending on one's point of view. Those of a biologist differ dramatically from those of a geologist. Even geologists consider the many aspects of water from different perspectives. A geomorphologist looks at the geomorphic cycle, a sedimentologist the transportation of sediments, a hydrologist the distribution and movement of water, and a low-temperature geochemist the distinctive chemical composition of the water.

Now, because of interest or economic reasons, geologists (and others in related sciences) are being trained (or retrained) in record numbers in the field of hydrogeology and pollution evaluation. They must become acquainted with complex mathematical models and be able to discuss, sometimes in court, fairly sophisticated chemical concepts.

The primary emphasis in this book is the interpretation of a water analysis or a group of analyses, with major applications on groundwater pollution or contaminant transport. It is assumed that at some stage in a hydrogeologic investigation, a series of water analyses will appear and have to be interpreted. Thus, the emphasis will be on the evaluation of the analyses rather than analytical techniques. A computer program (WATEVAL) aids in obtaining accurate, reproducible results, and helps alleviate some of the drudgery involved in water chemistry calculations.

This book is divided into nine chapters, and includes computer programs applicable to all the main concepts presented. After introducing some of the more fundamental aspects of water chemistry, the main emphasis of the book is on the interpretation of water chemical data.

Chapter 1 stresses the interrelationships between chemistry and geology. The dependence between the feedstocks available to the chemical industry and the occurrence of possible pollutants are also highlighted. Finally, the relationships between the various aspects of geochemistry are discussed.

Chapter 2 briefly reviews some basic geology and chemistry needed to understand the remainder of the text.

Chapters 3 and 4 discuss the origin and interpretation of the major elements, and some minor ones, that make up the main constituents of the dissolved inorganic components of a water—the water quality. The objective here is to use a water analysis to interpret the history of the water. Groundwater is stressed, although the techniques may be applicable to surface water. Inorganic water chemistry is also a useful finger-printing tool, when dealing with organic contamination.

Chapter 5 introduces the reader to the elementary thermodynamics necessary to understand both the use and results from water equilibrium computer programs.

Chapter 6 briefly discusses the range that may occur in some of the common water chemistry parameters, particularly pH and pe.

Chapter 7 is devoted to organic chemistry, particularly the naming of the simpler and environmentally important organic chemicals. Many of the chemicals included are important water contaminants. Others are included, however, to enable the reader to continuously use

the skills learned in everyday life, for example, reading food and drug labels listing organic compounds. A computer flash card system is included as a teaching tool for learning organic nomenclature.

Chapter 8 discusses methods of estimating the distribution of organic chemicals in the environment. Again, a computer program (ECOPLUS), aids in the calculations and presents some computer graphics to help convey the concepts.

Chapter 9 is devoted to the explanation of the computer programs included with the book.

The book grew as a result of my teaching experiences, aimed in large part, at adults returning to graduate school for retraining as hydrogeologists. I would like to thank those many students who made suggestions, corrected errors, and who in the end led me to the current presentation philosophy of teaching a complex topic in such a way that they could grasp challenging concepts despite a lack of possible prerequisites and recent formal education.

Wayne Pettyjohn, while head of the School of Geology at Oklahoma State University, was primarily responsible for initiating the writing of this book, as well as suggesting ways to make the computer programs more "user friendly." His encouragement, help, and friendship is deeply appreciated.

Phyllis Garman, a consulting hydrogeologist in Joelton, Tennessee, undertook the odious task of editing the entire book, and to her I owe a huge debt of gratitude.

Many thanks also to Kelly Goff, a computer programmer at Oklahoma State University, who assisted in writing some of the computer programs and who also reviewed chapter 9.

I would also like to extend sincere thanks to the following people, who reviewed sections of the book. Their invaluable contributions are greatly appreciated. They are:

- William Back, geochemist, U.S. Geological Survey, Reston, Virginia
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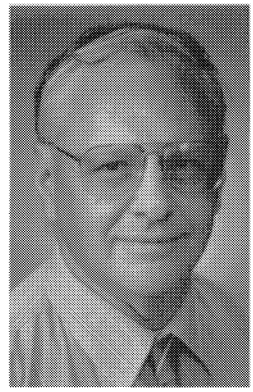
- John Veenstra, professor, Civil Engineering, Oklahoma State University
- Frank Wobber, geologist, U.S. Department of Energy, Washington, D.C.

Last, but by no means least, I would like to thank my wife Madeleine for her patience, help, encouragement, and love, for without these, this book would never have been written.

Arthur W. Hounslow

THE AUTHOR



Arthur W. Hounslow, Ph.D., is a geochemist with research interests in the interpretation of water quality data including brines, occurrence and mobility of trace elements, and organic pollutants. His primary philosophy is that computers are essential to reduce the drudgery of calculations and potential mistakes that often result from hand calculations, but only after understanding the logic behind the computer program. Areas of expertise encompass the prediction of rock water interactions, materials analysis, mineral chemistry, industrial mineralogy, assessment of groundwater retardation and biodegradation, and the determination of sources of pollutants and their environmental distribution.

Dr. Hounslow has scientific expertise resulting from over 30 years' diversified work experience in Australia, Canada, and the United States including seven years in industry, seven years in government agencies, and 17 years in teaching. He has been writing computer programs for over 30 years, has 25 published papers and reports, as well as numerous unpublished reports. Recent experience includes expert witness testimony for a variety of brine and organic pollutant litigations. Over the last seven years he has presented or was a major presenter in 42 short courses held throughout the United States. He teaches undergraduate courses in introductory geology, mineralogy, optical mineralogy, and graduate courses in organic geochemistry, environmental geochemistry, and trace elements in hydrogeology.

He obtained Fellowship and Associate Diplomas in chemistry and geology, respectively, from the Royal Melbourne Institute of Technology, and a B.Sc. degree from The University of Melbourne. Graduate studies in Canada led to M.Sc. and Ph.D. degrees from Carleton University, Ottawa. He served as a geochemist with the Robert S. Kerr Environmental Research Laboratory of the United States Environmental Protection Agency, was a senior project mineralogist with the Colorado School of Mines Research Institute, an analytical chemist with the Australian Government Agency, Commonwealth Scientific and Industrial Research Organization (CSIRO), and was an organic analyst with Imperial Chemical Industries of Australia and New Zealand (ICIANZ). He is a registered geologist in Oregon and is presently Professor of Geology at Oklahoma State University.

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CHAPTER 1

Introduction

INTRODUCTION

This text covers two somewhat different fields of water chemistry, namely, inorganic water geochemistry and organic geochemistry. When dealing with problems of environmental pollution it is necessary to integrate both of these areas if a solution to pollution problems is to be successful.

Whereas the background water quality is primarily one of inorganic geochemistry, many pollution problems arise from the manufacture of organic compounds and the use of trace metals in industrial processes. Considerable research, in what has been called organic geochemistry, has been conducted in areas relating to the origin of petroleum. It has included topics such as water washing and microbiological degradation of crude oil. Pressing environmental problems now center about the leakage of petroleum refinery products from underground storage tanks, the measurement of the fraction dissolved in water from nonaqueous phases, and the rate of microbiological degradation. In the past, considerable work has been conducted relative to the discovery of metalliferous ore deposits by using geochemical prospecting methods. Now the emphasis is on the transport and fate of a variety of toxic trace metals from known sources.

Some aspects of the various approaches to water chemistry will be discussed below. Several terms used to describe the study of geochemistry from a holistic viewpoint include Environmental Geochemistry, a Canadian term; Landscape Geochemistry, a Russian term; and Geochemical Ecology.

GEOCHEMICAL SPHERES

Geochemists have used the term *geochemical spheres* to describe the various parts of the earth being studied. They include the lithosphere (rocks), pedosphere (soils), biosphere (living organisms), atmosphere (air), hydrosphere (water), and anthroposphere (man's effect on the other spheres), Figure 1.1. The main processes occurring in these various spheres include the hydrologic cycle, which describes the distribution of water on the planet, and the rock cycle, which describes the distribution of rocks. In addition, when studying pollutant transport and fate, other aspects of the system and the various interactions between the various spheres must be considered. Minerals dissolve and contribute to water quality, as do several common gases—CO_2, which affects the pH of water, and H_2S and O_2, which often determine the redox of water. The texture and rock type determine the porosity and permeability of the rocks and hence their aquifer characteristics. The presence and amount of clay minerals, amorphous oxides, and natural organic matter exert a strong influence on the mobility or retardation of both trace metals and synthetic organic pollutants in the groundwater

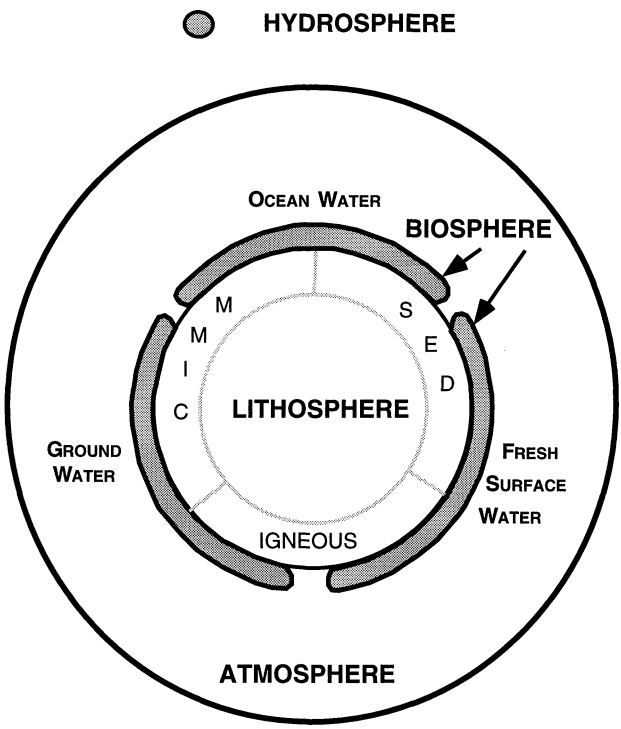


Figure 1.1. Geochemical spheres.

system. The microbiological population affects the biodegradation of synthetic organics, as well as catalyzes many of the redox reactions. These interactions are shown diagrammatically in Figure 1.2.

LITHOSPHERE

Rocks have been examined from various aspects in order to determine the mobility of various chemical elements in them. During the 1940s to 1960s, intensive work was conducted in trying to establish metallogenic provinces. These efforts were hampered by relatively poor analytical precision of trace metal analysis. The most common technique employed was optical emission spectroscopy, a time-consuming and very demanding procedure. This technique has been superseded by modern rapid and inexpensive instrumental methods.

Exploration geochemistry has been concerned with the origin of ore deposits, particularly base metals in the 1960s and uranium in the 1970s. The primary aim is the determination of the mobility of metals in order to determine the source of the metals. Soils were examined for underlying mineralization. Stream sediments were examined by selective screening, preferential dissolution, and heavy liquid separations. These allowed the examination of heavy minerals, adsorbed metals, clays, and coatings.

In agriculture, trace nutrients have been of major concern. For example, the need of Co for the well being of sheep in Australia in the 1940s, and toxic elements, such as Se—a small amount is essential, whereas too much is toxic.

Since the 1970s, pollution abatement and the transport and fate of synthetic organic chemicals has been of major interest. This has involved the determination of where the pollutants are going. Another topic on which the foregoing depends has been called subsurface characterization, that is, the study of constituents adsorbing and retarding the movement of

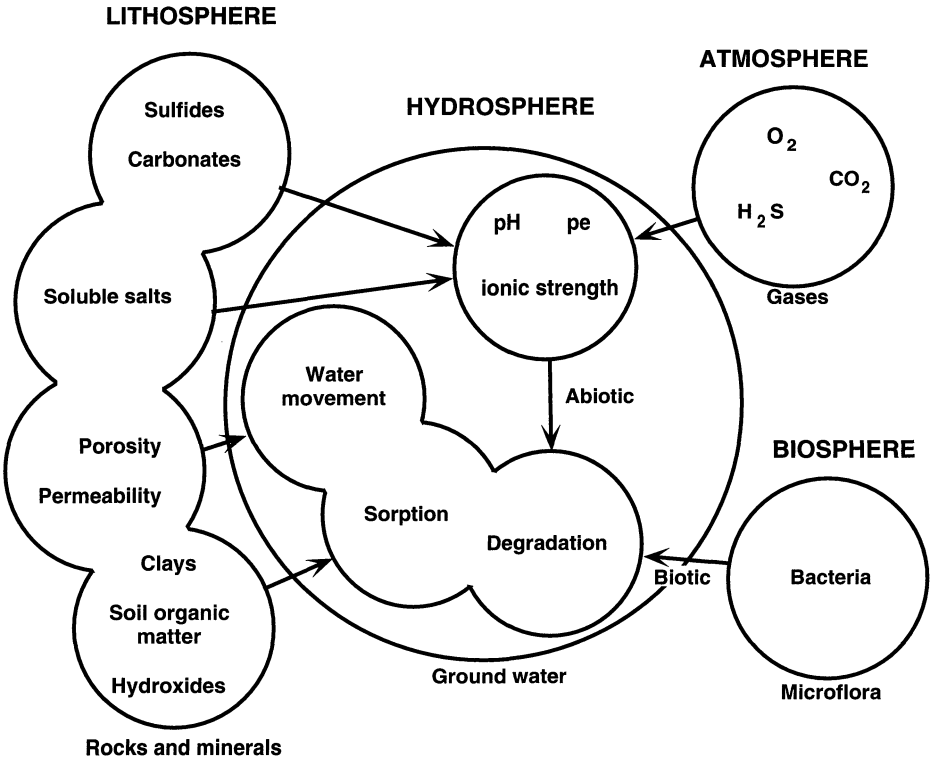


Figure 1.2. Groundwater chemistry.

pollutants. The compounds primarily involved in these processes are natural organic materials, amorphous hydroxides and oxides, and clay minerals.

Groundwater geochemical research involving the lithosphere includes studies of concretions such as gypsum, barite, chert, and agate; red beds; opal and turquoise deposits; uranium deposits, particularly roll fronts; dolomitization; and caliche formation.

The present emphasis on the lithosphere is the release of toxic trace elements during the mining, processing, and beneficiation of the multitude of elements used in our industrial society.

HYDROSPHERE

Water quality data have been collected for many years by the U.S. Geological Survey, as well as state surveys and individual water districts, and more recently by the U.S. Environmental Protection Agency. Surface water sample data dominate. Samples from streams and lakes are easier and much less expensive to collect than groundwater samples. Wells are expensive to install, although springs and seeps allow inexpensive sampling of groundwater in some areas. Streams can also be used to extract groundwater quality data by the mathematical separation of groundwater and surface water components using hydrograph separation techniques.

A major concern with water quality is human health and disease. Cancer may result from excessive Cd, Ni, and Pb. The study of potential carcinogens involves massive data collection and interpretation. Cardiovascular disease is also of great interest, and this involves the study of Ca, Mg, and water softening. Urolithiasis, that is, the occurrence of kidney stones, because of the build-up of Ca oxalate and Ca phosphate is also of continuing interest. The hydrosphere

contains the drinking water of the world. Therefore, the primary interest is to keep drinking water supplies free of toxic contaminants, whether they be heavy metals or trace amounts of toxic organic contaminants. In addition to the detection and attenuation of these compounds, the major concern is in the determination of their mobility.

ATMOSPHERE

Changes in the atmospheric composition of the earth can effect the climate of the earth directly. Excess CO_2 may increase its temperature via the greenhouse effect. Chlorofluorocarbons are important in ozone depletion, and hence, ultraviolet radiation onto the surface of the earth. Air pollution also results from CO, SO_2, NO_2, CO_2, and hydrocarbons, which produce peroxy acyl nitrate the main ingredient of smog. Atmospheric gases also affect water quality in a number of ways. Oxygen is a dominant redox buffer, and CO_2 affects the pH-buffering capacity. N_2 and the nitrogen cycle are also important redox variables. Acid rain results primarily from SO_3 and SO_2 produced by smelting and coal-fired furnaces, as well as some contributions from nitrogen oxides.

BIOSPHERE

Organic chemistry is the chemistry of carbon. During the history of the earth carbon has occurred in the various geochemical spheres. It is present in the atmosphere as CO_2, CO, and CH_4, in the lithosphere as carbon (graphite or diamond), carbonates (RCO_3), and as coal, petroleum, oil shale, and soil organic matter (SOM); in the hydrosphere as H_2CO_3, HCO_3^-, and CO_3^{2-} and in the biosphere as lipids, carbohydrates, and proteins. A diagrammatic representation of the carbon cycle is shown in Figure 1.3. The ultimate source of organic

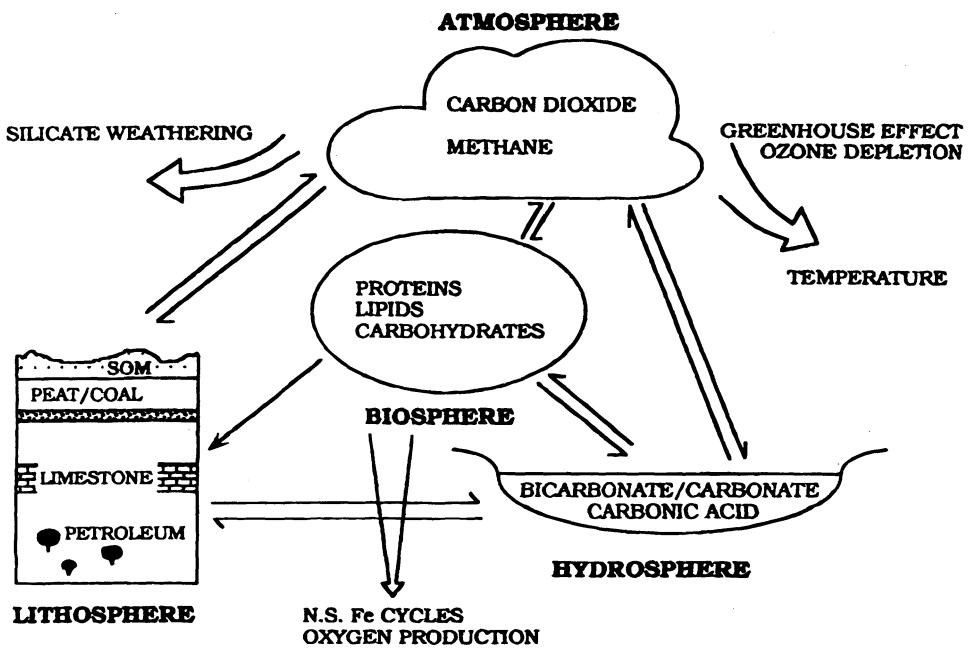


Figure 1.3. Carbon cycle.

compounds is the biosphere, specifically plants. They are formed by the process of photosynthesis by using the energy of the sun. The opposite reaction is respiration (Figure 1.4).

$$\text{plants} + CO_2 + H_2O + \text{energy} \underset{\leftarrow \text{ respiration}}{\overset{\text{photosynthesis} \rightarrow}{}} \text{simple sugars} + O_2$$

The bottom line is that the energy for the biosphere comes from the sun. The concept of a nuclear winter is that if there is no sun, then there is no life. Organic compounds are stored solar energy and may be divided pragmatically into renewable resources or biomass, such as wood, or as nonrenewable fossil fuels, such as oil shale, petroleum, or coal.

Two methods of geochemical prospecting using biosphere materials have been used. These are geobotany, or exploration using indicator plants, particularly for Ag, Au, Cu, Sn, and U. Trace metal anomalies are also traced by examining malformed plants and those with odd colors. The other biosphere technique used is biogeochemistry, whereby part of a plant is subjected to a chemical analysis. This also allows the detection of geochemical anomalies, such as Se in vetch (Astragalus), which was used as an indicator for U on the Colorado Plateau.

Soil Organic Matter

Soil organic matter consists of both humic and nonhumic substances. Nonhumic substances have physical and chemical characteristics that are still recognizable as proteins and carbohydrates. Humic substances, on the other hand, no longer have specific physical and chemical characteristics. Humic substances, the major organic constituents of soils and sediments, are widely distributed over the surface of the earth. They occur in almost all terrestrial and aquatic environments. About 60–70% of the total soil carbon occurs in humic materials. The decay of soil organic matter provides the largest CO_2 input into the atmosphere. Humic substances arise from the chemical and biological degradation of plant and animal residues and from the synthetic activities of microorganisms. The products so formed tend to associate into complex chemical structures that are more stable than the original materials.

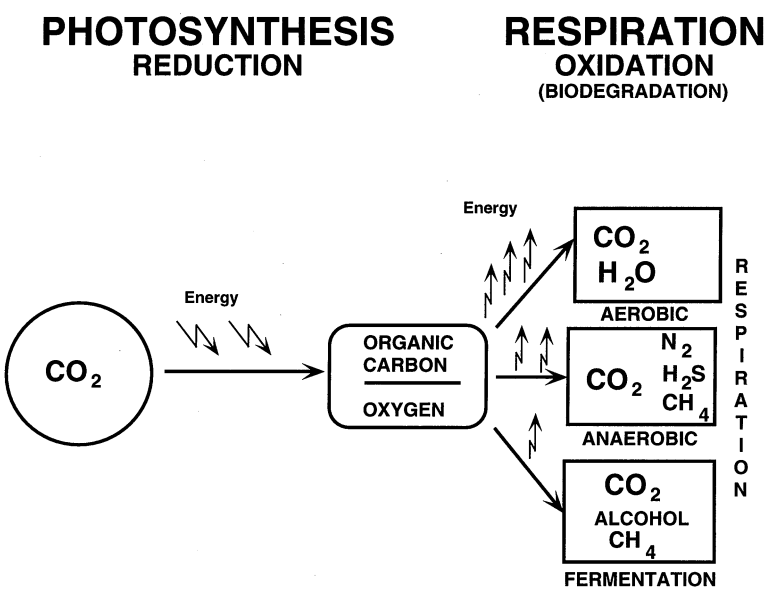


Figure 1.4. Photosynthesis and respiration.

Important characteristics of humic substances are their ability to form water-soluble and water-insoluble complexes with metal ions and hydrous oxides, and to interact with clay minerals and organic compounds. Humic substances are dark-colored, acidic, predominantly aromatic, hydrophilic, chemically complex, polyelectrolyte materials that range in molecular weight from a few hundred to several thousand. They are composed of three fractions:

1. Fulvic acid, which is soluble in both dilute alkali and acid.
2. Humic acid, which is soluble in dilute alkali, but precipitated on acidification.
3. Humin, which cannot be extracted by either dilute acid or alkali.

All are structurally similar, but differ in molecular weight, ultimate elemental analysis, and functional group content. Fulvic acid has the lowest molecular weight, more oxygen, less carbon and nitrogen, and more oxygen-containing functional groups. The structure of humin and humic acids is similar. The insolubility of humin is because it is firmly adsorbed on or bonded to inorganic soil and sediment constituents. The resistance to microbial degradation of humic material is possibly due to the formation of stable metal and/or clay organic complexes.

ANTHROPOSPHERE

In the 19th century the chemical industry centered around inorganic products obtained from minerals, especially salt and sulfur, and the refining of natural organic products, such as fats, soaps, and dyes. Some organic products were based on the fermentation of agricultural products, such as alcohol and acetic acid. During the 20th century there was rapid development in the production of organic chemicals based on coal. The coal-tar industry produced dyes, drugs, and other materials. The petrochemical industry began during World War I and progressed through the 1920s. However, it expanded rapidly during World War II because of the need for strategic materials, such as rubber and gasoline. Increase in the demand for gasoline was the main impetus in the U.S. It was much less in Europe, where there were far fewer automobiles. The diagrams and discussions in this chapter are given for the purpose of introducing the reader to the scope of industrial production using relatively simple starting materials. Many important industrial processes are not discussed, and some of those discussed may no longer be important industrially, even though they have been in the past.

INDUSTRIAL RAW MATERIALS

The feedstocks of industry are many and varied and tend to change over time, depending on new discoveries and economics. The primary sources of industrial raw materials are discussed briefly below.

BIOMASS

Fats and Oils

Fats and oils are triglycerides of C_{16} and C_{18} acids, consisting of glycerol and fatty acids (long-chain carboxylic acids). They may be saturated or unsaturated. Essential oils are volatile or aromatic oils, perfumes, or flavors. Soaps are obtained by hydrolyzing fat with NaOH or KOH (lye). NaOH is obtained from the electrolysis of brine. Glycerin is a soap by-product.

Sugar

Sugar is used extensively in the food industry. The main sources are cane sugar, beet sugar, and waste liquor—blackstrap molasses.

Starch

Starch is the principal energy reserve of the plant kingdom and is used to obtain ethanol (fermentation), citric acid, and lactic acid. Starch is the staple food of mankind, usually in the form of flour. Starch is also used as a source of sugar. Corn syrup (acid hydrolysis of starch), which is a high-fructose corn syrup, is much sweeter than glucose and as sweet or sweeter than sucrose. It is made by the conversion of glucose to fructose by using enzymes—a process developed in the 1960s. Starch is also a feedstock for the production of alcohol, either as a beverage or gasohol. Several enzymatic processes are involved in the conversion of starch to alcohol.

Wood

The major products of wood include lumber for construction, fuel, and pulp for paper manufacture. Methanol and acetic acid are obtained by dry distillation of wood (in the absence of oxygen), and vanillin is derived from the lignin. Some of the minor products obtained from wood include resins, tannins, turpentine, essential oils (perfume industry), natural rubber, and charcoal. Hardwoods also yield acetic acid, methanol, and acetone (Figure 1.5). Cellulose, used in the manufacture of paper, requires the removal of lignin from wood. It is also obtained from fibers in the form of cotton (seed hairs) and linen (stem fibers of flax plant). Rayon is obtained by dissolving and reforming cellulose. Sheets of such reformed cellulose are called cellophane. Acetate (cellulose acetate) is modified cellulose and releases acetic acid on heating.

COAL

Coal may be used directly as a fuel or indirectly as a nonfuel to produce a more convenient or more efficient fuel by carbonization, gasification, or hydrogenation. It has also been used to obtain a variety of compounds by the chemical treatment of coal tar (Figure 1.6). Many of the major constituents of coal tar are now known to be important carcinogens.

Carbonization

Carbonization produces coke residue and volatile matter. At low temperatures, that is, below 600°C, carbonization produces 15–22 gallons of tar per ton of coal. At high temperatures, above 600°C, carbonization produces 9–14 gallons of tar per ton (approximately 5%). However, this results in the maximum coke production. Coke is used extensively in metallurgy. The reaction of coke and lime in a high-temperature electric furnace produces calcium carbide, which, when treated with water, produces acetylene. This is the coal-base, synthetic route to many organic compounds. It does require high energy usage. The reactions are

$$CaO + 3C \rightarrow CaC_2 + CO$$

$$CaC_2 + H_2O \rightarrow CaO + C_2H_2$$

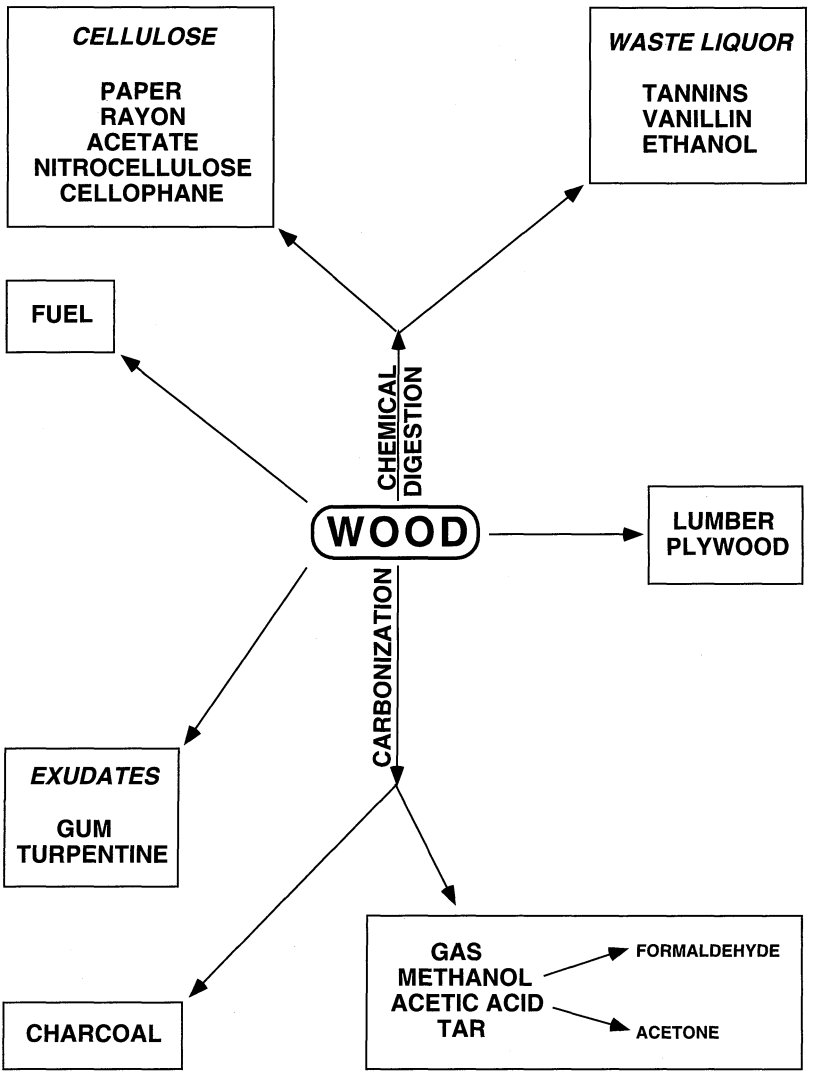


Figure 1.5. Chemical obtained from wood. (Adapted from Jubb, 1975.)

Gasification

Heating of coke in the presence of oxygen (O_2 or air) and/or water (steam) yields carbon monoxide, hydrogen, and methane. The amount of carbon dioxide, which does not burn, is minimized. Increased pressure favors the formation of methane (Lurgi process), and high temperature favors the formation of carbon monoxide.

Hydrogenation

In 1869 Berthelot converted coal to oil by using nascent hydrogen. In 1913 the process was performed catalytically by using molecular hydrogen. When comparing carbonization with hydrogenation, it is apparent that carbonization results in 8–10% tar, whereas hydrogenation yields 75% synfuel.

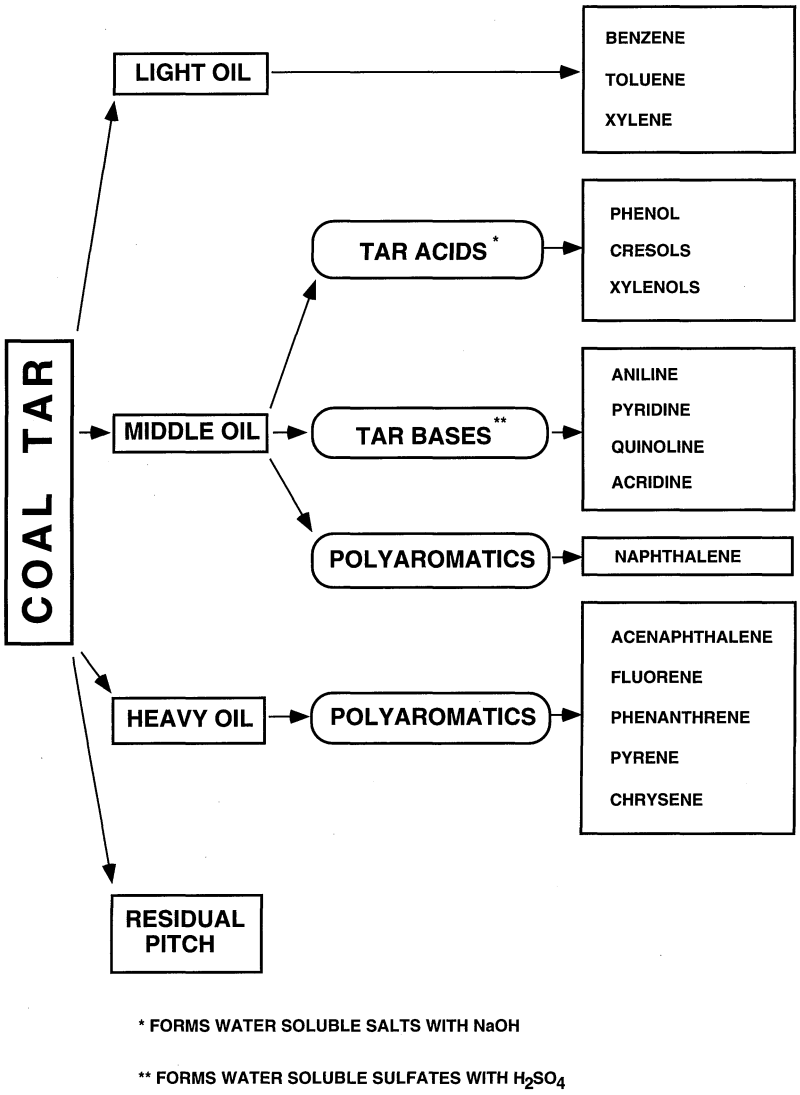


Figure 1.6. Products from the distillation of coal tar. (Adapted from Jubb, 1975.)

CRUDE OIL

Crude oils may be processed by either of two basic processes—fractional distillation, whereby the original composition of crude oil is retained, or refining, which results in new products being formed. The composition of crude oil and some of its products is shown diagrammatically in Figure 1.7.

Fractional Distillation

Fractional distillation is dependent on the fact that the boiling point of hydrocarbons is directly related to their molecular weights. The gasoline fraction of crude oil processed by fractional distillation is usually much smaller than desired, and the number and variety of products are too few. In order to overcome these problems, the larger hydrocarbon chains

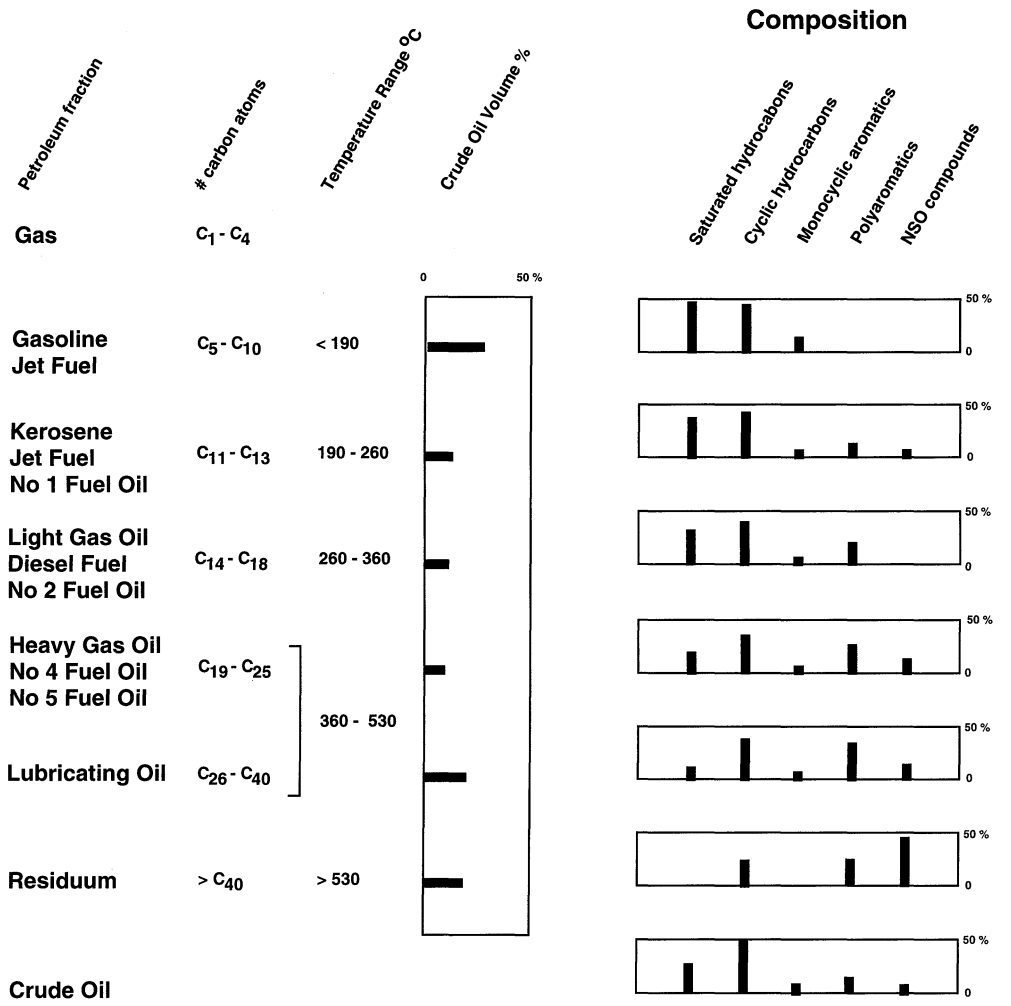


Figure 1.7. Crude oil and its products. (Data from Hunt, 1979, and Speight, 1980).

present in crude oil are broken into smaller pieces by using a variety of catalysts—a process called cracking. The kerosene fraction distilled at 150–300°C is often used for illuminating purposes. Paraffin wax is a major constituent of the lubricating oil fraction of petroleum. As it is a nonlubricant, which raises the viscosity of oil, it must be removed.

Refining

Refining modifies the nature of crude oil constituents by the following processes:

1. Cracking —Breakdown of large molecules to small molecules
2. Reforming —Molecular rearrangement
3. Alkylation —Increase in branching (higher octane rating)
4. Polymerization —Small molecules to large molecules
5. Isomerization —Straight chains to branched isomers

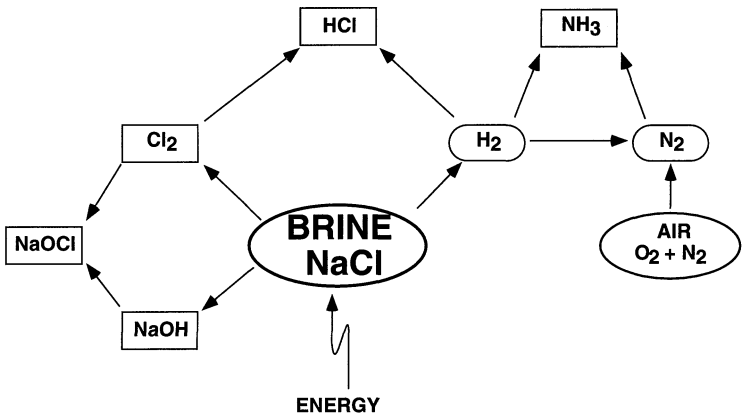


Figure 1.8. Products obtained by the hydrolysis of sodium chloride.

NATURAL GAS

Natural gas contains gaseous methane and ethane, as well as liquid hydrocarbons, propane, and butane. Some of the common products are

LNG —Liquefied natural gas, methane liquefied for transportation
LPG —Liquefied petroleum gas, a mixture of propane and butane
LRG —Liquefied refinery gas, containing varying amounts of unsaturated C_3 and C_4 hydrocarbons

BRINE-ROCK SALT

The most important source of common inorganic chemicals is brine, either as brine, seawater, or dissolved rock salt. Electrolysis yields chlorine, hydrogen, and sodium hydroxide. Other materials may be synthesized from these starting materials. Some are shown diagrammatically in Figure 1.8. The processes, however, are very energy intensive.

INDUSTRIAL PRODUCTION

The number of organic chemicals produced at the present time is almost overwhelming as any visit to a supermarket or drug store will demonstrate. Polymers probably make up the largest group of these materials, although other products are produced in prodigious quantities. Table 1.1 lists a selection of these products. In contrast, a much smaller number of chemical feedstocks is produced. However, many of these are produced in almost astronomical quantities. In many cases it is these chemicals that lead to many of the current pollution problems. Table 1.2 lists the top 50 or so organic chemicals produced in the U.S. Both the common and IUPAC chemical names are given for future reference.

WASTE PRODUCTS

In any manufacturing process, waste products are produced at every part of the process, from mining the raw materials, through the manufacturing process, to the disposal of the product at the end of its life cycle. Figure 1.9 illustrates this diagrammatically.

Table 1.1. A Summary of Some of the More Common Industrial Products

I. Plastics and elastomers
  Polymerization
  Additives
    stabilizers
    plasticizers
    extenders
    lubricants
II. Fibers
  Natural
    animal
    vegetable
  Regenerated
  Synthetic
III. Color chemistry
    dyestuffs
    pigments
IV. Pharmaceuticals
  Infectious diseases
    bacteria, fungi, parasitic
  Noninfectious diseases
    central nervous system, steroids, diuretics, antihypertension drugs
V. Agricultural chemicals
  Insecticides
    chlorinated hydrocarbons
    organophosphorus compounds
    carbamates
    natural products
  Fungicides
    surface
    systemics
    antibiotics
  Herbicides
  Growth regulators
VI. Detergents
  Soaps and soap products
  Synthetic surfactants
    anionic, cationic, nonionic
  Additives
    whitening, bleaching, foaming, enzymes, fabric softeners
VII. Food chemistry
  Oils and fats
  Bread making
  "Synthetic" foods, e.g., soybean steak!
VIII. Perfumes and flavors
IX. Photographic materials
  Silver halide processes
  Nonsilver processes
X. Chlorofluorocarbons
  Refrigerants, aerosols, solvents
  Foam-blowing, fire extinguishers

Based on Tedder et al. (1975).

POLLUTANT CLASSIFICATION

Pollutants may be classified into several groups. The first are the nutrients, such as nitrate, phosphate, and dissolved organics. A second group includes trace metals, such as chromium, lead, and arsenic. The third and largest group are the synthetic organics, which includes pesticides, industrial by-products, and solvents. Organic chemicals may also be divided into two classes based on solubility or lipid partitioning. These are hydrophobic compounds, which concentrate in lipids (fats), and hydrophilic compounds, which concentrate in water.

One of the great problems in organic pollution studies is the analysis of organic compounds in water. This includes their identification (many compounds have subtle differences) coupled with the fact that harmful quantities can occur in low concentrations. Quantification is usually

Table 1.2. U.S. Production of Organic Chemicals—1993

Common name	Billions of lbs.	IUPAC name (Other common name)
Ethylene	36.47	ethene
Propylene	21.85	propene
Ethylene dichloride	13.85	1,2-dichloroethane
Benzene	12.45	benzene
Vinyl chloride	10.62	chloroethene
Methyl *tert*-butyl ether	8.88	1,1-dimethyl-1-methoxyethane
1-Butanol	8.57	1-butanol
Ethylbenzene	8.37	ethylbenzene
Methanol	8.34	methanol
Styrene	8.02	phenylethene (vinylbenzene)
Teraphthalic acid, dimethyl ester	7.77	*p*-phthalic acid
Formaldehyde	6.72	methanal
Toluene	6.22	toluene
Isobutylene	6.00	2-methylpropene
Ethylene oxide	5.36	epoxyethane
p-Xylene	5.20	1,4-dimethylbenzene
Ethylene glycol	5.07	1,2-ethanediol
Cumene	4.31	isopropylbenzene
Acetic acid	3.75	ethanoic acid
Phenol	3.54	phenol
1,3-Butadiene	3.09	1,3-butadiene
Acrylonitrile	2.68	propenenitrile (vinyl cyanide)
Vinyl acetate	2.66	ethene ethanoate
Cyclohexane	2.46	cyclohexane
Acetone	2.33	propanone
Isopropyl alcohol	1.46	isopropanol
Caprolactam	1.38	2-oxohexamethyleneimine
Methyl methacrylate	1.18	methyl 2-methylpropenoate
Bisphenol A	1.15	2,2′-bis (4-hyroxyphenol)propane
Aniline	0.99	aniline
o-Xylene	0.94	1,2-dimethylbenzene
Phthalic anhydride	0.94	phthalic anhydride
Methylchloroform	0.80	1,1,1-trichloroethane
Methyl chloride	0.77	chloromethane
Propylene glycol	0.75	1,2-dihydroxypropane
Ethanolamines	0.73	2-aminoethanol
2-Ethylhexanol	0.65	2-ethylhexanol
Ethanol	0.55	ethanol
Chloroform	0.48	1,1,1-trichloromethane
Methyl ethyl ketone	0.47	2-butanone
Methylene chloride	0.46	dichloromethane
Maleic anhydride	0.42	2,5-furfurandione
Carbon tetrachloride	0.41	tetrachloromethane
Perchloroethylene	0.37	tetrachloroethene
Dioctyl phthalate	0.31	dioctyl phthalate
Ethyl chloride	0.15	chloroethane

Data from Anon, *Chemical & Engineering News*, 71(26), 1993.

preceded by separation and concentration procedures that involve expensive equipment and skilled operators.

The key words are expensive, difficult, and time consuming.

GEOCHEMICAL INVESTIGATIONS

SAMPLING AND SAMPLE COLLECTION

The number of samples to be taken for a given investigation must be determined from both statistical and economic considerations. Is one sample per square mile necessary, or

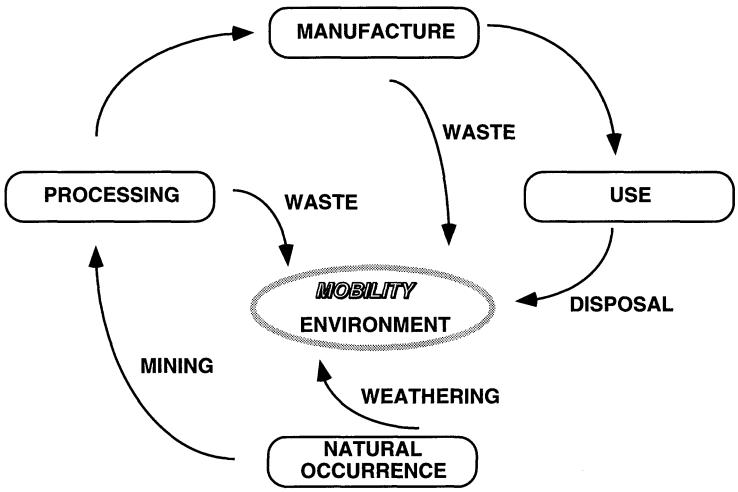


Figure 1.9. Environmental mobility of materials during and after manufacture.

would one sample per 100 square miles be sufficient for a stream sediment survey? How often should one sample wells? How many core samples should be analyzed? These questions can be answered only on an individual basis and project by project.

When collecting water samples, decisions must be made as to collection procedures (how often and when); the type of container (glass or plastic); and the method of preservation (ice, dark, or acid). Some chemical determinations must be conducted in the field. These include temperature, dissolved gases, pH, redox, and alkalinity. Most of these tests and procedures have been standardized and are included in EPA protocols.

In any investigation it is necessary to decide whether the analysis is to be done by oneself; to submit samples to commercial laboratories; to use published data; or to access data banks, such as the U.S. EPA database STORET or U.S. Geological Survey database WATSTORE. Each of these options has its own problems. Accuracy checks are also essential if there is to be any reliance on the results of the investigation. Quality assurance (QA) is imperative. This includes submission of duplicates, preparation of spikes, and inclusion of reference samples.

In groundwater investigations the source of a sample must also be determined. This is primarily a budgetary decision. Rivers can be used, although it is necessary to separate the groundwater and surface water components mathematically, or to use low-flow conditions. Wells are expensive to install and care must be taken to avoid contamination and to study any periodic changes that may occur. Springs, if present, are an important source of groundwater information, not only the water sample, but an analysis of any deposits that have formed as a result of that spring.

ANALYSIS INTERPRETATION

Individual analyses are to be subjected to accuracy checks. Their saturation, or otherwise with respect to dissolved minerals, is to be determined by using either mass balance or thermodynamic techniques. Thermodynamic water equilibrium studies are usually made with sophisticated computer programs, such as WATEQF, SOLMINEQ, and MINTEQ. These determine if the solution is saturated or unsaturated with respect to a variety of minerals, as well as determining the redox state of the water and the speciation of the components in it.

In order to discover anomalous samples or values within a collection of analyses they may be examined by using graphical methods, such as areal plots, or by cumulative frequency plots—a technique that was developed to distinguish between mixtures of two or more

populations. Mixed sources may be discovered by using factor analysis, a statistical procedure of multivariate analysis. Considerable use is still made of maps and diagrams, either spatial or temporal. Widely available computer programs make their production much less labor intensive than previously. It is important to note that the availability of contouring programs allows the replacement of the old graphical representation of analyses on maps.

Many water chemistry calculations are tedious and difficult to understand. However, when this step is accomplished a computer becomes imperative. It is rapid and avoids mistakes.

PRESENTATION OF MATERIAL IN THIS BOOK

The two major areas of water quality interpretation addressed in this book are water quality as it pertains to the natural processes of rock weathering and the chemical reactions typical of groundwater, and a discussion of the effect of organic and inorganic contaminants imposed on this system. The major inorganic contaminants considered here are brines. Brines are a major contaminant of drinking waters with sources as diverse as seawater encroachment, oil field brine disposal, and those derived from road salting. Organic contaminants, on the other hand, include almost any synthetic organic compound introduced into the ecosystem by man's activities. An outline of the various facets of water quality interpretation covered in this book are shown graphically in Figure 1.10.

Chapter 2 provides the reader a review of the fundamentals of chemistry and geology, which are assumed in the remainder of the book. It will give those in the geosciences a brief review of chemistry, and chemists and biologists an outline of geological thinking.

The major natural inorganic constituents of water are discussed in Chapter 3; mineralogic sources of the ions are emphasized. In addition, various parameters used by engineers, agronomists, etc., are discussed. The use of these parameters, such as hardness, in establishing the reliability of an analysis is emphasized. A computer flash-card system (MFLASH) may be used to recall selected rock and mineral compositions and the sources of common ions in waters.

Chapter 4 is a discussion of the interpretation of inorganic water quality data. After an evaluation of techniques for evaluating the reliability of a water analysis, it continues with details of rock weathering and methods for deducing the mineralogical composition of the aquifer matrix. This is followed by plotting techniques and their use in determining common groundwater reactions. The final part of the chapter discusses some of the techniques used for determining the source of brine contamination. The primary approach is one of mass balance, and the computer program WATEVAL is used extensively.

The basics of thermodynamics and water equilibrium thermodynamic modeling is presented in summary form in Chapter 5. The computer program used in this section is the U.S. Geological Survey program, WATEQ4F. Speciation, saturation, and redox as well as the interpretation of pe-pH diagrams also are included.

Discussed in Chapter 6 are selected geochemical environments from the viewpoint of redox, pH, and sorption. The discussion, primarily semiquantitative, is important to the understanding of the behavior of both organic and inorganic constituents. The speciation of many elements is often different in different pe or pH environments, and biodegradation of organic compounds also is strongly dependent on the geochemical environment.

Because many hydrogeologists have an inadequate background in organic chemistry, an attempt is made to introduce the basics of organic chemistry nomenclature. This is covered in Chapter 7. A computer flash card, OFCARD, may be used in conjunction with this chapter.

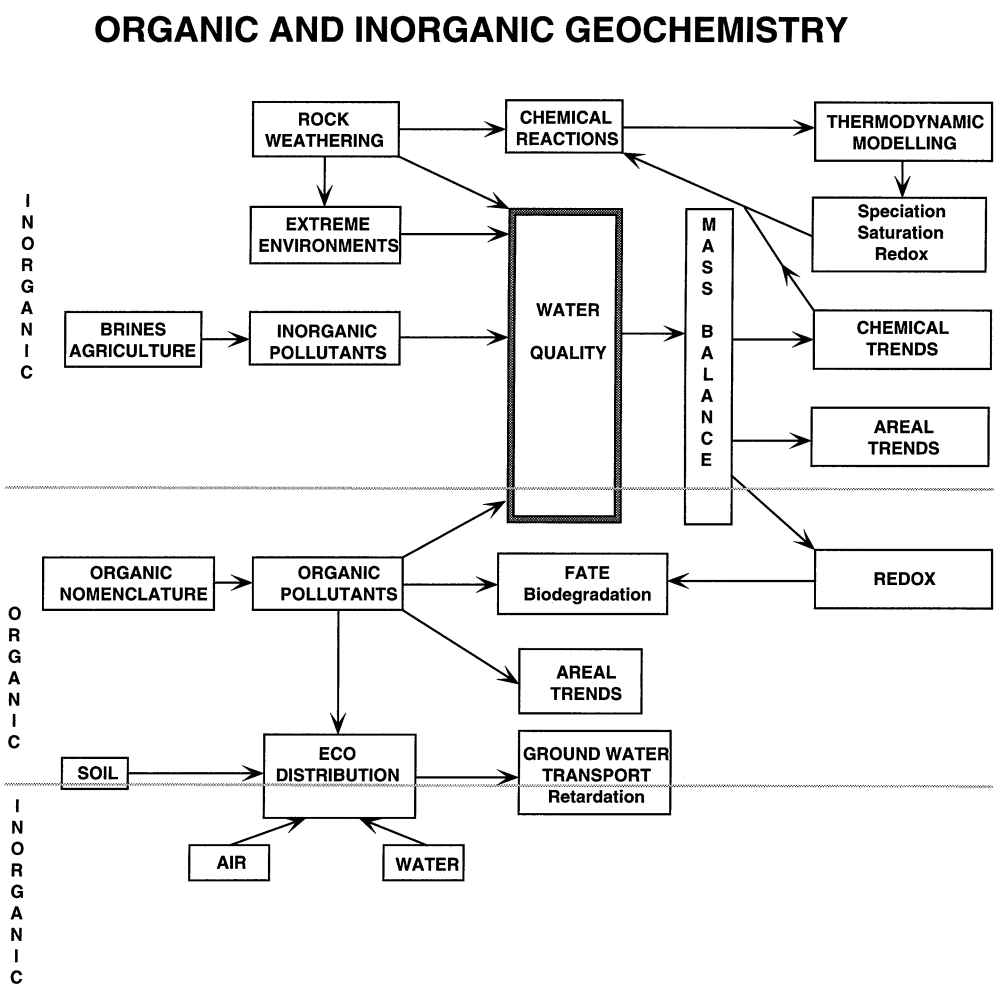


Figure 1.10. Topics covered in this book and their interrelationships.

The distribution of organic compounds in the ecosystem is discussed in considerable detail in Chapter 9. The program, ECOPLUS, is used as an aid in this process. This chapter and the ECOPLUS program emphasize the validation of the environmental partitioning parameters Koc, biological concentration factor (BCF), and Henry's law constant. Also included is a discussion of groundwater retardation and biodegradation in a groundwater system.

CHAPTER 2

Review of Basic Chemistry and Geology

INTRODUCTION TO ATOMIC STRUCTURE

An **element** cannot be changed to anything simpler by ordinary chemical processes. An **atom** is the smallest particle of an element that possesses the properties of that element. It consists of a positively charged central nucleus with negatively charged electrons surrounding this nucleus. The nucleus is 99.95% of the mass of the atom. The atomic size is determined by the size of the electron cloud surrounding the nucleus.

The **atomic nucleus** consists of a varying number of positively charged protons and neutral neutrons. The number of protons is called the **atomic number.** The total number of protons plus neutrons is called the **mass number.** Most elements consist of mixtures of atoms with different masses, that is, all have the same number of protons, but different numbers of neutrons. These are called isotopes. The average weight of the isotopes contained in a naturally occurring element is its atomic weight.

An **element** redefined means atoms of one **atomic number.**

ELECTRONIC STRUCTURE

The position and energy of each electron surrounding the nucleus of an atom may be described by a wave function, which is related to the probability of finding the electron at a particular point at an instant in time. Each electron may be described by its distance from the nucleus, the volumetric shape in which it is most likely to be found, the orientation of the shape with respect to spatial coordinates, and the direction of spin of the electron. This wave function may be written as the product of four factors that depend on the polar coordinates of the electron. These factors are

1. The radial function, which depends only on the radial distance of the electron from the nucleus;
2. and 3. Two angular functions, which may be described as the shape and orientation of the volumetric space in which the electron is most likely to be found;
4. A spin function, which is independent of the spatial coordinates.

Surfaces may be drawn to enclose the amplitude of the angular wave functions. These boundary surfaces are the atomic orbitals. The overall wave function and each of its component factors are expressed in terms of certain parameters called quantum numbers. There are four, which are designated by the symbols n, 1, m_l, m_s.

The Principal Quantum Number

The principal quantum number, n, is the *distance factor*, and relates to the average distance of the electron from the nucleus. It determines the nature of the radial part of the wave

function and has only positive integer values, from 1 to infinity. This is the most important factor in determining the energy of an electron. The lower the value of n, the lower the energy, other factors being the same. All electrons having the same principal quantum number are said to constitute a "shell" designated K, L, M, N for values of n = 1, 2, 3, 4. The maximum number of electrons that a shell can contain is $2n^2$.

The Azimuthal Quantum Number

The azimuthal quantum number, ℓ, is the *shape factor*, and relates to the shape of an orbital and occurs in the angular part of the wave function. It may be thought of as the angular momentum of an orbiting electron. It can have only integer values. Its maximum value is limited by the value of the principal quantum number, n, of that orbital, that is, ℓ ranges from 0 to n − 1.

For				
	n = 1	$\ell = 0$		
	n = 2	$\ell = 0$,	$\ell = 1$	
	n = 3	$\ell = 0$,	$\ell = 1$,	$\ell = 2$

Possible values of ℓ are 0, 1, 2, 3. The electrons having these values are referred to as the s, p, d, and f electrons. The state of an electron with respect to its principal and azimuthal quantum numbers is symbolized by a number representing the principal quantum number (n) and a letter representing the azimuthal quantum number (ℓ). For example, 1s refers to an electron in the K shell with $\ell = 0$, and 3d refers to an electron in the M shell with $\ell = 2$.

The number of electrons in a particular orbital is indicated by a superior following the symbol of the orbital. For example, $3d^5$ indicates five electrons in the d orbital of the M shell. Electrons in the same orbital have nearly the same energy. However, the energies of electrons in different orbitals of the same shell are appreciably different.

The order of electrons arranged in the order of increasing energy is 1s, 2s, 2p, 3s, 3p, 4s, 3d, 4p, 5s, 4d, 5p, 6s, 4f, 5d, 6p, 7s. This order is that of (n + ℓ) unless the values of (n + ℓ) are the same when the electron with the lower value of n comes first. Each orbital is of different shape and symmetry. The s orbitals are spherical and symmetrical. The p orbitals are three dumbbell-shaped orbitals oriented in space around three mutually perpendicular directions. The d orbitals are four differently oriented double dumbbells and one dumbbell with a ring around its center.

The Magnetic Quantum Number

The magnetic quantum number, m_l, is the orbital angular momentum. It may be called the Orientation Factor as it indicates the orientation of the electron cloud in space, or the directions of maximum extension in space of the electron cloud. It occurs in both angular factors of the wave function and has integer values ranging from $+\ell$ to $-\ell$. For example:

$\ell = 0$;	$m_l = 0$	One s orbital
$\ell = 1$;	$m_l = 0, +1, -1$	Three p orbitals
$\ell = 2$;	$m_l = 0, +1, -1, +2, -2$	Five d orbitals

The energies of the orbital with the same n and ℓ values, but different m_l values, are the same, except in the presence of a strong electric or magnetic field.

The Spin Quantum Number

The spin quantum number, m_s, is the *spin factor*, and spin angular momentum of an electron may be visualized as an electron spinning about some axis. As an electron is

negatively charged a magnetic field will be produced. Its direction depends on the sense of rotation of the electron, which may be either clockwise or anticlockwise. An electron with two kinds of spin is characterized by quantum numbers $m_s = +1/2$ and $m_s = -1/2$. For each space orbital characterized by quantum numbers n, ℓ, and m_l there are two possible arrangements of electron spin. These are generally of the same energy so each orbital can accommodate two electrons that spin in opposite directions. As a result, each s orbital may contain two electrons, the three p orbitals may contain six electrons, and the five d orbitals may contain ten electrons.

ENERGY LEVELS OF ORBITALS

Consider the distribution of electrons between the various possible atomic orbitals in their ground state. They will occupy the lowest possible potential energy subject to Pauli's Exclusion Principle, which is, that no two electrons in one atom can have an identical set of all four quantum numbers. The relative energy levels of the different atomic orbitals are not independent of atomic number, but vary with Z in a complicated way. The various orbitals of the same principal shell are shielded to different degrees by the core of electrons underneath.

Electronic Structure of the Elements — The Aufbau principle (or the building up of) refers to the distribution of electrons among the various orbitals.

Element	Number of electrons	Distribution
H	1	Electron is in the s orbital of the K shell, written: $1s^1$.
He	2	Electrons are in the 1s shell with different spins, written: $1s^2$.
Li	3	The third electron occupies the s orbital of the L shell, written: $1s^2\ 2s^1$.
Be	4	The 1s and 2s orbitals are fully occupied, written: $1s^2\ 2s^2$.
B	5	The fifth electron must occupy one of the three p orbitals, written: $1s^2\ 2s^2\ 2p^1$.

The question that now arises will be the position of the sixth electron of the element carbon. Will it occupy the same 2p orbital or one of the two as yet unoccupied p orbitals? This is answered by Hund's rule which states "As long as the exclusion principle permits, electrons with the same n and ℓ values will also have the same m_s value, thus occupying orbitals with different m_l values." More simply stated: as many orbitals as possible are occupied by a single electron before any pairing takes place. Thus, carbon (Z = 6) has the configuration $1s^2\ 2s^2\ 2p_x^1\ 2p_y^1$.

This electron building takes place until Ne (Z = 10), $1s^2\ 2s^2\ 2p^6$, when the K and L shells are fully occupied with two and eight electrons, respectively. The 11th electron, Na (Z = 11), $1s^2\ 2s^2\ 2p^6\ 3s^1$, must enter the M shell and so on until argon (Z = 18) when the 3s and 3p orbitals are filled: $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6$. Note that the M shell is not yet fully occupied as there is room for ten electrons in the five 3d orbitals. In the next two elements K (Z = 19), $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^1$, and Ca (Z = 20), $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2$, the extra electrons enter the 4s orbitals and not the 3d orbitals. After Ca the 3d orbital is more stable than the 4p orbitals. In the elements from Sc (Z = 21), $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2\ 3d^1$, to Zn (Z = 30), $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2\ 3d^{10}$, electrons enter the 3d orbitals rather than the 4p orbitals. These elements are termed the transition series.

THE PERIODIC TABLE

The periodic law states that when elements are arranged in order of their atomic numbers they exhibit a periodic recurrence of properties. The periodic table, Figure 2.1, is a tabular

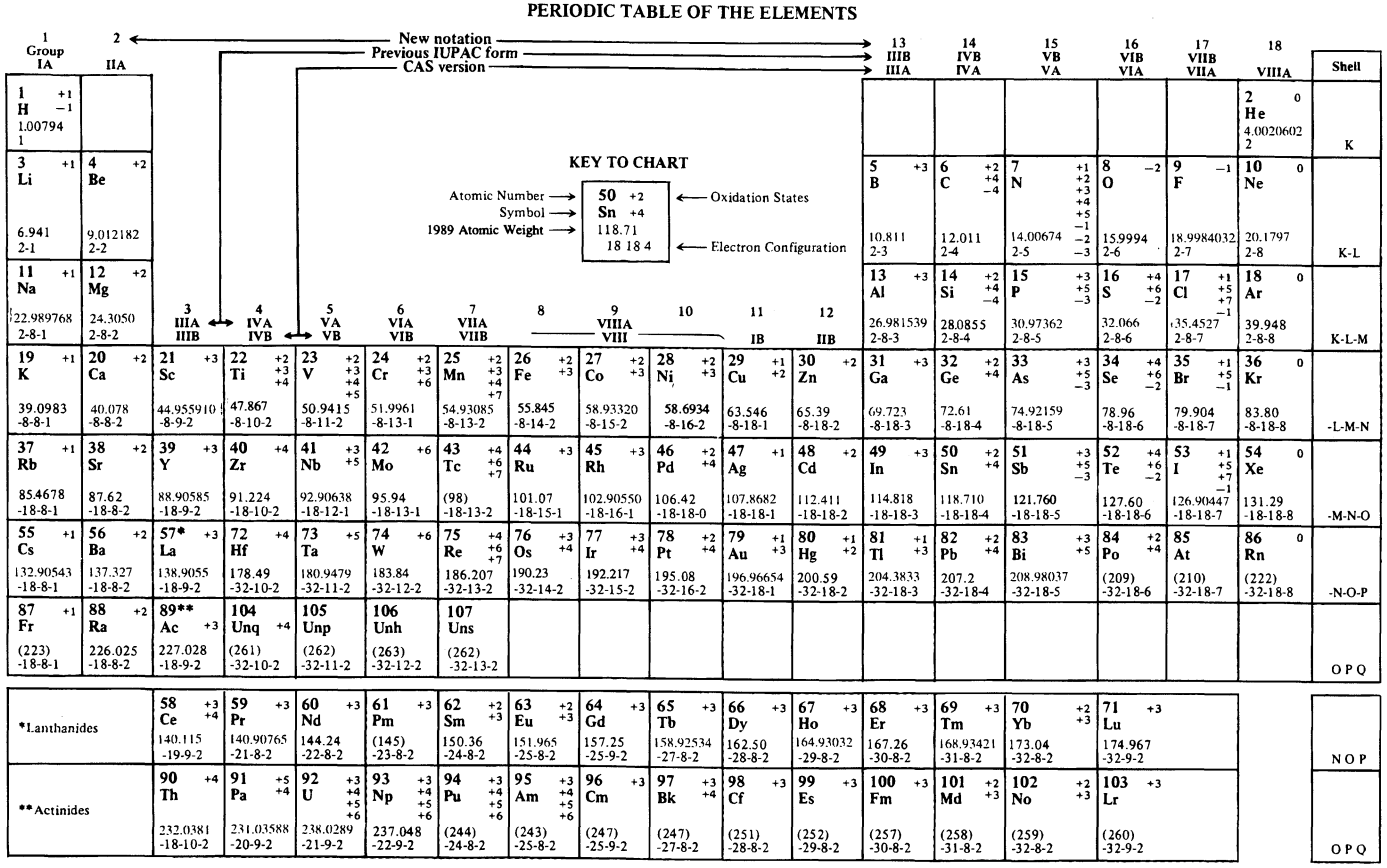


Figure 2.1. The new IUPAC format numbers the groups from 1 to 18. The previous IUPAC numbering system and the system used by Chemical Abstracts Service (CAS) are also shown. For radioactive elements that do not occur in nature, the mass number of the most stable isotope is given in parentheses. **REFERENCES:** G.J. Leigh, Editor, *Nomenclature of Inorganic Chemistry,* Blackwells Scientific Publications, Oxford, 1990, and *Chemical and Engineering News,* 63(5), 27, 1985. (From *CRC Handbook of Chemistry and Physics, 75th Ed.,* Lide, D.R., Ed., CRC Press, Boca Raton, FL.)

arrangement of elements. The elements are arranged in rows so that those having similar properties fall in the same vertical column. Periods are the horizontal rows of elements placed in order of increasing atomic number. They are designated by Arabic numerals. The first period contains 2 elements, the second and third periods contain 8, the fourth and fifth periods contain 18 elements, and the sixth and seventh periods contain 32. The lanthanides and actinides, usually located below the main table for convenience, belong in periods 6 and 7.

Periods	Number of elements	Configuration
1	2 elements	1s
2	8 elements	2s 2p
3	8 elements	3s 3p
4	18 elements	4s 3d 4p
5	18 elements	5s 4d 5p
6	32 elements	6s 4f 5d 6p
7	17 elements	7s 5f 6d

Groups are the 18 vertical columns. Each group consists of a family of elements having similar properties. These are designated by Roman numerals.

Representative elements are the elements in the eight main groups of the periodic table. They are also called the s and p groups, depending on the orbitals being filled. The groups are numbered from I to VIII and are called the A group elements.

Transition elements are the elements between the s and p groups. They are also called d-block elements, which result from the filling of the d orbitals and all are metals. The progression of properties (from left to right) is more gradual than in the representative elements. They differ from the p group in that their next to outer shells are being filled. The three rows are called first, second, and third transition series. These are numbered from I to VIII and are called the B group elements. The chemical properties of this group include multiple oxidation states, mostly colored compounds, and a strong tendency to form complex ions.

Inner Transition Elements—#1 (Lanthanides)

These are the lanthanide or rare earth elements. They range from Z = 57, lanthanum, to Z = 71 for lutetium. They are characterized by the filling of the 5f orbitals. Because this third outer shell is being filled, they each have very similar properties. All have an oxidation state of (III). In addition, a couple also have (IV) and a couple (II).

Inner Transition Elements—#2 (Actinides)

These are the actinide or uranium group elements, which result from the filling of the 6f orbitals. They have similar properties because the third outer shell is being filled. They are all radioactive. Many are man-made.

Chemical Properties of the Elements

The most distinctive chemical property of an atom is determined by the number of electrons in its outer shell. For each group A element the number of electrons in its outer shell corresponds to its group number in the periodic table. The ten group B, or transition elements, gain electrons in their next but outer shell, the d orbitals. The lanthanide (rare earths) and actinide (uranium elements) series are the result of filling the third outer shell, or f orbitals, with 14 electrons. These may also be called the inner transition series. The

chemical properties of elements in this group are even more closely related as one goes from left to right in the periodic table.

Metals lose electrons, conduct electricity and heat, and are generally ductile and malleable. They are found on the left-hand side of the periodic table. Generally, they have positive oxidation states. The metallic character decreases from left to right in a period and increases from top to bottom in a group. **Nonmetals** gain electrons and are poor conductors of heat and electricity. They are found on the right-hand side of the periodic table. **Metalloids** have properties intermediate between those of metals and nonmetals. They conduct electricity poorly. Atoms in the center of the periodic table tend to share electrons with other atoms. It is easier to gain or lose one electron than two electrons. Elements that lose one electron are generally more reactive than those that lose two electrons.

In the period 4 transition metals the outer s orbital is filled with two electrons, but differ in the number of electrons in the 3d orbitals. They are less active than Ca^{2+}, even though they lose the two s electrons to form ions Mn^{2+}, Fe^{2+}, Co^{2+}, and Ni^{2+}. The groups in the periodic table may be separated as follows:

Electrons Filling the s Orbitals

Alkali metals are those elements with one electron in the s orbital. They include lithium, sodium, potassium, rubidium, and cesium. Alkali metals have oxides that are very soluble in water and produce a strongly alkaline solution. Most of the alkali salts are soluble in water. They have an oxidation state of (I) only. They occur naturally in the secondary environment as evaporites and brines. They are also the dominant species in silicate minerals.

Alkaline earth metals are those elements with two electrons in the s orbital. They are beryllium, magnesium, calcium, strontium, barium, and radium. Alkaline earth metals also have oxides that give an alkaline reaction, but many of their compounds are of low solubility. They have an oxidation state of (II) only. The alkaline earth metals occur naturally in the secondary environment as carbonates, phosphates, and sulfates.

Electrons Filling the p Orbitals

These consist of the less metallic metals, unnamed metalloids, the halogen group, and the inert gases.

The **p-group metals** include aluminum, gallium, indium, thallium, tin, lead, and bismuth. Aluminum always occurs in the 3+ state. The others are called the post-transition metals. They have two oxidation states—the lower due to the loss of the outer p electrons, and the higher due to the additional loss of the two s electrons.

The **metalloids** include the elements boron, silicon, germanium, arsenic, antimony, tellurium, polonium, and astatine. The last two are radioactive and do not occur naturally, because of their short half-lives. The metalloids are semiconductors because they conduct electricity weakly. They are used extensively in the electronic industry.

The **halogen group** of nonmetals is highly reactive. Under natural aqueous conditions all have (I−) oxidation states. In the Chilean nitrate deposits iodine also occurs in the (V+) oxidation state as iodate $(IO_3)^-$. Halogens occur in the secondary environment as evaporites and brines, usually in conjunction with alkali metals.

The **inert gases,** sometimes called the noble gases, include He ($1s^2$). Their s and p orbitals are filled. They have low chemical reactivity and all except He occur in the atmosphere. Helium occurs in natural gas as a result of radioactive decay.

Electrons Filling the d Orbitals

The group VIII transition metals are different from the others in this group as they have greater horizontal similarities than vertical ones. They are often organized on the basis of horizontal groups of three elements called triads. Each triad is named after the best known element within it.

Iron triad	—	Fe, Co, Ni
Palladium triad	—	Ru, Rh, Pd
Platinum triad	—	Os, Ir, Pt

THE BONDING OF ATOMS

Most matter consists of groups of atoms joined by chemical bonds where only the outer part of the atoms is in contact. These are called the valence electrons. They may be represented by Lewis symbols—in which the atomic symbol is surrounded by a number of dots representing the outer shell of electrons—for example, Ca:, Na·.

Types of Bonding

Ionic bonds occur where one or more electrons are transferred from the valence shell of one element to the valence shell of another. Attraction takes place between ions of opposite charge—one atom losing electron(s), yielding a cation, and the other atom gaining electron(s), yielding an anion. Large numbers of atoms are involved in ionic reactions. The ionic solid does not contain discrete molecules, but contains atoms packed so that the attractive forces are maximized and repulsive forces are minimized. For example, in LiF each lithium ion is surrounded by six fluoride ions and each fluoride ion is surrounded by six lithium ions. The Octet rule states, "an atom tends to gain or lose electrons until there are eight electrons in its outer shell". Thus, the atom attains a stable, inert gas configuration. Exceptions to this rule include some of the transition elements. Ionic solids are dissociated by water dipoles and therefore tend to be relatively soluble in water.

Covalent bonds result from the equal sharing of electrons. An example is two atoms of the same element such as Cl_2, H_2. As two hydrogen atoms are brought together there is a decrease in energy as the electrons approach one another until a minimum energy is attained. This distance of minimum energy is the bond distance. At closer distance the energy rises abruptly because of the repulsion between the nuclei. Covalent compounds are true molecules held together by strong intramolecular forces. These forces must be distinguished from the intermolecular forces, which hold the molecules together in either the liquid or solid states.

Polar covalent bonds lie between the above extremes. The electrons are shared unequally by the adjoining atoms. The result is a molecule with positive and negative ends, called a dipole.

Van der Waals bonds are similar in some ways to polar covalent bonds except that they are much weaker. They are formed by oscillating dipolar atoms inducing opposite charges in neighboring atoms.

Electronegativity is a measure of the ability of an atom to attract shared electrons in a structure. The greater the difference in electronegativity of two bonded atoms, the more ionic (polar) the bond becomes.

Fluorine, nitrogen, and oxygen are highly electronegative. That is, they strongly attract electrons. The result is that the H atom is positively charged and is attracted to the unshared electron pair of a neighboring molecule. This forms a bridge called a hydrogen bond. The hydrogen bond strength is about ten times that of van der Waals bonds, but one tenth of a

covalent bond. Water molecules are held together by H bonds. In ice the hydrogen bonds form giant, three-dimensional networks where hydrogen atoms form bridges between the oxygen atoms.

Units for Atomic Sizes and Bond Lengths

μm	10^{-6} meter	—micrometer
nm	10^{-9} meter	—nanometer
pm	10^{-12} meter	—picometer
Å	10^{-10} meter	—Angstrom unit = 100 pm = 0.1 nm

OXIDATION NUMBERS

The oxidation number is the charge that an atom would have if both of the electrons in each bond were assigned to the more electronegative element. These numbers are assigned by a standard set of rules.

CALCULATION OF OXIDATION NUMBER

1. The maximum oxidation number of an element corresponds to its periodic group number. (Mg (II), N(V)).
2. The minimum (negative) oxidation number of a nonmetal equals the number of electrons required to fill its outer valence shell to eight. (N (III−), O(II−), F (I−)).
3. The oxidation number of an uncombined element is always (0).
4. The oxidation number of hydrogen is (I) in all compounds with the exception of metallic hydrides where it is (I−) (e.g., NaH).
5. The oxidation number of oxygen is (II−) in all compounds, with the exception of peroxides, where it is (I−) (e.g., H_2O_2).
6. Other exceptions include Cu, Fe, and Pb.
   Cu (I) and Cu (II) by losing an electron from their inner shell
   Pb (IV) uncommon; usually exists as Pb (II)
   Fe (II) and Fe (III)
7. All alkali metals have an oxidation number of (I).
8. All alkali earth metals have an oxidation number of (II).
9. The halogens have an oxidation number of (I−) except when combined with oxygen (e.g., $NaIO_3$ [iodate], I = (V)).

Examples of Finding an Oxidation Number from a Formula

1. SO_3; 3 × O = 6−, therefore S = 6+, written S(VI).
2. SO_2; 2 × O = 4−, therefore S = 4+, written S(IV).
3. PCl_3; Assume Cl = 1−, 3 × Cl = 3−, therefore P = 3+, written P(III).
4. HBrO; 1 × H + 1 × O = (1+) + (2−) = 1−, thus Br = 1+, written Br(I).
5. $MgSO_4$; 1 × Mg(II) + 4 × O(II−) = 6−, thus S = 6+, written S(VI).
6. $LiMnO_4$; 1 × Li(I) + 4 × O(II−) = 7−, thus Mn = 7+, written Mn(VII).
7. K_2CrO_4; 2 × K(I) + 4 × O(II−) = 6−, thus Cr = 6+, written Cr(VI).
8. $K_2Cr_2O_7$; 2 × K(I) + 7 × O(II−) = 12−, thus Cr = 12/2 = 6+, written Cr(VII).
9. KNO_3; 1 × K(I) + 3 × O(II−) = 5−, thus N = 5+, written N(V).
10. NH_4OH; 5 × H(I) + 1 × O(II−) = 3+, thus N = 3−, written N(III−).
11. H_2S; 2 × H(I) = 2+, thus S = 2−, written S(II−).
12. $Ca_3(PO_4)_2$; 3 × Ca(II) + 8 × O(II−) = 10−, thus P = 10/2 = 5, written P(V).

13. CO; $1 \times O(II-) = 2-$, thus $C = 2+$, written C(II).
14. CO_2; $2 \times O(II-) = 4-$, thus $C = 4+$, written C(IV).
15. CH_4; $4 \times H(I) = 4+$, thus $C = 4-$, written C(IV−).

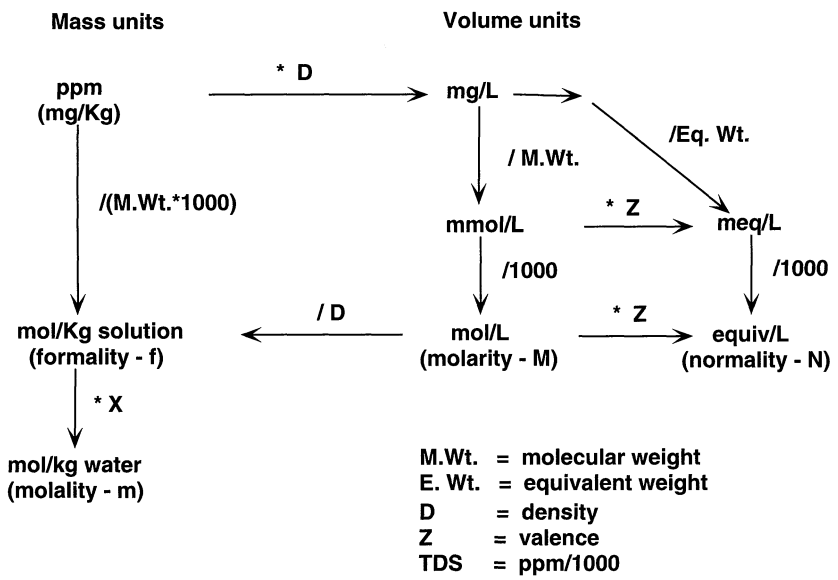
CONCENTRATION UNITS

The concentration of the individual ions or molecules in a solution may be expressed in a variety of ways. Two terms are used when expressing concentrations—one is the amount of the solute and the other is the amount of water or solution in which the solute is dissolved. The former is either mass units or moles and the latter is either volume, mass, or mole units. The relationship between these units is shown in Figure 2.2.

MOLES AND ATOMIC WEIGHTS

One mole of an item is defined as $6.023 * 10^{23}$ of that item. It applies to atoms, molecules, ions, golf balls, etc. This number is known as Avogadro's Number. A gram-atomic weight (atomic weight expressed in grams) of an element or a gram-formula weight of a compound contains 6.023E23 atoms * (formulas) of that material. Thus 1 mole of a compound equals the atomic or molecular weight of that compound in grams. The atomic weight of an atom is a relative measurement and is the mass of that atom compared to that of the carbon isotope $^{12}C_6$, which is exactly 12.00.

Different ways of expressing concentrations may be divided on the basis of the quantity of water or solution and the solute units used.



$$X = \frac{\text{wt. solution}}{\text{(wt. solution - wt. solute)}} = \frac{1000}{\text{(1000 - TDS g)}}$$

Figure 2.2. Units and conversions.

Concentration Expressed in Terms of Volume of Solution

g/l; gram/liter—low concentrations are expressed in **mg/l;** where 1 g = 1000 mg.
Molarity (M): moles/liter—low concentrations are expressed as **mmol/l;** millimoles/liter.

Concentration in Terms of Mass of Solution

Fraction: part of total which equals 1 (e.g., g solute/g solution).
Mole fraction (X_i): mole solute/mole solution.
Mole ratio is the ratio of the number of moles of a given constituent to the total number of moles of all constituents.

$$X_1 = \frac{n_1}{n_1 + n_2 + n_3 + n_x}$$

For example, the mole fraction of NaCl in a 1.0 molar solution of NaCl is

$$X_{NaCl} = \frac{1}{1 + 55.51} = 0.0177$$

where 55.51 is the number of moles of water in 1000 g water.
Percent (%): the parts in mass units of solute/hundred parts in the same mass units of solution. For example, g solute per 100 g of solution.
Salinity ($^o/_{oo}$): parts solute (mass)/thousand parts of solution (mass), for example, g solute per 1000 g of solution.
Ppm: parts solute (mass)/million parts (mass) of solution, which is equal to g solute per 1,000,000 g solution, or mg solute per 1,000,000 mg solution. Because 1,000,000 mg = 1,000 g = 1 kg, therefore 1 ppm = 1 mg/kg.
Formality: moles solute per kg solution.

Concentration Expressed in Terms of Mass of Water

Molality: moles solute/kg water; used extensively in thermodynamic calculations because it is always independent of temperature and pressure.

Conversions

$$\text{Mass/l} = \text{mass/kg} * \text{density of solution}$$

$$\text{Mol/l} = \text{mol/kg} * \text{density of solution}$$

$$\text{Mol/kg water} = \text{mol/kg solution} * \frac{\text{mass solution}}{\text{mass solution} - \text{mass solute}}$$

$$\text{Molality} = \text{formality} * \frac{1000\ \text{g}}{1000\ \text{g} - \text{TDS g}^-}$$

Examples:

1. As 55.85 g Fe contains 6.023E23 atoms of Fe, then 55.85 g Fe = 1 mol of Fe. Thus 173 g Fe contains 173/55.85 or 3.10 mol Fe.

2. As 70.91 g Cl_2 contains 6.023E23 molecules of Cl_2, then 70.91 g Cl_2 = 1 mol Cl_2. Thus 50 g Cl_2 contains 50/70.91 = 0.71 mol Cl_2.
3. As 18.015 g H_2O contains 6.023E23 molecules of H_2O, then 18.015 g H_2O = 1 mol H_2O. As 1 l of H_2O equals 1000 g H_2O, it contains 1000/18.012 or 55.51 mol H_2O.
4. As 44.009 g CO_2 contains 6.023E23 molecules of CO_2, then 44.009 g CO_2 = 1 mol CO_2. Thus 84 g CO_2 contains 84/44.009 = 1.91 mol CO_2.
5. A brine has a density of 1.018 and contains 12,000 ppm dissolved solids of which 3700 ppm is sodium.

Sodium concentrations:

ppm	= 3700	
mg/l	= ppm * D = 3700 * 1.018	= 3767 mg/l
Formality	= ppm/(1000 * M.Wt.) = 3700/(1000 * 23)	= 0.1609 mol/kg solution
mmol/l	= mg/l/M.Wt. = 3767/23	= 163.7826 mmol/l
Molarity	= mmol/l/1000	= 0.1638 mol/l solution
TDS (g)	= 12,000/1000	= 12 g/kg solution
Molality	= formality * 1000/(1000 − TDS g)	
	= 0.1609 * 1000/(1000 − 12)	= 0.1629 mol/kg water

where

D	= density
M. Wt.	= molecular weight
TDS	= total dissolved solids

Equivalents

Equivalent weights are the weight of a material that will combine with or furnish 1 mol of cationic or anionic charges, 1 mole of H^+, 1 mole of OH^- or 1 mole of e^-. The electrons take precedence in reactions involving both electron and hydrogen or hydroxyl ions.

$$\text{Equivalents/l} = \text{normality N}$$

$$\text{Normality (N)} = \frac{\text{g/l}}{\text{Eq. Wt}}$$

$$\text{Equivalents/million} = \text{epm}$$

$$\text{Milliequivalents/l} = \text{meq/l}$$

$$\text{epm} = \frac{\text{meq/l}}{\text{D}}$$

Calculation of equivalent weights are based on:

a. charge of an ion*

$$\text{Eq. Wt.} = \frac{\text{M. Wt.}}{\text{charge}}$$

for example, $Fe^{3+} + 3Cl^- \Leftrightarrow FeCl_3$; Eq. Wt. $Fe^{3+} = \frac{55.85}{3} = 18.62$

*Most common method of calculation.

b. number of electrons transferred in an oxidation-reduction reaction*

$$\text{Eq. Wt.} = \frac{\text{M. Wt.}}{\text{\# electrons transferred}}$$

for example, $Fe^{2+} \Leftrightarrow Fe^{3+} + e^-$, Eq. Wt. $Fe^{3+} = \frac{55.85}{1} = 55.85$

c. number of protons or hydroxyls transferred in an acid base reaction

$$\text{Eq. Wt.} = \frac{\text{M. Wt.}}{\text{\# of protons or hydroxyls transferred}}$$

For example, $H^+ + Cl^- \Leftrightarrow HCl$; Eq. Wt. $Cl^- = \frac{35.45}{1} = 35.45$

d. neutral salts

$$\text{Eq. Wt.} = \frac{\text{M. Wt.}}{\text{\# of H atoms equivalent to total cations}}$$

For example, Eq. Wt. of $Ca(NO_3)_2 = 164.088/2 = 82.044$

ROCKS AND MINERALS

The earth is 4.6 billion years old. It has a diameter of 8000 miles, yet we can directly study the outer few miles of the surface (maximum 8 miles). We can examine processes for only a few years, decades at most. Man has been observing the earth for 3000 years, although with some degree of scientific intelligence for only 200 years and with major insight during the last 50 years.

There are two major problems for the geologist:

1. Earth processes are usually infinitesimally slow, often at the speed of a growing fingernail, and proceed for millions of years. Consider movement of 1 cm/year for 1 million years (an instant in geologic time). The total movement would be 10 km (6.25 miles). Laterally this would not be too impressive; however, it would be quite impressive if the movement were vertical, as in mountain formation.
2. The second problem facing the geologist is that many earth materials are difficult to characterize because of their resistance to many of the usual wet-chemical techniques. Thus, minerals are studied by examining physical properties rather than chemical properties. A major breakthrough, which occurred during the 19th century, was the development of the technique of examining thin sections of rocks using the petrographic microscope.

The basic tenet of geology is that: "**The present is the key to the past.**" That is, the laws of nature do not change with time. This is also called the principle of uniformitarianism.

Absolute measurement of geologic time using radioactive decay is a relatively recent technique. Most advances in geology have been made using the concept of relative dating, where the chronological order of events is established even though the actual dates of the events are unknown. The principles used to establish the relative order of events are

1. The principle of superposition. In a sequence of undeformed sedimentary rocks, the oldest beds are on the bottom and the youngest ones on top.

2. The principle of faunal succession. Fossil assemblages (groups of fossils) change with time. This allows the recognition of similar time periods of rocks, although they may be separated by considerable distances.
3. The principle of cross-cutting relations. Fractures and injections of molten rock are younger (later) than the rocks they cut.
4. The principle of inclusion. Inclusions incorporated into igneous intrusions are older than the igneous bodies being intruded.

MINERALS

Minerals are naturally occurring inorganic compounds having a crystalline structure and a definite chemical composition. Minerals are the basic building blocks of the earth. They are more often than not resistant to chemical decomposition and are not readily amenable to the normal methods of qualitative chemical analysis. Because of this they are often identified on the basis of their physical properties. These same properties are often those for which the mineral is actually mined. In other cases the physical property is used in the recovery of the mineral. These minerals that are heated (smelted) to recover the metal in them are called ore minerals. Other minerals, often those more amenable to chemical solution, are used as raw materials by the chemical industry. These include many minerals formed by evaporation (evaporites).

Physical Properties

1. Color—used little in mineral identification; often used for ornamental purposes.
2. Streak (color of the powdered mineral)—pigments, gold testing, and mineral identification.
3. Specific gravity (relative heaviness)—gold, diamond, and other heavy-mineral recovery.
4. Hardness (resistance to abrasion)—abrasives such as sandpaper (quartz), garnet paper (garnet), emery (corundum), toothpaste (calcite), and lubricants (talc). Ten minerals form the basis of a hardness scale for use in mineral identification. These are

1. Talc	6. Orthoclase
2. Gypsum	7. Quartz
3. Calcite	8. Topaz
4. Fluorite	9. Corundum
5. Apatite	10. Diamond

5. Crystals (the symmetry of a crystal that reflects the internal arrangement of the atoms in the mineral)—ornament and mineral identification. The study of crystals is encompassed by the science of crystallography.
6. Cleavage (oriented breaking)—mica sheets, cleaving diamond, and selenite.
7. Magnetism (attraction to a magnet)—lode stone, mineral identification.
8. Radioactivity—can be detected by a Geiger counter.

ROCKS

Rocks are natural mixtures of minerals formed under a variety of conditions. They are divided into three groups on the basis of their mode of formation.

Igneous Rocks

Igneous rocks are formed by cooling and solidification of molten silicates. Their classification is based on the minerals present and their texture. Texture is defined as the size, shape, and mutual arrangement of minerals in the rock.

Igneous Textures and their Interpretation

1. Size.
   a. Glassy—without crystals—very rapid cooling.
   b. Aphanitic—small crystals—rapid cooling.
   c. Phaneritic—crystals seen with unaided eye—slow, uniform cooling, probably at depth.
   d. Porphyritic—two different crystal sizes.
      The larger crystals are called phenocrysts and the smaller crystals comprise the groundmass. They are formed by two stages of cooling—slow cooling, allowing the formation of large crystals, probably at depth, followed by a period of rapid cooling, possibly on the surface of the earth.
   e. Pyroclastic—broken fragments of volcanic rock.
      If they were deposited when still molten, the rock becomes welded together on cooling, forming welded tuffs.
2. Shape.
   a. Euhedral—having well-developed crystal faces.
      This indicates cooling and crystallization at widely separated centers in the rock mass.
   b. Anhedral—minerals crystallized without having definite crystal faces.
      This indicates crystallization of minerals in close proximity to each other, thus interfering with each other as they cool.
3. Mutual arrangement.
   a. Crystalline—minerals form interlocking meshwork of grains.
      This is characteristic of minerals crystallizing from a melt or from solution.
   b. Clastic—rocks formed from broken pieces of minerals or rocks.
      Characteristic of pyroclastic rocks and many sedimentary rocks.

Igneous Processes

Volcanism is the extrusion of molten rock (magma) at the surface of the earth which produces volcanic rocks. We can see the formation of lava flows and the piling up of volcanic ash. Little imagination is needed to infer the formation of volcanic necks and lava plains. Molten lava is converted to solid rock by rapid cooling.

Plutonic igneous rocks are those igneous rocks that cool slowly at great depth beneath the surface of the earth. A two-dimensional view of plutonic igneous rocks can be seen in LANDSAT imagery of the Canadian shield. An impressive three-dimensional view can be seen at Yosemite National Park. The texture of these rocks indicates slow, uniform cooling of igneous melt, presumably at great depth.

Earth Structure

The structure of the earth may be summarized as follows:

Crust, Upper mantle } lithosphere—solid
Lower mantle } asthenosphere—plastic
Core

Recent discussions of geology have invoked the idea of rigid lithospheric plates moving on a plastic asthenosphere. Most geologic activity occurs along the plate boundaries. They are classified as divergent plate boundaries, or spreading centers, represented by the mid-oceanic ridges; and convergent plate boundaries, or subduction zones, occurring at continental edges where the oceanic plate moves down into the mantle.

Examples of Common Igneous Rocks

Granites are coarse-grained igneous rocks occurring at continental edges. They consist of quartz and potash feldspar with smaller amounts or sodic plagioclase and some ferromagnesian minerals (containing iron and magnesium such as mica [biotite and/or muscovite] and sometimes hornblende). They are plutonic, resulting from the melting of marine sediments as they descend into the mantle. They are lighter than the surrounding rock, and therefore rise and intrude it. **Rhyolites** are fine-grained volcanic equivalents of granite.

Basalts are fine-grained igneous rocks containing calcic plagioclase and pyroxene, possibly with olivine. They are volcanic and occur around the Pacific Ocean. They are known as the Pacific ring of fire. They also occur at the mid-oceanic ridges. **Gabbros** are the coarse-grained plutonic equivalents of basalt.

Andesite is another common volcanic igneous rock that occurs at the continental edges. It consists primarily of plagioclase and amphibole, and usually contains no potash feldspar or quartz. The plutonic equivalent is **diorite.**

Peridotite is a coarse-grained igneous rock that occurs in the upper mantle. It consists of olivine and pyroxene.

Sedimentary Rocks

A sedimentary rock is a rock resulting from the consolidation of loose sediment, or a chemical rock formed by precipitation from solution, or an organic rock consisting of the remains of plants and animals.

Textural Classification

1. Clastic—fragments of other rocks, subdivided by size

Conglomerate	(>2 mm)
Sandstone	(<2 mm)
Shales	(mostly clays; <1/256 mm)

2. Chemical rocks—often crystalline

Limestone	—calcite	—$CaCO_3$
Dolostone	—dolomite	—$CaMg(CO_3)_2$
Rock salt	—halite	—NaCl
Gypsum	—gypsum	—$CaSO_4 \cdot 2H_2O$

Sedimentary Structures

(A result of method of deposition)

1. Stratification—layering.
2. Cross bedding—formation of channels or dunes, resulting from water or wind deposition.
3. Graded bedding—upward decrease in grain size. A mixture of fine to coarse material is allowed to settle; and the coarser and heavier grains sink more rapidly than the finer ones.
4. Ripple marks and mud cracks—usually indicating near-shore or exposed sediments.

Sedimentary Processes

1. Weathering
   Interaction of rocks with the atmosphere and hydrosphere. The primary decomposition agents

are carbonic acid (CO_2 and H_2O) and humic acids from vegetation. The type of reactions and their intensity depend to a great extent on climate.

2. Transportation
   Broken rock pieces or mineral grains are transported primarily by running water (streams), although wind and glaciers also transport sediment. The processes that occur during transportation are
   a. Sorting—separation into different size fractions.
   b. Rounding—abrading the rough edges of grains.
   c. Size reduction—primarily of grains with good cleavage.
3. Deposition
   The sedimentary environment is the place of deposition, which includes the physical, chemical, and biological conditions that exist at that place. Examples are
   a. Fluvial—river deposits
   b. Alluvial fans—sediment deposited by a stream where it emerges from an upland or mountain into a broad valley or plain (arid environment).
   c. Eolian—wind-borne sediments. Dune sands are well sorted, as the lighter wind-blown grains are deposited much farther away as loess.
   d. Glacial—transport by glaciers and their meltwaters. Ice-borne sediments are poorly sorted, whereas the water-borne ones are well sorted.
   e. Shallow marine—near shore (<200 m depth).
   f. Deep marine—deep ocean basins (>200 m depth).
   g. Deltas—sediment deposited at the mouth of rivers.
   h. Beaches—wave-washed sediment along coasts.
   i. Tidal flats—nearly horizontal land covered with water at high tide and exposed to air at low tide. Sediment is mostly fine grained.
   j. Reefs—solid structure composed of shells and other marine creatures.
4. Compaction and cementation
   The final stage in the formation of sedimentary rocks is the transformation of the loose, unconsolidated sediments into solid rock. This is accomplished by compaction (compression by the overlying rocks) and cementation (precipitation of minerals from the pore waters). Cements are commonly calcite, quartz, or limonite.

Examples of Common Sedimentary Rocks

Sandstones, which consist predominantly of quartz and sometimes potash feldspar grains in a matrix that may consist of clay, calcite, and sometimes iron oxide.

Shales, which are fine-grained rocks consisting primarily of clay minerals, although fine quartz and calcite may also be present.

Limestones, which are rocks composed of calcite and/or dolomite with lesser amounts of other minerals such as clays.

Evaporites, which are primarily chemical sediments that have been precipitated from water. They usually are the result of evaporation in arid climates. Minerals found in this environment include calcite, dolomite, gypsum, anhydrite, and halite.

Metamorphic Rocks

A metamorphic rock is a rock derived from pre-existing rocks by solid-state changes in response to changes in temperature, pressure, and stress.

Metamorphic Textures

1. Foliated—have a definite planar structure and are subdivided on the basis of type of foliation.
   a. **Slate**—is fine grained with slaty cleavage.

b. **Schist**—is medium to coarse grained with foliation. Foliation is caused by parallel arrangement of coarse minerals such as mica and chlorite.
c. **Gneiss**—is a coarse-grained rock where the foliation results from alternating layers of light and dark minerals.

2. Nonfoliated—are rocks with a granular texture. They are usually monomineralic.
Quartzite—quartz
Marble—calcite
Amphibolite—amphibole
Hornfels—very fine-grained, nonfoliated rock

Metamorphic Process

Metamorphism is a solid-state recrystallization process, although the presence of water is crucial. New minerals grow in the direction of the least stress, which gives the rocks the foliation—or preferred orientation—described earlier.

New textures and mineral assemblages develop with increases in temperature and pressure. The assemblages are used to determine the conditions of temperature and pressure under which the rocks were recrystallized. There are two kinds of metamorphism:

1. Contact or thermal metamorphism where temperature is the principle agent of change. This type of metamorphism occurs in the vicinity of igneous intrusions.
2. Regional metamorphism where the effects of increased pressure and temperature are combined with that of shearing stress. Regional metamorphic rocks occur over large areas associated with plate convergence and compression. When temperatures and pressures increase sufficiently, the conditions of regional metamorphism pass into those of magma generation.

Examples of Common Metamorphic Rocks

Schists and **gneisses**—have a mineralogic composition similar to granite with quartz, feldspars, micas, and other minerals such as chlorite, garnet, staurolite, cordierite, and alumino-silicates such as kyanite, sillimanite, and andalusite.

Marble is a coarse-grained metamorphic rock derived from limestone with a similar composition, although impurities may be present (e.g., diopside, forsterite, and others).

Quartzite is a coarse-grained metamorphic rock derived from sandstone and siltstone, composed of quartz. It is essentially monomineralic in composition.

Porosity and Rock Texture

One of the most important textures discussed above is that involving the mutual arrangement of mineral grains in the rock. The two textures that arise are crystalline—minerals that form an interlocking meshwork of grains, and clastic—rocks formed from broken pieces of minerals or rocks. A crystalline texture is characteristic of minerals crystallizing from a melt or from solution, or solid-state recrystallization. This texture, common in most igneous and metamorphic rocks as well as some sedimentary rocks, usually results in minimum primary porosity. Many of these rocks, however, because of stresses built up in them, may have significant secondary porosity because of fractures. Clastic textures, on the other hand, which are characteristic of pyroclastic rocks and many sedimentary rocks, lead to maximum primary porosity. Cementation of sedimentary rocks will usually result in lower porosity.

ROCK-WATER INTERACTIONS

Weathering of rocks involves the reaction of the minerals in rocks with water, carbon dioxide (combined to form carbonic acid), and possibly organic matter such as humic and fulvic acids. The results of such reactions are clays and organic polymers that remain in the soil and the soluble cations (bases), bicarbonate and silicic acid (silica). The soluble components are transported by the water. If sulfides or sulfates are present, they are decomposed (dissolved) and sulfate becomes an additional ion present in the water. Chloride may be added by the solution of halite. Composition of precipitation must not be overlooked. In many cases rainwater has a composition very similar to diluted seawater. It can add significant quantities of sodium, chloride, and sulfate to the infiltrating solution.

Types of weathering processes can be readily ascertained by the examination of a geologic map. However, a rudimentary knowledge of the mineralogic composition of the major rock type should be known.

SECONDARY WEATHERING ENVIRONMENT

Secondary weathering takes place primarily in the soil environment. Carbonic acid (formed from carbon dioxide and water) breaks down the rocks. A residue of clay minerals and hydrous oxides and hydroxides is left. The exact mineralogy depends on the environmental conditions (temperature, precipitation, biological activity), and other factors, such as drainage. The fluids (leachate) from this environment carry a variety of ions into the surface and groundwater systems. Under tropical weathering conditions almost all cations are leached out and the residual soils consist primarily of the oxides of iron (laterites) and aluminum (bauxites). Under conditions where organic decomposition is slow and large amounts of organic material accumulate, considerable quantities of organic acids such as humic or fulvic acids form. These acids may increase the amount of rock dissolved. Common soil minerals include kaolinite, montmorillonite, illite, limonite, and bauxite. Under arid conditions a caliche layer, calcite or gypsum, may form. If the soil is waterlogged pyrite may form.

CLAY MINERALOGY AND SOILS

Clay minerals are silicate minerals, which contain Si and O as well as other ions (e.g., Ca, Fe, Mg, Al, K, and Na). Major factors influencing their physical properties are the bond strengths between the different ions and the relative number of Si-O bonds. The bonds between the Si and O atoms are covalent. They are stronger than those between oxygen and metals.

The Si atom has four electrons in its outer shell, whereas the O atom has six. Silicon thus forms a Si^{4+} ion and oxygen an O^{2-} ion. Because of their relative sizes the oxygen forms a tetrahedral configuration with Si in its center. This is known as the $[SiO_4]^{4-}$ tetrahedra. As a result of this covalent sharing, each oxygen contains seven outer electrons; the eighth is supplied by the metals.

The silicate group of minerals is made up of various arrangements of the $[SiO_4]^{4-}$ tetrahedra. Different numbers of oxygen atoms are shared by other tetrahedra. The sheet silicates, which include the micas and clay minerals, have three of the four oxygen atoms shared by adjacent tetrahedra. The apices of all tetrahedra in a sheet point in the same direction. The sheets extend indefinitely in two directions. Each sheet is called a tetrahedra layer. The term phyllosilicate is applied to this group of minerals and comes from phyllon (Greek), a leaf; e.g., chloro*phyll* (green leaf). The silicon:oxygen ratio and charge are expressed as $(Si_4O_{10})^{4-}$.

Another layer structure may be formed in this group of minerals. It is the octahedral layer, where O or OH occur at the corners of an octahedron. The OH at each corner is shared by two or three other octahedra. An example is brucite, $Mg(OH)_{6/3} = Mg(OH)_2$. Because each corner is shared by three octahedra it is called a trioctahedral layer. Gibbsite, $Al(OH)_2$, also forms an octahedral layer except that each OH is shared by only two other octahedra. This is called a dioctahedral layer. It effectively leaves one out of three sites vacant.

Layer structures consist of different arrangements of these two basic layer types. One is a tetrahedral layer containing silicon-oxygen tetrahedra, arranged in a plane with all tetrahedra lying on one side. The second is an octahedral layer containing Mg or Al in the center of an octahedron composed of either oxygen atoms or hydroxyl ions. These also form a layer when all octahedra lie in a plane on one of their triangular faces. Several layer structures are illustrated in Figure 2.3.

1:1 Layer Silicates

The phyllosilicates can be described in terms of various combinations of these tetrahedral and octahedral layers. Each group has a characteristic ratio relating the number of tetrahedral

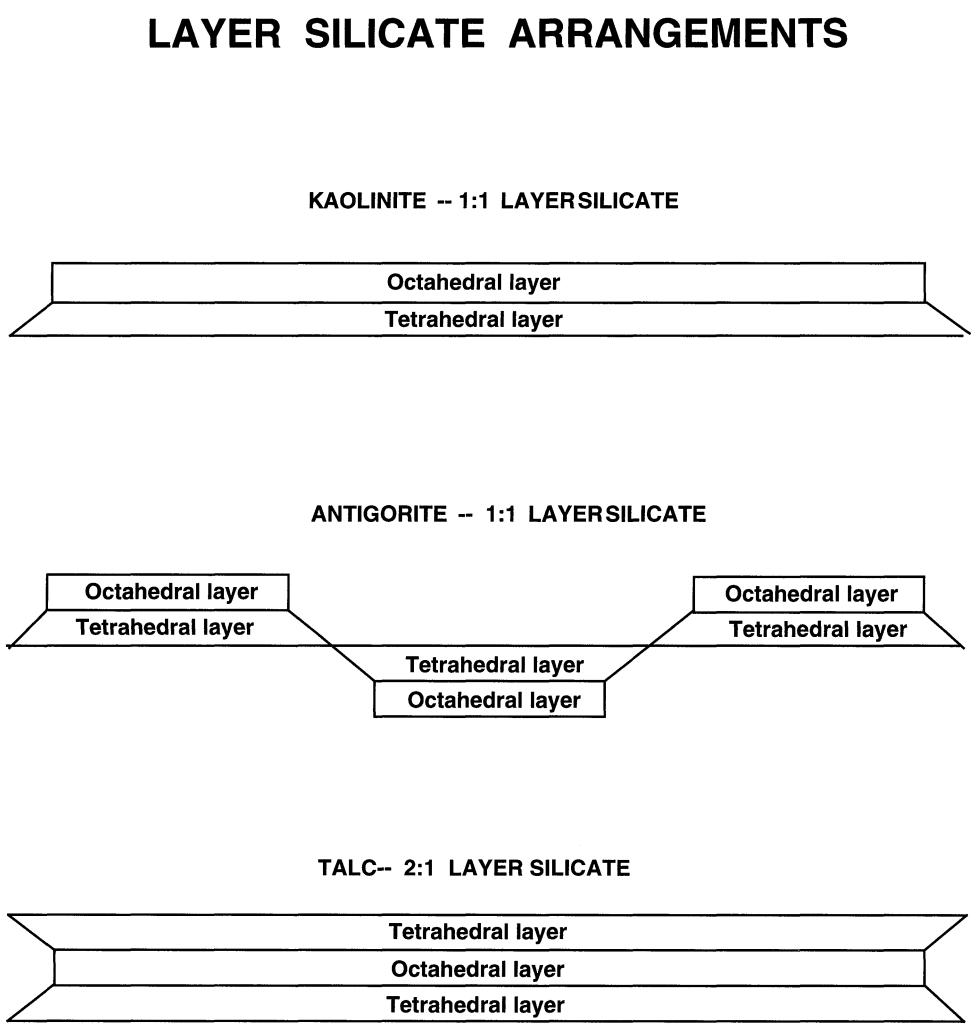


Figure 2.3. Layer structures.

layers to the number of octahedral layers. Therefore, a 1:1 layer silicate has one tetrahedral layer for every octahedral layer.

1:1 nonclay minerals:

These are the serpentine minerals—1:1 layer silicates containing one tetrahedral layer and one octahedral layer. They have an octahedral layer containing Mg. There are two common serpentine minerals, chrysotile asbestos and antigorite. In chrysotile asbestos the octahedral layer is larger than the tetrahedral layer, and the sheet bends or curls into fibers. This strong expansion force on the hydroxyl side tends to make each sheet curl into a cylinder with the Si-O sheet on the outside. This results in a fibrous microstructure. Antigorite, which is a platy serpentine, is a result of the octahedral and tetrahedral sheets reversing their direction at intervals in the sheet. This results in a corrugated form and a platy structure.

1:1 clay minerals:

The most important mineral in this category is kaolinite. It is a 1:1 layer silicate containing one tetrahedral layer and one octahedral layer. The octahedral layer contains octahedral Al. There is a very close match of O and OH of the tetrahedral and octahedral sheets. In the octahedral layer there are 3(OH) above and 3(OH) below. On the side next to the tetrahedral layer, two of the three corners of the octahedra contain the oxygen atoms shared by the Si. Thus, there are 4(OH) for each octahedron. For dioctahedral kaolinite the formula is $Al_2Si_2O_5(OH)_4$. One of the three octahedral sites is empty.

2:1 Layer Silicates

This group consists of two tetrahedral layers separated by one octahedral layer. Examples without Al substituting for Si in the tetrahedral layer are

Talc—Mg in octahedral layer	$Mg_3Si_4O_{10}(OH)_2$
Pyrophyllite—Al in octahedral layer	$Al_2Si_4O_{10}(OH)_2$

Substitution of Al for Si in tetrahedral layers, where one out of each four Si atoms is replaced by Al, are the micas. In this case K balances the charges and occupies the large hole between 12 oxygen atoms. The K-O bond is much weaker than other bonds; therefore it is easily broken. This accounts for the perfect basal cleavage.

Common micas are

Phlogopite	$KMg_3(AlSi_3O_{10})(OH)_2$
Muscovite	$KAl_2(AlSi_3O_{10})(OH)_2$
Biotite	$K(Mg,Fe)_3(AlSi_3O_{10})(OH)_2$

2:1 Clay Minerals

The simplest member of the 2:1 clay minerals is illite. It is essentially a poorly crystalline muscovite with a K deficiency. There is usually a deficit of positive charges near the surface because of tetrahedral substitution; therefore the K^+ ion is held tightly.

Illite $K_{0\text{-}1}Al_2(Al_{0\text{-}1}Si_{4\text{-}3})O_{10}(OH)_2$

2:1 Clay Minerals with Interlayer Water

There may be varying amounts of substitution of Mg^{2+} for Al^{3+}, and Al^{3+} for Si^{4+}. Both types of substitution leave a deficit of positive charges that are balanced by:

1. Interlayer cations.
2. Replacement of O^{2-} by $(OH)^-$
3. Excess cations in the octahedral layer (in dioctahedral clays these sites are only two thirds filled).
4. Adsorption of cations onto surface of individual layers.

The main example is montmorillonite. The primary substitution is of Mg for Al in the octahedral layer of pyrophyllite (dioctahedral with an Al or gibbsite layer). Minor replacement of Al for Si in the tetrahedral layer also occurs. These substitutions result in a small net layer charge balanced by a small number of interlayer cations. The main interlayer cations are Ca and Na. In Ca montmorillonite there are two layers of water, whereas in Na montmorillonite the number of water layers may be 1, 2, 3, to n.

For most cation substitutions the 15.6-Å spacing has wide stability. Trioctahedral montmorillonites are destroyed by dilute mineral acids or concentrated organic acids, leaving a residue of amorphous silica. The dioctahedral montmorillonites are much more stable. In soils the dioctahedral smectites are the more common. Smectites are responsible for most of the shrinking and swelling that occur in soils.

2:1:1 Layer Silicates with Interlayer Brucite

Each 2:1 part of the structure is separated by a brucite layer. The most important minerals in this group are the chlorites. Many substitutions are possible.

$$\text{talc} + \text{brucite} \rightarrow \text{chlorite } Mg_6Si_4O_{20}(OH)_8$$

Al may substitute for Si between Si_7Al and Si_4Al_4. Al may also substitute for Mg between $Mg_{11}Al$ and Mg_8Al_4. Replacement of Fe^{2+} for Mg^{2+} and Fe^{3+} for Fe^{2+} may also occur. If $Fe_2O_3 > 4\%$ they are called oxidized chlorites.

2:1:1 Type Clay Minerals

The most common 2:1:1 clay mineral is vermiculite, which is a Mg containing or trioctahedral clay mineral. The primary substitution is of Al for Si in the tetrahedral layer of the talc structural unit (trioctahedral with a Mg or brucite layer). This charge imbalance is compensated by the presence of interlayer cations, mainly magnesium. The Mg occurs in a double sheet of H_2O, although not all water sites are occupied. The water molecules form a distorted hexagonal pattern. Each oxygen is linked to an oxygen of the tetrahedral layer by a hydrogen bond. The resulting structure resembles that of chlorite, except that the brucite sheet is only partially filled. This results in a $[H_2O - Mg^{2+} - H_2O]$ double sheet. Two thirds of the available water molecule sites are filled and one ninth of the cation sites.

It should be noted that vermiculite and montmorillonite have similarities and may grade into one another. Vermiculite usually has the greater layer charge. Swelling in organic liquids (e.g., glycerol) usually occurs with minerals in this group. Expansion with water may also occur.

Layer charges for some of the more common minerals are listed in Table 2.1.

CATION EXCHANGE CAPACITY (CEC)

CEC is defined as the sum total of exchangeable cations adsorbed. It is expressed in milliequivalents per 100 g of oven-dried soil. Most layer silicates are negatively charged. If the charged sites are not affected by pH they constitute the permanent charge. If the exchange capacity increases with pH it is a pH-dependent charge. The relative ion exchange capacities for several common clay minerals are shown in Figure 2.4.

Charge deficiencies in clays result from:

1. Broken bonds around edges.
2. Removal of H from an exposed OH group,

$$R—Si—OH + OH^- \rightarrow R—Si—O^- + H_2O$$ (the higher the pH the higher the CEC).

Table 2.1. Layer Charges for Selected Clay Minerals

Mineral	Octahedral sheet	Tetrahedral sheet	Charge per unit formula	Exchangeable ions*	Fixed ions
Kaolinite	Al_2	Si_2	0	None	None
Montmorillonite	$Al_{1.7}Mg_{0.3}$	$Si_{3.9}Al_{0.1}$	−0.4	M^+ 0.4	None
Vermiculite	$Al_{1.7}Mg_{0.3}$	$Si_{3.6}Al_{0.4}$	−0.7	M^+ 0.7	xH_2O
Illite	Al_2	$Si_{3.0}Al_{1.0}$	−1.0	M^+ 0.1	K^+ 0.7

* Main interlayer ions are Na^+, Ca^{2+}, Mg^{2+}, and H^+.
Adapted from Brady, 1984.

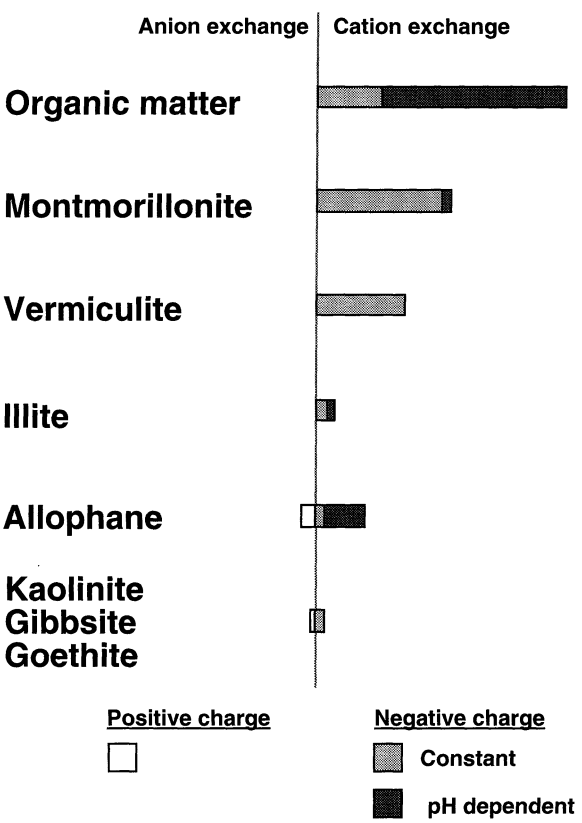


Figure 2.4. Relative ion exchange capacities for several common clay minerals.

3. Removal of structural cations (e.g., removal of Mg^{2+} from octahedral layer).
4. Substitution of low-valence cations for higher-valence cations in the structure (e.g., Al^{3+} for Si^{4+}).

Exchangeable Cations

Cations with greater valence are adsorbed more strongly than cations of lower valence. For a given valence the cation with the smallest hydrated radius will move closest to the adsorbing surface and therefore will be more strongly adsorbed. The energy of adsorption decreases as the square of the distance. Calcium is adsorbed more strongly than sodium because it has a greater valence and a smaller hydrated radius (Foth, 1984).

Percent Base and Hydrogen Saturation

The exchangeable bases are generally considered to include Ca^{2+}, Mg^{2+}, K^+, and Na^+. A particular clay may also contain H^+ on the exchange site. For example, if the exchangeable cations are Ca 14, Mg 3.4, K 0.5, Na 0.1, and H 9.3 meq/100 g, then the total CEC is 27.3. The 18 meq/100 g base exchange capacity represents 66% of the total CEC. The 9.3 meq/100 g of exchangeable H means the soil is 34% hydrogen saturated (Foth, 1984).

Anion Exchange

Anion exchange sites arise from the protonation of hydroxyls on the surfaces of clays. Anion exchange capacity thus increases as soil pH decreases. Gibbsite, goethite, and kaolinite display anion exchange capacity to some extent (Foth, 1984).

Stability Fields of Clay in Water

In groundwater, illite is stable in environments where K^+/H^+ is high; kaolinite is stable in environments where K^+/H^+ is low; and gibbsite is stable in environments where Si^{4+} is very low (Blatt et al., 1980). In rivers en route to the sea, montmorillonite tends to change to illite + chlorite. In seawater under what is called marine diagenesis, montmorillonite changes to mica, and K and Mg are always adsorbed preferentially over Na.

Progressive Diagenesis

Clays older than Upper Paleozoic consist only of illite and chlorite. Younger clays may be montmorillonite, kaolinite, or mixed layer clays.

SOIL

Products of chemical weathering include soluble constituents, which infiltrate to the groundwater system; insoluble residual primary minerals, such as quartz, which are incorporated in the soil profile; and insoluble materials formed in the secondary environment—primarily clays, hydroxides, or organic humic compounds. These materials usually form in the B soil horizon. The environmental factors affecting chemical weathering include climate, biological activity, parent material, topography, and time.

Soil is composed of five major components—mineral matter, water, air, organic matter, and a living population. The quantity of these constituents is not the same in all soils, but

varies with environmental factors. Of the inanimate portion, the amount of mineral and organic matter is relatively fixed at a single site; however, the proportion of air and water fluctuates. Air and water together account for approximately one half the soil volume. This portion of the volume represents the pore space. The living portion of the soil body generally makes up less than 1% of the total volume. The inorganic portion of the soil, because of its influence upon nutrient availability, aeration, and water retention, has a marked effect upon the microbial population. Because the chemical properties and activities of the particles are directly related to their surface area, the status of clay as a reactive constituent in the soil body assumes prominence. Three of the major clay minerals are kaolinite, montmorillonite, and illite.

Soil Texture

Soil texture is determined on the basis of the soil content of sand, silt, and clay. The soil aeration and water relationships, and hence its biological activity, are governed to a great extent by texture.

Soil Profile

As a rule, three major layers are designated in the soil profile—the A, B, and C horizons. The A horizon, the surface soil, designates the stratum subjected to marked leaching. It is also the layer of greatest biologic activity as roots, small animals, and microorganisms are most dense here. In this zone the concentration of organic matter is at its highest; hence, it is the dominant reservoir of microbial food. The B horizon, the subsoil underlying the A horizon, has little organic matter, few plant roots, and sparse microflora. In it iron and aluminum compounds often accumulate. At the very bottom of the profile is the C horizon. This layer contains the parent material of the soil proper. In this stratum organic matter is present in very small quantities and little life is noted.

Pedogenic Regimes

There are several basic trends in soil development, each leading to the formation of a distinctive soil group that is under the control of a particular climatic regime. These basic trends are referred to as pedogenic regimes.

Podzolization

Podzolization dominates in climates having sufficient cold to inhibit bacterial action, but sufficient moisture to permit larger green plants to survive. Such conditions exist at middle and high latitudes and at high elevations. Podzolization is usually associated with coniferous trees. These plants do not require Mg, Ca, and K and therefore do not restore them to the soil surface. The result is that humic acids, produced from the abundant leaf mold and humus, strongly leach the upper soil of bases, colloids, iron, and aluminum oxides. A characteristic ash-gray A horizon composed largely of silica is left. The materials leached from the A horizon accumulate in the B horizon, which may be dark in color and dense in structure.

Laterization

Laterization takes place in a warm climate having abundant rainfall distributed throughout the year (equatorial rain forest). A high mean annual temperature and a lack of severe winter season permit sustained bacterial action, which destroys dead vegetation as rapidly as it is

produced. Consequently, little or no humus is found upon or in the soil. In the absence of humic acids, the oxides of iron are insoluble and accumulate in the soil as red clays, nodules, and rock-like layers (laterite). On the other hand, silica is leached out of the soil and eventually disposed by stream flow in the process of desilication. No distinctive soil horizons are developed. In the absence of colloidal silicates, the soil tends to be firm and porous rather than sticky and plastic, and will transmit water readily.

Calcification

Calcification occurs in a climate in which the average evaporation exceeds precipitation. Rainfall is not sufficient to leach out the bases; therefore, Ca and Mg ions remain in the soil. Grasses, which use these bases, restore them to the soil surface. Colloids remain essentially in place and are not leached out. They are in a dense (flocculated) state and hold the soil into aggregate structures. Calcium carbonate brought upward by capillary water films and evaporates during the dry periods. It is precipitated in the B horizon in the form of nodules, slabs, and dense stony layers called caliche. Microbial activity is restricted, although humus may be abundantly distributed throughout the A and B horizons. Calcification is characteristically associated with grasslands, steppes, and semideserts.

Gleization

Gleization is characteristic of poorly drained (but not saline) environments under a moist and cool or cold climate. It is often associated with the tundra climate, but also occurs in bog environments where there are cold winters. Low temperatures permit heavy accumulations of organic matter to form a surface layer of peaty material. Beneath this is the glei horizon, a thick layer of compact, sticky, structureless clay of bluish-gray color. The glei horizon generally lies within the zone of saturation; consequently, the iron is in a partially reduced condition and imparts the bluish-gray color.

Salinization

Salinization results from the accumulation of highly soluble salts in the soil. It is associated with the desert climate and takes place in poorly drained locations where surface runoff evaporates. Sulfates and chlorides of calcium and sodium are common salts in these soils.

Clay Minerals in Soil

The products of weathering of silicic rocks, which make up the bulk of crystalline rocks, are illite (potassic clay), montmorillonite (containing divalent ions from ferromagnesian minerals), and kaolinite or gibbsite. The clay mineral is dependent on the intensity of weathering and the time during which weathering occurs. In moist temperate climates both illite and montmorillonite remain in the soil. Illite is found in many temperate soils, including podzols, where there has been only limited leaching. Montmorillonite is found in soils formed under neutral conditions, including chestnut and prairie soils, in highly alkaline soils in arid regions, in poorly drained clayey soils (gleys), and in black tropical soils. As the duration or intensity of weathering increases, Na and Ca are stripped from their interlayer positions in montmorillonite and K from its interlayer position in illite. Only kaolinite remains in the soil. Kaolinite is typical of acid tropical soils and red or yellow podzolic soils, all of which are characterized by heavy leaching. Under more severe weathering conditions, as in moist tropical climates, desilication of kaolinite occurs and gibbsite (AlOOH) is produced. Gibbsite

Table 2.2. Occurrence of Clay Minerals

1. Residual clays
   a. Solution of argillaceous limestone.
   b. Alteration of feldspathic rocks.
      —high-grade kaolinite.
      —transformation of crystalline rocks under the influence of deep hydrothermal solutions.
      —loss of silica and almost complete disappearance of alkalis.
      —kaolinization of quartz diorite at 150–300°C.
      —granite.
2. Alteration clays
   Weathering and devitrification of volcanic tuff or ash
      —montmorillonite.
   Result of
      a. hydrothermal action.
      b. groundwater alteration.
      c. weathering.
3. Transported clays
   a. Wind (eolian).
      loess—carbonate and clay, clay size fraction.
         Kansas—mostly montmorillonite.
         Europe—illite and chlorite.
   b. Ice (glacial).
      boulder clay—mainly illite.
   c. Water.
      i. rivers.
         flood-plain deposits.
            Mississippi—montmorillonite.
            Red River—kaolinite.
      ii. lakes.
            stream or glacial.
            often varved.
      iii. swamps.
            coal underclay.
            kaolinite, illite, mixed layers.
      iv. lagoons and deltas.
            often kaolinite.
      v. marine.
            Fuller's earth—montmorillonite.
            shale—illite/kaolinite.

Adapted from Bates, 1969.

and goethite (FeOOH) are the main constituents of laterites. A tabulation of the occurrence of some clay minerals is given in Table 2.2.

EXERCISES

1. How many moles of sulfur are needed to combine with 1 mol of iron to form pyrite (FeS_2)?
2. How many moles of iron are needed to combine with 1.44 mol of sulfur to form pyrite?
3. How many moles of sulfur are in 3 mol of pyrite?
4. How many moles of sulfur are in 1 mol of As_2S_3?
5. How many moles of CO_2 would be liberated from 1 mol of limestone ($CaCO_3$)?
6. For the following analysis calculate formality, molality, mg/l, molarity, and meq/l. Assume the density of solution is 1.11

Ion	ppm	f	m	mg/l	M	meq/l
Na^+	51,600					
K^+	2,650					
Ca^{2+}	1,360					
Mg^{2+}	1,720					
SO_4^{2-}	3,680					
Cl^-	86,600					

7. For each of the following reactions calculate the equivalent weight for the ion specified.

   a. $Ca^{2+} + CO_3^{2-} \rightarrow CaCO_3$ $\quad CO_3^{2-} =$
   b. $HCl + NaOH \rightarrow NaCl + H_2O$ $\quad HCl =$
   c. $CO_3^{2-} + H_2O \rightarrow HCO_3^- + OH^-$ $\quad CO_3^{2-} =$
   d. $O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$ $\quad O_2 =$

8. Calculate the concentrations of Na^+ and Cl^- in mg/l resulting from the solution of 1 g NaCl in 1 l of water.

ANSWERS TO EXERCISES

1. 2, 2. 0.72, 3. 6, 4. 3, 5. 1
6.

	ppm	f (a)	m (b)	mg/l (c)	M (d)	meq/l (e)
Na^+	51,600	2.2445	2.6312	57,276	2.4913	2,491.2
K^+	2,650	0.0678	0.0795	2,942	0.0752	75.23
Ca^{2+}	1,360	0.0339	0.0398	1,510	0.0377	75.33
Mg^{2+}	1,720	0.0708	0.0830	1,909	0.0785	157.07
SO_4^{2-}	3,680	0.0383	0.0449	4,085	0.0425	85.05
Cl^-	86,600	2.4429	2.8638	96,126	2.7116	2,711.6
TDS	147,610					

a. f = ppm/M.Wt/1,000
b. m = f * X
c. mg/l = ppm * D
d. M = mg/l/1,000/M.Wt
e. meq/l = mg/l/M.Wt * Z

Density of solution is 1.11

$$X = \frac{1000}{1000 - 147.61} = 1.1732$$

7.

   a. $Ca^{2+} + CO_3^{2-} \rightarrow CaCO_3$ $\quad CO_3^{2-} = 60/2$
      (valence)
   b. $HCl + NaOH \rightarrow NaCl + H_2O$ $\quad HCl = 36.5/1$
      (# of protons)
   c. $CO_3^{2-} + H_2O \rightarrow HCO_3^- + OH^-$ $\quad CO_3^{2-} = 60/1$
      (# of hydroxyls)
   d. $O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$ $\quad O_2 = 32/4$
      (# of electrons)

8. Na = 1000 * 23/58.4 = 393 mg/l
   Cl = 1000 * 35.45/58.45 = 607 mg/l

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CHAPTER 3

Major Inorganic Constituents of Water

INTRODUCTION

The major inorganic constituents of water originate when water in the form of precipitation dissolves atmospheric gases such as carbon dioxide and reacts with minerals on the surface of the earth. This process is called weathering. The solid phase formed is soil, and the leachate either runs off as surface water or infiltrates and becomes part of the groundwater system. When groundwater moves down gradient from its recharge area to discharge, other minerals are dissolved, some are possibly precipitated, and other various chemical reactions may also occur. These reactions are discussed in more detail in a later chapter.

WEATHERING

Weathering is caused by the interaction of rocks with the atmosphere and hydrosphere. The type of reactions and their intensity depend to a great extent on climate. The relationship and interaction of both the geologic cycle and the hydrologic cycle are shown in Figure 3.1. The primary decomposition agents are carbonic acid (CO_2 and H_2O) and humic acids from vegetation. Weathering processes produce both solids (soil) and liquids (leachate). Leachate may eventually enter groundwater or run off as surface water. The various products of weathering have been classified by geochemists according to their behavior in the secondary environment as follows:

1. Resistates, which are resistant to chemical and mechanical breakdown. They form sandstones or soils containing the minerals (elements)—quartz (Si), zircon (Zr), tourmaline (B), rutile (Ti), cassiterite (Sn), and gold (Au).
2. Hydrolysates, which are secondary products of the chemical breakdown of aluminosilicates such as feldspar. Depending on the conditions, they form shales, soils, or bauxites. They consist of clay minerals (hydrated aluminum silicates) or aluminum oxides/hydroxides. These may adsorb elements such as potassium.
3. Oxidates, which result from the oxidation of iron and precipitation as ferric hydroxide. The products may be redbeds, laterites, or soils. The precipitated ferric hydroxide transforms to limonite (FeOOH). Because the precipitated $Fe(OH)_3$ is a positively charged colloid it may adsorb anions. This is confirmed by the fact that iron ores contain Ni, As, V, P, Sb, Se, and Mo. On the other hand, MnO_2, which is a negatively charged colloid, adsorbs cations. This is substantiated by data that show manganese ores that contain Li, Ba, B, Co, Ni, Cu, Mo, As, V, Pb, and W.
4. Reduzates, which consist of organic material and sedimentary sulfides. These are coal (with many trace elements), oil (containing V, Ni), and sedimentary pyrite (with trace elements).

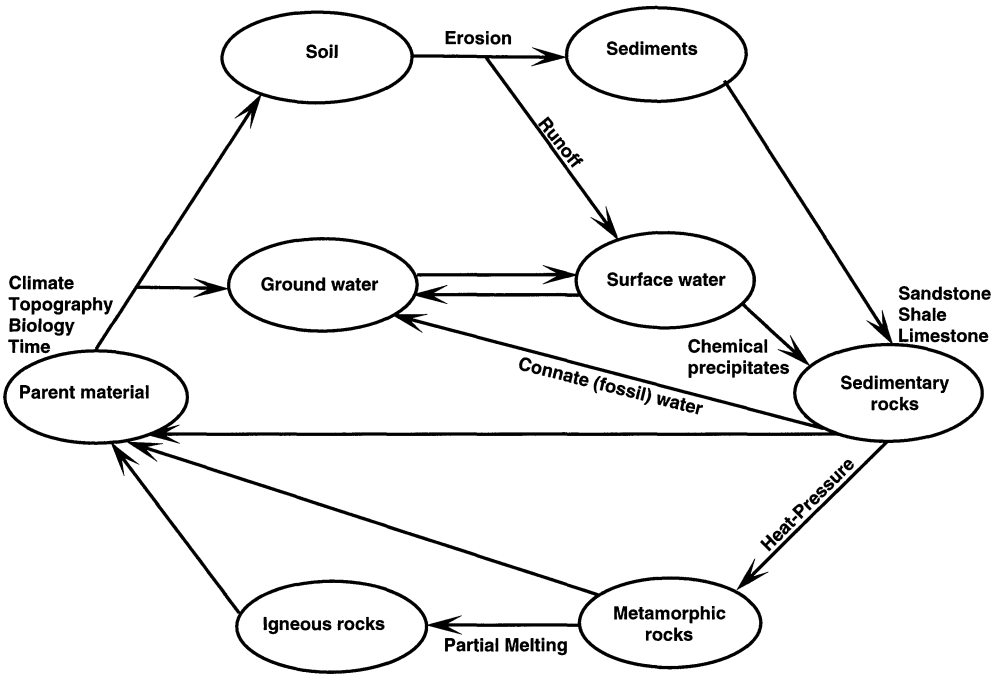

Figure 3.1. Hydrologic and geologic cycles.

5. Carbonates, which are the result of organic or inorganic precipitation of calcite (often containing trace amounts of Mg), aragonite (with traces of Sr), and dolomite (with Fe and Mn). They form limestones, dolomites, and travertines.
6. Evaporates, which are the relatively soluble salts that accumulate in oceans and later evaporate to form evaporites. They usually contain halite (NaCl), sylvite (KCl), gypsum ($CaSO_4 \cdot 2H_2O$), and possibly carnallite ($KCl \cdot MgCl_2 \cdot 6H_2O$).

BALANCING WEATHERING EQUATIONS

The weathering of rocks involves the reactions of their constituent minerals with atmospheric gases and water. The chemical composition of the minerals used in the weathering equations in this chapter are listed in Table 3.1. The simplest method of balancing the chemical equations pertaining to surface mineral weathering reactions involving CO_2 and H_2O is to follow the procedure below.

1. Select a mineral + CO_2 + H_2O and place on the left-hand side.
2. Decide the clay type to be formed (either kaolinite or montmorillonite) and place on the right-hand side.
3. Balance aluminum.
4. Balance cations released.
5. Set bicarbonate to balance cations released, maintaining an electrical balance.
6. Balance Si with H_4SiO_4.
7. Set the number of CO_2 molecules to balance HCO_3^-.
8. Set the number of H_2O molecules to balance the number of H atoms.
9. Count oxygen atoms on both sides to check balance.

Table 3.1. Mineral Composition and Occurrence

Mineral	Variety	Composition	Rock Type: Igneous	Rock Type: Metamorphic	Rock Type: Sedimentary
Quartz		SiO_2	X	X	X
		FELDSPARS			
PLAGIOCLASE					
	Albite	$NaAlSi_3O_8$	X	X	
	Anorthite	$CaAl_2Si_2O_8$	X	X	
Orthoclase/ microcline		$KAlSi_3O_8$	X	X	X
		FERROMAGNESIAN SILICATES			
AMPHIBOLES					
	Tremolite	$Ca_2(Mg,Fe)_4AlSi_7AlO_{22}(OH)_2$	X	X	
	Hornblende	$NaCa_2(Mg,Fe,Al)_5Si_8O_{22}(OH)_2$	X	X	
MICA GROUP					
	Biotite	$K(Mg,Fe)_3AlSi_3O_{10}(OH)_2$	X	X	
	Chlorite	$(Mg,Al,Fe)_6(Si,Al)_4O_{10}(OH)_8$	X	X	
PYROXENES					
	Diopside	$Ca(Mg,Fe)Si_2O_6$	X	X	
	Augite	$Ca(Mg,Fe,Al)(Al,Si)_2O_6$	X	X	
Olivine		$(Mg,Fe)_2SiO_4$	X	X	
Garnet		$Fe_3Al_2(SiO_4)_3$		X	
		HYDROUS ALUMINOSILICATES			
CLAY MINERALS					
	Kaolinite	$Al_2Si_2O_5(OH)_4$			X
	Montmorillonite	$Al_2Si_4O_{10}(OH)_2$			X
	Illite	$KAl_2(AlSi_3O_{10})(OH)_2$			X
		CARBONATES			
Calcite/ aragonite		$CaCO_3$			X
Dolomite		$CaMg(CO_3)_2$			X
		HALIDES			
Fluorite		CaF_2	X		
Halite		NaCl			X
		OXIDES/HYDROXIDES			
Bauxite		AlOOH			X
Hematite		Fe_2O_3			X
Limonite		FeOOH			X
		SULFIDES/SULFATES			
Pyrite/ marcasite		FeS_2	X	X	X
Gypsum		$CaSO_4 \cdot 2H_2O$			X
Anhydrite		$CaSO_4$			X
Barite		$BaSO_4$	X	X	

Example 1.

WEATHERING OF ORTHOCLASE TO KAOLINITE

1. Select mineral, CO_2, and H_2O

$KAlSi_3O_8 + ?CO_2 + ?H_2O \Leftrightarrow$

2. Clay type

$\Leftrightarrow$ KAOLINITE

$\Leftrightarrow$ $Al_2Si_2O_5(OH)_4$

3. Balance Al

$2KAlSi_3O_8 + ?CO_2 + ?H_2O \Leftrightarrow Al_2Si_2O_5(OH)_4$

4. Balance cations

$2KAlSi_3O_8 + ?CO_2 + ?H_2O \Leftrightarrow Al_2Si_2O_5(OH)_4 + 2K^+$

5. Balance cations with bicarbonate

$2KAlSi_3O_8 + ?CO_2 + ?H_2O \Leftrightarrow Al_2Si_2O_5(OH)_4 + 2K^+ + 2HCO_3^-$

6. Balance Si

$2KAlSi_3O_8 + ?CO_2 + ?H_2O \Leftrightarrow Al_2Si_2O_5(OH)_4 + 2K^+ + 2HCO_3^- + 4H_4SiO_4$

7. Determine CO_2

$2KAlSi_3O_8 + 2CO_2 + ?H_2O \Leftrightarrow Al_2Si_2O_5(OH)_4 + 2K^+ + 2HCO_3^- + 4H_4SiO_4$

8. Determine H_2O

$2KAlSi_3O_8 + 2CO_2 + 11H_2O \Leftrightarrow Al_2Si_2O_5(OH)_4 + 2K^+ + 2HCO_3^- + 4H_4SiO_4$

9. Check Oxygen

$16 + 4 + 11 = 9 + 6 + 16$

$31 \qquad\qquad\qquad\qquad 31$

Example 2.

WEATHERING OF BIOTITE TO MONTMORILLONITE

1. Select mineral, CO_2, and H_2O

$KMg_3AlSi_3O_{10}(OH)_2 + ?CO_2 + ?H_2O \Leftrightarrow$

2. Clay type

$\Leftrightarrow$ MONTMORILLONITE $Al_2Si_4O_{10}(OH)_2$

3. Balance alumina

$2KMg_3AlSi_3O_{10}(OH)_2 + ?CO_2 + ?H_2O \Leftrightarrow Al_2Si_4O_{10}(OH)_2$

4. Balance cations

$2KMg_3AlSi_3O_{10}(OH)_2 + ?CO_2 + ?H_2O \Leftrightarrow Al_2Si_4O_{10}(OH)_2 + 2K^+ + 6Mg^{2+}$

5. Balance cations with bicarbonate

$2KMg_3AlSi_3O_{10}(OH)_2 + ?CO_2 + ?H_2O \Leftrightarrow Al_2Si_4O_{10}(OH)_2 + 2K^+ + 6Mg^{2+} + 14HCO_3^-$

6. Balance Si

$2KMg_3AlSi_3O_{10}(OH)_2 + ?CO_2 + ?H_2O \Leftrightarrow Al_2Si_4O_{10}(OH)_2 + 2K^+ + 6Mg^{2+} + 14HCO_3^- + 2H_4SiO_4$

7. Determine CO_2

$2KMg_3AlSi_3O_{10}(OH)_2 + 14CO_2 + ?H_2O \Leftrightarrow Al_2Si_4O_{10}(OH)_2 + 2K^+ + 6Mg^{2+} + 14HCO_3^- + 2H_4SiO_4$

8. Determine H_2O

$2KMg_3AlSi_3O_{10}(OH)_2 + 14CO_2 + 10H_2O \Leftrightarrow Al_2Si_4O_{10}(OH)_2 + 2K^+ + 6Mg^{2+} + 14HCO_3^- + 2H_4SiO_4$

9. Check oxygen

$24 + 28 + 10 = 12 + 42 + 8$

$62 \qquad\qquad\qquad 62$

The results of weathering of other common minerals are listed in Table 3.2. The mineralogic composition of a typical granite with the weathering products are given in Figure 3.2.

INTRODUCTION TO WATER QUALITY

Water quality refers to the composition of a water sample. In this discussion it will be restricted to the inorganic constituents of the water. The interpretation of water quality data may be difficult and time consuming. All data are wasted if the collection, preservation, and analysis of the water sample is not done correctly and precisely. Sampling and preservation techniques are not the topic of this book; however, an abbreviated outline of procedures is presented below.

SOURCES OF GROUNDWATER QUALITY DATA

The various sources of groundwater samples include rivers, where the groundwater contribution is greatest under low-flow conditions; springs, where more direct samples may be obtained; and finally wells, which produce the most direct sampling of the groundwater. Deposits around springs will indicate water conditions changed upon exposure to atmospheric temperatures and pressures. Wells are the most difficult reliable samples to collect. Stringent procedures must be used to avoid contamination and changes in parameters that may occur during sample collection.

Before a sample is collected, the collection protocol must be established. This involves establishing a collection procedure, obtaining appropriate containers, and utilizing correct methods of preservation. For each constituent in a water analysis the EPA has a recommended

Table 3.2. Weathering Equations for Common Minerals

$2NaAlSi_3O_8 + 2CO_2 + 11H_2O \rightarrow Al_2Si_2O_5(OH)_4 + 2Na^+ + 2HCO_3^- + 4H_4SiO_4$	
albite	kaolinite
$2NaAlSi_3O_8 + 2CO_2 + 6H_2O \rightarrow Al_2Si_4O_{10}(OH)_2 + 2Na^+ + HCO_3^- + 2H_4SiO_4$	
albite	montmorillonite
$CaAl_2Si_2O_8 + 2CO_2 + 3H_2O \rightarrow Al_2Si_2O_5(OH)_4 + Ca^{2+} + 2HCO_3^-$	
anorthite	kaolinite
$2KMg_3AlSi_3O_{10}(OH)_2 + 14CO_2 + 15H_2O$	
biotite	
$\rightarrow Al_2Si_2O_5(OH)_4 + 2K^+ + 6Mg^{2+} + 14HCO_3^- + 4H_4SiO_4$	
kaolinite	
$2KMg_3AlSi_3O_{10}(OH)_2 + 14CO_2 + 10H_2O$	
biotite	
$\rightarrow Al_2Si_4O_{10}(OH)_2 + 2K^+ + 6Mg^{2+} + 14HCO_3^- + 2H_4SiO_4$	
montmorillonite	
$Ca_2Mg_4Al_2Si_7O_{22}(OH)_2 + 12CO_2 + 17H_2O$	
tremolite	
$\rightarrow Al_2Si_2O_5(OH)_4 + 2Ca^{2+} + 4Mg^{2+} + 12HHCO_3^- + 5H_4SiO_4$	
kaolinite	
$Ca_2Mg_4Al_2Si_7O_{22}(OH)_2 + 12CO_2 + 12H_2O$	
tremolite	
$\rightarrow Al_2Si_4O_{10}(OH)_2 + 2Ca^{2+} + 4Mg^{2+} + 12HCO_3^- + 3H_4SiO_4$	
montmorillonite	
$CaMgSi_2O_6 + 4CO_2 + 6H_2O \rightarrow Ca^{2+} + Mg^{2+} + 4HCO_3^- + 2H_4SiO_4$	
diopside	[no Al no clay mineral]
$Mg_2SiO_4 + 4CO_2 + 4H_2O \rightarrow 2Mg^{2+} + 4HCO_3^- + H_4SiO_4$	
olivine	[no Al no clay mineral]
$CaCO_3 + 2CO_2 + 2H_2O \rightarrow Ca^{2+} + 2HCO_3^-$	
calcite	[no Al no clay mineral]
$CaMg(CO_3)_2 + 2CO_2 + 2H_2O \rightarrow Ca^{2+} + Mg^{2+} + 4HCO_3^-$	
dolomite	[no Al no clay mineral]

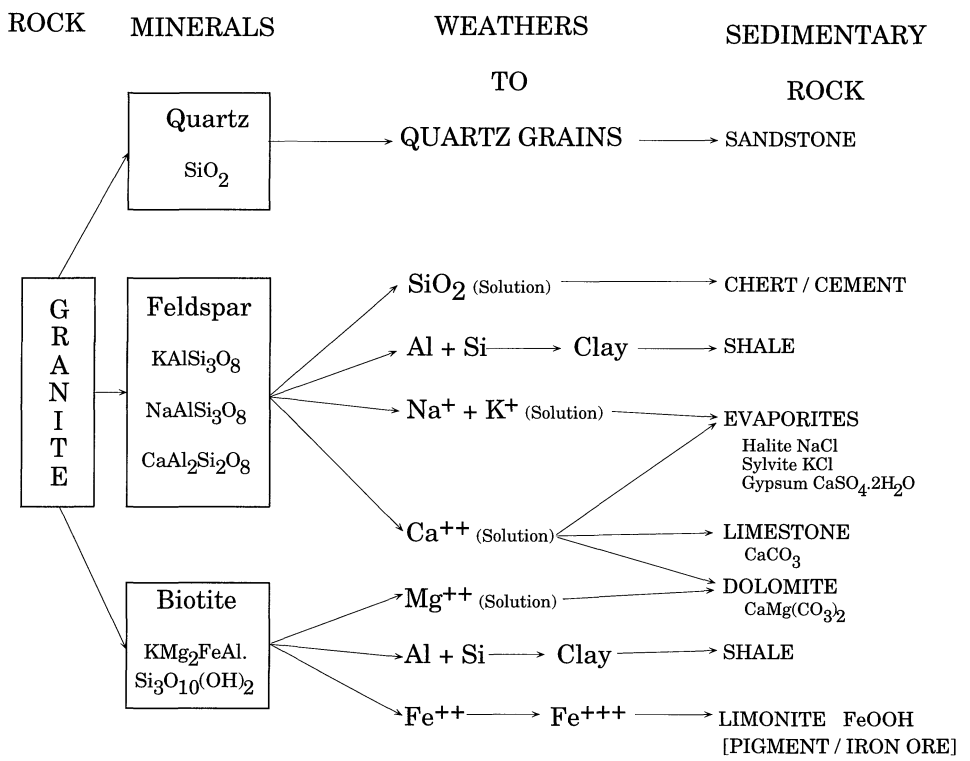

Figure 3.2. Minerals and weathering products of a granite. (Adapted from Levin, 1981.)

preservation and analysis procedure that must be followed. This is done in order to reduce the effects of adsorption or biodegradation. Samples must be collected and transported in special containers and preserved, either in ice or by the addition of acid or other preservative, depending on the constituent being considered.

Although most analyses are performed in the laboratory, some determinations must be conducted in the field. Determinations that are dependent on dissolved gases must be run as soon as possible after collection. For some groundwaters under pressure, even field measurements may be too late. Determinations usually performed in the field include temperature, pH, dissolved oxygen (DO), redox potential (Eh or pe), and alkalinity, which is very dependent on the partial pressure of CO_2.

After collection the samples may be analyzed by the collector or submitted to an analytical laboratory. In either case the appropriate quality assurance protocols must be adhered to in order to have confidence in the results.

If one does not have the resources for a sampling survey or if historical data are required, reference must be made to published data or data banks such as the U.S. EPA (STORET) or the U.S. Geological Survey (WATSTORE). However, one must be careful to evaluate each analysis with care, as poor and/or incomplete analyses are very common in data banks. If one must use partial analyses it may be necessary to estimate some of the missing parameters.

SOLUBILITY AND THE DISSOLVED CONSTITUENTS IN WATER

The solution of materials in water can be viewed from several perspectives. One perspective involves simply the amount of that material (solute) that is dissolved. It may vary from nothing to the maximum amount that may dissolve at the temperature and pressure of the

water. This maximum quantity is called the solubility for the solute in water. A solution containing this quantity is said to be saturated with respect to that solute. If the water contains less than this maximum quantity of solute in solution it is said to be undersaturated with respect to this constituent. If it contains more than the maximum it is said to be oversaturated. This implies that other factors are affecting the solubility. Some of the theoretical factors involved with this phenomena will be discussed later. The principal factor influencing solubility is temperature. The solubility of most salts will increase with an increase in temperature; however, the solubility of most gases will decrease with an increase in temperature.

Another phenomena that may occur when a material dissolves in water is known as dissociation, a mechanism whereby an ionic solid dissolves and in so doing breaks down into its individual ions. Various materials do this to different degrees. Sugar dissolves in water and exists in the water as individual sugar molecules. On the other hand, sodium chloride dissolves in water and dissociates almost completely into sodium (Na^+) and chloride (Cl^-) ions (in dilute solutions). In more concentrated solutions, some of the ions may be attracted to each other and form neutral $NaCl^0$ species in the water. The existence of charged ions in solution can be demonstrated by the fact that they can carry an electric current when electrodes are immersed in the solution. This phenomena is used when conductivity measurements are made on the solution.

In a typical water, the major ions existing in solution are Na^+, K^+, Ca^{2+}, Mg^{2+}, Cl^-, SO_4^{2-}, HCO_3^-, and CO_3^{2-}. Silicon is usually considered to exist as an uncharged SiO_2 species. Other minor species commonly occurring in water include NO_3^-, F^-, Br^-, Si^{2+}, Ba^2+, Fe^{2+}, Li^+, B^{3+}, and PO_4^{3-}. A common classification of aqueous species is given in Table 3.3.

COMMONLY DETERMINED CONSTITUENTS

Water samples are generally analyzed in a laboratory. However, some parameters must be analyzed in the field at the point of collection because their value will change with time and exposure to the atmosphere.

Field Parameters

The parameters usually measured in the field include temperature, pH, conductivity, alkalinity, and oxidation/reduction values.

Table 3.3. Major, Minor, and Trace Constituents of Water

Major constituents >5 mg/l	Minor constituents 0.01–10 mg/l	Trace constituents <0.1 mg/l
Sodium	Potassium	Aluminum
Calcium	Strontium	Arsenic
Magnesium	Iron	Barium
Chloride	Carbonate	Bromide
Sulfate	Fluoride	Cadmium
Bicarbonate	Nitrate	Chromium
Silica		Cobalt
		Copper
		Iodide
		Lead
		Lithium
		Manganese
		Molybdenum
		Phosphate
		Selenium
		Uranium
		Zinc

Basic Water Quality Parameters

The ions commonly determined in a water sample include:

$$Na^+, K^+, Ca^{2+}, Mg^{2+}, Cl^-, SO_4^{2-}, HCO_3^-, \text{and } CO_3^{2-}.$$

Other determinations include SiO_2 total dissolved solids (TDS) and hardness. Density should also be measured on brines. B^{3+}, Br^-, Sr^{2+}, Li^+, Ba^{2+}, F^-, and other less common elements may be reported in brine studies.

SOURCE OF MAJOR IONS IN WATERS

The following is a discussion on the sources of the common inorganic major elements that are found in waters. Included are the different ways by which their ions may be removed from solution, referred to as sinks.

Sodium

Sources of sodium (Na^+) are halite (NaCl), sea spray, hot springs, brines, some silicates, and rarer minerals such as nahcolite ($NaHCO_3$). Common sodic silicates include plagioclase—variety albite ($NaAlSi_3O_8$), and nepheline ($NaAlSiO_4$). Most sodium results from natural ion exchange. It is where Na-montmorillonite clay reacts with calcium and magnesium and releases sodium (sometimes called natural softening).

$$2\ \text{Na-clay} + Ca^{2+} \rightarrow \text{Ca-clay} + Na^+$$

The only common sink for sodium is reverse ion exchange (regeneration) that occurs when highly saline waters come in contact with calcium-rich clays.

Chloride

Common sources of chloride (Cl^-) are halite (NaCl), sea spray, brines, and hot springs. There are no common sinks for chloride except for evaporites.

Potassium

Sources of potassium (K^+) are potash feldspar ($KAlSi_3O_8$), mica ($KAl_2(AlSi_3)O_{10}(OH)_2$), and, less commonly, leucite ($KAlSi_2O_6$) and sylvite (KCl). The usual sinks are plants and clays. A common clay reaction is

$$\text{clays} + K^+ \rightarrow \text{illite}$$

Calcium

Sources of calcium (Ca^{2+}) are calcite ($CaCO_3$), aragonite ($CaCO_3$), dolomite ($CaMg(CO_3)_2$), gypsum ($CaSO_4 \cdot 2H_2O$), anhydrite ($CaSO_4$), fluorite (CaF_2), plagioclase (anorthite, $CaAl_2Si_2O_8$), pyroxene (diopside, $CaMgSi_2O_6$), and amphibole ($NaCa_2(Mg,Fe,Al)Si_8O_{22}(OH)_2$). Common sinks are calcite, gypsum, and montmorillonite (natural softening).

Sulfate

Sources of sulfate (SO_4^{2-}) are the minerals pyrite (FeS_2), gypsum ($CaSO_4 \cdot 2H_2O$), and anhydrite ($CaSO_4$). Under some conditions considerable quantities of sulfate may be obtained from organic sulfur compounds (e.g., combustion of coal and petroleum, smelting of sulfide ores, and geothermal waters). The more common sinks are pyrite, gypsum, and sulfate reduction. The generalized formula for sulfate reduction is

$$SO_4^{2-} + 2CH_2O \rightarrow 2HCO_3^- + H_2S$$

A saturated solution of gypsum in water would contain 636 mg/l Ca^{2+}, and 1600 mg/l SO_4^{2-}. However, this increases with NaCl concentration.

Magnesium

The most common source of large quantities of magnesium (Mg^{2+}) in natural waters is dolomite ($CaMg(CO_3)_2$). Magnesium is derived also from the silicates olivine ($(Mg,Fe)_2SiO_4$), pyroxene (diopside, $CaMgSi_2O_6$), amphibole ($NaCa_2(Mg,Fe,Al)Si_8O_{22}(OH)_2$), and mica ($K(Mg,Fe)_3(AlSi_3)O_{10}(OH)_2$). The main sink is montmorillonite. In saline waters, magnesium chlorite is considered to be a major sink.

Carbonate/Bicarbonate

Sources of carbonate species (HCO_3^- and CO_3^{2-}) are

the atmosphere (CO_2), e.g., [$H_2O + CO_2 \Leftrightarrow H_2CO_3 \Leftrightarrow H^+ + HCO_3^-$],

sulfate reduction, e.g., [$SO_4^{2-} + 2CH_2O$ v $H_2S + 2HCO_3^-$],

calcite, dolomite, and, much more rarely, nahcolite ($NaHCO_3$).

The most common sink is calcite. The amount of carbon dioxide in the atmosphere is 0.03% ($P_{CO2} = 0.0003$ atmospheres). The partial pressure of CO_2 (P_{CO2}) may be 10 to 100 times higher in soils because of decomposition of organic matter.

SOURCES OF MINOR IONS IN NATURAL WATERS

The following minor elements may be found in natural waters. Although they are far from ubiquitous, they may be in significant quantities in some waters. They are generally the result of specific reactions or they occur only in unique waters such as oil-field brines or saline-formation waters.

Strontium

Sources of strontium (Sr^{2+}) are strontianite ($SrCO_3$), celestite ($SrSO_4$), and aragonite ($CaCO_3$). The latter is probably the most common source because Sr^{2+} substitutes for Ca^{2+} in aragonite, but not in calcite. Thus, during diagenesis when aragonite is converted to the more stable polymorph calcite, the strontium is released to the water. The common sinks are the minerals strontianite and celestite, although ion exchange is probably more important. Strontium may occur in the 100–1000-mg/l range in oil-field brines. It has been reported in these waters as high as 11,600 mg/l (Collins, 1975). Seawater contains 8 mg/l Sr.

Barium

The main mineralogic source of barium (Ba^{2+}) is barite ($BaSO_4$). It most probably originates from oil-field brines. The solubility of barite in water is less than 1 ppm, whereas

oil-field brines commonly contain 5–50 mg/l, with one reported value of 670 mg/l (Collins, 1975). The only common sinks are barite and ion exchange. Seawater contains 0.02 mg/l Ba. High barium values usually occur in brines where the sulfate is low or absent.

Lithium

Lithium (Li^+)-bearing minerals include some pyroxenes and micas where lithium may replace magnesium. All, however, are relatively rare pegmatite minerals. Lithium does occur in some brines and evaporites. In subsurface waters the lithium content may increase with increasing temperature. Under the same conditions, magnesium tends to decrease. Thus Li/Mg ratios have been used as a chemical geothermometer (Kharaka and Mariner, 1987). Recent studies have shown that lithium is adsorbed by illite and other clays (Shaw and Sturchio, 1992). The lithium content of oil-field brines is typically 5–50 mg/l, although 400 mg/l has been reported (Collins, 1975). Seawater contains 0.17 mg/l Li.

Bromide

Seawater contains 67 mg/l Br^-. Natural brines typically contain 100–1000 mg/l, although values as high as 6000 mg/l have been reported (Collins, 1975). Because halite contains about 68 mg/l Br, a brine derived from a halite evaporite with a similar salinity to that of seawater would contain only 2.3 mg/l Br. The Br/Cl ratio is commonly used as an indicator of brine contamination (Whittemore, 1984, 1985).

Fluoride

Fluoride (F^-) in natural waters may originate from the solution of fluorite, apatite, or more commonly from the solution of fluoride-bearing micas and amphiboles. A common sink for fluoride is adsorption by kaolinite. This is an example of anion exchange. The adsorption is greatest at pH 6 and negligible below pH 4 and above pH 7.5 when desorption occurs. The result is that alkaline waters are commonly high in fluoride. The fluoride content of seawater is 1.3 mg/l. Most fresh waters contain less than 1 mg/l fluoride (Hem, 1992). Some slightly alkaline waters may contain more than 1 mg/l fluoride because of the desorption from kaolinite (Hounslow and Back, 1985).

Boron

Boron (B^{3+}) is not an uncommon element in minerals. It is a major constituent of the mineral tourmaline, a typical resistate mineral. It is seldom broken down during chemical weathering and generally occurs in the unweathered state in sandstones. Seawater contains 4.5 mg/l boron (Hem, 1992). The removal of dissolved boron from seawater and its adsorption by clay minerals is well known. This aspect of its behavior has been used as a paleosalinity indicator. Boron is richer in seawater than in river waters and is thought to be removed from seawater under estuarine conditions (Liss and Pointon, 1972). Boron commonly occurs in water as $B(OH)_3$ [or $H_3BO_3(aq)$] and $B(OH)_4^-$ [or $H_2BO_3^-$]. Below pH 8.7 $B(OH)_3$ predominates and is not adsorbed by clays to any great extent. $B(OH)_4^-$ predominates above pH 8.7 and is readily adsorbed by clay minerals (Spivack et al., 1987).

Nitrate

Nitrate (NO_3^-) occurs in almost all natural waters. Concentrations range up to hundreds of mg/l. Except when contamination is present, they seldom exceed 20 mg/l. However,

10 mg/l (as NO_3^-) or greater may be regarded as a probable indication of contamination from fertilizers, municipal wastewaters, feedlots, septic systems, and sometimes the cultivation of grasslands. Of the common nitrogen species the nitrate ion is not readily adsorbed by clay minerals. It moves freely through the aquifer, which is in contrast to ammonium ions that are strongly adsorbed by some clay minerals.

The primary source of all nitrates is atmospheric nitrogen gas. This is converted to organic nitrogen by some plant species by a process called nitrogen fixation. On the death of the plants the organic compounds are decomposed by microorganisms to inorganic ammonium salts (ammonification). These in turn are converted to nitrates by a process called nitrification. The intermediate product—nitrite—is generally short lived and seldom accumulates in significant quantities in any natural environment. In environments that are depleted in oxygen, some microorganisms can use nitrate in place of gaseous oxygen to carry out their metabolic processes. The products of this reaction are nitrogen gas and/or nitrous oxide (N_2O). This process, called denitrification, effectively removes nitrogen from the subsurface. Most of these reactions require either oxidizing or reducing conditions, thus may occur in different zones in the subsurface. pH may also be a critical parameter in these processes. Ammonia will only occur in very reduced waters where H_2S and/or CH_4 may also be present. The nitrogen cycle is discussed in more detail in Chapter 6, especially in Figures 6.2 and 6.4.

Iron

Iron is an abundant element and usually occurs in the ferric (Fe^{3+}) or oxidized form on the surface of the earth. In this form, except for very acid waters, it is to all intents insoluble and exists only in ppb quantities. Only in moderately reduced anaerobic waters does the reduced form of iron, ferrous iron (Fe^{2+}), exist in significant quantities, which is generally in the 1–10-mg/l range. Hem (1992) reports concentrations up to 50 mg/l are possible if the bicarbonate concentration is less than 61 mg/l. In highly reducing waters with H_2S present, ferrous iron is removed by precipitation as a sulfide—pyrite or marcasite.

Silica

The silica in most low-temperature waters is derived primarily from silicate weathering, as discussed earlier in this chapter. Geothermal waters, however, may contain considerable dissolved quartz or chalcedony. The solubility of quartz in hot waters is shown in Table 4.4 (Truesdell, 1984). Sinks for dissolved silica are clay minerals or secondary silica deposited as cement, overgrowths on quartz grains, or as chert deposits.

Summary

A listing of the common sources and sinks resulting from direct precipitation/solution and from some reactions is listed in Table 3.4.

COMMONLY REPORTED PARAMETERS

In addition to the ions described above, a variety of other parameters are often reported. Some are actual determinations and others are calculated values. For instance, hardness may be an experimental value, but generally is calculated from calcium and magnesium values.

Hardness

Hardness is the sum of the Ca and Mg concentrations expressed in terms of mg/l of calcium carbonate.

Table 3.4. Sources and Sinks of Ions

Sources and sinks of ions other than direct mineral solution/precipitation

Ion	Sources	Sinks
Sodium	Ion exchange	Reverse ion exchange
Potassium		Clay absorption, plant uptake
Calcium	Reverse ion exchange	Ion exchange
Magnesium	Reverse ion exchange [dedolomitization—dolomite and gypsum solution with calcite precipitation]	Ion exchange
Strontium	Aragonite → calcite diagenesis oil-field brines	Ion exchange
Chloride	Brine, seawater, rainwater	
Sulfate	Pyrite oxidation	Sulfate reduction
Bicarbonate	Rock dissolution; sulfate reduction; pyrite oxidation and neutralization	
Nitrate	Agriculture, sewage	Denitrification, plant uptake

Major sources of ions from mineral solution, and major mineral sinks

Ion	Sources	Sinks
Sodium	Halite, albite (plagioclase)	
Potassium	Mica, potash feldspar	
Calcium	Calcite, dolomite, gypsum (anhydrite), anorthite (plagioclase), pyroxenes	Calcite, gypsum
Magnesium	Dolomite, ferromagnesian silicates	
Chloride	Halite	
Sulfate	Pyrite, gypsum (anhydrite)	Gypsum
Bicarbonate	Rock weathering (atmospheric CO_2)	Calcite
Silica	Silicates	

Sources and sinks that may occur in formation waters

Ion	Sources	Sinks
Sodium		Reverse ion exchange
Potassium		Illite formation
Calcium		Anhydrite or calcite precipitation
Magnesium		Dolomitization, chlorite formation
Chloride		
Sulfate		Anhydrite precipitation Sulfate reduction and pyrite formation
Bicarbonate		
Silica	Clay mineral diagenesis	Secondary quartz

$$\text{Hardness} = \text{Ca(mg/l)} * \frac{\text{M.Wt. } CaCO_3}{\text{At.Wt. Ca}} + \text{Mg(mg/l)} * \frac{\text{M.Wt. } CaCO_3}{\text{At.Wt. Mg}}$$

Example: Ca = 200 mg/l Ca^{2+}, Mg = 30 mg/l Mg^{2+}

$$\text{Hardness} = 200 * \frac{100.088}{40.08} + 30 * \frac{100.088}{24.312}$$

$$= 499.4 \qquad +123.5$$

$$= 622.9 \text{ mg/l } CaCO_3$$

Calcium and magnesium form an insoluble residue with soap, which is typified as bathtub ring. Detergents were introduced to overcome this. Calcium carbonate precipitation is a major problem in boilers because it results in poor heat conduction. The hardness of streams may vary seasonally because of variation in groundwater and in surface water runoff. Groundwater is more likely to have a greater hardness than surface water. Total hardness is the sum of

calcium plus magnesium expressed as calcium carbonate. Other elements that could be included are strontium, barium, and some heavy metals. These, however, are seldom determined and are usually present in insignificant amounts relative to calcium and magnesium. Temporary hardness is the calcium and magnesium carbonate that would be removed by boiling, leaving a precipitate of $CaCO_3$. Permanent hardness (or noncarbonate) is the calcium and magnesium that would exist as sulfates or chlorides, which would not be removed by boiling.

Dissolved Solid Content—TDS

The dissolved solid content of a water, often called TDS, is calculated by adding the mass of ions plus SiO_2. This may differ from the chemically determined residue on evaporation, which is determined by evaporating to dryness a known volume of water at a specified temperature—usually 105–180°C. As a result of this heating, bicarbonates are converted to carbonates in the solid phase. At 180°C, CO_2 and H_2O are lost. Then bicarbonates are essentially completely converted to carbonate by the reaction:

$$2HCO_3^- \rightarrow CO_3^{2-} + CO_2 + H_2O$$

At temperatures below 180°C this reaction may not go to completion. The amount of carbonate formed

$$= \frac{\text{mg/l } HCO_3^-}{\text{M.Wt. } HCO_3^-} * \frac{\text{M.Wt. } CO_3^{2-}}{2}$$

The amount of H_2O and CO_2 lost

$$= \frac{\text{mg/l } HCO_3^-}{\text{M.Wt. } HCO_3^-} * \frac{\text{M.Wt. } H_2CO_3}{2}$$

Thus the analytical TDS or residue on evaporation (180°C)

$$= \text{sum of ions} + SiO_2 - \frac{\text{mg/l } HCO_3^-}{\text{M.Wt. } HCO_3^-} * \frac{\text{M.Wt. } H_2CO_3}{2}$$

$$= \text{sum of ions} + SiO_2 - \frac{\text{mg/l } HCO_3^-}{61.016} * \frac{62.02}{2}$$

$$= \text{sum of ions} + SiO_2 - \text{mg/l } HCO_3^- * 0.5082$$

In waters with high calcium and sulfate the residue at 180°C may still be slightly hydrated because of the formation of $CaSO_4 \cdot \frac{1}{2}H_2O$ (plaster of paris), thus giving high results. Some waters, especially brines, yield a very deliquescent (moisture-absorbing) residue, which is difficult to weigh accurately and often results in high numbers.

Conductivity

Conductivity is also called electrical conductivity (EC), specific conductivity, or conductance. Conductivity is the reciprocal of the resistance in ohms between the opposite faces

of a 1-cm cube of an aqueous solution at a specified temperature (usually 25°C). It is temperature dependent. The units are **mhos.** Because these units are large, micromhos are generally used, i.e., mhos * 10^6. The International Unit for conductivity is the **siemens,** which is numerically equivalent to the mhos.

Conductivity is a good estimator of TDS because TDS in mg/l is proportional to the conductivity in micromhos.

TDS (mg/l) = A * conductivity (μmhos), where A = 0.54–0.96 (usually 0.55–0.76).

Conductivity also may be estimated from the sum of cation expressed in meq/l.

Conductivity (μmhos) = sum of cations (meq/l) * 100.

Calculated Density

The density of a solution equals mass/volume. Considering 1 l of solution, the volume is 1000 cc. The mass of the solution is the mass of the solutes plus the mass of the water. The mass of the solutes is the TDS expressed in grams. The mass of the water is the volume of the water times the density of water, which is usually considered to be 1. The volume of the water is therefore the total volume less the volume of the solutes. The partial ionic volumes of dissolved constituents in water are used primarily to estimate the effects of pressure on solutions. A list of the molar volumes of some common ions is given in Table 3.5. They may also be used to estimate the density of a solution.

The volume of ions in solution is the sum of the product of the number of mol/l times the partial molar volume (Owen and Brinkley, 1941). Some of the values are negative and some are positive. The negative values occur when the ion in question has a tighter attraction to the water molecules than it would have to another without the additional ion. A positive partial molar volume indicates the water molecules are repelled to some extent by the additional ion.

Thus,

$$v = \text{sum } (n_i * v_i)$$

where

- v is the molar volume
- v_1 is the partial molar volume at 25°C
- n_1 is the concentration in mol/l of ion i

The total volume of solution = 1000 cm^3. The density of water is assumed to be 1.

Table 3.5. Partial Molal Ionic Volumes at 25°C

Cation	v_i	Anion	v_i
H^+	0	OH^-	−5.3
Na^+	−1.5	F^-	−2.1
K^+	+8.7	Cl^-	+18.1
NH_4^+	+17.9	Br^-	+25.0
Mg^{2+}	−20.9	NO_3^-	+29.3
Ca^{2+}	−17.7	HCO_3^-	+24.0
Sr^{2+}	−18.2	CO_3^{2-}	−3.7
Ba^{2+}	−12.3	SO_4^{2-}	+14.5

From Owen and Brinkley, 1941.

Mass of water = volume of water * density of water (D)

= (1000 − v) * 1 g

Mass of solids = TDS(mg/l)/1000 g

Mass of water + mass of solids

$$= (1000 - v) + \frac{TDS}{1000}$$

$$\text{Density} = \frac{\text{mass}}{\text{volume}}$$

$$= \frac{(1000 - v) * D + \frac{TDS}{1000}}{1000}$$

An example of a density calculation is given in Table 3.6.

pH

pH is a measure of the hydrogen ion concentration $[H^+]$, or more correctly, activity, which will be discussed later.

$$pH = -\log_{10}[H^+]$$

Note that mmol/l H^+ is approximately equal to mg/l H^+. Also, p(OH) = 14 − pH. At pH = 10:

$$[OH^-] = 10^{-4} \text{ mol/l} = 10^{-1} \text{ meq/l} = 10^{-1} * 17 = 1.7 \text{ mg/l}$$

pH may be raised by adding a base or by removing CO_2 from a solution, e.g., by photosynthetic assimilation. There are three main sources of hydrogen ions in natural waters.

a. Hydrolysis:

$$H_2O \rightarrow H^+ + OH^-; \text{ in pure water } [H^+] = 10^{-7}$$

Table 3.6. Example of Density Calculation

Ion	mg/l	mol/l n_i	Partial molar volume v_i	Molar volume $n_i * v_i$
Na^+	11,162	0.4855	−1.5	−0.7283
K^+	414	0.0106	8.7	0.0922
Ca^{2+}	427	0.0107	−17.7	−0.1894
Mg^{2+}	1,339	0.0551	−20.9	−1.1516
Cl^-	20,059	0.5658	18.1	10.2410
SO_4^{2-}	2,811	0.0293	14.5	0.4249
HCO_3^-	146	0.0024	24	0.0576
Total	36,358			8.75 cc

$$\text{Density} = \frac{[(1000 \text{ cc} - 8.75 \text{ cc}) * 1.0 \text{ g/cc}] \text{ g} + \left[\frac{36358}{1000}\right] \text{g}}{1000 \text{ cc}} = 1.028$$

b. Dissociation:

$$H_2CO_3 \rightarrow H^+ + HCO_3^-$$

c. Oxidation:

$$2FeS_2 + 7.5O_2 + 7H_2O \rightarrow 2Fe(OH)_3 + 8H^+ + 4SO_4^{2-}$$

Other sources of hydrogen ions include humic and fulvic acids, volcanic gases, acid rain, and short-chain organic acids present in some oil-field brines.

The $[H^+]$ in an aqueous solution is controlled by chemical reactions that produce or consume hydrogen ions. One of the most important of these is the set of reactions initiated when CO_2 is dissolved in water, i.e.,

$$CO_2(g) + H_2O(l) \rightarrow H_2CO_3(aq)$$

$$H_2CO_3(aq) \rightarrow H^+ + HCO_3^-$$

$$HCO_3^- \rightarrow H^+ + CO_3^{2-}$$

These are called buffered solutions. If, when acids and bases are added to such a solution, the pH changes very little, the solutions are said to be buffered. For example, if we add hydrogen ions to a solution of carbonate, then

$$CO_3^{2-} + H^+ \rightarrow HCO_3^-$$

or another ion—bicarbonate—is formed. It uses up the added hydrogen ions such that the pH does not decrease as it otherwise would. This is an important concept when dealing with acid rain or acid mine drainage.

Alkalinity and Acidity

It is important to distinguish between intensity and capacity values. Most quantities in chemical analyses are "intensity" functions, i.e., actual concentrations of a constituent. Thus pH measures the concentration of hydrogen ions in a solution. There are certain properties of solutions that are "capacity" functions that measure the response of the solution to change. For example, the capacity of a solution to neutralize acids or bases is called the buffering capacity of the solution. As an example, we have two solutions, A and B, both with a pH of 8.2, but A has no carbonate whereas B has a high concentration of carbonate. If we add acid to both solutions the pH of A will be lowered after only a few drops of acid, whereas the pH of B will remain relatively constant until sufficient acid has been added to change all the carbonate to bicarbonate.

Alkalinity and acidity are quantitative measurements of the capacity of a solution to react to acids and bases.

The alkalinity of a solution is defined as the capacity of a solution to react with strong acid. It is determined by a titration to specific end-points, namely, pH = 4.5—methyl orange, and pH = 8.3—phenolphthalein. A measured volume of the water is titrated with a strong acid such as HCl. Several different solute species contribute to the alkalinity of a natural water sample; however, the titration with acid does not specifically identify them. Alkalinity may be reported in several ways, the most common is in terms of an equivalent amount of $CaCO_3$, usually meq/l $CaCO_3$.

$$\text{meq/l } CaCO_3 = \frac{\text{mg/l } CaCO_3}{50}, \text{ where 50 is the equivalent weight of } CaCO_3$$

In most natural waters, alkalinity is produced by the dissolved CO_2 species, bicarbonate and carbonate. Noncarbonate contributors to alkalinity include hydroxide, silicate, borate, and the organic ligands, especially acetate and propanoate. The inclusion of these ions in the alkalinity value will be important if they are present in significant amounts.

Carbonate species are the most important participants in reactions that control the pH of natural waters. These relationships are often illustrated by a graph that shows the percent of each species present at a particular pH. A graph showing this relationship is given in Figure 3.3.

Acidity is the capacity of a solution to neutralize a strong base; that is, to react with hydroxyl ions and in so doing to convert all carbonate species to carbonate. This is determined by titrating a measured volume of water with a strong base, such as NaOH. Acidity may result from volcanic gases, acid rain, oxidation of sulfide minerals (such as would occur in spoil piles from coal), and metal mines. The major source of acidity is dissolved, undissociated CO_2 (H_2CO_3) in water; for example, 160 mg/l H_2CO_3 in a water has a pH = 5.2. Oil-field waters often contain dissolved acetic acid. Natural dissolved organic matter consists of large molecules of fulvic and humic acids with carboxylic acid (−COOH) and phenolic (−OH) sites. They originate in vegetation-rich areas and usually cause waters to be strongly colored.

Note that a solution possessing caustic alkalinity (OH^-) i.e., a very high pH, has no acidity; and a solution possessing mineral acidity, i.e., a very low pH, has no alkalinity.

Hardness-Alkalinity Relationships

Alkalinity may be greater than or less than the total hardness. If the alkalinity is less than the total hardness, then the alkalinity equals the temporary hardness. If the alkalinity is greater than the total hardness, then all hardness is temporary. On the other hand, if

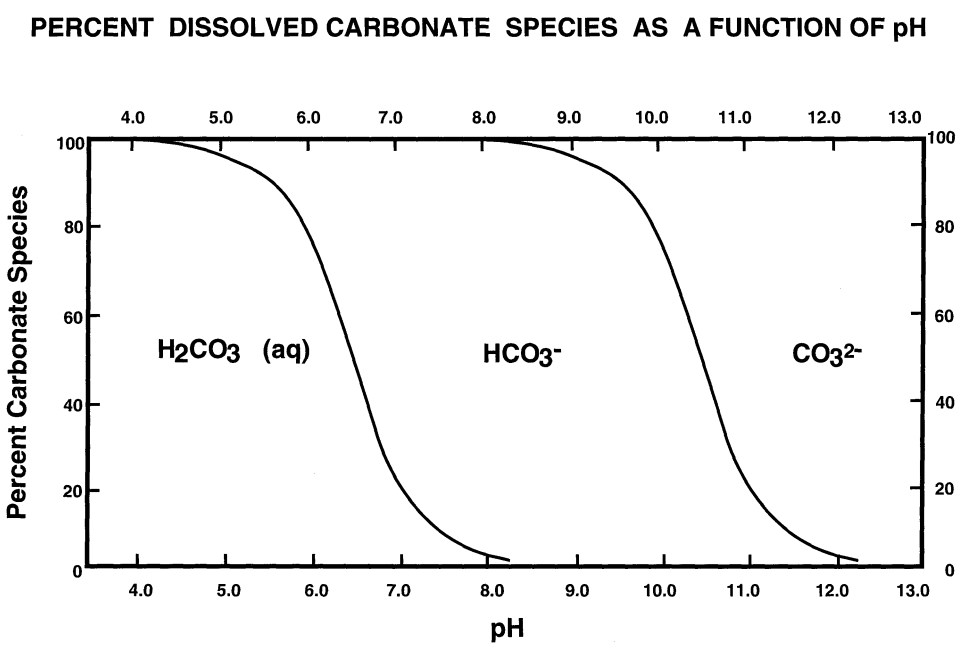

Figure 3.3. Carbonate species. (Adapted from Hem, 1992.)

temporary or permanent hardness are given, then alkalinity equals temporary hardness, or equals total hardness minus permanent hardness. This relationship is shown in Figure 3.4.

Hardness and alkalinity may be expressed in the following ways:

Total hardness	—Ca and Mg expressed as $CaCO_3$
Calcium hardness	—Ca expressed as $CaCO_3$
Magnesium hardness	—Mg expressed as $CaCO_3$
Temporary hardness	—Equals alkalinity, if alkalinity is less than total hardness
Permanent hardness	—The amount of hardness greater than temporary hardness
Noncarbonate hardness	—Permanent hardness
Total alkalinity	—Bicarbonate and carbonate alkalinity expressed as $CaCO_3$
Bicarbonate alkalinity	—Methyl orange alkalinity, expressed either as $CaCO_3$ or as HCO_3^-
Carbonate alkalinity	—Phenylphthalein alkalinity, usually expressed as $CaCO_3$

In calculating hardness-alkalinity relationships it is advisable to work in meq/l rather than mmol/l. The equivalent weight of $CaCO_3$ is molecular weight/2 or 50.

Sodium Adsorption Ratio (SAR) (Richards, 1969)

The SAR of a water is defined as

$$\frac{Na^+}{\sqrt{\frac{Ca^{2+} + Mg^{2+}}{2}}}$$

where the ion concentrations are expressed in meq/l.

SAR measures the degree to which sodium in irrigation water replaces the adsorbed (Ca^{2+} + Mg^{2+}) in the soil clays, and thus damages the soil structure. Irrigation waters are usually classified in terms of salinity hazard (conductivity or TDS) and sodium hazard (SAR).

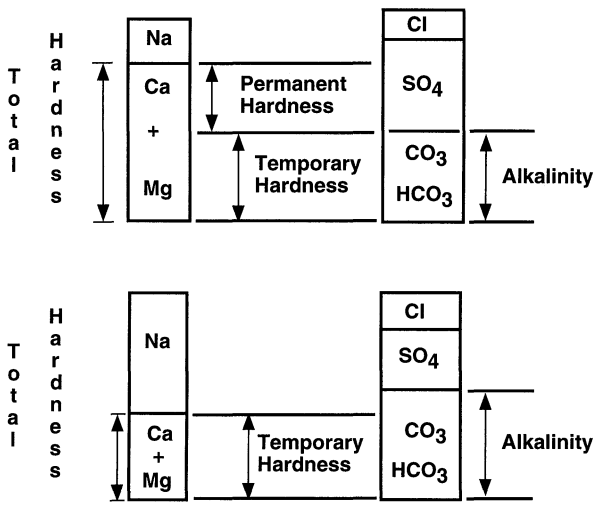

Figure 3.4. Hardness-alkalinity relationships.

The salinity hazard dividing points are 250, 750, and 2250 μmhos, resulting in four categories:

<250 umho	—Low-salinity water (C1)
250–750 umho	—Medium-salinity water (C2)
750–2250 umho	—High-salinity water (C3)
>2250 umho	—Very high-salinity water (C4)

The sodium hazard is a function of both SAR and salinity. The dividing lines are

$$S = 43.85 - 8.87 \log C$$
$$S = 31.31 - 6.66 \log C$$
$$S = 18.87 - 4.44 \log C$$

where S is the SAR and C is the conductivity.

The resulting four categories are

S1	—Low-sodium water
S2	—Medium-sodium water
S3	—High-sodium water
S4	—Very high-sodium water

The graph obtained from these calculations is shown in Figure 3.5 (Richards, 1969).

Langelier Index

When a mineral is dissolved in water the cations and anions of which it is composed will attain a specific concentration. Their sum essentially equals the solubility of that mineral. The mathematical product of these concentrations is given the name solubility product (K_{sat}). [These are actually the thermodynamic concentrations or activities.] See Chapter 5 for more details.

In any solution where the concentration of these ions is known, their product may be calculated. This number is called the ion activity product (IAP). The number so obtained may be compared to the solubility product of a mineral of interest. The comparison takes the form of the log of the ratio, which is called the saturation index (SI), namely:

$$\text{Saturation Index (SI)} = \log \frac{\text{IAP}}{K_{sat}}$$

If the SI equals zero, that is, IAP = K_{sat}, then the water is just saturated with the mineral phase in question. If SI is positive, or IAP > K_{sat}, then the water is oversaturated with respect to the mineral phase in question and will tend to precipitate. If SI is negative, or IAP < K_{sat}, then the water is undersaturated with respect to the mineral phase in question and will tend to dissolve more of the mineral if it is present.

The mineral whose SI is most commonly required is calcite ($CaCO_3$). When calcite is in equilibrium with water the solubility product of the Ca^{2+} and CO_3^{2-} ions in solution is expressed by their product $[Ca^{2}+][CO_3^{2-}] = K_{sat}$ for calcite = K_c.

Any solution that contains Ca^{2+} and CO_3^{2-} will have an IAP = $[Ca^{2+}][CO_3^{2-}]$ from solution. In the case of calcite the SI may be expressed in a different manner. It may be written as SI = $pH_{\text{of solution}} - pH_{\text{at which calcite precipitates}}$. When written in this form the SI is usually known as the Langelier index.

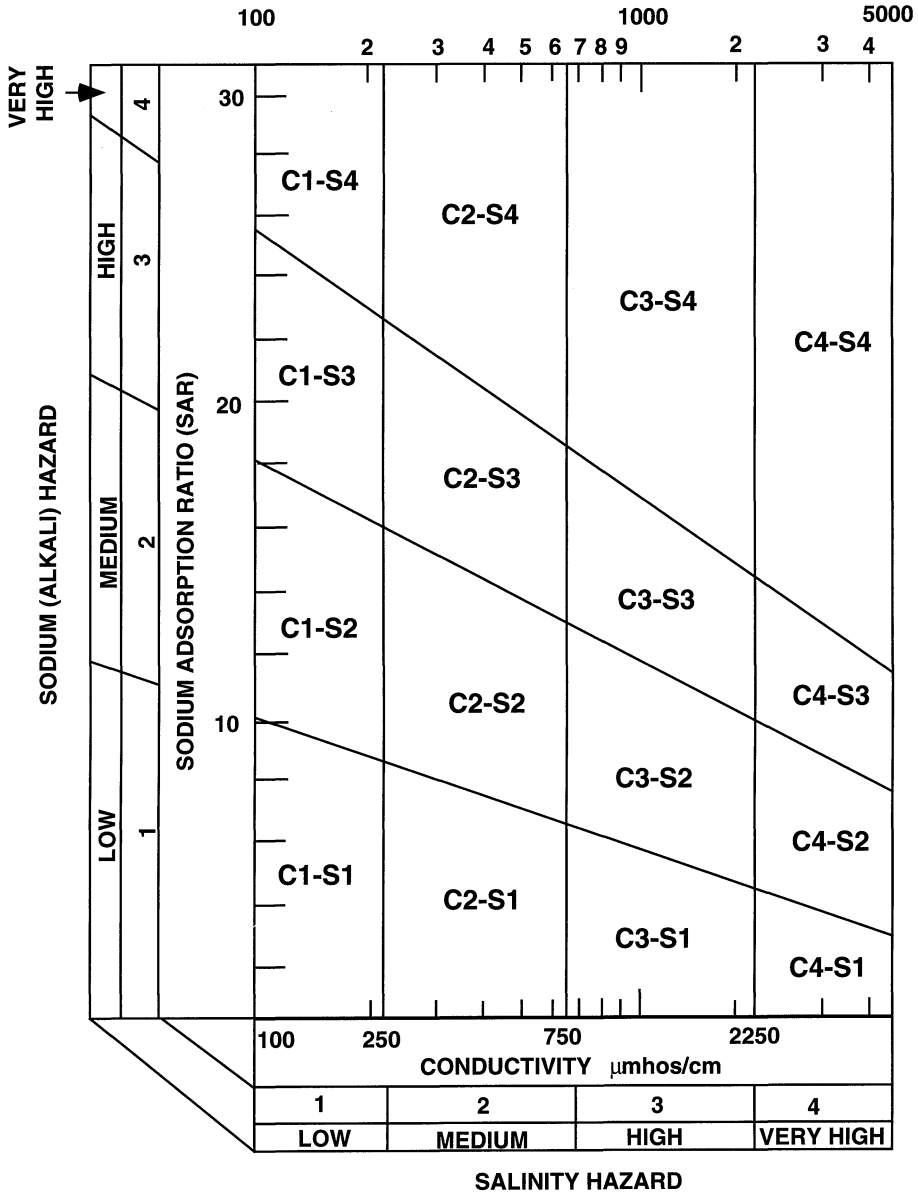

Figure 3.5. SAR-conductivity plot. (From Richards, 1969.)

Thus:

$$\text{Langelier Index} = \text{SI(calcite)} = \log \frac{\text{IAP}}{K_c} = \text{pH}_{\text{of solution}} - \text{pH}_{\text{at which calcite precipitates}}$$

If the Langelier index is positive, the solution is oversaturated, with respect to calcite, and if it is negative it is undersaturated with respect to calcite.

It should be noted that the $[CO_3^{2-}]$ concentration in solution depends on temperature, pH, and total ions in solution. Also, the presence of complex ions and neutral species will influence the concentration of both ions involved.

CONVERSIONS

If the units used for the parameters being measured are not in terms of the parameters expected, they may be converted by using ratios of the appropriate molecular or equivalent weights. Several important examples are given below.

a. Analysis reports Si (silicon) and silica (SiO_2) is required:

$$SiO_2 = \frac{Si}{\text{M.Wt. of Si}} * \text{M.Wt. of } SiO_2$$

$$= \frac{Si}{28.09} * 60.09 = Si * 2.1392$$

b. Analysis reports bicarbonate as alkalinity in terms of $CaCO_3$ and HCO_3^- is required:

$$HCO_3^- = \frac{CaCO_3}{\text{Eq. Wt. of } CaCO_3} * \text{Eq. Wt. } HCO_3^-$$

$$= \frac{CaCO_3}{50.044} * 61.016 = CaCO_3 * 1.2192$$

c. To convert carbonate (CO_3^{2-}) to bicarbonate (HCO_3^-):

$$HCO_3^- = \frac{CO_3^{2-}}{30.045} * 61.016 = CO_3^{2-} * 2.0308$$

d. To convert °F to °C:

$$°C = \frac{5 * (°F - 32)}{9}$$

Missing Values

A single missing value may be obtained by subtracting the sum of cations from the sum of anions or vice versa. However, this should not be done unless absolutely essential. The results obtained this way should be viewed with great caution.

Example

Given:

Permanent hardness = 75 mg/l $CaCO_3$.
Temporary hardness = 345 mg/l $CaCO_3$.
Mg = 6 mg/l; NaCl = 35 mg/l; pH = 7.1.

Then:

$$\text{Total hardness} = 345 + 75 = 420 \text{ mg/l } CaCO_3 = 8.4 \text{ meq/l.}$$

$$Mg = \frac{6}{12} = 0.5 \text{ meq/l}$$

Ca = 8.4 − 0.5 = 7.9 meq/l = 7.9 * 20 = 158 mg/l.
Alkalinity = temporary hardness = 345 mg/l $CaCO_3$.
At pH = 7.1, HCO_3^- is the only carbonate species present.
Thus alkalinity = $[HCO_3^-]$ = 345/50 * 61 = 421 mg/l.
Permanent hardness = 75 mg/l $CaCO_3$ = 75/50 = 1.5 meq/l $CaCO_3$
If permanent hardness is considered to be $CaSO_4$, then
SO_4^{2-} = 1.5 * 48 = 72 mg/l SO_4^{2-}
Given 35 mg/l NaCl

$$NaCl = \frac{35}{23 + 35.5} = 0.598 \text{ mmol/l NaCl}$$
$$= 0.598 * 23 = 13.8 \text{ mg/l } Na^+$$
$$= 0.598 * 35.5 = 21.2 \text{ mg/l } Cl^-$$

EXERCISES

1. Balance the equations for the weathering of the following minerals. Try each with the clay minerals kaolinite and montmorillonite. Do not add additional alumina or silica. If insufficient amount of either is present, the clay minerals will not form.

   a. Anorthite $CaAl_2Si_2O_8$
   b. Tremolite $Ca_2Mg_4AlSi_7AlO_{22}(OH)_2$
   c. Diopside $CaMgSi_2O_6$
   d. Dolomite $CaMg(CO_3)_2$

2. Rainwater percolates through gypsum beds to an unconfined aquifer. The sulfate content of the aquifer water was found to be 760 mg/l SO_4^{2-}. What is the sodium content of this water after passing through an ion exchange column?
3. Calculate the hardness in terms of $CaCO_3$ of a water containing 350 mg/l Ca^{2+} and 125 mg/l Mg^{2+}.
4. Given that a water has a hardness of 560 mg/l $CaCO_3$ and a Mg^{2+} content of 72 mg/l, calculate the concentration of Ca^{2+} in mg/l.
5. A water has a TDS(180°C) of 570 mg/l. It contains 155 mg/l HCO_3. What is the true TDS of the water?
6. A water contains 800 mg/l SO_4^{2-} and 500 mg/l Ca^{2+}. The measured TDS (180°C) was found to be 1750 mg/l. An X-ray diffraction examination of the residue revealed the presence of $CaSO_4 \cdot 0.5H_2O$, but not anhydrite or gypsum. What is the true TDS content of the water?
7. Estimate the TDS of a solution having a conductivity of 2730 umho.
8. Calculate the H^+ concentration in mg/l in waters having a pH of 2 and 7.
9. A groundwater is reported to have a hardness of 1000 mg/l expressed as calcium carbonate. The aquifer is known to be composed primarily of dolomite. What would you expect the Ca and Mg contents to be in mg/l?

10. Calculate the dissolved solid content of the following water. Concentrations in mg/l. $Na^+ = 2.14$; $Ca^{2+} = 48$; $Mg^{2+} = 3.6$; $HCO_3^- = 152$; $SO_4^{2-} = 3.2$; $Cl^- = 8.0$; $SiO_2 = 8.6$.
11. Calculate the density of the Red Sea brine whose analysis is given below (all values are in g/l):
    $Na^+ = 105$, $K^+ = 3.61$, $Mg^{2+} = 0.95$, $Ca^{2+} = 6.44$, $SO_4^{2-} = 1.14$, $Cl^- = 195$.
    Measured density = 1.196. Comment on the difference.
12. Comment on the reasonableness of the following water analyses using the carbonate/bicarbonate graph.

#	pH	mg/l HCO_3^-	mg/l CO_3^{2-}	Error
1	10.8	51	0	
2	5.9	23	23	
3	4.2	151	2	
4	11.7	162	0	
5	6.5	2	121	
6	12.6	170	20	
7	2	10	10	
8	7	500	50	

ANSWERS TO PROBLEMS

1. a. Anorthite → kaolinite.
   $CaAl_2Si_2O_8 + 2CO_2 + 3H_2O \rightarrow Al_2Si_2O_5(OH)_4 + Ca^{2+} + 2HCO_3^-$
   anorthite → montmorillonite will not occur because of insufficient silica.
   b. Tremolite → kaolinite.
   $Ca_2Mg_4AlSi_7AlO_{22}(OH)_2 + 12CO_2 + 17H_2O \rightarrow Al_2Si_2O_5(OH)_4 + 2Ca^{2+} + 4Mg^{2+} + 12HCO_3^- + 5H_4SiO_4$
   Tremolite → montmorillonite.
   $Ca_2Mg_4AlSi_7AlO_{22}(OH)_2 + 12CO_2 + 12H_2O \rightarrow Al_2Si_4O_{10}(OH)_2 + 2Ca^{2+} + 4Mg^{2+} + 12HCO_3^- + 3H_4SiO_4$
   c. Diopside will not form clay because it lacks alumina.
   $CaMgSi_2O_6 + 4CO_2 + 6H_2O \rightarrow Ca^{2+} + Mg^{2+} + 4HCO_3^- + 2H_4SiO_4$
   d. Dolomite will not form clays because of the lack of alumina and silica.
   $CaMg(CO_3)_2 + 2CO_2 + 2H_2O \rightarrow Ca^{2+} + Mg^{2+} + 4HCO_3^-$

2. 760 mg/l SO_4^{2-} = 7.912 mmol SO_4^{2-} = 7.912 mmol Ca^{2+}
   = 15.82 mmol Na^+ = 364 mg/l Na^+

3. $\frac{350}{40.08} * 100.09 = 874$ mg/l $CaCO_3$

   $\frac{125}{24.31} * 100.09 = 515$ mg/l $CaCO_3$

   Hardness = 1389 mg/l $CaCO_3$

4. Hardness = 560 mg/l $CaCO_3$ = 5.595 mmol $CaCO_3$

= mmol(Ca^{2+} + Mg^{2+})

72 mg/l Mg^{2+} = 2.962 mmol Mg^{2+};

Ca^{2+} = 5.595 − 2.962 = 2.663 mmol = 106 mg/l

5. TDS(180°C) = 570 mg/l; 155 mg/l HCO_3^- = 2.54 mmol/l

$2HCO_3^- \Leftrightarrow CO_3^{2-} + H_2O + CO_2$

2 mol bicarbonate loses 1 mol water + 1 mol CO_2

2.54 mmol bicarbonate loses 1.27 mmol water + 1.27 mmol CO_2

22.9 mg 55.9 mg

Total loss = 78.8 mg/l

True TDS = 570 + 79 = 649 mg/l

OR

$2HCO_3^- \Leftrightarrow CO_3^{2-} + H_2O + CO_2$

122.036 60.01 18.016 44.01

----------v----------

122.036 mg loses 62.026 mg

Loss is 50.83% HCO_3^- or loss = 0.5083 * 155 = 79 mg

6. TDS (180°C) = 1750 mg/l

800 mg/l SO_4^{2-} = 8.33 mmol/l

500 mg/l Ca^{2+} = 12.48 mmol/l Ca^{2+}

Limited by sulfate; $CaSO_4 \cdot \frac{1}{2} H_2O$ = 8.33 mmol/l

$2CaSO_4 \cdot \frac{1}{2} H_2O \Leftrightarrow 2CaSO_4 + H_2O$

2 mmol 1 mmol

8.33 mmol 4.165 mmol

= 75 mg/l H_2O

True TDS = 1750 − 75 = 1675 mg/l

7. TDS = A * conductivity where A = 0.55 − 0.76

As conductivity = 2730 then TDS = 1502 − 2075 mg/l

8. At pH = 2, $[H^+] = 10^{-2}$ mol/l = 10 mmol/l = 10.1 mg/l H^+.

At pH = 7, $[H^+] = 10^{-7}$ mol/l = 10^{-4} mmol/l = 1E − 4 mg/l H^+.

9. 1000 mg/l $CaCO_3$ = 10 mmol/l.

Dolomite contains an equal number of moles of Ca^{2+} and Mg^{2+}.

= 5 mmol/l Ca^{2+} and 5 mmol/l Mg^{2+}

= 5 * 40.08 = 200.4 mg/l Ca^{2+} and 5 * 24.31 = 121.6 mg/l Mg^{2+}

10. TDS = sum of all ions + SiO_2 = 225.54 mg/l

11.

Ion	g/l	M	v	M*v
Na^+	105	4.5652	−1.5	−6.848
K^+	3.61	0.0923	+8.7	+0.803
Mg^{2+}	0.95	0.0391	−20.9	−0.817
Ca^{2+}	6.44	0.1607	−17.7	−2.844
SO_4^{2-}	1.14	0.0119	+14.5	+0.172
Cl^-	195	5.5007	+18.1	+99.56
Sum	312.14			90.026

$$\text{Calculated density} = \frac{(1000 - 90.026) + 312.14}{1000} = 1.222$$

Measured density = 1.196

Error = 2%, which is well within experimental error.

12. If we assume that the pH is correct, then:

#	pH	mg/l HCO_3^-	mg/l CO_3^{2-}	Error
1	10.8	51	0	Should be 70% carbonate.
2	5.9	23	23	Carbonate absent.
3	4.2	151	2	Both carbonate and bicarbonate absent.
4	11.7	162	0	Mostly carbonate with <5% bicarbonate.
5	6.5	2	121	Carbonate essentially absent.
6	12.6	170	20	Bicarbonate essentially absent.
7	2	10	10	Both carbonate and bicarbonate absent.
8	7	500	50	Carbonate should be less than 10% of bicarbonate

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CHAPTER 4

Water Quality Interpretation

INTRODUCTION

There are two phases involved in the collection and interpretation of water quality data. The first is the collection and analysis phase, where due attention should be given to replication and analytical quality assurance. The second is where the analyses are checked for possible errors and inconsistencies and subjected to various interpretive procedures to try and solve the problem at hand. Unfortunately, these phases are often separated in both space and time—the group responsible for the collection and analysis having no contact with the group interpreting the data. Although this is far from ideal, it is a fact of life that has to be faced. Often there is no possibility of either obtaining more samples or having further analyses run.

The four basic steps involved may be summarized as follows:

1. Sampling
   a. sample collection.
   b. sample preservation.
   c. analyses of field parameters.
   d. collection and designation of duplicates.
2. Laboratory sample analysis
   a. analysis.
   b. laboratory quality assurance.
   c. laboratory manager—client dialog.
3. Determination of analysis reliability
   a. duplicate comparison.
   b. examination of quality assurance.
   c. anion-cation balance.
   d. miscellaneous checks.
   e. relative amounts of ions present.
4. Analysis interpretation
   a. source-rock deduction.
   b. areal trends.
   c. chemical trends.
   d. examination for mixing.
   e. mass-balance calculations.

Each of these steps will be discussed in detail in this chapter.

SAMPLING

This chapter will not include a discussion of sampling. The reader is directed to the EPA or U.S. Geological Survey protocol for detailed discussions of sampling. As these documents

are being updated on a regular basis, no references are given. It is suggested that the appropriate agency be contacted directly to obtain the latest information.

LABORATORY SAMPLE ANALYSIS

It is assumed that the reader will not be involved directly in the analysis of water samples. It is important, however, to establish a good working relationship with the laboratory manager in the lab being used. It is a fact of life that errors will occur. If possible errors are found early enough the lab may be able to reanalyze the sample. In some cases the error may be a simple transcription error. The quality assurance program will primarily be dependent on the laboratory being used, although usually EPA protocol will be followed.

ANALYSIS RELIABILITY

The following discussion lists the major ways to identify apparent inconsistencies in an analysis. It cannot be overemphasized that an inconsistency only indicates that an analysis is unusual, not necessarily wrong.

DUPLICATE COMPARISON

It is generally recommended that duplicate analyses be run on 10% of the samples. It should be noted that samples submitted together and run at the same time will often give a more favorable indication of precision than duplicates run on different days by different operators.

EXAMINATION OF QUALITY ASSURANCE

The objective of examining the quality assurance data is to obtain an estimate of the precision and accuracy of the data. A statistical analysis of the quality assurance data will not be discussed here. The terms precision and accuracy will, however, be compared.

Precision and Accuracy

Precision is the spread around the mean, that is, high precision means a low standard deviation. For optimum estimates of the precision obtainable from an analytical laboratory, duplicates should be submitted in different batches, and if possible, on different days. Different designations for samples should be used.

Accuracy, on the other hand, is how close to the true value are the analyses; an analysis may be accurate even if the standard deviation is high. The problem is that in most cases the true value is not known. Standard solutions are available that may be run with the samples as part of the quality assurance procedure. Also, one or more standard or spiked samples submitted with the samples would allow a relatively unbiased estimate of the laboratory accuracy.

ANION-CATION BALANCE

The accuracy of many water analyses may be readily checked because the solution must be electrically neutral. The sum of cations in meq/L should equal the sum of the anions in meq/L.

$$\text{meq/l} = \frac{\text{mg/l} * \text{valency}}{\text{formula wt.}}$$

Atomic, molecular, and equivalent weights for some of the more common ions are given in Table 4.1.

The charge balance is usually expressed as a percentage,
i.e., Balance = $(\Sigma C - \Sigma A)/(\Sigma C + \Sigma A) * 100$, where ΣC is the sum of cations and ΣA is the sum of anions.
If the balance calculated above is less than 5% the analysis is assumed to be good.
If the balance is exactly 0% it is likely that the Na or Na+K were determined by difference, especially in older analyses (prior to 1960).
If the balance is much greater than 5% then

a. The analysis is poor (inaccurate),
b. Other constituents are present that were not used to calculate the balance,
c. The water is very acid and the H^+ ions were not included, or
d. Organic ions are present in significant quantities (often indicated by colored water).

MISCELLANEOUS CHECKS

1. Calculated hardness should equal reported hardness. A discrepancy may indicate incorrect copying of reported data. This check assumes that hardness was calculated by the lab and not determined chemically.
2. Calculated TDS either as sum of ions plus silica or calculated residue at 180°C should equal reported TDS. Incorrect transcription is a frequent cause of nonequivalence.
3. TDS divided by measured conductivity should be between 0.55 and 0.76.
4. If carbonate is absent the pH should be less than 8.

Table 4.1. Atomic, Molecular, and Equivalent Weights

Species	Atomic or molecular weight	Valency	Equivalent weight	Partial molar volume
Na^+	22.991	1	22.991	−1.5
K^+	39.102	1	39.102	8.7
Li^+	6.939	1	6.939	−34
Ca^{2+}	40.08	2	20.04	−17.7
Mg^{2+}	24.312	2	12.156	−20.9
Sr^{2+}	87.62	2	43.81	−18.2
Ba^{2+}	137.34	2	68.67	−12.3
Fe^{2+}	55.847	2	27.924	0
Cl^-	35.453	−1	35.453	18.1
F^-	18.998	−1	18.998	−2.1
Br^-	79.909	−1	79.909	25.0
NO_3^-	62.004	−1	62.004	29.3
SO_4^{2-}	96.06	−2	48.03	14.5
HCO_3^-	61.016	−1	61.016	24
CO_3^{2-}	60.008	−2	30.004	−3.7
SiO_2	60.09	0	0	
B	10.811	0	0	
N	14.007			
O	15.999			
H_2O	18.015			
$CaCO_3$	100.088		50.044	

5. Conductivity divided by the sum of cations in meq/l is approximately 100. The usual range is 90–110.

6. Temporary hardness usually equals bicarbonate unless alkalinity is greater than total hardness.

RELATIVE AMOUNTS OF IONS REPORTED

Another approach to determining the accuracy of an analysis is to look for unusual ionic ratios. It is assumed that most aquifers yielding drinking water are sandstone (often with carbonate cement), limestone or dolomite, glacial till or granitic rocks. The following are only a guide, and it must be emphasized that many accurate analyses may reflect exceptions to these general statements. The objective is not to eliminate from consideration all analyses that do not comply with these generalizations, but to ensure their accuracy by bringing potential inconsistencies to the attention of the investigator. (Units used are meq/l.)

The following ratios are common in many groundwaters.

1. Na >> K, because the potassium is more readily removed from solution by plants and clay minerals than sodium. Both elements are equally common in most rocks originating as constituents from the weathering of feldspars (albite and K-feldspar) and micas. In addition, sodium commonly results from ion exchange reactions.

2. Ca >= Mg, because the most soluble minerals are the sedimentary carbonates, calcite and dolomite, and gypsum. A dolomite aquifer would show Ca = Mg, whereas other sedimentary rocks would have more Ca than Mg, unless Ca is removed by precipitation (such as dedolomitization) and/or ion exchange. Silicate weathering, on the other hand, would sometimes show Mg > Ca, particularly aquifers in ultramafic rocks, such as serpentinites.

3. Ca >= SO_4, because the main source of sulfate is some variety of $CaSO_4$ (such as anhydrite, gypsum, or sulfuric acid from pyrite neutralized by carbonate) unless Ca is removed by precipitation or ion exchange. In acid waters SO_4 is usually >Ca.

4. Na >= Cl, because the main source of chloride is NaCl. Sodium, on the other hand, has other sources such as silicates and ion exchange. Na, however, may be removed from the water by reverse ion exchange in brines (reverse softening).

The analytical checks described above are tabulated in Tables 4.2 and 4.3.

INTERPRETATION OF WATER QUALITY DATA

Water quality data may be interpreted on the basis of both individual analyses and sets of analyses from one sampling site or different sampling sites in an area or aquifer being examined. In the case of individual analyses, the first step is their examination as to accuracy, followed by estimation of source, mass balance examination of the minerals that may have dissolved or precipitated (using computer programs such as BALANCE and NETPATH), ion speciation, saturation with respect to individual phases or minerals, and the redox state of the water. The last three determinations are usually based on a thermodynamic water equilibrium study aided by computer programs such as WATEQ4F, MINTEQ, and others.

Collectively, water analyses may be compared and interpreted using areal plots, graphical methods, and statistical analyses (usually separated into those useful for qualitative comparisons, for example, stiff diagrams, and those designed to detect chemical trends or mixing such as Piper or Durov diagrams). Statistical analyses may be simple, such as showing ranges of variation, and more complex such as cumulative frequency plots that enable the recognition

Table 4.2. Summary of Important Formulas and Reliability Checks

	Concentration Units
mg/l	= ppm * density
mmol/l	$= \frac{\text{mg/l}}{\text{mol wt}}$
Molarity	$= \text{mole/l} = \frac{\text{mmol/l}}{1000}$
Mole fraction (dilute solutions)	$= \frac{\text{moles constituent}}{\text{moles constituent} + 55.51}$ approx. $= \frac{\text{moles constituent}}{55.51}$ where 55.51 = mol H_2O/l
Millequivalents/l (meq/l)	$= \text{mmol/l} * \text{valency} = \frac{\text{mg/l}}{\text{equivalent wt}}$
Equivalent weight	$= \frac{\text{mol. wt}}{\text{valency}}$
	Parameters
Total hardness in mg/l $CaCO_3$	$= Ca^{2+}\ (\text{mg/l}) * \frac{100.08}{40.08} + Mg^{2+}\ (\text{mg/l}) * \frac{100.08}{24.31}$
Alkalinity in mg/l $CaCO_3$	$= HCO_3^-\ (\text{mg/l}) * \frac{50.04}{61.02} + CO_3^{2-}\ (\text{mg/l}) * \frac{50.05}{30.00}$
Total dissolved solids	= sum ions + silica
Residue at 180°C	= sum ions + silica − 0.5082 * bicarbonate
Total dissolved solids	Approx. = conductivity * 0.66
Conductivity	Approx. = sum of cations (meq/l) * 100
	Weathering
Products (clays):	Kaolinite $Al_2Si_2O_5(OH)_4$
	Montmorillonite $Al_2Si_4O_{10}(OH)_2$
Mineral + xCO_2 + yH_2O − >	(Clay) + cations + bicarbonate (+SiO_2)
	Reliability Checks
Anion-cation balance	$= \frac{\text{sum cation} - \text{sum anions}}{\text{sum cations} + \text{sum anions}} * 100 < 5\%$
Calculated hardness	= reported hardness
Calculated TDS	= reported TDS
$\frac{\text{TDS}}{\text{conductivity}}$	Approx. 0.55–0.76
$\frac{\text{Conductivity}}{\text{sum meq cations}}$	Approx. = 100
pH < 8	Carbonate absent
Temporary hardness	= alkalinity (if alkalinity less than total hardness)
Na meq/l	>> K meq/l
Ca meq/l	>= Mg meq/l
Ca meq/l	>= SO_4 meq/l
Na meq/l	>= Cl meq/l

of multiple populations and anomalies. Factor analysis often allows the simplification of the number of variables into groups of variables (factors), which may represent different sources.

PRELIMINARY DATA MANIPULATION

When using analyses the constituents may not be expressed in the form you wish to use them, and in some cases analyses may be incomplete. Some simple conversions are given below.

Table 4.3. Analysis Evaluation Worksheet

Reliability checks	Attention value	Analysis value	Conclusion
Sample Designation:			
Balance $\frac{(C - A)}{(C + A)} * 100\%$	>5%		
Hardness $- \frac{\text{Entered} - \text{calculated}}{\text{Entered}} * 100\%$	>5%		
$\frac{\text{TDS entered} - \text{TDS calculated}}{\text{TDS entered}} * 100\%$	>5%		
$\frac{\text{TDS entered} - \text{TDS}_{180}\text{ calculated}}{\text{TDS entered}} * 100\%$	>5%		
$\frac{\text{TDS entered}}{\text{conductivity}}$	<0.55 & >0.75		
$\frac{\text{TDS calculated}}{\text{conductivity}}$	<0.55 & >0.75		
$\frac{\text{Conductivity}}{\text{sum MEQ cations}}$	<90 & >110		
Carbonate	Calculated		
$\frac{K^+}{Na^+ + K^+}$	>20%		
$\frac{Mg^{2+}}{Ca^{2+} + Mg^{2+}}$	>40%		
$\frac{Ca^{2+}}{Ca^{2+} + SO_4^{2-}}$	<50%		
$\frac{Na^+}{Na^+ + Cl^-}$	<50%		
Conclusion	Analysis acceptable:		Yes No

Completing Partial Analyses

a. Given any two of the following—hardness, Ca^{2+}, or Mg^{2+}—the other may be calculated.
b. Temporary hardness is equivalent to alkalinity if alkalinity is less than total hardness.
c. Carbonate-bicarbonate ratio—if HCO_3^- or CO_3^{2-} are inconsistent with the pH given, recombine to obtain more reasonable values, or check the pH.

Conversion Calculations

To convert:

a. Calcium hardness as $CaCO_3$ **to** Ca^{2+}, multiply by 0.4004.
b. Magnesium hardness as $CaCO_3$ **to** Mg^{2+}, multiply by 0.2429.
c. Noncarbonate hardness as $CaCO_3$ **to** HCO_3^-, multiply (total hardness minus noncarbonate hardness) by 1.2192.

d. Carbonate alkalinity—phenolphthalein (pp) alkalinity)—as $CaCO_3$ **to** CO_3^{2-}, multiply by 0.6004.
e. Total alkalinity and carbonate alkalinity as $CaCO_3$ **to** HCO_3^-, multiply (total alkalinity − carbonate alkalinity) by 1.2192.

SOURCE-ROCK DEDUCTION

The purpose of the technique described here is to gain insight into the possible origin of a water analysis. It is useful both as an analytical check or as an investigative procedure if the origin of the water is not known. The approach used is not infallible, but it can be very helpful. It is derived from a simplistic mass balance approach to water quality data (based on the work of Garrels and MacKenzie, 1967). Various elemental ratios resulting from the weathering of some common minerals are listed in Table 4.4. A flow chart of the technique is given in Figure 4.1.

The initial composition of groundwater originates from rainfall, which may be considered to be diluted seawater. During its return path to the ocean, the water composition is altered by rock weathering, evaporation (Gibbs, 1970), and aeration. During rock weathering, Ca^{2+}, Mg^{2+}, SO_4^{2-}, HCO_3^-, and SiO_2 are added to the water. The amount of each is dependent on the rock mineralogy. In many cases the source rock minerals may be deduced from the water composition, referred to in this text as source-rock deduction.

However, there are conditions where waters having unusual compositions may naturally occur. These may be called extreme environments. Some of the more common ones will be discussed in Chapter 6.

SYSTEMATIC SOURCE ROCK DERIVATION

Step 1. If the pH of the water is less than about 5–6, be cautious in applying the following steps as acid waters may not be able to be interpreted in this way. The primary reason why low pH causes an interpretation problem is that at low pH values, significant quantities of clay minerals may dissolve and release anomalously high silica (and alumina) to the water.

Step 2. The concentration of the various constituents, usually expressed as mg/l, must be converted to meq/l to be able to combine the various ions in a chemically meaningful

Table 4.4. Weathering Products of Common Minerals

Mineral	Clay formed[1]	meq/l				mmol/l	Ratios	
		Na^+	K^+	Ca^{2+}	Mg^{2+}	SiO_2	$\frac{SiO_2}{HCO_3^-}$	$\frac{Na^+ + K^+}{SiO_2}$
Cations and SiO_2 Based on 100 meq HCO_3								
Albite	K	100	—	—	—	200	2	0.5
Albite	M	100	—	—	—	100	1	1
Diopside	—	—	—	25	25	50	0.5	0
Tremolite	K	—	—	17	33	42	0.4	0
Tremolite	M	—	—	17	33	25	0.25	0
Forsterite	—	—	—	—	50	25	0.25	0
Phlogopite	K	—	14	—	43	29	0.29	0.5
Phlogopite	M	—	14	—	43	14	0.14	1
Anorthite	K	—	—	50	—	—	0	0
Calcite	—	—	—	50	—	—	0	0
Dolomite	—	—	—	25	25	—	0	0

[1]K = kaolinite
M = montmorillonite

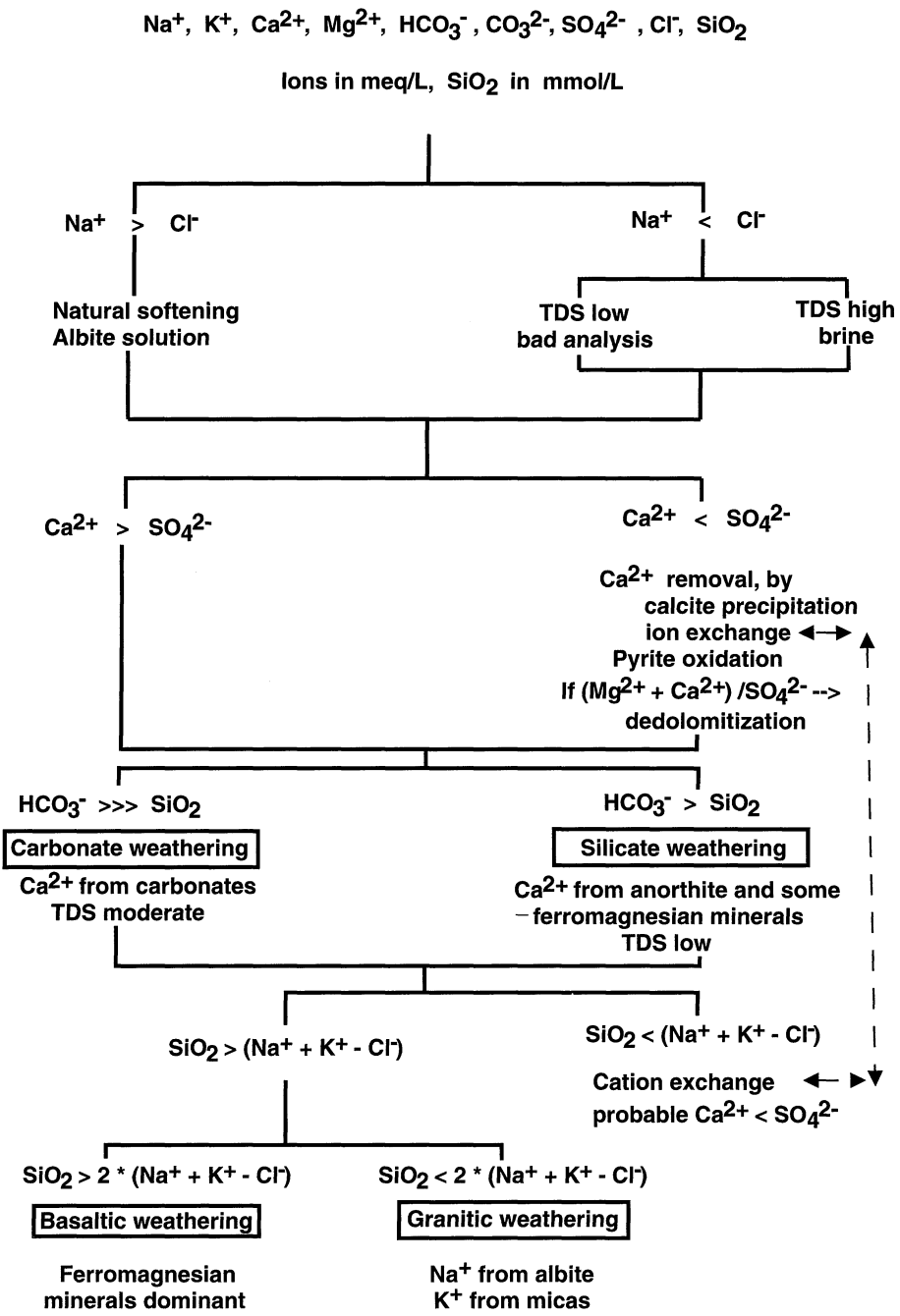


Figure 4.1. Weathering flow chart illustrating logic of water quality interpretation using simplified mass-balance technique.

way. Silica, which exists as a neutral complex, is converted to mmol/l. This is accomplished by dividing the ion concentration by its equivalent weight, and silica by its molecular weight.

Step 3. Sum the cations and the anions separately, omitting silica. Their totals should be within about 5% of each other; if not, proceed with caution or do not continue.

Sodium and Chloride

Step 4. Compare the chloride and sodium contents. We assume that the primary source of chloride in the water is from sodium chloride (directly from halite dissolution or indirectly from the ocean via rainfall). On the other hand, sodium can be derived from other sources (dissolution of albite—plagioclase, and ion exchange). Thus, if chloride > sodium, then there is either an analytical error or the composition of the water is derived from brines where reverse ion exchange or reverse natural softening has occurred (such as in oil-field brines). In the latter case, one would expect the dissolved solid content of the water to be high—at least over 500 mg/l. Also see Figure 4.2.

$Na^+ = Cl^-$ indicates halite dissolution.
$Na^+ < Cl^-$ indicates reverse softening (brine or seawater),

$$2Na^+ + Ca\text{—}Clay \rightarrow Ca^{2+} + 2Na\text{-}Clay$$

or a poor analysis.

$Na^+ > Cl^-$ indicates a Na source other than halite, such as albite (plagioclase), or natural softening.

$$Ca^{2+} + 2Na\text{-}Clay \rightarrow 2Na^+ + Ca\text{—}Clay$$

Calcium and Sulfate

Step 5. Compare the sulfate and calcium contents. The primary assumption is that sulfate is generally the result of direct dissolution of gypsum (or anhydrite) or the neutralization of acid waters by limestone or dolomite. In the latter case, magnesium may be prominent. If

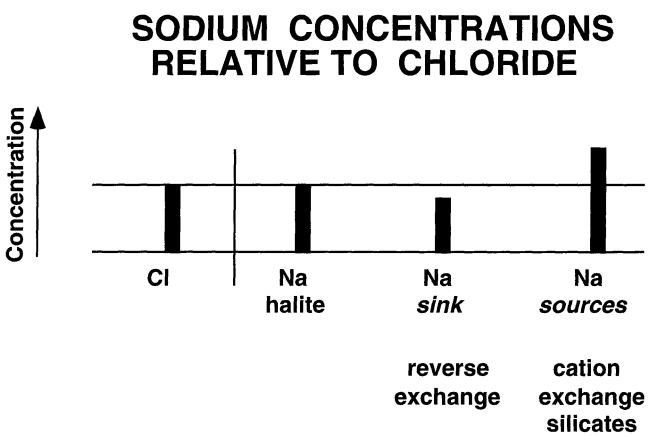


Figure 4.2. Chloride/sodium ratios relative to halite solution.

sulfate > calcium, then the inference is that calcium has been removed from solution, most likely by the precipitation of calcite or by ion exchange reactions. Also see Figure 4.3.

$Ca^{2+} = SO_4^{2-}$ indicates gypsum.
$Ca^{2+} < SO_4^{2-}$ indicates pyrite oxidation, or Ca^{2+} removal, such as by calcite precipitation, or natural softening.
$Ca^{2+} > SO_4^{2-}$ indicates a Ca^{2+} source other than gypsum, such as calcite/dolomite or silicates.

Bicarbonate and Silica

Step 6. Compare bicarbonate with silica. Bicarbonate is formed when carbon dioxide and water react with various minerals in a process called acid hydrolysis. Carbonates dissolve without releasing silica, whereas albite (plagioclase) releases considerable silica. Other silicates release a much lower amount (Table 4.2). An arbitrary division of bicarbonate/silica of <5 is used to indicate silicate vs. carbonate weathering and a ratio >10.

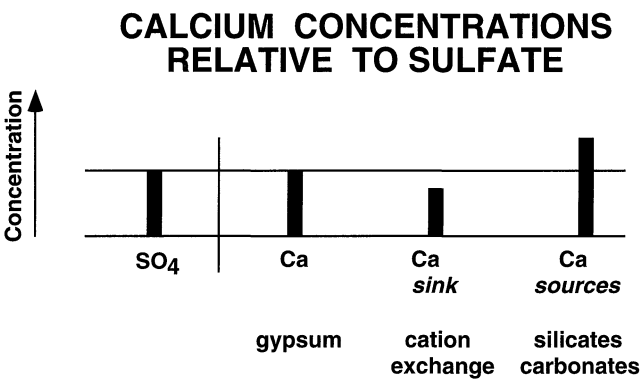


Figure 4.3. Sulfate/calcium ratios relative to gypsum.

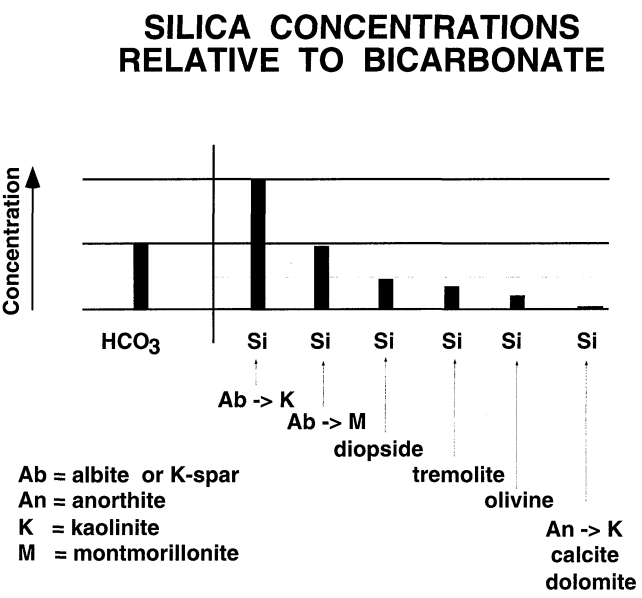


Figure 4.4. Bicarbonate/silica ratios for different minerals.

$HCO_3^- >>> SiO_2$ indicates carbonate rather than silicate weathering. (See Figure 4.4.)

Bicarbonate will be less than or equal to silica if albite (plagioclase) is weathered. In contrast, no silica will be released into solution if anorthite (plagioclase) is weathered. In fact, it would be impossible to distinguish calcite from anorthite (plagioclase) weathering on this basis alone. The total dissolved solids (TDS) from carbonate weathering will be moderate—often 500 mg/l or higher—whereas it usually will be low—100–200 mg/l—if there were silicate weathering. Calcium will be derived from calcite and dolomite if carbonate is present, and from anorthite (plagioclase) and some ferromagnesian minerals if derived from silicates. For the majority of rocks, other minerals will exist with anorthite (plagioclase) and the distinction between carbonate and silicate weathering will not be as difficult as indicated above. If the weathering of ferromagnesian minerals is occurring, it will also be manifest by the fact that magnesium will be greater than calcium. An arbitrary value of bicarbonate/silica > 10 is used to indicate carbonate weathering, and a value of <5 to indicate silicate weathering.

Silica and Nonhalite Sodium

Step 7. Compare silica with nonhalite sodium ($Na^+ + K^+ - Cl^-$). We assume that after subtracting the chloride from the sodium, then the remaining sodium is due to the weathering of albite (plagioclase) or ion exchange, and the potassium is due to the weathering of biotite and to a lesser extent potash feldspar. If other ferromagnesian minerals are present, silica will be present in considerable excess over sodium plus potassium. It is also assumed that the solid weathering product formed is either kaolinite or montmorillonite, the former releasing more silica to the water than the latter. Thus, we may conclude that if:

a. $SiO_2 < (Na^+ + K^+ - Cl^-)$ then cation exchange is probably the source of most of the excess sodium. In this case it is probable that calcium is less than the sulfate if carbonates were absent.
b. $SiO_2 > (Na^+ + K^+ - Cl^-)$ and $<2 * (Na^+ + K^+ - Cl^-)$, then albite (plagioclase) weathering is likely. The product is either kaolinite or montmorillonite.
c. $SiO_2 > 2 * (Na^+ + K^+ - Cl^-)$, then the rocks subjected to weathering contain a considerable quantity of ferromagnesian minerals, such as olivine, pyroxene, or amphibole. Under these conditions the source of much of the calcium is probably anorthite (plagioclase). See Figure 4.5, where the sodium listed is actually the nonhalite sodium.

$$(Na^+ + K^+ - Cl^-) = \text{nonhalite } Na^+$$

$$(Na^+ + K^+ - Cl^-) > SiO_2$$

indicates nonsilicate Na such as natural softening where Ca^{2+} may be $<SO_4^{2-}$ if carbonates are absent.

$$SiO_2 > (Na^+ + K^+ - Cl^-)$$

indicates granitic weathering primarily due to albite (plagioclase) dissolution.

$$SiO_2 >> (Na^+ + K^+ - Cl^-)$$

indicates basaltic weathering primarily due to the dissolution of sodium-poor ferromagnesian silicates.

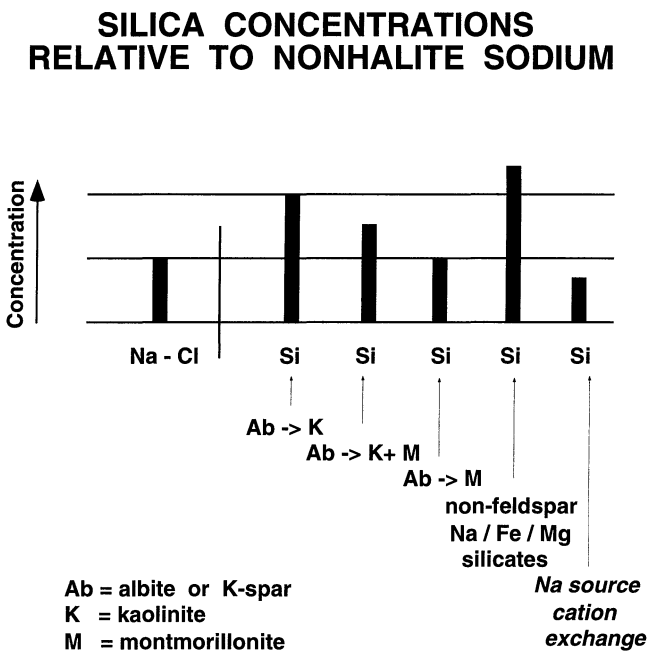


Figure 4.5. Nonhalite sodium/silica ratios for common weathering reactions.

OTHER COMPARISONS

Calcium and Magnesium

In sedimentary rocks the highest Mg^{2+}/Ca^{2+} ratio will occur with dissolution of dolomite where Ca^{2+} will be approximately equal to Mg^{2+} (Meisler and Becher, 1967). This is suggested by a moderate TDS of about 500 mg/l. If, however, the Mg^{2+} to Ca^{2+} ratio approaches one, it is very likely that Ca^{2+} has been removed from the solution. This process is commonly called dedolomitization. If Mg^{2+} is greater than Ca^{2+}, there are two common possibilities. The first is the dissolution of ferromagnesian minerals from mafic or ultramafic rocks where the TDS will be low—about 100–200 mg/l. The second would be seawater intrusion where the TDS would be high—probably greater than 500 mg/l.

Sodium and Potassium

Even though both Na^+ and K^+ may be produced in similar amounts by weathering of some igneous rocks, the Na^+ will generally be greater than K^+. Many sinks are available for K^+, but not for Na^+.

There are some occasions when the results of these calculations may have to be interpreted geologically. For example, if carbonate weathering is indicated, but the aquifer is a sandstone, it is the carbonate cement that is dissolving. Because of its low solubility the quartz would have little impact on the water composition.

Sodium and Calcium

It has been found that silicate weathering will result in a Na/Ca ratio of water similar to that of the plagioclase from which it was derived (Drever and Hurcomb, 1986). Further, this ratio may also be used as a way of distinguishing between silicate and carbonate weathering.

In carbonate weathering the Na/Ca ratio is usually very low unless considerable ion exchange has taken place.

Silica

In the above deductions it is assumed that the silica reported in the analysis is derived from silicate weathering and not from the dissolution of silica. The solubility of crystalline silica such as quartz is small at normal groundwater temperatures, although it may be considerable in geothermal waters (Truesdell, 1984). Silica gel, on the other hand, may dissolve to give equilibrium concentrations of 120 mg/l (Krauskopf, 1967). White et al. (1980) reported from 40–77 mg/l silica in a tuffaceous aquifer in Nevada, and White (1979) reported a similar range in silica from another tuffaceous aquifer in Nevada. Hearn et al. (1985) reported 38–110 mg/l silica in a basaltic aquifer in Washington. In all cases the high silica was attributed to the solution of volcanic glass that behaved like silica gel. These data suggest that if silica exceeds about 30 mg/l interpretations of the ratios using silica should be viewed cautiously. Silica concentrations could be used to distinguish between volcanic or plutonic rocks.

CHEMICAL REACTIONS

Many of the reactions discussed later in this chapter will complicate the source-rock deduction. If, however, it is cautiously applied, both the source rock and subsequent reactions may be deduced. Certain ratios may indicate various chemical reactions especially when used with other ratios or parameters. If the aquifer composition is known then the process of examining the data for possible reactions is considerably simplified.

The ratios and parameters used to determine both the source rock and the chemical reactions are tabulated in Tables 4.5 and 4.6. The reactions themselves are discussed later in this chapter. Examples of these deductions are given in Chapter 9. The ratios are calculated in the WATEVAL computer program.

GRAPHICAL METHODS

Graphical methods of illustrating water analyses have two main objectives. The first is to be able to plot analyses on a map and the second is to detect chemical trends.

The representation of analyses on maps may be accomplished in two ways. A common method is to use a variety of plots to represent the analyses. A better method that is becoming more common is the use of a computer contouring program. Either basic contour plots or fishnet 3-D plots of the data may be prepared. The latter are one-component plots—generally TDS or conductivity. Other elements of interest, or even ratios of ions or elements, may be plotted. These are readily contoured and, in some cases, easily interpreted. Graphical methods that are multi-component plots are extremely difficult to interpret. Interpretation involves a visual examination of both various shapes and different sizes on a map.

MULTIPLE-COMPONENT PLOTS

The more common multiple-component plots used are described below. A more extensive review and discussion is given by Hem (1992, pages 173–180).

Table 4.5. Source-Rock Deduction Worksheet

Parameter	Value	Conclusion
Sample Designation:		
SiO_2 (mmol/l)		
$\frac{HCO_3^-}{SiO_2}$		
$\frac{SiO_2}{Na^+ + K^+ - Cl^-}$		
$\frac{Na^+ + K^+ - Cl^-}{Na^+ + K^+ - Cl^- + Ca^{2+}}$		
$\frac{Na^+}{Na^+ + Cl^-}$		
$\frac{Mg^{2+}}{Ca^{2+} + Mg^{2+}}$		
$\frac{Ca^{2+}}{Ca^{2+} + SO_4^{2-}}$		
$\frac{Ca^{2+} + Mg^{2+}}{SO_4^{2-}}$		
TDS calculated (mg/l)		
$\frac{Cl^-}{\text{sum anions}}$		
$\frac{HCO_3^-}{\text{sum anions}}$		
Langelier index		
Conclusion	Aquifer mineralogy	
Conclusion	Reactions	

Bar Graphs

Units are usually in meq/l. This enables the sum of anions and the sum of cations to be drawn the same length.

Pie Diagrams or Circular Diagrams

Pie diagrams are drawn such that the diameters of the circles are proportional to the dissolved solid content. If the units are in meq/l, then one semicircle represents the cations and the other the anions.

Radial Diagrams

Concentrations are usually in meq/l or % meq/l. The arms of the plots are usually 60° apart and the ends connected to form a polygon.

Table 4.6. Source-Rock Deduction Summary of Reasoning

Parameter	Value	Conclusion
SiO_2 (mmol/l)	>0.5	Volcanic glass or hydrothermal waters possible
$\frac{HCO_3^-}{SiO_2}$	>10	Carbonate weathering
	>5 and <10	Ambiguous
	<5	Silicate weathering
$\frac{SiO_2}{Na^+ + K^+ - Cl^-}$	<1	Cation exchange
	>1 and <2	Albite weathering
	>2	Ferromagnesian minerals
$\frac{Na^+ + K^+ - Cl^-}{Na^+ + K^+ - Cl^- + Ca^{2+}}$	>0.2 and <0.8	Plagioclase weathering possible
	<0.2 or >0.8	Plagioclase weathering unlikely
$\frac{Na^+}{Na^+ + Cl^-}$	>0.5	Sodium source other than halite—albite, ion exchange
	= 0	Halite solution
	<0.5 TDS >500	Reverse softening, seawater
	<0.5 TDS <500 >50	Analysis error
	<0.5 TDS <50	Rainwater
	$\frac{HCO_3^-}{SiO_2} > 10$	Carbonate weathering
$\frac{Mg^{2+}}{Ca^{2+} + Mg^{2+}}$	= 0.5	Dolomite weathering
	<0.5	Limestone-dolomite weathering
	>0.5	Dolomite dissolution, calcite precipitation, or seawater
	$\frac{HCO_3^-}{SiO_2} < 5$	Silicate weathering
	>0.5	Ferromagnesian minerals
	<0.5	Granitic weathering
$\frac{Ca^{2+}}{Ca^{2+} + SO_4^{2-}}$	= 0.5	Gypsum dissolution
	<0.5 pH <5.5	Pyrite oxidation
	<0.5 neutral	Calcium removal—ion exchange or calcite precipitation
	>0.5	Calcium source other than gypsum—carbonates or silicates
$\frac{Ca^{2+} + Mg^{2+}}{SO_4^{2-}}$	>0.8 and <1.2	Dedolomitization
TDS	>500	Carbonate weathering or brine or seawater
	<500	Silicate weathering
$\frac{Cl^-}{\text{sum anions}}$	>0.8 TDS >500	Seawater, or brine, or evaporites
	>0.8 TDS <100	Rainwater
	<0.8	Rock weathering
$\frac{HCO_3^-}{\text{sum anions}}$	>0.8	Silicate or carbonate weathering
	<0.8 sulfate high	Gypsum dissolution
	<0.8 sulfate low	Seawater or brine
Langelier index	Positive	Oversaturated with respect to calcite
	0	Saturated with respect to calcite
	Negative	Undersaturated with respect to calcite
Conclusion	Aquifer mineralogy	
Conclusion	Reactions	

Vector Diagrams

Vector diagrams are similar to radial diagrams except that the vectors are plotted along predefined directions. The length of the vector is proportional to the concentration, which is usually expressed in meq/l. The ends of the plot are not usually connected.

Kite Diagrams

This configuration is limited to four concentrations and the axes are $Ca^{2+} + Mg^{2+}$, $Na^{+} + K^{+}$, $Cl^{-} + SO_4^{2-}$, and $HCO_3^{-} + CO_3^{2-}$, expressed in meq/l.

Stiff Diagrams

A stiff diagram uses four parallel, horizontal axes extending on each side of a vertical, zero axis. Four cations and four anions can thus be plotted on the left and right of the vertical axis, respectively. Concentrations are in meq/l. The resulting points are connected to give an irregular polygonal pattern. The size of the pattern is approximately equal to the total ionic content. Classically, the pairs are sodium-chloride, calcium-bicarbonate, magnesium-sulfate, and iron-carbonate. Usually the iron-carbonate line is small or nonexistent. In some computer programs, such as the author's WATEVAL, it is not drawn at all. In addition, the diagrams may be drawn using either a linear or a log meq/l scale.

The log plot is useful for wide ranges of water compositions without having to change the scale. This diagram may also be used to evaluate the source-rock deduction described above, if silica is represented by a line of appropriate length. Stiff diagrams of waters from aquifers of different rock types are shown in Figure 4.6. In the diagrams the axes are log meq/l.

CHEMICAL TRENDS

The determination of trends in a collection of water analyses is accomplished by using either an x-y plot or some type of trilinear plot. When considering plotting techniques, only major components are plotted, specifically Na^{+} ($+K^{+}$), Ca^{2+}, Mg^{2+}, Cl^{-}, SO_4^{2-}, and HCO_3^{-} ($+CO_3^{2-}$). This approximation provides six major ions or combinations of ions to be plotted.

In contrast to studying areal trends where individual analyses, each represented by an individual shape, are each plotted on a map, chemical-trend plots consist of all analyses plotted as points on one diagram. The simplest type of such a diagram is an x-y plot of two ions or variables, such as Na^{+} vs. Ca^{2+}. This is by far the simplest type of graph to interpret. Many computer statistical packages and spreadsheet programs are available to do these plots.

A more complex method of plotting is by using trilinear or triangular diagrams. The apices of trilinear diagrams represent 100% of a component and the opposite side of the triangle represents 0% of that component. Thus, for a three-component system—A, B, and C, the apex A represents 100% of A and the side B-C represents 0% of A. Similarly, apex B is 100% and side A-C 0% of component B; apex C is 100% and side A-B 0% of component C. Lines representing different percentages of each component are drawn parallel to the base opposite the apex of the component. The intersection of two lines representing two of the three components of a particular sample is the point representing that analysis. The third line is usually drawn as a verification; it too should pass through the same point. This procedure is shown in Figure 4.7. A point plotting on one side of a triangle represents a two-component mixture of the components at each end of that line. A disadvantage is that only three variables can be plotted on a triangle. This is overcome to some extent by plotting

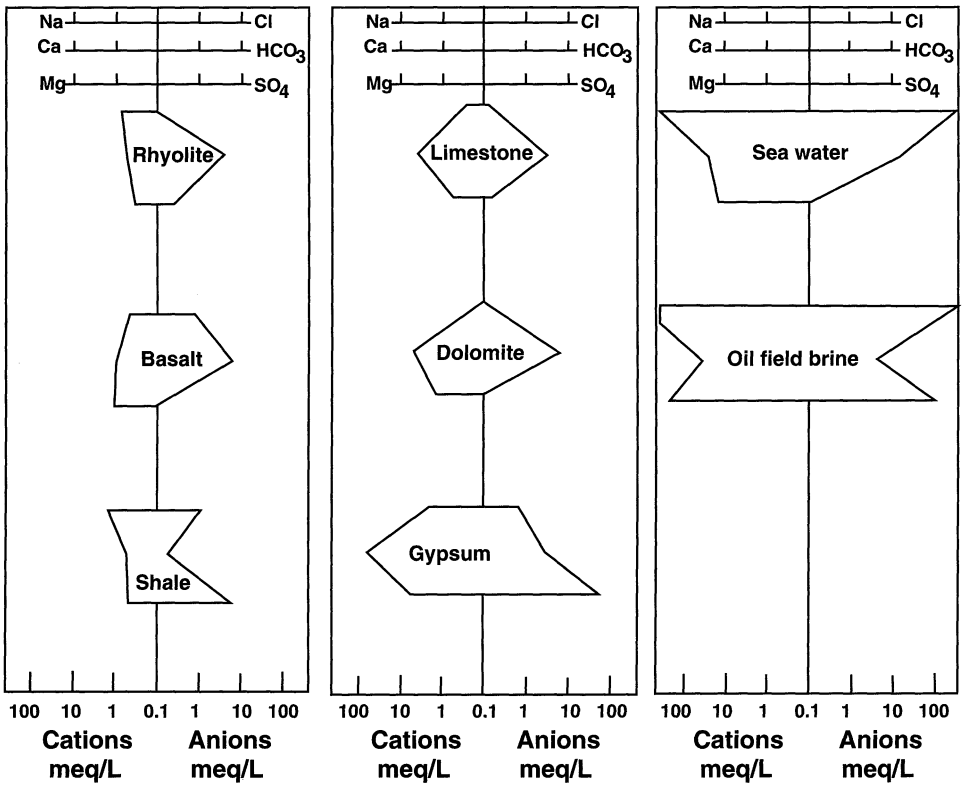


Figure 4.6. Stiff diagrams of waters from different rocks.

cations and anions on separate triangles and arranging the triangles in such a way that they can be related to one another.

A major problem with this type of diagram is that the analyses plotted are only ratios; therefore, the effect of dilution is not immediately apparent.

Two common techniques for plotting water data are Piper diagrams and Durov graphs. They are as follows:

Piper Diagrams

Piper diagrams are a combination anion and cation triangles that lie on a common baseline. Adjacent sides of the two triangles are then 60° apart. A diamond shape between them is used to replot the analyses as circles whose areas are proportional to their TDS. The position of an analysis that is plotted on a Piper diagram can be used to make a tentative conclusion as to the origin of the water represented by the analysis. However, the bicarbonate to silica ratio must also be considered when making this deduction.

Four basic conclusions can be derived from multiple analyses plotted on Piper diagrams. These are water type, precipitation or solution, mixing, and ion exchange. The study of Piper's 1944 paper is strongly recommended for anyone using these plots extensively.

Water Types

The diamond part of a Piper diagram may be used to characterize different water types. Piper divided waters into four basic types according to their placement near the four corners

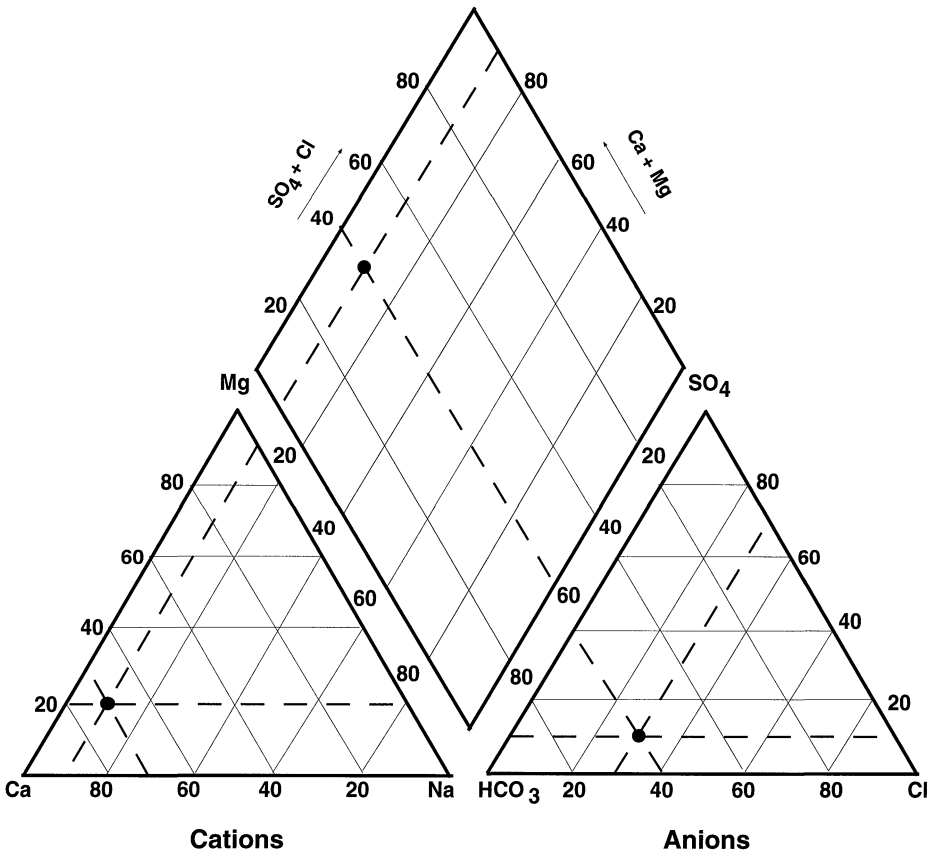


Figure 4.7. Triangular diagrams. Cation triangle plot of 70% Ca^{2+}, 20% Mg^{2+}, 10% Na^{-}; anion triangle plot of 60% HCO_3^{-}, 10% SO_4^{2-}, 30% Cl^{-}; intersection of cations and anions in diamond.

of the diamond. Water that plots at the top of the diamond is high in both $Ca^{2+} + Mg^{2+}$ and $Cl^{-} + SO_4^{2+}$, which results in an area of permanent hardness. The water that plots near the left corner is rich in $Ca^{2+} + Mg^{2+}$ and HCO_3^{-} and is the region of water of temporary hardness. Water plotted at the lower corner of the diamond is primarily composed of alkali carbonates ($Na^{+} + K^{+}$ and $HCO_3^{-} + CO_3^{2-}$). Water lying near the right-hand side of the diamond may be considered saline ($Na^{+} + K^{+}$ and $Cl^{-} + SO_4^{2-}$). These divisions are shown in Figure 4.8. Groundwater from aquifers within different rock types are shown in Figure 4.9.

Precipitation or Solution

If a series of water analyses plotted on a Piper diagram lie on a straight line, that when extrapolated passes through the corner of one or both of the triangles, then it is possible that the trend is indicative of precipitation or solution. The component at the corner of the triangle is either being added or removed from solution. Examples include calcite precipitation or solution (calcium and bicarbonate) or gypsum precipitation or solution (calcium and sulfate). Mass balance and solubility equilibrium may be used to confirm or disprove this hypothesis. Figure 4.10 shows Piper plots where Ca^{2+} and sulfate are either being removed or added. If addition of Ca^{2+} and sulfate occur together, the inference is that gypsum (or anhydrite) is dissolved. If ions are added, the TDS would be expected to increase unless another ion (or ions) is (are) removed at the same time.

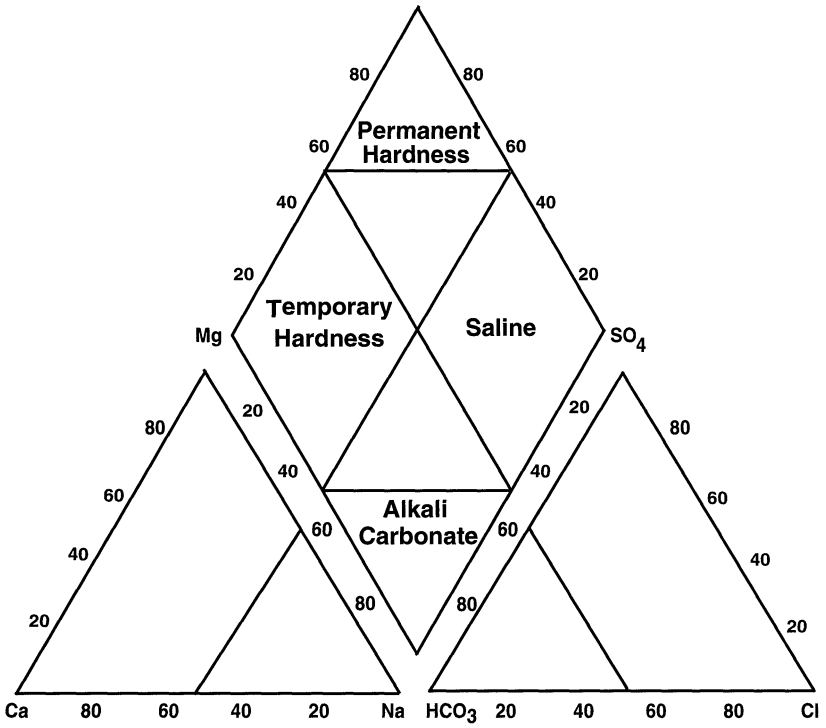


Figure 4.8. Different water types in the diamond portion of Piper diagram.

The removal of one ion from solution may be accompanied by a relatively constant TDS if the removal of this ion is accompanied by the addition of another ion. An example would be ion exchange. If both an anion and a cation were removed the TDS could also remain constant if the removal of the ions were a result of evaporation, that is, a reduction in water volume.

Mixing

If two waters mix, then the composition of the mixture will lie on a straight line joining the two end members. The relative amount of each end member in the mixture is inversely proportional to the distance of the mixture from that end member, that is, the closer the mixture is to an end member, the greater the amount of that end member in the mixture. If a water is strictly the result of mixing, without the addition or removal of any phase, then the mixture will exhibit exactly the same proportions between the end members on both cation and anion triangles as well as on the diamond. The method of calculating the proportions of the end members in a mixture is shown in Figure 4.11.

This is another application of the lever rule where the proportion of end member 1 equals the distance on the diagram from end member 3 to the mixture composition over the diagram distance from end member 1 to end member 3. Mathematically, if **a** is the distance from end member 1 to the mixture and **b** is the distance from the mixture to end member 3, then: the proportion of end member 1 = **b**/(**a** + **b**), and the proportion of end member 3 = **a**/(**a** + **b**). The result is that mixture contains about 66% of end member 3 and 34% of end member 1.

Although a semiquantitative estimate of the mixture proportions may be made from the Piper diagram, a quantitative estimate (assuming no solid or gas phases are lost or gained) may be calculated using the technique described in a later section of this chapter.

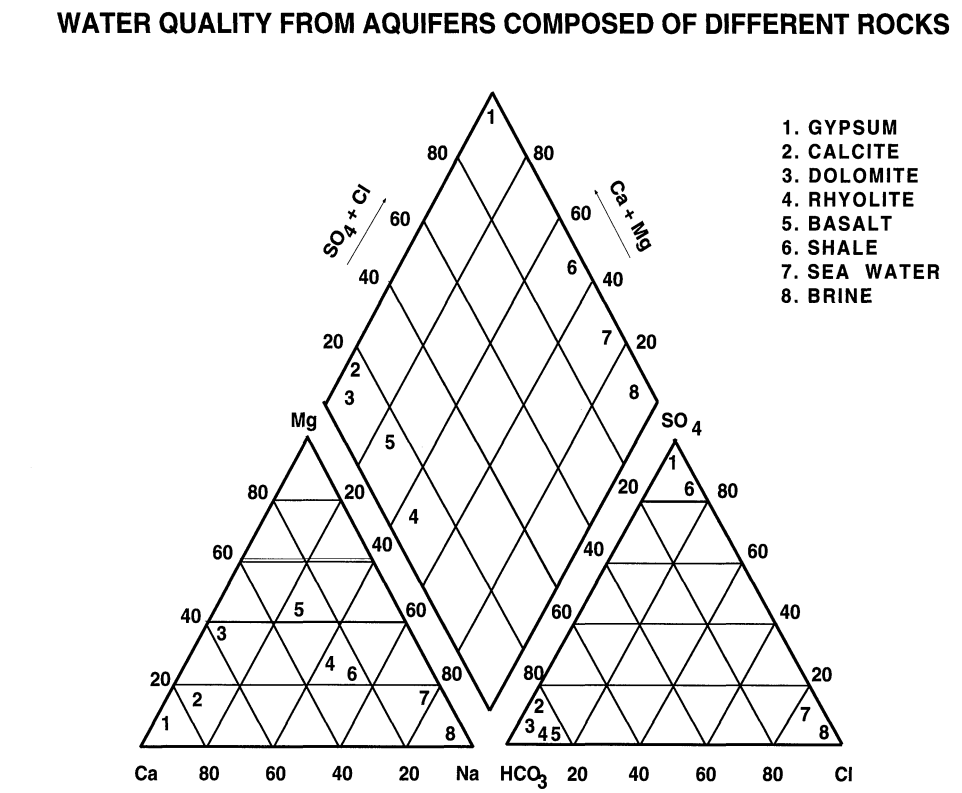


Figure 4.9. Piper plots of waters from different rocks.

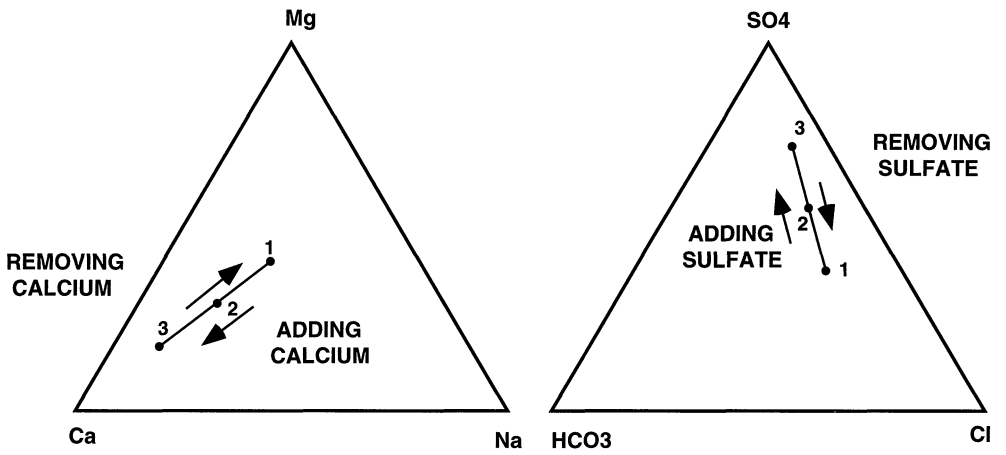


Figure 4.10. Solution and removal of ions on Piper diagrams.

Ion Exchange

The replacement of calcium and magnesium in solution by sodium is a special case of addition and removal from solution. The line on the Piper diagram connecting water compositions that are changed by ion exchange starts parallel to constant magnesium and then curves

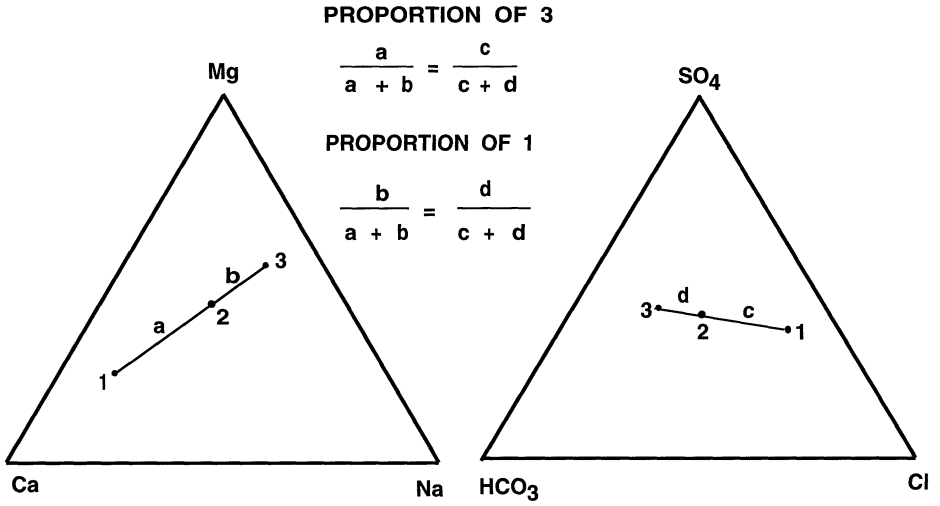


Figure 4.11. Mixing of two waters on Piper diagrams.

down towards the sodium apex. This suggests that more calcium is being exchanged than magnesium. The anions plot about the same position. If ion exchange alone is occurring, no anions are added or removed from solution. A hypothetical plot is shown in Figure 4.12.

Interpretation of Piper Diagrams when Analyses Are not Available

Occasionally the only data available pertaining to a particular sample(s) is in the form of a Piper diagram, often small and without scales on the triangles. As percent meq/l are plotted on Piper diagrams, approximate ratios may be calculated by measuring the placement of the sample on the diagram using a millimeter ruler. Once ratios are calculated they may be converted from x/y to y/x + y by calculating the reciprocal of (1 + x/y). For example, a Ca/Mg ratio of 2.2 is the same as a ratio of Mg/Ca + Mg = 1/(1 + Ca/Mg) = 1/(1 + 2.2) = 0.31.

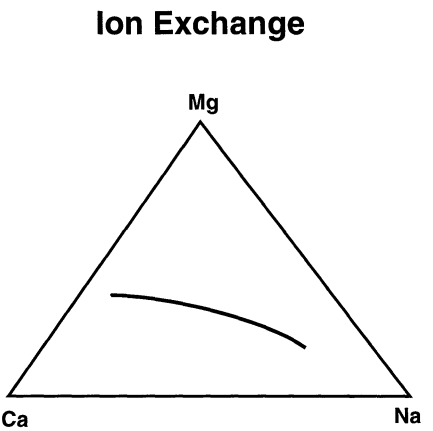


Figure 4.12. Ion exchange on Piper diagrams.

Example of some ratios are shown in Figure 4.13.

a. The percentage of A in the sample is a ratio of the distance above the base over the distance of the apex from the base.

b. The ratio of Ca/Mg in the sample is obtained by drawing a line (of constant Ca/Mg) from the Na apex through the sample point to the Ca-Mg side of the triangle. The ratio of Ca/Mg then is the ratio of the two segments of that side of the triangle.

c. The objective is to calculate an cation/anion ratio. Because both triangles are the same size they may be treated similarly. Thus, a Na/Cl ratio is obtained by measuring the placement of Na on the cation triangle and the placement of Cl on the anion triangle, and calculating their ratio by the ratio of their measurements.

d. Two samples with different cation ratios and the same anion ratio can be compared using the measurement technique used in (c) above.

Examples of the Interpretation of Piper Diagrams

Interpretation of Piper diagrams (1)—Figure 4.14

Analysis 1 has a TDS of 510 mg/l. **Estimate the relative amounts of each end member and suggest a possible source rock.**

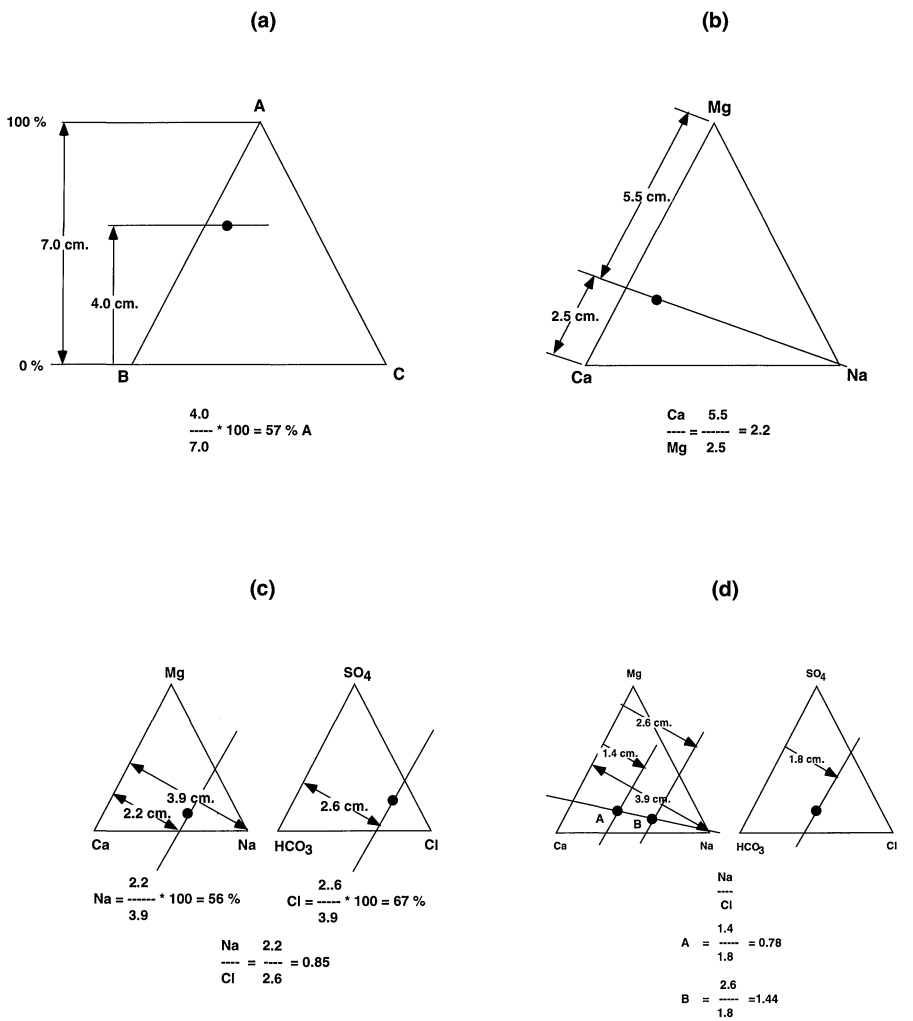


Figure 4.13. Calculation of ratios from Piper diagrams.

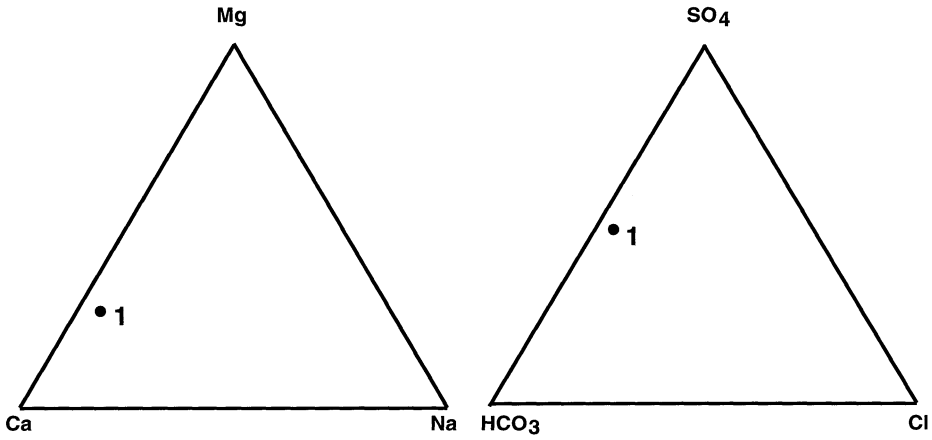


Figure 4.14. Interpretation of Piper diagrams (1).

Sample 1 contains about 68% Ca^{2+}, 26% Mg^{2+}, and about 6% Na^{+}. The anions consist of about 29% SO_4^{2-}, 29% HCO_3^{-} with 4% C^{-}. The bicarbonate indicates carbonic acid weathering, and if HCO_3^{-} much greater than SiO_2 (10× or more), then carbonate weathering is indicated. On the other hand, if HCO_3^{-} is only slightly greater than SiO_2 then silicate weathering is possible. The Na/(Na + Ca) of 0.08 and the relatively high TDS of 510 mg/l suggest carbonate weathering.

The Mg/(Mg + Ca) ratio of 0.27 also suggests limestone and some dolomite. The sulfate originates from gypsum or pyrite oxidation.

Interpretation of Piper diagrams (2)—Figure 4.15.

Analysis 2 has a TDS of 350 mg/l. **Estimate the relative amounts of each end member and suggest a possible source rock.**

Analysis 2 contains about 72% Ca^{2+}, 16% Mg^{2+}, and 12% Na^{+}. The anions are dominated by bicarbonate estimated to be 90%, with 5% Cl− and 5% SO_4^{2-}. With low TDS and Na/(Na + Ca) of 0.14 carbonate weathering is suggested, possibly near the recharge. A high HCO_3^{-}/SiO_2 silicate ratio would support this conclusion. A low Mg/(Mg + Ca) of 0.18 suggests some dolomite.

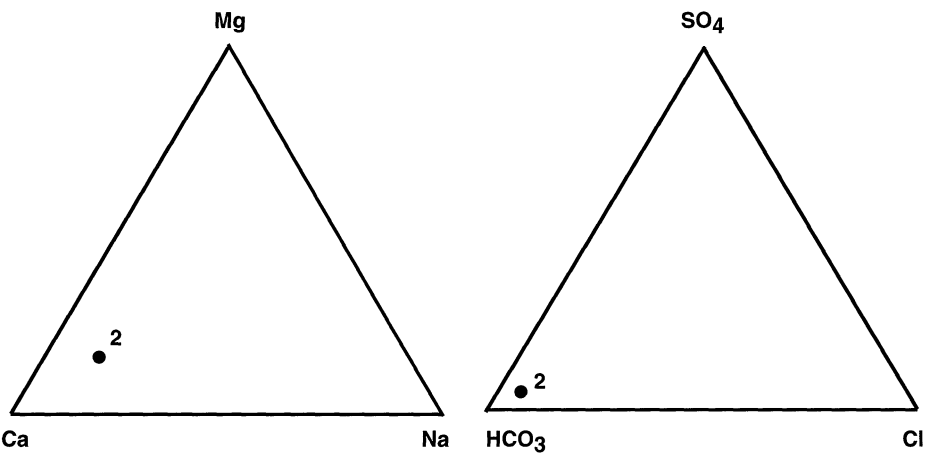


Figure 4.15. Interpretation of Piper diagrams (2).

Interpretation of Piper diagrams (3)—Figure 4.16.

Three analyses are shown lying in a line in this diagram with the TDS increasing from 1 to 3. **Discuss the possibility of sample 2 being the result of mixing of sample 1 and sample 3.**

The ratio (1 to 2)/(1 to 3) is different in the anion and cation triangles, and thus a simple mixture is unlikely. The cations align with the calcium apex, whereas the anions point midway between bicarbonate and sulfate. If we assume nonsilicate weathering is occurring, then calcite-gypsum solution is likely, or possibly calcite-pyrite solution. The uneven ratios between the anion and cation triangles is most likely the result of different proportions of dissolved calcite and gypsum. Both contribute calcium, but only gypsum or pyrite contributes sulfate. On the other hand, the Na/(Na + Ca) equals 0.6 and the Mg/(Mg + Ca) ratio is 0.7, both of which suggest mafic silicate weathering. These conflicting conclusions suggest that the samples may be quite unrelated.

Interpretation of Piper diagrams (4)—Figure 4.17.

Three analyses are shown lying in a line in this diagram with the TDS increasing from 1 to 3. **Discuss the possibility of sample 2 being the result of mixing of sample 1 and sample 3.**

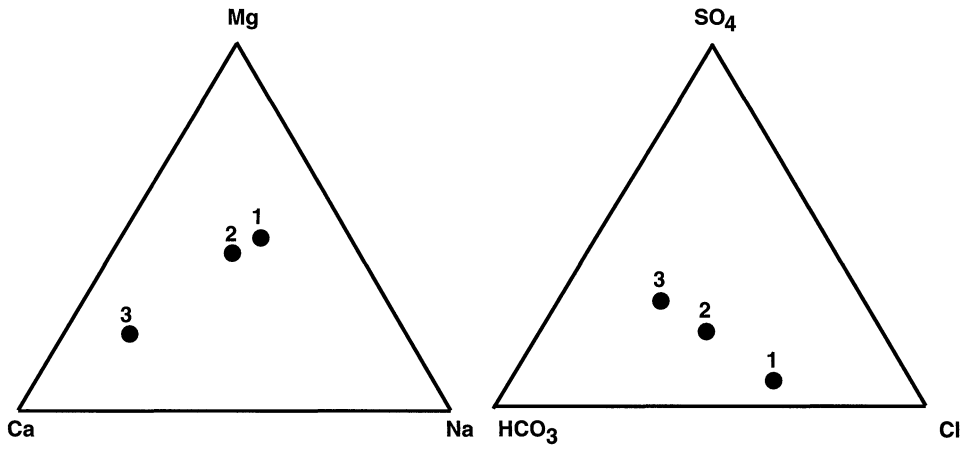


Figure 4.16. Interpretation of Piper diagrams (3).

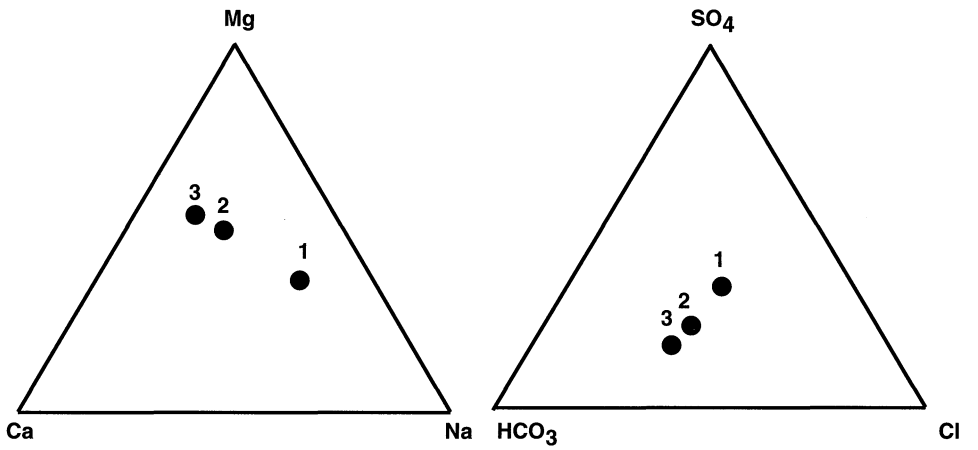


Figure 4.17. Interpretation of Piper diagrams (4).

In this case the ratio between the mixture and the two end members is about the same in both cation and anion triangles. Using the measured ratios, mixture 2 contains about 73% end member 3 and 27% end member 1. This ratio must, however, be the same as that calculated from the TDS ratios discussed later in this chapter.

Interpretation of Piper diagrams (5)—Figure 4.18.

Discuss the possible origin of the waters 1, 2, and 3 given that they were collected downgradient in an aquifer and that the TDS increase from sample 1 to sample 3.

Three analyses plot in a straight line pointing toward the Na^+ apex in the cation triangle and toward the Cl^- apex in the anion triangle. The basic indication is that of NaCl contamination by some source. Two possibilities that exist are progressive solution of halite solution (or mixing with saline groundwater formed by halite solution) or mixing with an oil-field brine. Sample 3 contains 87% Na and 87% Cl, resulting in a Na/(Na + Cl) ratio of 0.5. This suggests a halite origin, as most brines have a ratio lower than 0.5.

Interpretation of Piper diagrams (6)—Figure 4.19

Discuss the possible origin of the waters 1, 2, and 3 given that they were collected downgradient in an aquifer and that the TDS remains relatively constant.

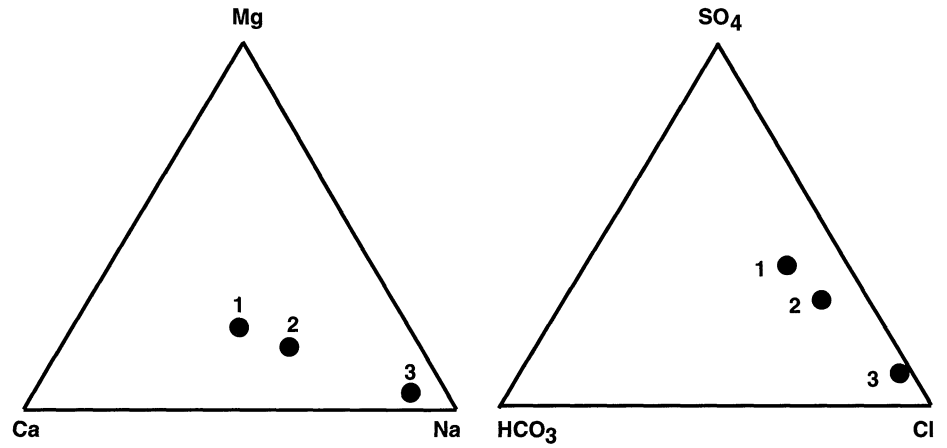


Figure 4.18. Interpretation of Piper diagrams (5).

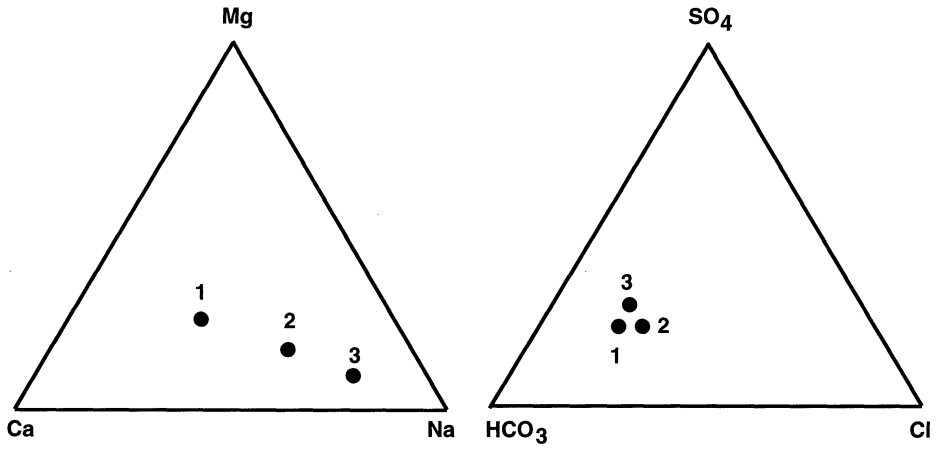


Figure 4.19. Interpretation of Piper diagrams (6).

This set of analyses lie in a line in the cation triangle, but clump together in the anion triangle. If these are groundwater and the downgradient direction is from 1 to 3, then the most likely reaction is cation exchange of Ca^{2+} and Mg^{2+} for Na^{+}. This explanation is preferred over the solution of halite because of the lack of a commensurate increase of Cl, or the solution of albite (plagioclase) because of the lack of increase in bicarbonate.

Durov Graphs

The Durov, or expanded Durov graphs, are similar to Piper diagrams in that the analyses are plotted on separate anion and cation triangles; however, the sides of the triangles are 90° apart. Also, in the expanded Durov the three corners of each triangle are physically separated from one another. The result is a square plot divided into nine areas, each characteristic of a different water type. These diagrams are commonly used by European water chemists. A detailed discussion of Durov diagrams is given in Lloyd and Heathcote, 1985.

RATIOS

Absolute concentrations are commonly used in the investigation of specific water types, such as oil field brines and geothermal waters. In contrast, groundwater contamination problems often involve mixtures of different waters, including dilution by rainwater or a fresher groundwater. In this case, absolute values of concentrations of the different water constituents is of marginal use in the interpretation of water quality data. To compensate for dilution and other effects, the use of ratios is recommended. The different forms these ratios can take can cause confusion. Some methods of plotting ratios are explained in this section.

Ratios vs. Log-Log Plots

If the ratio of B/A is considered, it is apparent that a linear plot of A against B is a straight line intersecting the origin. The slope of this line depends on the ratio of A to B, which is a constant for that data set. Thus B/A = k or B = k * A or **log B = log A + log k.** If A and B are plotted on log-log paper, the resultant graphs plot as a straight line with a 1:1 slope, regardless of the numerical value of k, which then becomes the intercept. Figure 4.20a shows a linear plot of three different ratios and Figure 4.20b shows a log-log plot of a wider range of ratios. The relationship discussed here is true if on the ratio being plotted intersects the origin, which is usually the case when concentrations are being plotted. The technique is often used in plotting ratios of elements in brines.

Ratio Plots vs. Trilinear Diagrams

If three values A, B, and C are reported in the ratio form of A/C and B/C then these ratios can readily be converted to the coordinates of a trilinear plot. An example of this calculation is given in Table 4.7. Thus if A/C = 0.5 and B/C = 0.2, then A $\approx$ 29%, B $\approx$ 12%, and C $\approx$ 59%. A result of this is that a linear plot of A/C vs. B/C is essentially the same as a trilinear plot. Three points in a straight line in one plot will result in three points in a straight line in the other plot. Figure 4.21a illustrates three points plotted on a linear ratio plot, and Figure 4.21b shows the same three points plotted on a trilinear diagram. Although the points lie on a line in both diagrams the proportionality between the points is different.

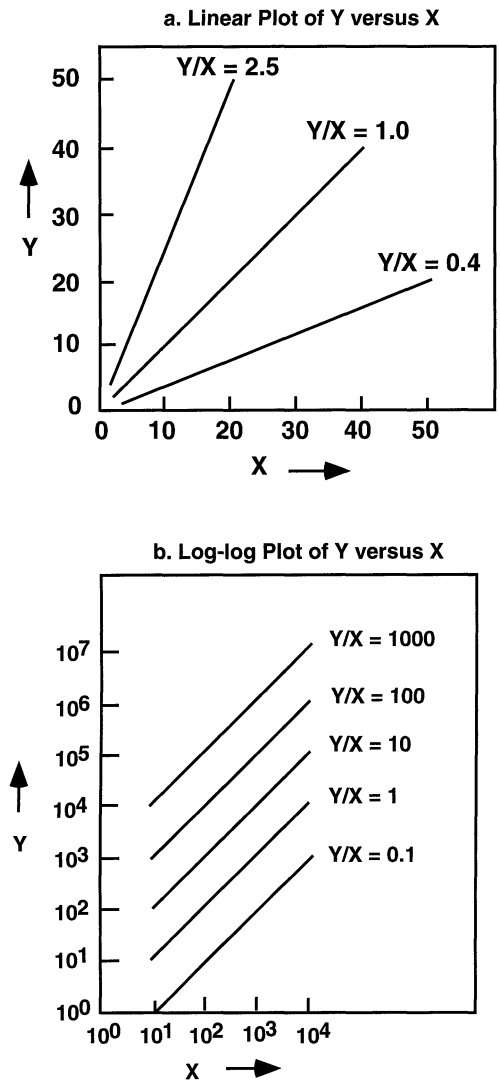


Figure 4.20. Ratio plots using linear and log-log graphs.

Ratio of Ratios

In dealing with ratios it is often useful to compare them with a standard. This technique is commonly used in isotope studies. The derivation of the formula used is given below.

$$\text{Ratio} = \frac{\left(\frac{X}{R}\right)_{\text{sample}}}{\left(\frac{X}{R}\right)_{\text{standard}}}$$ where X and R are measured constituents or $\frac{X}{R}$ is a measured ratio.

If the sample ratio equals the reference ratio, then the ratio equals one and there is no enrichment or depletion. If there is equality, or absence of enrichment or depletion, then we

Table 4.7. Conversion of Ratios to Trilinear Coordinates

	Ratios		
Sample	1	2	3
$\frac{A}{C}$	0.5	1.0	2.0
$\frac{B}{C}$	0.2	0.4	0.8

$A + B + C = 100$

$$\frac{A}{C} + \frac{B}{C} + 1 = \frac{100}{C}$$

$$C = \frac{100}{\left(\frac{A}{C} + \frac{B}{C} + 1\right)}$$

Sample	1	2	3
C	$\frac{100}{1.7}$	$\frac{100}{2.4}$	$\frac{100}{3.8}$

Above ratios converted to percent of each end member.

	Percentages		
Sample	1	2	3
C	58.8	41.7	26.3
A	29.4	41.7	52.6
B	11.8	16.6	21.1

define a value (delta) that is equal to zero. Thus, we define delta = (Ratio − 1). If delta is positive, then enrichment has occurred. If delta is negative, depletion has occurred.

$$\text{or} \qquad \text{Delta} = \frac{\frac{X}{R}\ \text{sample}}{\frac{X}{R}\ \text{standard}} - 1$$

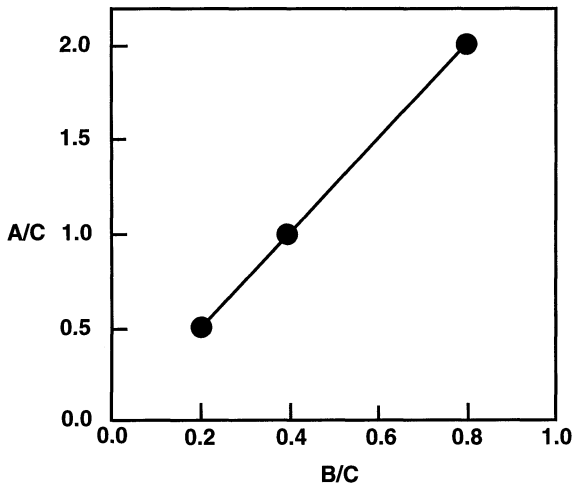
If the differences are small, a magnification factor may be used. For example, we can redefine delta as K * (Ratio − 1), where K is the magnification factor.

$$\text{Delta} = K^* \left[\frac{\frac{X}{R}\ \text{sample}}{\frac{X}{R}\ \text{standard}} - 1 \right]$$

If K = 1, delta is not changed. If K = 100, the change in the ratio is in parts per hundred or percent. If K = 1000 the change in the ratio is in $^{o}/_{oo}$ or parts per thousand. For nonisotope studies the choice of standard is open; however, seawater is probably the best choice for many investigations.

Examples:

If the Li/Cl ratio in a hydrothermal water is $6.98 * 10^{-3}$ and the Li/Cl ratio in sea water is $8.95 * 10^{-6}$, then the ratio of sample/seawater is 780. That is, the Li/Cl ratio of the hydrothermal water is 780 times that of seawater, or delta equals 779.



Ratios Plotted On Trilinear Diagram

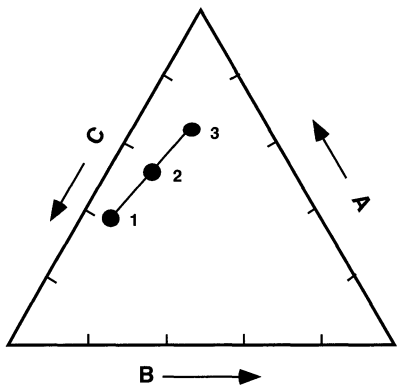


Figure 4.21. Ratios and trilinear diagrams.

Considering K/Na ratios, that of seawater is 0.03714, whereas that in a hydrothermal water is 0.01579. The ratio equals 0.425 or delta = (0.425 − 1) = −0.575, indicating depletion. A factor of 100 could be used as a magnifier. Thus the depletion is −58 parts per hundred.

GROUNDWATER REACTIONS

After an initial groundwater composition is established at the recharge area, the composition changes as the water moves downgradient toward the discharge point. These compositional changes may be the result of the following processes (see Figure 4.22):

1. Progressive dissolution of aquifer minerals—homogeneous aquifer.
2. Reactions resulting from changes in aquifer mineralogy—nonhomogeneous aquifer.

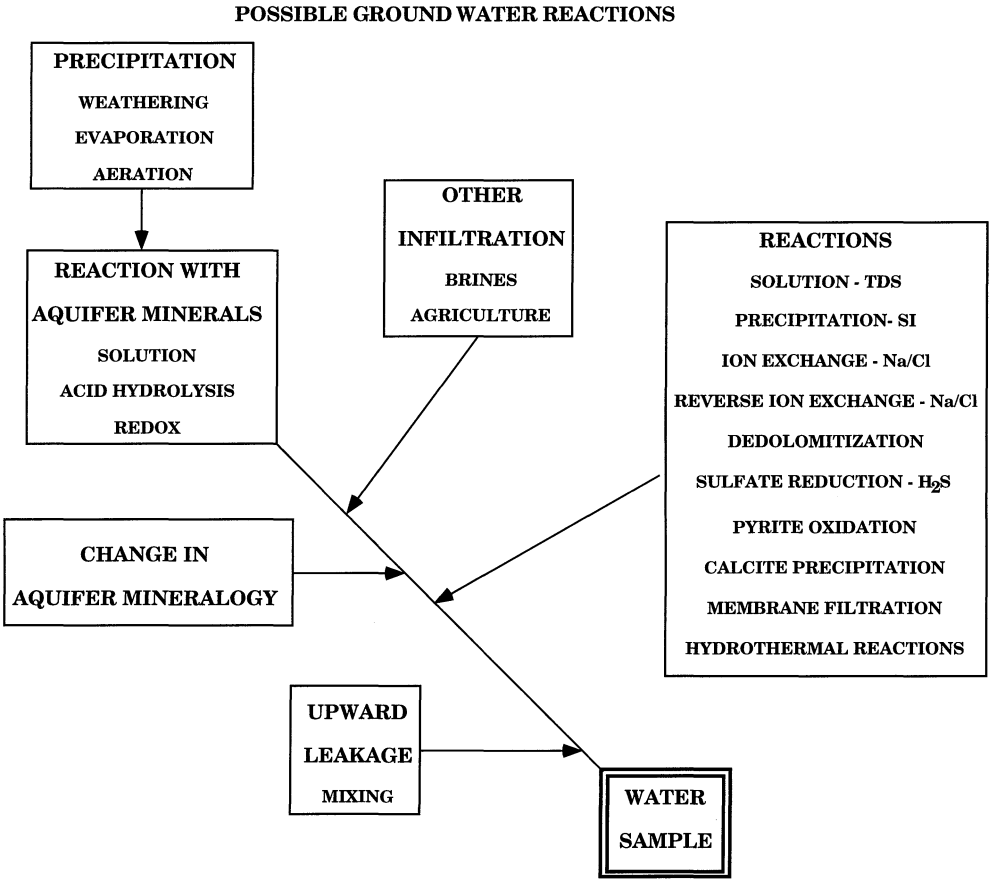


Figure 4.22. Possible groundwater reactions.

3. Deoxygenation by the reaction of dissolved oxygen with the organic carbon in the aquifer. This leads to redox changes that may increase the mobility of a variety of metal ions. Other redox reactions are possible, but deoxygenation is the most common.
4. Infiltration from other sources, such as irrigation water, brines, and landfill leachate, may result in major changes in water composition.
5. Upward leakage from underlying aquifers.

Some of the more common chemical reactions occurring in groundwater and methods of establishing their occurrence are discussed below.

DISSOLUTION

The progressive dissolution of minerals as groundwater moves downgradient in an aquifer will result in increases in the TDS content of the water. In sedimentary rocks the effect is noticeable because of the frequent occurrence of moderately to highly soluble minerals such as gypsum, anhydrite, or halite. In carbonate rocks progressive dissolution may slow down because of the depletion of the dissolved CO_2. The dissolution of gypsum is illustrated on a Piper diagram shown in Figure 4.10.

CHANGING MINERALOGY

An aquifer is often nonhomogeneous and some sections of it may have different mineralogic compositions. A limestone may have different carbonate minerals and may contain

sections rich in gypsum (or anhydrite). A sandstone aquifer may have different cements. Pyrite may not be homogeneously distributed in the aquifer. These variations may result in water composition changes that cannot readily be interpreted.

ION EXCHANGE

In aquifers containing montmorillonitic clay, natural softening or ion exchange may occur. Both Ca and Mg will be removed from the water and replaced by Na. Anions will remain unchanged. This is recognizable by a major increase of Na over Cl and, if most of the Ca comes from gypsum, then the meq/l ratio of $Ca^{2+}/(Ca^{2+} + SO_4^{2-})$ may be less than 0.5. The reaction for ion exchange may be written as follows:

$$Na_2\text{-}\mathbf{Clay} + Ca^{2+} \rightarrow 2Na^{+} + Ca\text{-}\mathbf{Clay}$$

The line connecting water compositions on a Piper diagram changed by ion exchange starts parallel to constant magnesium and then curves down towards the sodium apex. This suggests that more calcium is being exchanged than magnesium. A Piper diagram of this reaction is shown in Figure 4.12. The meq/l ratio of Na/(Na + Cl) is >0.5 when ion exchange occurs.

REVERSE ION EXCHANGE

Reverse ion exchange requires the presence of a clay with exchangeable calcium (usually montmorillonite) and a water higher in sodium than the clay-exchange equilibrium concentration. The effect is generally observed when seawater intrusion (Lloyd and Heathcote, 1985) or oil-field brine contamination occurs. It results in the release of calcium (and sometimes magnesium) and a decrease in sodium. Magnesium does not react reversibly as calcium (Piper et al., 1953). The result is often a meq/l Na/Cl of <1, often <<< 1. The reaction may be written as:

$$2Na^{+} + Ca\text{-}\mathbf{Clay} \rightarrow Na_2\text{-}\mathbf{Clay} + Ca^{2+}$$

Once the calcium in the clay has been removed, the process cannot continue any further. Normally it is detectable only in the leading front of a brine or seawater encroachment into a freshwater aquifer. If magnesium is held more strongly by clay than calcium, either by exchange or by incorporation into the clay structure, a calcium chloride water may be produced. Thus a $CaCl_2$ water may be considered to be the leading edge of a brine contamination front.

SULFATE REDUCTION

Sulfate reduction is usually recognized by the H_2S odor. It will result in decreased sulfate and increased bicarbonate. Sulfate reduction is the result of the microbial decomposition of sulfate as shown in the reaction below. A carbohydrate carbon source is assumed.

$$C_6H_{12}O_6 + 3SO_4^{2-} \rightarrow 6HCO_3^{-} + 3H_2S$$

The process is common in many aquifers. It is also the reason that many formation waters are low in sulfate.

PYRITE OXIDATION

Pyrite oxidation is another microbially mediated reaction resulting in the oxidation of pyrite to sulfuric acid. In the absence of carbonates this is a readily recognizable process, because of a low pH and high sulfate/chloride ratio. However, if carbonates are present then it may be difficult to differentiate pyrite oxidation and neutralization by carbonate from the dissolution of gypsum. It must be emphasized that pyrite oxidation will only occur in the presence of dissolved oxygen. The following reactions assume the precipitation of insoluble ferric hydroxide; however, ferric iron will remain in solution at low pH, and may accumulate in solution as ferrous iron under anoxic conditions.

The reactions are

$$\underset{\text{pyrite}}{FeS_2} + 3.75\ O_2 + 3.5\ H_2O \rightarrow \underset{\text{ferric hydroxide}}{Fe(OH)_3} + SO_4^{2-} + 4H^+$$

$$\underset{\text{calcite}}{2CaCO_3} + 4H^+ \rightarrow 2Ca^{2+} + 2H_2O + 2CO_2$$

The CO_2 may dissolve to form carbonic acid, which in turn dissolves more carbonate, or it may degas.

$$2CaCO_3 + 2H_2O + 2CO_2 \rightarrow 2Ca^{2+} + 4HCO_3^-$$

The resulting reaction is

$$FeS_2 + 3.75\ O_2 + 3.5\ H_2O + 4CaCO_3 \rightarrow Fe(OH)_3 + 2SO_4^{2-} + 4Ca^{2+} + 4HCO_3^-$$

On a Piper diagram the trend would be towards the 1:1 HCO_3^- : SO_4^{2-} side of the diagram rather than towards the sulfate corner, as would be the case with gypsum solution (Herr, 1991). A hypothetical Piper diagram for this reaction is shown in Figure 4.23.

CALCITE PRECIPITATION

Calcite is one of the most common minerals deposited from water. Surface water precipitates of calcite, both marine and nonmarine, have been discussed in considerable detail in the literature, as have spring deposits. The process of groundwater deposition of calcite in an aquifer has received little attention, although carbonate-cemented sandstones have been studied extensively by sedimentary petrologists. It must be concluded therefore that calcite precipitation is a common process in aquifers. Identifying a water that has precipitated calcite is the objective of this section. The chemical process involved is

$$Ca^{2+} + CO_3^{2-} \Rightarrow CaCO_3$$

$$\text{and } CaCO_3 \text{ will precipitate when } \frac{[Ca^{2+}][CO_3^{2-}]}{K_c} > 1$$

where K_c is the solubility product for calcite.

Thus calcite will precipitate when either Ca^{2-} or CO_3^{2-} is increased so that the solubility product is exceeded, or if the solubility product is reduced. Bricker (1971) stated that supersaturation and calcite precipitation can occur by warming (insolation or geothermal heating), pressure reduction, increased salinity (evaporation), decreased salinity (mixing of

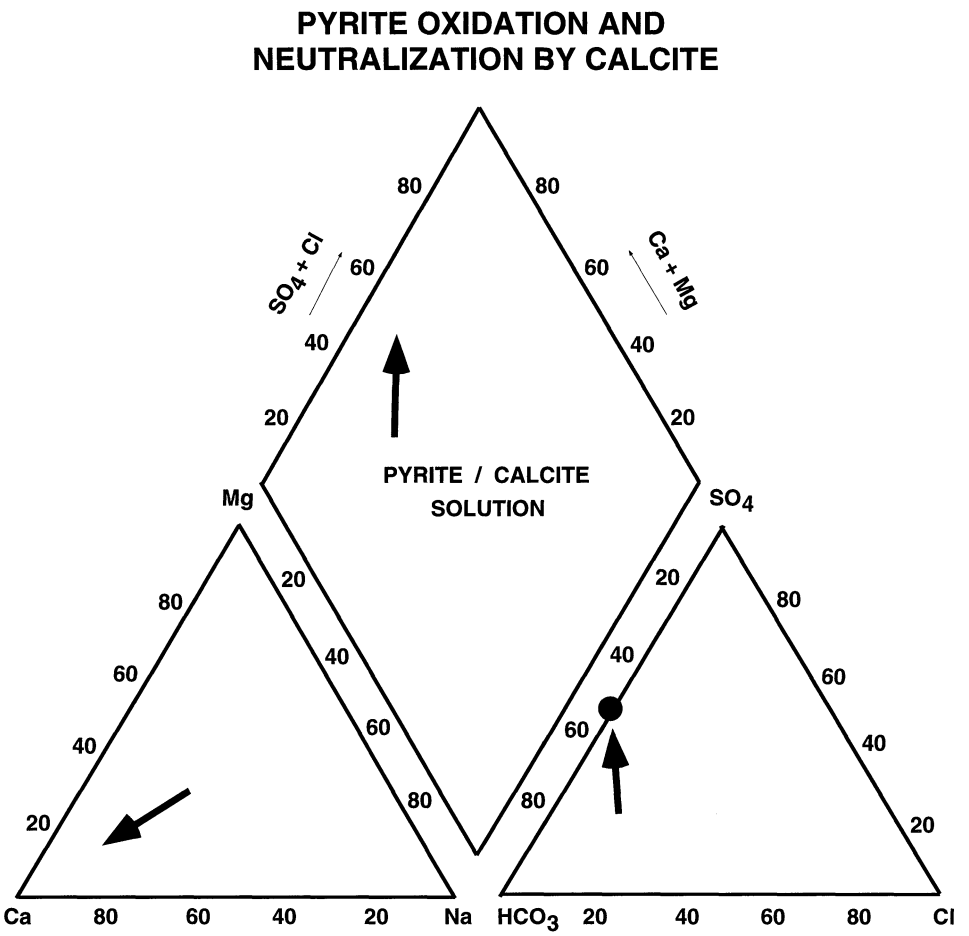


Figure 4.23. Pyrite oxidation and neutralization by calcite.

low- and high-salinity solutions), and loss of carbon dioxide (degassing or photosynthetic extraction).

Thus calcite will precipitate when:

a. The concentration of both constituents is increased, for example, by evaporation. Evaporite deposits from surface waters are of this type.
b. Decreasing the solubility product which is a function of temperature. Warming by insolation or by geothermal heating will do this.
c. Increasing the ion activity product by changing the ionic strength of the solution. An example is the mixing of low- and high-salinity solutions. An increase in ionic strength causes a decrease in the activity coefficients and increases calcite solubility (Dreybrodt, 1988).
d. By increasing the Ca^{2+} ion concentration, for example, by dissolving another soluble calcium mineral such as gypsum (common ion effect). This process is called dedolomitization and is discussed later.
e. By increasing the CO_3^{2-} concentration. Usually this occurs by decreasing the CO_2 content of the water, although increasing the bicarbonate content will have the same effect. The reaction is

$$CaCO_3 + 2H_2O + CO_2 \Leftrightarrow Ca^{2+} + 2HCO_3^-$$

Increasing carbonate concentration may result from:

i. decreased pressure, for example, springs depositing travertine, or cave deposits.
ii. photosynthesis, for example, algal deposits in lakes.
iii. adding HCO_3^-, such as through sulfate reduction (Berner 1971). Berner proposed that the bacterial process of sulfate reduction can result in the formation of excess HCO_3^-, which may cause the precipitation of $CaCO_3$ in marine sediment pore waters. He summarizes the reactions as:

$$SO_4^{2-} + 2CH_2O \rightarrow 2HCO_3^- + H_2S_{(aq)}$$

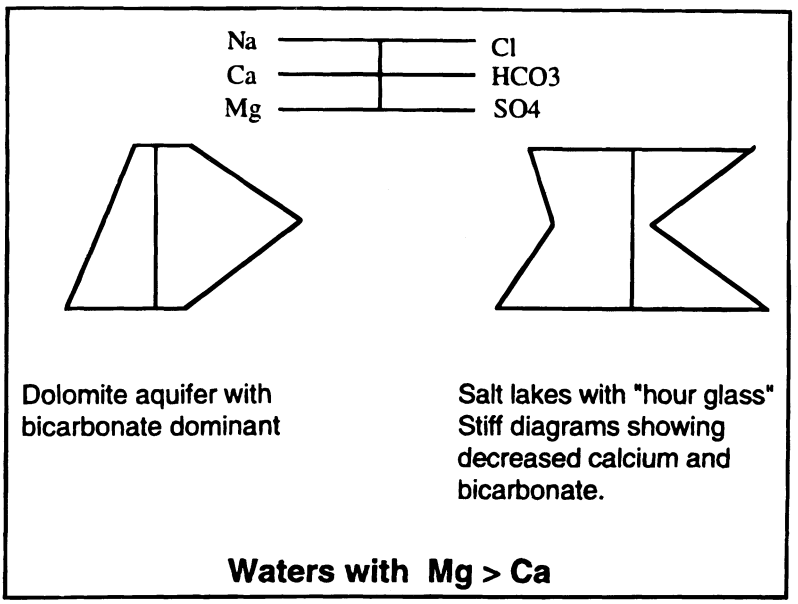
$$2HCO_3^- + Ca^{2+} \rightarrow CaCO_3 + CO_{2(aq)} + H_2O$$

Chapelle (1983) proposed a concurrent carbonate dissolution-precipitation reaction whereby magnesian calcite is dissolved and calcite is precipitated to account for secondary calcite cementation. The reactions proposed were

$$(Ca_{1-x}Mg_x)CO_3 + H_2O + CO_2 \Rightarrow (1 - x)Ca^{2+} + xMg^{2+} + 2HCO_3^-$$

$$Ca^{2+} + 2HCO_3^- \Leftrightarrow CaCO_3 + H_2O + CO_2$$

The waters examined had a saturation index for calcite of close to zero. In the area where this process was postulated the bicarbonate and pH remained relatively constant. The magnesian calcite being dissolved was thought to have $x = 0.1$. This theory could be extended to include dolomite as a source, in which case $x = 0.5$, in which case the magnesium concentration could easily exceed that of calcium. Hem (1992) discussed a high magnesium water where $Mg^{2+} > Ca^{2+}$ from a pool in Carlsbad Caverns, NM, where calcite is precipitating from a dolomite-derived water. In this case the saturation index for dolomite was +1.58, indication of major oversaturation of the water with respect to dolomite. The precipitation of calcite being deposited today from surface waters such as the Dead Sea and Great Salt Lake is reported by Blatt et al. (1980). Again this results in high magnesium waters. Eugster and Hardie (1978) report that in lakes with Mg as a major component the major anion is Cl (Dead Sea) or Cl + SO_4^{2-} (Basque Lakes, Hot Lake, Gulf of Karabogaz). The primary difference between surface- and groundwater situations is that in the surface water examples the bicarbonate decreases, because it is an open system, whereas in groundwater the bicarbonate remains constant because it is a closed system. Stiff diagrams of typical groundwater and surface waters with high magnesium that are known to be precipitating calcite are shown below.



A Piper diagram also showing these trends is shown in Figure 4.24.

DEDOLOMITIZATION

In its simplest form, dedolomitization is the replacement of dolomite by calcite according to the reaction:

$$CaMg(CO_3)_2 + Ca^{2+} \rightarrow 2CaCO_3 + Mg^{2+}$$

Petrographically, it is recognized with the replacement of rhombohedral dolomite crystals by an equigranular mosaic of anhedral calcite (Evamy, 1967).

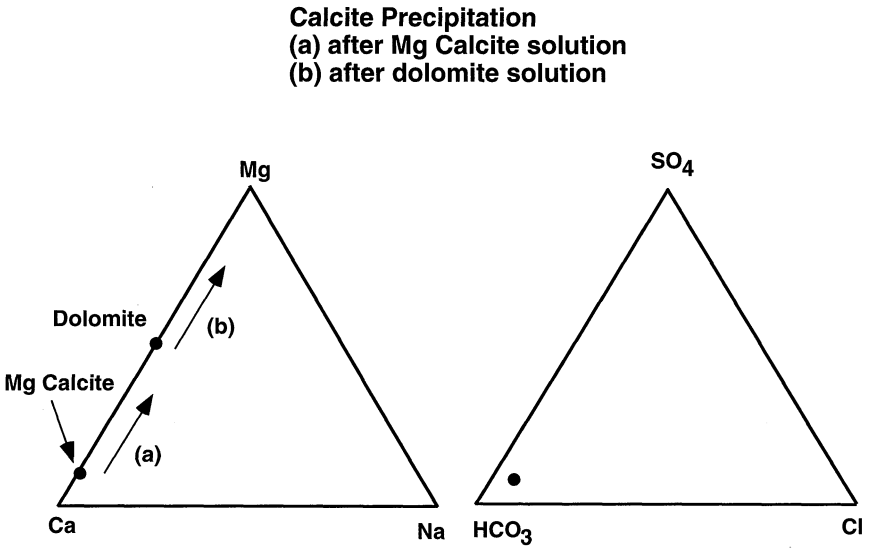


Figure 4.24. Calcite precipitation.

Back et al. (1983) consider dedolomitization as a result of four concurrent processes,

a. Dissolution of calcite,
b. Dissolution of dolomite,
c. Dissolution of gypsum, and
d. Precipitation of calcite.

They state that "The continual addition of calcium from gypsum thus leads to the precipitation of calcite owing to the common-ion effect. The precipitation of calcite decreases the pH and removes carbonate from solution, thereby causing further dissolution of dolomite."

The reaction is initiated by a Ca^{2+}/Mg^{2+} ratio >1, a low pCO_2, and temperatures less than 50°C. At high pCO_2, such as one atmosphere CO_2, dolomite dissolves without calcite precipitation. At pCO_2 pressures similar to that in the atmosphere (0.3E−3 atm), dedolomitization may occur. The high Ca^{2+}/Mg^{2+} ratio is usually accomplished by the introduction of dissolved gypsum or anhydrite into the system. However, the introduction of calcium sulfate into a system with high pCO_2 will not induce dedolomitization.

Mass-balance calculations of dedolomitization will show dolomite and gypsum dissolving and calcite precipitating. The Mg^{2+}/Ca^{2+} ratio will increase towards 1 and the sulfate content of the water will steadily increase. Saturation indices will show saturation with respect to calcite and slight undersaturation with respect to dolomite. The trend on a Piper diagram is shown in Figure 4.25 (Back et al., 1983), Richter and Kreitler (1986) suggest that dedolomitization is indicated by a molar ratio of $(Ca^{2+} + Mg^{2+})/SO_4$ approaching one.

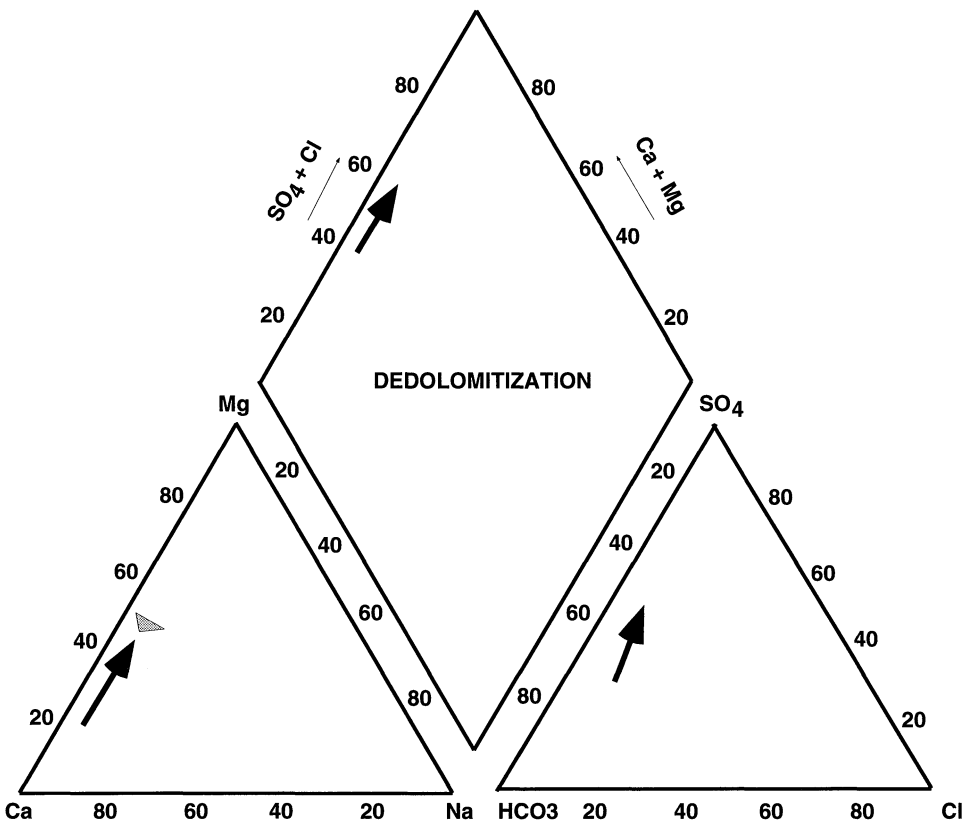


Figure 4.25. Dedolomitization.

MEMBRANE FILTRATION

Membrane filtration is also known as reverse osmosis, or hyperfiltration. Osmosis is a process whereby water molecules will tend to flow spontaneously from less saline to more saline sands through a semipermeable (usually shale) membrane. If the difference in hydraulic head across the shale membrane is sufficient, then water molecules can be forced to flow in the opposite direction—from sands of high salinity to sands of low salinity. The result is high salinity sands of even higher concentration. This is known as reverse osmosis.

White (1965) suggested that the observed increase in Ca/Na ratio of brines with depth in sedimentary basins could reflect membrane filtration. This would imply that monovalent sodium ions pass through shale membranes more readily than divalent calcium ions.

HYDROTHERMAL WATERS

The influence of temperature on ionic ratios of commonly determined constituents will be the only aspect of hydrothermal reactions discussed in this text. Much of this information occurs in discussions of geothermometry, such as Henley et al. (1984) and Kharaka and Mariner (1987). Water equilibrium programs, such as SOLMNEQ-86, incorporate many of these equations. Some of the equations are also calculated by WATEVAL and are listed in tabular form for easy comparison.

Silica content of hydrothermal waters is much higher than that in waters where silica is derived from low-temperature silicate dissolution, thus leading to the silica geothermometer. Lithium is also characteristically high in hydrothermal waters, whereas magnesium tends to be low. This has led to the use of a Li/Mg geothermometer. Frequently, lithium is greater than magnesium and may approach potassium in concentration. Typically, the molar Na/Li ratio lies in the range of about 10–100. Another common ratio used in geothermometry is Na/K, which assumes waters are in equilibrium with sodium and potassium feldspars.

Ellis and Mahon (1977) state that B, F, As, NH_3, and H_2S are usually present at much higher concentrations in hydrothermal waters than in low-temperature waters. Boron is particularly high if the hot waters pass through organic-rich sediments. Fluoride in geothermal waters is commonly in the range of 1–10 mg/l, cesium may be as high as 14 mg/l, and rubidium as high as 135 mg/l.

The solubilities of some minerals also increase with increasing temperature. Most of the work on the increase of solubilities of specific minerals with temperature has been done with the quartz minerals—quartz, cristobalite, and chalcedony. This has led to the development of the silica geothermometer. Table 4.8 lists the amount of quartz dissolved at different temperatures. Note that the dissolved silica observed in most low-temperature waters is a chemical weathering product of silicate minerals such as feldspars, and is not due to the dissolution of quartz per se. The silica geothermometer is only recommended for estimating temperatures above 150°C. Below 190°C the chalcedony equation is recommended and above 190°C the quartz equation is used.

Table 4.8. Solubility of Quartz at Various Temperatures

°C	ppm SiO_2	°C	ppm SiO_2
0	2	150	126
25	7	200	271
50	13	250	471
75	26	300	660
100	46		

After Truesdell, 1984.

In addition to the water constituents whose concentrations increase with temperature, the ratios of several cations in waters also increase with increasing temperature. The most common among the latter are the Li/Na, K/Na, Li/Mg, Cs/Na, and Rb/Na.

The ions Na, K, Ca, and H^+ determine the reactions between water and feldspars, micas, and clay minerals. The Na/K alkali geothermometer depends on the reaction:

$$NaAlSi_3O_8 + K^+ \} KAlSi_3O_8 + Na^+$$

whose equilibrium constant is

$$K_{eq} = \frac{[Na^+]}{[K^+]}$$

which is a function of temperature. The alkali geothermometer (Kharaka and Mariner, 1987) is recommended only for temperatures above 180°C. Using mg/l concentrations:

$$t°C = \frac{1180}{\log \frac{Na^+}{K^+} + 1.31} - 273$$

Calculated Na^+/K^+ ratios using the above equation are listed in Table 4.9.

This relationship gives a correlation coefficient of 0.4 for oil-field waters and 0.87 for all waters; thus it is of little use for oil-field waters.

The Mg-Li geothermometer (Kharaka and Mariner, 1987) is another geothermometer that depends on ratios. Mg concentration is usually much lower in groundwaters than in seawater, and decreases with increasing temperature. Li, on the other hand, increases with increasing temperature. Mg-Li substitutions occur in amphiboles, pyroxenes, micas, and clay minerals.

$$Li^+ + 0.5\ Mg\ (solid) \} 0.5\ Mg^{2+} + Li\ (solid)$$

$$\text{Thus } K_{eq} \text{ approx.} = \frac{\sqrt{[Mg^{2+}]}}{[Li^+]}$$

$$t°C = \frac{2200}{\log \frac{\sqrt{Mg^{2+}}}{Li^+} + 5.47} - 273$$

This relationship has a correlation coefficient of 0.9 for oil-field waters and 0.96 for all waters.

Similarly, the Na/Li ratio has a correlation coefficient of 0.8 for oil-field waters and 0.91 for all other waters. Thus the use of the Na-Li geothermometer is marginal for oil-field waters.

Table 4.9. Calculated Na/K Ratios at Various Temperatures

°C	$\log \frac{Na^+}{K^+}$	$\frac{Na^+}{K^+}$
100	1.85	71
200	1.18	15
300	0.75	6

MIXING

A common situation in many groundwater studies is a groundwater composition that may be the result of the mixing of two (or more) waters, such as groundwater and surface water, or waters from an upper and lower aquifer, or recharge water and deep groundwater. The approach to determining mixing ratios depends on the complexity of the mixing. If two waters are involved without the addition or removal of other phases, such as gases or minerals, then the procedure is relatively simple. If three waters are involved, the mathematics becomes slightly more difficult. If other phases are also involved, mass-balance programs must be used. These are described later in this chapter.

Two-Component Mixtures

On a Piper diagram two-component mixing may be readily apparent. If two waters mix, then the composition of the mixture will lie on a straight line joining the two end members. The relative amount of each end member in the mixture is inversely proportional to the distance of the mixture from that end member. If a water is the result of mixing without the addition or removal of any phase, then the mixture will exhibit exactly the same proportions between the end members on both cation and anion triangles as well as on the diamond. The TDS of the mixture must lie between the TDS values of the two end members. However, the converse is not necessarily true. If three waters lie on a straight line as described above they may not necessarily be the result of mixing. The final consideration is whether or not mixing is hydrologically possible. A further caution must be noted: if waters are dilute, then experimental errors may result in plots where waters do not lie on a straight line, although they are the result of mixing.

Quantitative Estimate of Mixing Proportions

Although a semiquantitative estimate of mixing proportions may be made from the Piper diagram, a quantitative estimate, assuming no solid or gas phases are lost or gained, may be calculated by using the following technique. The TDS values of three analyses thought to be two end members and a mixture are substituted in the equation below. The calculated fraction of each end member is then used to calculate an analysis of a hypothetical mixture of the two end members. The calculated amount of each ion is then compared with the amount of each ion in the proposed mixture. The agreement may be expressed as a correlation coefficient.

A simple mixing fraction can be calculated with any three input concentration values by using the following:

$$\text{loading} = \text{concentration} * \text{discharge} = C * Q$$

$$Cm * Qm = C_1 * Q_1 + C_2 * Q_2$$

where m = mixture, 1 = more concentrated solution, and 2 = the more dilute solution.

It is more convenient to use percentage volumes and calculate the fractions of the more dilute and more concentrated waters, which would have to mix to produce the water being examined.

$$\begin{aligned} 100 * C_m &= \%\ Q_1 * C_1 + (100 - \%\ Q_1) * C_1 \\ 100 * C_m &= \%\ Q_1 * C_1 + 100 * C_2 - \%\ Q_1 * C_2 \\ &= \%\ Q_1 * (C_1 - C_2) + 100 * C_2 \end{aligned}$$

$$\% Q_1 * (C_1 - C_2) = 100 * (C_m - C_2)$$
$$\% Q_1 = * (C_m - C_2)/(C_1 - C_2)$$

Any concentration or ratio values m: ; used in this calculation, but if the TDS values are used, the equation is the least squar(lution to the mixing problem and results in the most statistically valid solution.

Example:

Estimate the percent of a brine wast ering a stream given the following data. If the upstream river water TDS were 240 mg/l and the downstream river water TDS were 740 mg/l, then the percentage of brine waste with a TDS of 25,000 mg/l entering the river would be calculated as follows:

$$\% \text{ Brine} = \frac{(740 - 240)}{(25{,}000 - 240)} * 100 = 2.02\%$$

CORRELATION

The relationship between two variables is called correlation, and it measures the degree to which two variables vary together (or vary inversely). It is measured by an index called the correlation coefficient, r. If

r is +1 then there is perfect positive correlation,
r is −1 then there is perfect negative correlation,
r is 0 means that there is no correlation.

r is the square root of the explained variation over the total variation. The significance of the correlation is given by another index r^2, which measures the amount that the two measures have in common.

Example:

Measuring and comparing x and y resulted in an r = 0.7 and an r^2 of 0.49. This means that 49% of y is due to variations of x, and 51% of y is not related to x.

Calculation of R:

$$r = \frac{\Sigma (xy) - \frac{\Sigma x * \Sigma y}{N}}{\sqrt{\left(\Sigma x^2 - \frac{(\Sigma x)^2}{N}\right) * \left(\Sigma y^2 - \frac{(\Sigma y)^2}{N}\right)}}$$

The significance of r is determined using the t-distribution. A special formula is used to calculate t from the number of observations n and the correlation coefficient r. This formula is

$$t = \frac{r * \sqrt{n - 1}}{\sqrt{1 - r^2}}$$

If n = 7 and r = 0.95, then t = 6.8.

Three-Component Mixtures

Three-component mixtures can also be interpreted using Piper diagrams. The procedure used is discussed in detail in Piper (1944). More recent approaches have involved the use

of mixing curves, e.g., Mast, 1985. Mixing curves are used to calculate the composition of a mixture in terms of three unknown percentages of three end-member waters. Once two percentages are known, the third may be calculated by difference because they all must total 100%. There are two unknowns and therefore two parameters must be used to calculate them. Mast used three such pairs—chloride and sulfate, TDS and sulfate, and magnesium and sulfate. Whittemore (1984, 1988) made extensive use of Br/Cl and chloride. Either analytical values or ratios may be used to solve the equations. They are chosen so that the greatest discrimination is achieved. The two parameters chosen are then used to define the axes of the plot. The end members are then plotted using a log-log scale. On such a diagram mixtures plot as curves between the end members, hence, the common name ionic mixing curves.

The three equations involved are

$$\%Q_1 * C_{a1} + \%Q_2 * C_{a2} + \%Q_3 * C_{a3} = 100 * C_{am}$$

$$\%Q_1 * C_{b1} + \%Q_2 * C_{b2} + \%Q_3 * C_{b3} = 100 * C_{bm}$$

$$\%Q_1 + \%Q_2 + \%Q_3 = 100$$

where $\%Q_1$, $\%Q_2$, and $\%Q_3$ are the percentages of the three waters making up the mixture. C_{a1}, C_{a2}, C_{a3}, and C_{am} are concentrations, or ratios of concentrations, of component a. C_{b1}, C_{b2}, C_{b3}, and C_{bm} are concentrations, or ratios of concentrations, of component b. The numbers 1, 2, and 3 refer to the three end-member waters, and m refers to the mixture. An example of a three-component mixture is listed in Table 4.10 and a mixing curve diagram in Figure 4.26.

INTERPRETATION OF GROUNDWATER REACTIONS USING PIPER DIAGRAMS

If only groundwater reactions are considered, then it is often possible to come to a tentative conclusion as to the reactions taking place in the groundwater (if analyses have been taken in a downgradient direction). Usually, this implies an increase in TDS, or at least no decrease in TDS, in that direction. The interpretations discussed below also assume that only one of the reactions is taking place, and that complex mixing and multiple reactions are not occurring. The trends discussed below may be used as an aid for a preliminary interpretation.

Mixing of two end members is always a possibility, but it must again be emphasized that,

a. The placement of the end members and the mixture must always lie on a straight line; the proportionality must be preserved in the three areas of the Piper diagram; and
b. Mixing must be hydrologically possible.

Reactions may sometimes be ascertained by observing the linear trends in both cation and anion triangles. Some of the simpler trends are tabulated in Table 4.11 and Figures 4.27

Table 4.10. Three-Component Mixing

Component or ratio	End member 1	End member 2	End member 3	Mixture
Chloride	8000	3000	50	2525
$\frac{Cl}{Br} * 10^4$	200	10	5	45.5
Percent	20%	30%	50%	

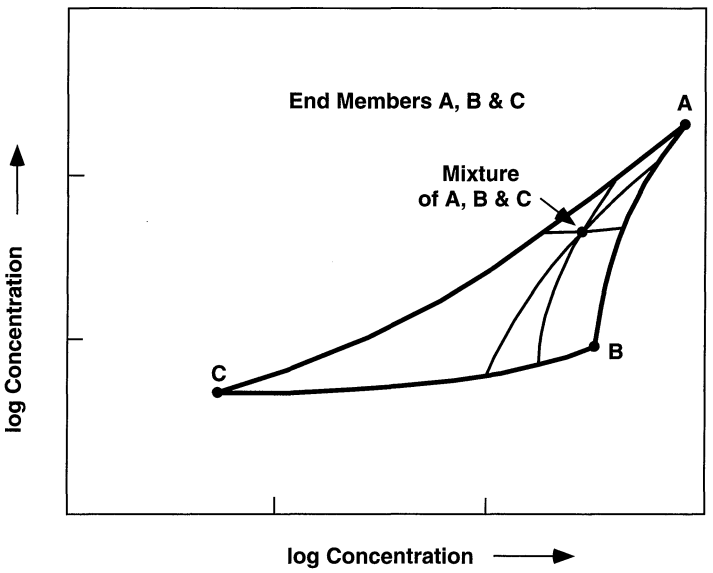


Figure 4.26. Three component mixture plot. The letters A, B, and C represent the compositions of three end-member samples. Each of the three outer curves joining these points represents the compositions of three two-end member mixtures. The point in the interior of this "triangle" represents the composition of a mixture of end-members A, B, and C. The inner curves represent the lines along which each of the three end-member percentages must lie.

Table 4.11. Nonmixing Trends on Piper Diagrams

First triangle	Second triangle	Interpretation
→ Ca apex	→ HCO_3 apex	Calcite solution
	→ SO_4 apex	Gypsum solution
	→ 1:1 HCO_3:SO_4	Pyrite oxidation and calcite solution or calcite and gypsum solution
	→ Cl apex	Reverse softening (brine contamination)
→ Na apex	→ HCO_3 apex	Albite solution or calcite solution and ion exchange
	→ SO_4 apex	Gypsum solution and ion exchange
	→ Cl apex	Halite solution no change ion exchange
→ Mg apex	→ HCO_3 apex	Ferromagnesian silicate solution (Mg often > Ca)
→ HCO_3 apex	→ Ca apex	Calcite solution
	→ Na apex	Albite solution or calcite solution and ion exchange
	→ Mg apex	Ferromagnesian silicate solution (Mg often > Ca)
	→ Ca-Mg side	Calcite-dolomite solution
→ SO_4 apex	→ Ca apex	Gypsum solution
	→ Na apex	Gypsum solution and ion exchange
	→ 1:1 Ca:Mg	Dedolomitization parallels Ca-Mg side & (Ca > Mg)
→ Cl apex	→ Ca apex	Reverse softening (brine contamination)
	→ Na apex	Halite solution

Note: These are assumed to be downgradient trends in groundwater systems, with increasing TDS in that direction.

* → means approaches.

to 4.32. The possible reactions are listed as trends towards an apex of one or the other triangle, with the various possibilities given for the other triangle.

MASS-BALANCE MODELING

Mass-balance calculations are a means whereby many of the reactions that are thought to be occurring may be quantified. This is not a verification that they are occurring, but

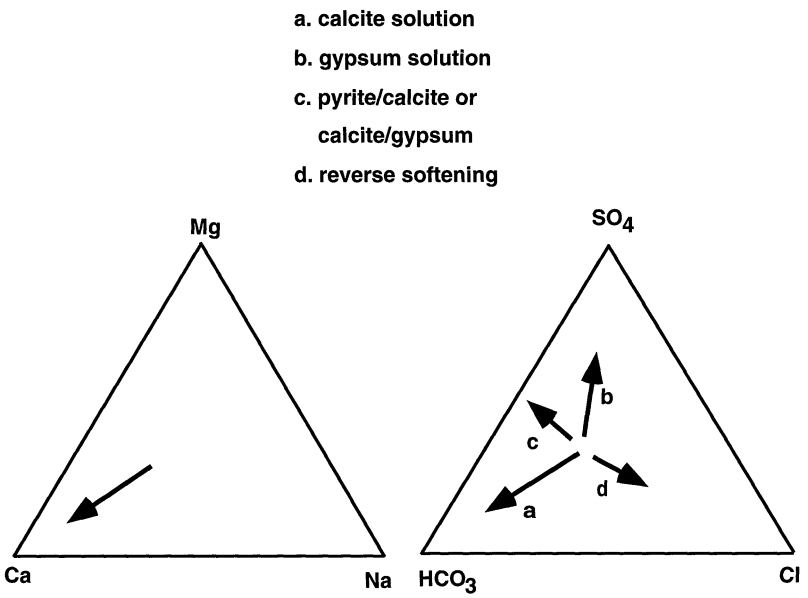


Figure 4.27. Groundwater reactions with Ca increase.

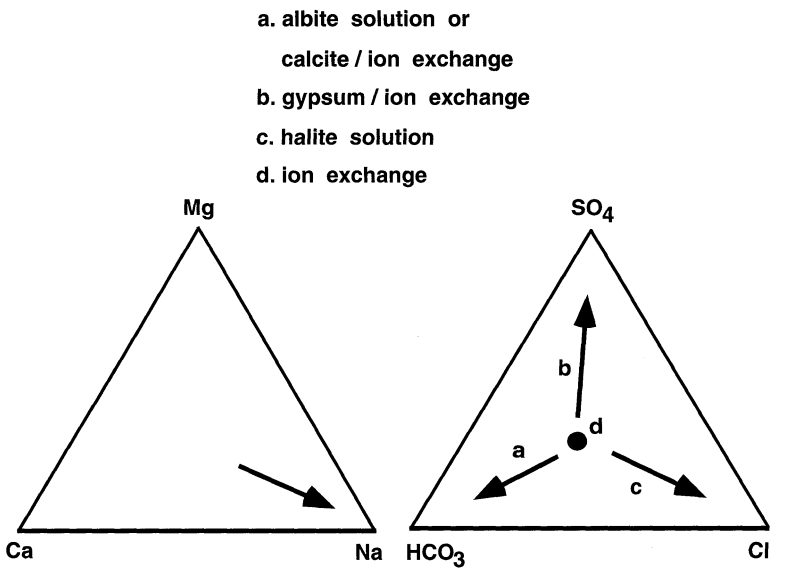


Figure 4.28. Groundwater reactions with Na increase.

rather a quantification of the reaction that is proposed. A detailed discussion of the technique and a computer program BALANCE, designed to do these calculations, is given in Parkhurst et al. (1982). NETPATH is an updated and much more comprehensive program also from the U.S. Geological Survey, written by Plummer et al. (1991).

A mass balance is simply the sum of what was originally present, plus whatever entered the system, minus whatever left the system. For example, the number of people in a room at any instant in time equals the number present in the room initially, plus those that entered, minus those that left.

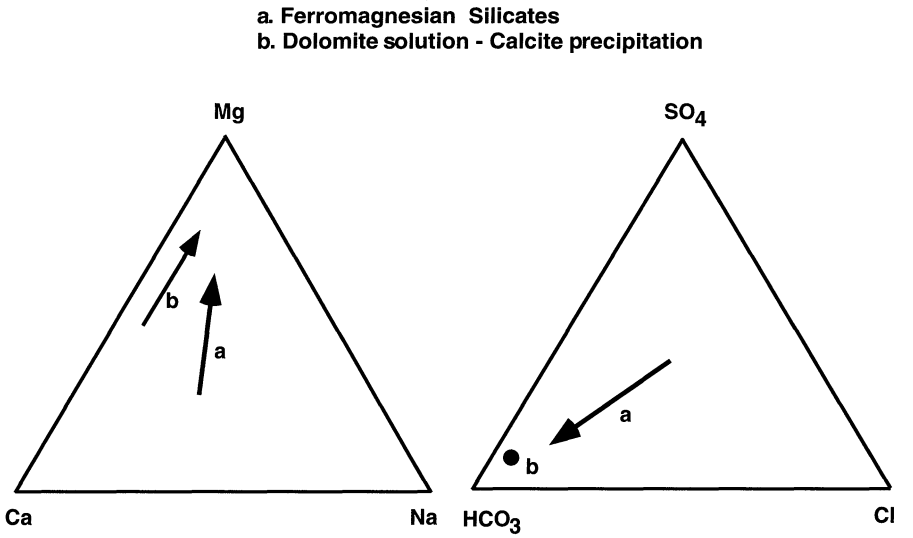


Figure 4.29. Groundwater reactions with Mg increase.

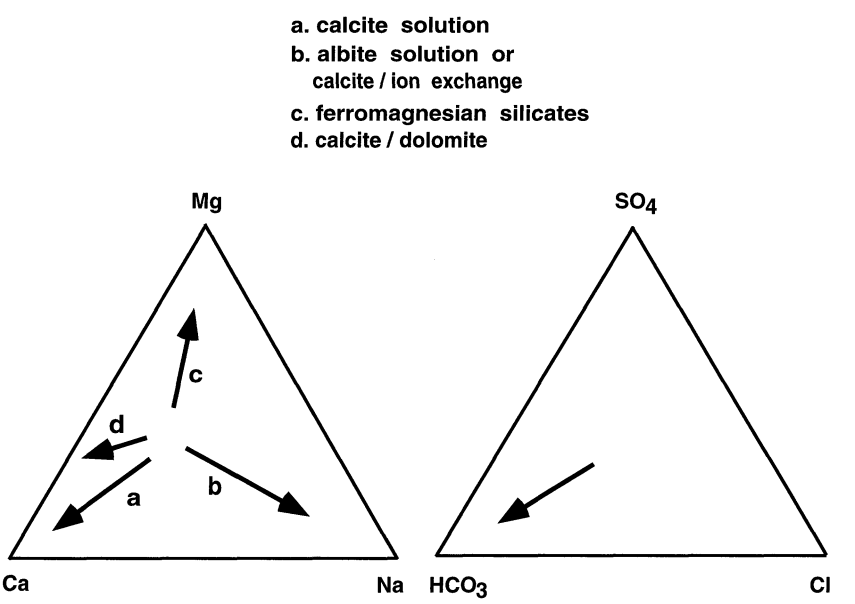


Figure 4.30. Groundwater reactions with HCO_3 increase.

Three major processes are considered:

1. Mineral dissolution or precipitation;
   positive results indicate dissolution.
   negative results indicate precipitation or loss.
2. Variable fluxes of CO_2, O_2, or other gases.
3. The mixing of two end-member waters.

These processes are shown diagrammatically in Figure 4.33.

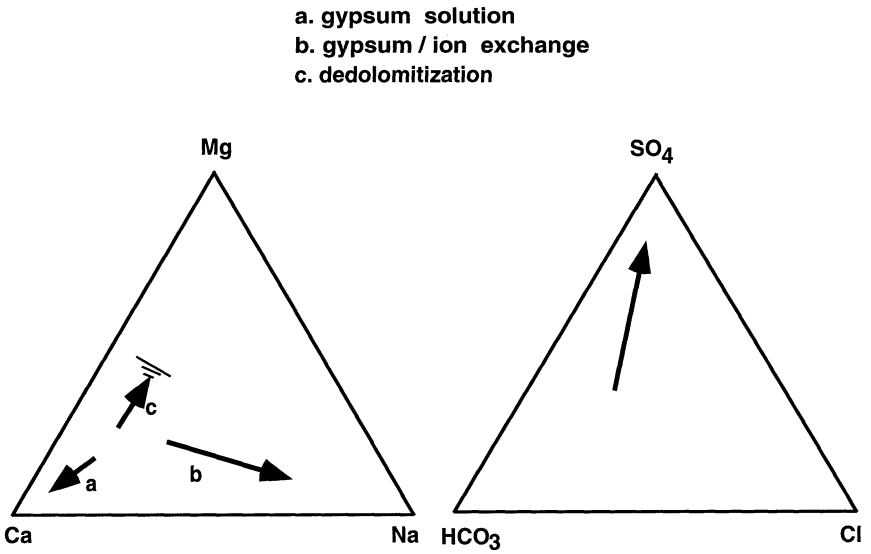


Figure 4.31. Groundwater reactions with SO_4 increase.

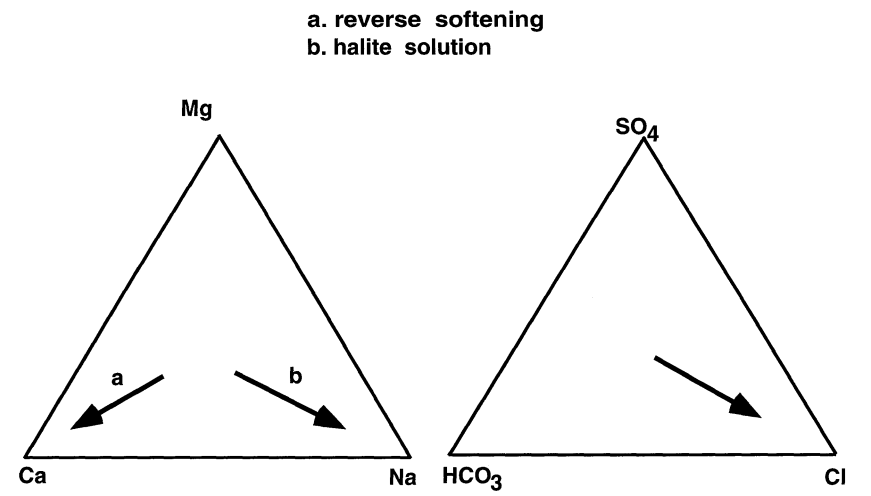


Figure 4.32. Groundwater reactions with Cl increase.

Compositional changes — A common application of water chemistry is the determination of change in chemical composition of water samples between two points along a flow path. The objective is to calculate the amount of solid phases (minerals) entering (dissolving) or leaving (precipitating) the aqueous phase. The minerals to be considered, as well as their chemical compositions, must be specified on the basis of geology, hydrology, and mineralogy of the system. Gases, ion exchangers, and other solutions may be considered in addition to minerals. In order to solve the equations, the number of phases must equal the number of elements. The objective in selecting phases is to provide a source, or sink, for each element in the initial and final solution. Although the calculated mass transfer for one or more phases might be zero, indicating that the phase(s) did not participate in the reaction, the phase(s) must still be included in order to perform the calculations.

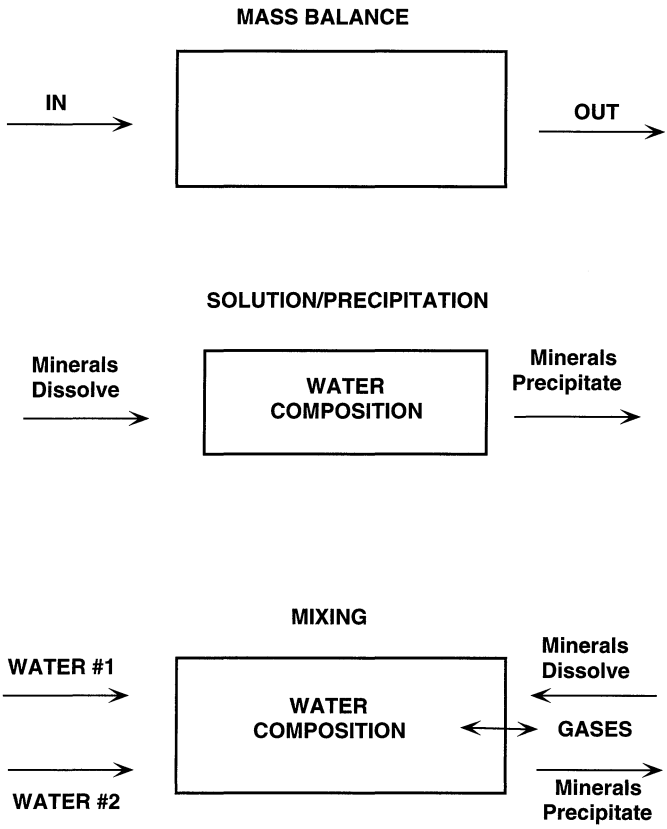


Figure 4.33. Mass-balance diagrams.

The inclusion of minerals whose composition can be derived by linear combinations of other minerals in the set will produce an unsolvable matrix. Thus, if calcite, magnesite, and dolomite are all included, the matrix cannot be solved because

$$CaCO_3 + MgCO_3 \rightarrow CaMg(CO_3)_2$$

The mass-balance approach can never prove that a reaction has taken place; however, it may indicate that a certain reaction could not happen as stated.

In general terms:

Consider elements x, y, and z with concentrations in water of (x), (y), and (z).

Also consider three solid phases A, B, and C such that A = xz, B = xyz_2, and C = z.

The coefficients giving the number of atoms of each element in each phase are

	Phases		
Water composition	A xz	B xyz_2	C z
(x)	1	1	0
(y)	0	1	0
(z)	1	2	1

The mass balance for each element is then:

(x) = 1*A + 1*B + 0*C
(y) = 0*A + 1*B + 0*C
(z) = 1*A + 2*B + 1*C

or

(x) = A + B
(y) = B
(z) = A + 2B + C

Solving for the amounts of A, B, and C:

B = y
A = (x) - B
C = (z) - A - 2B

Mixing — In addition to the determination of possible compositional changes along a flow path, the BALANCE program may be used to determine the composition of a water resulting from the mixing of two waters with or without the precipitation or solution of any other phases. In the simplest case, it may be used to calculate the composition that could result from evaporation and precipitation, although care must be taken to avoid the production of a singular matrix. If NETPATH is used, most of these problems are handled by the program. In addition, it determines only those reactions that result in a given composition.

EXAMPLES

1. What compounds would dissolve to give a water of the following composition?

Na = 0.8; K = 0.3; Cl = 1.5 mmol/l

Consider the phases NaCl, KCl, and HCl:

Na 0.8 + 0.8 Cl = 0.8 NaCl
K 0.3 + 0.3 Cl = 0.3 KCl
Cl 1.5 − 1.1 Cl = 0.4 HCl

Using matrix approach

	mmol/l	NaCl	KCl	HCl
Na	0.8	1	0	0
K	0.3	0	1	0
Cl	1.5	1	1	1

Na = 1 * NaCl + 0 * KCl + 0 * HCl = 0.8 or NaCl = 0.8

K = 0 * NaCl + 1 * KCl + 0 * HCl = 0.3 or KCl = 0.3

Cl = 1 * NaCl + 1 * KCl + 1 * HCl = 1.5

$$= 1 * 0.8 + 1 * 0.3 + 1 * HCl \quad = 1.5$$

$$\text{or } HCl = 1.5 - 0.8 - 0.3 \quad = 0.4$$

2. What minerals could dissolve to give the following water analysis and in what amounts?

	Ca	Mg	SO_4	HCO_3
mg/l	32	5	48	61
meq/l	1.6	0.4	1.0	1.0
mmol/l	0.8	0.2	0.5	1.0

Consider the minerals calcite, dolomite, and gypsum and CO_2 gas, that is, four phases and four elements. Once the analysis is converted to mol/l or mmol/l the next step is to determine the coefficients for each phase. That is, the number of each element present in each phase. Thus, calcite has 1 Ca and 1 C; dolomite has 1 Ca, 1 Mg, and 2 C; gypsum 1 Ca and 1 S; CO_2 gas 1 C. Note that we are dealing with moles and that 1 mol CO_3^{2-} equals 1 mol C.

Water composition		Phases number of elements in each phase			
	(mmol/l)	Calcite	Dolomite	Gypsum	CO_2 gas
Ca	0.8	1	1	1	—
Mg	0.2	—	1	—	—
S	0.5	—	—	1	—
C	1.0	1	2	—	1

Sulfur balance

$S = 0.5 = 1 * \text{Gypsum}$ $\qquad$ Gypsum = 0.5

Magnesium balance

$Mg = 0.2 = 1 * \text{Dolomite}$ $\qquad$ Dolomite = 0.2

Calcium balance

$Ca = 0.8 = 1 * \text{Calcite} + 1 * \text{Dolomite} + * \text{Gypsum}$ $\qquad$ Calcite = 0.8 − 0.2 − 0.5 = 0.1

Carbon balance

$C = 1.0 = 1 * \text{Calcite} + 2 * \text{Dolomite} + 1 * CO_2 \text{ gas}$ $\qquad$ CO_2 gas = 1.0 − 0.1 − 2 * 0.2 = 0.5

Thus the above water could be obtained by dissolving

0.5 mmol/l gypsum
0.1 mmol/l calcite
0.2 mmol/l dolomite
0.5 mmol/l CO_2 gas

3. What proportions of the two end-member waters are necessary and what minerals would dissolve or precipitate to give the following water composition? (Analyses are given in mmol/l.)

In this example two end-member waters mix in unknown proportions and, in addition, phases dissolve and precipitate to produce a final water. The two initial waters are treated exactly like other phases, and W_1 is the fraction of solution 1 and W_2 is the fraction of solution 2, which combine, along with mineral reactions, to produce the final solution.

An additional equation is automatically included to ensure that the two fractions are equal to 1, that is, $W_1 + W_2 = 1$.

As a result, the number of phases that can be included in the calculations (other than the solutions) is the number of elements minus 1.

	Final	Initial water 1 W_1	Initial water 2 W_2	Calcite C	Dolomite D
Ca	7	8	9	1	1
Mg	9	6	10	0	1
C	32	28	38	1	2
Mix	1	1	1	0	0

Mass balance for Ca $7 = 8W_1 + 9W_2 + C + D$ (1)

Mass balance for Mg $9 = 6W_1 + 10W_2 + D$ (2)

Mass balance for C $32 = 28W_1 + 38W_2 + C + 2D$ (3)

Mass balance for end members $1 = W_1 + W_2$ (4)

Thus from (4) $W_2 = 1 - W_1$ (5)

substitute in (2) $9 = 6W_1 + 10 - 10W_1 + D$

or $D = 4W_1 - 1$ (6)

Substitute (5) and (6) in (1) and (3)

$$(1)\quad 7 = 8W_1 + 9 - 9W_1 + 4W_1 - 1 + C$$

$$-1 = 3W_1 + C \qquad (7)$$

$$(3)\ 32 = 28W_1 + 38 - 38W_1 + 8W_1 - 2 + C$$

$$-4 = -2W_1 + C \qquad (8)$$

Subtracting (8) − (7)

$$3 = 5W_1 \quad \text{or} \quad W_1 = 0.6 \quad \text{and} \quad W_2 = 0.4$$

$$D = 1.4 \quad \text{and} \quad C = -2.8$$

Therefore, the final water could result from mixing 60% of water 1 and 40% of water 2, dissolving 1.4 mmol/l dolomite and precipitating 2.8 mmol/l calcite.

BRINE CONTAMINATION

Brines are one of the most common sources of drinking-water contamination. The brine may be the result of saltwater intrusion, oil-field brine contamination, or contamination by deicing salts. The major problem in deciding the source of contamination in many instances is the fact that absolute concentrations cannot be used because of dilution. Ratios are essential to interpret the data. In some oil-field brine contamination problems it may be necessary to decide which of several formation waters has caused the contamination. Each of the common

sources of brine contamination will be discussed individually followed by some methods whereby they may be differentiated.

RAINWATER

Rainwater is the main source of aquifer recharge. The composition of rainwater depends on the various proportions of sea-salt aerosols, terrestrial emissions (such as soil dust), anthropogenic sources (such as industrial emissions and burning vegetation), and gaseous reactions involving CO_2, SO_2, and NO_2 (Berner and Berner, 1987). Chloride is usually assumed to come primarily from sea salt; near the ocean, rain is primarily a sodium chloride solution, whereas further inland it changes to a calcium sulfate or calcium bicarbonate solution because of soil dust and gaseous reactions (Berner and Berner, 1987).

SEAWATER

The composition of seawater from Hem (1992) is given in Table 4.12. It is characterized by a molar Na/Cl ratio of 0.85 and a Mg/Ca ratio of 5.43 with a Cl/SO_4 ratio of 19.06.

EVAPORITES

Evaporites typically contain halite, gypsum, and calcite. The solution of halite results in a Br/TDS ratio less than that of seawater. Other elements in these waters may also be lower than in seawater. Such waters often contain half as much Ca, K, and Sr, and less than half as much Li, Mn, and B as does seawater. Mg, however, is only slightly lower.

It was found that ratios of Mg/Br and Mg/K remain constant until a magnesium salt begins to precipitate and that the ratio of K/Br remains constant until potash salts begin to precipitate. This relationship may be expressed as Br = 0.1634 * K. Thus water with 9240 mg/l K should contain 1510 mg/l Br. It must be remembered that the precipitation of an ion phase has a drastic effect on the ion ratios involving that element. Examination of the behavior of bromide during the evaporation of seawater reveals that calcite and gypsum contain very little bromide, and that the initial halite precipitated contains about 68 ppm Br. Further, brine saturated with halite contains about 510 ppm Br, whereas halite precipitating when sylvite is also precipitating contains 260 ppm Br. Various bromide ratios are listed in Table 4.13.

Table 4.12. Composition of Seawater

	mg/l
Cl	19,000
Na	10,500
SO_4	2,700
Mg	1,350
Ca	410
K	390
HCO_3	142
Br	67
Sr	8
SiO_2	6.4
B	4.5
F	1.3
N	0.67
Li	0.17

From Hem, 1992.

Table 4.13. Bromide Ratios During Seawater Evaporation

The distribution factor for halite is

$$\frac{\text{Br(crystals)}}{\text{Br(solution)}} = 0.073 - 0.16$$

Bromide in later crystallizing phases compared to that in halite:

Br(halite) (NaCl)	Br(sylvite) (KCl)	Br(carnallite) ($KMgCl_3 \cdot 6H_2O$)	Br(bischofite) ($MgCl_2 \cdot 6H_2O$)
1	5	9	13

$\frac{Br}{Cl}$ ratios in solids and solutions: $10^3 * \frac{Br}{Cl}$

	Ratio in solution		Ratio in solid
Ocean	3.4		
Onset of halite	4.7–5.5	Halite	0.014
Onset of sylvite	17.5–21.0	Sylvite	0.17
Onset of carnallite	20.1–23.8	Carnallite	0.32

Compiled from Sonnenfeld, 1984.

BITTERNS

Bitterns are the residual seawater remaining after halite has precipitated out, and are typically rich in magnesium. Rittenhouse (1967) suggests that Br/TDS greater than twice that of seawater are probably bitterns from rocks surrounding evaporites. The formation of evaporites has been studied by the experimental evaporation of seawater. Zherebtsova and Volkova (1966) from Carpenter (1978) showed that during the evaporation of seawater essentially all of the K, Rb, Li, and Br remain in solution until potash salts begin to precipitate, and that most of the Li and Br remain in solution during potash salt deposition.

OIL-FIELD BRINES

Much of the early work pertaining to the classification of oil-field brines was directed toward a method for identifying waters that would likely lead to the discovery of hydrocarbon deposits. That is, it was used as a prospecting tool. Toward that end, both ratios and absolute quantities were used. For example, Bojarski (1970) found that waters commonly associated with hydrocarbons in Poland had iodide >1 mg/l, bromide >300 mg/l, Cl/Br <350, Cl >100 * SO_4, and Na/Cl <1 (mole ratio), especially if H_2S present.

Sulfate — Sulfate waters near the surface are derived either from the solution of gypsum or anhydrite, or from the oxidation of pyrite in rocks. Low sulfate and high bicarbonate at depth is usually presumed to be the result of sulfate reduction in the organic-rich environment of oil-field waters. The lack of H_2S in some cases may be attributed to precipitation as pyrite. A low amount of carbonate species may be attributed to precipitation as carbonates. The net reaction involving sulfate reduction is

$$Ca^{2+} + SO_4^{2-} + 1.33\ CH_2 \Leftrightarrow H_2S + CaCO_3 + 0.33\ H_2O + 0.33\ CO_2$$

Strontium — Strontium in oil-field brines is most likely related to the recrystallization of aragonite to calcite. The orthorhombic structure of aragonite allows significant solid solution of strontium, whereas the trigonal calcite does not.

RATIOS USED TO DISCRIMINATE BETWEEN DIFFERENT SODIUM CHLORIDE WATERS

Some of the more important ratios used to discriminate between different sources of sodium chloride waters are discussed below. In comparing ratios it is important to establish the units being used. Commonly they are mg/l, molar, or epm (equivalents per million).

Sodium-chloride ratios — Schoeller (1955) introduced an index of base exchange (IBE), where IBE = (Cl − Na)/Cl (all in molar units). He postulated that those waters with an IBE equal or greater than 0.129 are usually petroleum reservoir waters. The IBE ratio can be recalculated to a molar Na/Cl ratio. If this is done an IBE ratio of 0.129 is equal to a Na/Cl molar ratio of 0.871 or a mg/l Na/Cl of 0.56. Leonard and Ward (1962), who examined Oklahoma, Kansas, and Texas waters, postulated a Na/Cl ratio (mg/l) of about 0.5 as indicative of oil-field waters. Bojarski (1970) suggested that the molar Na/Cl ratio was usually <1, especially if H_2S was present. Collins (1972) looked at 4000 brine analyses and found that many waters had molar Na/Cl ratios >0.85. A comparison of the ratios reported by different investigators is given in Table 4.14. One could conclude that most oil-field brines would have a molar Na/Cl ratio of <1.

Sulfate-chloride ratios — The ratio proposed by Bojarski (1970) in epm was SO_4 * 100/Cl < 1 or SO_4/Cl < 0.01. Collins (1972) found that generally the epm SO_4/Cl ratio ranged from 0–0.34, although usually it was <0.17. Hem (1992) suggests that sulfate in ionic proportions similar to seawater may indicate saltwater intrusion. The value of SO_4/Cl in seawater is 0.105 (meq/l).

Bromide-chloride ratios — The main ratio used to study bromide is the Br/Cl ratio. Seawater up to precipitation of halite has the same value as that of seawater. After halite starts to precipitate the ratio increases. The dissolution of halite would produce brines which are rich in chloride, but relatively low in bromide. Halite only contains 68 ppm Br in its crystal structure. Rittenhouse (1967) used bromide and TDS to differentiate several different water types. The Br/TDS ratio is approximately proportional to the Br/Cl ratio. This ratio remains the same if dilution and/or concentration of seawater occurs. Some waters were found to have a Br/TDS ratio about twice that in seawater. Their origin is not well understood, but it is thought to be the result of diagenesis or dissolution of organic matter containing higher Br (Rittenhouse, 1967). Some bromide-chloride ratios of seawater and the minerals crystallizing from it are listed in Table 4.13.

Calcium-magnesium ratios — Hem (1992) suggests that a low Ca/Mg ratio may indicate saltwater intrusion.

Table 4.14. Sodium/Chloride Ratios of Oil-Field Brines

Author	$\frac{Na}{Cl}$ mmol/l	$\frac{Na}{Cl}$ mg/l
	Sodium/Chloride Ratios	
Schoeller (1955)	<0.85	<0.55
Leonard and Ward (1962)	About 0.77	About 0.50
Bojarski (1970)	<1 (with H_2S)	<0.64
Collins (1972)	Many >0.85	Many >0.55

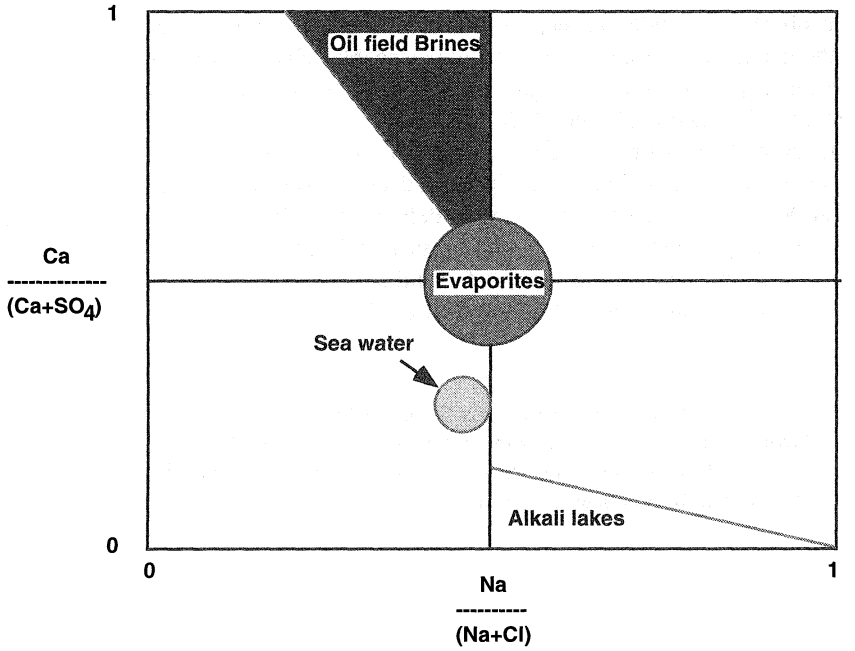


Figure 4.34. Brine differentiation plot.

Brine differentiation plots — Because bromide is seldom reported in a water analysis, a plot was devised by the author to differentiate brine-contaminated waters from waters of other origins using the major constituents of a water that are usually available. The plot uses molar Ca/Ca + SO_4 on the vertical axis and molar Na/(Na + Cl) on the horizontal axis (Figure 4.34). This method also allows waters to be plotted in a finite range, that is, from 0 to 1 on both axes. Mixing curves may also be plotted on this diagram. On this diagram, field characteristics of oil-field brine, evaporite solution, and seawater are separate and distinct.

EXERCISES

1. You are studying a limestone aquifer and have collected a sample that was sent to a commercial lab. The results obtained from the lab are listed below. At the same time that you took the sample you obtained a pH of 6.9 and a total alkalinity of 1400 mg/l bicarbonate using simple field equipment.

Ion	mg/l
Na^+	130
K^+	153
Ca^{2+}	57
Mg^{2+}	375
HCO_3^-	645
CO_3^{2-}	360
SO_4^{2-}	121
Cl^-	156
Hardness ($CaCO_3$)	1171
TDS (180°C)	1529
pH	6.72

Your job, if you decide to accept it, is to list the suspect numbers with all your evidence against them, and to replace them with more reasonable substitutes and appropriate documentation. Should you be caught juggling the figures, without the appropriate evidence the Department will disavow all knowledge of you.

[Note: Analytical errors as such are much less common than those involving arithmetic, transposing of figures or columns, or slipping a decimal point such as recording 67.0 as 6.70.]

To run WATEVAL, remain in the initial default menu. That is, input from keyboard and output to memory. From the main menu press 1 and ENTER. Input the data. If there is a data entry error, proceed with the next value and correct later. When finished press ENTER. Examine the data using options 2 and 3. Edit or change the data using option 5.
HINTS:

a. Start by examining Ca and Mg, then HCO_3^-/CO_3^{2-}.
b. TDS(180) is the residue on evaporation and drying at 180°C.
c. To convert carbonate to bicarbonate work in meq/l and remember that carbonate is divalent and bicarbonate is univalent.

2. Piper exercise (look at cation triangle only). Analyses in meq/l

	A	B	C	D	E	F	G	H	I
Ca	12.2	4.6	4.6	6.3					
Na	1.2	1.0	4.0	1.1					
Mg	0.8	6.4	2.4	5.0					
Cl	14.2	12.0	11.0	12.4					

Enter analyses A, B, C, and D into WATEVAL and save to a file. The four water analyses are given in meq/l. Also enter into the same file analyses E, F, and G below.

E—remove 1/4 of the Ca from A
F—remove 1/2 of the Ca from A
G—remove 3/4 of the Ca from A.

Again, using the same file, add analyses H and I below.

H—combine A and B in the proportions 1:1
I—combine A and B in the proportions 3:1

Plot these analyses on a Piper diagram and discuss the possible origin or analyses C and D. What general conclusions can be drawn from this exercise?

NOTE: When you are reading the file as an input to obtain your Piper diagram you must change the units from meq/l to mg/l.

3. Mixture exercises

a. A waste brine with Cl = 25,000 mg/l is polluting a river with an upstream Cl of 270 mg/l and a downstream Cl of 900 mg/l. Calculate the percentage contribution of the brine to the downstream water.
b. A town water supply draws water from two sources, 30% coming from a well and 70% from a surface water supply. The TDS of the surface water supply is 120 mg/l and the TDS of the drinking water is 360 mg/l. What is the TDS of the groundwater?

c. Water from a pumping well contains 30 mg/l nitrate. The nitrate level of the unconfined aquifer is 70 mg/l and the nitrate in the lower confined aquifer is 5 mg/l. What is the percentage contribution from each aquifer?

4. How much KCl and $CaCl_2$ would dissolve (mg/l) to give a water composition of:

	mg/l	mmol/l	KCl	$CaCl_2$
K	105			
Ca	289			
Cl	606			

5. How much KNO_3, KCl, and NH_4NO_3 would dissolve (mg/l) to give a water composition of:

	mg/l	mmol/l	KNO_3	KCl	NH_4NO_3
K	182				
NH_4	135				
Cl	95				
NO_3	588				

6. How much NaCl, KCl, $CaCl_2$, and K_2SO_4 would dissolve (mg/l) to give a water composition of:

	mg/l	mmol/l	NaCl	KCl	$CaCl_2$	K_2SO_4
Na	79					
K	195					
Ca	72					
Cl	344					
SO_4	110					

7. The following analyses are in mmol/l, and A and B refer to an upgradient well and a downgradient well, respectively.

	Na	Ca	Cl	S
A	0.2	0.5	0.2	0.5
B	1.7	0.4	0.6	1.0

Using the phases halite, gypsum, sylvite, and ion exchange, calculate the amount of each phase added or removed from the solution as the water moves downgradient. K is present, but is not used in the calculation. In this example ion exchange may be written as:

$$Na_2X + Ca^{2+} \rightarrow 2Na^{+} + CaX$$

In this case the coefficients are Na = 2, Ca = −1. That is, two Na ions are added to the water for every Ca removed.

	mmol/l difference (B − A)	NaCl HL	KCl SY	$CaSO_4 \cdot 2H_2O$ GY	Cation exchange EX
Na	1.5				
Ca	−0.1				
Cl	0.4				
SO_4	0.5				

8. Calculate by hand the concentration of minerals (in mmol/l) that would give a water of the following composition when dissolved.

	Na	K	Ba	Cl	HCO_3
mg/l	46	20	7	71	37

Use minerals $BaCO_3$ (witherite), $NaHCO_3$ (nahcolite), halite, sylvite, and CO_2 gas. Note: use moles of C.

	mg/l	mmol/l	NaCl	KCl	$NaHCO_3$	$BaCO_3$	CO_2 (gas)
Na	46						
K	20						
Ba	7						
Cl	71						
HCO_3	37						

ANSWERS TO EXERCISES

1.

a. If Ca and Mg are reversed the hardness value is reproducible.
b. Field and lab pH agree; therefore, carbonate in error.
   Bicarbonate = 645 + 360/30*61 = 1377 mg/l (close to the field value)
   Carbonate = 0 mg/l as pH = 6.7 (lab) − 6.9 (field)
c. Potassium is too high relative to Na, probably by an order of magnitude, possibly decimal point was displaced on copying analysis.

2. Piper

D is a mixture of A and B in the ratio of 1:3.
C is the result of removing Ca from A.

3. Mixing

1. % brine = 900 − 270/25000 − 270 * 100 = 2.55%
2. % from well = 30 = 360 − 120/x − 120 * 100 and x = 920 mg/l TDS
3. % from upper aquifer = 30 − 5/70 − 5 * 100 = 38.5%
4. How much KCl and $CaCl_2$ would dissolve (mg/l) to give a water composition of:

	mg/l	mmol/l	KCl Mol. Wt = 74.55	$CaCl_2$ Mol Wt = 110.98
K	105	2.69	1	
Ca	289	7.21		1
Cl	606	17.09	1	2

K = 2.69 = 1 * [KCl] or [KCl] = 2.69 mmol/l = 200.5 mg/l

Ca = 7.21 = 1 * [$CaCl_2$] or [$CaCl_2$] = 7.21 mmol/l = 800.2 mg/l

Cl = 17.07 = 1 * [KCl] + 2 * [$CaCl_2$] = 2.69 + 14.42

= 17.11 (check)

5. How much KNO_3, KCl, and NH_4NO_3 would dissolve (mg/l) to give a water composition of:

	mg/l	mmol/l	KNO_3 (101.1)	KCl (74.55)	NH_4NO_3 (80.05)
K	182	4.65	1	1	
NH_4	135	7.48			1
Cl	95	2.68		1	
NO_3	588	9.48	1		1

$NH_4 = 7.48 = 1 * [NH_4NO_3]$ or $[NH_4NO_3] = 7.48$ mmol/l = 598.8 mg/l

$Cl = 2.68 = 1 * [KCl]$ or $[KCl] = 2.68$ mmol/l = 199.8 mg/l

$K = 4.65 = 1 * [KNO_3] + 1 * [KCl]$

or $[KNO_3] = 4.65 - 2.68 = 1.97$ mmol/l = 199 mg/l

$NO_3 = 9.48 = 1 * [KNO_3] + 1 * [NH_4NO_3] = 1.97 + 7.48 = 9.45$ (check)

6. How much NaCl, KCl, $CaCl_2$, and K_2SO_4 would dissolve (mg/l) to give a water composition of:

	mg/l	mmol/l	NaCl (58.44)	KCl (74.55)	$CaCl_2$ (110.98)	K_2SO_4 (174.26)
Na	79	3.43	1			
K	195	4.99		1		2
Ca	72	1.80			1	
Cl	344	9.70	1	1	2	
SO_4	110	1.14				1

$Na = 3.43 = 1 * [NaCl]$ or $[NaCl] = 3.43$ mmol/l = 200 mg/l

$Ca = 1.80 = 1 * [CaCl_2]$ or $[CaCl_2] = 1.80$ mmol/l = 199.8 mg/l

$SO_4 = 1.14 = 1 * [K_2SO_4]$ or $[K_2SO_4] = 1.14$ mmol/l = 198.7 mg/l

$K = 4.99 = 1 * [KCl] + 2 * [K_2SO_4]$

or $[KCl] = 4.99 - 2 * 1.14 = 2.71$ mmol/l = 202 mg/l

$Cl = 9.70 = 1 * [NaCl] + 1 * [KCl] + 2 * [CaCl_2] = 3.43$

$+ 2.71 + 2 * 1.80 = 9.74$ (check)

7. The following analyses are in mmol/l, and A and B refer to an upgradient well and a downgradient well, respectively.

	Na	Ca	Cl	S
A	0.2	0.5	0.2	0.5
B	1.7	0.4	0.6	1.0

Using the phases halite, gypsum, sylvite, and ion exchange, calculate the amount of each phase added or removed from the solution as the water moves downgradient. K is present, but is not used in the calculation. In this example ion exchange may be written as:

$$Na_2X + Ca^{2+} \rightarrow 2Na^{+} + CaX$$

In this case the coefficients are Na = 2, Ca = −1. That is, two Na ions are added to the water for every Ca removed.

	Difference (B − A) mmol/l	NaCl HL	KCl SY	$CaSO_4 \cdot 2H_2O$ Gyp	EX
Na	1.5	1			2
Ca	−0.1			1	−1
Cl	0.4	1	1		
SO_4	0.5			1	

$SO_4 = 0.5 = 1 * GYP$ or $GYP = 0.5$ mmol/l

$Ca = -0.1 = 1 * GYP - 1 * EX$ or $EX = (0.1 + 0.5) = 0.6$ mmol/l

$Na = 1.5 = 1 * HL + 2 * EX$ or $HL = 1.5 - 1.2 = 0.3$ mmol/l

$Cl = 0.4 = 1 * HL + 1 * SY$ or $SY = 0.4 - 0.3 = 0.1$ mmol/l

8. Calculate by hand the amounts of minerals which when dissolved would give a water of the following composition.

	Na	K	Ba	Cl	HCO_3
mg/l	46	20	7	71	37

Use minerals $BaCO_3$ (witherite), $NaHCO_3$ (nahcolite), halite, sylvite, and CO_2 gas. Note: use moles of C.

	mg/l	mmol/l	NaCl	KCl	$NaHCO_3$	$BaCO_3$	CO_2 (gas)
Na	46	2.000	1	—	1	—	—
K	20	0.512	—	1	—	—	—
Ba	7	0.051	—	—	—	1	—
Cl	71	2.003	1	1	—	—	—
HCO_3	37	0.606	—	—	1	1	1

$K = 0.512$ mmol/l: $KCl = 0.512 * 74.555 = 38.2$ mg/l

$Cl = 2.003 = (NaCl) + 0.512$: $NaCl = 1.491 * 58.443 =$a 87.1 mg/l

$Ba = 0.051$ mmol/l: $BaCO_3 = 0.051 * 197.351 = 10.1$ mg/l

$Na = 2.000 = (NaCl) + NaHCO_3 = 1.491 + NaHCO_3$

$NaHCO_3 = 0.509$ mol/l $= 0.509 * 84.016 = 42.8$ mg/l

$C = 0.606 = (NaHCO_3) + (BaCO_3) + (CO_2) = 0.509 + 0.051 + (CO_2)$

$CO_2 = 0.046$ mol/l $= 0.046 * 44.011 = 2.0$ mg/l

CHAPTER 5

Geochemical Equilibrium Modeling

INTRODUCTION

The interpretation of water quality data discussed in previous chapters uses what is commonly called the mass-balance approach. This approach determines what minerals are likely to have dissolved or precipitated, or what reactions may have occurred to give a water a specific composition. The conclusions depend entirely on the expertise of the person making the interpretation. A hypothesis is tested, and the results are dependent on the validity of the hypothesis. The approach in this chapter allows conclusions to be based on a body of knowledge from the science of thermodynamics. Thermodynamics is derived from three apparently simple concepts (laws). It has been developed to enable conclusions to be made relative to the validity of chemical predictions. These predictions may not always be correct, but are derived by using a base of common knowledge and a set of specific rules. Thus, different researchers should reach the same conclusions, given the same data. Unfortunately, the calculations involved are complex and require the use of a computer. The programs that make these calculations are called water equilibrium-calculation programs. A list of some of the main programs used is given in Table 5.1. In this book the program discussed and used is the U.S. Geological Survey program WATEQ4F. This program was chosen because of its small size, availability, and relative ease of use. Although the calculations are by computer, an understanding of the rationale behind the calculations is necessary if an intelligent interpretation of the output is to be made. To this end, a pragmatic discussion of chemical thermodynamics is presented in this chapter.

Table 5.1. Some Common Water Equilibrium Programs

	USGS Wateq Series	
WATEQ	—PL/1	(Truesdell and Jones, 1974)
WATEQF	—FORTRAN IV	(Plummer et al., 1976)
WATEQ3	—Uranium equilibria	(Ball et al., 1981)
WATEQ2	—Trace elements	(Ball et al., 1979; 1980)
WATEQ4F	—FORTRAN 77 for PC	(Ball et al., 1987)
	EPA Soil Chemists	
REDEQL		(Morel and Morgan, 1972)
REDEQL2		(McDuff and Morell, 1973)
GEOCHEM		(Sposito and Mattigod, 1980)
MINEQL		(Westall et al., 1976)
MICROQL		(Westall, 1979)
	USGS and Others—Hot Waters and Brines	
SOLMNEQ		(Kharaka and Barnes, 1973)
SOLMNEQ-88		(Kharaka et al., 1988)
	EPA and Battelle Northwest	
MINTEQ—(MINEQL and WATEQ)		(Felmy et al., 1984)

CHEMICAL THERMODYNAMICS

The chemical quality of water results from:

a. Solution of solids (minerals),
b. Precipitation of solids,
c. Solution or evolution of gases, and
d. Sorption/ion exchange.

The first step in interpreting a water analysis using a thermodynamic approach is the acquisition of the following information, which may be obtained from a reasonably complete water analysis:

Speciation — the ratio of the different species of an element in a water. For example, what is the relative amount of carbonate and bicarbonate that should be present in a solution at a specified pH?

Saturation — information regarding specific minerals, as to whether or not a solution is saturated, undersaturated, or in equilibrium with the phase specified. For example, is a water saturated or undersaturated with respect to calcite?

Oxidation/reduction — the oxidation/reduction environment of the water. For example, at what pe would the Fe^{2+}/Fe^{3+} ratio of a water be equal to one?

To obtain this information it is necessary to compare the water analysis with theoretically determined parameters that are calculated by using thermodynamic reasoning. The primary objective is the calculation of an equilibrium constant for a reaction at 25°C and correcting it to the temperature of the water being studied. In all but the most dilute solutions, the concentration is an overestimate of the amount of the ions present, and a thermodynamic parameter (activity) must be calculated.

Chemical thermodynamics is concerned primarily with the distribution and changes in the energy of the system. There are three laws of thermodynamics:

1. The first law is the principle of conservation of energy. The total amount of energy in the universe remains constant, although the forms that this energy takes may change.
2. The second law implies that energy transfer occurs only along favorable potential gradients, such as:
   —water flows downhill,
   —heat passes from hot objects to cooler ones, and
   —electrical currents flow from points of high potential to points of lower potential.
   The second law also implies that energy in a closed system tends to become evenly distributed. That is, the degree of disorder (called entropy, with symbol S) increases.
3. The third law implies that at a temperature of absolute zero (−273.15°C or 0 K) there is perfect order, that is, the entropy is zero.

CHEMICAL ENERGY

The chemical energy stored in a substance at constant temperature and pressure is termed enthalpy (H). Enthalpy is usually expressed relative to an arbitrary standard state or zero point. It is represented by the symbol ΔH. The Δ represents a departure from the standard state. For chemical elements this standard reference state is that of 1 mol of the element in its elemental form at 25°C and 1 atmosphere pressure. For example:

Compound	Enthalpy ΔH kcal/mol
Ca	0
Ca^{2+}	−129.91
$CaCO_3$ (calcite)	−288.59

Enthalpy (ΔH), Entropy (ΔS), and Free Energy (ΔG)

Enthalpy may be thought of as having two components:

1. The internal component, or entropy (ΔS), which is a measure of the organization or order within the system. The entropy of a substance at absolute zero (T = 0) is zero. If ΔS = 0 there is perfect order.
2. The available energy, or free energy (ΔG). The equation relating these variables is

$$\Delta H = \Delta G + T\Delta S,$$

where T is the absolute temperature (= 273.15 + °C) and ΔS is the entropy relative to its standard state.

The relationship between ΔH, ΔG, and ΔS is shown in Figure 5.1. The values of enthalpy, entropy, and free energy are expressed in terms of heat units. In the U.S., kcal is usually used, whereas in the International system of units Joule or Kjoule is used.

$$1 \text{ calorie} = 4.184 \text{ joules}.$$

EQUILIBRIUM CONSTANT (K)

The rate of a reaction is proportional to the product of the effective concentrations of the reacting substances.

For a reaction:

$$A + 2B \Leftrightarrow C \quad \text{or} \quad A + B + B \Leftrightarrow C$$

where A, B, and C represent different chemical species.

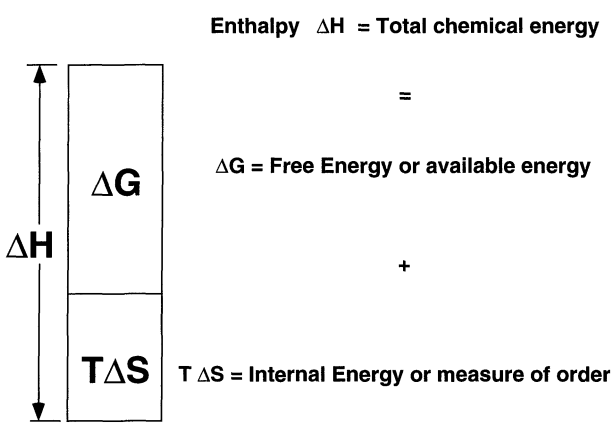


Figure 5.1. Chemical energy.

The forward rate is proportional to $[A][B][B] = [A][B]^2$ where [ ] represents the concentration in mol/l of the species enclosed.

In a more general case:

$$aA + bB \Leftrightarrow cC + dD$$

where a, b, c, and d represent the number of moles of species A, B, C, and D, respectively.

$$\text{The forward rate} = K_f * [A]^a[B]^b$$
$$\text{The reverse rate} = K_r * [C]^c[D]^d$$

At equilibrium, forward rate = reverse rate, or

$$K_f * [A]^a[B]^b = K_r * [C]^c[D]^d$$

thus:

$$\frac{K_f}{K_f} = K = \frac{[C]^c[D]^d}{[A]^a[B]^b}$$

K is known as the equilibrium constant for that reaction. It may be used to determine the concentration of each ion in solution.

ESTIMATION OF K USING FREE ENERGY OF REACTION

The standard free energy of a reaction, ΔG^o_r, is the algebraic sum of the standard free energies of the **products** minus the sum of the standard free energies of the **reactants.** Like the ΔH^o_f the ΔG^o_f are standard state, thermodynamic free energies of formation that may be computed for any reaction.

For example, for the reaction $aA + bB \Leftrightarrow cC + dD$

$$\Delta G^o_r = (c*\Delta G^o_{fC} + d*\Delta G^o_{fD}) - (a*\Delta G^o_{fA} + b*\Delta G^o_{fB})$$

where the standard free energy of the reaction equals the sum of standard free energies of formation of the products times their stoichiometric coefficients less that of the reactants times their stoichiometric coefficients.

Gibb's free energy of a reaction, ΔG_r, is a useful parameter which expresses the tendency of a reaction to proceed (the departure of the reaction from equilibrium). It is related to the standard free energy of the reaction and the activities of the reactants and products. (The effective concentrations or activities will be discussed later in this chapter.)

$$\Delta G_r = \Delta G^o_r + RT \ln \frac{[D]^d[C]^c}{[A]^a[B]^b}$$

where R is the gas constant and T the absolute temperature:

If $\Delta G_r > 0$, the reaction will proceed from right to left.
If $\Delta G_r < 0$, the reaction will proceed from left to right.
If $\Delta G_r = 0$, the reaction will not go in either direction.
Thus, if $\Delta G_r = 0$, it will be at equilibrium; then

$$\Delta G_r^o = -RT \ln \frac{[D]^d[C]^c}{[A]^a[B]^b}$$

$$= -RT \ln K$$

$$\text{and } K = \frac{[D]^d[C]^c}{[A]^a[B]^b}$$

Thus, the standard free energy of a reaction is mathematically related to the equilibrium constant for the reaction. This allows the calculation of equilibrium constants from readily obtainable standard free-energy data.

Thus: $\Delta G_r^o(\text{cal}) = -RT \ln K$

or $\Delta G_r^o(\text{cal}) = -2.303\ RT \log K$

As R = 1.98726 cal/degree/mol, T = 298.15 K (= 25°C).

ΔG_r^o	$= -1.364 \log K$
or $\log K$	$= -\frac{\Delta G_r^o}{1.364}$
where ΔG_r^o is in kcal/mol.	

Note:

What is the meaning of $10^{-4}M$? Consider iron with an atomic weight of 55.85.

$$10^{-4}M \text{ Fe} = 56 * 10^{-4} \text{ g/l} = 56 * 10^{-4} * 10^3 \text{ mg/l} = 5.6 \text{ mg/l}$$

Express $10^{-6}M$ Fe in mg/l.

$$10^{-6}M \text{ Fe} = 56 * 10^{-6} \text{ g/l Fe} = 56 * 10^{-6} * 10^3 \text{ mg/l Fe} = 0.056 \text{ mg/l} = 56 \text{ ppb}$$

EXAMPLES OF THE USE AND CALCULATION OF EQUILIBRIUM CONSTANTS

The ΔG^o_f values used in the following examples are listed in Table 5.2. It should also be noted that the free energy of formation of elements in their standard state are given a ΔG^o_f of 0. It is also assumed that solid phases and water have concentrations of 1.

Example 1.

What is the equilibrium constant for the reaction:

$$\begin{array}{lcccccc} \Delta G_f^o & HCO_3^- & \Leftrightarrow & CO_3^{2-} & + & H^+ & \\ & & & -140.26 & & -126.17 & 0 \end{array}$$

$$\Delta G_r^o = -126.17 - (-1.40.26) = -126.17 + 140.26 = 14.09 \text{ kcal/mol}$$

$$\log K = -\frac{\Delta G_r^o}{1.364} = -\frac{14.09}{1.364} = -10.3$$

$$K = \frac{[CO_3^{2-}][H^+]}{[HCO_3^-]} = 10^{-10.3}$$

Table 5.2. Enthalpy and Free Energy of Formation of Species Commonly Found in Water

Temperature of 298.15 K (25°C)				
Species and formula	Formula weight	$\Delta H°_f$ kcal/mol	$\Delta G°_f$ kcal/mol	Source[a]
Ba^{2+} (aq)	137.34	−128.50	−134.02	1
$BaSO_4$ (barite)	233.402	−352.1	−325.6	1
Ca^{2+} (aq)	40.08	−129.74	−132.30	1
$Ca(OH)_2$	74.095	−235.68	−214.76	1
CaF_2 (fluorite)	78.077	−291.5	−279.0	1
$CaSO_4$ (anhydrite)	136.142	−342.76	−315.93	1
$CaSO_4 \cdot 0.5H_2O$	145.149	−376.85	−343.41	1
$CaSO_4 \cdot 2H_2O$ (gypsum)	172.172	−483.42	−429.60	1
$CaCO_3$ (calcite)	100.089	−288.46	−269.80	1
$CaCO_3$ (aragonite)	100.089	−288.51	−269.55	1
$CaAl_2Si_2O_8$ (anorthite)	278.210	−1009.2	−955.5	1
$CaMg(CO_3)_2$ (dolomite)	184.411	−556.0	−517.1	1
$Ca_2Mg_5Si_8O_{22}(OH)_2$ (tremolite)	812.410	−2954.0	−2780.0	1
CO_2 (aq)	44.0100	−98.90	−92.26	1
CH_4 (aq)	16.0430	−21.28	−8.22	1
HCO_3^- (aq)	61.0174	−165.39	−140.26	1
CO_3^{2-} (aq)	60.0094	−161.84	−126.17	1
H_2CO_3 (undissociated)	62.0253	−167.22	−148.94	1
Cl^- (aq)	35.453	−39.952	−31.372	1
F^- (aq)	18.9984	−79.50	−66.64	1
H^+ (aq)	1.0080	0	0	1
OH^- (aq)	17.0074	−54.970	−37.594	1
H_2O (liq)	18.0153	−68.315	−56.687	1
Fe^{2+} (aq)	55.847	−21.3	−18.85	1
Fe^{3+} (aq)	55.847	−11.6	−1.1	1
Fe_2O_3 (hematite)	159.6922	−197.0	−177.4	1
FeOOH (goethite)	88.8538	−133.6	−117.21	1,2
$Fe(OH)_3$ (precipitated)	89.8617	−196.7	−166.5	1
FeS_2 (pyrite)	119.975	−42.6	−39.9	1
Mg^{2+} (aq)	24.312	−111.58	−108.7	1
$MgSO_4 \cdot 7H_2O$ (epsomite)	246.4810	−809.92	−686.4	1
$MgCO_3$ (magnesite)	84.3214	−261.9	−241.9	1
$Mg(OH)_2$	58.3267	−220.97	−199.23	1
Mg_2SiO_4 (forsterite)	140.7076	−519.6	−491.2	1
Mn^{2+} (aq)	54.9380	−52.76	−54.5	1
MnO_2 (pyrolusite)	86.9368	−124.29	−111.18	1
NO_3^- (aq)	62.0049	−49.56	−26.61	1
NH_4^+ (aq)	18.0386	−31.67	−18.97	1
K^+ (aq)	39.102	−60.32	−67.70	1
$KAl_2Si_3O_{10}(OH)_2$ (muscovite)	398.3133	−1430.3	−1340.5	1
SiO_2 (quartz)	60.0848	−217.72	−204.75	1
Na^+ (aq)	22.9898	−57.39	−62.593	1
$NaAlSiO_4$ (nepheline)	142.0549	−500.2	−472.8	1
Sr^{2+} (aq)	87.62	−130.45	−133.71	1
$SrSO_4$ (celestite)	183.682	−347.3	−320.5	1
$SrCO_3$ (strontianite)	147.629	−291.6	−272.5	1
SO_4^{2-} (aq)	96.0616	−217.32	−177.97	1
H_2SO_4 (aq)	98.0775	−217.32	−177.97	1
H_2S	34.08	−9.5	−6.66	1

[a] (1) Weast, 1989; (2) Hem, 1992.

a. What is the ion ratio at pH = 7.3?

$$10^{-10.3} = \frac{[CO_3^{2-}] * 10^{-7.3}}{[HCO_3^-]}$$

$$\frac{[CO_3^{2-}]}{[HCO_3^-]} = 10^{-10.3} * 10^{7.3} = 10^{-3} = \frac{1}{1000}$$

b. At what pH would $[HCO_3^-] = [CO_3^{2-}]$

$$10^{-10.3} = [H^+] \quad \text{or} \quad pH = 10.3$$

Example 2.

a. What is the equilibrium constant for the reaction:

$$\begin{array}{lcccccc} & Al(OH)_3 & + & 3H^+ & \Leftrightarrow & Al^{3+} & + & 3H_2O \\ \Delta G_f^o & -276.08 & & 0 & & -115.95 & & 3 * -56.69 \end{array}$$

$$\Delta G_r^o = [-115.95 + (3 * -56.69)] - [-276.08] = -9.94 \text{ kcal/mol}$$

$$\log K = -\frac{\Delta G_r^o}{1.364} = -\frac{-9.94}{1.364} = 7.29$$

b. At what pH would $[Al^{3+}] = 10^{-4}M$?

$$K = 10^{7.29} = \frac{[Al^{3+}] * [H_2O]^3}{[Al(OH)_3] * [H^+]^3} = \frac{[Al^{3+}]}{[H^+]^3} = \frac{10^{-4}}{[H^+]^3}$$

As $[Al(OH)_3]$ and $[H_2O] = 1$ then

$$[H^+]^3 = \frac{10^{-4}}{10^{7.29}} = 10^{-11.29}$$

$$[H^+] = 10^{-3.76} \text{ or } pH = 3.76$$

Example 3.

a. What is the equilibrium constant for the reaction:

$$\begin{array}{lcccccc} & & Al(OH)_3 & + & OH^- & \Leftrightarrow & Al(OH)_4^- \Leftrightarrow AlO_2^- + 2H_2O \\ \Delta G_f^o & -276.08 & & -37.594 & & -198.58 & 2 * -56.69 \end{array}$$

$$\Delta G_r^o = [-198.58 + 2 * -56.69] - [-276.08 + (-37.594)] = 1.714 \text{ kcal/mol}$$

$$\log K = -\frac{\Delta G_r^o}{1.364} = -\frac{1.714}{1.364} = -1.256$$

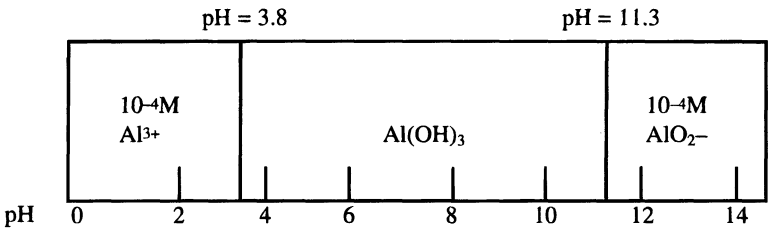
For the above reaction:

$$K = 10^{-1.26} = \frac{[AlO_2^-][H_2O]^2}{[Al(OH)_3][OH^-]} = \frac{[AlO_2^-]}{[OH^-]}$$

Again $[Al(OH)_3]$ and $[H_2O] = 1$.
At what pH would $[AlO_2^-] = 10^{-4}M$?

$$[OH^-] = \frac{10^{-4}}{10^{-1.26}} = 10^{-2.74}$$

$$pOH = 2.74 \text{ or } pH = 14 - pOH = 14 - 2.74 = 11.26$$



Example 4.

What is the equilibrium constant for the reaction:

$$\begin{array}{lccccc} & Mg^{2+} & + & 2H_2O & \Leftrightarrow Mg(OH)_2 & + 2H^+ \\ \Delta G_f^o & -108.7 & & 2 * -56.69 & -199.21 & 0 \end{array}$$

$$\Delta G_r^o = [-199.21] - [-108.7 + (2 * -56.69)] = 22.87 \text{ kcal/mol}$$

$$\log K = -\frac{22.87}{1.364} = -16.77$$

At what pH will $Mg(OH)_2$ precipitate? Assume $[Mg^{2+}] = 10^{-3}$

$$K = 10^{-16.77} = \frac{[Mg(OH)_2] * [H^+]^2}{[Mg^{2+}] * [H_2O]^2} = \frac{[H^+]^2}{[Mg^{2+}]}$$

$$[H^+]^2 = 10^{-16.77} * 10^{-3} = 10^{-19.77}$$

$$[H^+] = 10^{-10.0} \text{ or } pH = 10$$

Sulfate-Carbonate Boundaries

Example 5.

a. At what pH would calcite be replaced by gypsum in the presence of sulfate?

$$2H_2O + CaCO_3 + 2H^+ + SO_4^{2-} \Leftrightarrow CaSO_4 \cdot 2H_2O + H_2CO_3$$

$$\begin{array}{lccccc} \Delta G_r^o & 2 * -56.69 & -269.79 & 0 & -177.95 & -429.56 & -149.00 \end{array}$$

$$\Delta G_r^o = [-429.56 + (-149.00)] - [2 * -56.69 + (-269.79) + (-177.95)]$$

$$= -17.44 \text{ kcal/mol}$$

$$\log K = -\frac{-17.44}{1.364} = 12.78$$

$$K = 10^{12.78} = \frac{[CaSO_4 \cdot 2H_2O][H_2CO_3]}{[H_2O]^2[CaCO_3][H^+]^2[SO_4^{2-}]} = \frac{[H_2CO_3]}{[H^+]^2[SO_4^{2-}]}$$

Assume $[H_2CO_3] = 10^{-3}$ and $[SO_4^{2-}] = 10^{-3}$

$$[H^+]^2 = 10^{-12.78} \text{ or } [H^+] = 10^{-6.4} \text{ or } pH = 6.4$$

b. At what pH would $[Ca^{2+}]$ be equal to $10^{-3}M$?

Consider the reaction:

$$\begin{array}{lccccccc} & CaSO_4 \cdot 2H_2O & + & H^+ & \Leftrightarrow & Ca^{2+} & + & HSO_4^- & + & 2H_2O \\ \Delta G_f^\circ & -429.56 & & 0 & & -132.31 & & -180.67 & & 2 * -56.69 \end{array}$$

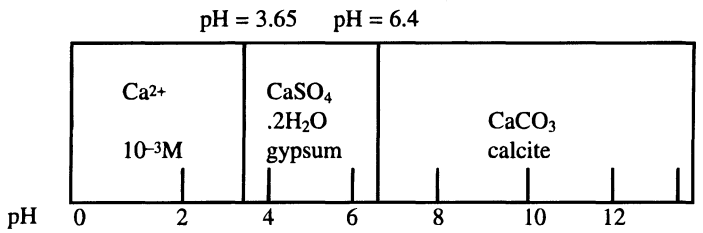
$$\Delta G_r^\circ = [-132.31 + (-180.67) + (2 * -56.69)] - [-429.56] = 3.2 \text{ kcal/mol}$$

$$\log K = -\frac{3.2}{1.364} = -2.35$$

Assume $[HSO_4^-] = 10^{-3}M$

$$K = 10^{-2.35} = \frac{[Ca^{2+}][HSO_4^-]}{[H^+]}$$

$$[H^+] = 10^{-6} * 10^{2.35} = 10^{-3.65} \text{ and pH} = 3.65$$



Dissociation of an Acid

Example 6.

$$\begin{array}{lccccc} & H_3PO_4 & \Leftrightarrow & H^+ & + & H_2PO_4^- \\ \Delta G^\circ_f & -273.07 & & 0 & & -270.14 \end{array}$$

$\Delta G^\circ_r = 2.93$ kcal/mol and log K = −2.15

If $H_3PO_4 = H_2PO_4^-$ then pH = 2.15

$$\begin{array}{lccccc} & H_2PO_4^- & \Leftrightarrow & H^+ & + & HPO_4^{2-} \\ \Delta G^\circ_f & -270.14 & & 0 & & -260.31 \end{array}$$

$\Delta G^\circ_r = 9.83$ kcal/mol and log K = −7.21

If $H_2PO_4^- = HPO_4^{2-}$ then pH = 7.21

$$\begin{array}{lccccc} & HPO_4^{2-} & \Leftrightarrow & H^+ & + & PO_4^{3-} \\ \Delta G^\circ_f & -260.31 & & 0 & & -243.48 \end{array}$$

$\Delta G^\circ_r = 16.83$ kcal/mol and log K = −12.34

If $HPO_4^{2-} = PO_4^{3-}$ then pH = 12.34

CHANGE OF K WITH TEMPERATURE

As described above, an equilibrium constant can be calculated from free energy data. However, this only applies at a temperature of 25°C. In order to be useful, this equilibrium constant must be corrected to the temperature of the water being examined. This may be done with thermodynamic calculations by using enthalpy or with an empirical method.

Thermodynamic Method

Chemical equilibria can be defined in terms of energy. The thermodynamic treatment of energy involves three parameters. These are enthalpy (ΔH), or heat content at constant pressure; entropy (ΔS), or a measure of the disorder of the system; and Gibb's free energy (ΔG), the difference between total chemical energy and internal energy, which is defined by $\Delta G = \Delta H - T\Delta S$, where T is the absolute temperature. It is not possible to measure the actual values, but only changes during a reaction, i.e., ΔG, ΔH, and ΔS. Changes in enthalpy record the amount of heat energy absorbed or liberated during a chemical reaction—the heat of a reaction.

$\Delta H = H_{products} - H_{reactants}$
If ΔH is positive, then the reaction is endothermic (heat absorbed).
If ΔH is negative, then the reaction is exothermic (heat liberated).

The enthalpy change in forming 1 mol of a compound from its elements (at 25°C and 1 atmosphere pressure) is known as the heat of formation of that compound. Thus, by adding or subtracting the heat of formation, the enthalpy change for any reaction can be computed (see example below). The computation of the change in the equilibrium constant with temperature is made possible with the van't Hoff equation:

$$\frac{d\ln K}{dT} = \frac{\Delta H_r^o}{R * T^2}$$

Thus at two temperatures T_1 and T_2 with ΔH^o_r in calories,

$$\log \frac{K_1}{K_2} = \log K_1 - \log K_2 = \frac{\Delta H_r^o}{2.303R} * \left[\frac{1}{T_2} - \frac{1}{T_1}\right]$$

or

$$\log K_2 = \log K_1 - \frac{\Delta H_r^o}{2.303R} * \left[\frac{1}{T_2} - \frac{1}{T_1}\right]$$

where ΔH^o_r is the standard partial molal enthalpy, T is the absolute temperature, and R is the gas constant (=1.98 cal/degree/mol).

If T_1 = 25°C or 298.15 K and ΔH^o_r is in kcal,

$$\text{then } \log K_2 = \log K_1 - \Delta H_r^o \text{ (kcal)}\left[\frac{219.30}{T_2} - 0.7355\right]$$

A list of ΔH_f^o and ΔG_f^o are listed in Table 5.2.

Calculate the equilibrium constant for the reaction below at 25°C and 15°C.

$$\begin{array}{cccccccc} & CaCO_3 & + & H^+ & \rightarrow & Ca^{2+} & + & HCO_3^- \\ \Delta G_f^o & -269.78 & & 0 & & -132.18 & & -140.31 \end{array}$$

$$\Delta G_r^o = (-132.18 + (-140.31)) - (-269.78 + 0) = -2.71 \text{ kcal/mol}$$

$$\log K = \frac{2.71}{1.364} = 1.99 \text{ at } 25°C$$

Calculate K at 15°C

Enthalpy of reaction

$$\begin{array}{lccccc} & CaCO_3 & + H^+ \rightarrow & Ca^{2+} & + & HCO_3^- \\ \Delta H_f^o & -288.45 & 0 & -165.18 & & -288.45 \end{array}$$

$$\Delta H_r^o = -129.77 + (-165.18) - (-288.45) = -6.5 \text{ kcal/mol}$$

At T = 15°C or 288.15 K,

$$\log K_2 = \log K_1 - \Delta H_r^o \text{ (kcal)}\left[\frac{219.30}{T_2} - 0.7355\right]$$

$$\log K_2 = 1.99 - 6.5\left[\frac{219.30}{288.15} - 0.7355\right] = 1.99 + 0.166 = 2.15$$

Empirical Method

If several equilibrium constants are known at different temperatures, the coefficients of the following equation may be calculated using:

$$\log K = A + BT + \frac{C}{T} + D^*\log T$$

where A, B, C, and D are derived constants.

Example 7.

For the reaction $HCO_3^- \rightarrow H^+ + CO_3^{2-}$ an empirical equation is

$$\log K = 5.388 - 0.02199 * T - \frac{2730.7}{T}$$

where T is in Kelvin

From example 1 using free energy $\log K_{25} = -10.3$

Using this equation:

At 25°C (298 K) $\log K_{25} = -10.33$

At 15°C (288 K) $\log K_{15} = -10.42$

ACTIVITY (a)

Thermodynamics is a predictive science. In water chemistry it enables one to determine whether a mineral may dissolve in, or precipitate from, a particular solution. At low concentrations of ions, concentrations are used in the calculations. However, as a solution becomes more concentrated, the ions interact with each other and may no longer act as separate ions. Thus, only a portion of the ions actually act in a predictable way. This predictable concentration is called the activity.

ACTIVITY COEFFICIENT (γ)

In thermodynamic calculations the concentration of a component is usually expressed in molality, m (approximated in dilute solutions by molarity, M). This molality is then used to calculate the effective concentration or activity that is used in most calculations. The activity is a measure of the concentration of the true ions capable of reacting in the solution. It removes the effect of those ions that have formed complexes or are otherwise not available for the reaction being considered. The activity is usually obtained by calculating a factor called an activity coefficient, with a value between 0 and 1, which when multiplied by the concentration gives the activity. Thus, the activity is proportional to concentration:

$$\text{activity} = \text{activity coefficient} * \text{concentration}$$

or symbolically $a = \gamma * c$

where a is the activity, γ is the proportionality constant or activity coefficient, and c is the concentration.

The activity coefficient varies with:

a. The ionic strength of the solution,
b. The charge of the ion,
c. The size of the ion, and
d. The temperature.

At infinite dilution γ approaches 1. In water chemistry the trick is to find γ. There are several formulas that have been proposed to do this.

Calculating Activity Coefficient

Ionic Strength (I)

The ionic strength of a solution is an estimate of the number of total ions in the solution. It may be calculated as follows:

$$\text{Ionic strength} = I = 0.5 * \sum (c_i * z_i^2)$$

where c_i is concentration in mol/l (M) of ion i
z_i is charge on ion i

Debye-Huckel Equation

This equation is used if ionic strength (I) < 0.1.

$$\log \gamma = \frac{-Az_i^2\sqrt{I}}{1 + Ba_o\sqrt{I}}$$

Extended Form of Debye-Huckel Equation

This equation is used if $I > 0.1$ (Truesdell and Jones, 1974).

$$\log \gamma = \frac{-Az^2\sqrt{I}}{1 + Ba_o\sqrt{I}} + bI$$

Davies Equation

This equation may be used for $I < 0.5$. This equation is used for many trace element calculations where a_o is not known.

$$\log \gamma = -Az_i^2 \frac{\sqrt{I}}{1 + \sqrt{I}} - 0.3I$$

a_o is theoretically the hydrated radius of a particular ion (Table 5.3).

b is a computer-calculated value obtained only for major ions (Table 5.3).

A and B are constants that depend only on temperature and pressure, and can be calculated from the dielectric constant of water and temperature (Truesdell and Jones, 1974).

$$A = \frac{1.82483 * 10^6 * d^{0.5}}{(eT)^{3/2}} \text{ mol}^{-1/2}(10^3 \text{ g } H_2O)^{1/2}$$

$$B = \frac{50.2916 * 10^8 * d^{0.5}}{(eT)^{1/2}} \text{ cm}^{-1} \text{ mol}^{-1/2}(10^3 \text{ g } H_2O)^{1/2}$$

where

d = density of water
T = absolute temperature K
e = dielectric constant of water (= 78.25 at 25°C)

OR

$$A = 0.48863 + T * 7.48 * 10^{-4} + T^2 * 3.85 * 10^{-6}$$

$$B = [0.32415 + T * 1.65 * 10^{-4} + T^2 * 2.00 * 10^{-7}] * 10^8$$

and T is in degrees C (Wigley, 1977).

At 20°C; A = 0.5051 and B = $0.3275 * 10^{+8}$.

Example 8.

Calculate the activity coefficients for Ca^{2+} and Cl^- in a solution assuming a temperature of 20°C, with Ca^{2+} = 100.2 mg/l and Cl^- = 177.3 mg/l.

Table 5.3. a_o and b of Common Ions for Debye-Huckel Equation

$a_o * 10^{-8}$	Ions
9	Al^{3+}, Fe^{3+}, H^+
8	Mg^{2+}
6	Ca^{2+}, Mn^{2+}, Fe^{2+}, Li^+
5	Sr^{2+}, Ba^{2+}, S^{2-}, CO_3^{2-}
4	PO_4^{3+}, SO_4^{2-}, Na^+, HCO_3^-
3	OH^-, F^-, Cl^-, Br^-, NO_3^-, K^+, NH_4^+

Ion	b
Ca^{2+}	0.165
Mg^{2+}	0.20
Na^+	0.075
K^+	0.015
Cl^-	0.015
SO_4^{2-}	−0.04
HCO_3^-	0.0
CO_3^{2-}	0.0

From Truesdell and Jones, 1974.

$$\text{Molarity is } Ca^{2+} = 2.5 * 10^{-3} \text{ mol/l and } Cl^{-} = 5.0 * 10^{-3} \text{ mol/l}$$

$$\text{Ionic strength (I)} = \frac{2.5E-3 * (2)^2 + 5.0E-3 * (1)^2}{2} = 0.0075$$

$$\sqrt{I} = 0.0866$$

$$\log \gamma_{Ca^{2+}} = \frac{-0.5051 * (2)^2 * 0.0866}{1 + 0.3275E + 8 * 6E - 8 * 0.0866} = -0.149$$

$$\gamma_{Ca^{2+}} = 0.71$$

$$\log \gamma_{Cl^{-}} = \frac{-0.5051 * (1)^2 * 0.0866}{1 + 0.3275E + 8 * 3E - 8 * 0.0866} = -0.0402$$

$$\gamma_{Cl^{-}} = 0.91$$

COMPLEX FORMATION

By far the most important consideration in the calculation of true activities is the presence in the solution of charged and uncharged complexes, which are not immediately apparent from the analysis. Some programs such as MINTEQ calculate the activity coefficients of neutral complexes from the expression $\log \gamma = 0.1$ I (Felmy et al., 1984).

Terminology of charged and uncharged complexes — A dissolved complex is a combination of an anion and a cation and their net charge difference is the charge of the complex. If a complex is uncharged it is designated as a complex by a superscripted °. If charged, a superscript indicating the net charge is used. It is important to understand that these complexes are dissolved species. Several examples are given below.

$CaCO_3$ is **solid** phase calcium carbonate,
$CaCO_3^{\circ}$ is a **dissolved** calcium and carbonate neutral complex,
$CaHCO_3^{+}$ is a positively charged **dissolved** calcium and bicarbonate complex, and
$NaCO_3^{-}$ is a negatively charged **dissolved** sodium and carbonate complex.

ACTIVITY OF GASES

For gaseous phases the activity is replaced by their partial pressure. The relationship between their partial pressure and their concentration in the aqueous phase is obtained by using Henry's law constant.

$$P \text{ (atmos)} = H * C_w \text{ (mg/l)}$$

Henry's law constants for some common gases are given in Table 5.4. Note that the values are temperature dependent.

SPECIATION

One of the objectives of the thermodynamic calculation described above is the calculation of each concentration of a set of related species. The most common of these is the calculation of each of the carbonate species that exist at different pHs. Some of the species and complexes that occur in seawater are given in Table 5.5.

Table 5.4. Henry's Law Constants of Some Common Gases

°C	CO_2	H_2S	N_2	O_2	CH_4
0	0.0002988	0.0001415	0.03399	0.01440	0.02526
5	0.0003604	0.0001666	0.03846	0.01647	0.02933
10	0.0004314	0.0001956	0.04325	0.01863	0.03384
15	0.0005076	0.0002267	0.04796	0.02082	0.03848
20	0.0005924	0.0002600	0.05260	0.02305	0.04312
25	0.0006901	0.0002962	0.05711	0.02544	0.04782

Usage: What is the dissolved oxygen content of water at 0°C in contact with atmosphere?

$$C_w = \frac{P}{H} = \frac{0.2}{0.01440} = 13.9 \text{ mg/l}$$

Note: P (atmos) = H (atmos-liter/mg) * C_W (mg/l) where P is partial pressure; H is Henry's law constant; C_W is concentration in water.
Modified from Dean, 1985.

Table 5.5. Species of Some Common Ions in Seawater

	m_{Total}	% free ion	% MSO_4	% $MHCO_3$	% MCO_3
		Cations			
Na^+	0.4855	98.6	1.37	0.03	0.01
Mg^{2+}	0.0550	88.9	10.6	0.40	0.16
Ca^{2+}	0.0107	88.7	10.8	0.31	0.21
		Anions			
	m_{Total}	% free ion	% NaA	% MgA	% CaA
SO_4^{2-}	0.0291	53.2	22.8	20.0	3.95
HCO_3^-	0.0019	78.2	8.57	11.6	1.72
CO_3^{2-}	0.0002	17.5	30.4	41.7	10.4

Data from Plummer, Jones, and Truesdell, 1976.

CARBONATE EQUILIBRIA

The carbonate system may be described by five equations with five associated equilibrium constants. The [] imply activities, although concentrations may be used as an approximation. Equilibrium constants for these reactions are listed in Table 5.6.

Henry's Law Constant

$$CO_2 + H_2O \Leftrightarrow H_2CO_3 \qquad H_{CO_2} = \frac{[H_2CO_3]}{P_{CO2}}$$

First Ionization Constant for Carbonic Acid

$$H_2CO_3 \Leftrightarrow H^+ + HCO_3^- \qquad K_1 = \frac{[H^+] * [HCO_3^-]}{[H_2CO_3]}$$

Second Ionization Constant for Carbonic Acid

$$HCO_3^- \Leftrightarrow H^+ + CO_3^{2-} \qquad K_2 = \frac{[H^+] * [CO_3^{2-}]}{[HCO_3^-]}$$

The Solubility Product for Calcite

$$CaCO_3 \Leftrightarrow Ca^{2+} + CO_3^{2-} \qquad K_c = \frac{[Ca^{2+}] * [CO_3^{2-}]}{[CaCO_3]}$$

Table 5.6. pK Values of Carbonate Species at Different Temperatures

T °C	pK_{CO2}	pK_1	pK_2	pK_w	pK_c
0	1.11	6.58	10.63	14.93	8.38
5	1.19	6.52	10.55	14.73	8.39
10	1.27	6.46	10.49	14.53	8.41
15	1.34	6.42	10.43	14.35	8.43
20	1.41	6.38	10.38	14.17	8.45
25	1.47	6.35	10.33	14.00	8.48

From Plummer and Busenberg, 1982.

The Ionization Constant for Water

$$H_2O \Leftrightarrow H^+ + OH^- \qquad K_w = \frac{[H^+] * [OH^-]}{[H_2O]}$$

Example 9.

What is the concentration of carbonate in a solution at pH 7 containing 700 mmol/l HCO_3^-? Use concentrations, not activities. The equation for the reaction is

$$HCO_3^- \Leftrightarrow CO_3^{2-} + H^+$$

The equilibrium constant is

$$K = \frac{[CO_3^{2-}][H^+]}{[HCO_3^-]} = 10^{-10.33} \text{ at } 25°C$$

At pH = 7, $[H^+] = 10^{-7}$, therefore

$$\frac{[CO_3{}^{2-}]}{[HCO_3{}^-]} = 10^{-10.33 + 7} = 10^{-3.33}$$

Thus if $[HCO_3{}^-] = 0.7M$ (= 700 mmol/l)

$[CO_3^{2-}] = 10^{-3.33} * 0.7\ M = 0.000327M = 0.000327 * 1000$ mmol/l = 0.3274 mmol/l.

Example 10.

A solution contains 0.01 m HCO_3^- at 20°C and has a pH of 9. What is the carbonate concentration?

$$mCO_3^{2-} = \frac{K_2 * HCO_3^-}{mH^+}$$

$$= 10^{-10.38} * \frac{10^{-2}}{10^{-9}} = 10^{-3.38} = 4.17 * 10^{-4}$$

Converting to mg/l

$$CO_3^{2-} = 4.17 * 10^{-4} * 60.008 * 1000 = 25 \text{ mg/l}$$

$$HCO_3^- = (10^{-2} - 4.17 * 10^{-4}) * 61.016 * 1000 = 585 \text{ mg/l}$$

MINERAL SATURATION INDEX (SI)

One of the objectives of the thermodynamic calculation listed earlier was the determination of the degree of saturation or unsaturation of the solution with respect to a particular mineral or solid. This is determined by comparing the equilibrium constant for the solubility of the mineral with the product of the activities of the ions actually in the solution, that is,

$$\text{Saturation Index} = \text{SI} = \log \frac{\text{IAP}}{K_{sat}}$$

where SI is the saturation index, K_{sat} is the equilibrium constant for the solution of a solid, usually called solubility product, and IAP (ion activity product) is the product of the activities of the ions in solution. A comparison of IAP/K_{sat} and log IAP/K_{sat} is given in Table 5.7.

SOLUBILITY PRODUCT

Solubility product is a special type of equilibrium constant that enables us to predict the concentration of ion released when a substance dissolves in water.

$$\text{In general, if } A_xB_y \Leftrightarrow xA^+ + yB^-$$

The equilibrium constant, here called the solubility product, is

$$K_{sat} = \frac{[A^+]^x[B^-]^y}{[A_xB_y]}$$

By convention, activity or concentration of solid $A_xB_y = 1$.
Thus,

$$K_{sat} = [A^+]^x[B^-]^y$$

Example 11.

Calculate the solubility product of gypsum.

$$\begin{array}{lccccc} & CaSO_4 \cdot 2H_2O & \Leftrightarrow & Ca^{2+} & + \; SO_4^{2-} & + \; 2H_2O \\ \Delta G_f^o \text{ (Kcal/mol)} & -429.54 & & -132.30 & -177.97 & 2 * -56.69 \end{array}$$

$$\Delta G_r^o = -132.30 + (-177.97) + (2 * -56.69) - (-429.54) = 5.89 \text{ Kcal/mol}$$

$$\log K_{sat} = \frac{-5.89}{1.364} = 4.32 \text{ or } K_{sat} = 10^{-4.32}$$

Table 5.7. Meaning of Saturation Indices

	$\log \frac{IAP}{K}$	$\frac{IAP}{K}$	$\log \frac{IAP}{K}$
	SATURATION INDICES log IAP/K		
1/1	0.0		
1/2	−0.3	2/1	0.3
1/5	−0.7	5/1	0.7
1/10	−1.0	10/1	1.0
1/100	−2.0	100/1	2.0
1/1000	−3.0	1000/1	3.0

Example 12.

Calculate the solubility product for barite.

a. Determine the standard free energy of the reaction:

$$\begin{array}{rccccc} & BaSO_4 & \Leftrightarrow & Ba^{2+} & + & SO_4^{2-} \\ \Delta G_f^o(\text{Kcal/mol}) & -325.6 & & -134.0 & & -178.0 \end{array}$$

$$\Delta G_r^o = \text{sum } \Delta G_f^o \text{ products} - \text{sum } \Delta G_f^o \text{ reactants}$$

$$= [-134.0 + (-178.0)] - [-325.6] = 13.6 \text{ Kcal/mol}$$

b. Calculate the solubility product,

$$\log K_{sat} = \frac{-13.6}{1.364} = -9.97$$

c. Calculate the solubility of barite.

The equation for the reaction is

$$BaSO_4 \Leftrightarrow Ba^{2+} + SO_4^{2-}$$

$$K_{sat} = [Ba^{2+}][SO_4^{2-}]$$

$$\text{As } [Ba^{2+}] = [SO_4^{2-}]$$

$$K_{sat} = [Ba^{2+}][Ba^{2+}]$$

$$\text{or } [Ba^{2+}] = \sqrt{K_{sat}}$$

$$K_{sat} = 10^{-9.97}$$

$$[Ba^{2+}] = 10^{-4.99} * 1000 * 137.34$$

$$= 1.42 \text{ mg/L } Ba^{2+}$$

ION ACTIVITY PRODUCT (IAP)

The steps involved in calculating an IAP are

a. Calculate ionic strength.
b. Calculate activity coefficients. At first assume no complexes.
c. Calculate activities, e.g., $[Ca^{2+}]$, $[SO_4^{2-}]$, $[CaSO_4^o]$.
d. Repeat steps a to c until activities remain the same.

The total concentration of dissolved species includes:

a. Free ions, for example, Ca^{2+} expressed as an activity requires the calculation of an activity coefficient using the Debye-Huckel or Davies equation, and
b. Ion pairs, for example, $CaSO_4^o$ calculated by relationships such as:

$$\frac{[CaSO_4^o]}{[Ca^{2+}][SO_4^{2-}]} = K_{CaSO_4^o}$$

c. The concentrations of each of these species are calculated using mass balances for each ion.
   For example: $mCa(T) = mCa^{2+} + mCaSO_4^o + mCaCO_3^o + mCaHCO_3^+ + —$
   where $mCa(T)$ is the molality of the total Ca in solution.
d. For all ions the simultaneous equations are solved using iterative methods.

Note: In some texts free energies and enthalpies may be in Kjoule/mol; do the summation and then divide by 4.18331 to convert to kcal/mol, or use the appropriate gas constant without converting. [R = 1.98726 cal/degree/mol = 8.31470 joules/degree/mol, 1 calorie = 4.18331 joules].

SATURATION ESTIMATE

If IAP is the ion activity product and K_{sat} is the solubility product, then:

If $IAP > K_{sat}$ the solution is oversaturated and precipitation may occur,
$IAP = K_{sat}$ the solution is saturated and in equilibrium,
$IAP < K_{sat}$ the solution is undersaturated and more of the solid phase may be dissolved.

LANGELIER INDEX

The Langelier index is the saturation index (SI) for calcite, usually calculated somewhat differently. It is defined as:

$$\text{Langelier Index (LI)} = pH_a - pH_s$$

where pH_a is the actual pH of the solution and pH_s is the pH of the same solution that would be at saturation with calcite, that is, would be in equilibrium with calcite (when $IAP = K_{sat}$ for calcite). It is usually calculated from the HCO_3^- and Ca^{2+} concentrations in several steps.

a. Calculate the activity coefficients for HCO_3^- and Ca^{2+}.
b. Calculate the carbonate concentration from the bicarbonate and pH values using the dissociation constant of the reaction:

$$K_2\ HCO_3^- \Leftrightarrow H^+ + CO_3^{2-}.$$

c. Calculate the solubility product of calcite:

$$K_c\ CaCO_3 \Leftrightarrow Ca^{2+} + CO_3^{2-}.$$

These values are all dependent on temperatures, so the appropriate equilibrium constants must be used. Ball, Nordstrom, and Zachmann (1987) give regression equations based on temperature in Kelvin from which these values may be calculated.

$$\log K_2 = -107.8871 - 0.03252849 * T + \frac{5151.79}{T} + 38.92561 * \log_{10} T - \frac{563713.9}{T^2}$$

$$\log K_c = -171.9065 - 0.077993 * T + \frac{2839.319}{T} + 71.595 * \log_{10} T$$

As $K_c = [Ca^{2+}] * [CO_3^{2-}]$ at saturation and $[CO_3^{2-}] = K_2 * [HCO_3^-]/[H^+]$
by substituting for $[CO_3^{2-}]$, then $K_c = [Ca^{2+}] * K_2 * [HCO_3^-]/[H^+]$
taking $\log_{10}$, then $-\log[H^+] = pH_s = \log K_c - \log K_2 - \log [Ca^{2+}] - \log [HCO_3^-]$
converting from concentrations to activities by $a = \gamma * c$

$$pH_s = \log K_c - \log K_2 - \log \gamma_{(Ca^{2+})} - \log[Ca^{2+}] - \log \gamma_{(HCO_3^-)} - \log[HCO_3^-]$$

If IAP is not equal to K_{sat} for calcite (K_c), the saturation index may be calculated in the same way as pH_s was calculated above.

$$\log[CO_3^{2-}] = K_2 + \log[HCO_3^-] - \log[H^+]$$

or

$$pH_a = \log[CO_3^{2-}] - \log K_2 - \log[HCO_3^-]$$

converting to activities

$$pH_a = \log \gamma(CO_3^{2-}) + \log[CO_3^{2-}] - \log K_2 - \log \gamma(HCO_3^-) - \log[HCO_3^-]$$

$$pH_a - \log \gamma(CO_3^{2-}) - \log[CO_3^{2-}] = -\log K_2 - \log \gamma(HCO_3^-) - \log[HCO_3^-]$$

Substituting in the equation

$$pH_s = \log K_c - \log \gamma_{(Ca^{2+})} - \log[Ca^{2+}] - \log K_2 - \log \gamma_{(HCO_3^-)} - \log[HCO_3^-]$$

results in the expression:

$$pH_s = \log K_c + pH_a - \log \gamma_{(Ca^{2+})} - \log[Ca^{2+}] - \log \gamma_{(CO_3^{2-})} - \log[CO_3^{2-}]$$

or

$$pH_a - pH_s = -\log K_c + \log \gamma_{((Ca^{2+})} + \log[Ca^{2+}] + \log \gamma_{(CO_3^{2-})} + \log[CO_3^{2-}]$$

$$= \log \gamma_{(Ca^{2+})} + \log[Ca^{2+}] + \log \gamma_{(CO_3^{2-})} + \log[CO_3^{2-}] - \log K_c$$

Thus $SI = \log IAP/K_{sat} = pH_a - pH_s$, which is identical to the Langelier index.
Thus SI = Langelier index = $pH_a - pH_s$ ($= pH_{actual} - pH_{saturated}$).
The Langelier index is used extensively in corrosion studies. Solutions oversaturated with respect to calcite, or with a positive Langelier index, are likely to precipitate calcite. As a result, the water is less likely to corrode the metal pipes through which it passes.

REDUCTION/OXIDATION (REDOX) REACTIONS

Redox reactions, or reduction-oxidation reactions, are those chemical reactions in which the participating elements change their valence (oxidation number), that is, they either gain or lose electrons. The reaction representing the reduction of ferric iron to ferrous iron is

$$Fe^{3+} + e^- \Leftrightarrow Fe^{2+}$$

The symbol e^- represents an electron or a unit negative charge.

In order for a reduction to take place a source of electrons must be available, either as an associated oxidation reaction or an electric current. If we exclude those electrolysis reactions involving an external source of electric current, all natural aqueous reactions occur in pairs. There is an accompanying oxidation reaction for every reduction so that there is no net change in the number of electrons in the system, i.e., $\Delta e = 0$. Each such reaction, either oxidation or reduction, is known as a half reaction or redox couple. The electron concentration is produced by a reductant:

$$\text{e.g., } Zn \Leftrightarrow Zn^{2+} + 2e^-$$

However, the restriction is that an electron acceptor or oxidant must be present.

$$\text{e.g., } Cu^{2+} + 2e^- \Leftrightarrow Cu$$

The oxidant (oxidizing agent) becomes reduced and the reductant (reducing agent) becomes oxidized. A reducting reaction is one where an oxidant accepts electrons and an oxidizing reaction is one where a reductant donates electrons.

The relative strength of oxidants and reductants can be estimated by looking at the following examples:

$$F_2 + 2e^- \Leftrightarrow 2\,F^-$$

Under surface conditions F^- is present and not F_2, thus the reaction uses electrons and moves to the right, i.e.,

$$F_2 + 2e^- \rightarrow 2\,F^-$$

Thus F_2 is a strong oxidizing agent or F^- is a weak reducing agent.

Similarly,

$$Na^+ + e^- \Leftrightarrow Na$$

Under surface conditions Na^+, and not Na, is present. Thus, the reaction releases electrons and the reaction moves to the left, i.e.,

$$Na^+ + e^- \leftarrow Na$$

Na is a strong reducing agent, or Na^+ is a weak oxidizing agent.

During an oxidation (where reduced $\rightarrow$ oxidized) electrons are lost, i.e.,

$$Fe^{2+} \text{ (reduced)} \rightarrow Fe^{3+} \text{ (oxidized)} + e^-$$

During a reduction (where oxidized $\rightarrow$ reduced) electrons are gained, i.e.,

$$Fe^{3+} \text{ (oxidized)} + e^- \rightarrow Fe^{2+} \text{ (reduced)}$$

Note that the oxidized side of the equation contains the electrons.

DERIVATION OF pe

pe is defined the same way as pH, that is, the negative log of the electron activity, specifically pe = $-\log [e^-]$. Consider the reduction of ferric iron:

$$Fe^{3+} + e^- \Leftrightarrow Fe^{2+}$$

Note that the reaction is written as a reduction, that is, oxidized form + electrons $\Rightarrow$ reduced form

$$K = \frac{[Fe^{2+}]}{[Fe^{3+}][e^-]} = \frac{[\text{reduced}]}{[\text{oxidized}][e^-]}$$

Therefore, $\log K = \log [Fe^{2+}] - \log [Fe^{3+}] - \log [e^-]$
Substituting pe = $-\log [e^-]$, the above equation becomes:

$$pe = \log K + \log[Fe^{3+}] - \log[Fe^{2+}]$$

Also, as $\log K = -\Delta G^o_r/1.364$, at unit activity $pe^o = \log K$.

$$pe = pe^o + \log \frac{[Fe^{3+}]}{[Fe^{2+}]} \frac{-\text{oxidized}}{-\text{reduced}}$$

In the more general case npe = log K + log [oxidized/reduced]

$$\text{or } pe = \frac{\log K}{n} + \frac{1}{n} * \log\left[\frac{\text{oxidized}}{\text{reduced}}\right]$$

Where $pe^o = \log K/n$, if there are n electrons participating in the reaction.

$$pe = pe^o + \frac{1}{n} * \log\left[\frac{\text{oxidized}}{\text{reduced}}\right]$$

Note the reversal in the log part of the expression of the oxidized form and the reduced form in the pe expression and the K expression above.

Example 13.

	Fe^{3+} +	e^-	$\Leftrightarrow$	Fe^{2+}
ΔG^o_f	−1.11	0		−18.85

$\Delta G^o_r = -18.85 - (-1.11) = -17.74$ Kcal/mol

Note again that the signs of the tabulated values are the result of writing the reaction as oxidized form + electrons $\Rightarrow$ reduced form.

$$\text{As } \log K = \frac{-\Delta G^o_r}{1.364} \text{ then } \log K = \frac{17.74}{1.364} = 13.00 = pe^o$$

pe therefore becomes:

$$pe = 13.00 + \log\left\{\frac{[Fe^{3+}]}{[Fe^{2+}]}\right\}$$

NOTE:

$pe^o = \frac{1}{n} * \log K$

n = number of electrons participating in the reaction

Example 14.

Considering the F_2 and Na reactions quantitatively:

$$\begin{array}{rccc} & F_2 + & 2e^- \Leftrightarrow & 2\,F^- \\ \Delta G_f^o & 0 & 0 & 2 * -66.64 \end{array}$$

$\Delta G_r^o = -133.28$ kcal/mol and log K = 97.71

$$pe^o = \frac{\log K}{n} = 48.86$$

$$\begin{array}{rccc} & Na^+ & + e^- \Leftrightarrow & Na \\ \Delta G_f^o & -62.59 & 0 & 0 \end{array}$$

$\Delta G_r^o = 62.59$ kcal/mol and log K = −45.89

$$pe^o = \frac{\log K}{n} = -45.89$$

Example 15.

Determine the upper stability limit in surface environment at 25°C:

$$\begin{array}{rcccc} & O_{2(g)} + & 4H^+ + & 4e^- \Leftrightarrow & 2\,H_2O \\ \Delta G_f^o & 0 & 0 & 0 & 2 * -56.68 \end{array}$$

$\Delta G_r^o = -133.36$ kcal/mol; log K = 83.11; and $pe^o = 20.77$.

$$K = \frac{1}{P_{O_2} * [H^+]^4} \text{ and } \log K = -\log P_{O_2} - 4 * [H^+] = -\log P_{O_2} + 4\,pH$$

Thus $pe = 20.77 + 0.25 * \log P_{O_2(g)} - pH$.

If $P_{O_2} = 0.2$ atmos then $pe = 20.6 - pH$.

Determine the lower limit in surface environment at 25°C:

$$\begin{array}{rcccc} & 2\,H_2O & + 2e^- \Leftrightarrow & H_2 + & 2OH^- \\ \Delta G_f^o & 2 * -56.68 & 0 & 0 & 2 * -37.59 \end{array}$$

$\Delta G_r^o = 38.17$ kcal/mol; log K = −27.98; and $pe^o = -14.0$

$$pe = pe^o - 0.5 \log P_{H_2}[OH^-]^2 = -14 + pOH$$

As pOH = 14 − pH and the max P_{H_2} is 1 atmosphere, then pe = −pH.

Tabulating the above data and assuming all at 25°C:

Above upper stability limit of surface environment
$F_2 + 2e^- \Leftrightarrow 2F^-$ $pe^o = 48.86$
Upper stability limit in surface environment
$O_2(g) + 4H^+ + 4e^- \Leftrightarrow 2\ H_2O$ $pe^o = 20.77$
Lower stability limit in surface environment
$2\ H_2O + 2e^- \Leftrightarrow H_2 + 2OH^-$ $pe^o = -14$
Below stability lower limit of surface environment
$Na^+ + e^- \Leftrightarrow Na$ $pe^o = -45.89$

DERIVATION OF Eh

Under standard conditions, defined as 25°C, 1 atmosphere, and unit activity, the potential of a reaction (in volts) is represented by the symbol E^o. Also by convention, the potential of a reaction involving the reduction of hydrogen ions to hydrogen gas is taken as zero.

$$\text{i.e., } 2H^+ + 2e^- \Leftrightarrow H_2(g)\ E^o = 0 \text{ volts}$$

The sign of the potential associated with a half reaction is negative if it is a reducing reaction and positive if it is an oxidizing reaction. The magnitude of E^o is a measure of the oxidizing or reducing tendency of the system. When the activities of the participating species in a system differ from unity, then the potential observed at equilibrium is termed the redox potential and is given the symbol Eh. It is a function of the standard potential E^o and the activities of the participating species. The relationship is known as the Nernst equation. At equilibrium the standard free energy of a system is given by the following equation:

$$\Delta G_r = \Delta G^o + RT \ln \frac{[\text{products}]}{[\text{reactants}]} \frac{-\text{reduced}}{-\text{oxidized}}$$

In order to convert the energy units from thermal to electrical units we use the relationship,

$$-\Delta G_r = nFE$$

where:

F is the Faraday constant.
= 96,490 coulombs/mol (joules).
= 96,490 * 0.239/1000 = 23.0611 kcal.

Thus, there are 23.06 kcal/volt.
n = number of electrons appearing in the balanced half cell.
E = the electrical potential.

$$\text{Thus, } -nFE = -nFE^o + RT \ln \frac{[\text{reduced}]}{[\text{oxidized}]}$$

dividing both sides by −nF we obtain:

$$E = E^o - \frac{RT}{nF} * \ln \frac{[\text{reduced}]}{[\text{oxidized}]}$$

inverting logs and changing sign:

$$E = E^o + \frac{RT}{nF} * \ln \frac{[\text{oxidized}]}{[\text{reduced}]}$$

Converting to base 10, the equation becomes:

$$Eh = E^o + \frac{1}{C*n} * \log \frac{[\text{oxidized}]}{[\text{reduced}]}$$

$$Eh = E^o + \frac{0.0592}{n} * \log \frac{[\text{oxidized}]}{[\text{reduced}]}$$

CONVERSION OF Eh TO pe

Comparing

$$Eh = E^o + \frac{1}{C*n} * \log \frac{[\text{oxidized}]}{[\text{reduced}]}$$

with

$$pe = pe^o + \frac{1}{n} * \log \frac{[\text{oxidized}]}{[\text{reduced}]}$$

Thus, pe = Eh * C, where C = F/R * T * ln(10)

$$C = \frac{1000}{R} * \frac{F}{1} * \frac{1}{T} * \frac{1}{\ln(10)} = \frac{1000 * 23.0611}{1.987 * 298.15 * 2.303} = 16.906$$

Where R is in cal/°/mol, T = 25°C, then Eh = pe/16.906
Thus, a pe of 12.67 has an Eh of 0.75 V.

EXAMPLE 16.

Calculate the pe^o value for the reaction:

$$\underset{\text{(goethite)}}{FeOOH} + 3H^+ + e^- \Leftrightarrow Fe^{2+} + 2H_2O$$

$$\Delta G_f^0 \quad -117.21 \qquad 0 \qquad 0 \qquad -18.85 \qquad 2 * -56.68$$

ΔG_r^o = sum of free energies of products − sum of free energies of reactants

= (−18.85 − (2* −56.594)) − (−117.21 + 0 + 0) = −15.00 kcal/mol

$$\log K = \frac{15.00}{1.364} = 11.00 = pe^o$$

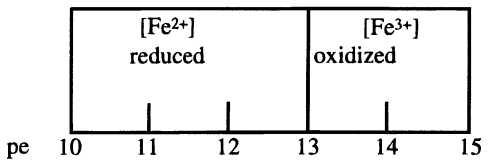
EXAMPLE 17.

What is the transition pe of the pH independent reaction:

$$\begin{array}{lccc} & Fe^{3+} + e^- & \Leftrightarrow & Fe^{2+} \\ \Delta G_f^o & -1.1 \quad 0 & & -18.85 \end{array}$$

$\Delta G_r^o = -17.75$ kcal/mol and log K = 13.01 = pe^o

Assume $[Fe^{3+}] = [Fe^{2+}]$ then pe = 13.01



EXAMPLE 18.

What is the transition pe of the pH-dependent reaction:

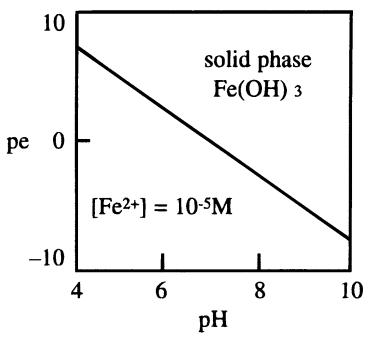
$$Fe(OH)_3 + e^- + 3H^+ \Leftrightarrow Fe^{2+} + 3H_2O$$

ΔG_f^o $\quad -166.5 \quad 0 \quad 0 \quad -18.85 \quad 3 * -56.68$

$\Delta G_r^0 = -22.39$ and log K = 16.41 = pe^o

$$pe = 16.41 + \frac{1}{n} \log \frac{[H^+]^3}{[Fe^{2+}]}$$

Assume $[Fe^{2+}] = 10^{-5}M$
At pH = 4 then pe = 16.41 − 12 + 5 = 9.41
At pH = 10 then pe = 16.41 − 30 + 5 = −8.6
In general pe = 16.41 − 3pH + 5 = 21.41 − 3pH
This may be shown as:



BALANCING HALF REACTIONS

As discussed above, a redox reaction consists of two parts or half reactions. These are the oxidation reaction in which a substance loses or donates electrons, and the reduction reaction in which a substance gains or accepts electrons. These reactions must accompany

each other because free electrons cannot exist in a solution. In order to balance a redox reaction the following technique may be used. For each half cell:

a. Identify the principal reactants and products other than hydrogen ions, hydroxyl ions, and water.
b. Balance atoms other than hydrogen and oxygen.
c. Balance oxygen using H_2O.
d. Balance H using H^+.
e. Balance charge with electrons.

To balance two half cells continue as follows:

f. Multiply each half cell by an integer so that both half cells contain the same number of electrons.
g. Add the two balanced half reactions.
h. Steps a–g may produce a reaction with H^+ as a reactant or product. If the reaction is known to take place in an alkaline solution, then add the reaction for the dissociation of water to eliminate the H^+ and form water.

Note that the equivalent weight of an oxidizing or reducing agent is the formula weight divided by the number of electrons taking part in the reaction.

EXAMPLE 19.

Using the steps listed above:

Balance a reaction where Fe^{2+} is oxidized to Fe^{3+}.

Step (a). $Fe^{2+} \rightarrow Fe^{3+}$ (oxidation)

Step (e). balance charge $Fe^{2+} \rightarrow Fe^{3+} + e^-$

Balance reduction of nitrate to ammonia.

Step (a). $NO_3^- \rightarrow NH_4^+$

Step (c). balance oxygen $NO_3^- \rightarrow NH_4^+ + 3H_2O$

Step (d). balance hydrogen $NO_3^- + 10\ H^+ \rightarrow NH_4^+ + 3H_2O$

Step (e). balance electrons $NO_3^- + 10\ H^+ + 8e^- \rightarrow NH_4^+ + 3H_2O$

[N + V] [N − III]

Balance reduction of limonite to ferrous iron.

Step (a). $FeOOH \rightarrow Fe^{2+}$

Step (c). balance oxygen $FeOOH \rightarrow Fe^{2+} + 2H_2O$

Step (d). balance hydrogen $FeOOH + 3H^+ \rightarrow Fe^{2+} + 2H_2O$

Step (e). balance electrons $FeOOH + 3H^+ + e^- \rightarrow Fe^{2+} + 2H_2O$

[Fe + III] [Fe + II]

EXAMPLE 20.

a. Balance the reaction: $FeOOH \rightarrow FeS_2$

From 19 above: $FeOOH + 3H^+ + e^- \rightarrow Fe^{2+} + 2H_2O$

Also require reaction: $SO_4^{2-} \rightarrow S^-$

$2SO_4^{2-} + 16H^+ + 14e^- \rightarrow 2S^- + 8H_2O$

(S VI) (S − I)

Combining

$$2SO_4^{2-} + FeOOH + 19H^+ + 15e^- \rightarrow FeS_2 + 10H_2O$$

b. Calculate pe^o and pe of the reaction:

$$\begin{array}{lccccccc} \Delta G_f^o & 2SO_4^{2-} & + & FeOOH & + & 19H^+ + 15e^- \rightarrow & FeS_2 & + & 10H_2O \\ & 2 * -177.97 & & -117.21 & & & -39.9 & & 10 * -56.68 \end{array}$$

$\Delta G_r^o = -133.55$ and $\log K = 97.96/15 = 6.53 = pe^o$

$$pe = 6.53 + \frac{2 * \log[SO_4^{2-}]}{15} - \frac{19 * pH}{15}$$

c. Calculate the pe at a pH of 12 (assume $[SO_4^{2-}] = 10^{-2}M$):

$$pe = 6.53 - \frac{4}{15} - \frac{19 * 12}{15} = -8.95$$

INTRODUCTION TO pe(Eh)/pH DIAGRAMS

Thermodynamic data may be used to construct figures called pe-pH (or Eh-pH) diagrams. Such diagrams are invaluable in determining the mobility of various ions in the environment. They show fields (areas) where different ions or compounds exist within the boundaries set by the pH and pe limits. The boundaries that separate these fields have directional significance, and are also the result of specific conventions used in the construction of such diagrams.

Diagram Conventions

Some of the conventions used are

a. If the phases on both sides of a boundary are soluble, then the boundary line is placed where the activities of the ions are equal. If we consider the pe boundary between Fe^{2+} and Fe^{3+} it is placed at the pe value for which the activity of Fe^{2+} is equal to that of Fe^{3+}. Using the redox equation given in Table 5.8 where $pe = 13.0 + \log \{ [Fe^{3+}]/[Fe^{2+}] \}$ the boundary lies at pe = 13.0.

b. If a boundary separates a soluble and an insoluble phase, then its placement depends on some prespecified value for the activity of the soluble phase. Often $10^{-4}M$ or $10^{-6}M$ is chosen. For example, the boundary between Fe^{2+} and $Fe(OH)_3$ may be chosen so that the activity of Fe^{2+} is $10^{-4}M$ or 5.6 mg/l. Again, using the equation from Table 5.8 where $pe = 16.1 - \log[Fe^{2+}] - 3pH$, then if Fe^{2+} is $10^{-4}M$, $pe = 16.1 - (-4) - 3pH = 20.1 - 3pH$. At pH = 6, then pe = 2.1; at pH = 4, then pe = 8.1.

Boundary Types

Boundaries may be parallel to either the horizontal or vertical axes or inclined to them. These orientations are the result of the reactions requiring hydrogen ions, electrons, or both.

a. Horizontal boundaries parallel to the pH axis separate phases, which differ in oxidation number. The change from one phase to the other phase, however, is independent of pH. An example is the reaction:

Table 5.8. Redox Equations and Formulas with pe° Values

1. MnO_2 (g) + H^+ + $2e^- \Leftrightarrow Mn^{2+}$ + $2H_2O$	pe = 20.8 − 0.5 log $[Mn^{2+}]$ − 2pH
2. Fe^{3+} + $e^- \Leftrightarrow Fe^{2+}$	pe = 13.0 + log $[Fe^{3+}]/[Fe^{2+}]$
3. $Fe(OH)_3$ (s) + $3H^+$ + $e^- \Leftrightarrow Fe^{2+}$ + $3H_2O$	pe = 16.41 − log$[Fe^{2+}]$ − 3pH
4. FeOOH + $3H^+$ + $e^- \Leftrightarrow Fe^{2+}$ + $2H_2O$	pe = 11.0 − log$[Fe^{2+}]$ − 3pH
5. NO_3^- + $10H^+$ + $8e^- \Leftrightarrow NH_4^+$ + $3H_2O$	pe = 15.0 − 0.125*log$[NH_4^+]$ + 0.125*log$[NO_3^-]$ − 1.25 pH
6. $2NO_3^-$ + $12H^+$ + $10e^- \Leftrightarrow N_2$ (g) + $6H_2O$	pe = 21.0 − 0.1*log P_{N2} + 0.2*log$[NO_3^-]$ − 1.2*pH
7. O_2 (g) + $4H^+$ + $4e^- \Leftrightarrow 2H_2O$	pe = 20.8 + 0.25*log P_{O2} (g) − pH
8. O_2 (aq) + $4H^+$ + $4e^- \Leftrightarrow 2H_2O$	pe = 21.5 + 0.25*log$[O_2]$ − pH
9. SO_4^{2-} + $10H^+$ + $8e^- \Leftrightarrow H_2S$ (g) + $4H_2O$	pe = 5.75 − 0.125*log P_{H_2S} + 0.125*log$[SO_4^{2-}]$ − 1.25*pH
10. CO_2 (g) + $8H^+$ + $8e^- \Leftrightarrow CH_4$ (g) + $2H_2O$	pe = 2.87 − 0.125*log P_{CH4} + 0.125*log P_{CO2} − pH
11. $2H_2O$ + $2e^- \Leftrightarrow H_2$ + $2OH^-$	pe = −14.0 − 0.5*log$[P_{H_2}]$ − log$[OH^-]$

$$Fe^{2+} - e \rightarrow Fe^{3+}$$

b. Vertical boundaries are parallel to the pe axis. They separate phases that have the same oxidation number, but hydrogen ions participate in the reaction. An example is

$$HCO_3^- - H^+ \rightarrow CO_3^{2-}$$

c. Boundaries inclined to both axes involve reactions where both electrons and hydrogen ions participate. An example is

$$Fe(OH)_3 + e^- + 3H^+ \rightarrow Fe^{2+} + 3H_2O$$

Upper and Lower Limits of Diagram

The strongest oxidizing agent in nature is the oxygen in the atmosphere. The potential of this half cell is strongly dependent on pH. From Table 5.8 the equation is pe = 21.5 + 0.25 log$[O_2]$ − pH. Assuming 1 atmosphere of O_2 then pe = 21.5 − pH. Then at pH = 0 pe = 21.5; at pH = 14 pe = 7.5. These points then describe the position of the upper limiting values in nature.

Similarly, the lower limiting redox potential is that of the hydrogen electrode. From Table 5.8 pe = − 14.0 − 0.5log$[p_{H2}]$ − log$[OH^-]$. At 1 atmosphere then pe = −14 + pOH or pe = −pH.

At pH = 0, then pe = 0 and at pH = 14, then pe = −14.

The redox conditions in natural waters are usually effected by only a few elements—namely C, N, O, Fe, and Mn. These reactions, however, are frequently catalyzed by microbiota; therefore, thermodynamic predictions may not always be correct.

pe-pH Diagram of Some Common Iron Species

A simplified pe-pH diagram for iron is given in Figure 5.2. The convention used is soluble iron species set at 10^{-4} M, or 5.6 mg/l, and sulfate set at 10^{-2} M, or 961 mg/l. The $Fe^{3+} - Fe^{2+}$ border is independent of pH, whereas the $Fe^{3+} - FeOOH$ border is independent of pe. It is apparent that at pH greater than about 5, goethite (FeOOH) is the stable phase, except at very low pe where pyrite is stable, which is indicated by H_2S gas resulting from

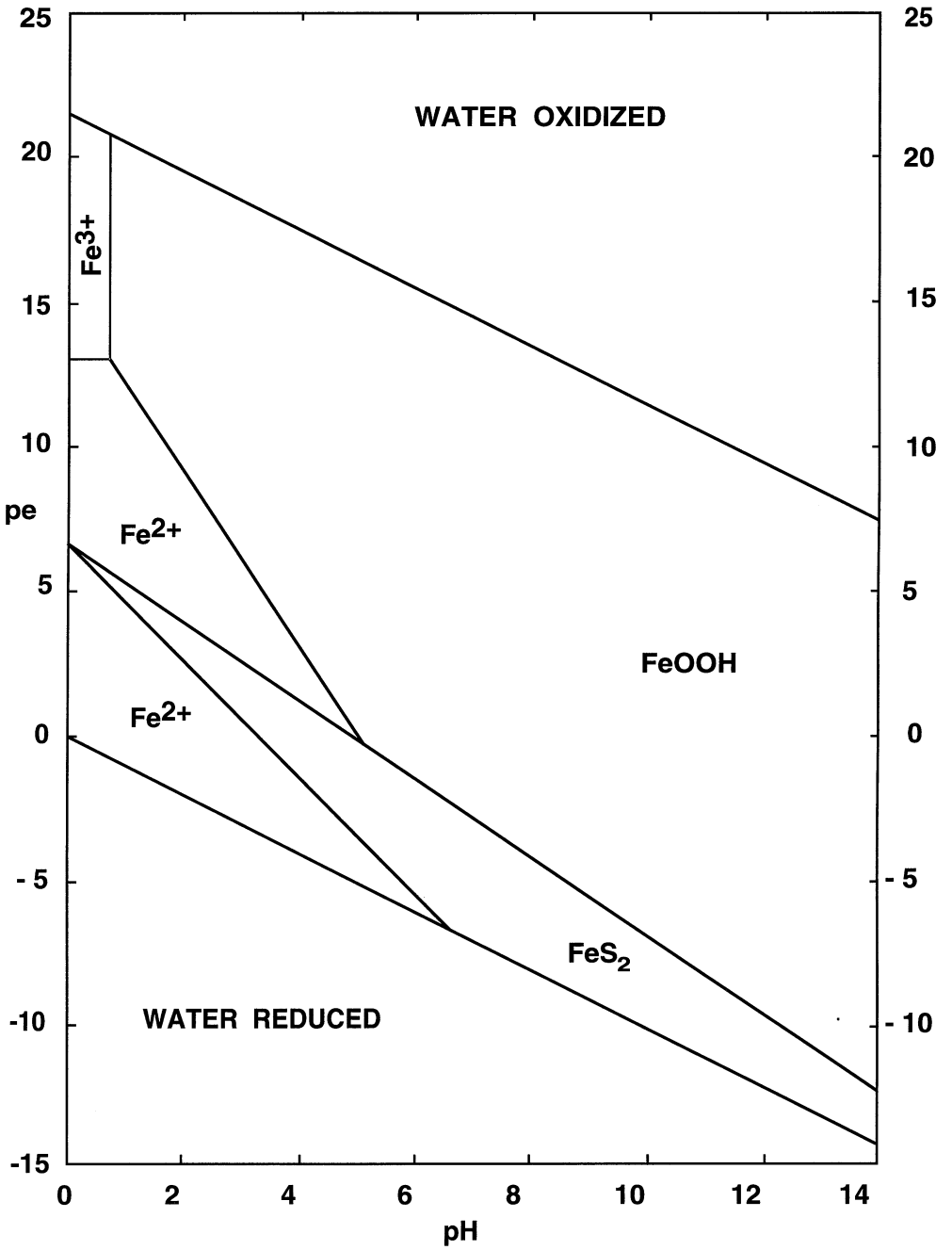


Figure 5.2. Simplified pe-pH diagram for common iron species assuming 10^{-4}M Fe and 10^{-2}M SO_4^{2-}.

sulfate reduction. At pH less than 5, reducing waters would yield either goethite, pyrite, or ferrous iron, dependent upon the redox potential. The presence of carbonate and the absence of sulfate would allow the formation of siderite ($FeCO_3$) rather than pyrite at lower pe values. In the event that a lower Fe concentration, such as 10^{-6} M (or 0.06 mg/l), were chosen, then the goethite boundary would move towards the higher pH side of the diagram by about 0.7 pH units.

The main formulas discussed in this chapter are summarized in Table 5.9.

EXERCISES

Thermodynamic calculations:

1. Calculate the pH of a suspension of $Ca(OH)_2$ in water at 25°C. Calculate the Ca^{2+} concentration in this solution in mg/l.

Reaction is

$$Ca(OH)_2 \Leftrightarrow Ca^{2+} + 2(OH)^-$$

$$\Delta G_f^0$$

$$\Delta G_r^o =$$

$$\log K =$$

$$K =$$

Let x mol/l = concentration of Ca^{2+}, whereupon the concentration of $(OH)^-$ = 2x mol/l.

$$x = Ca^{2+} \text{ (mol/l)} =$$

$$Ca^{2+} \text{ (mg/l)} =$$

$$2x = (OH)^- =$$

$$pOH =$$

$$pH =$$

2. Is the following solution saturated, undersaturated, or in equilibrium with calcite at 20°C? This is most easily calculated using a spreadsheet.

	(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)
Ion	mg/l	mmol/l	mol/l	Z	$a^{o*}10^{-8}$	logγ	γ	a
Ca^{2+}	300							
Na^+	70							
HCO_3^-	915							
Cl^-	106							
pH	7.1							

(5) Ionic strength =

Debye-Huckel A = 0.5042 B = 0.3273E8

(9) Using $K_2 = [H^+] * [CO_3^{2-}]/[HCO_3^-]$ (Table 5.6)

where [] = activity

$[CO_3^{2-}]$ =

Table 5.9. Basics of Water Chemistry Thermodynamics

Absolute temperature	= °C + 273.15; e.g., 25°C = 298.15 K
Gas constant	= 1.98 cal/degree/mol; 1 calorie = 4.18331 joules
Equilibrium constant K_{25} (25°C)	Using $\Delta G°_f$ values in Table 5.8
	$\Delta G°_r = -R * T * \ln K_{25}$, or $\Delta G°_r$ (cal) $= -2.303\ RT \log K$
	If T = 298.15K (= 25°C) and $\Delta G°_r$ is in kcal, then $\Delta G°_r = -1.364$ log K or $\log K = \frac{-\Delta G°_r}{1.364}$
Equilibrium constant K_T (T°C)	From $\Delta H°_f$ values in Table 5.8, using the van't Hoff equation
	$\text{Log } K_2 = \log K_1 - \frac{\Delta H°_r}{2.303R} * \left[\frac{1}{T_2} - \frac{1}{T_1}\right]$
	K_1 = equilibrium constant at temperature T_1 K
	K_2 = equilibrium constant at temperature T_2 K
	$\Delta H°_r$ = enthalpy of the reaction in cal/degree/mol
	If T_1 = 25°C or 298.15 K and $\Delta H°_r$ is in kcal, then $\log K_2 = \log K_1 - \Delta H°_r$ (kcal) $\left[\frac{219.30}{T_2} - 0.7355\right]$
Ionic strength	From concentrations and ionic charges
	There is one value of I for each solution
	Ionic strength = $I = 0.5 * \Sigma (c_i * z_i^2)$
Activity coefficient	Calculated for each ion using Debye-Huckel equation or Davies equations
Debye-Huckel equation	Used if ionic strength (I) < 0.1, i.e., $\log \gamma = \frac{-Az_i^2\sqrt{I}}{1 + Ba_o\sqrt{I}}$
	a_o is related to the size of each ion, Table 5.2
	A and B are temperature dependent, $A = 0.48863 + T * 7.48 * 10^{-4} + T^2 * 3.85 * 10^{-6}$, $B = [0.32415 + T * 1.65 * 10^{-4} + T^2 * 2.00 * 10^{-7}] * 10^8$ where T is in degrees C (Wigley, 1977)
Davies equation	Used if ionic stength (I) < 0.5, i.e., $\log \gamma = \frac{-Az_i^2\sqrt{I}}{1 + \sqrt{I}} - 0.3I$
Activity	$a_i = \gamma_i * c_i$
Ion activity product (IAP)	Of ions in solution
Saturation index (SI)	$SI = \log (IAP/K_{sat})$ If SI = 0, then solution is saturated
	If SI is negative solution is undersaturated
	If SI is positive solution is oversaturated
Langelier index	Saturation index for calcite = $pH_a - pH_s$
	pH_a = actual pH of solution
	pH_s = pH of same solution just saturated with calcite
Oxidation	Loss of electrons
	During an oxidation (reduced form → oxidized form) electrons are lost, e.g., Fe^{2+} (reduced) → Fe^{3+} (oxidized) + e^-
Reduction	Gain of electrons
	During a reduction (oxidized form → reduced form) electrons are gained, e.g., Fe^{3+} (oxidized) + e^- → Fe^{2+} (reduced)
	Note: The oxidized side of equation contains the electrons

Table 5.9. *Continued*

pe	Defined the same way as pH, i.e., the negative log of the electron activity, specifically: pe = $-\log [e^-]$
pe°	Note that the reaction is written as a reduction, i.e., oxidized form + electrons ⇒ reduced form
K	= [reduced]/[oxidized][e^-] and as pe = $-\log [e^-]$
pe	$= \log K + 1/n * \log\left[\frac{\text{oxidized}}{\text{reduced}}\right]$ at unit activity where there are n electrons participating in the reaction
pe°	$= \frac{\log K}{n}$ and $pe = pe^\circ + 1/n * \log\left[\frac{\text{oxidized}}{\text{reduced}}\right]$ Note the reversal in the log part of the expression of the oxidized form and the reduced form in the pe expression and the K expression above
Eh	= pe/16.906
Balancing reactions	(a) Identify principal reactants and products other than hydrogen ions, hydroxyl ions, and water. (b) Balance atoms other than hydrogen and oxygen. (c) Balance oxygen using H_2O. (d) Balance H using H^+. (e) Balance charge with electrons. To balance two half cells: (f) Multiply each half cell by an integer so that both half cells contain the same number of electrons. (g) Add the two balanced half reactions.

(10) IAP = $[CO_3^{2-}] * [Ca^{2+}]$ =

(11) K_{sat} (calcite) = (from Table 5.6)

(12) IAP/K_{sat} =

Conclusion:

3. A solution contains 200 mg/l HCO_3^-. Calculate the concentrations of CO_3^{2-} and H_2CO_3 present in mg/l at 25°C at a pH of 11. Assume solution density = 1 and concentrations equal activity. Use equilibrium constants from Table 5.4.

4. Prepare a graph of the solubility product of barite for a series of barium and sulfate concentrations. Use a K_{sat} of barite of 0.988E − 10. Plot 6 to 20 values in the range 1E − 6 to 50E − 6 M Ba. This problem is accomplished most readily using a spreadsheet.

5. Plot on a vertical scale the pe range for the following reactions assuming a pH of 7. Use concentrations and not activities for the calculations.

a. 0.01 mg/l dissolved oxygen
b. 10 mg/l dissolved oxygen
c. equal concentrations of ferrous and ferric iron
d. 0.1 mg/l Mn^{2+} in contact with solid MnO_2
e. 10 mg/l Mn^{2+} in contact with solid MnO_2
f. equal concentrations of nitrate and ammonium ions
g. 0.01 mg/l H_2S and 200 mg/l SO_4^{2-}
h. 2 mg/l H_2S and 200 mg/l SO_4^{2-}
i. equal molar ratio of carbon dioxide and methane

ANSWERS TO EXERCISES

Thermodynamic calculations:

1. Calculate the pH of a suspension of $Ca(OH)_2$ in water at 25°C. Calculate the Ca^{2+} concentration in this solution in mg/l.

Reaction is

$$Ca(OH)_2 \Leftrightarrow Ca^{2+} + 2(OH)^-$$

ΔG_f^o $\quad -214.76 \quad -132.30 \quad -37.594$

$\Delta G_r^o = -132.30 - 2 * 37.594 + 214.76 = 7.272$ kcal/mol

$\log K = \Delta G_r^o/1.364 = -5.3314$

$K = 4.4688E-6$

let x mol/l = concentration of Ca^{2+}

Thus concentration of $(OH)^-$ = 2x mol/l

$K = [x][2x]^2 = 4x^3$

$x = Ca^{2+}$ (mol/l) = 1.0378E−2

Ca^{2+} (mg/l) = 1.0378E−2 * 1000 * 40.08 = 416 mg/l

$2x = (OH)^- = 2.0755E-2$

pOH = 1.68

pH = 12.32

2. Is the following solution saturated, undersaturated, or in equilibrium with calcite at 20°C?

Ion	mg/l	mmol/l	mol/l	Z	a^{o*} 10^{-8}	logγ	γ	a
Ca^{2+}	300	7.485	7.485E−3	+2	6	−0.2450	0.57	$10^{-2.37}$
Na^+	70	3.044	3.044E−3	+1	4	−0.0666	0.86	$10^{-2.58}$
HCO_3^-	915	15.000	1.500E−2	−1	4	−0.0666	0.86	$10^{-1.89}$
Cl^-	106	2.990	2.990E−3	−1	3	−0.0697	0.85	$10^{-2.59}$
pH	7.1							

(5) Ionic strength = 1000/2 * (4 * 7.485 + 3.044 + 15.00 + 2.99) = 0.0255

$\sqrt{I}$ = 0.1597

Debye-Huckel A = 0.5042 B = 0.3273E8

(9) Using $K_2 = \dfrac{[H^+] * [CO_3^{2-}]}{[HCO_3^-]}$

where [ ] = activity

$[CO_3^{2-}] = \dfrac{10^{-10.38} * 10^{-1.89}}{10^{-7.1}} = 10^{-5.17}$ (= 6.76E−6)

(10) IAP $= [CO_3^{2-}] * [Ca^{2+}]$

$= 10^{-5.17} * 10^{-2.37} = 10^{-7.54}$ (= 2.88E−8)

(11) K_{sat} (calcite) $= 10^{-8.28}$

(12) $\dfrac{IAP}{K_{sat}} = \dfrac{10^{-7.54}}{10^{-8.28}} = 10^{0.74}$

Thus SI = log $(10^{0.74})$ = 0.74

Conclusion: solution is oversaturated with respect to calcite.

3. A solution contains 200 mg/l HCO_3^-. Calculate the concentrations of CO_3^{2-} and H_2CO_3 present in mg/l at 20°C at a pH of 11. Assume solution density = 1 and concentrations equal activity. Use equilibrium constants from Table 5.4.

$$K_1 = \frac{[H^+] * [HCO_3^-]}{[H_2CO_3]} = 10^{-6.38}$$

$$K_2 = \frac{[H^+] * [CO_3^{2-}]}{[HCO_3^-]} = 10^{-10.38}$$

$$[HCO_3^-] = 200 \text{ mg/l} = 200/61.019/1000 \text{ M} = 10^{-2.48} \text{ M}$$

$$[H^+] = 10^{-11}$$

$$[CO_3^{2-}] = \frac{10^{-10.38} * 10^{-2.48}}{10^{-11}} = 10^{-1.86} \text{ M}$$

$$= 10^{-1.86} * 60.011 * 1000 = 828.38 \text{ mg/l}$$

$$[H_2CO_3] = 10^{6.38} * 10^{-11} * 10^{-2.48} = 10^{-7.1} \text{ M}$$

$$= 10^{-7.1} * 62.027 * 1000 = 4.93 * 10^{-3} \text{ mg/l}$$

4. Prepare a graph of the solubility product of barite for a series of barium and sulfate concentrations. Use a K_{sat} of barite of 0.988E−10. Plot 6 to 20 values in the range 1E−6 to 50E−6 M Ba. This problem is accomplished most readily using a spreadsheet.

$$1E-6 \text{ M Ba} = 1E-6 * 1000 * 137.34 = 0.137 \text{ mg/l}$$

$$SO_4^{2-} = 0.988E-10/1E-6 \text{ M} = 98.8E-6 \text{ M}$$

$$= 98.8E-6 * 96.0616 = 9.49 \text{ mg/l}$$

Ba^{2+}M	Ba^{2+}mg/l	SO_4^{2-}M	SO_4^{2-} mg/l
1E−6	0.13	98.8E−6	9.49
2E−6	0.27	49.4E−6	4.74
3E−6	0.41	32.9E−6	3.16
4E−6	0.54	24.7E−6	2.37
5E−6	0.68	19.7E−6	1.89
6E−6	0.82	16.4E−6	1.58
8E−6	1.09	12.3E−6	1.18
10E−6	1.37	9.88E−6	0.94
12E−6	1.64	8.23E−6	0.79
15E−6	2.06	6.58E−6	0.63
20E−6	2.74	4.94E−6	0.47
30E−6	4.12	3.29E−6	0.31
35E−6	4.80	2.82E−6	0.27
40E−6	5.49	2.47E−6	0.23
43E−6	5.90	2.29E−6	0.22
45E−6	6.18	2.19E−6	0.21
47E−6	6.45	2.10E−6	0.20
49E−6	6.72	2.01E−6	0.19
50E−6	6.86	1.97E−6	0.18

The above results are plotted in Figure 5.3.

5. Plot on a vertical scale the pe range for the following reactions, assuming a pH of 7. Use concentrations and not activities for the calculations.

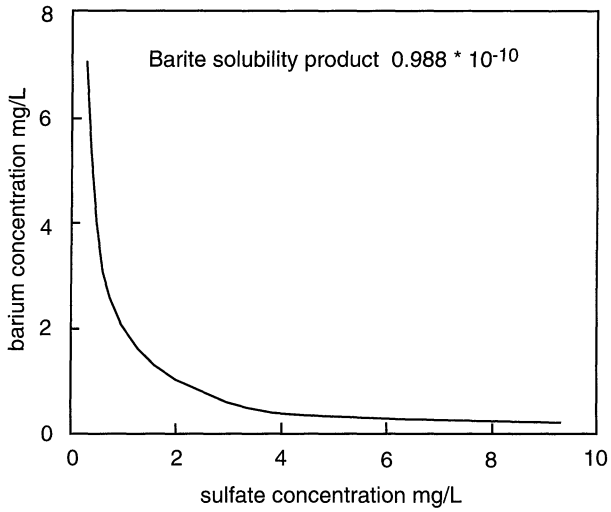


Figure 5.3. Barite solubility product for different Ba^{2+} and SO_4^{2-} concentrations (Exercise 4).

a. 0.01 mg/l dissolved oxygen pe = 12.9

$$\text{pe} = 21.5 + 0.25 \log[O_2] = \text{pH}$$

$$\log[O_2] = \log\left\{\frac{0.01}{1000 * 32}\right\} = -6.505$$

$$\text{pe} = 21.5 - \frac{6.505}{4} - 7 = 12.87$$

b. 10 mg/l dissolved oxygen pe = 13.6

$$\text{pe} = 21.5 + 0.25 \log[O_2] = \text{pH}$$

$$\log[O_2] = \log\left\{\frac{10}{1000 * 32}\right\} = -3.505$$

$$\text{pe} = 21.5 - \frac{3.505}{4} - 7 = 13.62$$

c. equal concentrations of ferrous and ferric iron pe = 13.0

$$\text{pe} = 13.0 + \log\frac{[Fe^{3+}]}{[Fe^{2+}]} = 13.0$$

d. 0.1 mg/l Mn^{2+} in contact with solid MnO_2 pe = 9.7

$$\text{pe} = 20.8 - 0.5 \log[Mn^{2+}] - 2\text{pH}$$

$$\log[Mn^{2+}] = \log\left\{\frac{0.1}{1000 * 54.94}\right\} = -5.74$$

$$\text{pe} = 20.8 + \frac{5.74}{2} - 14 = 9.67$$

e. 10 mg/l Mn^{2+} in contact with solid MnO_2 pe = 8.7

$$\text{pe} = 20.8 - 0.5 \log[Mn^{2+}] - 2\text{pH}$$

$$\log[Mn^{2+}] = \log\left\{\frac{10}{1000 * 54.94}\right\} = -3.74$$

$$\text{pe} = \frac{20.8 + 3.74}{2 - 14} = 8.67$$

f. equal concentrations of nitrate and ammonium ions pe = 6.2

$$\text{pe} = 15.0 + 0.125 \log \frac{[NO_3^-]}{[NH_4^+]} - 1.25\ \text{pH}$$

$$= 15 - 8.75 = 6.25$$

g. 0.01 mg/l H_2S and 200 mg/l SO_4^{2-} pe = −3.4

$$\text{pe} = 5.75 - 0.125 \log \left\{\frac{pH_2S}{[SO_4^{2-}]}\right\} - 1.25\ \text{pH}$$

$$\log[SO_4^{2-}] = \log\left\{\frac{200}{1000 * 96.06}\right\} = -2.68$$

$$\log(pH_2S) = \log(0.01 * H) = \log(0.01 * 3.1483E{-}04) = -5.50$$

$$\text{pe} = 5.75 - 0.068 - 0.335 - 8.75 = -3.40$$

h. 2 mg/l H_2S and 200 mg/l SO_4^{2-} pe = −3.40

$$\text{pe} = 5.75 - 0.125 \log \frac{pH_2S}{[SO_4^{2-}]} - 1.25\ \text{pH}$$

$$\log[SO_4^{2-}] = \log\left\{\frac{200}{1000 * 96.06}\right\} = -2.68$$

$$\log(pH_2S) = \log(2 * H) = \log(2 * 3.1483E{-}04) = -3.20$$

$$\text{pe} = 5.75 - 0.40 - 0.335 - 8.75 = -3.73$$

i. equal molar ratio of carbon dioxide and methane pe = −4.2

$$\text{pe} = 2.87 - 0.125 \log \frac{pCH_4}{pCO_2} - \text{pH} = 2.87 - 7 = -4.13$$

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CHAPTER 6

Geochemical Environments

INTRODUCTION

The purpose of this chapter is to acquaint the reader with some of the principles of ion mobility in the aquatic environment. Goldschmidt (1958) used the concept of ionic potential to help explain element behavior. Ionic potential is the ratio of the charge of the ion divided by the ionic radius. A threefold grouping was proposed. The first group consists of those elements with large radii and low charge which included the alkali metals, alkaline earth metals, ferrous iron, manganous iron, copper, and others which occur primarily as simple cations and which are usually mobile. The second group with intermediate ionic potentials are those elements that are readily precipitated as hydroxides, and include aluminum, ferric iron, titanium, and manganic manganese. The third group with high ionic potential occurs as very soluble and mobile oxy-anions and include the elements boron, carbon, phosphorus, and sulfur.

Whereas the above approach is useful in some cases, it does not take into account the chemical differences that occur in most groundwater environments. Garrels and Christ's (1965) fence diagram and the more elaborate geochemical barrier concept introduced by Perel'măn (1967, 1986) aid in estimating the mobility of some ions in the more complex geochemical environments.

The rocks comprising an aquifer, through which groundwater flows, usually contain substances that provide sinks (removal from the water) or sources (addition to the water) of hydrogen ions or electrons, or contain soluble salts which in turn determine the pH, redox potential, or ionic strength of the water passing through it. Changes in these parameters in turn may change the chemical composition of the water because of precipitation, solution, or change of valence. When such conditions exist, they may be referred to as geochemical barriers.

The quality of groundwater reflects the mineralogic composition of the rocks with which the water has been in contact. As water moves slowly through the subsurface its composition gradually changes, reflecting the increasing saturation of some ions or the end products of various rock-water interactions. Many of these reactions define the geochemical environment, including such parameters as pH, pe, and ionic strength, which in turn determine the adsorptive properties of the subsurface and the types of microbial processes that may occur, which, in turn, may affect the mobility of many trace elements.

FACTORS INFLUENCING THE MOBILITY OF TRACE ELEMENTS

Several processes may remove (or release) trace elements from (to) the aqueous phase.

pH-DEPENDENT REACTIONS

pH measures the ability of the environment to supply (or remove) hydrogen ions to (from) the solution. Examples of pH-dependent reactions are hydroxide precipitation and

carbonate formation. Trace elements, because of their low concentrations, may only be removed from the water if major components are being precipitated. For example, gallium probably would not be precipitated on its own due to its low natural abundance, but would be coprecipitated with aluminum. In general, many metals are dissolved at low pH values and precipitated at higher values. However, some may redissolve again at even high pH values. The pH of some common environments is shown in Figure 6.1. A variety of reactions may cause the release or removal of hydrogen ions, with the resultant formation of the following environments.

Strongly Acid—pH < 4

Strongly acid waters, with a pH of less than 4, include acid geothermal waters and waters resulting from the oxidation of pyrite.

Ellis and Mahon (1977) list two primary types of acid geothermal waters. One type results in acid sulfate water created by the oxidation of H_2S in condensed steam rising to the surface. The proposed reaction is

$$H_2S + 2O_2 \Leftrightarrow SO_4^{2-} + 2H^+$$

This was characterized by Truesdell (1984) as having a pH range from 1–5, and sulfate as the major anion with minor chloride. A second acid water type is one where hot water reacts with sulfur-containing rocks at depth. This proposed reaction is

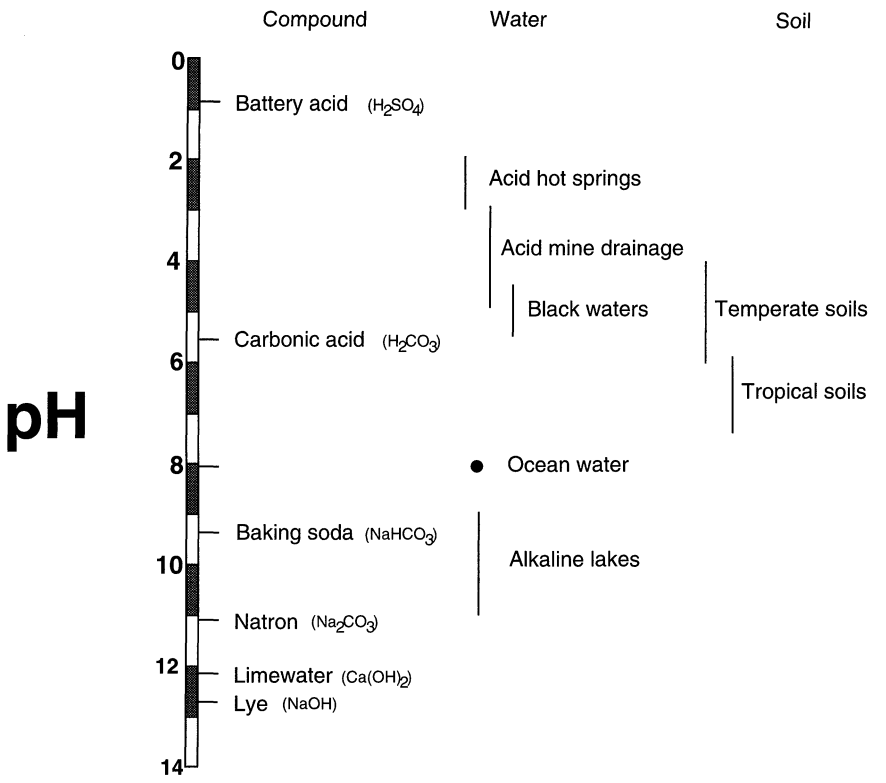


Figure 6.1. pH Ranges of common material and environments.

$$4S + 4H_2O \Leftrightarrow 3H_2S + 2H^+ + SO_4^{2-}$$

Truesdell (1984) describes this water as having a pH range from 1–5, and sulfate and chloride as principal anions.

Waters resulting from the solution of pyrite include acid waters draining coal mines and metallic ore deposits. In the absence of carbonate they will be high in sulfuric acid. They result from the oxidation of pyrite and other sulfides common in ore deposits and the pyrite or marcasite in coal mines. The acidity is the result of strong or mineral acids, weak acids being absent. The oxidation of pyrite may be written as:

$$FeS_2 + 3.5O_2 + H_2O \Leftrightarrow Fe^{2+} + 2SO_4^{2-} + 2H^+$$

$$2Fe^{2+} + 0.5O_2 + 2H_2O \Leftrightarrow Fe_2O_3 + 4H^+$$

$$Fe_2O_3 + H_2O \Leftrightarrow 2FeOOH$$

OR

$$FeS_2 + 3.75O_2 + 2.5H_2O \Leftrightarrow FeOOH + 2SO_4^{2-} + 4H^+$$

Another source of low-pH water is acid rain. Rain unaffected by man's activities will have a pH of 5.5–6.5 because of dissolved CO_2. Minor quantities of nitric acid may be present because of the oxidation of N_2 by lightning and forest fires. Anthropogenic causes of acid rain with pH ranges of 1.4–5 (Kahan, 1986) include the sulfur and nitrogen oxide gases released by the combustion of fossil fuels, forest fires started by man, and the release of ammonia by feces/urine decomposition, coal burning, and fertilizer applications. Ammonia is also released by the decomposition of organic matter. Ammonia may be oxidized to NO_x and then to HNO_3, but it is generally thought to be converted to the ammonium ion (NH_4^+) and washed out of the atmosphere, possibly as ammonium sulfate (Berner and Berner, 1987).

The combustion of fossil fuels consists of two different processes. The first is the oxidation of the sulfur and nitrogen contained in the fuel to SO_2 and NO_x, respectively. The second process is oxidation of atmospheric nitrogen to NO_x by the heat of the combustion (Berner and Berner, 1987). Other natural processes that may result in the formation of nitrogen oxides are denitrification and nitrification (Berner and Berner, 1987).

Once the nitrogen and sulfur gases are in the atmosphere they are readily oxidized to NO_x and SO_3 and thence to HNO_3 and H_2SO_4, respectively. The series of reactions are as follows:

$$H_2S \rightarrow SO_2 \rightarrow SO_3 \rightarrow H_2SO_4$$

$$NO \rightarrow NO_x \rightarrow HNO_3$$

$$N_2O_3 \xrightarrow[\text{stratosphere}]{} NO_x \rightarrow HNO_3$$

The various reactions of the different nitrogen gases are shown diagrammatically in Figure 6.2 (based on Berner and Berner, 1987).

In this environment clay minerals are destroyed, aluminum becomes mobile, and many trace metals, such as Cu and Zn, also become mobile. The concentrations of many of these species increase in the groundwater after rain, and their concentrations may vary seasonally. In such waters sulfate is usually much greater than chloride, and bicarbonate is absent.

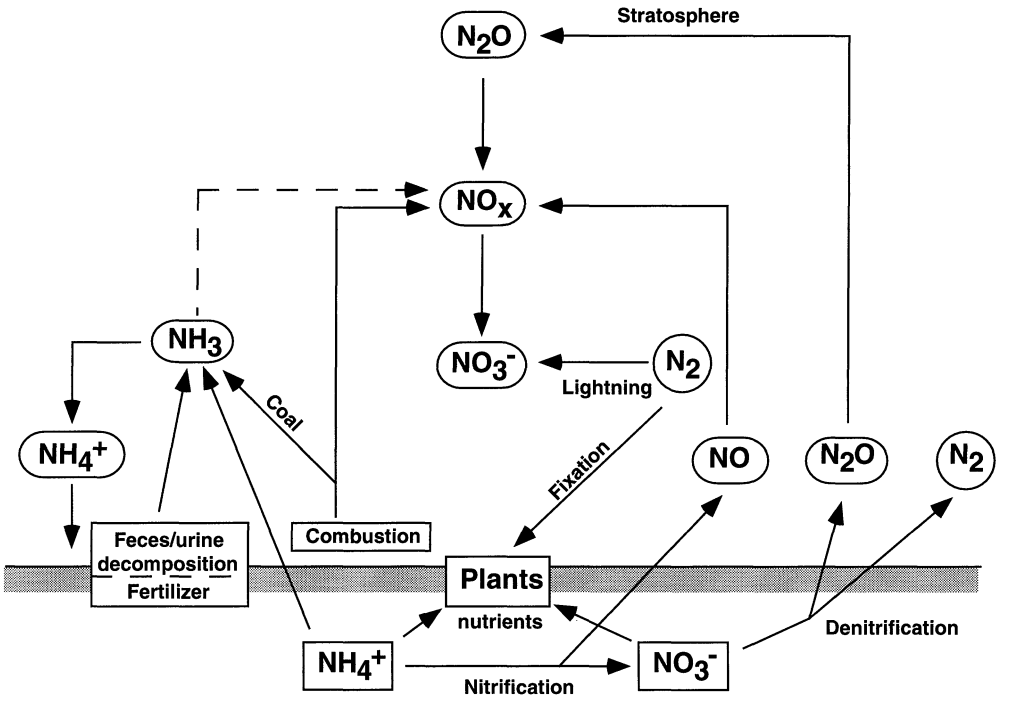


Figure 6.2. Simplified atmospheric nitrogen cycle. (After Berner and Berner, 1987.)

Moderately Acid—pH 4–6.5

The low pH in this environment is usually the result of weak acids such as carbonic acid (a result of precipitation) or dissolved organic acids (derived from decaying organic matter). The organic acids are common in podzolic soils (with a leached A− horizon). The high organic matter content is a result of the lack of microbiological decomposition. This situation occurs in cool coniferous forests, and results in the formation of large amounts of humic and fulvic acids from the partial breakdown of organic material. The replacement of cations by H^+ ions may also occur. Theses organic waters are also typical of typical waters, rivers, and lakes, that result from the solution of brown humic compounds that are derived from forests growing on poor soils of leached white sand. These have a low TDS and a pH of 4.6–5.2 (Payne, 1986). The Rio Negro is probably the most well-known river of this type.

Carbonic acids result from the solution of atmospheric CO_2 or from the solution of CO_2 generated in the soil zone as a result of the oxidation of soil organic material. The latter solution contains more CO_2 and often results in a higher pH than that formed from atmospheric CO_2 solution. The reaction may be written as follows:

$$CO_2 + H_2O \Leftrightarrow H_2CO_3$$

Under normal atmospheric conditions the pH is about 5.7 (Berner and Berner, 1987). In both these environments feldspars usually alter to clay minerals. Some trace elements may become mobile because of complexation with dissolved fulvic acid.

Neutral—pH 6.5–7.8

In this neutral environment bicarbonate is often the dominant anion, and the cations are mainly Ca and Mg. It is common in humid climates and results in karst topography, solution

cavities, and other karst features. In dry climates where karst topography is unlikely there may be a caliche layer in the soil and possible carbonate concretions. This environment is also a good buffer for acids, and extreme pH conditions are unlikely. In this environment manganese is often mobile as a bicarbonate, which on oxidation results in black stains of pyrolusite, MnO_2. The chemical equations for the environment may be written as:

$$CO_2 + H_2O \Leftrightarrow H_2CO_3$$

$$H_2CO_3 + CaCO_3 \underset{\leftarrow \text{ dry}}{\overset{\text{humid} \rightarrow}{\longrightarrow}} Ca^{2+} + 2HCO_3$$

In this environment Na^+, K^+, Ca^{2+}, Mg^{2+}, Cl^-, SO_4^{2-}, and HCO_3^- are common and reflect the composition of the rocks with which they are in contact.

Moderately Alkaline—pH 7.8–9

In moderately alkaline environments carbonates are precipitated, and many trace metals co-precipitate with them. Seawater has a pH of about 8.1 and is of this type of environment. These environments are often close to saturation with calcite. There is measurable carbonate (CO_3^{2-}) in the water, and silica is often soluble and mobile. As a result of such conditions silica may replace carbon in wood, yielding silicified or fossil wood.

Strongly Alkaline—pH > 9

This environment is rare under natural conditions, but occurs if Na, Ca, or Mg hydroxides are present. Alkaline lake waters containing dominant Na^+, CO_3^2, and HCO_3^- may form when the alkalinity of surface waters is greater than the Ca^{2+} and Mg^{2+} content. After precipitation of the alkaline earth carbonates, the water contains Na^+ as the dominant cation and bicarbonate as the dominant anion. Leaching of fresh cement may result in the presence of $Ca(OH)_2$ in water. This usually lasts only a short time before it reacts with the other cement constituents and forms the calcium aluminosilicates of the cement. It is often observed in freshly cemented wells.

pe (+/− pH)-DEPENDENT REACTIONS

Electrons may also be released under certain conditions. A measure of the electron flow in a solution is the pe value, which is the negative log of the electron concentration. It may also be considered as a potential, in which case it is called an Eh value, where $Eh = \frac{pe}{16.9}$. A major point of difference between pH and pe is that in order for electrons to be released from a reducing agent an electron acceptor must also be available. That is, the reactions must be coupled; for a reduction to take place an oxidation must also take place.

The ability of a natural environment to bring about an oxidation or reduction process is defined by what is called its redox potential. This measures the ability of the environment to supply electrons to an oxidizing agent or remove electrons from a reducing agent. Because many elements have more than one oxidation state and the stability of a particular oxidation state depends on the availability of electrons, the ratio of two such oxidation states of a particular element in a water will also depend on the environment.

The few common redox elements in natural waters shown also in Figure 6.3 are

O	—	O_2/H_2O
C	—	CO_2/CH_4
Fe	—	Fe^{2+}/Fe^{3+}; $Fe^{2+}/FeOOH$, $Fe^{2+}/Fe(OH)_3$
Mn	—	Mn^{2+}/MnO_2
S	—	SO_4^{2-}/H_2S
N	—	NO_3^-/NO_2^-; NO_3^-/N_2; NO_3^-/NH_4^+

Dissolved Oxygen

Dissolved oxygen may range in concentration from 8 to 10 mg/l in a cold, well-aerated stream (depending on the temperature), to zero in an anaerobic groundwater. Warm surface streams will have a dissolved oxygen content of 3–5 mg/l. The organic carbon in an aquifer

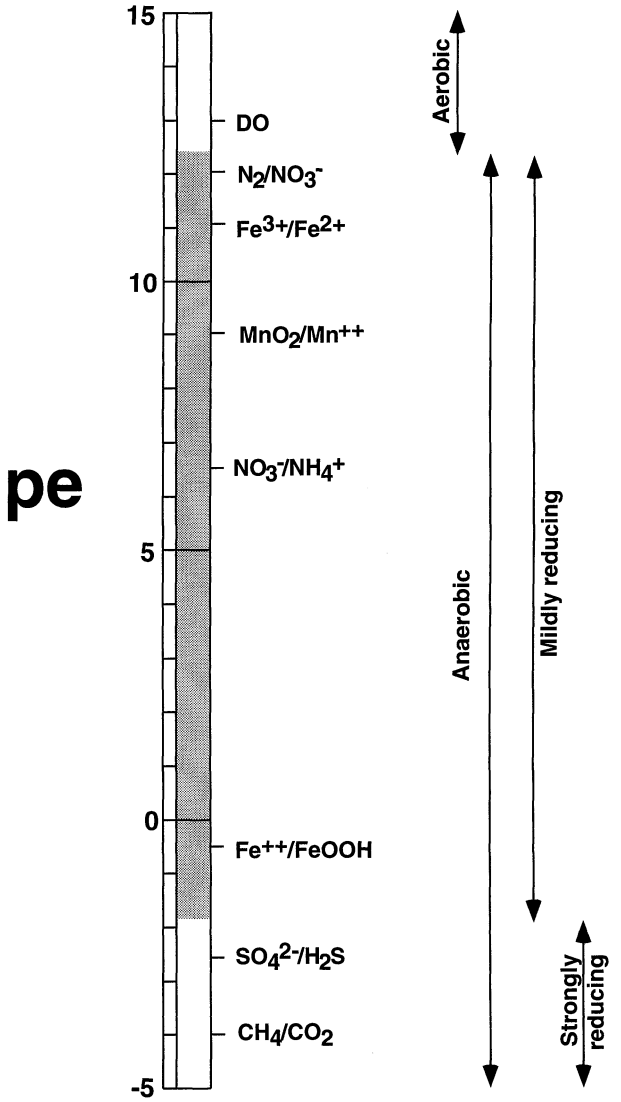


Figure 6.3. pe Range of common redox couples.

will react with dissolved oxygen, and as water moves from recharge to discharge in an aquifer a progressive decrease in dissolved oxygen may result. This organic carbon (natural organic carbon or natural organic matter, NOM) may be thought of as a redox "buffer". When the dissolved oxygen is depleted the water becomes anaerobic, and sometimes highly reducing such that H_2S, CH_4, or NH_4^+ may be present.

Dissolved Iron

Iron has a high natural abundance, is ubiquitous, and exists in two valence states, Fe^{2+} (ferrous), the reduced form, and Fe^{3+} (ferric), the oxidized form. Iron forms low solubility oxides, hydroxides, and sulfides. At a pH greater than 3, ferric iron is insoluble and forms colloidal hydroxides. This means that in the presence of dissolved oxygen or hydrogen sulfide iron forms insoluble compounds. In their absence, iron may occur in water in the ferrous state. Of great significance with respect to many trace metals is the fact that the iron colloids have high adsorption capacity. The transformation of ferric hydroxide to limonite and hematite is basically one of dehydration, namely:

$$2Fe(OH)_3 \rightarrow 2FeOOH + H_2O \rightarrow Fe_2O_3 + H_2O$$

Dissolved Manganese

The most common mineral species containing manganese in most oxidizing environments is MnO_2 (pyrolusite). Under mildly reducing conditions manganese will dissolve to form the mobile manganous ion Mn^{2+}.

Sulfur Species

The dominant sulfur species in most natural environments are sulfate (SO_3^{2-}) and sulfide (S^{2-}). The two most common minerals containing sulfur are pyrite (FeS_2) and gypsum ($CaSO_4 \cdot 2H_2O$). Pyrite is common in sulfide ore deposits and reduced rocks like coal and some shales. The microbiological oxidation of pyrite at the surface of the earth leads to the common problem of acid mine drainage, where the sulfur is present as sulfate (or sulfuric acid). The reduction of sulfate occurs, usually in the deeper groundwater zones, as a result of a microbiologically catalyzed reaction known as sulfate reduction, where the oxygen of the sulfate is utilized by the microorganism, and H_2S is released. Some of the organic carbon used as the source of energy for the reaction is converted to bicarbonate. The presence of detectable H_2S in water is an indication of strongly reducing conditions.

Nitrogen Species

The primary source of all nitrogen species is atmospheric nitrogen gas (N_2). This is converted to organic nitrogen by a process called nitrogen fixation. On the death of the plants the organic compounds are decomposed by microorganisms to inorganic ammonium salts (ammonification). These in turn are converted to nitrates by a process called nitrification. In environments depleted in oxygen, some microorganisms can use nitrate in place of gaseous oxygen to carry out their metabolic processes. The products of this reaction are nitrogen gas and/or nitrous oxide (N_2O). This process is called denitrification. Most of these reactions require either oxidizing or reducing conditions and thus may occur in different zones in the subsurface. pH may also be a critical parameter in these processes. Ammonia will only occur

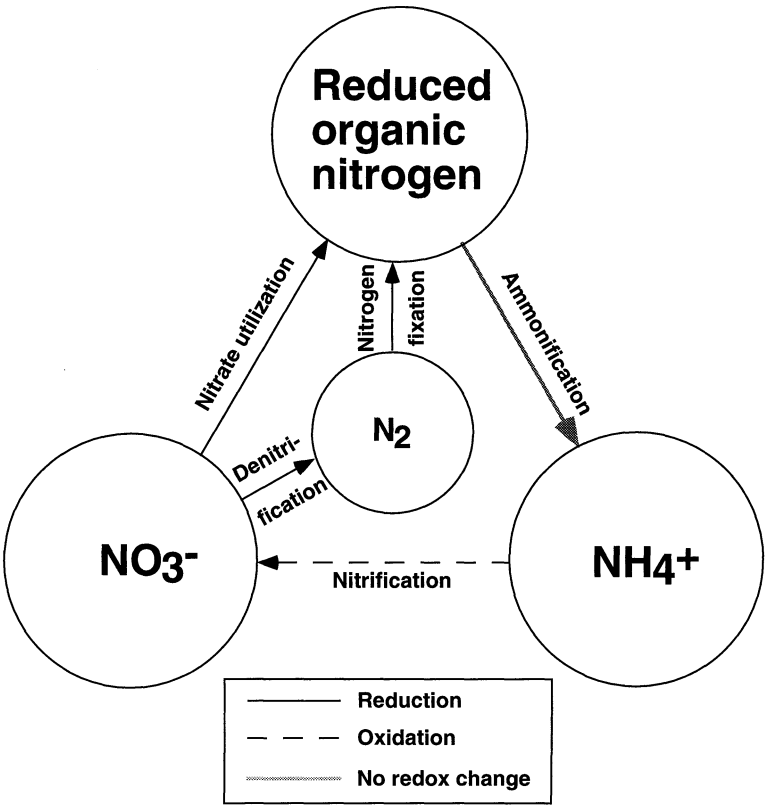


Figure 6.4. Simplified subsurface nitrogen cycle.

in very reduced waters where H_2S and/or CH_4 may also be present. The major parts of the nitrogen cycle are shown in Figures 6.4.

GEOCHEMICAL REDOX ZONES

It is possible to describe redox zones in a similar manner to pH zones (Hounslow, 1980). Such a classification allows us to consider a limited number of geochemical environments that may affect the mobility of trace elements in a predictable way. The zones, shown in Figure 6.5 and described below, are also of great importance in organic biodegradation because the degradation rates vary dramatically in the different zones. Also, as the redox condition of waters containing organic contaminants are seldom measured, estimates based on the following zoning are often useful to arrive at biodegradation rates. These zones are described below.

Aerobic Waters

Aerobic waters by definition contain measurable dissolved oxygen, with H_2S and CH_4 absent. In this environment iron occurs as solid and gelatinous $Fe(OH)_3$, unless the pH is very low (pH $<$ 3). Ferric hydroxide may adsorb a number of trace metals such as arsenic. The dissolved oxygen will react with organic matter present in the environment, forming carbon dioxide. The reactions may be written:

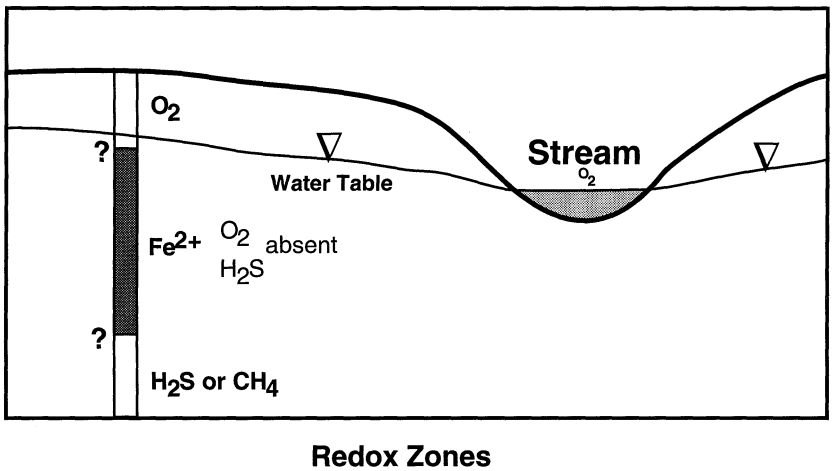


Figure 6.5. Redox zones. (Modified from Hounslow, 1980.)

$$C + O_2 \rightarrow CO_2$$

$$Fe^{3+} \rightarrow FeOOH \text{ or } Fe(OH)_3$$

Extremely oxidizing (corrosive) conditions may occur in a desert with little or no organic matter to reduce the oxygen content of the infiltrating water.

Anaerobic Waters (1)—Mildly Reducing

By definition, anaerobic waters are without oxygen. Two distinct kinds of anaerobic water may exist. The first is a mildly reducing or gley water. In addition to dissolved oxygen being absent, H_2S is also absent. Soluble Fe^{2+} is characteristic of these waters. Because ferric oxides/hydroxides are also absent, toxic trace metals tend to be mobile in this environment. Soluble arsenite, which is very toxic, is mobile under these conditions if sufficient arsenic is present. Also characteristic of this environment is the presence of Mn^{2+} and nitrate.

Anaerobic Waters (2)—Strongly Reducing

The second type of anaerobic water is strongly reducing with oxygen absent, but with H_2S and/or CH_4 present. If H_2S is present, insoluble sulfides such as FeS_2 (pyrite or marcasite) may occur and many coprecipitated heavy metal sulfides may be found with the pyrite. The H_2S is usually the result of sulfate reduction; however, if sulfate is low or absent methane may be the only gas present. In the absence of sulfides, iron commonly occurs as $FeCO_3$ (siderite). The reactions for sulfate reduction and fermentation (methanation) are shown below.

sulfate reduction

$$2C + SO_4^{2-} + 2H_2O \Leftrightarrow H_2S + 2HCO_3^-$$

$$Fe^{2+} \rightarrow FeS_2$$

fermentation or methanation

$$2C + 2H_2O \Leftrightarrow CH_4 + CO_2$$

$$Fe^{2+} + CO_2 \rightarrow FeCO_3$$

This environment is characteristic of coal swamps where bubbles of marsh gas (methane) are common. In many wells where the water contains sulfate, the introduction of organic material, such as plastic tubing, initiates sulfate reduction, which may or may not be characteristic of the aquifer.

A pe-pH diagram showing some common geochemical environments is shown in Figure 6.6.

SORPTION REACTIONS

Many ions may be removed from solution by adsorption or ion exchange onto clay minerals, amorphous hydroxides, or organic matter in the soil or sediment. Examples would be the adsorption of selenium onto iron hydroxide, or barium onto manganese dioxide. Other examples are Ca^{2+}/Na^{+} cation exchange on montmorillonite and F^{-}/OH^{-} anion exchange on kaolinite. The mobility of organics in the subsurface are also dependent on the presence and type of material in the aquifer.

The most common adsorbents in the subsurface are clay minerals, amorphous oxides and hydroxides, and NOM. These materials are abundant in soils, but are present in smaller quantities in deeper aquifers. The physical nature of subsurface adsorbents as well as their presence and distribution patterns may be highly significant. For example, humic acids may occur as spheres, sheets, or as bundles of fibers, depending on pH (Schnitzer and Khan, 1978). Grim (1968) describes electron microscope studies showing that kaolinite may often occur as hexagonal flakes, whereas halloysite is elongate and tubular, and illite, chlorite, vermiculite, and some smectites often occur as irregular flakes. On the other hand, elongate laths and fibers are the characteristic form of the attapulgate-sepiolite-palygorskite series and some smectites. The area to thickness ratio of smectites is also orders of magnitude greater than that for kaolinite. Further, the movement of water and the sorption of pollutants may both be strongly dependent on the shape and size of the voids in the subsurface materials. Similarly, amorphous hydroxides often occur as coatings on other minerals, a habit that allows them to exert chemical activity far out of proportion to their total concentration (Jenne, 1968).

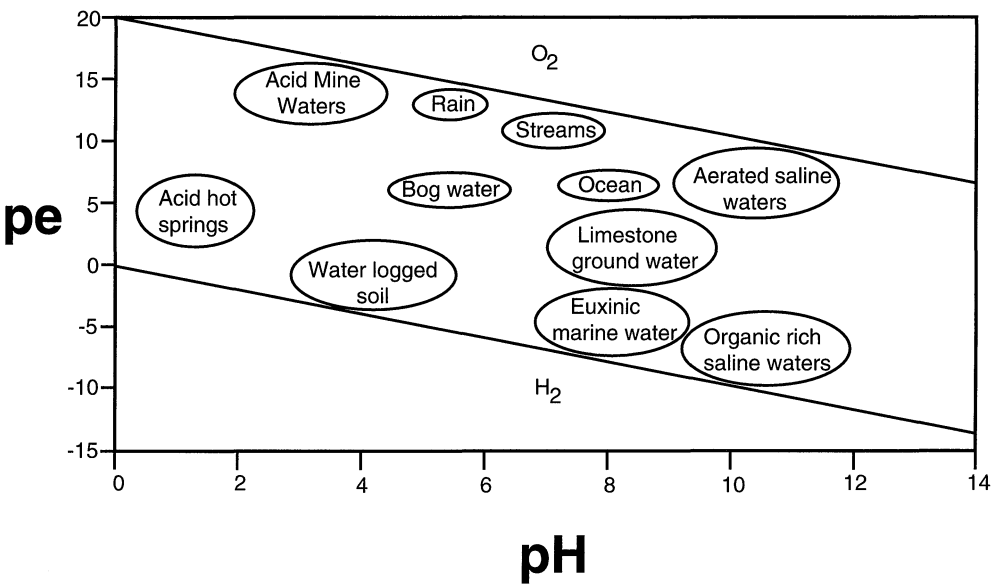


Figure 6.6. Natural environments.

The materials discussed above all have the capacity to influence the mobility of trace metals in solution. The dominant process depends on the type and relative amount of each of the adsorbents present.

Clay Minerals

Clay minerals, which are the insoluble products of chemical weathering of silicate minerals, are usually concentrated in the B soil horizon. They have the property of adsorbing certain anions and cations and retaining them in an exchangeable state. These exchangeable ions are held around the outside of the silica-alumina clay-mineral structural unit, and the exchange reaction generally does not affect the structure of the silica-alumina packet. The most common exchangeable cations are Ca^{2+}, Mg^{2+}, H^+, K^+, NH_4^+ and Na^+; frequently in that order of abundance (Grim, 1968). Different clay minerals are formed under different conditions, and although most are capable of adsorbing metals to some extent, this ability varies greatly. The principal factors affecting the ability of clay minerals to adsorb metals are particle size, surface area, moisture content, and degree of crystallinity (the more amorphous the clay, usually the greater the adsorption). Further, a specific clay will adsorb different elements to different extents, even under the same conditions. Grim (1968) emphasizes that there is no single universal replaceabilty series. Generally, the dissolved alkaline earth metals such as Mg^{2+}, Ca^{2+}, and Ba^{2+} are more strongly adsorbed than the univalent alkali metals such as Rb^+ and Cs^+; however, both groups are adsorbed by clays more frequently than base metals (Levinson, 1974).

Amorphous Hydroxides

The principal controls on the mobility of Co, Ni, Cu, and Zn in soils and freshwater sediments are the hydrous oxides of Mn and Fe (Jenne, 1968). He also established that the adsorption/desorption of these heavy metals occurs in response to the following factors:

1. Aqueous concentration of the metal in question
2. Aqueous concentrations of other heavy metals
3. pH
4. Amount and strength of organic chelates and other complex ions

In a study of heavy metal relationships beneath a municipal landfill in central Pennsylvania, Suarez and Langmuir (1976) found that the major source of heavy metals in these soils was hydrous manganese oxide. The manganese oxide exceeded iron oxide adsorption by at least a factor of 10 for some heavy metals, possibly because of the greater crystallinity of the iron oxides as well as the lower pH. They also noted that the metal oxides and trace metals existed predominantly in coatings on quartz grains and were not significantly concentrated in the < 15-μm fraction. These conclusions differ little from well-established geochemical data such as reported by Rankama and Sahama (1950), namely, that oxidate sediments rich in Mn commonly contain notable amounts of Li, K, Ca, Ba, B, Ti, Co, Ni, Cu, Zn, Tl, Pb, and W.

Amorphous oxides/hydroxides adsorb many compounds. Adsorption by Mn and Fe hydroxides is often greater than clays. Adsorption depends on metal concentrations, associated heavy metal concentrations, and the presence or absence of organic chelates. Often, adsorption by Mn is much greater than adsorption by Fe hydroxides, sometimes by ten times. This difference depends on the crystallinity of the material and on whether or not it occurs as coatings on quartz grains. Examples include the adsorption of selenite (SeO_3^{2-}) and molybdate (MoO_4^{2-}) by goethite, and the adsorption of barium (mineral wad) by Mn oxide.

Organic Matter

Opinions differ widely as to the role of organic matter in the adsorption of small amounts of heavy metals. That the organic layer of soil accumulates certain metals is not surprising, because the exchange capacity of humic materials can be as high as 500 meq/100 g, whereas clay minerals rarely exceed 150 meq/100 g (Levinson, 1974). Organic matter in swamps and bogs is also likely to show high metal values, although all metals are not necessarily adsorbed equally by organic matter. Horsnail and Elliott (1971) found that, in some swamps in British Columbia, Co and Mo were markedly enriched in organic swamp deposits, whereas Fe, Mn, Co, Ni, and Zn were not.

Takamatsu and Yoshida (1978), studying complexes of the divalent metals Co, Pb, and Cd with a variety of humic acids, found that the bonding is mainly through two −COOH (carboxylic acid) groups such as in the polycarboxylic acids and through −COOH and −OH (phenolic) groups. Saxby (1973) suggested that incorporation of a metal into a sediment may involve several processes, such as a reaction between a metal and organic in solution, followed by adsorption into clay minerals. Parfitt et al. (1977) showed that the principal mode of interaction between the hydrous oxides of iron and aluminum, on one hand, and fulvic and humic acid, on the other, is ligand exchange between the humate-carboxylate groups and the surface hydroxides of the hydrous oxides. Kodama and Schnitzer (1968) demonstrated that the amount of fulvic acid adsorbed by montmorillonite depends on the cation with which the montmorillonite was saturated. The actual isolation of naturally occurring clay-organic matter complexes has as yet met with limited success.

NOM has a cation exchange capacity of 500 meq/100 g compared to clay (maximum 150 meq/100 g). It contains humic acid-divalent metal complexes because of −COOH and −OH bonds. The reaction is between the humic-COOH and HO-metal hydroxide bonds. NOM is the major absorbent that influences the mobility or degree of retardation of synthetic organics in the subsurface. This is discussed in more detail in a later chapter.

Relative Importance of Adsorbates

The most commonly accepted relative adsorption sequence for heavy metals (from highest to lowest) is manganese oxide, humic acid, iron oxide, and clay minerals (Guy and Chakrobarti, 1975).

Adsorption Barriers

Adsorption barriers commonly result from the presence of four different kinds of adsorbents, namely, montmorillonite and kaolinite clays, ferric oxide/hydroxide, and organic matter.

Montmorillonite Clays

Montmorillonite clays absorb Ca^{2+} and Mg^{2+} under normal conditions and release Na^{+} into the water. This ion-exchange process is called natural softening. It is reversed by saline solutions, when sodium is adsorbed and calcium released. This may be called regeneration or reverse softening. The reaction may be written as:

$$Na_2\text{-clay} + Ca^{2+} \Leftrightarrow Ca^{2+}\text{-clay} + 2Na^{+}$$

Kaolinite Clay

Kaolinite reacts as an anion exchanger. Typically, it will adsorb phosphate, sulfate, and fluoride. In the latter case F^{-}/OH^{-} exchange will occur under acid conditions which are reversed at neutral pH.

Goethite (FeOOH)

Goethite is also an anion exchange adsorbent and commonly sulfate, selenate, and molybdate may be adsorbed. This adsorption may be reversed under reducing conditions.

Natural Organic Matter

NOM involves the metals in question bonding to humic/fulvic acids, where the strength of the adsorption is

$$UO_2 > Hg > Cu > Pb > Zn > Ni > Co$$

The adsorption is pH dependent and, for example, Pb is more strongly adsorbed under alkaline conditions than under acid conditions.

Remobilization of Heavy Metals

Sorption of heavy metals onto inorganic or organic substrates is often only a temporary condition; changes in geochemical parameters or the addition of organic or inorganic complexing agents may release the heavy metals in a slug that may be environmentally catastrophic. Forstner and Wittmann (1979) list five such types of reactions, described below.

Elevated Salt Concentrations

Elevated salt concentrations could lead to replacement of adsorbed heavy metals by alkali and alkaline earth metals, particularly from clays. Elevated salt concentrations may be caused by seawater encroachment, contamination by leakage from an upper or lower aquifer, or by increased salt contamination from the surface. Because of the preferred adsorption by clays of Na relative to heavy metals, the latter are likely to be released. Also, destabilization of colloids is another potential effect of high salt concentration, which could lead to the precipitation of materials such as metal-organic complexes.

Changes in Redox

Changes in redox conditions, such as a decrease in dissolved oxygen, could lead to the solution of iron and manganese hydroxides as well as their adsorbed heavy metals. The most common cause of a decrease in dissolved oxygen and thus a decrease in pe is the reaction of the oxygen with any organic matter that may be present. This could lead to the redistribution of iron and manganese in the subsurface and possibly the release of adsorbed heavy metals once adsorbed on these hydroxides, such as selenium or molybdenum. Further, the presence of H_2S could render many trace metals insoluble because of their precipitation as sulfides or coprecipitation with iron sulfide.

Changes in pH

A decrease in pH could lead to the dissolution of carbonates and hydroxides as well as decreased adsorption because of competition with the more strongly adsorbed hydrogen ion. As a general rule (Khalid et al., 1977), low pH and low pe in sediments tend to favor the formation of soluble species of many metals, whereas in an oxidized, nonacid system the slightly soluble or insoluble forms tend to predominate. The classic example of increasing the acidity of groundwater and surface water is acid mine drainage. Acid precipitation and

the surface introduction of acids such as pickling liquors to a disposal site (Pettyjohn, 1975) may also be primary causes in changes in the pH of ground or surface waters.

Complexing Agents

Increased amounts of natural or synthetic complexing agents entering the system could lead to the formation of highly stable heavy metal complexes that would otherwise be adsorbed to solid particles. The most common natural organic complexing agent is dissolved organic matter, which consists of the remains of biologically produced compounds of low molecular weight, principally fulvic acid. Synthetic organic compounds that have strong chelation capabilities are nitrilotriacetic acid, ethylenediaminetetracetic acid, and many others. These chelating agents of whatever origin will drastically change the adsorption properties of many heavy metals. Sholkavitz and Copland (1981) have shown that in surface waters Fe, Mn, Cu, Ni, Co, and Cd may be held in the dissolved phase by natural organic substances such as humic acids, between a pH of 3 and 9. However, when such a solution contacts a high concentration of salt, such as seawater, precipitation of some of these elements may occur due to the destabilization of the colloids.

Microbial Activity

Microbial activity can lead to the formation of highly soluble and highly toxic alkyl derivatives of a variety of heavy metals, such as methyl mercury. Microbial activity often has a significant effect on many of the above reactions. However, our knowledge of the full extent of the activity of microorganisms in the subsurface, especially the deeper subsurface, is limited. Forstner and Wittmann (1979) postulate three major processes that lead to the mobilization of heavy metals by microbial activity:

i. breakdown of organic matter to more soluble forms,
ii. changes in the geochemical parameters of the environment by microbial activity, and
iii. conversion of inorganic compounds into soluble metal-organic complexes.

The complexing of heavy metals by fulvic acid has been discussed above. In addition, Theis and Singer (1973, 1974) have shown that soluble humic acids produced by the microbial decay of humic material form complexes with ferrous iron, which inhibits the formation of insoluble ferric compounds under the appropriate oxidizing conditions.

The production of acid waters by bacteria-catalyzed oxidation of the sulfide components of mine dumps, known as acid mine drainage, is well known. In addition to the acid formation, the release and solution of many toxic heavy metals (and aluminum) is a major environmental problem. The release of acid and trace metals may continue for decades (Forstner and Wittmann, 1979). In waters of little buffer capacity (that is, in carbonate-poor areas), dissolved metals may be transported for great distances. The bacterial leaching of metals is also used industrially for the recovery of some metals, primarily Cu and U, from low-grade ore deposits or waste dump material. It has been found that pyrite not only provides the source of the acid, but also stimulates the bacterial oxidation of other sulfides.

A more subtle effect of microorganisms, at least in surface waters, is the alkylation of heavy metals. When uptake of a toxic metal occurs, microorganisms are often able to detoxify their environment through organometal transformation. This product, however, may be extremely toxic to higher organisms. This is particularly true of methyl mercury. Microorganisms do not seem to require mercury in their diet, but deal with it in this manner when it occurs in their food supply. The mechanism of biologic methylation is also effective in the formation of volatile compounds of Ag, Pb, and Se as alkyl arsines, tetramethyl lead, and

dimethyl selenite. Methylation of tin compounds can be catalyzed by some bacteria. Other metal alkyls, which are stable in water and can be synthesized by methylcobalamin reactions, include Te, Pd, Pt, Au, and Tl.

EXERCISES

Arrange in order of decreasing pe (giving your reasons) the following environments, and estimate the possible pH of each of them:

A. Water from a small mountain stream.
B. A swamp where bubbles of an odorless gas sporadically rise to the surface.
C. Groundwater containing 0.5 mg/l Fe^{2+}.
D. Water from a swamp in northern Canada.
E. Groundwater smelling of hydrogen sulfide.
F. Pore water from a deep lake sediment.
G. Lake water above a thermocline.
H. Lake water below a thermocline.

ANSWERS TO EXERCISES

A. Water from a small mountain stream.

The water would be cool and turbulent. It would contain close to the maximum dissolved oxygen possible and therefore be oxidizing. The pH would most likely be moderately acid because of dissolved CO_2.

B. A swamp where bubbles of an odorless gas sporadically rise to the surface.

The gas would most likely be methane (swamp gas) and the redox state of the water would be strongly reducing. The copious dissolved organic matter would probably result in a slightly acid water because of dissolved humic and fulvic acids.

C. Groundwater containing 0.5 mg/l Fe^{2+}.

The presence of ferrous iron would indicate the absence of dissolved oxygen and hydrogen sulfide and thus the water would be classified as mildly reducing. The presence of other dissolved metals in this water should also be anticipated. The pH of the water cannot be determined from these data.

D. Water from a swamp in northern Canada.

The cold climate would limit the decay of organic material and the amount of weathering. Thus the TDS of the water would be low. The organic matter would most likely have removed the dissolved oxygen and the water would be mildly reducing. The pH would probably be moderately acid because of the dissolved organic matter and the lack of bases in the water.

E. Groundwater smelling of hydrogen sulfide.

The presence of hydrogen sulfide indicated a strongly reducing water. The pH, however, is indeterminant.

F. Pore water from a deep lake sediment.

The sediment at the bottom of a deep lake is most likely very rich in organic matter, and depending on the presence or absence of sulfate in the water, either sulfate reduction or

methanation is likely. In either case the water is probably strongly reducing. The removal of CO_2 or the production of bicarbonate would probably lead to a pH close to 7.

G. Lake water above a thermocline.

The water would probably be expected to be somewhat oxygenated, although considerably less so than a stream. The pH would depend on the inflow to the lake, which is not described.

H. Lake water below a thermocline.

Below a thermocline the dissolved oxygen present before the thermocline formed would be removed by the rain of organic matter from above the thermocline. Mildly reducing conditions would generally be expected, although in some cases strongly reducing conditions may be possible. The pH is indeterminant without more information.

Aerobic waters—A, G
Mildly reducing—C, H, D
Strongly reducing—B, E, F

CHAPTER 7

Organic Chemistry Nomenclature

INTRODUCTION

Organic compounds are composed primarily of variable numbers of carbon and hydrogen atoms, usually with smaller numbers of oxygen, nitrogen, sulfur, phosphorus, and halogen atoms—chlorine, fluorine, and bromine. Other elements may be incorporated in organic compounds to form organometallic compounds, but those will not be discussed here. Although specific references are generally not practical in this chapter, the text "Nomenclature of Organic Compounds" by Fletcher et al. (1974) was relied on extensively when nomenclature problems arose.

The carbon atoms are joined to one another as chains, branched structures, or in rings. The carbon-carbon bonds may be single (sharing one electron pair), double (sharing two electron pairs), or triple (sharing three electron pairs). The most important ring structure, benzene, is one that consists of six carbon atoms and six hydrogen atoms in a planar ring. If a noncarbon atom replaces a carbon in a ring structure, the compound is called a heterocyclic compound. Most of the variation among organic compounds is caused by special groups of organic atoms attaching to the carbon atoms. They are called functional groups and contain at least one noncarbon atom. It is the presence of these groups that give organic compounds their unique properties. Organic compounds containing only carbon and hydrogen are called hydrocarbons. If they contain one or more halogen atoms they are called halogenated hydrocarbons. They may be divided into two groups, depending on whether the benzene ring is present or not. These are listed in Table 7.1.

EARLY ORGANIC CHEMISTRY

The term organic chemistry was originally used to designate those substances of plant and animal origin thought to be more closely related to one another than to subsıances of mineral origin. It was known that organic substances form CO_2 and H_2O when burned in air. The number of organic compounds was small and each was named individually. During the first half of the 19th century, most people thought that organic compounds could not be synthesized in the laboratory. Some of the major breakthroughs in organic chemistry include:

1828 Wohler converted ammonium cyanate (NH_4CNO—inorganic) into urea (H_2N-CO-NH_2–organic).
1831 First quantitative analysis of carbon and hydrogen.
1845 Kolbe synthesized acetic acid (CH_3COOH).
1866 Kekule proposed formula C_6H_6 for benzene.
1930 International Commission on the Nomenclature of Organic Chemistry. Called IUPAC nomenclature.

Table 7.1. Classification of Hydrocarbons

Benzene absent - aliphatic compounds
  branched or unbranch chains
    no double or triple bonds
    - saturated
    - paraffins
    double and/or triple bonds present
    - unsaturated
    double bonds
    - olefins
  cyclic compounds
    saturated - naphthenes
    unsaturated - cyclo-olefins
Benzene present - aromatic compounds
  one benzene ring
  - substituted benzenes
  two or more benzenes fused (or sharing carbon atoms)
  - polyaromatic hydrocarbons (PAH), or
  - polynuclear aromatics (PNA)—seldom used
  two benzene rings joined by one C–C bond
  - biphenyls
  three benzene rings each joined by one C–C bond
  - terphenyls

The separation of organic and inorganic chemistry remains today. There are many more carbon compounds than there are compounds of all other elements combined, at present count approximately 9 million.

BONDING

Most matter consists of groups of atoms joined by chemical bonds where only the outer part of the atoms are in contact. These are called the valence electrons. They may be represented by Lewis symbols in which the atomic symbol is surrounded by a number of dots representing the outer shell of electrons. Examples are Ca: and Na·.

Several types of bonding that may be distinguished.

Ionic bonds are formed where one or more electrons are transferred from the valence shell of one element to the valence shell of another. Attraction takes place between ions of opposite charge—one atom loosing electron(s), yielding a cation, and the other atom gaining electron(s), yielding an anion. In ionic reactions large numbers of atoms are involved. An ionic solid does not contain discrete molecules, but does contain atoms packed so that the attractive forces are maximized and repulsive forces are minimized. For example, in LiF each of many lithium atoms is surrounded by six fluoride ions.

The Octet rule states that an atom tends to gain or lose electrons until there are eight electrons in its outer shell, thus attaining a stable, inert gas configuration. Exceptions to this rule include some of the transition elements. Ionic solids are dissociated (separated) by water dipoles.

Covalent bonds result from the equal sharing of electrons, for example, two atoms of the same element such as Cl_2 and H_2. If the energy is measured as two hydrogen atoms brought together, a decrease in energy occurs as the electrons approach one another until a minimum energy is attained. This distance of minimum energy is the bond distance. At closer distances the energy rises abruptly because of the repulsion between the nuclei. Covalent compounds are molecules held together by strong intramolecular forces, and not, as commonly occurs in inorganic chemistry, an ionic lattice. These forces must be distinguished from the intermolecular forces holding the molecules together in either the liquid or solid state.

Polar covalent bonds lie between the above extremes. Electrons are shared unequally by the adjoining atoms, which results in molecules with positive and negative ends (often called dipoles).

Electronegativity is a measure of the ability of an atom to attract shared electrons in a structure; the greater the difference in electronegativity of two bonded atoms, the more ionic (polar) the bond.

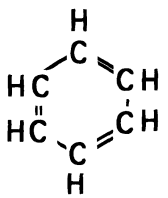
BONDING OF ORGANIC COMPOUNDS

Single bonds such as C-C or C-H result when a pair of electrons shared between two carbon atoms or one carbon and a hydrogen atom. These bonds are concentrated at, and are symmetrical about, an axis joining the two atoms. The resulting compounds are a series of organic compounds called saturated hydrocarbons or paraffins.

Multiple bonds are the result of sharing more than one pair of electrons between two atoms. Double bonds are the sharing of two pairs of electrons and triple bonds are the sharing of three pairs of electrons. The hydrocarbons containing multiple bonds are called unsaturated compounds, whereas those with only single bonds are called saturated compounds. In multiple-bond compounds one pair of electrons is found between the two atoms, but the other pair or two pairs of electrons are found perpendicular to this axis in lobes extending above and below the axis. This sideward overlap prevents rotation around the two-atom axis.

Aromatic compounds are a particular group of organic compounds, usually made up of six carbon atoms forming a planar ring. In older texts they were thought to be rings with apparent alternating single and double bonds. In fact, the second pair of electrons associated with the double bond of each carbon is "delocalized". It may be thought of as spreading and sharing around the ring. This results in a greater stability than any similar structure with normal unsaturated bonds.

An example is benzene, with a molecular formula C_6H_6. It is a planar molecule with a ring structure where each carbon is bonded to two other carbons and one hydrogen. It cannot be adequately represented by a single structure. It is currently explained by the resonance hybrid theory, which proposes a combination of two structures. Each bond is a cross between single and double bond, that is, a hybrid between two structures. The six-carbon structure, or benzene ring, is represented by an outer hexagon and an inner ring representing the delocalized electron pairs. In older texts it is shown as a hexagon with alternating single and double bonds.



NAMING ORGANIC COMPOUNDS

The primary problem faced by hydrogeologists and other non-chemist environmental scientists in discussing organic pollutants is twofold. First, many have not had a formal course in organic chemistry, and second, the large number of names that may be used to refer to one compound is confusing. The latter problem is further complicated by the fact that acronyms and trade names are used frequently.

Many organic compounds that have been known for a long time have one or more common names: an older systematic name and a more modern systematic (IUPAC) or Chemical Abstracts (CAS) name. Also, most complex compounds such as pesticides are referred to by common names or trade names because of the complexity of their systematic name and also for marketing purposes.

One may compare the naming of a person and an organic compound as follows:

Person		Organic compound
Bluey	Common name	PERC
Bill Smith	Semisystematic name	Perchloroethylene
William A. Smith	Systematic name	Tetrachloroethene
SS# 123-45-6789	Unique number	CAS # 127-18-4

The systematic name of an organic chemical is the International Union of Pure and Applied Chemistry name, or IUPAC name, and the number is the Chemical Abstracts System number. Most of the rest of this chapter will be devoted to the methods whereby systematic names may be derived. Common names and some semisystematic names will be noted in the following discussion. Because the key to most of the chemical literature is the Chemical Abstracts System, one must be able to locate the chemical of interest in these abstracts. For on-line searches the CAS number is of major importance. For paper searches the name used by Chemical Abstracts is important. This is usually, but not always the IUPAC name.

CHEMICAL ABSTRACTS REGISTRY NUMBERS

All new substances in the CAS database are given registry numbers. Each is a unique identification number, which overcomes the problem common in organic chemistry of a substance having many different names. The number has up to nine digits separated by hyphens into three groups. The first part of the number, starting from the left, has up to six digits, the second part two digits, and the third and final part a single check digit (Schulz, 1988).

CHECK DIGIT

The CAS number digits are designated from 1 to n (placement number) starting with the second to last number on the right and moving left. Each digit in turn is multiplied by its placement number. The products are added and the result is divided by 10. The remainder becomes the last figure of the number (check digit).

Example 1: 7732-18-5

7		7		3		2	−	1		8	−	5
6		5		4		3		2		1		check digit
42	+	35	+	12	+	6	+	2	+	8	=	105
$\frac{105}{10}$	has remainder which is the last number										=	5

Example 2: 75-15-0

7		5	−	1		5	−	0
4		3		2		1		
28	+	15	+	2	+	5	=	50
$\frac{50}{10}$	has remainder						=	0

Example 3:53469-21-9

5		3		4		6		9	−	2		1	−	9
7		6		5		4		3		2		1		
35	+	18	+	20	+	24	+	27	+	4	+	1	=	129
													=	9

$\frac{129}{10}$ has remainder

The CAS Registry Handbook Number Section starts with the 1965–71 volumes with numbers from 35-66-5 through 4599-99-9, and continues to the 1989 volume with numbers to 124535-32-6. Note, however, there are volumes entitled CAS Registry Handbook—Registry Number Update 1965–1989 that contain changes or deletions.

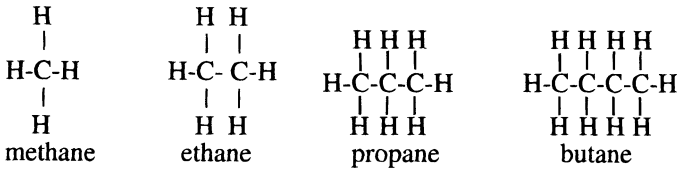
HYDROCARBONS

Hydrocarbons are compounds made up of carbon and hydrogen atoms. They may be combined as chains or cyclic compounds, and may be saturated (containing single bonds only) or unsaturated (with double and/or triple bonds). A more complete classification is given in Table 7.1. Early chemists usually named a compound on the basis of its history, such as methane, which has one carbon atom. Methyl alcohol was originally obtained by the destructive distillation (distillation in the absence of oxygen) of wood, and therefore was named wood spirits, methic—wine; hule—wood. Acetic acid was named after Latin acetum, for vinegar. Ethane, or ethyl, was named after ether—from Latin aether or sky. Propane is from propionic acid (first of fatty acids) from Greek pion or fat. Butane is from butyric acid (hydrolysis product of butter—from Latin buterium or butter). Hydrocarbons with five or more carbon atoms are named after the number of carbon atoms in the molecule by using Latin numbers. One exception is that in the older literature pentane derivatives were also called amyl from amyl alcohol, which was first obtained from starch, Latin amylum. These compounds also include most of the petroleum compounds that are designated LNAPL—light nonaqueous-phase liquids that commonly occur as contaminants floating on groundwater.

ALIPHATIC HYDROCARBONS

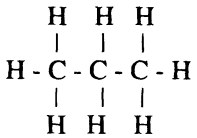
Aliphatic hydrocarbons include those organic compounds without benzene rings.

Saturated alkanes or paraffins have the molecular formula C_nH_{2n+2} and may be straight or branched chains. Methane is the simplest hydrocarbon—CH_4. From a three-dimensional aspect, it consists of a tetrahedron (opposite corners of cube) with bonds that are about 100% covalent. Methane is also known as fire damp, marsh gas, or natural gas. It is prepared in the laboratory by heating oxalic acid and by anaerobic fermentation of organic compounds. Other alkanes are ethane (C_2H_6), propane (C_3H_8), and butane (C_4H_{10}).



These compounds may be represented as a 3-D space-filling model (spheres), as ball and stick models, or in 2-D as:

1) an expanded molecular diagram,



2) a condensed structural formula,

$$CH_3—CH_2—CH_3$$

3) or as a molecular formula.

$$C_3H_8$$

Hydrocarbons are named by assigning a prefix that indicates the number of carbon atoms in the chain and a suffix indicating the degree of unsaturation. If saturated, that is, the compound contains only single bonds, then the ending is -ane. Examples are methane, ethane, propane, butane, and pentane, each designating saturated hydrocarbons with one, two, three, four, and five carbon atoms, respectively. A more comprehensive listing is given in Table 7.2. Compounds with double or triple bonds have endings -ene or -yne, respectively. A two-carbon compound with one double bond is ethene (old name ethylene). A three-carbon compound with one triple bond is propyne.

Isomers

Isomers are organic compounds with the same molecular formulas, but with different geometric structures. They are analogous to polymorphs in inorganic chemistry, e.g., calcite and aragonite have the same formula, namely $CaCO_3$, but different crystal structures.

Structural isomers are compounds with the same molecular formula, but with a different carbon skeleton, that is, amount of branching. They contain four or more carbons. For example, butane may consist of a normal (*n*-butane) straight chain or a branched (iso-butane) isomer. Another type of branching is designated neo. The numbers of possible isomers for a variety of carbon atoms is shown in Table 7.3. The compounds described above are straight-

Table 7.2. Naming Hydrocarbons

# C	Name	# C	Name	# C	Name
1	Methane	11	Undecane	21	Henicosane
2	Ethane	12	Dodecane	22	Docosane
3	Propane	13	Tridecane	23	Tricosane
4	Butane	14	Tetradecane	24	Tetracosane
5	Pentane	15	Pentadecane	25	Pentacosane
6	Hexane	16	Hexadecane	26	Hexacosane
7	Heptane	17	Heptadecane	27	Heptacosane
8	Octane	18	Octadecane	28	Octacosane
9	Nonane	19	Nonadecane	29	Nonacosane
10	Decane	20	Eicosane	30	Triacontane
36	Hexatriacontane	40	Tetracontane	50	Pentacontane
60	Hexacontane	70	Heptacontane	80	Octacontane
90	Nonacontane				

Table 7.3. Numbers of Hydrocarbon Isomers

Formula	# Isomers	Formula	# Isomers
CH_4	1	C_6H_{14}	5
C_2H_6	1	C_7H_{16}	9
C_3H_8	1	C_8H_{18}	18
C_4H_{10}	2	C_9H_{20}	35
C_5H_{12}	3	$C_{10}H_{22}$	75
$C_{20}H_{42}$	366,319		
$C_{30}H_{62}$	4,111,846,763		

From Richter, 1943.

or branched-chain compounds called aliphatic compounds. These alkanes are commonly called paraffins.

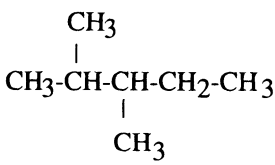
Older Nomenclature

Straight-chain compounds are called normal and are written *n*-propane. Branched compounds are iso- if the branch is one carbon from the end, and neo- if one carbon atom has four other carbon atoms attached to it. The IUPAC names and the older names are given for some compounds in Table 7.4.

IUPAC Naming of Alkanes

The basis for naming aliphatic organic compounds is to determine the number of carbon atoms in the longest chain and to specify the position of branches.

1. Find the longest unbranched chain, count the number of carbon atoms in this chain, designate by the appropriate stem, and add the suffix -ane. The names of the hydrocarbon stem for a variety of hydrocarbons are given in Table 7.2.

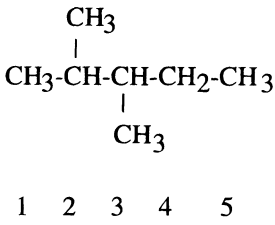


The longest chain contains five carbon atoms and are all single bonds; the stem is then pentane.

Table 7.4. Older nomenclature and IUPAC Names for Some Common Hydrocarbons

Formula	Old name	IUPAC name
$CH_3—CH_2—CH_2—CH_3$	*n*-Butane	Butane
$CH_3—CH_2—CH_2—CH_2—CH_3$	*n*-Pentane	Pentane
$CH_3—\underset{\displaystyle CH_3}{\underset{\vert}{CH}}—CH_3$	Isobutane	2-Methylpropane
$CH_3—\underset{\displaystyle CH_3}{\underset{\vert}{CH}}—CH_2—CH_3$	Isopentane	2-Methylbutane
$\overset{\displaystyle CH_3}{\overset{\vert}{CH_3}}—CH—CH_3$	Neopentane	2,2-Dimethylpropane
$\overset{\displaystyle CH_3}{\overset{\vert}{CH_3}}—CH—CH_2—CH_2—CH_3$	Isohexane	2-Methylpentane

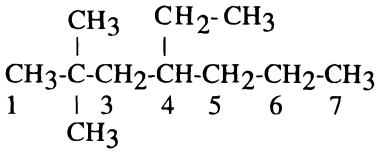
2. Starting at the end nearest a branch, number each carbon in sequence. This numbering should result in the lowest numbers possible for the side chain positions.



The name is then 2,3-dimethylpentane and not 3,4-dimethylpentane.

3. Identify the side chains by using the hydrocarbon name, removing the terminal -ane, and replacing it with -yl. Thus methane becomes methyl, ethane becomes ethyl, and propane becomes propyl. See Table 7.5. If two or more different side chains are present their names are listed in alphabetical order. However, the di- or tri- prefixes are discounted when deciding alphabetical order. Thus, ethyl is listed before dimethyl and iso is considered as part of the name.

An example of a more complex hydrocarbon is



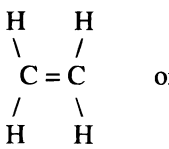
4-ethyl-2,2-dimethylheptane

Note that each methyl group must have its own locator number, that is, '-2,2-dimethyl' in the above example

Unsaturated hydrocarbons are those with double or triple bonds.

Hydrocarbons with double bonds are called alkenes (olefins). An example is ethene (ethylene) $CH_2=CH_2$. Those with triple bonds are called alkynes. An example is ethyne (acetylene) HC≡CH.

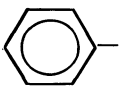
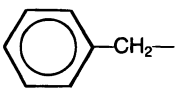
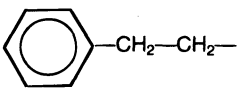
Double bonds result in a configuration where the three bonds around a carbon atom lie in one plane and are 120° apart. An example of a hydrocarbon with a double bond is ethene or ethylene (old name):



or $CH_2=CH_2$

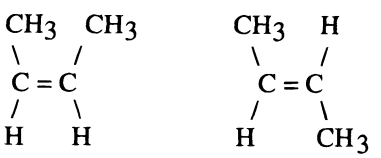
The double bond leads to the formation of an important group of isomers called geometric isomers. The presence of a double bond prevents free rotation between the two carbon atoms. This allows for two possible arrangements on either side of the double bond. If two substituent groups (groups that replace hydrogen atoms) are on the same side they are called cis- orientations, if they are on opposite sides they are called trans- orientations. The isomers have different physical and many different chemical properties. Sometimes the **Z** and **E** terminology is used. This comes from the German **Z**usammen—together, and **E**ntgegen—opposite. This terminology is often used if multiple double bonds occur in one compound.

Table 7.5. Hydrocarbon Combining Forms

Formula	Alternate formula	IUPAC name	Common name
CH_3—		Methyl	Methyl
CH_3—CH_2—	C_2H_5—	Ethyl	Ethyl
CH_2=CH—		Ethenyl	Vinyl*
CH_3—CH_2—CH_2—		Propyl	*n*-Propyl
CH_3 CH_3—CH—	or $(CH_3—)_2CH$—	1-Methylethyl	isoPropyl*
CH_2=CH—CH_2-		2-Propenyl	Allyl*
CH_3—CH_2—CH_2—CH_2—		Butyl	*n*-Butyl
CH_3 CH_3—CH_2—CH—		1-Methylpropyl	sec-Butyl*
CH_3 CH_3—CH—CH_2—	or $(CH_3—)_2CH—CH_2$—	2-Methylpropyl	isoButyl*
CH_3 CH_3—C— CH_3	or $(CH_3—)_3C$—	1,1-Dimethylethyl	Tert-Butyl*
	or C_6H_5—	Phenyl	Phenyl
	or $C_6H_5—CH_2$—	Phenylmethyl	Benzyl*
		2-Phenylethyl	2-Phenylethyl

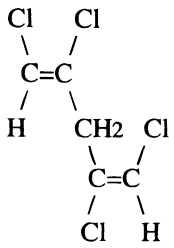
*May be used for the unsubstituted radicals only.

Examples:



cis-2-butene trans-2-butene

(Z)-2-butene (E)-2-butene



(1Z,4E)-1,2,4,5-tetrachloro-1,4-pentadiene

Triple bonds form a linear molecule, with the two single bonds at each end. An example is ethyne or acetylene: H—C≡C—H or CH≡CH. Most of these compounds are too unstable to be found in water.

IUPAC Naming of Alkenes and Alkynes

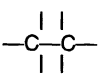
1. Find the longest chain containing the double or triple bonds. Name the stem to indicate the number of carbon atoms in the chain. A prefix locator number is used to indicate the carbon atom just before the double or triple bond. A suffix is used to indicate the degree of saturation.
2. Start numbering at the end with the closest double or triple bond and name the appropriate alkyl groups.
3. If both double and triple bonds are present, then number from the end nearest to the double bond and use the ending - enyne.

$HC{\equiv}C{-}CH{=}CH_2$ butenyne

$HC{\equiv}C{-}CH_2{-}CH{=}CH_2$ 1-penten-4-yne

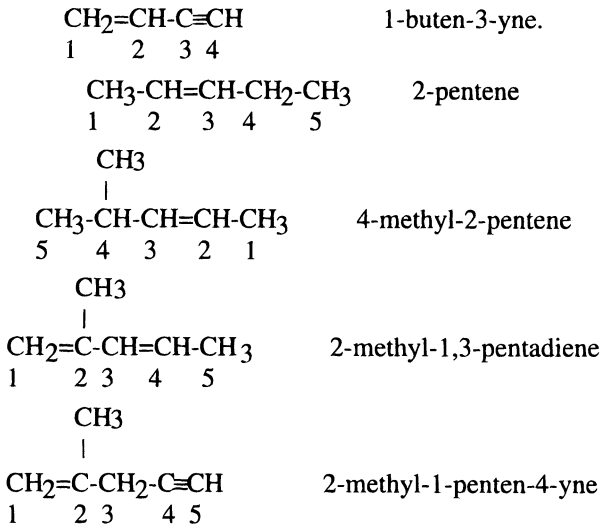
4. If more than one double bond is present, then the various locator numbers are indicated first and the ending is expressed as diene, triene, etc. If multiple double bonds and a triple bond are present, then the double bonds are designated in the main stem, dropping the -e and designating the triple bond by an extra suffix. The priority of the various bonds and branches is given in Table 7.6.

Table 7.6. Hydrocarbon Nomenclature Priority, from Highest to Lowest

Functional group	Prefix	Suffix
		-ene
—C≡C—		-yne
		-ane
—F	Fluoro-	
—Cl	Chloro-	
—Br	Bromo-	
—I	Iodo-	
$-CH_3$	Methyl-	
$-C_6H_5$	Phenyl-	

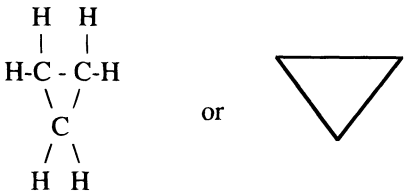
5. Unsaturated side chains are named by using the prefix of the side chain without the terminal -e and adding -yl. An example is ethene as a side chain becomes ethenyl.

Examples of unsaturated hydrocarbons:

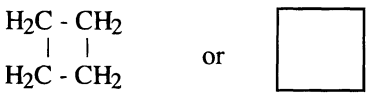


Cyclic Hydrocarbons

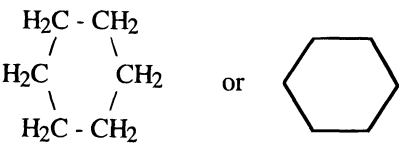
Cyclic hydrocarbons are similar to the chain hydrocarbons except they form ring structures. These must be distinguished from the aromatic rings (see following section). Cyclic hydrocarbons are not flat structures like the aromatic hydrocarbons. Substituted cyclic hydrocarbons are named so that each substituent is given the lowest possible locator number. The numbering starts with a double bond if present. These compounds are often represented by a single geometric shape, such as a triangle, square, or hexagon.



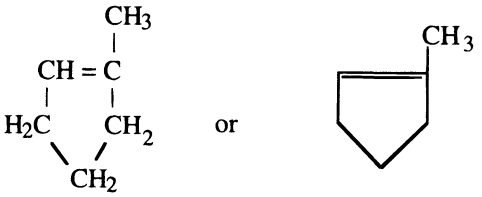
cyclopropane



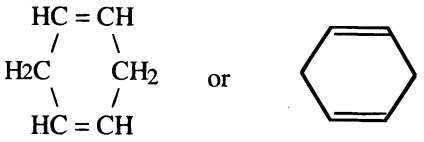
cyclobutane



cyclohexane



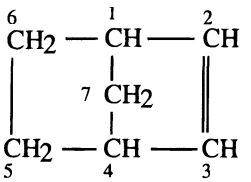
1-methyl-cyclopentene



1,4-cyclohexadiene

Multiple-Ring Cyclic Hydrocarbons

Cyclic hydrocarbons containing one or more pairs of atoms common to two or more rings are called bridged cyclic hydrocarbons. The carbon atoms common to two or more rings are called bridge carbons. The number of rings is defined as being equal to the minimum number of bonds that would need to be "cut" to convert the bridged ring system to an acyclic hydrocarbon having the same number of carbon atoms. They are designated as bicyclo-, tricyclo-, etc. The carbon atoms are numbered starting at one of the bridge carbons by the longest path to the second bridge carbon and back to the first by the longest unnumbered path. The numbering is then completed by the shortest path. The number of carbon atoms between each of the bridge carbon atoms is indicated in square brackets in descending order. In the example below carbons 1 and 4 are the bridge carbons. There are two carbons to the left of the bridge atoms, two to the right, and one vertically between them.



bicyclo [2.2.1]hept-2-ene

AROMATIC HYDROCARBONS

Aromatic hydrocarbons are compounds containing a benzene ring with six carbon atoms and six hydrogen atoms.

The benzene ring has six identical bonds, neither single nor double bonds. The ring has been drawn with alternating single and double bonds. In recent texts the benzene ring is drawn as a hexagon enclosing a circle, indicating the ring of delocalized electrons. This gives rise to the two symbols used for the benzene ring, namely:

In some literature it is designated as C_6H_5— when acting as a substituent.

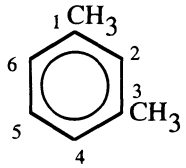
IUPAC Naming of Aromatics

The basis for naming monocyclic aromatic compounds is to specify what atoms are on each of the six carbon atoms making up the benzene ring.

Most monosubstituted derivatives of benzene are named as benzene derivatives. The two major exceptions are phenol and aniline, which will be discussed later. On the other hand, all the disubstituted benzenes are named as derivatives of benzene with locator numbers indicating the position of the substituted groups. Other methods of naming aromatics are in common use and must also be known. The three major alternative methods are

1. Numeric system (standard IUPAC).

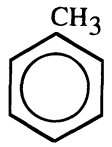
The benzene ring carbon atoms are numbered from 1 to 6, starting with one substituent and continuing either clockwise or counterclockwise so that the lowest numbers for each substituent are obtained. In naming complex compounds with functional groups (see later), the numbering starts with the functional group of highest nomenclature priority.



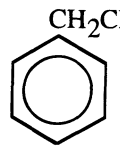
1,3-dimethylbenzene
not
1,5-dimethylbenzene

2. Specific names based on long usage.

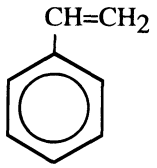
benzene



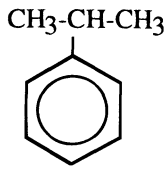
toluene
or
methylbenzene



ethylbenzene



styrene
ethenylbenzene

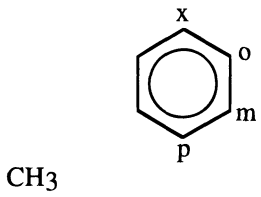


cumene
1-methylethylbenzene
isopropylbenzene
2-phenylpropane

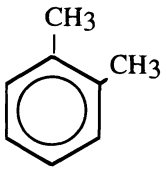
3. Based on the ortho, meta, and para system.

ortho-, abbreviated *o*-, (1, 2-),
meta-, abbreviated *m*-, (1, 3-), and
para-, abbreviated *p*-, (1, 4-), benzene (or benzene derivative).

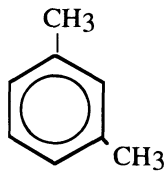
This system is commonly used for disubstituted benzene derivatives. It should be emphasized that the *o, m,* and *p* prefixes are lowercase letters.



x is any constituent
o ortho position
m meta position
p para position



1,2-dimethylbenzene
o-xylene

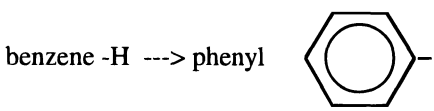


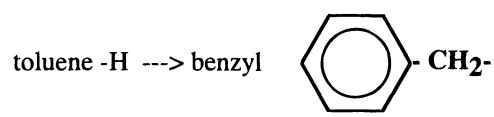
1,3-dimethylbenzene
m-xylene

1,4-dimethylbenzene
p-xylene

Aromatic Combining Forms

Combining names for two common benzene containing groups are





Aromatics Commonly Found in Groundwater

An important group of aromatic compounds includes benzene, toluene, ethylbenzene, and xylenes that are often called BTEX. They occur in gasoline and related petroleum fractions. Because of their high water solubility they present an immediate hazard to drinking water supplies. The solubilities of these compounds are given in Table 7.7. A summary of hydrocarbon nomenclature is given in Table 7.8.

Table 7.7. Solubility of some Common Aromatic Hydrocarbons

Aromatic hydrocarbon	Solubility in distilled water ppm	Source
Benzene	1696	(1)
Toluene	580	(1)
o-Xylene	171	(2)
p-Xylene	156	(2)
m-Xylene	146	(2)
Ethylbenzene	161	(2)

Note: Xylenes and ethylbenzene are all isomers.
(1) Keeley et al. 1988.
(2) Sutton and Calder, 1975.

Table 7.8. Hydrocarbon Nomenclature

SUMMARY: HYDROCARBON NOMENCLATURE

SATURATED	single bonds only
UNSATURATED	double or triple bonds
ALIPHATIC	branched or straight chains; cyclics without benzene
AROMATIC	contains at least one benzene ring

UNBRANCHED ALIPHATIC HYDROCARBONS

STEM-	designates number of carbon atoms
ENDING-	indicates degree of unsaturation
STEM + ANE	saturated
STEM + ENE	double bond
STEM + YNE	triple bond

BRANCHED ALIPHATIC HYDROCARBONS

CHOOSE: longest chain containing as many double and triple bonds as possible

COUNT number of carbon atoms in this chain to derive STEM
Use Greek or Latin names given in Table 7.2.

NUMBER carbon atoms from end closest to:
a. double bond
b. triple bond
c. side chain
PRIORITY is in the order given; a. highest and c. lowest

SIDE CHAIN nomenclature
STEM + YL; methyl, ethyl, propyl, butyl, pentyl, hexyl
LIST in alphabetical order not including di- or tri- prefix

DOUBLE or TRIPLE bonds
DESCRIBE placement using the number of the carbon atom preceding it.

CYCLIC HYDROCARBONS

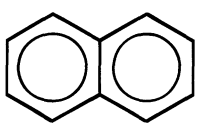
BASE on noncyclic name with CYCLO-prefix.
NUMBER from double bonds or substituents in that order.

AROMATIC HYDROCARBONS

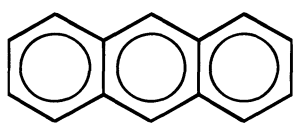
BASE on the benzene ring.
DESIGNATE a carbon atom of the benzene ring with a constituent as carbon number 1, and designate all other substituent groups by their appropriate locator number.

POLYAROMATIC HYDROCARBONS

Polyaromatic hydrocarbons (PAH) or polycyclic aromatic hydrocarbons contain two or more benzene rings fused together. An example is naphthalene. Each ring shares at least two carbon atoms of an adjacent ring. Polyaromatics are planar structures that when they become infinite in extent consist only of carbon atoms. This is in fact the structure of the mineral graphite. Many of this group of compounds occur in coal tars and are known carcinogens. Two common polyaromatics are



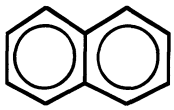
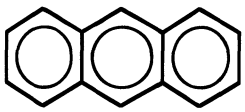
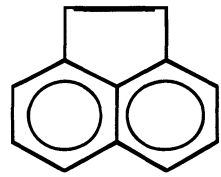
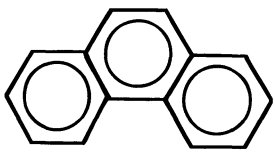
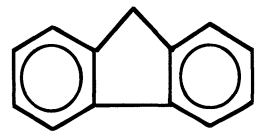
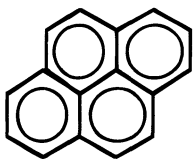
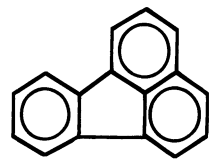
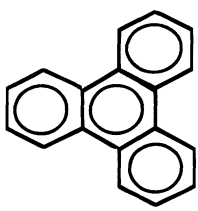
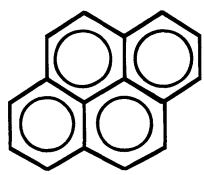
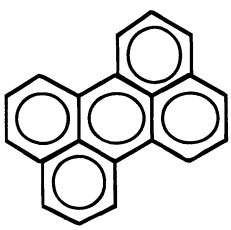
naphthalene



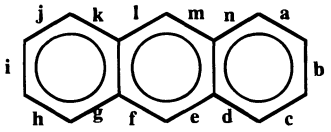
anthracene

A more complete list showing several configurations based primarily on Weast (1989) is given in Table 7.9.

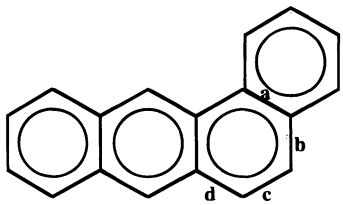
Table 7.9. Polyaromatic Hydrocarbons

Ring Types		
All 6 ring		**One 5 ring**
	Two Cycle	
 naphthalene		
	Three Cycle	
 anthracene		 acenaphthylene
 phenanthrene		 fluorene
	Four Cycle	
 pyrene		 fluoranthene
 triphenylene	 pyrene	
	Five Cycle	
 perylene		

For more complex polyaromatic compounds the sides of a base compound may be designated by lowercase letters, a–z, and the compound named by considering other groups as substituents on this. The names of the substituent rings are shortened from benzene to benzo-, anthracene to anthra-, and naphthalene to naphtho-. The side designations for anthracene are shown below as well as the more complex benzo[a]anthracene. Note that the side designator is enclosed in square brackets.



anthracene



benz[a]anthracene

HALOGENATED ORGANIC COMPOUNDS

The halogenated organic compounds discussed here include the halogenated hydrocarbons whose nomenclature is identical to that of the hydrocarbons from which they are derived, except that the halogen atoms are listed as substituents. These compounds include most of the solvents that are designated—dense nonaqueous-phase liquids (DNAPL). These commonly occur as contaminants in groundwater. Some of the more common acronyms referring to concentrations of organic halogen compounds in water are total organic carbon (TOC) and total organic halogen (TOX). The procedure for calculating the concentrations of TOC and TOX is shown in Table 7.10.

Table 7.10. Calculation of TOC and TOX

	Example 1	
Carbon tetrachloride, CCl_4		
Molecular weight	= 153.8 g	
Chloride	= 4*35.453	= 141.812 g
Carbon	= 1*12.011	= 12.011 g
Given 500 μg/l CCl_4		
TOC	= 500 * 12.011/153.8	= 39 μg/l
TOX	= 500 * 141.812/153.8	= 461 μg/l
	Example 2	
Chlorobenzene, C_6H_5Cl		
Molecular weight	= 112.56 g	
Chloride	= 1*35.453	= 35.453 g
Carbon	= 6*12.011	= 72.07 g
Given 500 μg/l chlorobenzene		
TOC	= 500 * 72.07/112.56	= 320 μg/l
TOX	= 500 * 35.453/112.56	= 158 μg/l

OLD NOMENCLATURE

Number of carbon atoms	Old name	IUPAC
	ALKENES	
2	Ethylene	Ethene
2	Vinyl	Ethenyl
3	Propylene	Propene
	ALKYNES	
2	Acetylene	Ethyne

Halogen Derivatives of Hydrocarbons

	Old name	IUPAC
1 Halogen/carbon atom	Methyl chloride	Chloromethane
	Ethyl chloride	Chloroethane
	Ethylene chloride	1,2-Dichloroethane
2 Halogens/carbon atom	Methylene chloride	Dichloromethane
	Ethylidene chloride	1,1-Dichloroethane
	Vinylidene chloride	1,1-Dichloroethene
3 Halogens/carbon atom: suffix-form	Chloroform	Trichloromethane
	Bromoform	Tribromomethane
	Iodoform	Triiodomethane
4 Halogens/carbon atom	Carbon tetrachloride	Tetrachloromethane
All hydrogen atoms replaced: prefix perchloro-	Perchloroethane	Hexachloroethane
	Perchloroethylene	Tetrachloroethene

HALOGENATED ALIPHATIC HYDROCARBONS

Many of the following compounds are priority pollutants or occur on the appendix IX Superfund list. The chlorofluorocarbon (CFC) is often referred to as Freon® in the United States. The Freon® number is derived by the following method:

Freon® numeric code for CFCs

Units digit - number of F atoms
Tens digit - number of H atoms + 1
Hundreds digit - number of C atoms − 1

Examples:

	# C − 1	#H + 1	#F	Freon #
CCl_3F	1 − 1	0 + 1	1	11
$Cl_2FC—CClF_2$	2 − 1	0 + 1	3	113
$CHClF_2$	1 − 1	1 + 1	2	22
CCl_2F_2	1 − 1	0 + 1	2	12

Saturated hydrocarbons
Methane derivatives

NAME	FORMULA
Chloromethane	CH_3Cl
Bromomethane	CH_3Br
Dichloromethane	CH_2Cl_2
Trichloromethane	$CHCl_3$
Tribromomethane (heavy liquid—S.G. 2.85)	$CHBr_3$
Bromodichloromethane	$CHCl_2Br$
Dibromochloromethane	$CHClBr_2$
Chlorodifluoromethane	$CHClF_2$
Dichlorofluoromethane	$CHCl_2F$
Tetrachloromethane	CCl_4
Trichlorofluoromethane	CCl_3F
Dichlorodifluoromethane	CCl_2F_2

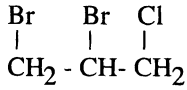
Ethane derivatives

Chloroethane	$CH_3—CH_2Cl$
1,2-Dichloroethane	$ClCH_2—CH_2Cl$
1,1-Dichloroethane	$Cl_2CH—CH_3$
1,2-Dibromoethane	$BrCH_2—CH_2Br$
1,1,2-Trichloroethane	$Cl_2CH—CH_2Cl$
1,1,1-Trichloroethane (methyl chloroform)	$CH_3—CCl_3$
1,1,2,2-Tetrachloroethane	$Cl_2CH—CHCl_2$
1,1,1,2-Tetrachloroethane	$Cl_3C—CH_2Cl$
Pentachloroethane	$Cl_3C—CHCl_2$
Hexachloroethane	$Cl_3C—CCl_3$
1,2-Dichloro-1,1,2,2-tetrafluoroethane $F_2ClC—CClF_2$	
1,1,2-Trichloro-1,2,2-trifluoroethane $Cl_2FC—CClF_2$	

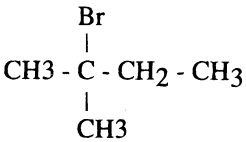
Miscellaneous saturated

2-Chloropropane $CH_3—CHCl—CH_3$

1,2,-Dibromo-3-chloropropane (DBCP)

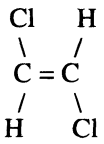


2-Bromo-2-methylbutane

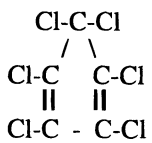


Unsaturated hydrocarbons

Chloroethene (vinyl chloride)	$CH_2=CHCl$
1,1-Dichloroethene (vinylidene chloride)	$CH_2=CCl_2$
1,2-*Trans*-dichloroethene (*trans*-1,2-dichloroethylene)	

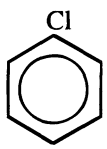


Trichloroethene (TCE)	$ClCH=CCl_2$
Tetrachloroethene (perchloroethylene) (PCE)	$Cl_2C=CCl_2$
1-Chloropropene	$ClCH=CH—CH_3$
1,2-Dichloropropane	$ClCH_2—CHCl—CH_3$
1,3-Dichloropropene (dichloropropylene)	$ClCH=CH—CH_2Cl$
Hexachlorobutadiene	$Cl_2C=CCl—CCl=CCl_2$
Hexachlorocyclopentadiene	

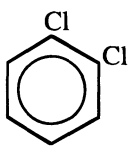


HALOGENATED AROMATIC HYDROCARBONS

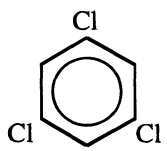
There are a large number of possible monocyclic aromatic hydrocarbons. Many are derived from benzene, and some from toluene. Some examples are given below.



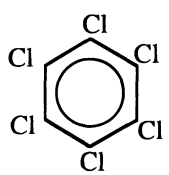
chlorobenzene



1,2-dichlorobenzene

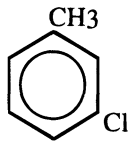


1,3,5-trichlorobenzene

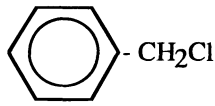


hexachlorobenzene

It is important to distinguish between substitution of hydrogens on the benzene ring and substitution of the hydrogens on the methyl group of toluene.



3-chlorotoluene



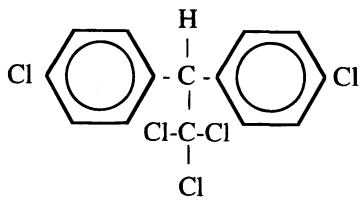
phenylchloromethane
benzyl chloride

HALOGENATED CYCLIC HYDROCARBONS

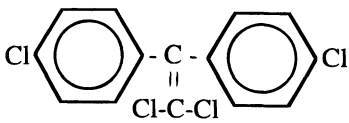
Hexachlorocyclohexane (alpha, beta, gamma, delta isomers)
lindane: gamma isomer
Benzene hexachlorides—acronym BHC—not aromatics!

Halogenated Insecticides (DDT Type)

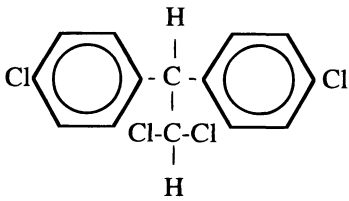
4,4′-DDT
Dichlorodiphenyltrichloroethane
1,1,1-Trichloro-2,2-bis(*p*-chlorophenyl)ethane



4,4′-DDE
Dichlorodiphenyldichloroethylene
1,1-Dichloro-2,2-bis(*p*-chlorophenyl)ethene
(degradation product of DDT)



4,4′-DDD
Dichlorodiphenyldichloroethane
TDE
Tetrachlorodiphenylethane
1,1-Dichloro-2,2-bis(*p*-chlorophenyl)ethane

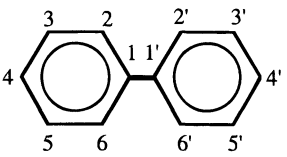


Halogenated Biphenyls

Polychlorinated Biphenyls (PCB)

Biphenyls consist of two benzene rings joined by a single bond. Substituents on each ring are designated by separate number and prime number, for example, 1 or 1′ designate

the same relative position on each of the two rings. Terphenyls consist of three benzene rings each joined by single bonds. In this case they may be ortho-, meta-, or para- configurations as shown below. Much of the following is from Waid (1986).



biphenyl

The 209 different PCB have the general molecular formula $C_{12}H_{10-n}Cl_n$.

Examples of some PCB are

Mono
2-, 3-, 4-
Di
2,4-, 2,2′-, 2,4′-, 4,4′-
Tri
2,4,4′-, 2′,3,4-
Tetra
2,2′,5,5′-, 2,2′,3,3′-, 2,2′,4,4′-, 2,2′3,5′-,
2,3′,4,4′-, 2,3′,4′,5-, 3,3′,4,4′-
Penta
2,2′,3,4,5′-, 2,2′,4,5,5′-
Hexa
2,2′,4,4′,5,5′-
Octa
2,2′,3,3′,4,4′,5,5′-

In the United States PCB is called Arochlor®—with a four-digit number following. The first two numbers indicate the type of molecule, e.g., 12 for chlorinated biphenyls, and 54 for chlorinated terphenyls. The last two numbers indicate the percent by weight of chlorine in the compound. For example, Arochlor® 1221 is a biphenyl (first two numbers 12) with 21% chlorine (last two numbers are 21).

PCB are chemically and thermally stable, extremely inert, and have excellent dielectric properties. They are also characterized by low volatility, low water solubility, and high resistance to chemical and biological breakdown. However, they are destroyed if held at a temperature of >800°C for a minimum of 10 seconds. PCB have been used in high-power transformers and capacitors, and as plasticizers in paint, plastics, and sealants. Also, they have been used as constituents in resins, inks, printing, copy paper, and adhesives.

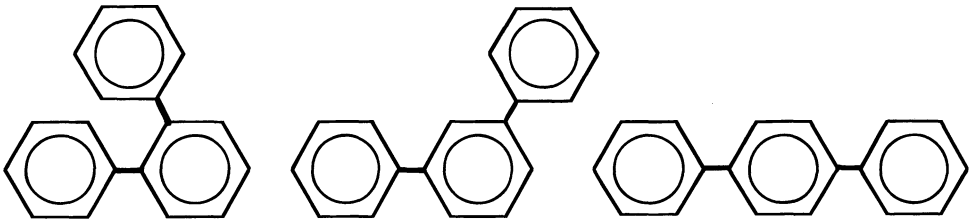
The first patent for the manufacture of PCB was in 1881 and the first commercial product prepared in the U.S. was in 1930. Peak production, however, occurred in 1970. The cumulative production to 1970 was approximately 1 million tons. After this time there was a voluntary cutback for environmental reasons related to their use in transformers, electric capacitors, vacuum pumps, and gas turbines.

In soil their half-life is about 5 years. Photodecomposition by ultraviolet light may produce polychlorinated benzofurans (PBF). PCB are soluble in nonpolar solvents and lipids. Thus they are rapidly adsorbed by fatty tissue, although uptake is also influenced by the stereochemistry of the molecule. PCB are often associated with bottom sediments and are thought to be adsorbed by clay soil organic matter complexes.

Small quantities of polychlorinated dibenzofurans (PCDF) and polychlorinated terphenyls (PCT) are present as occasional impurities.

Polychlorinated Terphenyls

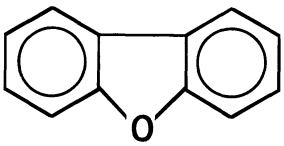
PCT are by-products of manufacturing processes.



o-terphenyl *m*-terphenyl *p*-terphenyl

Dibenzofurans

The most common hazardous impurities in PCB are the dibenzofurans (PBF), which are related to dioxins. They are more toxic than the parent PCB. PCB from different manufacturers have different toxicities based upon their PBF content. They are thought to be 1/2–1/4 times as toxic as dioxins.

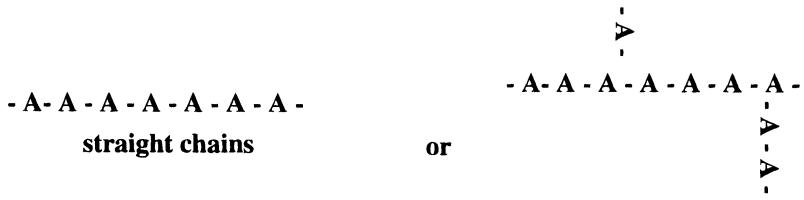


dibenzofuran

POLYMERS

Polymers are molecules of high molecular weight whose structures are composed of a large number of simple repeating units. Polymer chains may have identical composition, but differing molecular weights. Examples of man-made polymers are synthetic fibers (Orlon®, nylon, Dacron®), elastopolymers or synthetic rubbers (neoprene, butyl rubber), and plastics (vinyl, Lucite®, polyethylene). Natural polymers are either biopolymers such as polysaccharides, lignin, or proteins, or geopolymers such as kerogen.

The basic polymer repeating unit is usually formed from low-molecular weight compounds referred to as monomers, while the conversion process, monomer → polymer, is known as polymerization. Polymers may form straight chains or they may be branched, forming a network which extends in several directions.



Polymers may form from a single monomer (homopolymers) or from two or more different monomers (copolymers).

Homopolymer may be represented as: nA → n -(-A-)-; for example, polyethylene.
Copolymers may be represented as: nA + nB → n -(-A-B-)-; for example, polyester.
The copolymer structure may be either alternating or random.

Synthetic polymers may also be described on the basis of their reaction to heat. Thermoplastic polymers become plastic and are therefore capable of being molded when heated. Most simple polymers are of this type, for example, polyethylene. On the other hand, thermosetting polymers when formed cannot be softened when heated again. Examples of this group are Melamine® and bakelite. The essential difference between the two types is that the thermosetting types are cross linked, that is, each polymer chain is attached to adjacent chains.

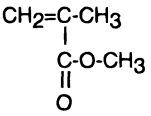
Classification — Polymers may be divided into two categories: addition polymers and condensation polymers. The former will be discussed here and the latter under esters.

Addition Polymers — All addition polymer units are alkenes. Addition polymers are formed by the addition of one polymer unit to another. The final structure incorporates all the atoms of the original structure. The characteristic reaction of alkenes is addition to the double bond, e.g., hydrogen, water, and halogens. If alkene molecules add to the double bonds of each other, an addition polymer is formed, thus (ethylene) $nH_2C{=}CH_2 \rightarrow$ (polyethylene) $-(-CH_2-CH_2-)-_n$ where n may be 1000.

$$n\ CH_2{=}CH \rightarrow -[CH_2-CH-]-$$
$$\qquad\quad\ |\qquad\qquad\quad\ |$$
$$\qquad\quad\ X\qquad\qquad\quad\ X$$

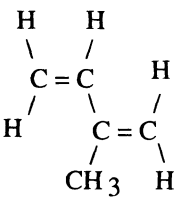
Also, vinyl monomer reacts in the same way:
Examples of common addition polymers are

Monomer	Polymer	Uses
Ethylene, ethene, $CH_2{=}CH_2$	Polyethylene	Plastic pipe, sheeting, containers
Propylene, propene, $CH_3{-}CH{=}CH_2$	Polypropylene (Herculon®)	Outdoor carpets, water pipe
Isobutylene, 2-methylpropene, $(CH_3{-})_2\ C{=}CH_2$	Polyisobutylene	Inner tubes (tires)
Vinyl chloride, chloroethene, $CH_2{=}CH{-}Cl$	Polyvinyl chloride (PVC®)	Garden hose, water pipe, shoe soles, records, floor covering, synthetic fibers
Acrylonitrile, vinyl cyanide, $CH_2{=}CH{-}CN$	Polyacrylonitrile (Orlon®, Acrilan®)	
Vinylidene chloride, $CH_2{=}C{-}Cl_2$	Self-adhering wrappers (Saran®)	
Tetrafluoroethylene, tetrafluoroethene, $F_2{-}C{=}C{-}F_2$	Polytetrafluoroethylene (Teflon®)	Lubricant, chemical resistant applications
Styrene, phenylethene, $C_6CH_5{-}CH{=}CH_2$	Polystyrene	Insulators, molded objects, foam/ styrofoam
Vinyl acetate, $CH_2{=}CH{-}O{-}\overset{\overset{O}{\|}}{C}{-}CH_3$	Polyvinyl acetate	Adhesives, chewing gum, fabric coatings
Methyl methacrylate, methyl 2-methyl-2-propenoate,	Polymethyl methacrylate (Plexiglass®, Lucite®)	glass substitute, transparent sheets and rods

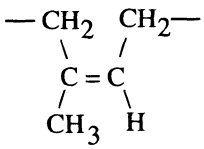


Isoprene, $CH_2=C—CH=CH_2$, written structurally, forms synthetic rubber, a cis-isomer polymer shown below:

isoprene

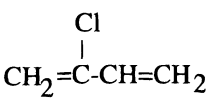


synthetic rubber
cis-isomer



The chlorinated isoprene is a monomer for neoprene.

chloroprene,
2-chloro-1,3-butadiene,



Neoprene®

Synthetic rubber, oil and grease resistant, soles of shoes

Examples of addition copolymers are

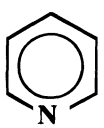
Vinyl chloride + vinyl acetate	→	vinylite—phonograph records
Vinyl chloride + vinylidene chloride	→	Saran®—Saran wrap
Acrylonitrile + butadiene	→	ABS—crash helmets, luggage

HETEROCYCLICS

When nitrogen, sulfur, oxygen, and phosphorus atoms join with carbon atoms to form a ring, they are called heterocyclic compounds. They have two or more types of atoms making up the ring. A large number of naturally occurring substances are heterocyclics. There are three common nomenclature conventions.

1. Common names.

Many heterocyclics have well-established common names.



pyridine

2. Replacement nomenclature based on carbon structure.

If heteroatoms are present in a compound they are denoted by prefixes ending in "-a", and if two or more are present they are cited in their order listed below. The location of the heteroatom is indicated by a number. Numbering starts with the heteroatom in single-ring compounds, although in double- or triple-ring compounds, such as naphthalene or anthracene, the numbering is based on the parent hydrocarbon.

Element	Valency	Prefix name
Oxygen	2	Oxa-
Sulfur	2	Thia-
Nitrogen	3	Aza-
Phosphorus	3	Phospha-

Using this system, pyridine would be called azabenzene.

3. Use of special endings.

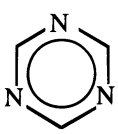
Endings are used to indicate the number of heteroatoms in the ring and whether or not the ring is saturated or unsaturated. The prefix name in the table above is used to indicate the type of heteroatom present.

Ring members	Containing nitrogen		Without nitrogen	
	Unsaturated	Saturated	Unsaturated	Saturated
3	-irine	-iridine	-irene	-irane
4	-ete	-etidine	-ete	-etane
5	-ole	-olidine	-ole	-olane
6	-ine	* see below	-in	-ane

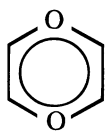
* perhydro ..... -ine

Examples

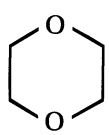
Name	# Heteroatoms	Saturation	Ring size
Triaz**ine**	3 N	Unsaturated	6 with N
Diox**in**	2 O	Unsaturated	6 without N
Diox**ane**	2 O	Saturated	6 without N



triazine

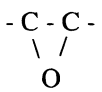


dioxin

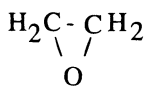


dioxane

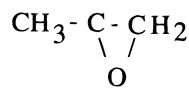
Oxygen heterocyclics — A special type of cyclic ether (see later) consisting of two carbons and one oxygen is called an epoxide. Their nomenclature is derived by naming the longest carbon chain and indicating by locator numbers the oxygen bonds. They may also be named using heterocyclic nomenclature as discussed above.



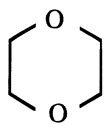
epoxide



1,2-epoxyethane
(ethylene oxide)
oxacyclopropane
oxirane

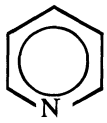


1,2-epoxypropane
(propylene oxide)
2-methyloxacyclopropane
methyloxirane

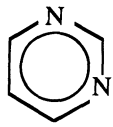


1,4-dioxane
1,4-diethylene dioxide
1,4-dioxacyclohexane

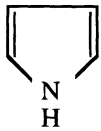
Nitrogen heterocyclics — Some simple nitrogen heterocyclics are given below.



pyridine
azabenzene



pyrimidine
1,3-diazabenzene



pyrrole
azacyclopent-2,4-diene
(1H-pyrrole)

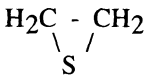
Pyrrole occurs as part of the porphyrin ring (tetrapyrrole) in chlorophyll and hemoglobin.

Sulfur heterocyclics and thiophenes — Examples of sulfur heterocyclics are

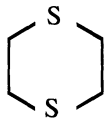
Thiophenes are unsaturated five-membered rings containing one sulfur and four carbon atoms. They are also examples of heterocyclics.

thiophene
thiacyclopenta-2,4-diene

Other sulfur heterocyclics include:



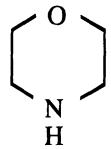
thiacyclopropane
thiirane



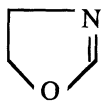
1,4-dithiacyclohexane

Mixed heteroatoms

Examples of heterocyclics with more than one type of heteroatom are



1-oxa-4-azacyclohexane
(morpholine)

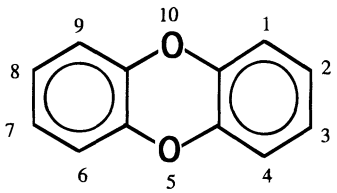


1-oxa-3-azacyclopent-2-ene
1,3-oxazolin-2-ene

Dibenzo-p-Dioxins

The chlorinated heterocyclics based on the dibenzo-*p*-dioxin structure are often considered as some of the most toxic organic compounds known.

The rings are numbered as shown below for indicating the position of substituents:



Dibenzo-*p*-dioxin

These are substituted at 1–4 and 6–9. This family of substituted dibenzo-*p*-dioxins was never intentionally released to the environment. They formed as a result of contamination of commercial chemical products. They have a very high toxicity and physiological activity. Tetrachlorodibenzo-p-dioxin (TCDD) is formed during the manufacture of 2,4,6-trichlorophenol from 1,2,4,6-tetrachlorobenzene. Dioxins are also found in the fly ash from municipal incinerators and in chlorine-bleached paper made from the Kraft process. There are 75 possible chlorinated dioxins, they have high thermal stability, and are not decomposed until the temperature exceeds 700°C. They lack reactive groups and are extremely lipophilic. Do not confuse with common solvent—dioxane.

RING SYSTEM DESCRIPTION

As the complexity of a ring system increases, finding information on the compound in Chemical Abstracts becomes almost insurmountable because of the difficulty in naming the compound. This complexity results from the number of rings and the number and diversity of heteroatoms. To overcome this problem, ring compounds have been assigned a simplified descriptor under which it is indexed (Schulz, 1988). There are three components to this index:

1. Number of component rings,
2. Ring size, given as the number of atoms in each ring arranged in order of size, and
3. Formula index of each ring.
   Formula for each ring contains:
   a. the number of carbon atoms and
   b. the number of heteroatoms in the ring listed in alphabetical order.

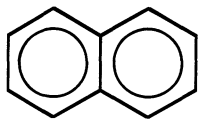
For rings of the same size, those with the smallest number of carbon atoms are listed first.

Examples:

Pyridine

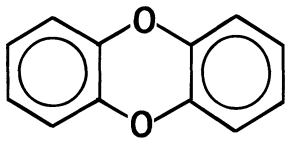
1. 1 (ring)
2. 6 (atoms)
3. C_5N

Naphthalene



1. 2 (rings)
2. 6,6
3. C_6 - C_6

Dibenzo[b,e][1,4]dioxin



1. 3 (rings)
2. 6,6,6
3. C_4O_2 - C_6 - C_6

The information obtained from Chemical Abstracts after such a search includes the CAS # and the CA preferred name.

OXYGEN FUNCTIONAL GROUPS

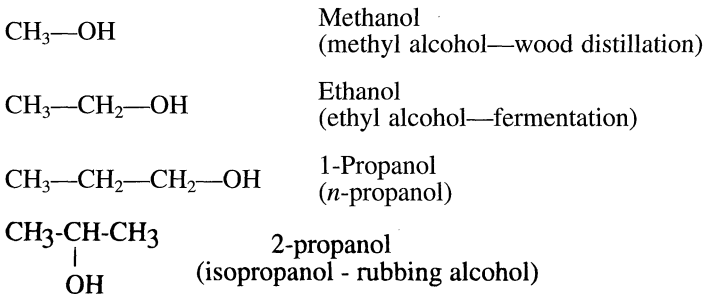
Organic chemicals can consist of compounds having a wide variation in the number of carbon atoms, sometimes with only minor variation in properties. However, major variations in activity result from the presence of special groups of atoms containing noncarbon atoms, such as oxygen, nitrogen, sulfur, or phosphorus. These groups of atoms are called functional groups.

Nomenclature — The following is a summary of IUPAC rules for naming organic compounds with functional groups:

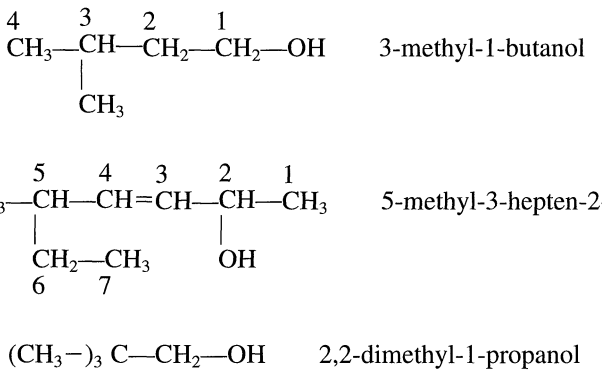
1. Select longest continuous carbon chain containing the functional group or groups.
2. Use the appropriate ending to indicate the principal functional group.
3. Number the chain starting at the end closest to the principal functional group.
4. Locate the functional groups by the number of the carbon atoms to which they are attached.
5. Name and locate by number any other atom or group of atoms attached to the selected chain.

ALCOHOLS

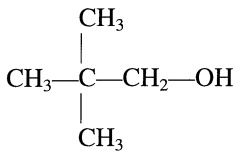
Alcohols contain the hydroxyl functional group, —OH. Their general formula being R-OH, where R is used to represent any carbon-containing group. Alcohols are named by changing the -e ending of the parent alkane to -ol. The position of the hydroxyl group is indicated by adding a number in front of the name. The older naming system for the simpler alcohols changes the alkane to an alkyl group and adds alcohol.



Examples of IUPAC nomenclature:

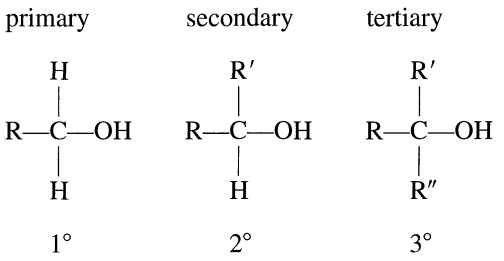


When written out in full the structure becomes:

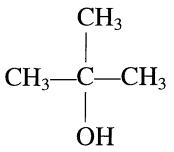


2,2-dimethyl-1-propanol

In older literature a distinction is also made between primary, secondary, and tertiary alcohols which depends on the number of other carbon atoms (1, 2, or 3) bonded to the carbon atom with the hydroxyl group.



Example:



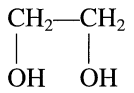
2-methyl-2-propanol
(tert-butyl alcohol)

Alcohols may also be classified based on the number of hydroxyl groups:

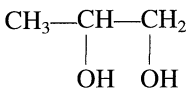
Number	Name	Example
1 hydroxyl group	Monohydric	Ethanol
2 hydroxyl groups	Dihydric	1,2-Ethanediol
3 hydroxyl groups	Trihydric	1,2,3,-Propanetriol
n hydroxyl groups	Polyhydric	Glucose

Common examples of these are

Dihydric:

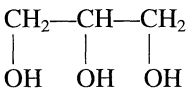


1,2-ethanediol (IUPAC)
(ethylene glycol)



1,2-propanediol (IUPAC)
(propylene glycol)

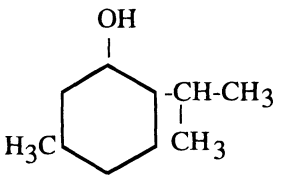
Trihydric:



1,2,3-propane-triol (IUPAC)
(glycerol or glycerine)

Polyhydric: sugars and their polymers such as starches and cellulose.

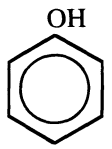
Cyclic alcohols



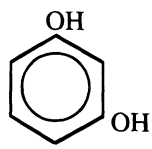
Menthol
(IUPAC: 2-isopropyl-5-methylcyclohexanol)

Aromatic alcohols

The mono-hydroxy substituted benzene is given the IUPAC name of phenol. However, the dihydroxy substituted benzenes are named after benzene.

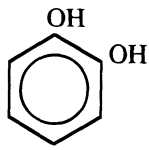


IUPAC: phenol



1,3-benzenediol
1,3-dihydroxybenzene
m-hydroxyphenol
resorcinol

4-methylphenol
p-cresol
p-hydroxytoluene

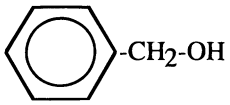


1,2-benzenediol
1,2-dihydroxybenzene
catechol

1,4-benzenediol
1,4-dihydroxybenzene
hydroquinone
quinol

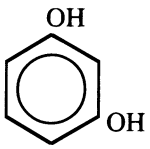
Industrially important alcohols and pollutants:

Formula	Common name	IUPAC name
$CH_2{=}CH{-}CH_2{-}OH$	allyl alcohol	2-propen-1-ol
$CH_3{-}CH(CH_3){-}CH_2{-}OH$	isobutyl alcohol	2-methylpropanol

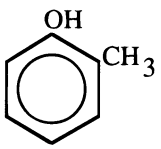


benzyl alcohol phenylmethanol

phenol phenol

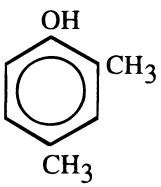


resorcinol 1,3-benzenediol



o-cresol 2-methylphenol

p-cresol 4-methylphenol



2,4-dimethylphenol

Chlorinated phenol derivatives of environmental importance:

2-Chlorophenol
4-Chloro-3-methylphenol (4-chloro-*m*-cresol)
2,3-Dichlorophenol
2,4-Dichlorophenol
2,4,6-Trichlorophenol
3,3,4-Trichlorophenol
2,3,4,5-Tetrachlorophenol
Pentachlorophenol
2,4-Dichloro-5-methylphenol

Chlorinated catechol (1,2-benzenediol) derivatives of environmental importance:

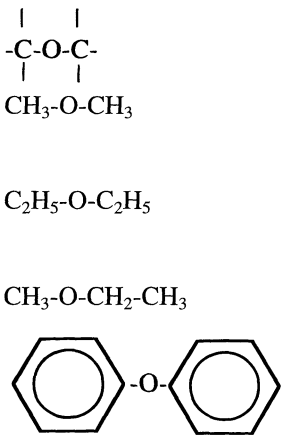
4,5-Dichlorocatechol	(4,5-dichloro-1,2-benzenediol)
4-Chloro-5-methylcatechol	(4-chloro-5-methyl-1,2-benzenediol)
3,4,5-Trichlorocatechol	(3,4,5-trichloro-1,2-benzenediol)
3,4,6-Trichloro-5-methylcatechol	(3,4,6-trichloro-5-methyl-1,2-benzenediol)
Tetrachlorocatechol	(tetrachloro-1,2-benzenediol)

ETHERS

The ether functional group is comprised of an oxygen atom bonded to two carbon atoms. They are commonly named by naming the two alkyl or aryl groups and adding the word ether. If both groups are the same, then its name is only given once and the presence of the second group is assumed. In the IUPAC system, the nomenclature is different. The smaller of the two groups is combined with the oxygen. As such it is located as a substituent group on the parent hydrocarbon. The CH_3O- group becomes a methoxy group and C_6H_5O- group is called a phenoxy group. If both groups on either side of the oxygen are equal, then the more complex ethers are termed **bis,** meaning twice. See Table 7.11 for the distinction between di, bi, and bis.

Table 7.11. Multiplying Prefixes

Numerical designation	Simple groups	Complex groups	Ring assemblies
2	di-	bis	bi-
3	tri-	tris	ter-
4	tetra-	tetrakis	quater-



or R-O-R' , ether formula

methoxymethane
methyl ether
dimethyl ether

ethoxyethane
ethyl ether ("ether" anesthetic)
diethyl ether

methoxyethane
ethyl methyl ether

phenoxybenzene
(di)phenyl ether

methoxybenzene
methyl phenyl ether
anisole

3-methoxypentane

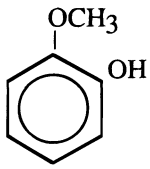
trimethoxymethane

Examples of some halogenated ethers are

$ClCH_2—CH_2—O—CH=CH_2$	1-ethenoxy-2-chloroethane chloroethylvinylether
$ClCH_2—O—CH_3$	chloromethoxymethane chloromethylmethylether

Guaiacol (methyl catechol ether or 2-methoxyphenol)* derivatives

Guaiacol is a degradation product of lignin. Therefore, guaiacol and chlorinated guaiacol derivatives may be expected in effluents from the pulp and paper industry.



Guaiacol
methyl catechol ether
2-methoxyphenol

3-Chloro-5-methylguaiacol
(6-chloro-4-methyl-2-methoxyphenol)

4,5-Dichloro guaiacol
(4,5-dichloro-2-methoxyphenol)

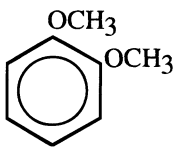
3,4-Dichloro-5-methyl guaiacol
(5,6-dichloro-4-methyl-2-methoxyphenol)

3,4,5-Trichloro guaiacol
(4,5,6-trichloro-2-methoxyphenol)

3,4,6-Trichloro-5-methyl guaiacol
(3,5,6-trichloro-4-methyl-2-methoxyphenol)

Tetrachloro guaiacol
(tetrachloro-2-methoxyphenol)

Veratrole (catechol diether or 1,2-dimethoxybenzene)* derivatives:

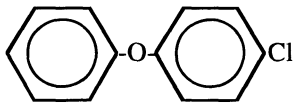


Veratrole
catechol diether
1,2-dimethoxybenzene

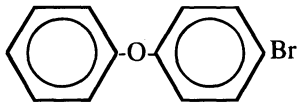
Trichloromethylveratrol
(trichloro-1,2-dimethoxybenzene)

Halogenated aromatic ethers:

*IUPAC



4-chloro-phenoxybenzene
4-chlorophenylphenyl ether



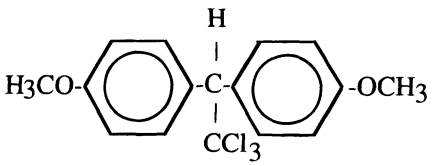
4-bromo-phenoxybenzene
4-bromophenylphenyl ether

The following examples illustrate the use of the Latin term "bis", meaning twice. Chloroalkyl ethers:

$CH_2Cl—O—CH_2Cl$	bis(chloromethyl)ether
$CH_2Cl—CH_2—O—CH_2—CH_2Cl$	bis(2-chloroethyl)ether
$CH_2Cl—CH(CH_3)—O—CH(CH_3)—CH_2Cl$	bis(2-chloroisopropyl)ether
$(ClCH_2—CH_2—O)_2—CH_2$	bis(2-chloroethoxy)methane

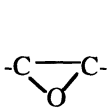
Pesticide:

methoxychlor

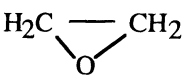


2,2-bis(4-methoxyphenyl)-1,1,1-trichloroethane

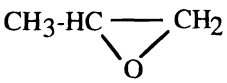
Cyclic ethers — A special type of cyclic ether consisting of two carbons bonded to one oxygen is called an epoxide. Their nomenclature is derived by naming the longest carbon chain and indicating the oxygen bonds by locator numbers. They may also be named by using heterocyclic nomenclature.



epoxide



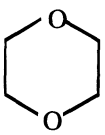
1,2-epoxyethane
(ethylene oxide)
(Oxacyclopropane)
(methyloxirane)



1,2-epoxypropane
(propylene oxide)
(2-methyloxacyclopropane)

See under heterocyclics

Priority pollutants — ethylene oxide or (1,2-epoxyethane)



1,4-dioxane
(1,4-diethylene dioxide)

These ethers may also be named as heterocyclic compounds where oxygen replaces a carbon in the structure:

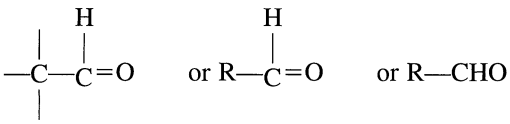
Ethylene oxide → oxacyclopropane
1,4-Dioxane → 1,4-dioxahexane

ALDEHYDES

Aldedehydes contain the carbonyl functional group that consists of an oxygen atom doubly bonded to a carbon atom.

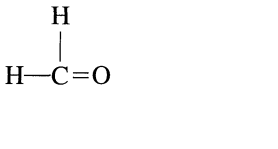
Carbonyl group —C=O

Aldehydes contain a terminal carbonyl group. That is, the carbonyl group is bonded to only one carbon atom.

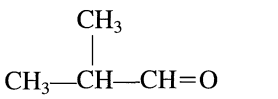


Aldehydes are identified by the suffix -al and the numbering starts from the carbonyl carbon atom.

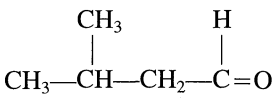
Examples:



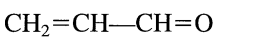
methanal
(formaldehyde)
(40% formaldehyde = formalin)



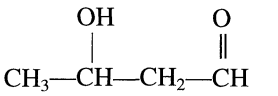
2-methylpropanal



3-methylbutanal

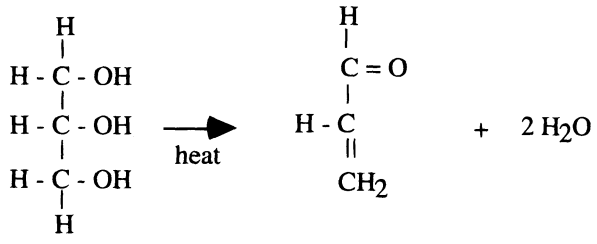


2-propenal or acrolein



3-hydroxybutanal

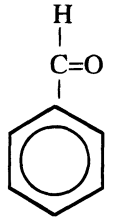
Acrolein is formed by the thermal breakdown of glycerol, resulting in the acrid smell of burning fat.



Glycerol

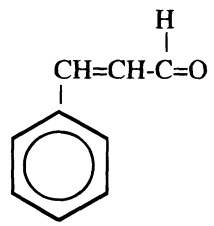
Acrolein
2-propenal

Aromatic aldehydes — The IUPAC name of the simplest aromatic aldehyde is benzenecarbaldehyde, although it is usually called benzaldehyde.



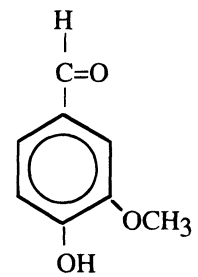
benzenecarbaldehyde

benzaldehyde
(almond flavoring)



3-phenyl-2-propenal

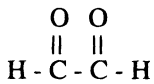
cinnamaldehyde



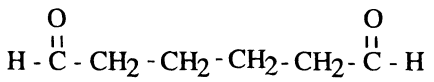
4-hydroxy-3-methoxy-
benzenecarbaldehyde

vanillin

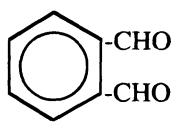
Compounds with two aldehyde groups are named by retaining the -e of the stem and adding dial. The carbonyl carbon atoms are included in the stem.



ethanedial
glyoxal

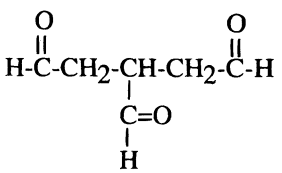


hexanedial



1,2-benzenedicarbaldehyde
phthalaldehyde

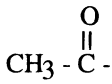
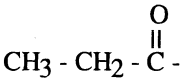
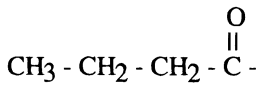
Compounds with three aldehyde groups are named by selecting and naming a stem that does not include the carbonyl carbon atoms and adding tricarbaldehyde.

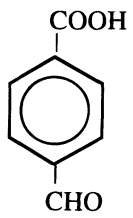


1,2,3-propanetricarbaldehyde

Aldehyde as a substituent — When aldehydes occur as substituents on compounds of higher nomenclature priority they are named after the appropriate carboxylic acid, and thought of as removing the —OH from the —COOH. The name is obtained by removing the -ic

from the appropriate acid and adding -oyl if it is an IUPAC name or -yl if it is a common name. Formic acid becomes formyl, methanoic acid becomes methanoyl.

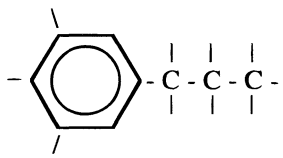
	Common name	IUPAC
	formyl	methanoyl
	acetyl	ethanoyl
	propionyl	propanoyl
	butyryl	butanoyl
	benzoyl	benzoyl



4-methanoylbenzenecarboxylic acid
4-formylbenzoic acid

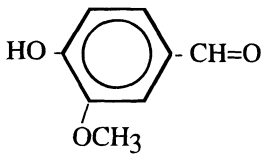
Aldehydes derived from lignin polymers — Lignin is an important natural polymer. Wood is a lignin plastic reinforced by cellulose fibers that contain 15–36% lignin. Lignin is a network or chicken wire polymer where each molecule is attached to two or three other molecules. It is not a chain polymer, and has many variants. It is one of the most inert of plant substances. Its function is to reduce cell wall permeation, impart rigidity to the cell wall, and help cell walls resist attack by microorganisms. There are two common types of fungi that decompose wood, the first is white rot, which attacks all components of wood, including lignin, and the second is brown rot, which decomposes all components except lignin, and leaves a brown residue.

The structure of the lignin polymer unit is not a sugar. It is an alcohol based on phenyl propane.



phenylpropane

The oxidation of lignin results in the formation of three products, all aldehydes—vanillin, syringaldehyde, and *p*-hydroxybenzaldehyde. Vanillin has the formula:



vanillin

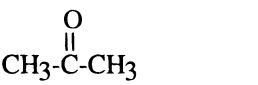
Thus, different woods produce different products. Monocots give three different aldehydes, dicots two different aldehydes, and gymnosperms only one aldehyde. Primitive vascular plants contain little lignin.

KETONES

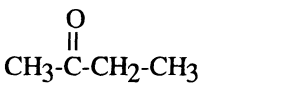
Ketones contain a carbonyl group that appears in the middle of the molecule, bonded to two other carbon atoms.

Ketones are named after the parent hydrocarbon containing the carbonyl group with the suffix -one, and a locator number indicating the position of the carbonyl group if greater than four carbons. The older nomenclature includes the groups on either side of the carbonyl group plus the name ketone. If a carbonyl group occurs as a substituent on an aldehyde or carboxylic acid, then it is referred to by the prefix oxo-. Two ketone groups in a compound are called diones.

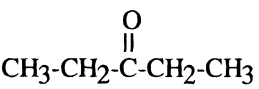
Examples:



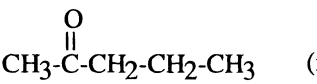
propanone
(dimethyl ketone)
(acetone)



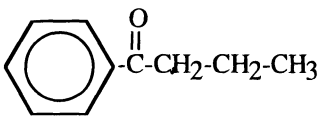
butanone
(methyl ethyl ketone)
(MEK)



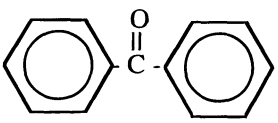
3-pentanone
diethyl ketone



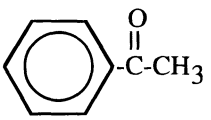
2-pentanone
(methyl n-propyl ketone)



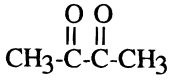
1-phenyl-1-butanone



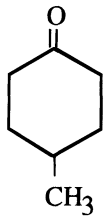
diphenylmethanone
(benzophenone)
(diphenyl ketone)



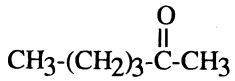
phenylethanone
(acetophenone)
(methyl phenyl ketone)



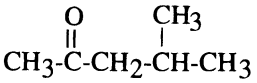
2,3-butanedione
diacetyl (butter flavor)
dimethyl diketone
dioxobutane



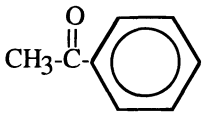
4-methylcyclohexanone



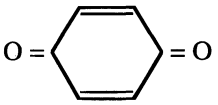
2-hexanone



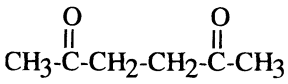
4-methyl-2-pentanone



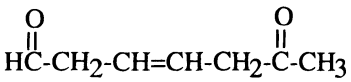
phenylethanone
(acetophenone)
(methyl phenyl ketone)



2,5-cyclohexadiene-1,4-dione
(*p*-benzoquinone)

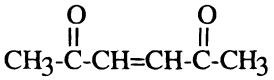


2,5-hexanedione

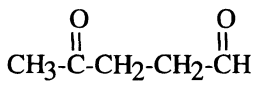


6-oxo-3-heptenal

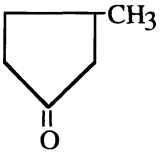
(The terminal aldehyde is the highest priority functional group.)



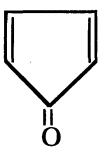
3-hexene-2,5-dione



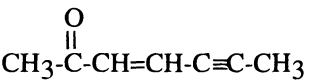
4-oxopentanal



3-methyl-1-cyclopentanone



2,4-cyclopentadien-1-one



3-hepten-5-yne-2-one

Carbohydrates

Carbohydrates are sugars or sugar polymers. The simplest carbohydrate unit is a sugar, also called a monosaccharide. It consists of three to seven carbon atoms. They are aldehyde or ketone derivatives of polyhydric alcohols and must have an asymmetric (CHIRAL) carbon atom. They are the principal source of energy for living organisms. Carbohydrates are made by plants through the process of photosynthesis, whereby atmospheric CO_2 and H_2O are converted to simple sugars. Some of the sugar is converted to starch, a sugar polymer, for storage and some is converted to cellulose, a macropolymer, for structural support.

An asymmetric carbon atom is a carbon atom that has four different atoms or groups of atoms attached to it. The molecule is NOT identical to its mirror image. The result is optical isomerism, whereby one isomer rotates the vibration direction of polarized light to the left, and the other isomer rotates it to the right.

The classification of carbohydrates is based on the number of simple sugar units in the compound:

Name	# Sugar units
Oligosaccharides	few
Monosaccharides	one
Disaccharides	two
Trisaccharides	three
Polysaccharides	many

The naming of simple sugars is based on:

a. Number of C atoms + -ose, for example, five carbons are pentoses, six are hexoses, seven are heptoses, and eight are octoses.
b. Functional group present + -ose, for example, aldose has an aldehyde group and ketose a ketone functional group.

The two most common sugars are hexoses (with six carbon atoms), one an aldose containing an aldehyde group, called glucose (dextrose), and the other a ketose, with a ketone group, called fructose. Their formulas and the formula of the disaccharide sucrose are given below.

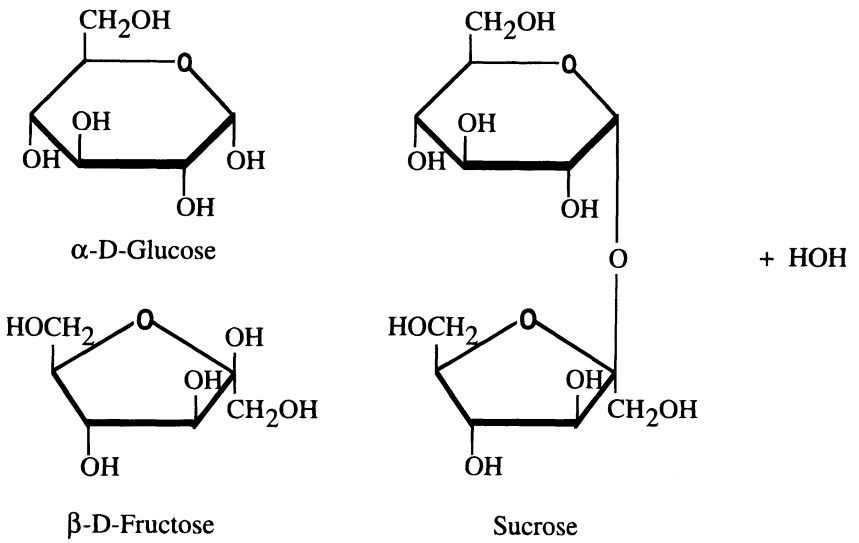


Figure based on Baum, 1987.

The number of isomers depends on the number of asymmetric carbon atoms (ACA) which in turn depends on the number of carbon atoms in the sugar structure. This relationship is shown below:

# C	# ACA	# isomers
n	2^n	
3	1	2
4	2	4
5	3	8
6	4	16

Disaccharides

Sucrose—plant sugar (glucose + fructose) cane sugar or sugar beets.
Lactose—milk sugar (glucose + galactose).
Maltose—germinating grain sugar (glucose + glucose).

Polysaccharides — Polysaccharides are sugar polymers that on hydrolysis with acids yield simple sugars.

Starch is the primary means by which plants store food reserves. It consists of glucose polymers stored as granules. Natural starches are a mixture of two types of polysaccharides. Amylose is a linear polysaccharide made up of glucose with a molecular weight of about 50,000. Amylopectin has a molecular weight of about 300,000 and is a highly branched glucose polymer. Starch grains consist of a framework of amylopectin with amylose coiled around it.

Inulin is a fructose polymer making up the food reserves of many Compositae such as dandelion, dahlia, and sunflower.

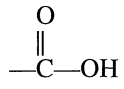
Glycogen is a carbohydrate used by animals for energy storage. It is a glucose polymer with much more branching than that of amylopectin. It may be considered to be an animal starch that is stored in the liver and muscles. It is also soluble in water.

Cellulose makes up the structural parts of plants and is a straight chain polymer of about 10K glucoses (mol. wt. 150K–1M). The strength and rigidity that cellulose gives to plants result from hydrogen bonding between the cellulose molecules. Over 50% of the total organic matter in the living world is cellulose.

Hemicellulose is another type of structural plant material consisting of several different types of sugars. It is composed of the equivalent of 100–200 glucose units.

CARBOXYLIC ACIDS

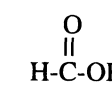
Carboxylic acids are organic acids that contain a hydroxyl group attached to a carbonyl group.



carboxylic acid group

Carboxylic acids are named by replacing the -e of the parent alkane by -oic acid. The older nomenclature system is given in Table 7.12.

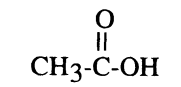
Examples:



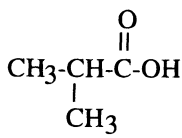
methanoic acid
(formic acid - ants)

Table 7.12. Older Nomenclature of Carboxylic Acids

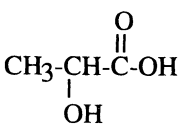
# C	Common name	IUPAC name	Derivation	Notes
1	Formic	Methanoic	< L formica—ant	
2	Acetic	Ethanoic	< L acetum—vinegar	
3	Propionic	Propanoic	Pro -to + <Gk pion—fat	First of fatty acids (liquid) found in beet root molasses
4	Butyric	Butanoic	<L butyrum—butter <Gk boutyron—butter = bous —cow + tyros—cheese	
5	Valeric	Pentanoic	<L valere—strong	Valerian—herb
6	Caproic	Hexanoic	<L caper—goat	
8	Caprylic	Octanoic	<L caper—goat	
10	Capric	Decanoic	<L caper—goat	
12	Lauric	Dodecanoic	<L laurus—laurel	Mediterranean evergreen shrub, Bay laurel, laurel wreath
14	Myristic	Tetradecanoic	<NL nux myristica—nutmeg <Gk myrizein—anoint	Found in nutmeg butter
16	Palmitic	Hexadecanoic	<L palma—palm tree	Palm oil, especially African oil palm—*Elaeis guineensis*
18	Stearic	Octadecanoic	<Gk stear—suet	



ethanoic acid
(acetic acid - vinegar)



2-methylpropanoic acid



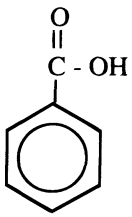
2-hydroxypropanoic acid
(lactic acid)
(yogurt, sour cream)

Aliphatic carboxylic acids are sometimes called fatty acids because many of them are contained in natural fats. The common names of some carboxylic acids are listed in Table 7.12.

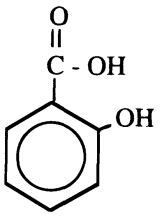
C_4	butyric acid—rancid butter
C_6, C_8, C_{10}	odor of goats
C_{10+}	waxlike solids
$CH_3(CH_2)_{16}-COOH$	stearic acid—from beef (steers)

Na or K salts of long-chain fatty acids are known as soaps.

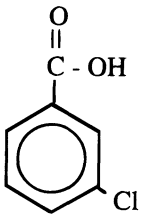
Aromatic acids — The IUPAC name for the simplest aromatic acid is benzenecarboxylic acid. It is seldom used because the common name benzoic acid has almost universal acceptance.



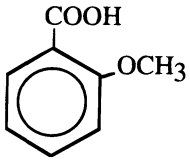
benzenecarboxylic acid
benzoic acid



2-hydroxybenzenecarboxylic acid
salicylic acid

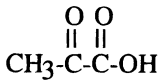


3-chlorobenzenecarboxylic acid
m-chlorobenzoic acid

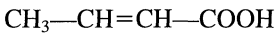


2-methoxybenzoic acid

In older books this may be written as *o*—OCH_3—C_6H_4COOH.



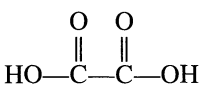
2-oxopropanoic acid



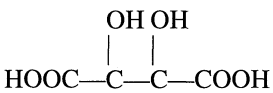
2-butenoic acid

4-hydroxy-2-pentenoic acid

Di- and tricarboxylic acids — Dicarboxylic acids are carboxylic acids with two —COOH groups. They are named by counting the total number of carbons in a chain including the carboxyl group and adding dioic acid.

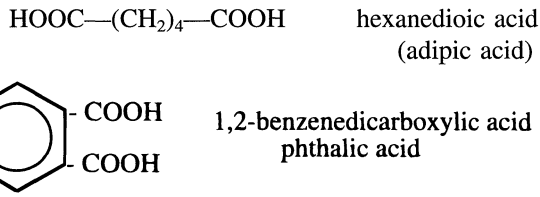


ethanedioic acid
oxalic acid
(kidney stones, rhubarb leaves)
(Commonly used as a rust remover)

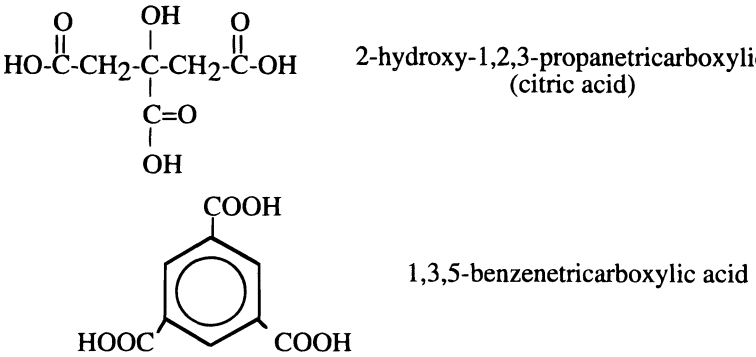


2,3-dihydroxy-butanedioic acid
(tartaric acid)

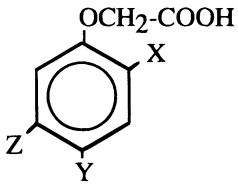
Cream of tartar is potassium hydrogen tartrate.



Tricarboxylic acids are named on the hydrocarbon without the carboxylic acid groups, which are then denoted as carboxylic acid substituents.



Phenoxy Acid Herbicides



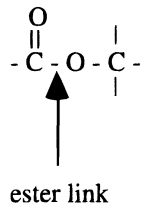
If X = Y = Cl, then the compound is 2,4-dichlorophenoxyacetic acid or 2,4-D.
If X = Y = Z = Cl, then the compound is 2,4,5-trichlorophenoxyacetic acid or 2,4,5-T.
If X = CH_3, Y = Cl, and Z = H, then the compound is 2-methyl-4-chlorophenoxyacetic acid or MCPA.

ESTERS

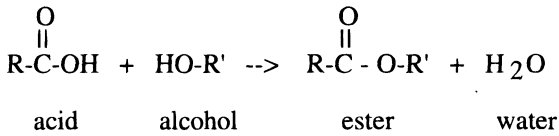
Esters are derived from carboxylic acids and alcohols. The reaction is called a condensation reaction and water is removed. The group includes fats (solids) and oils (liquids), and waxes (solids composed of alcohols and esters of high molecular weight).

Condensation is a special type of elimination reaction resulting in the formation of esters or amides (see nitrogen functional groups). Two compounds combine to form one with the elimination of a small compound such as water or alcohol. This may also be called esterification. Hydrolysis is the breaking of esters and amides by addition reactions with water (the reverse of condensation). Saponification is alkaline hydrolysis where the bonds of the esters are broken with an aqueous solution of a strong base giving an acid salt (soap) and an alcohol.

The ester functional group is



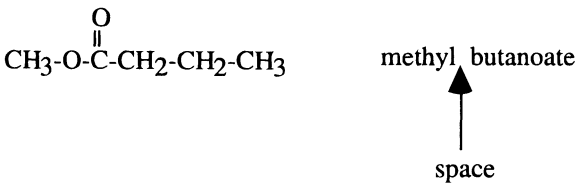
Condensation reaction



Esters are named by listing the alcohol portion with a -yl ending and the acid portion with an -oate ending. There is always a space between the alcohol part of the name and the acid part of the name.

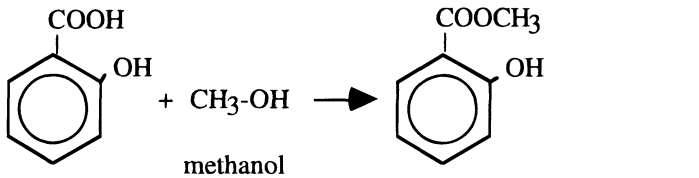
methanoic acid → methanoate

Example:



The nomenclature system used in Chemical Abstracts is somewhat different in that they index esters with the carboxylic acids. For example, methyl butanoate is listed as butanoic acid, methyl ester.

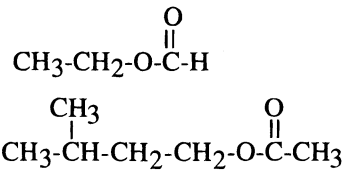
Important esters:



2-hydroxybenzene-carboxylic acid (salicylic acid)

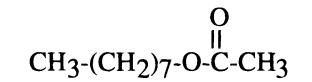
2-hydroxybenzenecarboxylic acid, methyl ester (methyl salicylate) (oil of wintergreen)

Flavorings

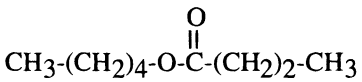


ethyl methanoate (rum flavoring)

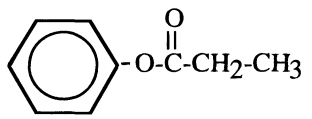
3-methylbutyl ethanoate (isoamyl acetate) (banana flavoring)



octyl ethanoate
(octyl acetate)
(orange flavoring)

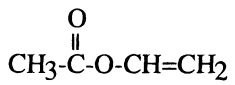


pentyl butanoate
(amyl butyrate)
(apricot flavoring)



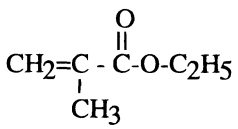
phenyl propanoate

Priority pollutants



vinyl acetate
(ethenyl ethanoate)

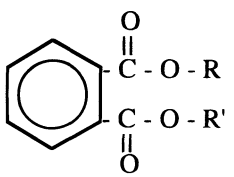
vinyl acetate
(ethenyl ethanoate)



2-propenoic acid, 2-methyl-, ethyl ester
ethyl methacrylate

Other naturally occurring esters are fats and waxes. Fats will be considered later. Waxes are monohydric (one OH) alcohols and a fatty acid, usually saturated. Examples are sperm oil (a liquid wax), and bee's wax (an ester of myricyl alcohol ($C_{30}H_{61}OH$) and palmitic acid (CH_3— $(CH_2)_{14}COOH$)).

Esters of dicarboxylic acids:



Phthalate esters

bis(2-Ethylhexyl) phthalate	R = R′ = 2-ethylhexyl
Butylbenzyl phthalate	R = butyl; R′ = benzyl
di-*n*-Butyl phthalate	R = R′ = butyl
di-*n*-Octyl phthalate	R = R′ = octyl
Diethyl phthalate	R = R′ = ethyl
Dimethyl phthalate	R = R′ = methyl

Esters of Trihydric Alcohols

This group of biological compounds (fats) are classified into the category of lipids along with the waxes described above. Lipids are biological compounds that are insoluble in water. There are two major types: (a) complex lipids or fats, which are composed of groups of fatty acids (fatty acids are carboxylic acids made up of 14–22 carbon atoms); triglycerides that are three fatty acids linked together by means of a glycerol molecule (this type of lipid is used for fat storage and the formation of cell membranes); and alkaline hydrolysis of fat, which forms soap (a K or Na salt of fatty acid); and (b) simple lipids which do not contain

fatty acids. They are nonsaponifiable and are either terpenes which occur in plant oils and are the main component of lignin and chlorophyll, or complex steroids.

Saponifiable lipids can be hydrolyzed by a base. They consist of fats and oils that in turn are esters of a trihydric alcohol (three OH), glycerol and

One type of fatty acid	simple lipid
Two types of fatty acids	mixed lipids
Two types of fatty acids and a phosphate group plus a N compound	phospholipids
Two types of fatty acids and a sugar	glycolipids

This is shown diagrammatically below.

Simple	Mixed	Phospholipid	Glycolipid
CH_2—OH + FA*	CH_2—OH + FA_1	CH_2—OH + FA_{sat}	CH_2—OH + FA
CH—OH + FA	CH—OH + FA_2	CH—OH + FA_{unsat}	CH—OH + FA
CH_2—OH + FA	CH_2—OH + FA_3	CH_2—OH + PO_4—N	CH_2—OH + SUGAR

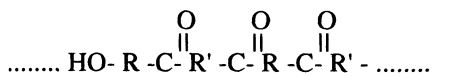
The number of unsaturated bonds in a fat may be measured by the Iodine Number, which is a reaction of unsaturated bonds with iodine. It is reported as the number of grams of iodine reacting with 100 g of fat. Fat has an Iodine Number <70, and oil an Iodine Number >70.

Hydrogenation is the saturation of double bonds with H_2. It is the change from vegetable oils to shortenings (solid). Rancidity is the hydrolysis and oxidation of fats to butanoic acid, and oils (unsaturated) to either acids or aldehydes.

Saponification is the hydrolysis of fats with a strong base, giving a Na salt of fatty acids (soap) + glycerol. Soaps have a polar head (Na acid) that remains in water and a nonpolar chain that dissolves in grease. Hard water forms insoluble Ca and Mg salts with soap. Detergents will not form insoluble products with Ca and Mg and are prepared by treating fatty acids with sulfuric acid and alkyl halides, giving alkyl sulfonates.

Polyesters — Polyesters are polymers in which monomers are joined by ester linkages. They form the condensation of dihydric alcohol and a dicarboxylic acid; for example:

HO—R—OH + HOOC—R′ − COOH + HO—R—OH + ⋯ →
dihydric alcohol dicarboxylic acid dihydric alcohol



polyester

They may also be called condensation polymers. In a condensation polymer a small fragment, such as water, is eliminated during the polymerization process from the reaction between monomer functional groups. There are two basic types of condensation polymers:

Those resulting in the formation of esters are

*FA is a fatty acid; FA_1, FA_2, and FA_3 are different fatty acids; FA_{sat} is a saturated fatty acid and FA_{unsat} is an unsaturated fatty acid.

Polyester formation

and those resulting in the formation of polyamides are

Polyamide formation

These will be described later under nitrogen functional groups.

A typical example of a polyester is the fiber, Dacron®. It is synthesized by the condensation of teraphthalic acid and ethylene glycol with the elimination of water. Because it is made up of two different monomers, it is a copolymer. Acetate rayon, one of the first synthetic polymers, is a polyester made by reaction between cellulose (which has many hydroxyl groups) and acetic anhydride. Acetic acid is the molecule eliminated in this reaction. If one of the monomers used in the preparation of a polymer has three functional groups, it may form branched chains or cross links between polymer chains.

OXYGEN FUNCTIONAL GROUP NOMENCLATURE

1. Choose the longest continuous carbon chain containing the functional group, if there is one.
2. Location of the other groups are indicated by a location number.
3. The functional group of highest nomenclature priority should have the lowest locator number.

A summary of the nomenclature priority of functional groups containing oxygen is given in Table 7.13. A key to the identification of oxygen functional groups is given in Table 7.14.

Table 7.13. Oxygen Functional Group Nomenclature Priority

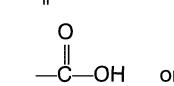
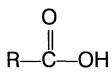
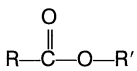
Name	Functional group	Prefix	Suffix
Carbonyl group			
Carboxylic acid			-oic acid carboxylic acid
Aldehydes		-oyl	-al
		-yl	carbaldehyde
Ketone		oxo-	-one
Single bond	C—O		
Alcohol	—OH	hydroxy-	-ol
Ether	—O—	alkoxy- phenoxy-	ether
Hydrocarbons			
Alkene	—C=C—		-ene
Alkyne	—C≡C—		-yne
Alkane	—C—C—		-ane
Substituents			
Alkyl	—R		
Halo-	—X		
Chloro-	—Cl		
Fluoro-	—F		
Bromo-	—Br		
Iodo-	—I		

Table 7.14. Key to the Simple Oxygen Functional Groups

Note:
R or R′ are groups containing a bonding carbon atom such as CH_3—.

is a carbonyl group

1. Oxygen functional groups without a carbonyl group.
   a. oxygen bonded to H and C atoms, e.g., R—O—H alcohol
   b. oxygen bonded to two C atoms, e.g., R—O—R′ ether
2. One carbonyl group present
   The carbonyl carbon atom bonded to
   a. two H atoms, e.g., aldehyde—methanal
   b. H (and a carbon) atom, e.g., aldehyde
   c. two carbon atoms, e.g., ketone
   d. one carbon atom and an OH group, e.g.,  carboxylic acid
   e. one carbon atom and an oxygen atom (bonded to a carbon),

e.g.,  ester;

R′ is alcohol group (bonded to O atom),
R is carboxylic acid group (bonded to carbonyl carbon atom).

ORGANIC NITROGEN COMPOUNDS

Nitrogen can form single, double, or triple covalent bonds. The most important N functional groups are listed in Table 7.15.

Single-Bond Nitrogen Compounds

These are based on the ammonia structure (NH_3) with one or more of the hydrogen atoms replaced by carbon.

AMINES

Amines are organic derivatives of ammonia which are classified by the number of hydrogen atoms replaced by alkyl groups. The simpler amines are named by giving the alkyl groups on the nitrogen, followed by the ending amine, e.g., methylamine; or by naming the parent hydrocarbon, dropping the -e and adding amine, e.g., ethanamine. More complex compounds are named by using the word amino to identify the -NH_2 group in the molecule. An N appearing before the name of a substituted group (e.g., *N*-ethyl. . . .) indicates that the group named after the N is attached to the N of the amino group.

Table 7.15. Nitrogen Functional Groups

N only		N and O atoms	
	Single	**bond**	
$R—NH_2$	Amine	$R—C(=O)—NH_2$	Amide
$H_2N—NH_2$	Hydrazine	$R—CH(NH_2)—C(=O)—OH$	Aminoacid
$H_2N—C_6H_4—C_6H_4—NH_2$	Benzidine		
	Double	**bonds**	
$R_2C=NH$	Imine	$R—N=O$	Nitroso
		$R—N(R')—N=O$	Nitrosamine
		$R—N(=O)=O$ or $R—NO_2$	Nitro
	Triple	**bond**	
$R—C\equiv N$	Nitrile		

H-N-H	R-N-H	R-N-R'	R-N-R'
ammonia	primary	secondary amines	tertiary

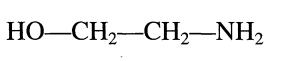
Examples:

CH_3-NH-H	methylamine methanamine
$CH_3-NH-CH_3$	dimethylamine N-methylmethanamine
$CH_3-N(CH_3)-CH_3$	trimethylamine N,N-dimethylmethanamine

Where the amino group is not terminal, its location is indicated by a locator number, for example:

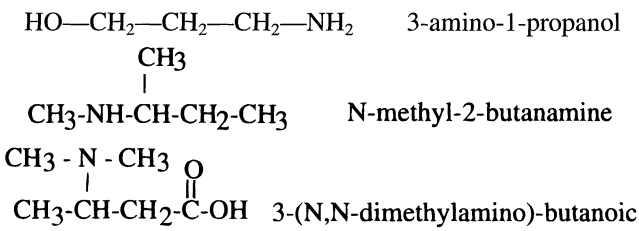
$CH_3-CH(NH_2)-CH_2-CH_3$ 2-butanamine

Some older names do not use nomenclature priority, for example:



ethanolamine
2-aminoethanol (IUPAC)

The IUPAC names for other amines are

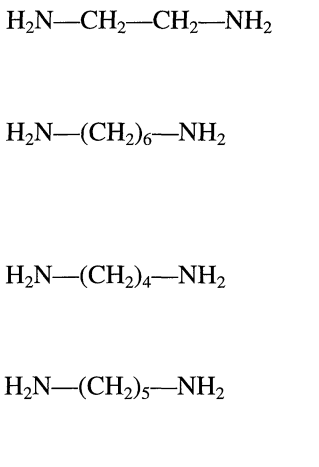


3-amino-1-propanol

N-methyl-2-butanamine

3-(N,N-dimethylamino)-butanoic

DIAMINES



1,2-ethanediamine
1,2-diaminoethane
ethylene diamine

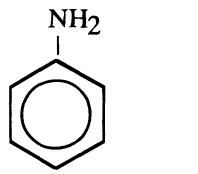
1,6-hexanediamine
1,6-diaminohexane
hexamethylene diamine
(used in manufacture of nylon)

1,4-butanediamine
1,4-diaminobutane
putrescine

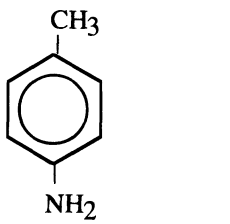
1,5-pentanediamine
1,5-diaminopentane
cadaverine

AROMATIC AMINES

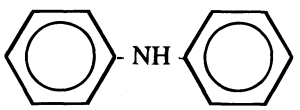
The IUPAC naming of monoamino aromatic amines is based on aniline. Diamino aromatic amines are named as substituted benzenes, in a manner similar to the phenol nomenclature.



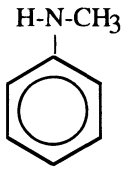
aniline



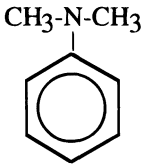
4-methylaniline
(p-toluidine)



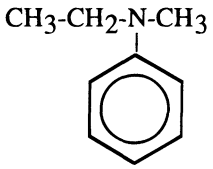
N-phenylaniline
diphenylamine
N-phenylbenzamine



N-methylaniline

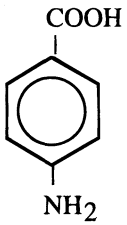


N,N-dimethylaniline

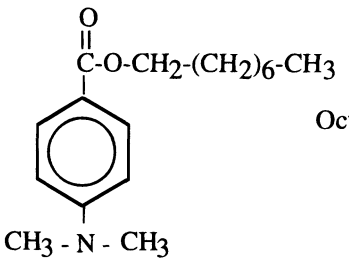


N-ethyl-N-methylaniline

1,4-diaminobenzene
p-phenylene diamine



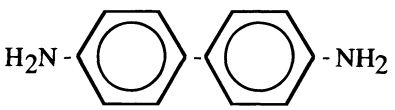
p-aminobenzene carboxylic acid
p-aminobenzoic acid
PABA



Octyl N,N-dimethyl-p-aminobenzoate
(Presun® sunscreen)

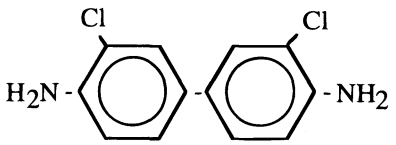
Benzidines—a special group of diamines

4,4'-biphenyldiamine



benzidine
(p,p'-diaminobiphenyl)

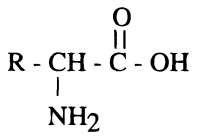
Chlorinated benzidine priority pollutant:



3,3'-dichlorobenzidine

AMINO ACIDS

These are a very important group of amines occurring in proteins that also contain a carboxylic acid group. The amino group is always on the carbon next to the carbonyl carbon atom. The general structure is

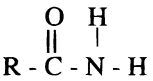


Amino acid structure

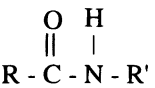
The R side chain group determines many of the properties of these compounds. It may be hydrophobic (mainly hydrocarbon chains), polar but uncharged (containing hydroxyl or amide groups), or polar and charged (containing carboxylate anions, ammonium cations, and similar groups).

AMIDES

Amides are derivatives of carboxylic acids in which the hydroxyl group has been replaced by an amino group. The bond between the carbonyl group and the N atom is called the amide linkage. It is very stable and occurs in many large molecules (polymers) such as protein and nylon.

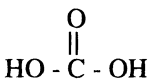


unsubstituted amides

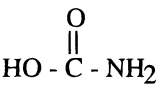


monosubstituted amides

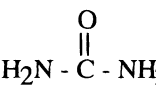
disubstituted amides



carbonic acid

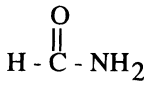


carbamic acid
aminomethanoic acid

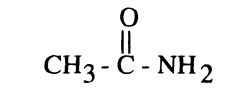


urea
1-aminomethanamide

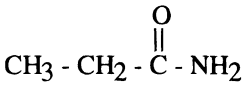
Unsubstituted amides with two hydrogen atoms on the nitrogen atom are named by dropping the -oic ending of the original acid and adding -amide.



formamide
methanamide

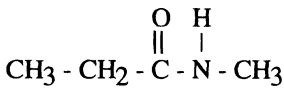


acetamide
ethanamide

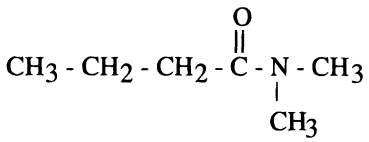


propanamide

Substituted amides with groups other than H attached to the N atom are named as alkyl groups with the N in front to indicate that they are attached to the N.



N-methylpropanamide



N,N-dimethylbutanamide

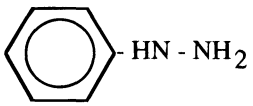
PROTEINS

Proteins are high-molecular weight polymers of amino acids. They differ from other polymers, such as carbohydrates, in that they may consist of many different amino acids in one protein in which the amino acids are arranged in a specific sequential arrangement. This arrangement is dictated by the DNA sequence from which they are transcribed.

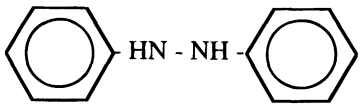
HYDRAZINES

Hydrazine may be thought of as two ammonia molecules combined by losing two hydrogen atoms.

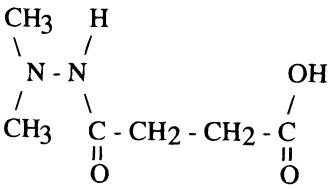
hydrazine
diazane



phenylhydrazine



1,2-diphenylhydrazine

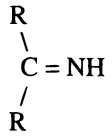


ALAR®
(daminozide)
butanedioic acid, mono(2,2-dimethylhydrazide)
or
succinic acid, (2,2-dimethylhydrazide)

Double-Bond Nitrogen Compounds

IMINES

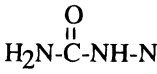
Imines may be thought of as having two of the bonds from an ammonia molecule attached to a carbon atom. The result is a carbon-nitrogen double bond, that is



imine structure

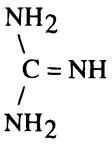
Thus, imines contain carbon to nitrogen double bonds. These compounds result from the reaction of primary amines with the carbonyl bonds of aldehydes and ketone. Imines derived from special types of amines are given names as follows:

a. those derived from hydroxylamine ($HO—NH_2$) are called oximes,
b. those derived from phenylhydrazine ($C_6H_5—NH—NH_2$) are called phenylhydrazones, and
c. those derived from semicarbazide are called semicarbazones.

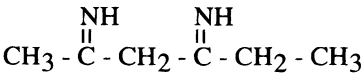


semicarbazone

Examples:



guanidine



2,4-hexanediimine

Triple-Bond Nitrogen Compounds

NITRILES

Nitriles are cyanides where the H of hydrogen cyanide (HCN) has been replaced by an organic group. They are named after the carboxylic acid to which they would oxidize.

$H^+ {}^-C{\equiv}N$	$R—C{\equiv}N$
hydrogen cyanide	nitrile

They may be thought of as part of the sequence:

$R—C—NH_2$	amine
$R—C{=}NH$	imine
$R—C{\equiv}N$	nitrile

These compounds may be named in two ways:

1. nitrile, where the functional group is ≡N, and
2. cyanide, where the functional group is —C≡N.
   The number of carbon atoms in the parent cyanide compound is one less than that of the same nitrile compound.

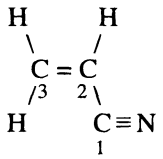
Nitriles may be polymerized to form synthetic fibers, e.g.,

$CH_2=CH—C\equiv N$ → Orlon® (synthetic fiber)
2-propenenitrile
(vinyl cyanide, acrylonitrile, cyanoethylene).

Cyanide is released on combustion of this polymer and has caused many deaths in hotel fires.

Laetrile is a complex organic nitrile extracted from apricot pits.

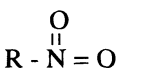
$CH_3–C\equiv N$ acetonitrile
methyl cyanide
ethane nitrile



acrylonitrile
vinyl cyanide
2-propenenitrile
cyanoethylene

NITRO GROUP

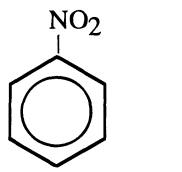
The nitro group is a functional group containing N and O. It also is an organic derivative of nitric acid (HNO_3). These groups are designated only by the prefix "nitro-".



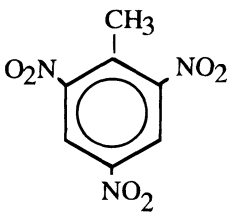
or $R\text{-}NO_2$ nitro group

$CH_3\text{-}NO_2$ nitromethane

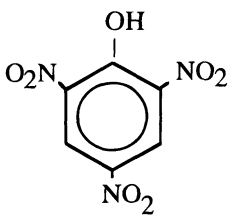
$CH_3\text{-}CH_2\text{-}NO_2$ nitroethane



nitrobenzene



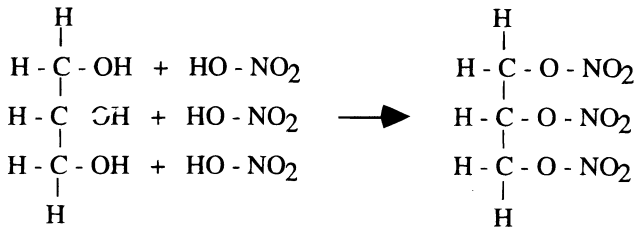
2,4,6-trinitrotoluene
(TNT)
explosive



2,4,6-trinitrophenol
(PICRIC ACID)
explosive

Picric acid is a bright yellow compound normally stored under water. On aging the water often evaporates and the chemical recrystallizes, forming a potentially violent explosive.

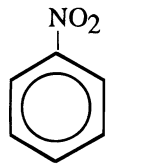
Nitric acid esters are formed by the reaction of nitric acid and an alcohol.



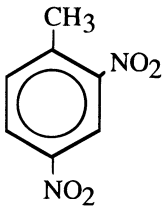
glycerol nitric acid nitroglycerine

Nitrification of cellulose with many —OH groups results in nitrocellulose, another explosive. This was also used as the base for the first movie films.

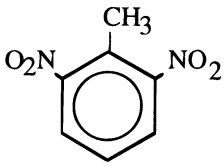
Priority pollutants:



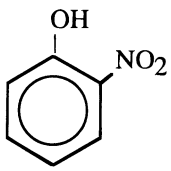
nitrobenzene



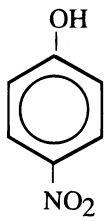
2,4-dinitrotoluene



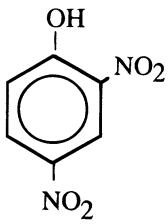
2,6-dinitrotoluene



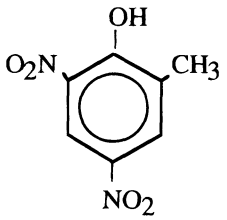
2-nitrophenol



4-nitrophenol



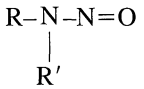
2,4-dinitrophenol



4,6-dinitro-o-cresol
2-methyl-4,6-dinitrophenol

N-NITROSAMINES

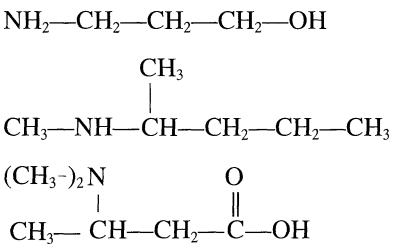
These compounds are derived from nitrous acid (HNO_2 or HO—N=O). They are named only by means of the prefix "nitroso-". The nitroso functional group is therefore —N=O. Amine groups with the nitroso group are called nitrosamines. Most nitrosamines are thought to be carcinogenic.

 nitrosamine structure

Priority pollutants:

N-nitrosodimethyl amine R=R′=methyl
N-nitrosodiphenyl amine R=R′=phenyl
N-nitrosodipropyl amine R=R′=propyl

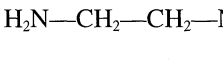
Examples of nitrogen functional groups:



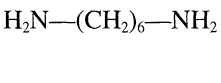
3-amino-1-propanol

1-methyl-N-methylbutanamine
2-(N-methylamino)-pentane

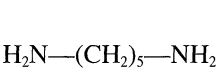
3-(N,N-dimethylamino)-butanoic acid



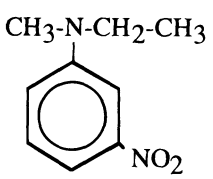
1,2-ethanediamine
1,2-diaminoethane



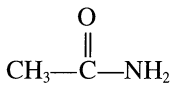
1,6-hexanediamine
hexamethylene diamine
1,6-diaminohexane



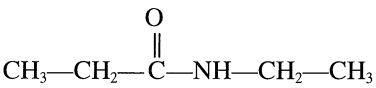
1,5-pentanediamine
cadaverine
1,5-diaminopentane



N-ethyl-N-methyl-3-nitroaniline



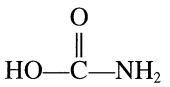
acetamide
ethanamide



N-ethylpropanamide

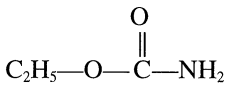
CARBAMATES

Carbamates are extensively used as pesticides and synthetic resins. Thiocarbamates are also included in this section. They have the formula shown below:



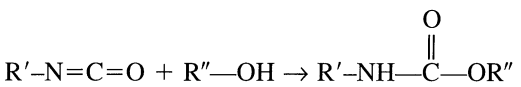
carbamic acid, or
aminoformic acid

Esters of carbamic acid are carbamates, which are also called urethanes.



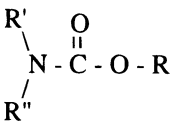
ethyl carbamate
(urethane)

Polyurethanes are made by reacting diisocyanates with a dihydric alcohol.



Methyl isocyanate: $CH_3—N=C=O$ (extremely toxic)
Isocyanic acid: $H—N=C=O$
Diisocyanates contain two ($—N=C=O$) groups.

Carbamate Insecticides



R' = CH_3-
R" = CH_3- or H
R = Aryl, Heterocyclic, or Imine (-C=N-)

Examples of different carbamate insecticides are tabulated below.

Aryl:

- Carbaryl® (sevin)® [l-naphthyl-N-methylcarbamate]
- Propoxur®
- Methiocarb®
- Metalkamate®

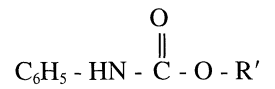
Heterocyclic:

- Carbofuran®
- Pirimicarb®

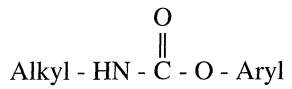
Imine:

Aldicarb®
Methomyl®
Oxamyl®

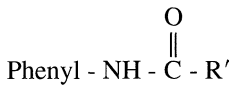
Carbamate Herbicides
Esters of phenylcarbamic acid



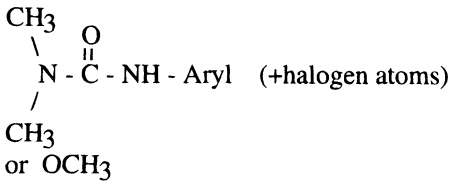
Examples include chlorpropham, propham, chlorbufam, and carbetamide.
Esters of alkylcarbamic acid



An example is carbaryl.
Nonesters, phenyl-substituted amides



An example is propanil.
Urea herbicides



Examples are diuron, fluometuron, linuron, chlorbromuron, chlortoluron, fenuron, metobromuron, metoxuron, monolinuron, and chloroxuron.

ORGANIC COMPOUNDS CONTAINING SULFUR

One of the reasons for the variety of organic sulfur compounds is that sulfur has a number of oxidation states. Many common organic sulfur compounds may be thought of as resulting from the replacement of one or two hydrogen atoms in H_2S. The simplest carbon-sulfur compound is carbon disulfide, CS_2. It is usually considered to be an inorganic compound, although it is used extensively in organic syntheses and as a solvent. It has the molecular structure S=C=S. Organic sulfur compounds form three major groups of compounds. One, where the oxygen of a functional group is replaced by sulfur; second, the sulfur atom forms functional groups surrounded by varying numbers of oxygen atoms; and third, is the group

that contains the sulfur heterocyclics. See Table 7.16. Many of the examples of sulfur-containing organic compounds in this section were based on those described in Baum, 1987.

MERCAPTO- OR THIOL GROUP

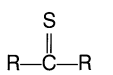
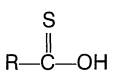
Present terminology uses mercapto- as a prefix only; however, in the older literature these compounds were called mercaptans. They are usually unpleasant, strongly smelling compounds. They are alcohols where the oxygen has been replaced by sulfur.

R—SH (mercaptan) is analogous to R—OH (alcohols)

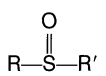
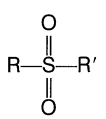
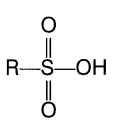
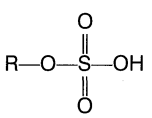
$CH_3—CH_2—SH$	Ethanethiol or ethyl mercaptan LPG odorant (liquefied petroleum gas)
$CH_3—CH_2—CH_2—SH$	propanethiol Found in onions

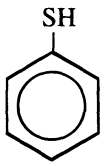
Table 7.16. Sulfur Functional Groups

Group 1. Oxygen replacement

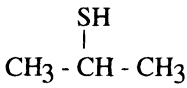
Formula	S group	Analogous O group
R—S—H	Thiol	[Alcohol]
R—S—R′	Sulfide	[Ether]
	Thione	[Ketone]
	Thioacid	[Carboxylic acid]

Group 2. Carbon replacement

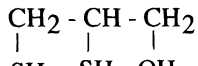
	Sulfoxide
	Sulfone
	Sulfonic acid
	Sulfate



thiophenol or benzenethiol



2-propanethiol
(isopropyl mercaptan)



2,3-dimercaptopropanol
BAL - British Anti-Lewisite
Antidote to organic arsenicals
such as Lewisite, and other heavy metals.
The -SH group bonds to these metals.

DISULFIDES

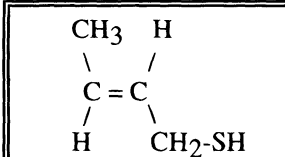
Disulfides contain two sulfur atoms joined together by a single bond. They have the formula: R—S—S—R′.

This group commonly occurs in some proteins, such as wool, and is responsible for cross linking, which results in stabilizing that protein.

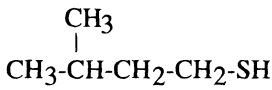
CH_3—S—S—CH_3 dimethyl disulfide

Other more notable examples of thiols and disulfides are

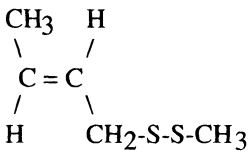
S K U N K



(trans-2-butene)-1-thiol



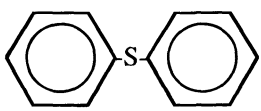
3-methyl-1-butanethiol



methyl-1-(trans-2-butenyl) disulfide

SULFIDES

Sulfides are analogous to ethers (R—O—R′) where the oxygen has been replaced by S, giving sulfides (R—S—R′).

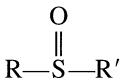


diphenyl sulfide

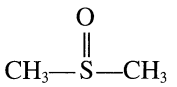
$CH_3—S—CH_3$	dimethyl sulfide
$CH_2=CH—CH_2—S—CH_2—CH=CH_2$	allyl sulfide bis(2-propenyl) sulfide garlic odor
$Cl—CH_2—CH_2—S—CH_2—CH_2—Cl$	bis(2-chloroethyl) sulfide Mustard gas (used in World War I)

SULFOXIDES

Sulfoxides are analogous to ketones where the carbonyl carbon has been replaced by sulfur.



sulfoxide



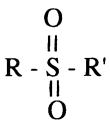
dimethyl sulfoxide
DMSO

Dimethyl sulfoxide (DMSO) is a by-product of the sulfite paper pulping process. Its major use is as a solvent. It is miscible with both polar and nonpolar compounds, e.g., alcohol and benzene. It is also absorbed through the skin and is sometimes used as an analgesic.

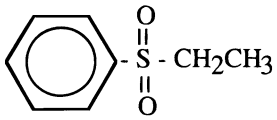
SULFONES

The sulfur in sulfones has six bonds, four of which are used up as two =O, and the remaining two bonded to carbon compounds.

Prefix is sulfonyl-.



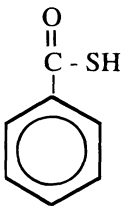
sulfones



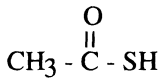
(ethylsulfonyl) benzene

THIO ACIDS

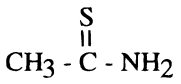
Thio acids are a carboxylic acid where one or the other of the oxygens in a carboxylic acid group has been replaced by a sulfur atom. It is considered as existing in both states alternately, that is, it resonates between the two.



thiobenzoic acid



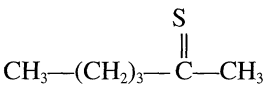
thioacetic acid



thioacetamide

THIO OR THIONE

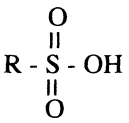
These compounds are analogous to ketones where the oxygen has been replaced by sulfur.



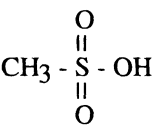
2-hexanethione

SULFONIC ACID

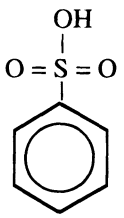
The sulfonic acids are organic derivatives of sulfurous acid, H_2SO_3, that is, R—SO_3H.



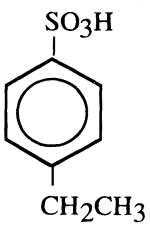
sulfonic acid



methylsulfonic acid

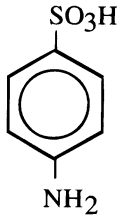


phenylsulfonic acid



4-ethylbenzene sulfonic acid

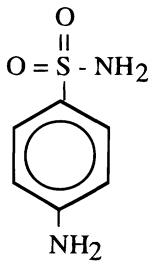
Sulfanilic acid is a sulfonic acid derivative of aniline.



4-aminobenzenesulfonic acid
sulfanilic acid

SULFONAMIDES

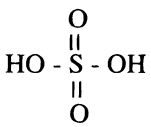
This group of chemicals, which has the basic structure of *p*-aminobenzenesulfonamide, comprised the main group of bactericides in the 1930s prior to the introduction of penicillin. The formula is $NH_2—C_6H_4—SO_2—NH_2$. Numerous derivatives are manufactured by adding various groups to the sulfone radical. They often have unpleasant or toxic side effects.



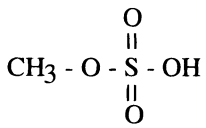
4-aminobenzenesulfonamide

SULFATES

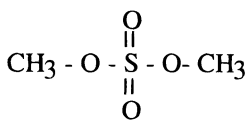
These are esters of inorganic sulfuric acid—H_2SO_4.



sulfuric acid



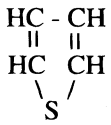
methyl hydrogen sulfate



dimethyl sulfate

THIOPHENES

Thiophenes are unsaturated, five-membered rings containing one sulfur and four carbon atoms. They are also examples of aromatic heterocyclics.

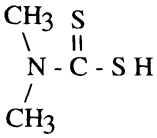


thiophene
thiacyclopenta-2,4-diene

DITHIOCARBAMATE FUNGICIDES AND HERBICIDES

Dithiocarbamate fungicides

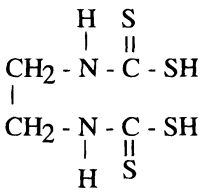
Derivatives of dimethyldithiocarbamic acid:



dimethyldithiocarbamic acid

Examples are ziram (zinc complex), thiram (disulfide).

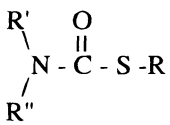
Derivatives of ethylene bis-dithiocarbamate:



ethylene bis-dithiocarbamate

Examples are Zineb (Zn), Maneb (Mn), and Mancozeb (Mn and Zn).

Thiocarbamate herbicides



Thio(l)carbamates

Examples include (S-ethyl di-N,N-propylthiocarbamate), vernolate, cycloate, butylate, diallate, triallate, pebulate, molinate, benthiocarb.

ORGANIC PHOSPHORUS COMPOUNDS

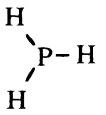
This group includes some of the important phosphorus-containing insecticides and war gases (nerve gases). They are generally called organophosphates. They exert a powerful inhibitory effect upon the transmission of nerve impulses. The classification and many examples in this section are from Corbridge (1980). A summary of organic phosphorus nomenclature is given in Table 7.17.

Table 7.17. Organic Phosphorus Nomenclature

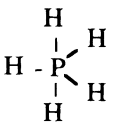
The names of organophosphorus compounds are made up of three parts: prefix—center—suffix.		
1. Prefix:	phosph-, indicating phosphorus atom	
2. Center:		
	-in-, indicating 1 hydroxyl	
	-on-, indicating 2 hydroxyl	
	-or-, indicating 3 hydroxyl	
3. Suffix:		
	-ous (acid) or -ite (ester)	trivalent phosphorus
	-ic (acid) or -ate (ester)	pentavalent phosphorus

Organic phosphorus compounds are a diverse group which may be subdivided in several ways. One is on the basis of valence. Most phosphorus compounds are either trivalent or pentavalent. The second method of subdividing is on the basis of the number of P-C bonds relative to the number of P-O-C linkages.

Compounds with only P-C linkages may be considered to be derived from phosphine PH_3 or phosphane PH_5.



phosphine



phosphane

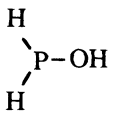
CH_3—PH_2 methylphosphine

CH_3—PH_4 methylphosphane

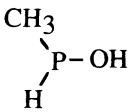
Compounds with one or more P-O-C linkages are derived by progressive replacement of the H in the above structures by -OH. They may be either acids or esters. See Table 7.17.

Examples of phosphorus compounds

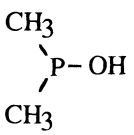
Trivalent with one hydroxyl group:



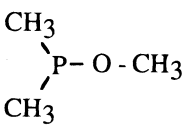
phosphinous acid



methylphosphinous acid

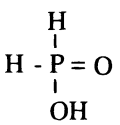


dimethylphosphinous acid

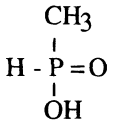


methyl dimethylphosphinite

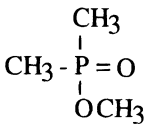
Pentavalent with one hydroxyl group:



phosphinic acid

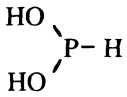


methylphosphinic acid

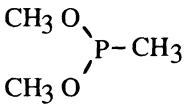


methyl dimethylphosphinate

Trivalent with two hydroxyl groups:

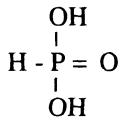


phosphonous acid

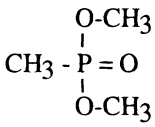


dimethyl methylphosphonite

Pentavalent with two hydroxyl groups:

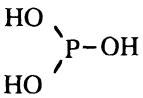


phosphonic acid

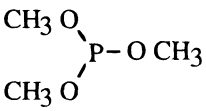


dimethyl methylphosphonate
(one P - C bond)

Trivalent with three hydroxyl groups:

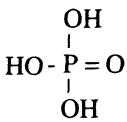


phosphorous acid

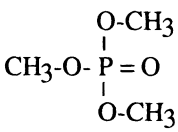


trimethyl phosphite

Pentavalent with three hydroxyl groups:

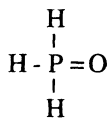


phosphoric acid



trimethyl phosphate
(no P - C bonds)

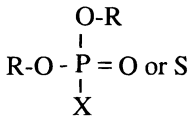
Pentavalent without any hydroxyl groups:



phosphine oxide

Organophosphorus insecticides:

These are either phosphates or phosphonates.
They have the following general formula:

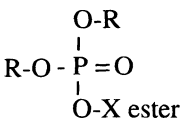


Generally the R group is the same, either methyl or ethyl, and the X is some complex group, which may be joined to the P in one of three ways:

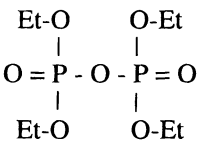
a. P—X directly—phosphonate or thionphosphonate,
b. P—O—X ester—phosphate, or
c. P—S—X thioester, a thiol group.

Also, the carbonyl group may be a thione group, P=S.

1. Orthophosphates
Hydrophilic and low persistence, often extremely toxic.

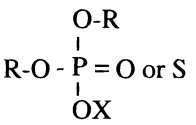


dichlorvos
mevinphos

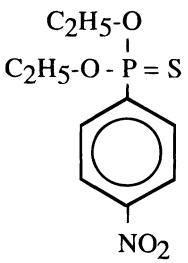


tetraethylpyrophosphate
TEPP
Et = ethyl

2. Thionophosphates
Hydrophobic, but more persistent than 1. above.

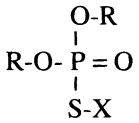


thionophosphates
parathion
methyl parathion
fenitrothion
diazinon



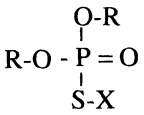
Parathion
O,O-diethyl-O-(p-nitrophenyl) phosphorothionate

3. Thiolphosphates (or phosphotiolates)



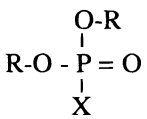
demeton-S-methyl
vamidothion

4. Dithiophosphates (or phosphorothiolthionates)



phorate
malathiondimethoate
disulfoton
menazon

5. Phosphonates
(Minor group)



trichlorphon
butonate

COMPLEX NOMENCLATURE

A priority listing of the more common organic functional groups is given in Table 7.18. Some examples of more complex nomenclature are given in tabular form in Tables 7.19a and 7.19b.

EXERCISES IN CHECKING CAS REGISTRY NUMBERS

Verify the following CAS registry numbers. If you have access to the CAS Registry Handbooks, give the CAS preferred name. Comment on the names for numbers 9 and 10.

1. 71-43-2
2. 95-48-8
3. 680-20-6
4. 1336-36-3
5. 12764-91-9
6. 7488-56-4
7. 7647-14-5
8. 67-66-3
9. 12015-73-5
10. 1306-05-4

Naming Hydrocarbons

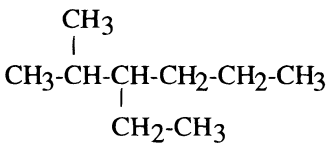
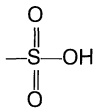
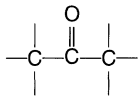
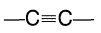
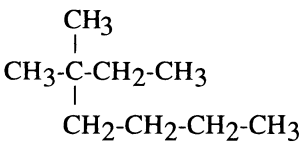
1. 

Table 7.18. Functional Group Nomenclature Priority, from Highest to Lowest

Functional group	Prefix	Suffix
		-oic acid carboxylic acid
		-sulfonic acid carbonyl chloride
		-oyl chloride
		Amide -carboxamide
	-oyl or -yl	-al -carbaldehyde
	Oxo-	-one
	Cyano- -carbonitrile	-nitrile
	Hydroxy-	-ol
	Mercapto- Amino-	-thiol -amine
	Alkoxy- Phenoxy-	Ether
		-ene
		-yne
		-ane
-F -Cl -Br -I $-CH_3$ $-C_6H_5$ $-NO_2$	Fluoro- Chloro- Bromo- Iodo- Methyl- Phenyl- Nitro-	

2. 

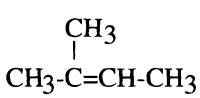
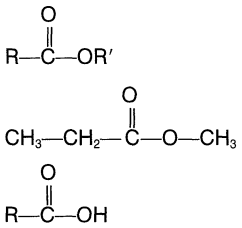
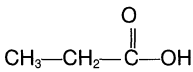
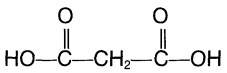
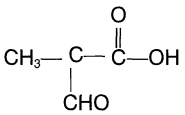
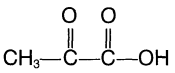
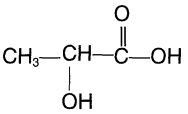
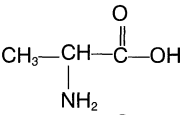
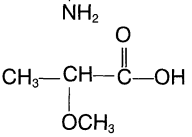
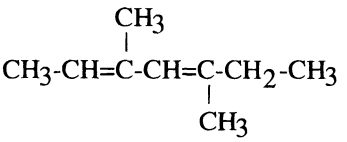
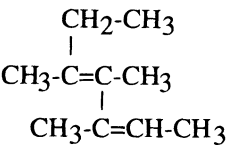
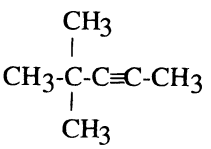
3. 

Table 7.19a. Examples of More Complex Nomenclature

Esters	
	Methyl propanoate propanoic acid, methyl ester
Carboxylic Acids	
	Propanoic acid
	Propanedioic acid
	2-Methanoylpropanoic acid (aldehyde substituent)
	2-Oxopropanoic acid (ketone substituent)
	2-Hydroxypropanoic acid
	2-Aminopropanoic acid
	2-Methoxypropanoic acid

4. 

5. 

6. 

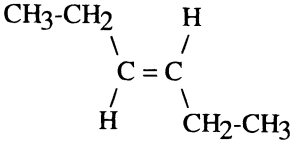
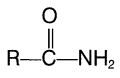
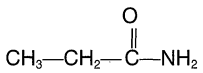
7. 

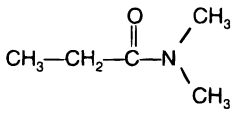
Table 7.19b. Examples of More Complex Nomenclature

Amides



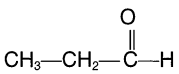


Propanamide

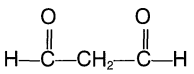


N,N-Dimethylpropanamide

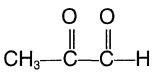
Aldehydes



Propanal

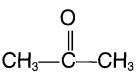


1,3-Propanedial



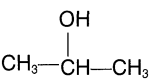
2-Oxopropanal

Ketones

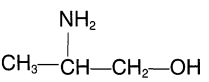


Propanone

Alcohols

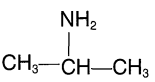


2-Propanol



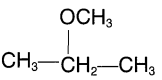
2-Amino-1-propanol

Amines



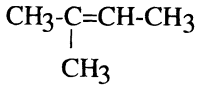
2-Aminopropane

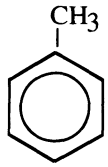
Ethers

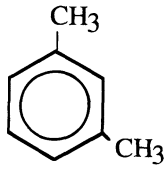


2-Methoxypropane

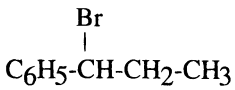
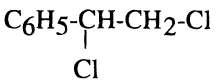
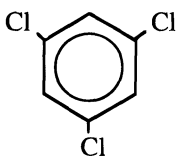
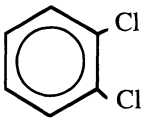
8. $(CH_3\text{-})_2C{=}CH\text{-}CH_3$ =



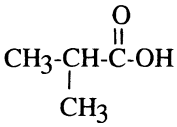
9. 

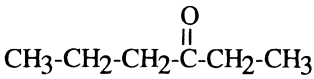
10. 

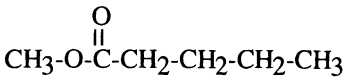
Naming Halogenated Hydrocarbons

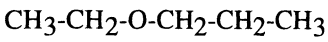
1. $C_6H_5—CH_2—Cl$
2. $Br—CH_2—CH_3$
3. $CH_2{=}CH—CH_2—Cl$
4. $Cl—CH_2—CH_2—CH_2—CH_2—Cl$
5. $CH_2{=}CH—Cl$
6. 
7. $CH_3—CF_3$
8. 
9. 
10. 

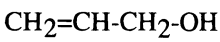
Naming Compounds with Oxygen Functional Groups

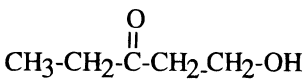
1. 

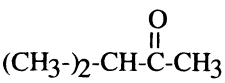
2. 

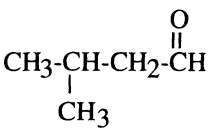
3. 

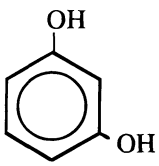
4. 

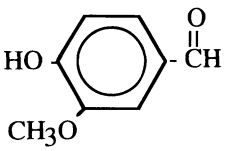
5. 

6. 

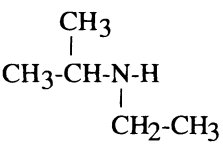
7. 

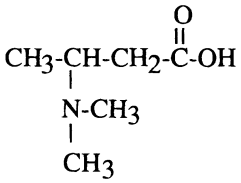
8. 

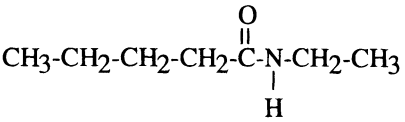
9. 

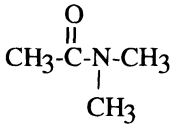
10. 

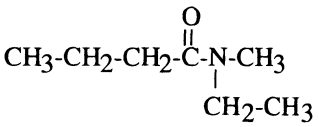
Naming Compounds with Nitrogen Functional Groups

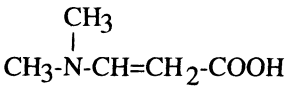
1. 

2. 

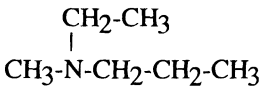
3. 

4. 

5. 

6. 

7. $N{\equiv}C{-}(CH_2)_4{-}C{\equiv}N$

8. 

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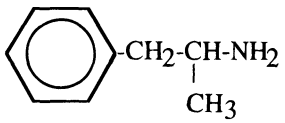
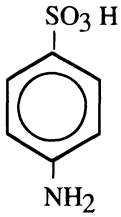
10. 

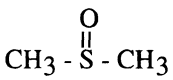
Naming Sulfur and Phosphorus Compounds

1. $CH_3{-}CH_2{-}CH_2{-}SH$

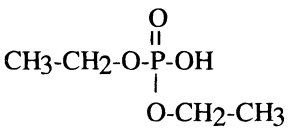
2. $Cl{-}CH_2{-}CH_2{-}S{-}CH_2{-}CH_2{-}Cl$

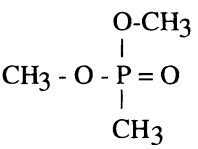
3. 

4. $CH_3—CH_2—S—S—CH_2—CH_3$

5. 

6. S=C=S

7. 

8. 

9. PH_3

10. $CH_3—PH_2$

ANSWERS TO EXERCISES

CAS Registry Numbers

Verify the following CAS registry numbers, and, if correct, give the CAS preferred name. Comment on numbers 9 and 10.

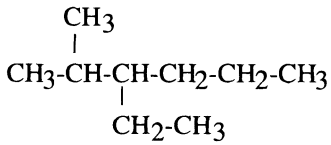
1. 71-43-2 benzene: check = 42/10 → 2
2. 95-48-8 check = 67/10 → 7 mistake
   o-xylene 95-47-6: check 66/10 → 6
3. 680-20-6 1,1,1,2-tetrachloroethane: check = 66/10 → 6
4. 1336-36-3 polychlorinated biphenyls [PCSs]
   check = 63/10 → 3
5. 12764-91-9 Aglypt: check = 109/10 → 9
   → 21087-63-8 check = 88/10 → 8
   1,2,4-triazin-5(4H)-one, 4-amino-3-(methylthio)-6-phenyl
6. 7488-56-4 selenium sulfide SeS_2: check = 134/10 → 4
7. 7647-14-5 sodium chloride: check = 115/10 → 5
8. 67-66-3 chloroform: check = 63/10 → 3

9. 12015-73-5 calcium fluoride phosphate $Ca_5F(PO_4)_3$
   check = 55/10 → 5
10. 1306-05-4 apatite $Ca_5FO_{12}P_3$: check = 44/10 → 4

Note: Two different numbers are used, one for the mineral and one for the chemical compound. In each case the chemical formula is represented differently.

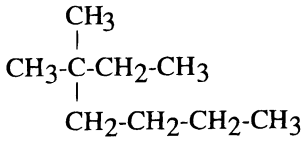
Hydrocarbons

1.



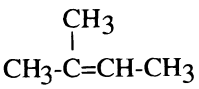
3-ethyl-2-methylhexane

2.



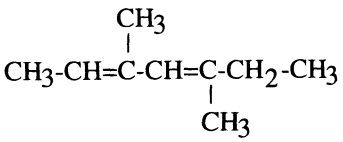
3,3-dimethylheptane

3.



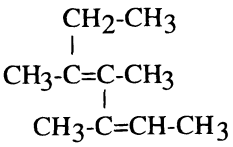
2-methyl-2-butene

4.



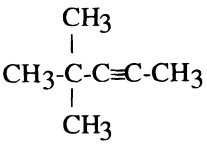
3,5-dimethyl-2,4-heptadiene

5.



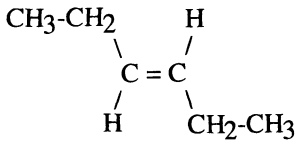
3,4,5-trimethyl-2,4-heptadiene

6.



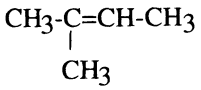
4,4-dimethyl-2-pentyne

7.



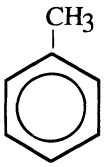
trans-3-hexene

8. $(CH_3\text{-})_2C{=}CH\text{-}CH_3$ =



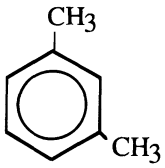
2-methyl-2-butene

9.



toluene

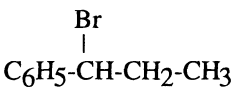
10.



m-xylene (1,3-dimethylbenzene)

Halogenated Hydrocarbons

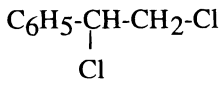
1. $C_6H_5—CH_2—Cl$ — phenylchloromethane or benzyl chloride
2. $Br—CH_2CH_3$ — bromoethane
3. $CH_2{=}CH—CH_2—Cl$ — 3-chloropropene or allyl chloride
4. $Cl—CH_2—CH_2—CH_2—CH_2—Cl$ — 1,4-dichlorobutane
5. $CH_2{=}CH—Cl$ — chloroethene or vinyl chloride
6.



1-bromo-1-phenylpropane

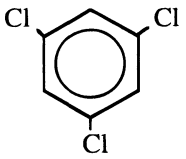
7. $CH_3—CF_3$ — 1,1,1-trifluoroethane

8.



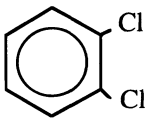
2-phenyl-1,2-dichloroethane

9.



1,3,5-trichlorobenzene

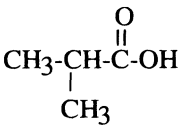
10.



1,2-dichlorobenzene or o-chlorobenzene

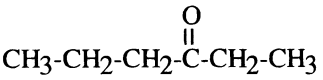
Oxygen Functional Groups

1.



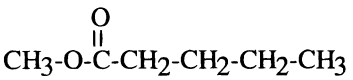
2-methylpropanoic acid

2.



3-hexanone

3.

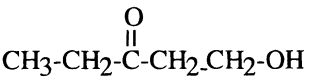


methyl pentanoate or pentanoic acid, methyl ester

4. $CH_3—CH_2—O—CH_2—CH_2—CH_3$ ethyl-n-propyl ether or 1-ethoxypropane

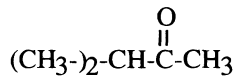
5. $CH_2=CH—CH_2—OH$ 2-propene-1-ol

6.



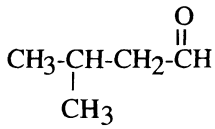
3-pentanone-1-ol

7.



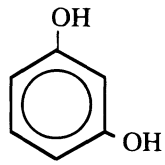
3-methyl-2-butanone

8.



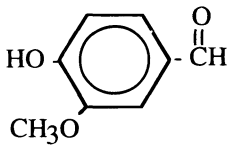
3-methylbutanal

9.



1,3-dihydroxybenzene

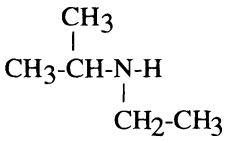
10.



4-hydroxy-3-methoxybenzaldehyde or vanillin

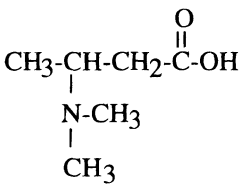
Nitrogen Functional Groups

1.



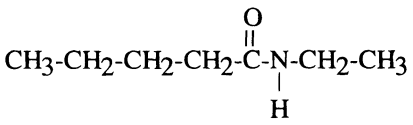
N-ethyl-2-propanamime
or ethyl isopropylamine
or N-ethylisopropanamine

2.



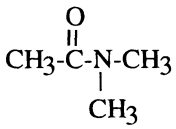
3-(N,N-dimethylamino)-butanoic acid

3.



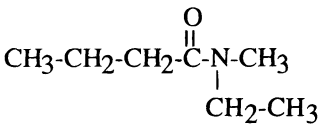
N-ethylpentanamide

4.



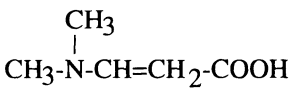
N,N-dimethylethanamide
or N,N-dimethylacetamide

5.



N-ethyl-N-methylbutanamide

6.

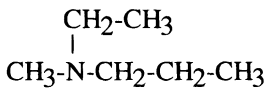


3-(N,N-dimethylamino) propenoic acid

7. $N{\equiv}C{-}(CH_2)_4{-}C{\equiv}N$

hexanedinitril
or (adiponitrile—nylon intermediate)

8.

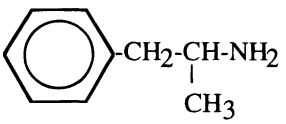


N-ethyl-N-methylpropanamine or
ethylmethylpropylamine

9.

4-nitroaniline

10.

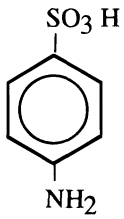


1-phenyl-2-propanamine
or 1-methyl-2-phenylethanamine
or 2-amino-1-phenylpropane
or benzedrine or amphetamine

Sulfur and Phosphorus Functional Groups

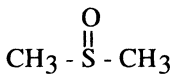
1. $CH_3—CH_2—CH_2—SH$ propanethiol

2. $Cl—CH_2—CH_2—S—CH_2—CH_2—Cl$ bis(2-chloroethyl) sulfide or (mustard gas)

3. 

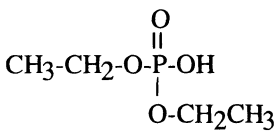
p-aminobenzene sulfonic acid or sulfanilic acid

4. $CH_3—CH_2—S—S—CH_2—CH_3$ diethyl disulfide

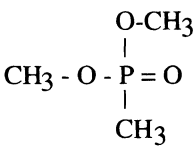
5. 

dimethylsulfoxide

6. $S=C=S$ carbon disulfide

7. 

diethyl phosphate

8. 

dimethyl methylphosphonate

9. PH_3 phosphine

10. $CH_3—PH_2$ methylphosphine

CHAPTER 8

Ecosystem Partitioning and Solute Transport

INTRODUCTION

Over the last 3 decades it has become increasingly apparent that the organic and inorganic constituents of the soil and deeper subsurface play an important part in the mobility (retardation) of introduced organic and inorganic chemicals. Early research by agronomists on the retardation of synthetic organic chemicals centered about the movement of pesticides and herbicides in the soil environment. Exploration geochemists studied the mobility of trace metals in order to locate ore deposits. In recent years the movement of many organic and inorganic pollutants in this zone has become a primary concern.

This chapter will describe the factors that influence the movement of organic pollutants in the subsurface and address the issue of the partitioning of organic chemicals in air, soil, and water. Some methods of estimating biodegradation will be discussed.

ECOSYSTEM PARTITIONING

An ecosystem may be thought of as a series of homogeneous compartments such as air, water, soil, sediment, and biological material. The concentration of an organic chemical in any compartment is related to the concentration in any other compartment by a specific distribution coefficient. Each distribution coefficient is known by a specific name. That relating air and water is called Henry's law constant; that relating concentrations in solid and water is called the distribution constant; and that relating concentrations in fish to that in water is called the bioconcentration factor.

LIQUID-LIQUID PARTITIONING

A distribution coefficient is a ratio of the concentration of the solute in each of the two immiscible phases. This is illustrated in Figure 8.1. The actual amount of the solute in each phase is thus dependent on two factors:

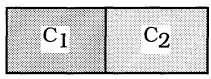
a. The distribution coefficient
b. The volume of each phase present

Calculations applicable to liquid-liquid and solid-liquid partitioning are derived in Table 8.1.

PARTITIONING

GIVEN CONCENTRATION IN PHASE 1

DETERMINE CONCENTRATION IN PHASE 2



$$C_2 = K * C_1$$

Figure 8.1. Partitioning between two immiscible phases.

Table 8.1. Distribution Coefficient

CASE 1: Immiscible Liquid (i)/ Water

$$K_i = \frac{C_i}{C_w} = \frac{\frac{M_i}{V_i}}{\frac{M_w}{V_w}} = \frac{M_i * V_w}{V_i * M_w} \frac{mg/L}{mg/L} \text{ unitless}$$

$$M_i = M_w * \frac{V_i}{V_w} * K_i$$

If the total mass of solute in the system is the loading, then

$$\text{Loading (LD)} = M_w + M_i = M_w * \left[1 + \frac{V_i}{V_w} * K_i\right]$$

CASE 2: Solid (s)/ Water

$$K_s = \frac{C_w}{C_w} = \frac{\frac{M_s}{MASS_s}}{\frac{M_w}{V_w}} \frac{mg/kg}{mg/L} = \frac{L}{kg} = ml/g$$

As mass = density * volume

$$K_s = \frac{C_s}{C_w} = \frac{\frac{M_s}{(V_s * D_s)}}{\frac{M_w}{V_w}} = \frac{M_s * I * V_w}{V_s * D_s * M_w}$$

$$M_s = M_w * \frac{V_s}{V_w} * D_s * K_s$$

$$\text{Loading (LD)} = M_w + M_s = M_w * \left[1 + \frac{V_s}{V_w} * D_s * K_s\right]$$

Octanol/Water Partition Coefficient

Octanol/water partition coefficient (K_{ow}) describes the distribution of a solute between two immiscible phases (that remain separate from one another), octanol and water, such that

$$K_{ow} = \frac{\text{conc. in octanol } (C_o)}{\text{conc. in water } (C_w)} \text{ (dimensionless)}$$

Example:

Consider an octanol/water system containing 200 ml octanol and 500 ml water with 10 mg solute distributed between them. The log K_{ow} for solute is 1.

$$K_{ow} = \frac{C_o}{C_w} = 10^1 = 10$$

If water contains x mg solute, then octanol contains (10 − x) mg of solute:

$$C_w = \frac{x \text{ mg}}{500 \text{ ml}} = 2x \text{ mg/L}$$

$$C_o = \frac{(10\text{-}x) \text{ mg}}{200 \text{ ml}} = 5*(10\text{-}x) \text{ mg/L}$$

thus as

$C_o = C_w * K_{ow}$

$5 * (10\text{-}x) = 2x * 10$ [K_{ow}] or $50 - 5x = 20x$

$50 = 25x$ or $x = 2$ and $(10\text{-}x) = 8$

$C_w = 4$ mg/L; $C_o = 40$ mg/L

[check $C_o/C_w = 10$]

Calculate concentrations for log $K_{ow} = 2.1$:

$K_{ow} = 10^{2.1} = 125.9$ and $5*(10\text{-}x) = 2x * 125.9$

$x = 0.195$ and $C_w = 0.39$ mg/L

$(10\text{-}x) = 9.805$ and $C_o = 49$ mg/L

[check $C_o/C_w = 49/0.39 = 125.6$; $\log(125.6) = 2.099$]

If the amount of solute in each phase is expressed as a percentage of the total amount of solute, and the volume of each phase is expressed as a percentage of the total volume, then

Let $\%M_o$ = % of solute mass in octanol
$\%M_w$ = % of solute mass in water
$\%V_o$ = volume of octanol expressed as % of total volume
$\%V_w$ = volume of water expressed as % of total volume

Then the concentration of solute in octanol $C_o = \%M_o/\%V_o$ and the concentration of solute in water $C_w = \%M_w/\%V_w$ and

$$K_{ow} = (\%M_o/\%V_o)/(\%M_w/\%V_w) \text{ or } \%M_o/\%V_o = K_{ow} * (\%M_w/\%V_w)$$

$$\text{Thus } \%M_o = K_{ow} * \frac{\%V_o}{\%V_w} * \%M_w \quad (1)$$

As $\%M_o = 100 - \%M_w$

then $100 - \%M_w = K_{ow} * (\%V_o/\%V_w) * \%M_w$ or
$100 = \%M_w * [1 + K_{ow} * (\%V_o/\%V_w)]$

Resulting in:

$$\%M_w = \frac{100}{\left(1 + K_{ow} * \frac{\%V_o}{\%V_w}\right)} \tag{2}$$

$$\text{And } M_w = \%M_w * \text{Loading} \tag{3}$$

If the size of the compartments and the distribution coefficient are known, then the amount of each phase in each compartment may also be calculated (Figure 8.2).

Using the first example above:

$$V_o = 200 \text{ ml}; V_w = 500 \text{ ml}$$

$$\%V_o = \frac{200}{700} * 100 = 28.6\%$$

$$\%V_w = \frac{500}{700} * 100 = 71.4\%$$

Substituting in Equation (2):

$$\%M_w = \frac{100}{\left(1 + 10 * \frac{28.6}{71.4}\right)} = 20\%$$

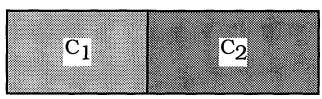
Substituting in Equation (1):

$$\%M_o = 10 * \frac{28.6}{71.4} * 20 = 80\%$$

LOADING - CONCENTRATION RELATIONSHIP

GIVEN SOLUTE LOADING
(TOTAL AMOUNT)

DETERMINE CONCENTRATION
IN EACH PHASE



V_1 V_2

VOLUMES MUST BE SPECIFIED

LOADING = $C_1 * V_1 + C_2 * V_2$

Figure 8.2. Calculation of loading (total solute in system) from concentration and volume.

Substituting in Equation (3):

$$M_w = \frac{20}{100} * 10 = 2 \text{ mg}$$

Bioconcentration Factor

The bioconcentration factor (BCF) describes the distribution of a solute between a fish and water; it is defined as

$$\text{BCF} = \frac{\text{conc. in fish } (C_f)}{\text{conc. in water } (C_w)}$$

$$\text{BCF} = \frac{\frac{M_f}{V_f}}{\frac{M_w}{V_w}} = \frac{M_f * V_w}{M_w * V_f}$$

where M is the mass of solute in compartment with volume V.

$$M_f = \text{BCF} * \frac{V_f}{V_w} * M_w$$

Examples:

1. Given a log BCF of 3.2 and a concentration of a chemical in a pond of 20 μg/l, what is the concentration of the chemical in the fish?

$$C_f = \text{BCF} * C_w = 10^{3.2} * 20 = 31{,}698 \text{ μg/l} = 31.7 \text{ mg/l}$$

2. Assume a 1-kg spill of a material in a pond having dimensions of 100 * 100 * 10 m^3. If the fish make up 1 ppm of the pond, and log BCF is 3.2, find the concentration of the material in the pond.

Volumes: $\text{pond} = 10^5 \text{ m}^3$; $\text{fish} = \frac{\text{pond}}{10^6} = 0.1 \text{ m}^3$

$$\text{BCF} = 10^{3.2} = 1585$$

concentrations:

$$\text{LD} = M_w * \left[1 + \frac{V_f}{V_w} * K_f\right]$$

$$1 \text{ kg} = M_w * \left[1 + \frac{0.1}{10^5} * 1585\right]$$

$$M_w = \frac{1000 \text{ g}}{1.001585}$$

$$= 998.418 \text{ g } C_w = \frac{M_w}{V_w} = \frac{988.418}{10^5} = 9.984\text{E-}3 \text{ g/m}^3 \text{ (= mg/l)}$$

$$= 0.01 \text{ mg/l}$$

$$M_f = 1000 - 998.418 = 1.583 \text{ g}$$

$$C_f = \frac{1.583}{0.1} = 15.83 \text{ g/m}^3$$

CHECK log(BCF) = log(15.8/0.009984) = 3.199

BCF-K_{ow} Relationship

$$\ln BCF = 0.935 * \ln K_{ow} - 3.443$$

$$(\ln X = \log_e X, \log X = \log_{10} X \text{ and } \log X = \frac{\ln X}{\ln(10)}$$

Calculate relationship in terms of log BCF and log K_{ow}.

$$\log BCF * \ln 10 = 0.935 * \log K_{ow} * \ln 10 - 3.443$$

$$\log BCF = 0.935 * \log K_{ow} - \frac{3.443}{\ln 10}$$

$$\log BCF = 0.935 * \log K_{ow} - 1.495$$

Nonaqueous Phase Liquid Partitioning

Partitioning of liquid solutes between nonaqueous phase liquids (NAPL) and water may be calculated by the relationship:

$$\frac{C_{NAPL}}{C_{water}} = K_{NAPL}$$

If units of C_{NAPL} are mole fraction – X_i, and those for C_{water} are in mg/l – S_i^e (called effective solubility), then K_{NAPL} is $1/S_i$, where S_i is the pure phase solubility of compound i.

The equation presented by Feenstra et al. (1991) is

$$S_i^e = X_i * S_i$$

where

S_i is the maximum solubility of a solute in water,
X_i is the mole fraction concentration in the nonaqueous phase, and
S_i^e is the effective solubility of a solute in water partitioning from a nonaqueous phase liquid in which it is in contact.

Example:

If a dense nonaqueous phase liquid (DNAPL) contains 0.10 mole fraction of trichloroethene (TCE), then its solubility in water in contact with it is

$$0.1 * 1100 \text{ mg/l} = 100 \text{ mg/l}$$

In order to calculate the partitioning of a solid solute between NAPL and water, the liquid solubility must be obtained. This may be calculated from the solid solubility by the equation:

$$C_l = C_s * \exp\left\{6.8 * \left[\frac{T_M}{T} - 1\right]\right\}$$ Shiu, et al., 1988.

where

C_l is the liquid solubility
C_s is the solid solubility
T_M is the melting point (K)
T is the system temperature (K).

Examples of calculated liquid solubilities of some common pollutants are given in Table 8.2. The result of these calculations shows that liquid-phase solubility values for the solutes may be considerably higher than the solid-phase solubility values, and that the difference is greater for the compounds with higher melting points (Feenstra, 1990). Thus, an oily waste product containing a small fraction of a high-melting point solid may present a much greater hazard to the groundwater than a concentrated pile of the solid component.

SOLID-PHASE PARTITIONING

Partitioning between water and a solid phase usually presents an additional problem. That is, the concentration in the solid phase is usually expressed in terms of the weight of the solid, for example, mg/kg of soil (equals ppm). Most measurements of the amount of solid phase are usually expressed as a volume. The relationship mass = volume * density is used. The derivation of this is given in Table 8.1.

Adsorption Isotherms—Equations

An adsorption isotherm is a graph of the amount of solute adsorbed by a given weight of a solid phase vs. the concentration of the solute in solution. The constant relating of these two parameters is called the distribution coefficient. The distribution coefficient is not always a constant and may vary with the concentration of the solute in the liquid phase. The graph that allows the distribution coefficient to be obtained at different concentrations is known as an adsorption isotherm. An adsorption isotherm determined experimentally is a plot of the amount of material adsorbed per gram of adsorbent (solid) vs. the concentration of the adsorbate (solute) in solution. The result may be a straight line or an exponential curve. This curve will become a straight line on a log-log plot. Linear adsorption isotherms result when the distribution coefficient is independent of concentration, that is,

$$C_s = K_d * C_w$$

Table 8.2. Liquid Solubility of some Solids, Calculated by the Method of Shiu et al., 1988

Compound (1)	Melting point °C	Solubility (mg/l) solid	Solubility solid reference	Solubility (mg/l) liquid*	Factor C_l/C_s
Chrysene	255.5	0.0020	(2)	0.583	292
Anthracene	216.4	0.073	(2)	8.46	116
Pentachlorophenol	191	14	(3)	891	64
Pyrene	156	0.135	(2)	3.76	28
Phenanthrene	101	1.29	(2)	9.82	8
Naphthalene	80.5	31.7	(2)	149	5
2-Methylnaphthalene	34.6	25.4	(2)	40.3	2

Source of data:
(1) Lide, 1992
(2) Mackay and Shiu, 1977.
(3) Howard, 1989.

*Calculated at 15°C.

Note: The high values obtained would result in much higher aqueous solubilities than would otherwise be expected.

where

C_s is the amount of solute adsorbed by the solid phase.
C_w is the concentration of solute in the liquid phase.
K_d is the distribution coefficient (linear distribution coefficient).

This is commonly the relationship observed where partition occurs between two liquid phases up to their solubility limit. Most chromatography models used for describing pollutant transport assume this model. Freundlich isotherms are an empirical attempt to describe nonlinear relationships. They are defined by the equation:

$$C_s = K_d * C_w^n$$

where K_d and n are constants. This equation is usually presented in the linear form:

$$\log C_s = K_d + n * \log C_w$$

where n is the slope of the line and K_d the distribution coefficient.

Although generally considered an empirical relationship, Sposito and Mattigod (1980) derived it theoretically for the trace adsorption of an ion participating in an exchange reaction. Elution curves illustrating the phenomena of tailing for isotherms where $n = 1$, $n < 1$, and $n > 1$ are shown in Figures 8.3 and 8.4.

Activated Carbon Partitioning

Activated carbon is commonly used as a method of removing trace amounts of organic chemicals from aqueous solutions, such as an activated carbon filter. The distribution of solute is described by the equation:

$$\frac{x}{M} = K * C_W^n$$

where

x/M represents the concentration in the solid phase,
x is the amount of solute adsorbed by the carbon,
M is the concentration of carbon in the solution,
K is the activated carbon distribution coefficient,
C_w is the concentration of solute in the solution, and
n is the Freundlich isotherm exponent

Units: $\frac{x}{M}$—mg/g; C_w—mg/l; K—l/g

Example:

A liter of solution containing 10 mg/l solute contains 3 mg/l after adding 2 g of activated carbon. If $n = 1$, what is the distribution coefficient?

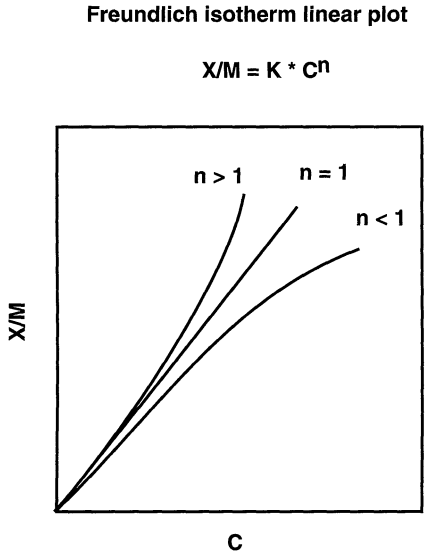


Figure 8.3. Freundlich isotherm plotted using linear axes showing the departure from linearity when the exponent n is not equal to 1. The curve is concave up when $n > 1$ and convex up when $n < 1$. A straight line results when $n = 1$.

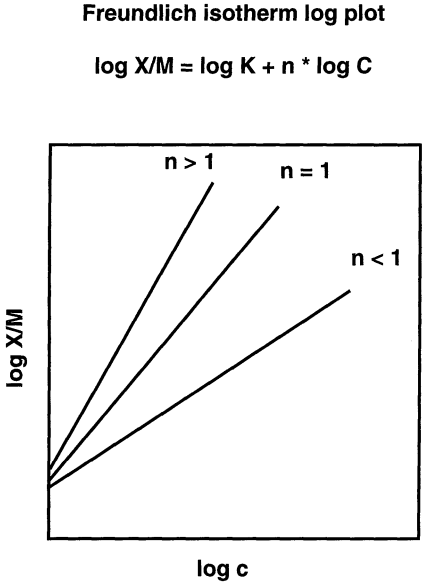


Figure 8.4. Freundlich isotherm plotted using log-log axes. When plotted on a log-log graph the slope is 45° when $n = 1$, steeper when $n > 1$ and less steep when $n < 1$.

Concentration of solute in water = 3 mg/l
Concentration of carbon = 2 g/l
Mass of solute in carbon (10 − 3) = 7 mg

$$\frac{x}{M} = K * C_w$$

$$K = \frac{(10 - 3)}{2 * 3} = 1.17 \text{ l/g}$$

If K = 50 and n = 0.7, how much activated carbon would be required to reduce a solute from 15 to 2 mg/l?

Concentration of solute in water is 2 mg/l

Concentration of solute in carbon is (15 − 2) = 13 mg/l

$$\frac{13}{M} = 50 * 2^{0.7}$$

$$\text{or } \frac{13}{M} = 50 * 1.625$$

M = 0.16 g carbon/l

Soil Sorption Constant

The soil sorption coefficient describes the behavior of a solute in water with respect to soil. K_d (ml/g) is defined as:

$$K_d = \frac{\text{conc. in soil } (C_s)}{\text{conc. in water } (C_w)} = \frac{\dfrac{M_s}{\text{mass soil}}}{\dfrac{M_W}{\text{mass water}}}$$

Mass soil = $V_s * D_s$, where D_s is the bulk density.

$$K_d = \frac{\dfrac{M_s}{(V_s * D_s)}}{\dfrac{M_w}{V_w}} = \frac{M_w * V_w * 1}{M_w * V_s * D_s}$$

$$M_s = K_d * \frac{V_s}{V_w} * D_s * M_w$$

Soil is a complex multiphase system where components vary considerably from one area to another. The three solid-phase constituents most likely to be important in the adsorption reactions are soil organic matter (SOM), clay minerals, and amorphous hydroxides of iron, aluminum, and manganese.

SOM is a mixture of complex organic polymers of doubtful composition, which is generally assumed to have a large number of phenolic —OH and carboxylic acid (—COOH) groups attached to it. It may be physically and chemically separated into three main components: alkali-soluble fulvic and humic acids, and insoluble humin. The interactions between the SOM-clay minerals and amorphous hydroxides that may affect the adsorption characteristics are essentially unknown.

A vast amount of literature has been developed over the last 3 decades on the adsorption of organic compounds (primarily herbicides and pesticides) by soil components. In 1954, Sherburne and Freed published one of the earlier papers to report experimental data that showed an unequivocal correlation between adsorption of a specific organic compound and SOM. Since then, many papers have been written expanding the number of organic compounds for which this relationship holds true.

Normalized K_d

It has become a fairly common practice to normalize distribution coefficients obtained from soils to their organic matter or organic carbon content, as in the following equation,

$$K_{oc} = K_d * \frac{100}{\%oc}$$

where K_{oc} is the normalized distribution coefficient and K_d is the distribution coefficient obtained using a soil containing **oc** percent organic carbon.

Historical background — The sorbing medium is thus considered to be the som rather than the total mass of soil. Lambert (1967) and Furmidge and Osgerby (1967) normalize to percent SOM, whereas Karickhoff (1981) normalizes the distribution coefficient to percent of organic carbon. It has been found empirically that som contains 58% organic carbon; thus K_{oc} can be derived from K_{som}. Although som has been shown to be the primary factor in many adsorption experiments, it is not the only one. In 1960, Leopold et al. showed that for 17 of the chlorinated derivatives of phenoxyacetic acid there was a strong inverse correlation between their adsorption and solubility. In a more practical mode, Harris (1964) noted that in most soils the adsorption (inactivation) of insecticides is proportional in the organic content of the soil; however, in dry soils this inactivation is related to the adsorption capacity of the mineral fraction. Bailey and White (1964) presented the first review of the adsorption and desorption of organic pesticides by soil colloids, including som clays, and amorphous hydroxides. Stevenson (1976) reviewed many aspects of organic matter-pesticide reactions in soils. His discussion is based on the premise that adsorption by organic matter has been shown to be a large factor in the behavior of many pesticides in soil. He also stated that the mechanisms of pesticide-organic matter interactions will remain obscure until more is known about the nature of chemical composition of the organic fraction of soils. Khan (1978) further reviews the nature and classification of pesticides and various mechanisms that have been proposed for their adsorption by som. For example, 2-4D is strongly adsorbed by humic acid, although the effect of illite may be important (Haque, 1975). Similarly, 1-naphthol is primarily adsorbed by som although a high montmorillonite/SOM ratio has a significant effect on the adsorption isotherm (Hasset et al., 1981).

Thus the distribution coefficient is normalized to the amount of organic carbon in the soil. That is, K_d is expressed in terms of 1% organic carbon. The reason is that it has been established that the primary adsorbing material in the soil is the som (organic carbon). Thus K_{oc} is defined as:

$$K_{oc} = \frac{\mu g \text{ chemical/g organic carbon}}{\mu g \text{ chemical/g water}}$$

$$= K_d * \frac{100}{\%oc}$$

Solute Distribution in an Aquifer

$K_d = K_{oc} * TOC$ (expressed as a fraction)
Expressing solute as a percent,

then $100 = M_w * \left[1 + V_s/V_w * D_s * K_d\right]$ derived in Table 8.1.

Assuming a porosity n, then $V_s/V_w = (1 - n)/n$ and
D_s (bulk density) = 2.65 * (1 − n) for a quartz matrix, then:

$$100 = M_w * \left[1 + \frac{(1 - n)}{n} * 2.65 * (1 - n) * K_{oc} * \text{TOC (fraction)}\right]$$

Critical Sediment Concentration

For an acute maximum concentration of a toxic material in water, there exists a maximum critical concentration in the sediment in equilibrium with it.

$$K_{oc} = \frac{K_d}{\text{TOC (as a fraction)}}$$

$$K_{oc} = \frac{C_s}{(C_w * \text{TOC})}$$

$$C_s = K_{oc} * C_w * \text{TOC}$$

If acute concentration (C_{w-ac}) in water is 0.16 μg/l (ppb); K_{oc} = 1950

$$C_{s\text{-}ac} = \frac{1950 * 0.16}{000\ \mu g/g} = 0.31\ \mu g/g\ (\text{ppm})$$

(per gram of organic carbon in sediment).

Pond Ecosystem

Consider an ecosystem consisting of a pond containing only water and sediment. Then if:

$\%M_w$ = % solute in water phase
$\%M_s$ = % solute in sediment phase
$\%V_w$ = % total volume occupied by water
$\%V_s$ = % total volume occupied by sediment
D_s = bulk density of the sediment, typically about 2.0
D_w = density of water, essentially 1.0
C_w = concentration of solute in water

$$= \frac{\%M_w}{\text{mass water}} = \frac{\%M_s}{(\%V_w * D_w)} = \frac{\%M_w}{\%V_w}$$

C_s = concentration of solute in sediment

$$= \%M_s/\text{mass of sediment} = \frac{\%M_w}{(\%V_s * D_s)}$$

$$= \frac{\%M_s}{(\%V_s * 2.0)}$$

Distribution coefficient

K_d = distribution coefficient

$$= K_{oc} * \frac{\%oc}{100} = \frac{C_s}{C_w} = \frac{\%M_s}{2.0 * V_s} * \frac{\%V_w}{\%M_w}$$

$$\%M_s = \frac{K_d * 2.0 * \%V_s}{\%V_w} * \%M_w = X * \%M_w$$

$$100 = \%M_s + \%M_w = X * \%M_w + \%M_w = \%M_w * (X + 1)$$

$$\%M_w = \frac{100}{X + 1}$$

Concentration in ppm (mg/kg)

$$\text{Mass of solute in phase x in mg} = \frac{\%M_x}{100} * \text{loading (kg)} * 1E6$$

$$\text{Mass of phase x in kg} = \frac{\%V_x}{100} - *Vt(m^3) * 1E3 * D_x$$

D_x = density of phase x

$$\text{Concentration of solute in phase x} = \frac{\%M_x * LD(kg) * 1E3}{\%V_x * Vt(m^3) * D_x}$$

Example of a Pond Ecosystem

Assume:

Pond diameter	= 100m		
% oc in sediment	= 5%		
Water depth	= 4 m		
K_{oc} solute	= 1000 mg/g		
Sediment depth	= 5 cm		
Loading of solute	= 1 kg		
Volume of water	$= \pi * 50 * 50 * 4$	$= 31{,}416\ m^3$	
Volume of sediment	$= \frac{\pi * 50 * 50 * 5}{100}$	$= 392.7\ m^3$	
$\%V_w$	= 98.77%		
$\%V_s$	= 1.23%		
K_d	$= K_{oc} * \%oc/100$	$= 1000 * 5/100$	$= 50$
$K_d * 2.0 * \%V_s/\%V_w$	$= 50 * 2.0 * 1.23/98.77$	= 1.254	
$\%M_w$	$= 100/(1.254 + 1)$	= 44.4%	
$\%M_s$		= 55.6%	
C_w (ppm)	$= \frac{\%M_w * LD * 1E3}{\%V_w * V_t * D_w}$	$= \frac{44.4 * 1 * 1E3}{98.77 * 31808.7 * 1}$	= 0.014 ppm
C_s (ppm)	$\frac{\%M_s * LD * 1E3}{\%V_s * V_t * D_s}$	$\frac{55.6 * 1 * 1E3}{1.23 * 31808.7 * 2}$	= 0.71 ppm

AIR-WATER PARTITIONING

The main problem when considering air-water partitioning is the large variety of units that are used to describe the distribution constant, called Henry's law constant. Some of these are described below.

Henry's Law Constant—H

Some of the different expressions that result in different units for Henry's law constant are given below.

a. H (atmos-liter/gram)

$$H = \frac{P\ (\text{atmos})}{C_w\ (\text{g/l})}$$

b. H (atmos-liter/mole)

$$H = \frac{P\ (\text{atmos})}{C_w\ (\text{mol/l})}$$

c. H (atmos/mole fraction)

$$H = \frac{P\ (\text{atmos})}{X_w\ (\text{mole fraction})}$$

d. H (dimensionless)

$$H = \frac{Ca\ (\text{mol/l})}{C_w\ (\text{mol/l})}$$

Conversion Equation

GAS LAW:

$$PV = nRT \text{ where } n = \frac{w}{M}$$

$$P * V = \frac{w * R * T}{M}$$

$$P = \frac{w * R * T}{M * V}$$

$$C_a\ (\text{mol/l}) = \frac{w}{M * V}$$

$$P = C_a * R * T$$

Thus:

$$H = \frac{P}{C_w} = \frac{C_a * R * T}{C_w} \text{ if } C_w \text{ in mol/l}$$

$$H \text{ (dimensionless)} = \frac{C_a}{C_w} = \frac{H \text{ (atmos-liter/mole)}}{R * T}$$

Gas constant (R) = 0.08205 liter-atmos/degree/mole

= 8.20562E-05 m^3-atmos/degree/mole

H—Approximation

$$C_a \text{ (g/l)} = \frac{w * P * M}{V * R * T}$$

At saturation $C_w = C_{sat}$ (solubility)
For pure solute P = Po atmos

Thus

$$\frac{C_a}{C_w} = \frac{Po * M}{R * T * C_{sat}}$$

$$\text{If Po is in mm Hg, then Po (atmos)} = \frac{Po \text{ (mm Hg)}}{760}$$

$$\text{If } C_{sat} \text{ is in mg/l then } C_{sat} \text{ (g/l)} = \frac{C_{sat} \text{ (mg/l)}}{1000}$$

R (liter-atmos/degree/mole) = 0.082054

T = 25°C = 298.16 K

$$\text{Factor} = \frac{1000}{(0.082 * 760)} = 16.04$$

$$\frac{C_a}{C_w} = 16.04 * \frac{Po \text{ (mm Hg)} * M}{T \text{ (°K)} * C_{sat} \text{ (mg/L)}} \text{ (Dilling, 1977)}$$

Example:

What is the Henry's law constant for tetrachloromethane?

Formula = CCl_4, molecular weight (M) = 153.823, solubility (C_{sat}) = 800 ppm, vapor pressure (Po) = 113 mm Hg

$$T = 25°C = 298.15 \text{ K}$$

$$H = 16.04 * \frac{113 * 153.823}{298.15 * 800} = 1.169$$

Note: The larger the Henry's law constant, the greater will be the concentration of the contaminant in the air. Thus, contaminants having larger Henry's law constants are more easily removed by air stripping.

Air-Water Distribution

$$H = \frac{\text{conc. in air}}{\text{conc. in water}} = \frac{C_a}{C_w}$$

$$H = \frac{\frac{M_w}{V_a}}{\frac{M_w}{V_w}} = \frac{M_a * V_w}{M_w * V_a}$$

$$M_a = K_H * \frac{V_a}{V_w} * M_w$$

AQUIFER ECOSYSTEM

Another simplified ecosystem is the aquifer system or saturated system consisting of rock and water. It is numerically similar to the pond ecosystem except that the solid phase is dominant and the aqueous phase equals the pore space.

Thus

$$\frac{V_{sed}}{V_w} = \frac{(1 - n)}{n}$$

and

$$M_{sed} = K_d * \frac{V_{sed}}{V_w} * D * M_w$$

$$= K_d * \frac{(1 - n)}{n} * D * M_w$$

FULL ECOSYSTEM CALCULATIONS

The above calculations can be extended to a multiphase system if there are partitioning coefficients available for all pairs of phases. The amount of solute in each phase may be expressed relative to a common phase, usually water. For convenience in calculations the percent solutes and volumes are used rather than the actual values. This means that the loading is assumed to be 100 and may be changed when the actual loading is known without altering the equations. The partition coefficients of the various phases are shown in Figure 8.5. A list of log K_{oc}, log BCF, and Henry's law constant for some common organic chemicals are given in Table 8.3. This ecosystem was proposed by McCall et al. (1983) and is shown in Figure 8.6. A plot of some common organic chemicals in McCall's ecosystem is shown in Figure 8.7.

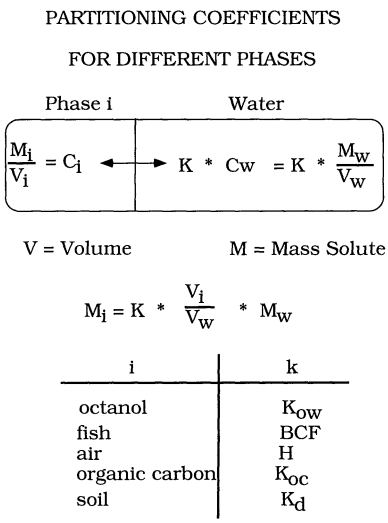


Figure 8.5. Partition coefficients for different phases.

Using the BCF when considering the fish-water system, then

$$BCF = \frac{C_f}{C_w} = \frac{M_f * V_w}{V_f * M_w}$$

and

$$M_f = M_w * \frac{V_f}{V_w} * BCF$$

Using the sediment distribution coefficient K_d when considering the sediment-water system, then

$$K_d = \frac{C_s}{C_w} = \frac{M_s * V_w}{V_s * D_s * M_w}$$

where

$$D_s = \text{bulk density of sediment, approximately 2.0}$$

and

$$M_s = M_w * \frac{K_d * V_s * D_s}{V_w}$$

This equation is used for both K_{d-sed} and K_{d-soil}. It must be noted that although the same K_{oc} is used, the percent organic matter will usually be different.

Using Henry's law constant (H) when considering the air-water system

$$H = \frac{C_a\ (mol/l)}{C_w\ (mol/l)} = \frac{V_w * M_a}{M_w * V_a}$$

and

$$M_a = M_w * \frac{V_a}{V_w} * H$$

Table 8.3. K_{oc}, BCF, and Henry's Law Constant of Selected Organic Chemicals

Chemical	log K_{oc}	log BCF	H unitless
DDT	5.18	4.79	0.00213
Pentachlorophenol	4.72	3.18	0.00011
Tetrachlorobiphenyl	4.51	4.86	0.50000
Hexachlorobutadiene	4.46	2.97	186.79703
Hexachloroethane	4.30	2.81	0.10178
1.2.4-Trichlorobenzene	3.96	2.53	0.09442
1.2.3-Trichlorobenzene	3.87	2.35	0.17290
Chlorpyrifos	3.79	2.67	0.00030
1.3.5-Trichlorobenzene	3.79	2.38	0.97690
Hexachlorocyclopentadiene	3.68	3.22	0.55998
Hexachlorobenzene	3.59	3.40	0.02784
2.4.6-Trichlorophenol	3.30	2.12	0.00016
Pentachloroethane	3.28	1.21	0.99734
1.2-Dichlorobenzene	3.23	1.87	0.07889
1.3-Dichlorobenzene	3.23	1.87	0.14674
2-Chlorotoluene	3.20	1.70	0.25547
Lindane	3.11	2.51	0.00333
Naphthalene	3.11	1.72	0.04701
3-Chlorotoluene	3.08	1.57	0.65399
Ethylbenzene	3.04	1.45	0.26282
m-Xylene	2.99	1.55	0.43736
p-Xylene	2.94	1.45	0.28817
o-Xylene	2.92	1.26	0.20846
Nitrapyrin	2.75	1.91	0.00087
4-Chloro-*m*-cresol	2.69	1.30	0.00010
Tetrachloromethane	2.64	0.97	0.98508
2-Chlorophenol	2.60	0.53	0.00043
2.4-Dichlorophenol	2.58	1.22	0.00011
Tetrachloroethene	2.56	0.94	1.05865
Toluene	2.48	1.06	0.26037
Trichlorofluoromethane	2.20	0.87	4.49621
1.1.1-Trichloroethane	2.18	0.84	0.58859
Bromobenzene	2.18	1.27	0.07848
Trichloroethene	2.10	0.73	0.37196
1.1.2.2-Tetrachloroethane	2.07	0.74	0.01557
Tribromomethane	2.06	0.75	0.02256
Trichloroethene	2.06	1.02	0.41525
2.4.5-Trichlorophenol	1.95	1.98	0.00891
Dibromochloromethane	1.92	0.46	0.04047
Benzene	1.92	0.49	0.22849
1,3-Dichloropropene	1.83	0.48	0.05556
1.1-Dichloroethene	1.81	0.23	1.38974
Bromodichlorobenzene	1.79	0.26	0.09810
2,4-D	1.78	0.48	7.7E−09
1.2-Dichloroethene (*trans*)	1.77	−1.05	0.26814
Chloroethene	1.76	−0.20	3.34763
Dichlorodifluoromethane	1.76	0.53	121.39765
Benzyl chloride	1.70	0.96	0.00207
1.2-Dichloroethene (*cis*)	1.69	−0.84	0.30983
Trichloromethane	1.67	0.35	0.11743
Chloromethane	1.54	−1.52	1.79848
1.1-Dichloroethane	1.48	0.18	0.17617
Chloroethane	1.23	−0.05	0.02514
Dichloromethane	0.94	−0.28	0.08298

Data from Mercer et al., 1990

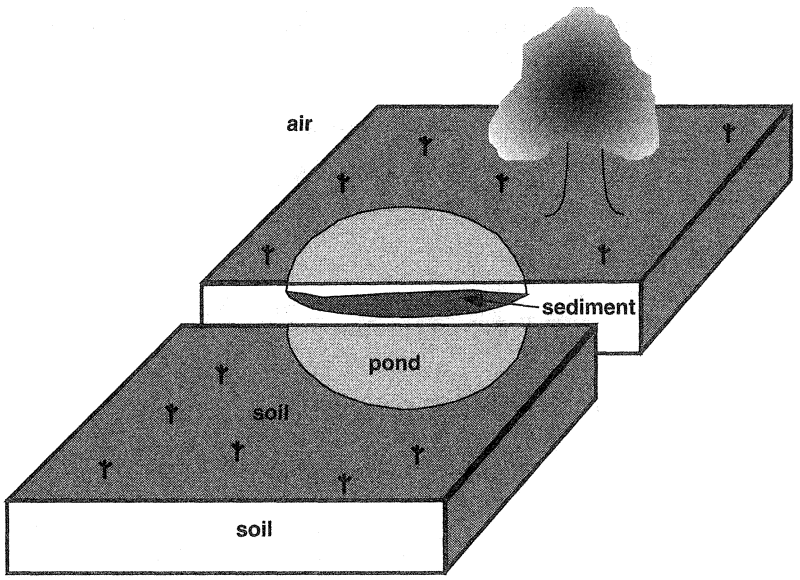


Figure 8.6. Ecosystem proposed essentially by McCall et al., 1983. It consists of soil of specified thickness with air, water, soil organic matter, a percentage of the total area under water of specified depth containing sediment, suspended sediment, and fish. The natural organic content of the sediment may be different to that of the soil. The entire region is overlain by a column of air of some specified height.

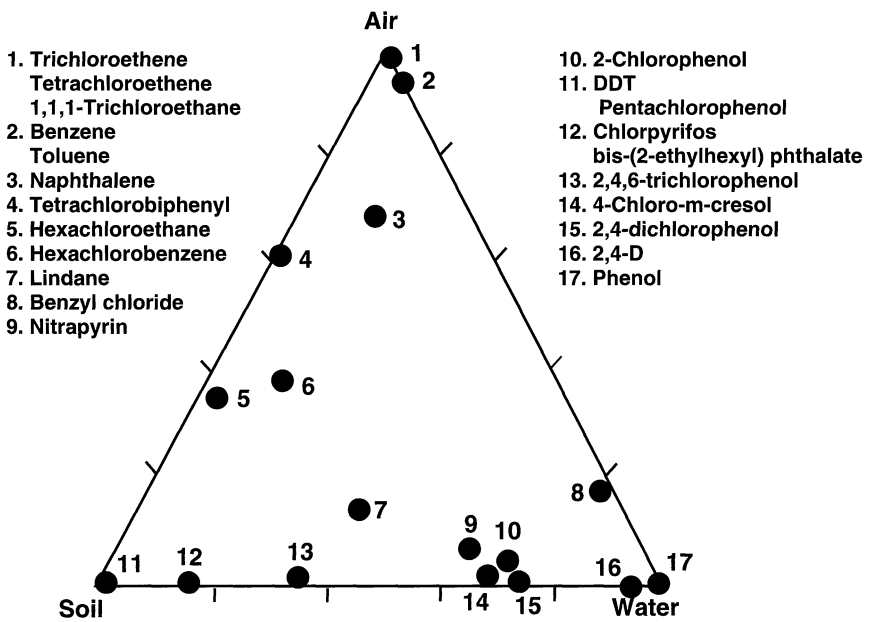


Figure 8.7. Plot of some organic chemicals in the soil-air-water system.

When considering the air-soil water system the equations for both the air-soil and the air-water systems must be combined:

$$H = \underset{\text{air-soil water}}{\frac{V_{sw} * M_a}{M_{sw} * V_a}} = \underset{\text{air-water}}{\frac{V_w * M_a}{M_w * V_a}}$$

Therefore

$$\frac{V_{sw}}{M_{sw}} = \frac{V_w}{M_w} \quad \text{and} \quad M_{sw} = \frac{M_w * V_{sw}}{V_w}$$

The final equation is formed by adding all fractions:

$$\begin{aligned} \text{loading} &= M_w + M_f + M_a + M_{sw} + M_{sed} + M_{soil} \\ &= M_w * \left[1 + BCF * \frac{V_f}{V_w} + H * \frac{V_a}{V_w} + \frac{V_{sw}}{V_w} + K_{d\text{-}sed} * 2.0 * \frac{V_{sed}}{V_w} \right. \\ &\quad \left. + K_{d\text{-}soil} * 2.0 * \frac{V_s}{V_w} \right] \end{aligned}$$

PARTITIONING ESTIMATES USING PARAMETER RANGES

The fundamental parameters for estimating environmental partitioning parameters are solubility and vapor pressure.

Solubility

Many regression equations have been proposed for relating solubility and K_{ow}, solubility and K_{oc}, K_{ow} and K_{oc}, and K_{ow} and BCF. As K_{ow} and solubility are actually different expressions of the same property, it is readily apparent that solubility, K_{ow}, K_{oc}, and BCF are related. All these parameters have been used to classify organic pollutants into simple categories; however, the divisions used are usually somewhat arbitrary.

In the following discussion, several solubility divisions are used and the related parameter values are calculated using various regression equations such that all are consistent and that as many as possible related organic chemicals fall into the same category. The divisions used are solubilities of 65 ppm and 2000 ppm. The matching parameter ranges are

solubility ppm	65	and	2000
log Kow	4.0	and	2.5
log Koc	2.9–3.6	and	2.1–2.4
log BCF	2.2	and	0.8

Vapor Pressure

The only common parameter used to estimate solute volatility is vapor pressure. The partition coefficient used to estimate water/air partitioning is Henry's law constant. This parameter has numerous unit choices, but the one most commonly used in distribution

calculations is the unitless one. This value is often calculated from solubility and vapor pressure. Molecular weight and temperature are also used in the computation.

The vapor pressure divisions used are 0.1 mm Hg and 10 mm Hg. In Table 8.4 below Henry's law values increase from the high-solubility/low-vapor pressure side to the low-solubility/high-vapor pressure side. Several other organic chemicals are shown in Table 8.5. A similar plot showing solubility, vapor pressure and Henry's law relationships is shown in Figure 8.8.

ESTIMATION OF PARTITIONING COEFFICIENTS

Conversion Factors

1 mm Hg	= 1 Torr (vacuum technology)
	= atmos. * 760
	= kPa (kilo Pascals) * 7.501
	= psia * 51.72
	= bars * 750.1
Note:	
psia	= pounds/square inch absolute (measured with respect to zero pressure)
psi	= pounds/square inch (measured with respect to atmospheric pressure)
°C	= (F − 32) * 5/9
K	= °C + 273.15
log x	= ln x/ ln 10
H (dimensionless)	= H′/R * T with R in similar units to H′
R	= 0.082054 liter-atmos/deg/mol

Table 8.4. Selected Organic Chemicals in the Selected Solubility-Vapor Pressure Ranges

	Solubility		
Vapor pressure	**Low**	**Medium**	**High**
Low	Anthracene **H medium**	Diethyl phthalate	2,4-Dichlorophenol **H low**
Medium	Naphthalene	*m*-Xylene **H medium**	Aniline
High	Octane **H high**	Benzene	Vinyl chloride **H medium**

Table 8.5. Organic Compounds with a Range of Solubility and Vapor Pressures

	Solubility		
Vapor pressure mm Hg	**Low <65 mg/L**	**Medium 65–2000 mg/L**	**High >2000 mg/L**
Low <0.1 mm	Chlordane DDT PCP Dibutyl phthalate Pyrene Anthracene	1,3-Butadiene Diethyl phthalate	2,4-Dinitrophenol 4-Chloro-*m*-cresol 2,4-Dichlorophenol
Medium 0.1–10 mm	Naphthalene 1,4-Diethylbenzene 2,2,5,5-Tetramethylhexane	Ethylbenzene	*o*-Cresol Aniline Chlorotoluene 2-Chlorophenol
High >10 mm	Octane Butane Cyclohexane Isobutane 1-Hexene	Toluene Benzene Tetrachloromethane 1-Pentene	Trichloromethane Dichloromethane Chloroethene 2-Butanone

R	= 8.20562E−05 atmos-m^3/deg/mol
K_{oc}	= K_{som} * 1.724
D_s	= (1 − porosity) * 2.65 (specific gravity of quartz)
K_d	= K_{oc} * % organic carbon/100
R_d	= 1 + K_d * bulk density/porosity

The equations listed below are used for estimating critical partitioning parameters in the ECOPLUS computer program. The relationships between the various parameters and the partitioning parameters that they are used to estimate are shown in Figure 8.9.

Estimated Boiling Point—T_b

$\log T_b = 3 - 4/5 * \sqrt{M}$ for M > 200 (Banks, 1939)

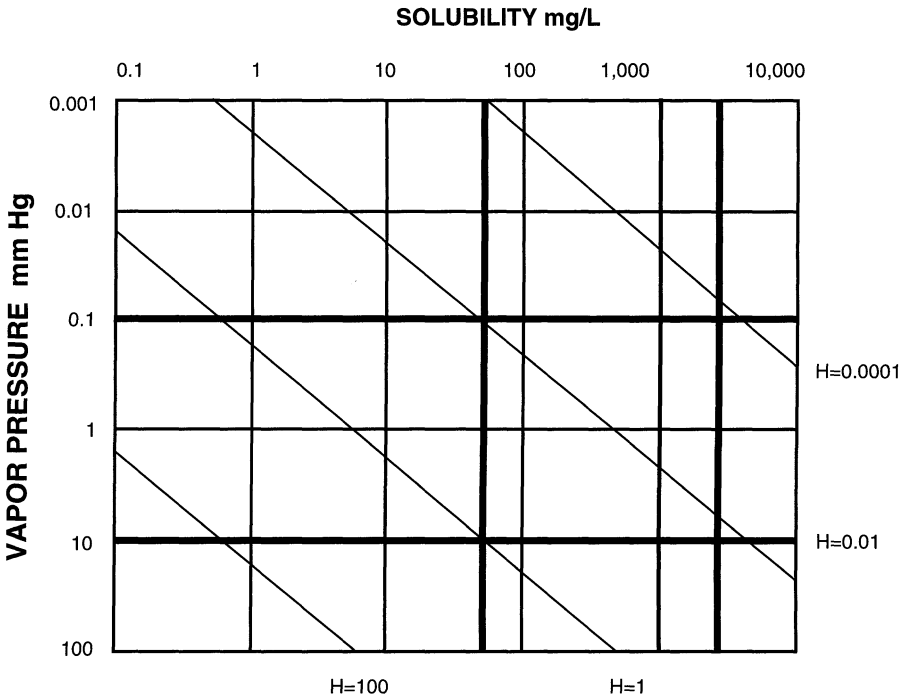


Figure 8.8. Graphical relationship between solubility, vapor pressure, and Henry's law constant, showing that high vapor pressure alone does not necessarily mean a high Henry's law constant. A high Henry's law constant does, however, result if the vapor pressure is high and the solubility is low.

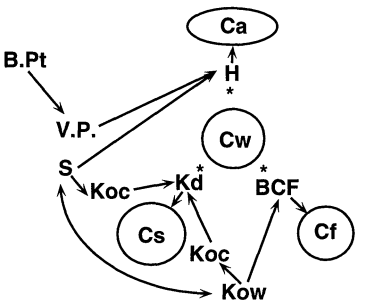


Figure 8.9. A plot of the various distribution coefficients and their relationship to solute concentrations in the various ecosystem compartments—air, soil/sediment, fish—and aqueous phases.

T_b = boiling point in K
M = molecular weight

Estimated Melting Point—T_m

T_m = 0.5839 T_b (Gold and Ogle, 1969)
T_m = melting point in K

Vapor Pressure

Mackay et al., 1982b.

$$\ln P = -(4.4 + \ln T_b) * \left[1.803 * \left(\frac{T_b}{T} - 1\right) - 0.803 * \ln \frac{T_b}{T}\right] - 6.8 * \left(\frac{T_m}{T} - 1\right)$$

P = vapor pressure in atmospheres
T_b = boiling point (K)
T_m = melting point (K)

When $T_m > T$ the last term is ignored.

Solubility

log S = − log Kow + 0.76 − 0.01 * Tm (Yalkowsky et al., 1983)
S = solubility in mole/liter
T_m = melting point in °C

For liquids T_m is set to 25°C

Henry's Law Constant

Dilling, 1977
H (dimensionless) = 16.04 * Po * M/(T * S)

Po = vapor pressure of pure compound (mm Hg)
S = solubility in mg/l (maximum solubility 1 mol/l)
M = molecular weight
T = temperature K
This equation cannot be used for miscible solutes.

Mackay et al., 1982a.

$$H\ (\text{atm m}^3/\text{mol}) = 10.6 * \left[1 - \frac{T_b}{T}\right] + 6.8 * \left[1 - \frac{T_m}{T}\right] + 0.0318 * (Tb - 273) - 5.15$$

T_b = boiling point (K)
T_m = melting point (K) solids

Estimates of Normalized Distribution Coefficients—K_{oc}

Estimates of normalized distribution coefficients are commonly obtained from solubility or octanol/water partition coefficients rather than by the difficult and time-consuming direct

determination of adsorption isotherms. Note that some authors use the organic carbon content, whereas others use the percent som. If an assumption is made that 58% of som is organic carbon, then:

$$K_{oc} = \frac{K_{som}}{0.58}$$

K_{oc} from Solubility

Solubility estimates of adsorption were discussed by Cassidy (1951). Lundelius, 1920 (Cassidy 1951) proposed that the Freundlich K is inversely proportional to the solute in question.

That is

$$\log K = A - n * \log S$$

where

n = is the Freundlich exponent,
S = is the solubility, and
K = is the Freundlich distribution coefficient

The constants in the equations are largely dependent on the solubility units used and to a lesser extent on the group of compounds investigated.

Kenaga and Goring (1980) collected data for 106 organic chemicals, primarily pesticides, and obtained a regression equation:

$$\log K_{oc} = 3.64 - 0.55 \log S \text{ (ppm)}$$

They estimated the results would be within +1.23 orders of magnitude from the actual value, assuming 95% confidence limits.

Chiou et al. (1979) obtained a relationship between distribution coefficients and solubility for a large number of nonionic organic compounds. Their relationship covers more than 7 orders of magnitude in S and 4 orders of magnitude in K_{oc}. They found that

$$\log K_{som} = 4.040 - 0.557 \log S \text{ (micromoles/liter)}$$

Assuming that SOM = 58%oc,

$$K_{oc} = 3.80 - 0.557 \log S.$$

Karickhoff et al. (1979) found the relationship to be

$$\log K_{oc} = 0.44 - 0.54 \log S \text{ (mole fraction).}$$

Only hydrophobic compounds such as aromatic hydrocarbons and chlorinated hydrocarbons were considered.

Means et al. (1979) found a relationship:

$$\log K_{oc} = 4.070 - 0.82 \log S \text{ (mg/ml)}$$

Karichoff (1981) gives:

$$\log K_{oc} = -0.197 - 0.594 \log S \text{ (mole fraction solubility)}$$

Karickhoff also recommended the incorporation of a crystal energy term in the equation.

The equations used in the ECOPLUS program were those recommended by Lyman et al. (1982).

The solubility units used in the expressions to calculate the distribution coefficient so far encountered include mg/l, ppm, μmol/l, and mole fraction.

Thus:

$$\text{mg/l} = \text{ppm for dilute solutions}$$

$$\text{micromoles/l} = \text{mg/l} * \frac{1000}{\text{molecular weight}}$$

$$\text{mole/l} = \text{micromoles/l}/10^6$$

$$\text{mole fraction} = \frac{\text{moles/l}}{(\text{mole/l}) + 55.51}$$

(1) $\log K_{oc} = -0.55 * \log S + 3.64$ (Kenaga and Goring, 1980)
S in mg/l

(2) $\log K_{oc} = -0.54 * \log S + 0.44$ (Karickhoff et al., 1979)
S in mole fraction

(3) $\log K_{oc} = -0.557 * \log S + 4.277$ (Chiou et al., 1979)
S in μmol/l

A graph showing these K_{oc} solubility estimates is given in Figure 8.10.

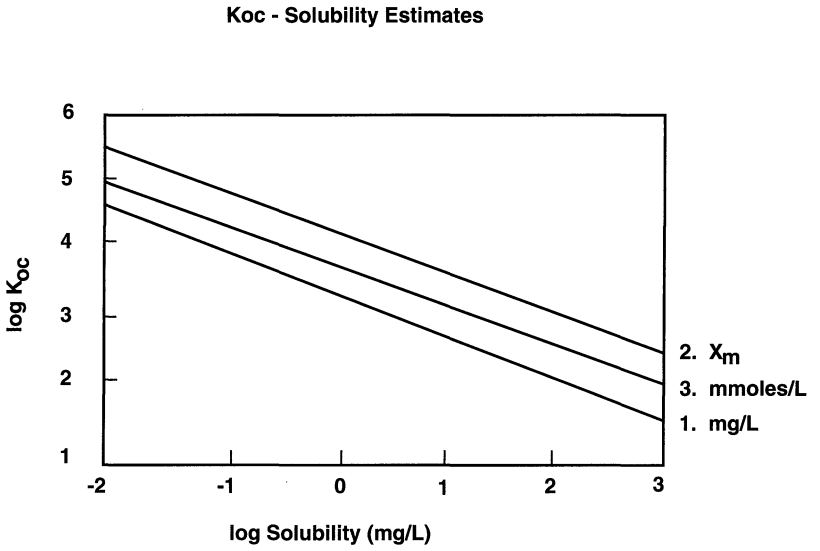


Figure 8.10. K_{oc} estimates based on solubility regression equations. Solubility-K_{oc} estimates are based on equations proposed by: Kenega and Goring (1980), mg/L; Karickhoff et al. (1979), mole fraction; Chiou et al. (1979), μmol/l.

K_{oc} from Octanol/Water Partition Coefficients

The partitioning of a solute between water and an immiscible organic solvent has been used extensively to estimate biological concentration tendency solutes. Generally, octanol-water partition coefficients are those most commonly measured. Leo et al. (1971) made an extensive compilation of these coefficients in 1971. Ward and Holly (1966) found a linear relationship between the amount of sorption and the degree of partitioning between cyclohexane and water of *S*-triazines.

Chiou et al. (1979) used octanol/water partition coefficients to obtain better estimates of solubility, that is,

$$\log K_{ow} = 5.00 - 0.670 \log S \text{ (}\mu\text{mol/l)}$$

These equations were found to be valid over 6 orders of magnitude in K_{oc} (10 to 10^7).

Karickhoff et al. (1979) examined ten hydrophobic pollutants with water solubilities ranging from 1 ppb to 1000 ppm and obtained excellent correlations of K_{oc} vs. K_{ow}, and poor correlation between K_{oc} and solubility. One of the following equations was suggested:

$$\log K_{oc} = 1.00 \log K_{ow} - 0.21 \text{ or } K_{oc} = 0.63\ K_{ow}$$

Means et al (1979) obtained similar partition coefficients for pyrene and 7, 12-dimethylbenz [a] anthracene (DMBA), respectively:

$$K_{oc} = 0.53\ K_{ow} \text{ and } 0.50\ K_{ow}$$

Banerjee et al. (1980) correlated *n*-octanol/water partition coefficients with solubility and found that

$$\log K_{ow} = 5.2 - 0.68 \log S \text{ (}\mu\text{mol/l)}$$

For solids with known melting points they suggest:

$$\log K_{ow} = 6.5 - 0.89 \log S - 0.015 * Tm$$

where Tm is the melting point in °C. A value of 25°C is used if the solute is a liquid.

Chiou and Schmedding (1980) state that most inaccurate data on water solubility and partition coefficients are generated with impure compounds or solvents. They discuss methods of ensuring purity of phases and suggest at a minimum that a melting point of a solid phase is minimal and that poor phase separations or persistent emulsions are often an indication of undesirable solvents. Experimentally, they found that for 36 organic chemicals, which ranged over 6 orders of magnitude, that

$$\log K_{ow} = -0.862 \log S \text{ (mol/l)} + 0.710$$

Kenaga and Goring (1980) obtained the following relationship for 45 organic chemicals:

$$\log K_{oc} = 1.377 + 0.544 \log K_{ow}$$

Karickhoff (1981) obtained the equation for hydrophobic solutes:

$$\log K_{oc} = 0.989 \log K_{ow} - 0.346.$$

The near unity of the coefficient suggests that

$$K_{oc} = 0.411\ K_{ow} \text{ is a good approximation.}$$

Briggs (1981) gives the relationship

$$\log K_{om} = 0.52 \log K_{ow} + 0.64.$$

He presents the data of Felsot and Dahm (1979) in the form

$$\log K_{om} = 0.52 \log K_{ow} + 0.78$$

the data of Lord et al. (1978) as,

$$\log K_{om} = 0.53 \log K_{ow} + 0.98$$

and his own earlier data as

$$\log K_{om} = 0.52 \log K_{ow} + 0.62.$$

Brown and Flagg (1981) found another empirical equation for nine compounds:

$$\log K_{oc} = 0.937 \log K_{ow} - 0.006.$$

The equations used in ECOPLUS were those recommended by Lyman et al., 1982. Note that K_{ow} is a unitless number that is often listed in its log form.

(1)	$\log K_{oc} = 0.544 * \log K_{ow} + 1.377$	(Kenaga and Goring, 1980)
(2)	$\log K_{oc} = 0.937 * \log K_{ow} - 0.006$	(Brown and Flagg, 1981)
(3)	$\log K_{oc} = 1.00 * \log K_{ow} - 0.21$	(Karickhoff et al., 1979)
(4)	$\log K_{oc} = 0.94 * \log K_{ow} + 0.02$	(Brown, 1979)
(5)	$\log K_{oc} = 1.029 * \log K_{ow} - 0.18$	(Rao and Davidson, 1980)
(6)	$\log K_{oc} = 0.524 * \log K_{ow} + 0.855$	(Briggs, 1973)

A graph showing these $K_{oc} - K_{ow}$ estimates is given in Figure 8.11.

Bioconcentration Factor

(1) $\ln BCF = 0.935 * \ln K_{ow} - 3.443$ (Kenaga and Goring, 1980)

or

$$\log BCF = 0.935 * \log K_{ow} - 1.495$$

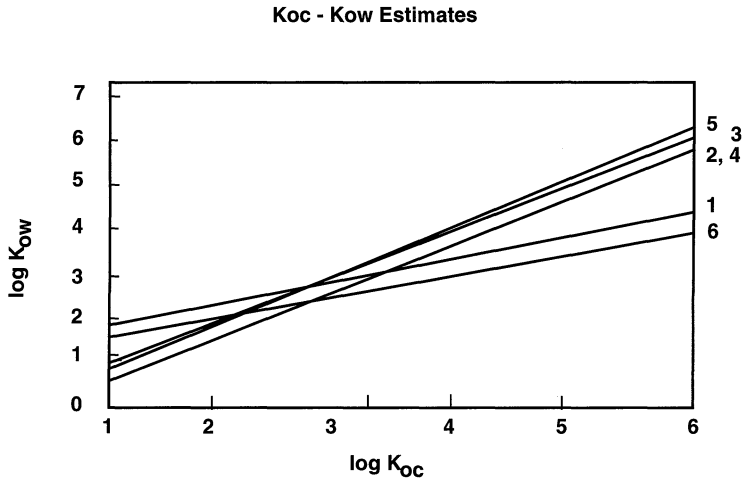


Figure 8.11. K_{oc} estimates based on K_{ow} regression equations. K_{ow}-K_{oc} relationships are based on equations proposed by: (1) Kenega and Goring, 1980; (2) Brown and Flagg, 1981; (3) Karickhoff, et al., 1979; (4) Brown, 1979; (5) Rao, et al., 1980; (6) Briggs, 1973.

GROUNDWATER FLOW MODELS

Any model that attempts to predict the movement of solutes in the subsurface requires a knowledge of the groundwater flow regime. This is usually referred to as a groundwater flow model. Input requirements are the mass balance of water, the hydraulic head distribution, the hydraulic conductivity, and the porosity. The computational method used is Darcy's law, that is, Q = K*I*A, where Q is the discharge, K is the hydraulic conductivity, I is the hydraulic gradient, and A is the cross-sectional area. The usual output is a velocity distribution where the velocity v = Q/A. Details of this procedure are discussed in detail in most texts in hydrogeology, and will not be pursued here. It is important to keep in mind the following restrictions related to groundwater movement.

Laminar flow — Laminar flow occurs only when velocities are relatively low, and the water particles move along parallel paths called streamlines. These are parallel to the solid pore boundaries. In laminar flow the viscous forces are dominant. Most groundwater flow is laminar. Darcy's equation is valid only for laminar flow, in which case head loss is proportional to velocity.

Turbulent flow — Turbulent flow occurs under conditions where velocities are high and inertial forces dominate. Under these conditions water molecules travel in irregular paths called eddies, even in a straight tube. This type of flow is common in streams, but rare for groundwater flow unless pores and hydraulic gradients are both large, such as in the vicinity of pumped wells or in highly porous formations. Darcy's law then becomes invalid as head loss for turbulent flow is proportional to the square of the velocity. The distinction between laminar and turbulent flow is shown in Figure 8.12.

Reynolds number — The Reynolds number is used to make the distinction between laminar and turbulent flow. It is calculated from the expression:

$$N_r = \frac{\rho * v * D}{\mu}$$

where

- v = velocity (cm/s)
  For groundwater the velocity is the Darcy velocity or Q/A
- ρ = density of fluid (g/cc)
- μ = viscosity of fluid (Poise)
- D = characteristic diameter (cm)
- D = diameter of full flowing pipe
- D = hydraulic radius of stream

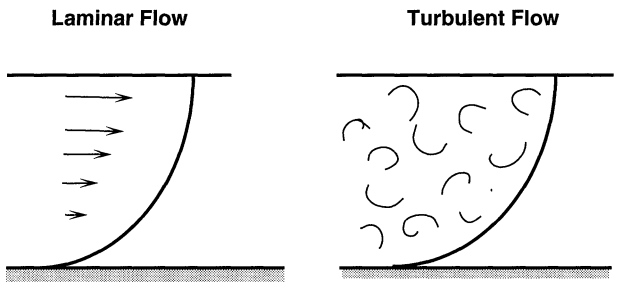


Figure 8.12. Distinction between laminar and turbulent flow. (Modified from Morisawa, 1968.)

D = cross-sectional area/wetted perimeter
D = average particle size in groundwater flow = D_{50}

For groundwater, turbulent flow starts at N_r = 60–700
For streams, turbulent flow starts at N_r = 500–2000
For pipe flow, turbulent flow starts at N_r = 2100.

True velocity: = Darcy velocity/porosity

SOLUTE TRANSPORT MODELS

Solute transport models or water quality models are designed to determine the concentration of a solute at point x downgradient from the source after time t. Information required by such models includes the velocity distribution (furnished by a groundwater flow model), a mass balance for solute species, and information on any chemical reactions that may occur. The mathematical method used is called the solute transport equation. It is usually solved in two steps, the first using conservative solutes with no chemical reactions, that is, considering only advection and dispersion, and the second step, which incorporates various chemical reactions, such as retardation and degradation. The objective is to be able to calculate the solute concentration at a certain point downgradient after a certain time (Figure 8.13).

The movement of solutes in solution whereby the concentration of solute at distance x downgradient after time t is calculated requires the determination of the following parameters:

1. Advection—where the solutes move with the same velocity as water (Latin: ad- = to, vehere = carry, cf. vehicle)

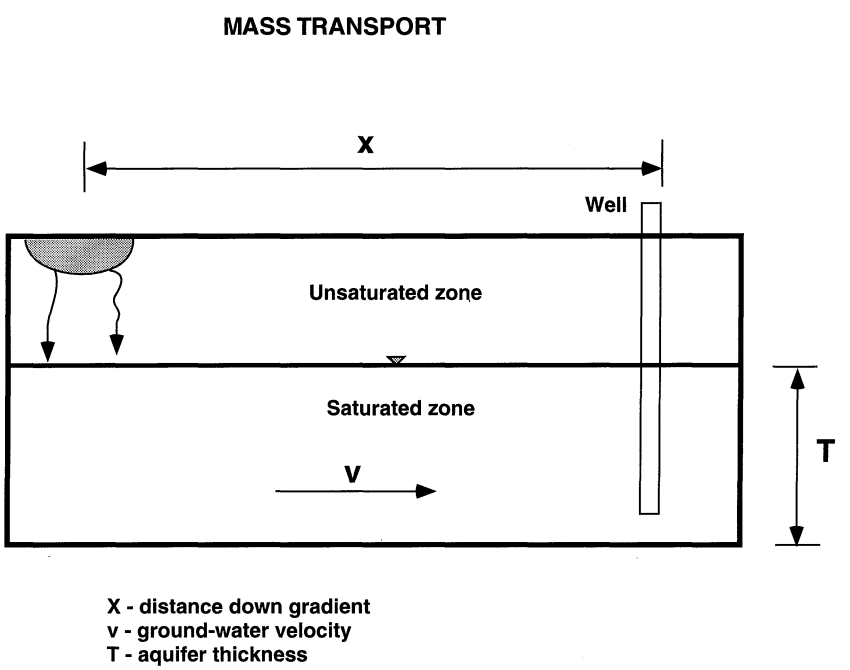


Figure 8.13. Factors influencing the transport of solutes downgradient in an aquifer. Mass Transport or the movement of the solute downgradient, is characterized by the determination of the concentration at a specified distance downgradient after a specified time. A distance transverse to the downgradient direction may also be specified.

2. Attenuation of solute (dilution, Latin: tenuis = thin, ad + tenuare = make thin). As the more concentrated solute moves away from its source, it gradually becomes less concentrated by three main mechanisms:

   a. dispersion, or the spreading of solute,
   b. retardation, where the solute moves with velocity less than that of the water, and
   c. degradation, or the removal of the solute by reactions that may be either or both of:
      i. biodegradation, or decomposition by microorganisms, or
      ii. abiotic degradation, or chemical decomposition.

Dispersion

Dispersion (disperse—to cause to scatter, to dissipate) occurs with laminar flow and has a similar effect in groundwater as turbulence has in surface water. The process affects all solutes equally and may be considered as dilution. The body of solute will spread by a nonuniform movement in the porous medium. There are two types of dispersion:

1. Hydraulic dispersion is the spreading of the solute both along the direction of flow and transverse to it. The three factors that result in longitudinal dispersion are

   a. velocity differential, which results from the slower movement of the fluid near the pore walls relative to movement at the center of the pore space; and
   b. velocity differential caused by the water traveling faster in the larger pores than in the smaller or narrower ones; and
   c. in general, the solution meanders randomly; therefore, movement within long vs. short flow paths also affects the longitudinal spread.

These variables depend on grain size and grain size distribution, but are independent of grain shape, grain roughness, or angularity. Field measurements are usually greater than laboratory measurements, indicating large-scale heterogeneities. The main contribution to transverse dispersion is from the different solute paths branching—the greater the distance from the source, the greater the divergence. A pictorial view of dispersion is given in Figure 8.14.

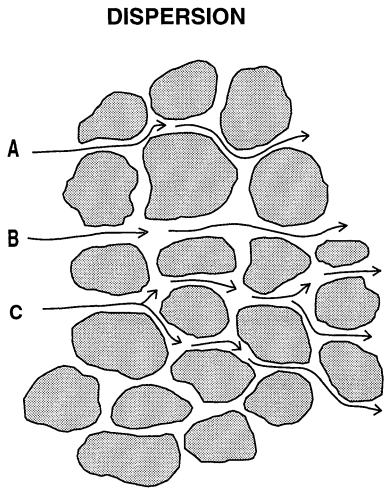


Figure 8.14. Movement of water particles around grains that results in dispersion. (Adapted from Heath, 1980.)

2. Molecular dispersion occurs at very slow velocities, such as under stagnant groundwater conditions. It is thought to be the result of Brownian movement.

Dispersion can be measured because the concentration of contaminants decreases with increasing distance of flow. It is described by two parameters:

1. Longitudinal dispersion, which occurs in the direction of flow; and
2. Transverse dispersion, which occurs normal to the direction of flow. The latter results from repeated splitting and deflection of flow by the solid particles in the aquifer.

A dispersion plume commonly results from point sources of pollution where longitudinal and transverse dispersion affect the flow of contamination downgradient from the source. The resulting plume has a Gaussian curve that becomes wider and flatter with increasing distance from the source (Figure 8.15). Two related terminologies used to describe dispersion are dispersion itself, expressed in units of area/time, and dispersivity, which equals dispersion/velocity and is in units of distance.

$$\text{dispersivity } (a_l) = \frac{\text{dispersion}}{\text{velocity}} = \frac{D_l}{v_x}$$

Retardation Coefficient

The retardation coefficient (R_d) represents a ratio of the velocity of the water over the velocity of the solute. Thus, if a solute having a retardation coefficient of 10 traveled 10 feet, the water would have traveled 100 feet. The reciprocal of R_d which is the chemical R_f factor, is more readily understood because solute movement is defined in terms of water movement. That is, during the time that water has moved a distance x the solute has moved a distance R_f times x. Assuming an R_f of 0.1 and a water movement of 100 feet, the solute has moved $100 \times 0.1 = 10$ feet.

The following concepts must be considered when examining pollution movement:

1. Chromatography, which is the process whereby differential solute movement results when a solution moves through a porous solid (e.g., polluted groundwater moving through sediments);
2. Adsorption, which is described quantitatively by an adsorption isotherm (a graph of the

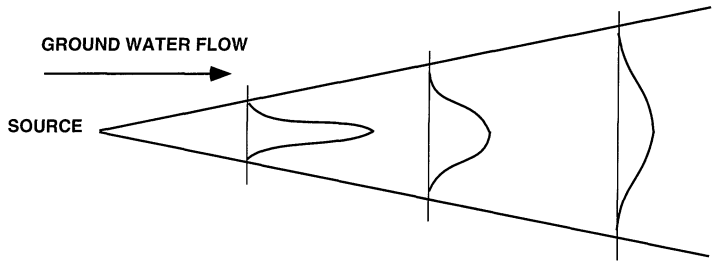


Figure 8.15. Effect of dispersion of solutes by spreading transverse to the flow direction as a result of slowing near the grain surfaces and splitting of the flow paths. This reduces the maximum concentration and increases the concentration further from the direction of the flow path. The total solute loading remains the same but is spread over a greater area. (Adapted from Heath, 1980.)

amount of solute—pollutant—absorbed per gram of solid vs. the concentration of solute in solution), and

3. Mass transport equation, which enables the concentration of a pollutant to be determined at a specified place after a specified time.

Adsorption Term

The total mass of solute per unit volume of porous medium is the sum of the solute in solution plus that adsorbed on the soil. If the porous medium is 100% saturated with solution, the volume of solution per unit volume of porous media is equal to the effective porosity, n. The mass of soil per unit volume of porous medium is D_s, the bulk density. Thus, if the total mass of solute per unit volume is C_T, then

$$C_T \text{ (total)} = n * C_w \text{ (liquid)} + D_s * C_s \text{ (solid)}$$

The change in total concentration with time can thus be written as:

$$\frac{\mathbf{d}C_T}{\mathbf{d}t} = n * \frac{\partial C_w}{\partial t} + D_s * \frac{\partial C_s}{\partial t} \tag{1}$$

where C_w is the solute concentration in water and C_s is the adsorbed concentration on the solid. In general, C_s is a function of C_w; that is, the relationship is defined by the distribution coefficient. The change in the mass of solute adsorbed on the solid (C_s) with time can be expressed as:

$$\frac{\partial C_s}{\partial t} = \frac{\partial C_s}{\partial C_w} * \frac{\partial C_w}{\partial t} \tag{2}$$

[Note: a partial derivative is shown as ∂, e.g., $\partial C_w/\partial t$]

After combining Equations (1) and (2), the change in total mass of solute per unit volume of porous medium with time is

$$\frac{\mathbf{d}C_T}{\mathbf{d}t} = n * \frac{\partial C_w}{\partial t} + D_s * \frac{\partial C_s}{\partial C_w} * \frac{\partial C_w}{\partial t}$$

$$= \frac{\partial C_w}{\partial t} * \left[n + D_s * \frac{\partial C_s}{\partial C_w} \right]$$

$$= n * \frac{\partial C_w}{\partial t} * \left[1 + \frac{D_s}{n} * \frac{\partial C_s}{\partial C_w} \right]$$

where the term

$$1 + \frac{D_s}{n} * \frac{\partial C_s}{\partial C_w} \tag{3}$$

is defined as the retardation coefficient R_d. Thus,

$$\frac{\partial C_T}{\partial t} = Rd * n * \frac{\partial C_w}{\partial t} \tag{4}$$

The retardation coefficient, as defined in Equation (3) above, contains two readily obtainable terms n, the effective porosity, and D_s, the bulk density of the soil. The third variable

is the ratio $\partial C_s/\partial C_w$, which is derived from the distribution coefficient, K_d. Thus the retardation coefficient is

$$R_d = 1 + K_d * \frac{D_s}{n}$$

Integration with the Mass Transport Equation

The primary objective of the preceding discussion is to describe chromatographic movement, the role of the distribution coefficient, and the various methods of obtaining estimates of this parameter. In this section the manner in which the distribution coefficient is integrated into the mass transport equation is examined.

Once a general understanding of adsorption chromatography is obtained, it must be applied to the problem of predicting the rate of movement of chemical pollutants in the soil-sediment environment. The mobile phase is, of course, water, and the solid phase is soil. The retardation coefficient term in the mass transport equation contains the variable $\partial C_s/\partial C_w$, which is directly related to the distribution coefficient. It equals K_d in the linear case, but the relationship becomes more complex for nonlinear isotherms. In the linear case where

$$C_s = K_d * C_w \quad \text{or} \quad \frac{\partial C_s}{\partial C_w} = K_d$$

In the Freundlich case where

$$C_s = K_d * C_w^n \quad \text{then} \quad \frac{\partial C_s}{\partial C_w} = n * K_d * C_w^{n-1}$$

Chromatographic R_f Factor

R_f is defined as the velocity of the point of maximum concentration of the solute (V_s) over the average linear velocity of the groundwater (V_w) (Freeze and Cherry, 1979). That is,

$$R_f = \frac{V_s}{V_w} = \frac{1}{\left[1 + K_d * \frac{D_s}{n}\right]}$$

The reciprocal of $R_f = V_w/V_s$ is the retardation coefficient, namely:

$$R_d = \left[1 + K_d * \frac{D_s}{n}\right]$$

Assuming linear isotherms, a pore fraction (n), and a bulk density (D_s), the retardation

$$R_d = 1 + K_d * \frac{D_s}{n}$$

and as $D_s = D * (1 - n)$, where D is the average specific gravity of rock minerals. K_{oc} is defined as 100 * K_d / %oc, where %oc is % organic carbon therefore, K_d = %oc * K_{oc} / 100 the retardation $R_d = 1 + (1 - n) * K_{oc} * \%oc / (100 * n) = 1 / R_f$

As a guide, a number of organic chemicals with normalized distribution coefficients ranging over 5 orders of magnitude are listed in Table 8.3. With these data are listed the calculated K_d value for 1% organic carbon, retardation coefficients R_d, R_f values, and the amount they may be considered to have moved if the water moved a distance of 10 miles. It must be understood that linear adsorption is assumed and that degradation and diffusion are ignored. The effect of tailing (nonlinear isotherms) is shown in Figure 8.16.

Aquifer Characteristics

The calculation of the retardation coefficient requires the organic carbon content of the aquifer as well as its bulk density and porosity.

Organic carbon content — The organic carbon content of the aquifer may be entered directly, or the percent soil organic matter may be entered and the organic carbon content calculated. The assumption made in the program is that 58% of som is organic carbon.

$$K_{oc} = \frac{K_{som}}{0.58}$$

Bulk density and porosity — Both these values may be entered directly, or one or the other may be entered and the other calculated from the relationship:

$$\text{bulk density} = \text{mineral density} * (1 - \text{porosity}).$$

The assumptions are that the mineral density will be very close to that of quartz, namely 2.65, and that the amount of organic carbon will not be significantly large.

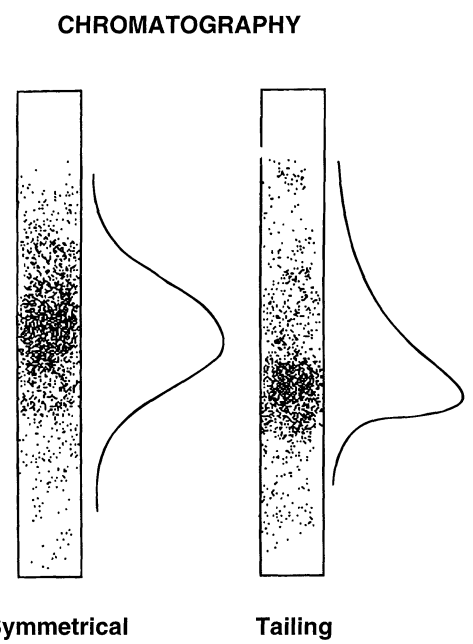


Figure 8.16. Representation of symmetrical and tailing chromatographic movement.

Solute under consideration — The distribution coefficient may be estimated from a variety of empirical regression equations relating various forms of solubility and the octanol/water partition coefficient of the solute. It must be emphasized that the units of the input data are known, whether or not it is log form or, as is sometimes given, a minus log form. These coefficients are variously given in the form of K_{oc}, K_{som}, or K_d. The relationships between them are

$$K_{oc} = K_d * \frac{100}{\text{percent organic carbon}}$$

$$K_{oc} = \frac{K_{som}}{0.58}$$

Calculation of retardation coefficient — The retardation coefficient is calculated from the distribution coefficient, bulk density, and porosity using the following equation:

$$\text{Retardation coefficient} = 1 + K_d * \frac{Ds}{n}$$

where the K_d is calculated from the estimated K_{oc} by the expression:

$$K_d = K_{oc} * \frac{\text{percent organic carbon}}{100}$$

The effect of porosity and organic carbon content in shown as a function of solute movement using lindane as an example in Table 8.6.

POLLUTANT DEGRADATION

Biological oxygen demand (BOD) is a measure of the amount of oxygen consumed by an organic compound undergoing decomposition. It may be expressed in two ways:

1. BOD_5 is defined as the mg oxygen consumed per liter of solution, or as gram of O_2 consumed per gram of compound, over a period of 5 d.

Table 8.6. Example of Solute Movement vs. Porosity and % OC

LINDANE K_{oc} = 911
Assume water travels 1000 ft.
OC = organic carbon

	Lindane Movement (ft.)	
Porosity	**0.1% OC**	**1.0% OC**
0.01	4	0.4
0.05	21	2
0.1	44	5
0.2	94	10

2. Theoretical oxygen demand (ThOD) is the amount of oxygen needed to oxidize hydrocarbons to CO_2 and H_2O. A graph showing BOD and ThOD is given in Figure 8.17.

ThOD is expressed as:

$$C_nH_{2m} + \left(n + \frac{m}{2}\right)O_2 \Rightarrow n\,CO_2 + m\,H_2O$$

$$\text{ThOD of } (C_nH_{2m}) = \frac{32 * \left(n + \frac{m}{2}\right) g}{(12.011 * n + 2 * m)\,g} = \frac{8(2n + m)}{(6n + m)}$$

Other elements may have to be considered and determinations made as to their end products formed. Some other reactions are

$$2H_2 + O_2 \rightarrow 2\,H_2O$$

$$2N + 3O_2 \rightarrow 2\,NO_3^-$$

$$S^= + 2O_2 \rightarrow SO_4^=$$

$$2\,SO_3^= + O_2 \rightarrow 2\,SO_4^=$$

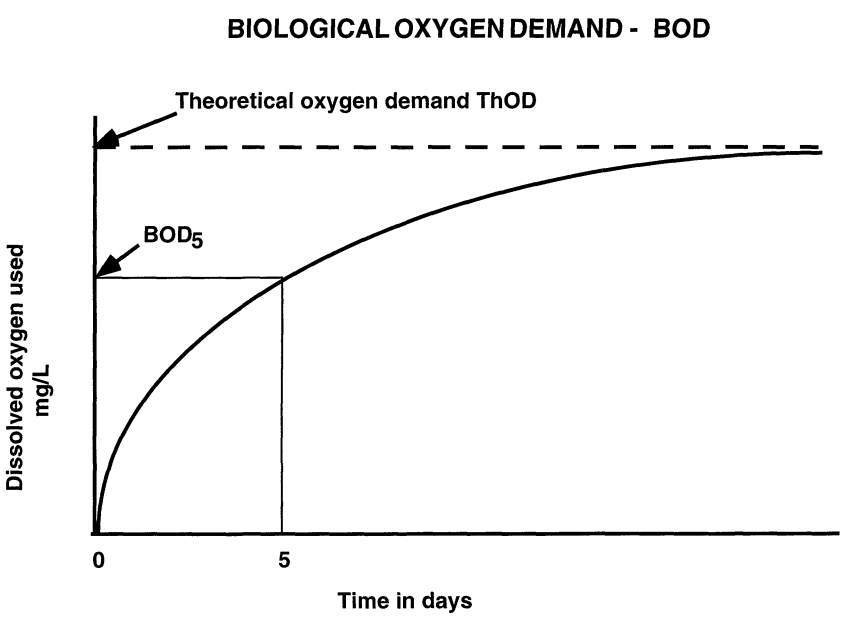


Figure 8.17. Graphical representation of biological oxygen demand (BOD). This is a first-order reaction where the rate of the reaction is dependent on the amount of the biodegradable organic matter present. This is approximated by theoretical oxygen demand (ThOD). (Adapted from Snoeyink, V.L., and Jenkins D., *Water Chemistry,* John Wiley & Sons, New York, 1991, p. 49. With permission.)

In each case the mass of oxygen used is divided by the molecular weight of the compound oxidized.

$$\text{ThOD} = \frac{32 * \text{number of moles of oxygen}}{\text{molecular weight} * \text{number of moles of compound}}$$

Example:

Ammonium acetate M.Wt. = 77 − $C_2H_3O_2\ NH_4$
If N remains as NH_{4+}

$$CH_3COONH_4 + 2\ O_2 \rightarrow 2\ CO_2 + H_2O + NH_4^+ + OH^-$$

$$\text{ThOD} = \frac{32 * 2}{77 * 1} = 0.83\ \text{g/g}$$

If N → N_2

$$2CH_3COONH_4 + 5.5\ O_2 \rightarrow 4\ CO_2 + 7\ H_2O + N_2$$

$$\text{ThOD} = \frac{(32 * 5.5)}{(77 * 2)} = 1.14\ \text{g/g}$$

If N → NO_3^-

$$2CH_3COONH_4 + 7.5\ O_2 \rightarrow 4\ CO_2 + 5\ H_2O + 2\ NO_3^- + 4\ H^+$$

$$\text{ThOD} = \frac{(32 * 7.5)}{(77 * 2)} = 1.56\ \text{g/g}$$

HALF-LIFE CALCULATIONS

The rate of degradation of a substance with time is the rate of decrease in concentration with time, which in turn is proportional to the concentration (assuming a first-order reaction). A graphical view if a zero order reaction is given in Figure 8.18 and that of a first order reaction is given in Figure 8.19.

Mathematically:

$$-\ dC/dt = kC,$$

where k is the proportionality constant or rate constant.

Solving this differential equation, we obtain:

$$C_t = C_o * e^{-kt}$$

where C_o is the initial concentration and C_t is the concentration after time t.

Taking logs (base e) of both sides

$$\ln C_t = \ln C_o - kt$$

This equation then plots as a straight line with intercept ($\ln C_o$) and slope (−k) (Figure 8.20).

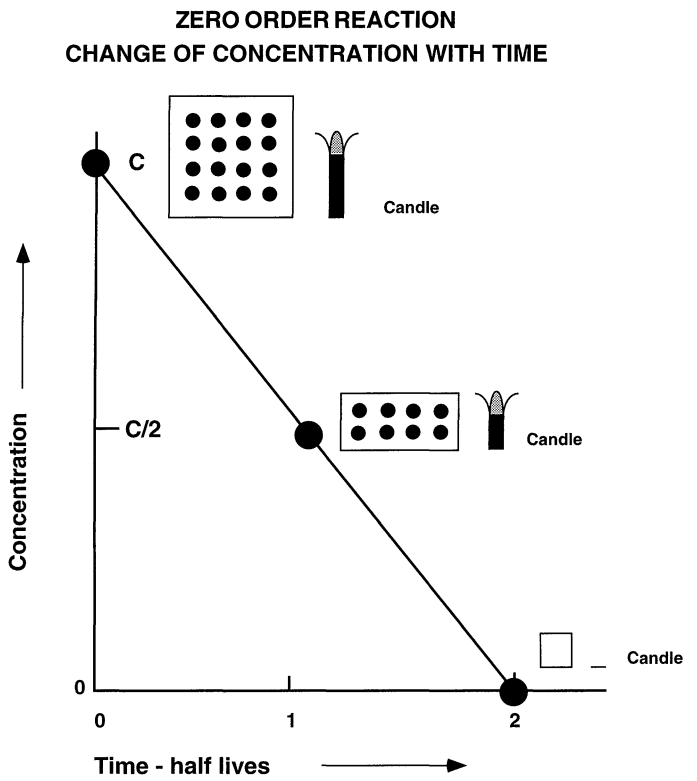


Figure 8.18. Rate of degradation independent of concentration remaining.

Again, considering the equation:

$$C_t = C_o * e^{-kt}$$

If we set $C_t = C_o/2$, then $2 = e^{kt}$ or $\ln 2 = kt = .693$

Then the time t with the designation $t_{1/2} = 0.693/k$ where $t_{1/2}$ is called the half-life. Thus, for each half-life the concentration is reduced by half.

The half-life of organic chemicals in groundwater or soil is also a function of initial concentration and inversely proportional to temperature (Laskowski et al., 1983). This is shown in Figures 8.21 and 8.22.

Determination of Half-Life

Surface Waters

The main problem encountered in the determination of half-lives of compounds in surface waters (by measuring their concentrations at two points in time) is that water evaporation or dilution may have occurred. In some cases this variation may be factored out by measuring the concentration of an element or ion, which has not been added to or removed from the water, during the time period of interest. In many cases, chloride fulfills this condition. Using the above assumption, the actual concentration of compound x after time t is

$$C'_x = C_s * \frac{\text{original (Cl)}}{\text{present (Cl)}}$$

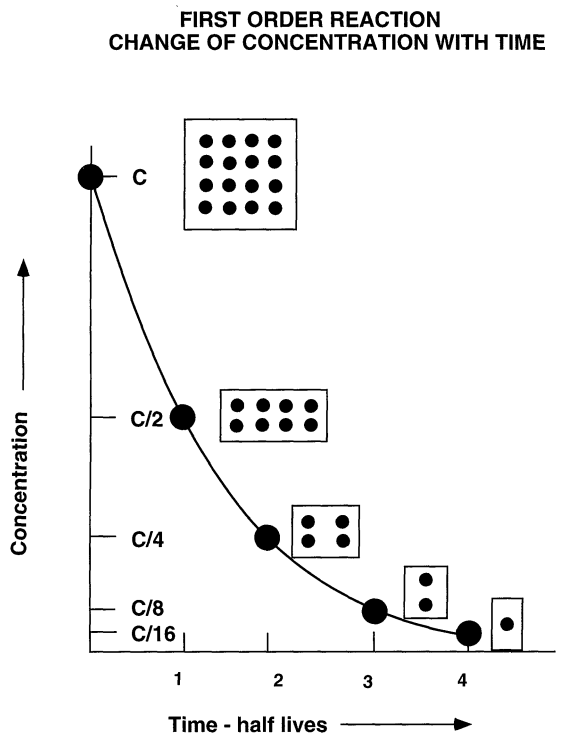


Figure 8.19. Rate of degradation is dependent on the concentration remaining. Concept of half-life. The plot of concentration vs. time shows the decrease in concentration by 50% after each half-life.

Groundwaters

The estimation of half-life from groundwater data is exceedingly complex, as many poorly known variables must be included in the calculations. These include aquifer parameters, solute loading, and time of entry into the groundwater system.

Derived from BOD_5 and % ThOD

For example, given a 16% ThOD, what is the equivalent half life?
Half-life calculation

$$\frac{C_t}{C_o} = e^{-kt} \quad \text{and} \quad t_{1/2} = \frac{0.693}{k}$$

Thus, % ThOD is amount lost and 100 − % ThOD is amount remaining.
Thus

$$\frac{(100 - 16)}{100} = e^{-5k}$$

$$k = \frac{\ln \dfrac{100}{100 - 16}}{5} = 3.487\text{E-}02$$

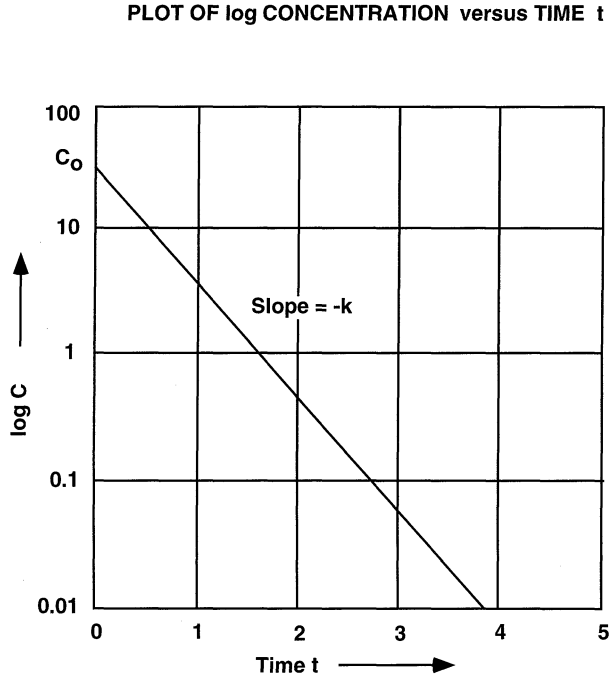


Figure 8.20. Semi-log plot of log concentration vs. time typical of first-order reaction. The plot shows that the concentration intercept equals the initial concentration and the slope of the line is the rate constant.

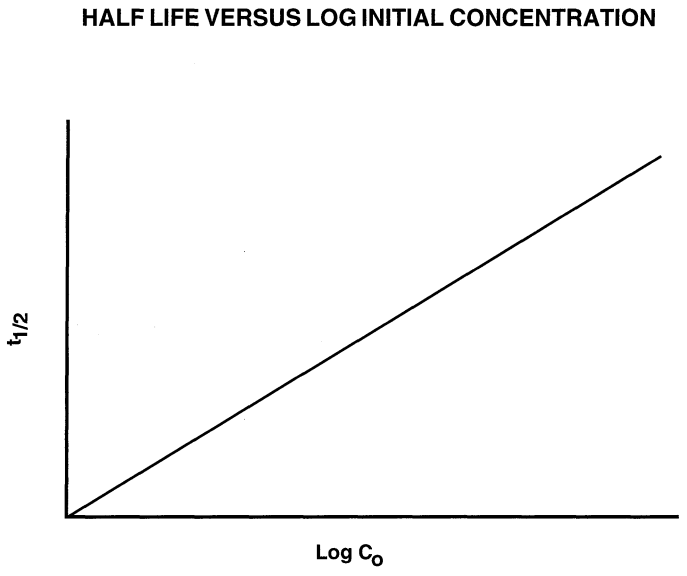


Figure 8.21. Plot of half-life vs. log of initial concentration. The plot shows that the half life increases with increasing initial concentration. (After Laskowski et al., 1983.)

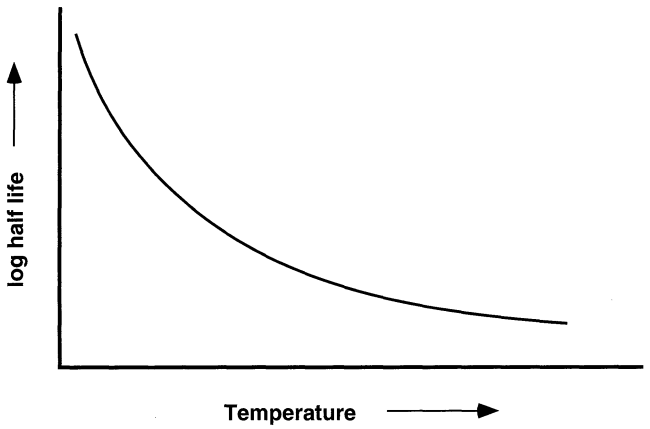


Figure 8.22. Plot of log half-life vs. temperature. This plot is derived from Laskowski et al. (1983) who showed a linear relationship between log half-life and reciprocal temperature. It may be seen that at low temperatures the half-life may be very large, indicating slow biodegradation, and at higher temperatures the half-life would increase to a lower limiting value (greater rate of degradation), presumably dependent on the other environmental conditions.

$$t_{1/2} = \frac{0.693}{k} = 19.9 \text{ days}$$

$$t_{1/2} = \frac{0.693 * t \text{ (days)}}{\ln\left[\frac{100}{(100 - \% \text{ ThOD})}\right]}$$

If % ThOD > 50%, then half-life <5 d.

Contaminant Properties

Contaminant properties such as retardation may change the apparent half-life in major ways. In some (probably rare) occasions the aquifer parameters may be estimated from the behavior of conservative constituents; the retardation of the solute in question may be estimated from K_{oc}, K_{ow}, or solubility. The difference between the observed concentration and the estimated concentration may be used to estimate half-life.

Estimates from Aerobic and Anaerobic Data

Howard et al. (1991) used several approximations to arrive at a half-life of an organic compound if it were not available. He assumed that:

1. The groundwater half-life would be about twice that of the soil, surface water, or unacclimated aerobic half-lives if they were available.
2. The groundwater half-life would be equal to the unacclimated anaerobic half-life if that were available.
3. The unacclimated anaerobic half-life would be about four times the unacclimated aerobic half-life.

In either case, the upper and lower limits of the available data in the literature were

noted. These calculations are shown diagramatically in Figure 8.23. The half-lives of some common organic chemicals are listed in Table 8.7. The effect of half-life on the remaining concentration of biodegraded solutes is shown in Figure 8.24.

Examples

1. A compound decreased from 15 mg/l to 1 mg/l over a period of 90 d. a. What is its half-life? b. What would be the concentration after 1 year?

Formula used:

$$C_t = C_o * e^{-kt} \qquad e^{kt} = \frac{C_o}{C_t} \qquad t_{1/2} = \frac{\ln 2}{k} \quad \text{or} \quad k = \frac{\ln 2}{t_{1/2}}$$

$$t = \frac{\ln \frac{C_o}{C_t}}{k} = \frac{\ln \frac{C_o}{C_t}}{\ln(2)} * t_{1/2}$$

$$e^{kt} = \frac{15}{1} \quad \text{and} \quad k = \frac{\ln 15}{t} = \frac{2.708}{90} = 0.03009$$

Table 8.7. Half-Lives of Selected Organic Chemicals

	Half-life in days			
	Aerobic		Anaerobic	
Compound	Minimum	Maximum	Minimum	Maximum
Cresol(s)	<1	29	10	49
Phenol	<1	4	8	28
Naphthalene	1	20	25	258
Acetone	1	7		
Butanone	1	7		
Dibutyl phthalate	1	23	2	23
Pyridine	1	7	7	28
Captan	2	60		
Toluene	4	22	56	210
Malathion	4	52		
Benzene	5	16	112	720
Xylene(s)	7	28	180	360
Acenaphthalene	12	102		
Heptachlor	15	65		
Methyl parathion	15	70	1	7
Phenanthrene	16	200		
Aldecarb	20	361	62	635
Pentachlorophenol	23	178	42	1520
1,4-Dichlorobenzene	28	180		
1,4-Dioxane	28	180		
Chloroethene	28	180		
Methyl *tert*-butyl ether	28	180		
Lindane	31	413	6	31
Anthracene	50	460		
1,1,1-Trichloroethane	140	273		
Dieldrin	175	1080	1	7
Methoxychlor	180	365	50	180
Tetrachloroethene	180	360	98	1653
Trichloroethene	180	360	98	1653
Pyrene	210	1900		
Chlordane	238	1386	1	7
Kepone	312	720		
DDT	730	5708	16	100

Note: The table lists the ranges in half-lives for some selected organics under both aerobic and anaerobic conditions (Howard et al., 1991). Because these data were derived from soil, river, groundwater, and laboratory experiments it would be unwise to apply them directly to groundwater contamination problems without further verification.

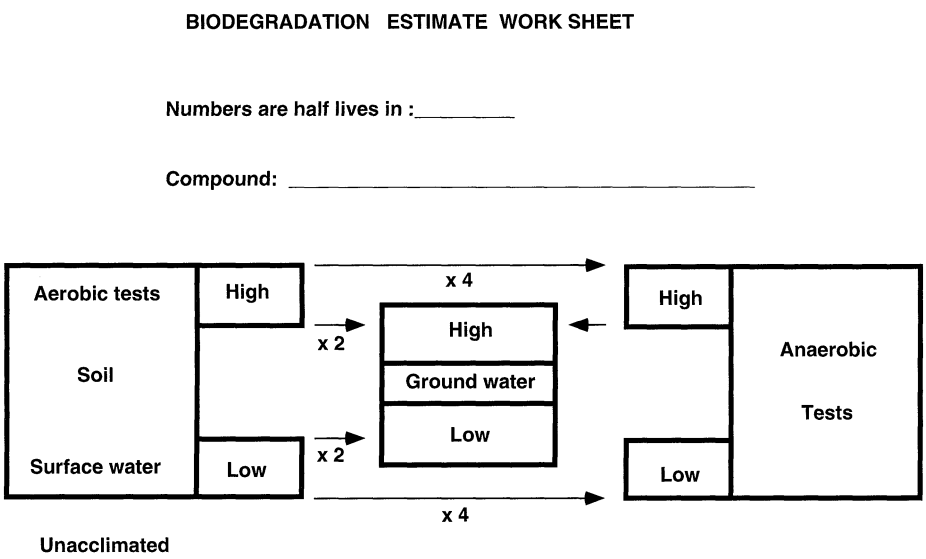


Figure 8.23. Biodegradation estimates. (Based on Howard et al., 1991.)

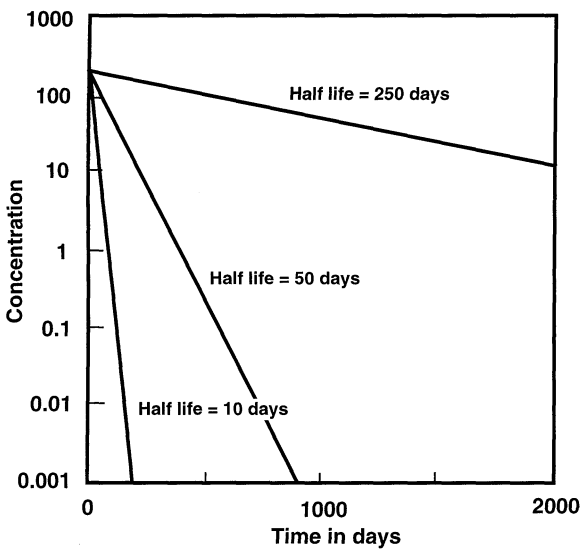


Figure 8.24. Effect of half-lives on amount of solute remaining. The plot shows the effect of different half-lives on the amount of solute remaining as a function of time. An initial concentration of 200 units is assumed.

$$t_{1/2} = \frac{\ln 2}{k} = 23 \text{ days}$$

$$C_t = \frac{15}{e^{(0.03009*365)}} = .00025 \text{ mg/l}$$

2. How long would it take for a compound to decrease from 10 mg/l to 1.0 mg/l given the following half-lives: a. 1 week, b. 1 month, c. 1 year?

a. $$\ln \frac{C_o}{C_t} = t * k = t * \frac{\ln 2}{t_{1/2}}$$

$$t = \frac{\ln \frac{C_o}{C_t}}{\ln(2)} * t_{1/2} = \frac{\ln \frac{10}{0.1}}{\ln(2)} * 7 = 45 \text{ days}$$

b. $t = 206$ d

c. $t = 2425$ d $= 6.64$ years

SUMMARY

A form that may be used to collect partitioning and biodegradation data is given in Table 8.8. Some of the more important partitioning formulas are listed in Table 8.9.

EXERCISES

Parameter Estimation

1. Calculate Henry's law constant for diazinon given:
   M.Wt = 304.34
   Solubility = 40 mg/l
   Vapor pressure = 1.4E−04 mm Hg at 20°C

Table 8.8. Environmental Partitioning Data Form

Data for hydrologic modeling of compounds

IUPAC name: _____
CA entry name: _____
Common names: _____ _____ _____

	VALUE	REFERENCE
a. CAS #		
b. Formula		
c. Molecular weight		
d. Melting point °C		
e. Boiling point °C		
f. Vapor pressure		
g. Density		
h. Log K_{ow} or K_{ow}		
i. Solubility		
j. H or $K_w = \left[\frac{1}{H}\right]$		
k. K_{oc}		
l. BCF		
m. Biological $t_{1/2}$		
i. aerobic		
ii. anaerobic		
n. Hydrolysis $t_{1/2}$		
o. Critical conc.		
p. Calculated value:		

H (calc) _____ K_{oc} (calc) _____ BCF (calc) _____
Researched by: _____ Date: _____

Table 8.9. Ecosystem Distribution Formulas

T (K) =	273.15 + T °C
R =	8.2054E−05 atm-m^3/deg/mol
1 atmos	= 760 mm Hg
°C =	$\frac{(F - 32) * 5}{9}$
H (dimensionless) =	$16.04 * \frac{Po\ (mm\ Hg) * M.Wt}{T\ (K) * Sol.\ (mg/l)}$
H (dimensionless) =	$\frac{H\ (atm\text{-}m^3/mol)}{R * T\ (K)}$
K_{oc} =	$K_{som} * 1.724$
log S =	$-\log K_{ow} + 0.76 - 0.01\ T_m$, S in mol/l, T_m is melting point (°C) or 25 if a liquid
log K_{oc} =	−0.55 * log S (mg/l) + 3.64
log K_{oc} =	0.544 * log K_{ow} + 1.377
log BCF =	0.935 * log K_{ow} − 1.495
K_d =	K_{oc} * f_{oc} (fraction organic carbon)
Bulk density =	(1 − porosity) * 2.65 (quartz)
R_d =	$1 + K_d * \frac{\text{bulk density}}{\text{porosity}}$
	NAPL
S_i^e =	$X_i * S_i$ S is pure phase solubility in water, X is mole fraction in NAPL, S^e = partitioning concentration in water
Mole fraction =	$\frac{\text{moles solute}}{\text{total moles of liquid}}$
C_l =	$S * \exp\left[6.8\left(\frac{T_m}{T} - 1\right)\right]$, C_l is liquid solubility, T_m is melting point (K), T is system temperature (K)
	Half-life
C_t =	$C_o * e^{-kt}$ and $t_{1/2} = 0.693/k$

2. Henry's law constant for methylene chloride is reported as 0.003319 atmos-m^3/mol. What is the dimensionless number?
3. Estimate Henry's law constant for methylene chloride and compare with 2. above.
   M.Wt. = 84.93
   Solubility = 16,000 mg/l
   Vapor pressure = 360 mm Hg at 20°C
4. If groundwater were contaminated by the above chemicals (diazinon and methylene chloride), which would be more effectively removed by air stripping?
5. For DDT and malathion, calculate their BCF values and determine which would be more highly concentrated in fish.

DDT — K_{ow} = 960,000
Malathion — K_{ow} = 780

6. Given that 500 ml of a water contains 10 mg/l of an organic solute, but after adding 1 g of carbon the concentration is reduced to 2 mg/l. Calculate the linear distribution coefficient.
7. Calculate the amount of granulated carbon necessary to reduce 10 mg/l lindane to 0.1 mg/l. Lindane has a K = 256 and n = 0.49.
8. Recalculate problem 4 in two steps, reducing lindane from 10 to 1 mg/l and then from 1 to 0.1 mg/l. Comment on the result.
9. Chloroform has a K = 2.6 and n = 0.75 for carbon adsorption. How much carbon is required to reduce 10 mg/l chloroform to 0.1 mg/l in one step? Compare your result with question 5 above. Comment on your result.
10. Derive the relationship between bulk density (D_s) and porosity (n) assuming a quartz aquifer with a specific gravity of 2.65.

Consider a total volume V of sand and air.
a. volume of sand =
b. mass of sand =
c. total mass (sand + air) =
d. bulk density = total mass/total volume =

a. Given a porosity of 0.15, calculate the bulk density.
b. Given a bulk density of 1.85, calculate the porosity.

Groundwater Calculations and Retardation

11. An alluvial aquifer has a hydraulic conductivity of 2000 gal/d/ft^2, a porosity of 0.2. Two wells 1 mile apart have water levels of 1525 and 1515 ft, respectively. Calculate:
    a. the Darcy velocity in ft/day.
    b. the actual velocity in ft/day.
    c. the time in years that a chloride spill would travel downgradient from one well to another.
    d. the Reynolds number for the groundwater movement. Assume a density of 1 g/cc, a viscosity of 1.002 cP, and an average grain size of 0.8 mm.
    e. What linear distribution coefficient would a solute need to have to travel at 1/4 the velocity of the water?
12. Calculate the retardation coefficient for a compound having a K_{oc} of 115 in a sandstone aquifer with a porosity of 0.23 and an SOM content of 0.87%.
13. Make a table of R_o, R_f, K_{oc}, log K_{oc}, and K_{ow} for compounds having solubilities of 0.001, 0.1, and 10 mg/l. Assume a sandstone aquifer with a porosity of 0.3 and an organic carbon content of 0.1% OC.

To calculate K_{ow} use the relation 0.989 log K_{ow} = log K_{oc} + 0.346
To calculate K_{oc} use the relation log K_{oc} = − 0.55 * log S + 3.64
where S is in mg/l.

Solubility mg/l	R_d	R_f	K_{oc}	log K_{oc}	log K_{ow}
0.001					
0.1					
10					

14. For this exercise use the following hydrologic parameters:

Velocity	= 1.5 ft/d
Effective porosity	= 0.35
Aquifer thickness	= 110 ft
Longitudinal dispersivity	= 70 ft
Transverse dispersivity	= 14 ft
Half-life	= 2000 years

    a. Calculate the loading in lb/d of a recharge rate of 20,000 gpd of a waste with a solute concentration of 500 mg/l. Use a hand calculator and show your reasoning.
    b. Assume the solute is conservative (retardation = 1) and estimate by hand calculations the time it would take for the solute concentration to reach a maximum at a well 600 ft downgradient. Again show all reasoning.
    c. Assume a second solute with a retardation coefficient of 15, and estimate the time it would take for the solute concentration to reach a maximum at the well.

Half-Life Exercises

Calculate the half-life from the following data (consider the solutes to be nonvolatile):

15. An aquifer contained 155 μg/l of chemical X on 5/10/86 and 107 μg/l chemical X on 4/1/87. Both samples contain 157 mg/l Cl.
16. A pond with no input other than precipitation contained 15.2 mg/l Cl and 5.1 μg/l chemical Y on 2/12/85, and 9.7 mg/l Cl and 1.3μg/l chemical Y on 5/24/86.
17. Calculate the concentration of chemical Z (on 6/1/87) having a half-life of 3.5 years for each of the following cases.
    a. Assume a groundwater where chemical Z had a concentration of 52 μg/l on 3/17/86. The chloride content was found to be constant over time.
    b. Assume a surface pond with 58 mg/l Cl and 87 μg/l of chemical Z on 3/3/84. The chloride concentration on 6/1/87 was 116 mg/l.
18. An effluent must not be released into a waterway unless the concentration of chemical x is less than 1 μg/l. The chemical is known to be biodegradable. The concentration of chemical x in water pumped into a holding pond was 5.3 μg/l on 5/7/84. The chloride content of this water was 15 mg/l at this time. Measured again on 7/2/85, the concentration of chemical x was 2.1 μg/l and the chloride 9 mg/l.

What is the minimum time that the effluent would have to be kept in the holding pond before discharge? What precautions would you have to take to minimize the holding time?

ANSWERS TO EXERCISES

Parameter Estimation

1. Diazinon

$$H = 16.04 * \frac{P_o \text{ (mm Hg)}}{T \text{ (°K)} * C_s \text{ (ppm)}} * M = 16.04 * \frac{1.4\text{E-}04 * 304.34}{293.15 * 40} = 5.83\text{E-}05$$

2. Methylene chloride

$$H \text{ or } \frac{C_a}{C_w} = \frac{H \text{ (atm-m}^3\text{/mole)}}{R * T} = \frac{0.003319}{293.15 * 8.20562\text{E-}05} = 0.138$$

3. Methylene chloride

$$H = 16.04 * \frac{360 * 84.93}{293.15 * 16000} = 0.105$$

4. Diazinon H = 5.83E − 05; methylene chloride H = 0.105
Methylene chloride has the largest H, and thus would be more readily removed by air stripping.

5. DDT and malathion

ln BCF	= 0.935 * ln K_{ow} − 3.443 (Kenaga and Goring, 1980)
ln BCF (DDT)	= 0.935 * ln (960,000) − 3.443 = 9.436
BCF (DDT)	= 1.2536E + 04 = 12,536
ln BCF (malathion)	= 0.935 * ln (780) − 3.443 = 2.783
BCF (malathion)	= 1.6175E + 01 = 16.2

As BCF = C_f/C_w

Thus the compound with the higher value will be concentrated in the fish, that is, the DDT.

6. Activated carbon
Isotherm equation is

$$\frac{X}{m} = K * C_w^n$$

Express concentrations in g/l

$$n = 1, X = (10 - 2) \text{ mg/l}, m = \frac{1 \text{ g}}{500 \text{ g}} = 2 \text{ g/l}$$

thus (10 − 2)/2 = K * 2 or K = 2 mg/g

7. Lindane—one step

$$\frac{(10 - 0.1)}{m} = 256 * 0.1^{0.49}$$

$$m = 0.12 \text{ g} = 120 \text{ mg/l}$$

8. Lindane—two steps

$$\frac{(10 - 1)}{m} = 256 * 1^{0.49}; \; m = 0.035 \text{ g} = 35 \text{ mg}$$

$$\frac{(1 - 0.1)}{m} = 256 * 0.1^{0.49}; \; m = 0.011 \text{ g/L} = 11 \text{ mg}$$

Total = 46 mg/l carbon

The greater the number of steps, the greater the efficiency, suggesting that a column of carbon would be most efficient, i.e., infinite number of steps.

9. Chloroform

$$\frac{(10 - 0.1)}{m} = 2.6 * 0.1^{0.75} \text{ or } m = 21.4 \text{ g/l}$$

The less strongly adsorbed chloroform requires 465 times as much carbon to remove an identical amount of the more strongly adsorbed lindane.

10. Bulk density

Volume of sand	= V*(1 − n)	
Mass of sand	= V * S.G.	= V*(1 − n)*2.65 (quartz)
Total mass	= mass sand + mass air	= V* (1 − n)*2.65
Bulk density	= Total mass / total volume	
	= V*(1 − n)*2.65/V	= (1 − n)*2.65
A. Bulk density	= (1 − 0.15)*2.65 = 2.25	
B. Porosity	= 1 − 1.85/2.65 = 0.30	

Groundwater Calculations and Retardation

11.

a. $V = Q/A = k * I = \frac{2000 * 10}{7.48 * 5280} = 0.51$ ft/d

b. $V_a = \frac{0.51}{0.2} = 2.53$ ft/d

c. $\text{time} = \frac{\text{distance}}{\text{velocity}} = \frac{5280}{2.53} = 2085 \text{ days} = 5.7 \text{ years}$

d. $N_r = \frac{\rho \text{ (g/cc)} * V \text{ (cm/sec)} * D \text{ (cm)}}{\mu\text{(Poise)}}$

$$= \frac{1 * \frac{0.51 * 12 * 2.54}{(24*60*60)} * \frac{0.8}{10}}{\frac{1.002}{100}} = 1.436 \text{ E-3}$$

e. $R_d = \frac{V_{water}}{V_{solute}} = \frac{4}{1} = 1 + \frac{D_s * K_d}{n}$

$D_s = (1 - n) * 2.65 = 0.8 * 2.65 = 2.12$

$K_d = \frac{(4 - 1)}{2.12} * 0.2 = 0.28$

12. Retardation coefficient

$K_{oc} = 115$; SOM = 0.87%; n = 0.23

$D_s = (1 - 0.23) * 2.65 = 2.04$

%OC = 58 * 0.87 = 0.50%

$$K_d = \frac{K_{oc} * \%OC}{100} = \frac{115 * 0.50}{100} = 0.58$$

$$R_d = 1 + \frac{B * K_d}{n} = 1 + \frac{2.04 * 0.58}{0.23} = 6.14$$

13. To calculate K_{ow} use the relation: $0.989 \log K_{ow} = \log K_{oc} + 0.346$

Solubility mg/l	R_d	R_f	K_{oc}	$\log K_{oc}$	$\log K_{ow}$
0.001	1207	0.0008	0.19E+06	5.29	5.70
0.1	97	0.0103	0.15E+05	4.19	4.59
10	9	0.12	0.12E+04	3.09	3.47

14.

a. $$\text{loading } \frac{\text{lbs}}{\text{day}} = \frac{\text{x gal}}{\text{day}} *\& \frac{\text{y mg}}{\text{l}} * \frac{\text{1 g}}{\text{1000 mg}} * \frac{\text{1 lb}}{\text{453.6 g}} * \frac{\text{3.785 l}}{\text{1 gal}}$$

$$= \frac{\text{x (gpd)} * \text{y (mg/l)}}{119841.5}$$

As x = 20,000 gpd, y = 500 mg/l, then

loading = 83.4 lb/day

OR

$$\text{loading } \frac{\text{lbs}}{\text{day}} = \frac{\text{x gal}}{\text{day}} * \frac{\text{y mg}}{\text{l}} * \frac{\text{1 cft}}{\text{7.48 gal}} * \frac{\text{1 g}}{\text{1000 mg}} * \frac{\text{1 lb}}{\text{453.6 g}} * \frac{\text{28.317 l}}{\text{1 cft}}$$

as $\frac{1}{7.48} = 0.13366$ then

$$\text{loading} = \frac{0.1337}{16019} * \text{x (gpd)} * \text{y (mg/l)}$$

b. $$\text{Velocity} = \frac{\text{distance}}{\text{time}}$$

$$\text{Time} = \frac{600 \text{ (ft)}}{1.5 \text{ (ft/day)}} = 400 \text{ days}$$

c. $$\text{Retardation} = \frac{\text{velocity of water}}{\text{velocity of solute}}$$

$$\text{Velocity of solute} = \frac{\text{velocity of water}}{\text{retardation}}$$

$$= \frac{1.5 \text{ (ft/day)}}{15} = 0.1 \text{ ft/day}$$

$$\text{Time} = \frac{600 \text{ (ft)}}{0.1 \text{ (ft/day)}} = 6{,}000 \text{ days} = 16.44 \text{ years}$$

Half-Life Exercises

15. No evaporation or precipitation during time period

$k = \ln (C_o/C_t)/t = \ln (155/107)/326$ (days)

$= 0.0011368$/day

$t_{1/2} = 0.693/k = 1.67$ years

16.

	Y	Cl
2/12/85	5.1	15.2
5/24/86	1.3	9.7

Final concentration of X corrected for precipitation

$$= 1.3 * \frac{15.2}{9.7} = 2.04 \text{ μg/l}$$

$$k = \frac{\ln \frac{5.1}{2.04}}{466} = 0.001966$$

$$t_{1/2} = \frac{0.693}{k} = 352 \text{ days} = 0.96 \text{ years}$$

17.

a. $t_{1/2} = 3.5$ years $= 1277.5$ days; $k = 0.0005425$

Date 3/17/86 = 52μg/l,
Date 6/1/87 = ? μg/l
Time difference = 441 days

$$\ln \frac{C_o}{C_t} = k * t = 0.0005425 * 441 = 0.2392$$

$C_t = 40.94$ μg/l

b.

Date	Z μg/l	Cl mg/l
3/3/84	87	58
6/1/87	?	116

$t = 1185$ days; $k = 0.0005425$

$C_t = 45.74$ μg/l
corrected for evaporation is 91.5 μg/l

18.

a. Half-life calculation

	X μg/l	Cl mg/l
5/7/84	5.3	15
7/2/85	2.1	9

true concentration $= 2.1 * 15/9 = 3.5$
$t = 423$ days; $k = 0.00098$

b. Maximum holding time t

$$t = \frac{\ln \frac{5.3}{1.0}}{0.00098} = 1700 \text{ days without evaporation or dilution,}$$

or

$$t = \frac{\ln \frac{2.1}{1.0}}{0.00098} = 756 \text{ days longer.}$$

CHAPTER 9

Computer Programs

INTRODUCTION

The computer programs included with this book are meant to be an integral part of the book and not an afterthought. Several programs, such as MFLASH and OFLASH, are flashcard systems written to ease the pain of remembering some of the basics necessary to understand the topics. Others, such as WATEVAL and ECOPLUS, may be used to evaluate the inorganic and organic constituents of waters, respectively. The calculations used in these programs, with the exception of the groundwater routine in ECOPLUS, are simple and easily done by hand. The computer version is, however, much more rapid and less subject to errors. An additional program, WATEQ4F (Ball et al., 1987), a water equilibrium program, is included for use in conjunction with the chapter on thermodynamics. The thermodynamics chapter is written primarily to aid in the use and understanding of the output from WATEQ4F.

COMPUTER HARDWARE

The computer programs other than WATEQ4F are written in Microsoft QuickBASIC 4.0. Compiled code only is available. The programs require an IBM or clone with a Colorgraphics adapter (CGA) graphics adapter or better, DOS 2.1 or later and 640 K RAM. Only WATEQ4F requires a math coprocessor. No alterations are permitted to be made to the programs and the banners must be left intact. Any changes will result in the programs abruptly terminating.

WATEQ4F is a U.S. Geological Survey program written in FORTRAN. It is compiled for use with a math coprocessor. The source code may be obtained from the USGS, but is not included here.

NOTE: To obtain hard copies of any graphic screen, the Shift PrtSc keys must be used. The program GRAPHICS.COM must be run before loading the program. This is done either by incorporating it in the AUTOEXEC.BAT file or by typing GRAPHICS at the DOS prompt. If run from the Windows environment, a Print Screen command will copy the screen to the Windows clipboard from which it may be pasted into other graphics/word-processing programs.

The computer programs and the book chapters with which they may best be used are tabulated below.

Chapter 1	Introduction	———
Chapter 2	Review of Basic Chemistry and Geology	MFLASH
Chapter 3	Major Inorganic Constituents of Water	MFLASH
Chapter 4	Water Quality Interpretation	WATEVAL
Chapter 5	Geochemical Equilibrium Modeling	WATEQ4F
Chapter 6	Geochemical Environments	———

Chapter 7	Organic Chemistry Nomenclature	OFCARD
Chapter 8	Ecosystem Partitioning and Solute Transport	ECOPLUS
Chapter 9	Computer Programs	———

MFLASH

MFLASH is a microcomputer flash card system written by A. W. Hounslow to aid in the learning of basic mineral formulas, rock mineralogy, and sources of dissolved constituents in water.

Running MFLASH — To run MFLASH type MFLASH and press ENTER. After the first question appears on screen press ENTER for the answer to be shown, as well as the various function key options. After each question you may type in the answer for your convenience only—the program will ignore the entry—and then press ENTER for the answer to appear on the screen.

The various options that may be obtained by using function keys are

F1 Formulas	Shows name	Reply - formula
F2 Minerals	Shows formula	Reply - name
F3 Rocks	Shows rock	Reply - mineral composition
F4 Ions	Shows ion	Reply - mineral source
F5 All	Shows any of above in random order.	
F6 Sequential	Same as (F5) above, but in sequential order moving from (F1) to (F4).	

OFCARD

OFCARD is a microcomputer flash card system of organic chemistry nomenclature written by A. W. Hounslow. The coded data file for this program is COMP.ORG.

Running OFCARD — To run OFCARD type OFCARD and press ENTER. When requested press ENTER again and the program will read in the data. The structure number is shown in the upper left-hand corner of the screen. The selection of compound types is accomplished using function keys. The selection criteria has three parts—the functional groups, the level of difficulty, and the selection of either formula or name.

F1 - hydrocarbons and chlorinated hydrocarbons.
F2 - oxygen functional groups.
F3 - nitrogen, sulfur, and phosphorus functional groups.
F4 - random selection of any of the above.
F5 - Level 1 - simple compounds.
  F1 - simple hydrocarbons.
  F2 - simpler oxygen functional groups.
  F3 - amines and nitro groups.
F6 - Level 2 - more complex compounds.
  F1 - chlorinated hydrocarbons.
  F2 - esters and unsaturated compounds with oxygen functional groups.
  F3 - amides.
F7 - Level 3 - most complex compounds.
  F1 - complex hydrocarbons.
  F2 - multiple oxygen functional groups.
  F3 - sulfur, phosphorus, and complex nitrogen functional groups.

F8 - formula given.
F9 - name given.

allows you to choose a structure number.
(Press ENTER to start at #1.)
X allows you to work sequentially through the structures.
(You need only press X, not ENTER.)

L is a list of the number of compounds in each category.
H is a nomenclature help screen for hydrocarbons.
O is a nomenclature help screen for oxygen functional groups.
N is a nomenclature help screen for nitrogen functional groups.
S is a nomenclature help screen for sulfur functional groups.
P is a nomenclature help screen for phosphorus functional groups.

WATEVAL

WATEVAL is a water quality evaluation program written by A. W. Hounslow and Kelly D. Goff. The purpose of the program is to evaluate water quality data from several points of view. These include:

a. An intensive evaluation of the analysis for a determination of its reliability.
b. A deduction of the aquifer mineralogy from the analysis.
c. A plot of one or more analyses on Piper, Stiff, and SAR diagrams used to determine chemical trends such as mixing and ion exchange, or relative compositions of water samples.
d. A comparison of two analyses and estimates of the likelihood of two analyses mixing to give a third analysis.
e. An estimate of the REDOX state of the water by using input values of Fe^{2+}/Fe^{3+}, NO_3^-/NH_4^+, dissolved O_2, Mn^{2+}, SO_4^{2-}/H_2S, and CH_4/CO_2.

The program has the capability of editing the input data; making some simple calculations, such as calculating HCO_3^- from alkalinity or temporary hardness; converting CO_3^{2-} to HCO_3^-; estimating pH from HCO_3^-/CO_3^{2-} ratios; calculating the third parameter given any two of the following three: Ca, Mg, or hardness; and calculating SiO_2 from Si.

A variety of input/output options are available including saving to RAM (computer memory—random access memory—program array) or disk files. A maximum of five analyses may be saved to memory. Input may be from keyboard, RAM, or disk file.

An outline of the various program options is shown in Figure 9.1. The main menu options and program configuration menu are given in Tables 9.1 and 9.2.

FILE-HANDLING PROCEDURES

The program is designed to automatically open and close files. Thus, when a file used for output is required for input, it is closed and reopened for input. It then is not available for output until reopened as such. In the event that two files are opened for output (input), the first one opened is closed, and the second opened. Most disk errors allow for correction; the most common, however, is the most time consuming. This occurs when the program is being run from hard disk (C:) and the drive default (A:) is not changed. At this error you may insert a floppy in drive A: or wait until the program returns to the default menu.

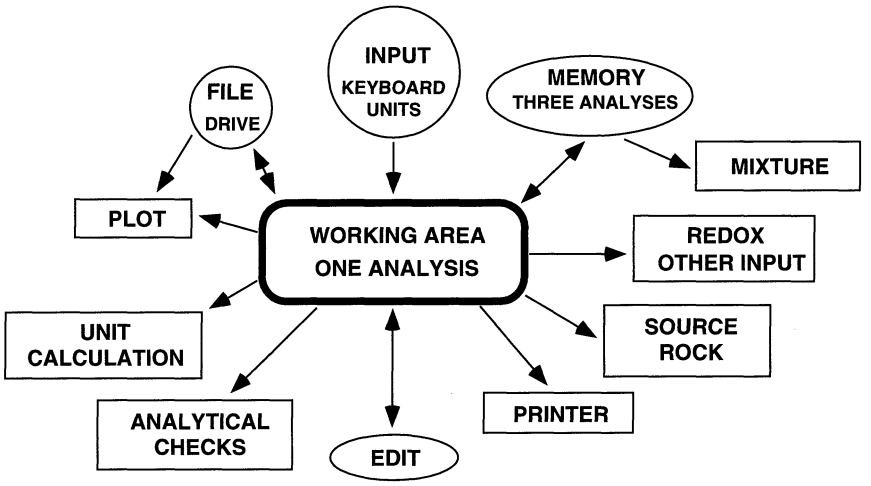


Figure 9.1. WATEVAL program outline.

Table 9.1. Main Menu Options

-- WATEVAL MAIN MENU OPTIONS --

1. Input analysis—the default option is input from the keyboard. The units for the input data may be mg/l, ppm, meq/l, or mmol/l. The default is mg/l. The previous analysis will be overwritten and the analysis lost unless it has been saved. If data files exist they may also be input. They will have the extension .H20.
2. View analysis—print a table with analyses in mg/l, mmol/l, meq/l, and % meq anion and % meq cations.
3. View analysis checks—a table of a variety of analysis checks is printed and major discrepancies are highlighted for further investigation.
4. View source-rock deduction—deduces from a series of ratios the type of mineralogy of the aquifer. This may also be used as an analysis check if the aquifer mineralogy is known.
5. Edit data—this allows the editing of the sample designation, sample data, or the calculation of some parameters as described above. Several conversions may be made from this menu.
6. Print hard copy—this enables a printer output of items 2, 3, and 4 above.
7. Plot diagram—Piper, Stiff, SAR, and BDP (brine differentiation plot) diagrams may be plotted in either high- or medium-resolution graphics. The default is medium resolution. Each analysis may be plotted when entered (default option) or a series of analyses may be plotted from a file or from RAM. A hard copy of the plot is obtained by using the Shift-Prt Sc keys. See note on GRAPHICS.COM above.
8. Redox equilibria—allows the calculation of pe values from a variety of input parameters (pH and SO_4^{2-} are required from the main program). It also allows the calculation of some ion ratios if given a specific pe and pH.
9. Save analysis—the default is to memory (RAM). The input and output options currently in operation are given at the top of the screen above the menu. When an item is saved the sample designation and destination are given below the menu. All analyses should be saved to a disk file. The RAM option is used to calculate mixtures and compare analyses (see option 11 below). Only five analyses may be saved to RAM.
10. Set program configuration—this enables changes to be made to the default settings. Additional options are listed below. The main use of this option is fast operation without program prompts. It is not recommended unless you are familiar with the program.
11. Mixture and comparison calculation—three analyses previously saved to memory (RAM) are sorted into two end members and the third as a mixture of the first two based on TDS (in meq/l). A correlation coefficient is then calculated. Two of the analyses saved to memory may also be compared directly using several bar graphs.
12. Exit program—the program exits to DOS and data stored in memory (RAM) is **LOST!**

-- END OF MAIN MENU OPTIONS --

ADDITIONAL OPTIONS
H—Help screens.
F—Fast operation based on settings of configuration menu.
No program prompts will appear.
Toggles (moves) back and forth between fast and normal operation.

Table 9.2. Program Configuration Menu

-- Program Configuration Menu --

If you do not wish to change the settings highlighted, press ENTER and they will remain unchanged.

1. MONITOR	**1.—Color**	**—default**
	2.—Monochrome	
	3.—No graphics (or Hercules graphics)	
2. DRIVE	**1.—A:**	**—default**
	2.—B:	
	3.—C:	
	4.—D:	
	5.—E:	
3. UNITS	**1.—Concentrations in mg/l**	**—default**
	2.—Concentrations in ppm	
	3.—Concentrations in meq/l	
	4.—Concentrations in mmol/l	
4. GRAPHICS	**1.—Medium resolution**	**—default**
	2.—High resolution.	

If a monochrome monitor is chosen this defaults to high resolution.

5. PLOT TYPE	**1.—Piper plot**	**—default** (only option if user code not entered)
	2.—SAR plot	
	3.—Stiff(6) plot	(six analyses per screen)
	4.—Stiff(9) plot	(nine analyses per screen)
	5.—BDP graph	(brine differentiation plot)

All Stiff diagrams are plotted on the same scale, which is log meq/l.

6. PLOT FROM	**1.—Last entry**	**—default**
	2.—Analyses in file	
	3.—Analyses in memory	

Plotting the last entry means that only the last analysis entered is plotted. For multiple analyses you have the option of plotting all analyses or selecting those you wish to plot one at a time. As each analysis is plotted the ENTER key must be pressed for the next analysis to be plotted. When first entered each new analysis is plotted in a color different from that of the earlier entries. This is changed back when a subsequent analysis is entered.

7. DATA	**1.—Enter from keyboard**	**—default**
	2.—Enter from file	
	3.—Enter from memory	

You have the option of running through the file or memory to select the analysis you wish to examine.

8. SAVE	**1.—Analysis to memory**	**—default**
	2.—Analysis to file	
	3.—Memory to file	
	4.—Reset memory to zero	

In most instances analyses should be saved to a disk file. If you save your analyses to memory you should use the **save memory to file** option before leaving program or all analyses will be lost. When you save analyses in MEMORY to FILE, the analyses will be saved and the program will default to memory after clearing (resetting to zero) the RAM memory array. If you have already saved an analysis, the program will alert you to this if you try and save it again. You should not, however, change the analysis and save it to the same file unless you rename it.

9. RETURN **TO MAIN MENU**

-- End of Program Configuration Menu --

The various INPUT/OUTPUT options are summarized below and in Figure 9.2.

INPUT
- KEYBOARD—default.
- RAM
  - Select option.
  - Choose sample.
- FILE
  - Select option.
  - Choose drive.
  - Select file.
    - Choose sample, or
    - Process all analyses in file and write output to .PRN file, or
    - Process all analyses in file and write analyses check summary to .CHK file.

OUTPUT (SAVING ANALYSIS)
- RAM (MEMORY)—default.
- FILE
  - Select option.
  - Choose drive.
  - Name file.
  - Save EACH analysis.
- SAVE RAM TO FILE
  - Select option.
  - Choose drive (default A:).
  - Name file.
  - Save RAM.
  - Program closes file and resets to default.

WATEVAL "*.H2O" FILE

The format of the WATEVAL "*.H2O" file is the "sample name" followed by 30 parameters separated by commas. It may be set up using a spreadsheet if this order is followed. Several parameters are not used in this program. Sometimes a correct output can only be obtained from a spreadsheet if a zero is entered in each space that does not have a parameter. The order of entry, on a single line, is

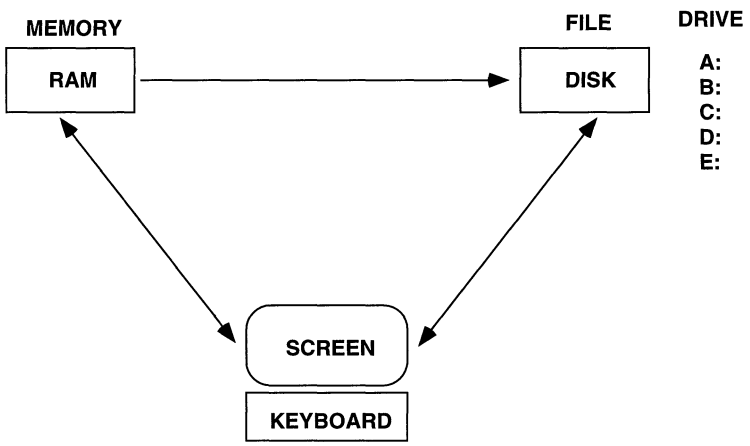


Figure 9.2. WATEVAL file routines.

"Sample name", temperature (C), pH, TDS, conductivity, hardness ($CaCO_3$), density (a zero will default to l), x-coordinate (**not used**), y-coordinate (**not used**), ***units code*** (1–4) **see below,** rock type (**not used**), sodium, potassium, calcium, magnesium, chloride, sulfate, bicarbonate, carbonate, silica, lithium, strontium, barium, ferrous iron, nitrate (NO_3^-), fluoride, bromide, boron (B), **(not used), (not used), (not used) [Carriage Return].**

The units code consists of a number between 1 and 4 indicating the units used for the data as shown below:

1. mg/l
2. ppm
3. meq/l
4. mmol/l

WATEVAL PROCEDURE FOR PIPER PLOTS

Before running the program make sure that the program GRAPHICS has been run from DOS—this enables you to use a screen dump to obtain a hard copy of any graphics screen. To run WATEVAL type WATEVAL and press ENTER.

If you have:

a. No graphics type WATEVAL/H and press ENTER.
b. Monochrome graphics type WATEVAL/M and press ENTER.
c. EGA or VGA graphics type WATEVAL/E and press ENTER. This option may also be changed in the program.

When requested press ENTER. This should take you to the main menu. For each selection follow the prompts. DO NOT attempt to use the fast mode until you are familiar with the program as it will not prompt you. The fast mode is governed by the setting selected in the configuration menu (Item 10). If you wish to change graphics modes select the GRAPHICS option of the configuration menu.

The general procedure is

1. From the main menu input the first analysis from the keyboard, examine it for errors (option 2 and 3), and edit if necessary (option 5). When finished save analysis to file (or memory)—option 9. Enter the next analysis using the same procedure. The current analysis may be viewed on the plot by choosing option 7 at any time.
2. When all analyses have been entered and SAVED change to plot analyses from file (or memory). The analyses will appear one at a time by pressing the ENTER key after each is plotted. The first two characters of the sample name will appear at the top left-hand portion of the screen. When all the analyses have been plotted a hard copy of the plot may be obtained by pressing **Shift and PrtSc.** If the program is run from windows a **PrtSc** will save the screen to the windows clipboard which may be pasted into other programs such as Microsoft WORD™.

EXAMPLES OF THE USE OF WATEVAL

Examine each analysis given in Table 9.3 (White et al., 1963) for reliability and determine as far as possible the source rock and any reactions that may have occurred. How do your conclusions compare with the stated source? Tables of the analytical checks and source rock ratios are given in Tables 9.4a to 9.4p.

Table 9.3. Analyses Used to Illustrate the Use of WATEVAL

	A	B	C	D	E	F	G	H
Na^+	20	12	36	4	2.0	17	11,500	5,872
K^+	5.2	5.3	3.5	0.7	0.6	17	390	133
Ca^{2+}	14	24	15	48	34.0	636	410	376
Mg^{2+}	5.8	15	7.5	5.8	14.0	43	1,350	116
HCO_3^-	112	156	3.2	168	160.0	143	142	540
SO_4^{2-}	7.7	1.6	128	6.4	3.7	1,570	2,700	1.6
Cl	4	15	21	4.8	2.5	24	19,000	9,929
SiO_2	62	50	22	8.9	9.2	29	6.4	47.4
pH	7.6	7.7	4.9	7.7	7.5		8.1	7.5
T °C	14.4				16.7		20	49.5
TDS	234	280	236	247		2,480	35,490	17,100
Cond. umhos	217	427	373	287	259	2,510		25,800

Note: A. Table 1 Number 4—Rhyolite well 251′
B. Table 2 Number 9—Basalt well
C. Table 5 Number 2—Shale spring
D. Table 6 Number 3—Limestone spring 71,000 gpd
E. Table 7 Number 2—Groundwater (Harvey spring), Dolomite, AL
F. Table 8 Number 5—Gypsum spring 5 gpm
G. Seawater
H. Table 12 Number 2—Oil field brine 4952′

Analyses from U.S. Geological Survey Professional Paper 440-F (White et al., 1963).

Table 9.4a. Sample A Reliability Checks. A. Table 1 Number 4—Rhyolite Well 251′

Reliability check	Attention value	Analysis value	Conclusion
$\frac{(C - A)}{(C + A)}$ %	>5%	1.6%	
Hardness $- \frac{\text{Entered} - \text{Calc}}{\text{Entered}}$	>5%	***	
$\frac{\text{Entered TDS} - \text{TDSC}}{\text{Entered TDS}}$	>5%	1%	Entered TDS is sum of ions
$\frac{\text{Entered TDS} - \text{TDS 180}}{\text{Entered TDS 180}}$	>5%	26%	
$\frac{\text{Entered TDS}}{\text{Conductivity}}$	<0.5 and >0.75	1.08	
$\frac{\text{TDS calc}}{\text{Conductivity}}$	<0.5 and >0.75	1.06	High
$\frac{\text{Conductivity}}{\text{sum MEQ cations}}$	<90 and >110	100	
Carbonate	0.2 (calc)	0.0	
$\frac{K}{K + Na}$	>0.2	0.13	
$\frac{Mg}{Mg + Ca}$	>0.4	0.41	
$\frac{Ca}{Ca + SO_4}$	<0.5	0.81	
$\frac{Na}{Na + Cl}$	<0.5	0.89	
Conclusion	Analysis acceptable		Yes No

Table 9.4b. Sample A SourceRock Evaluation. A. Table 1 Number 4—Rhyolite Well 251

Parameter	Value	Conclusion
SiO_2 (mmol/l)	1.03	Volcanic glass or hydrothermal water possible
$\frac{HCO_3}{SiO_2}$	1.78	Silicate weathering
$\frac{SiO_2}{Na + K - Cl}$	1.16	Albite
$\frac{Na + K - Cl}{Na + K - Cl + Ca}$	0.72	Plagioclase weathering possible
$\frac{Na}{Na + Cl}$	0.89	Albite or ion exchange
$\frac{Mg}{Mg + Ca}$	0.41	Granitic weathering
$\frac{Ca}{Ca + SO_4}$	0.81	Ca source other than gypsum, carbonates, or silicates
$\frac{Ca + Mg}{SO_4}$	7.3	Dedolomitization unlikely
TDS calculated (mg/l)	231	Silicate weathering possible
$\frac{Cl}{\text{sum anions}}$	0.05	Silicate or carbonate weathering
$\frac{HCO_3}{\text{sum anions}}$	0.87	Silicate or carbonate weathering
Langelier index	−0.72	Undersaturated with respect to calcite
Conclusion	Aquifer mineralogy	Rhyolitic composition strongly suggested; high silica suggests volcanic origin
Conclusion	Reactions	None obvious

Table 9.4c. Sample B Reliability Checks. B. Table 2 Number 9—Basalt Well

Reliability check	Attention value	Analysis value	Conclusion
$\frac{(C - A)}{(C + A)}$ %	>5%	1.2%	
Hardness $- \frac{\text{Entered} - \text{Calc}}{\text{Entered}}$	>5%	***	
$\frac{\text{Entered TDS} - \text{TDSC}}{\text{Entered TDS}}$	>5%	0%	Entered TDS is sum of ions
$\frac{\text{Entered TDS} - \text{TDS 180}}{\text{Entered TDS 180}}$	>5%	29%	
$\frac{\text{Entered TDS}}{\text{Conductivity}}$	<0.5 and >0.75	0.66	
$\frac{\text{TDS calc}}{\text{Conductivity}}$	<0.5 and >0.75	0.65	
$\frac{\text{Conductivity}}{\text{sum MEQ cations}}$	<90 and >110	138	High
Carbonate	0.2 (calc)	0.0	
$\frac{K}{K + Na}$	>0.2	0.21	
$\frac{Mg}{Mg + Ca}$	>0.4	0.51	High
$\frac{Ca}{Ca + SO_4}$	<0.5	0.97	
$\frac{Na}{Na + Cl}$	<0.5	0.55	
Conclusion	Analysis acceptable		Yes No

Table 9.4d. Sample B source Rock Evaluation. B. Table 2 Number 9—Basalt Well

Parameter	Value	Conclusion
SiO_2 (mmol/l)	0.83	Volcanic glass or hydrothermal water possible
$\frac{HCO_3}{SiO_2}$	3.07	Silicate weathering
$\frac{SiO_2}{Na + K - Cl}$	3.55	Ferromagnesian minerals
$\frac{Na + K - Cl}{Na + K - Cl + Ca}$	0.28	Plagioclase weathering possible
$\frac{Na}{Na + Cl}$	0.55	Albite or ion exchange
$\frac{Mg}{Mg + Ca}$	0.51	Ferromagnesian minerals
$\frac{Ca}{Ca + SO_4}$	0.97	Ca source other than gypsum, carbonates, or silicates
$\frac{Ca + Mg}{SO_4}$	73.0	Dedolomitization unlikely
TDS calculated (mg/l)	279	Silicate weathering possible
$\frac{Cl}{\text{sum anions}}$	0.14	Silicate or carbonate weathering
$\frac{HCO_3}{\text{sum anions}}$	0.85	Silicate or carbonate weathering
Langelier index	−0.51	Undersaturated with respect to calcite
Conclusion	Aquifer mineralogy	Basaltic composition strongly suggested; high silica suggests volcanic origin
Conclusion	Reactions	None obvious

A. Table 1 Number 4—Rhyolite well 251′—Table 9.4a and b

Analysis acceptable. It is evident that the reported TDS is the sum of the ions. Source rock deduction

Bicarbonate/silica = 1.8 (<<10), suggesting silicate weathering.
TDS (234 mg/l) relatively low, suggests silicate weathering.
Silica/excess sodium = 1.2 suggests silicic silicates.
Chloride and sulfate low, suggests precipitation.
Relatively high potassium (5 mg/l), suggests mica weathering.
Na, Ca, and Mg, possible rhyolite/granite composition.
Na:Ca suggests sodic plagioclase.
The relatively high silica suggests volcanic glass and therefore rhyolite.

Conclusion: silicate weathering, most likely rhyolite origin.

B. Table 2 Number 9—Basalt well—Table 9.4c and d

Analysis acceptable. It is evident that the reported TDS is the sum of the ions. Source rock deduction

Bicarbonate/silica = 3.1 (<<10), suggests silicate weathering.
TDS (280 mg/l), suggests mafic silicate weathering.
Silica/excess sodium = 3.6 (> 2), suggests mafic silicate weathering.

Table 9.4e. Sample C Reliability Checks. C. Table 5 Number 2—Shale Spring

Reliability check	Attention value	Analysis value	Conclusion	
$\frac{(C - A)}{(C + A)}$ %	>5%	−4.6%		
Hardness − $\frac{\text{Entered} - \text{Calc}}{\text{Entered}}$	>5%	***		
$\frac{\text{Entered TDS} - \text{TDSC}}{\text{Entered TDS}}$	>5%	***		
$\frac{\text{Entered TDS} - \text{TDS 180}}{\text{Entered TDS 180}}$	>5%	***		
$\frac{\text{Entered TDS}}{\text{Conductivity}}$	<0.5 and >0.75	***		
$\frac{\text{TDS calc}}{\text{Conductivity}}$	<0.5 and >0.75	0.63		
$\frac{\text{Conductivity}}{\text{sum MEQ cations}}$	<90 and >110	123	High	
Carbonate	0.2 (calc)	0.0		
$\frac{K}{K + Na}$	>0.2	0.05		
$\frac{Mg}{Mg + Ca}$	>0.4	0.45		
$\frac{Ca}{Ca + SO_4}$	<0.5	0.22	Low	
$\frac{Na}{Na + Cl}$	<0.5	0.73		
Conclusion	Analysis acceptable		Yes	No

Sodium, chloride, and sulfate low, suggests mafic silicate weathering.
Potassium of 5 mg/l, suggests some micas and therefore mafic rather than ultramafic weathering.
Mg/(Mg + Ca) = 0.5, suggests mafic silicate weathering.
Na:Ca suggests calcic plagioclase.
The relatively high silica suggests volcanic glass and therefore basalt.

Conclusion: silicate weathering, most likely basalt.

C. Table 5 Number 2—Shale spring—Table 9.4e and f

Analysis acceptable
Source rock deduction

Bicarbonate/silica equals 0.14, primarily because of very low bicarbonate which suggests neither carbonate nor silicate weathering.
TDS (236 mg/l) relatively low.
Ca < SO_4^{2-}; and Na > Cl, suggests ion exchange.
The low bicarbonate (3 mg/l) and the pH of 4.9 strongly suggest pyrite oxidation and subsequent partial neutralization of the sulfuric acid generated.
The relatively high chloride (21 mg/l) suggests some halite, although rain water concentration is also possible.
Mg/(Mg + Ca) = 45%, suggests dolomite except for the very low bicarbonate.

Conclusion: the interpretation of this water analysis is not straightforward. A possible origin may be pyrite oxidation, partial neutralization by dolomitic limestone, coupled with some cation exchange.

Table 9.4f. Sample C Source Rock Evaluation. C. Table 5 Number 2—Shale Spring

Parameter	Value	Conclusion
SiO_2 (mmol/l)	0.37	
$\frac{HCO_3}{SiO_2}$	0.14	Silicate weathering
$\frac{SiO_2}{Na + K - Cl}$	0.34	Cation exchange
$\frac{Na + K - Cl}{Na + K - Cl + Ca}$	0.74	Plagioclase weathering possible
$\frac{Na}{Na + Cl}$	0.73	Albite or ion exchange
$\frac{Mg}{Mg + Ca}$	0.45	Granitic weathering
$\frac{Ca}{Ca + SO_4}$	0.22	Pyrite oxidation
$\frac{Ca + Mg}{SO_4}$	0.5	Dedolomitization unlikely
TDS calculated (mg/l)	236	Silicate weathering possible
$\frac{Cl}{\text{sum anions}}$	0.18	Silicate or carbonate weathering
$\frac{HCO_3}{\text{sum anions}}$	0.02	Sea water, brine, or evaporites
Langelier index	−5.04	Undersaturated with respect to calcite
Conclusion	Aquifer mineralogy	Pyrite oxidation and partial neutralization with dolomitic limestone
Conclusion	Reactions	Some ion exchange

D. Table 6 Number 3—Limestone spring 71,000 gpd—Table 9.4g and h

Analysis acceptable
Source rock deduction

Bicarbonate/silica = 18.6 (>>10), suggesting carbonate weathering.
TDS (247 mg/l) somewhat low for carbonates unless near the recharge area.
Langelier index = 0.2, indicating saturation or oversaturation with respect to calcite.
Na, K, Cl, and SO_4^{2-} low, suggesting mostly precipitation origin.
Mg/(Mg + Ca) = 0.17, indicating some dolomite.
The water is primarily calcium and bicarbonate, indicating a limestone origin.

Conclusion: limestone origin close to the recharge area with some dolomite present.

E. Table 7 Number 2—Groundwater (Harvey spring), Dolomite, AL—Table 9.4i and j

Analysis acceptable
Source rock deduction

Bicarbonate/silica = 17.1 (>>10), suggesting carbonate weathering.
TDS (226 mg/l) relatively low, suggesting recent recharge if carbonate origin.
Sodium, potassium, chloride, and sulfate are all low, indicating precipitation origin.

Table 9.4g. Sample D Reliability Checks. D. Table 6 Number 3—Limestone Spring 71,000 gpd

Reliability check	Attention value	Analysis value	Conclusion
$\frac{(C - A)}{(C + A)}$ %	>5%	0.7%	
Hardness $-\frac{\text{Entered} - \text{Calc}}{\text{Entered}}$	>5%	***	
$\frac{\text{Entered TDS} - \text{TDSC}}{\text{Entered TDS}}$	>5%	***	
$\frac{\text{Entered TDS} - \text{TDS 180}}{\text{Entered TDS 180}}$	>5%	***	
$\frac{\text{Entered TDS}}{\text{Conductivity}}$	<0.5 and >0.75	***	
$\frac{\text{TDS calc}}{\text{Conductivity}}$	<0.5 and >0.75	0.86	Slightly high
$\frac{\text{Conductivity}}{\text{sum MEQ cations}}$	<90 and >110	94	
Carbonate	0.2 (calc)	0.0	
$\frac{K}{K + Na}$	>0.2	0.09	
$\frac{Mg}{Mg + Ca}$	>0.4	0.17	
$\frac{Ca}{Ca + SO_4}$	<0.5	0.95	
$\frac{Na}{Na + Cl}$	<0.5	0.56	
Conclusion	Analysis acceptable		Yes No

Mg/(Mg + Ca) = 40%, suggesting dolomite with some limestone.
Slight excess of sodium over chloride suggests ion exchange.

Conclusion: dolomite with minor limestone close to recharge area, possibly with some ion exchange.

F. Table 8 Number 5—Gypsum spring 5 gpm—Table 9.4k and l

Analysis acceptable. Conductivity possibly high.
Source rock deduction

Bicarbonate/silica = 4.9 (<1.0) borderline.
TDS (2479) is very high, indicating the solution of a soluble salt such as gypsum.
$Ca^{2+} > SO_4^{2-}$ and the excess Na relative to Cl indicates ion exchange.
Mg/(Mg + Ca) = 0.10 probably indicating that some dolomite was also dissolved.
The potassium relative to sodium is somewhat high.
$(Ca + Mg)/SO_4^{2-}$ is 1.1, which suggests dedolomitization.

Conclusion: gypsum with some dolomite. Ion exchange and dedolomitization are possible reactions.

G. Seawater—Table 9.4m and n

Analysis acceptable—some unusual values that are typical of seawater.
Source rock deduction

Table 9.4h. Sample D Source-Rock Evaluation. D. Table 6 Number 3—Limestone Spring 71,000 gpd

Parameter	Value	Conclusion
SiO_2 (mmol/l)	0.15	
$\frac{HCO_3}{SiO_2}$	18.59	Carbonate weathering
$\frac{SiO_2}{Na + K - Cl}$	2.62	Ferromagnesian minerals
$\frac{Na + K - Cl}{Na + K - Cl + Ca}$	0.05	Plagioclase weathering unlikely
$\frac{Na}{Na + Cl}$	0.56	Albite or ion exchange
$\frac{Mg}{Mg + Ca}$	0.17	Limestone-dolomite weathering
$\frac{Ca}{Ca + SO_4}$	0.95	Ca source other than gypsum, carbonates, or silicates
$\frac{Ca + Mg}{SO_4}$	21.6	Dedolomitization unlikely
TDS calculated (mg/l)	247	Silicate weathering possible
$\frac{Cl}{\text{sum anions}}$	0.04	Silicate or carbonate weathering
$\frac{HCO_3}{\text{sum anions}}$	0.91	Silicate or carbonate weathering
Langelier index	0.20	Oversaturated with respect to calcite
Conclusion	Aquifer mineralogy	Limestone with some dolomite
Conclusion	Reactions	

Mg/(Mg + Ca) = 84 is very high, suggesting Ca removal.
Langelier index = 0.43 indicates calcite probably precipitating.
$Ca^{2+}/(Ca^{2+} + SO_4^{2-}) = 0.27$ suggests Ca removal.

Conclusion: typical seawater. Calcite precipitation is the main reaction suggested.

H. Table 12 Number 2—Oil field brine 4952′—Table 9.4o and p

Analysis acceptable
Source rock deduction

Bicarbonate/silica = 11.2, indicates carbonate weathering.
TDS (17,100) very high, indicating brine.
$Na^+ < Cl^-$, indicates reverse exchange.
Mg/(Mg + Ca) = 33.7%, indicates dolomite solution.

Conclusion: typical oil field brine characteristics, especially Na < Cl.

Table 9.4i. Sample E Reliability Checks. E. Table 7 Number 2—Groundwater (Harvey Spring), Dolomite, AL

Reliability check	Attention value	Analysis value	Conclusion
$\frac{(C - A)}{(C + A)}$ %	>5%	3.2%	
Hardness $- \frac{\text{Entered} - \text{Calc}}{\text{Entered}}$	>5%	***	
$\frac{\text{Entered TDS} - \text{TDSC}}{\text{Entered TDS}}$	>5%	***	
$\frac{\text{Entered TDS} - \text{TDS 180}}{\text{Entered TDS 180}}$	>5%	***	
$\frac{\text{Entered TDS}}{\text{Conductivity}}$	<0.5 and >0.75	***	
$\frac{\text{TDS calc}}{\text{Conductivity}}$	<0.5 and >0.75	0.87	Slightly high
$\frac{\text{Conductivity}}{\text{sum MEQ cations}}$	<90 and >110	88	
Carbonate	0.2 (calc)	0.0	
$\frac{K}{K + Na}$	>0.2	0.15	
$\frac{Mg}{Mg + Ca}$	>0.4	0.40	
$\frac{Ca}{Ca + SO_4}$	<0.5	0.96	
$\frac{Na}{Na + Cl}$	<0.5	0.55	
Conclusion	Analysis acceptable		Yes No

WATEQ4F

WATEQ4F is a water equilibrium computer model distributed by the U.S. Geological Survey.

A variety of water equilibrium programs are available, and a partial listing is given in Table 5.1 in Chapter 5. Those selected illustrate the development and evolution that the programs undergo over time. The program included here is the U.S. Geological Survey Model WATEQ4F. Its selection was based on the ability to run it on a floppy disk system and the relative ease of use as an introduction to equilibrium programs.

WATEQ4F is a FORTRAN version of a program originally written in PL-1. It calculates the equilibrium distribution of inorganic aqueous species of major and important minor elements in natural waters using the chemical analysis of the water and *in situ* measurements of temperature, pH, and redox potential. From this model the saturation state of the water with common minerals is calculated. A BASIC program that formats the input data is included.

By far the most important consideration in the calculation of the activities is the presence in the water of charged and uncharged complexes that are not immediately apparent from the analysis. The program calculates the activities of these complexes by an iterative procedure using the mass-balance equations for each element.

The WATEQ4F database consists of a list of minerals, ions, and complexes with their equilibrium constants (at 25°C) and enthalpies. If these data are not available, then the coefficients for empirical equations are stored. These data are stored in files TABLE1, TABLE2, TABLE3, and TABLE4.

Table 9.4j. Sample E Source Rock Evaluation. E. Table 7 Number 2—Groundwater (Harvey Spring), Dolomite, AL

Parameter	Value	Conclusion
SiO_2 (mmol/l)	0.15	
$\frac{HCO_3}{SiO_2}$	17.13	Carbonate weathering
$\frac{SiO_2}{Na + K - Cl}$	4.81	Ferromagnesian minerals
$\frac{Na + K - Cl}{Na + K - Cl + Ca}$	0.04	Plagioclase weathering unlikely
$\frac{Na}{Na + Cl}$	0.55	Albite or ion exchange
$\frac{Mg}{Mg + Ca}$	0.40	Limestone-dolomite weathering
$\frac{Ca}{Ca + SO_4}$	0.96	Ca source other than gypsum, carbonates, or silicates
$\frac{Ca + Mg}{SO_4}$	37.0	Dedolomitization unlikely
TDS calculated (mg/l)	226	Silicate weathering possible
$\frac{Cl}{\text{sum anions}}$	0.03	Silicate or carbonate weathering
$\frac{HCO_3}{\text{sum anions}}$	0.95	Silicate or carbonate weathering
Langelier index	−0.27	Undersaturated with respect to calcite
Conclusion	Aquifer mineralogy	Limestone-dolomite
Conclusion	Reactions	Possibly some ion exchange

The sequence of operations performed by WATEQ4F is

a. Calculation of the equilibrium constants at 25°C followed by an adjustment to the temperature of the water, generally using the Van't Hoff equation.
b. Next the ionic strengths and activity coefficients are calculated. These are based on the Debye-Huckel or Davies equations, depending on the ionic strength of the solution.
c. A series of mass-balance equations are then formulated for each species in the analysis. This includes the ions as well as the charged and uncharged complexes.
d. This set of equations is solved and the process (a to c) repeated until convergence is attained.
e. The final step is the calculation of the solubility products of a series of minerals and a comparison of them with the appropriate ion activity products (IAP).

The log ratio of the IAP/solubility product (Sp) is known as the saturation index. If this ratio equals 0, then the solution is in equilibrium with the mineral. If IAP $<$ Sp, then the solution is undersaturated with respect to that mineral. If IAP $>$ Sp, then the solution is oversaturated with respect to that mineral.

RUNNING WATEQ4F

To run, enter WQ4FINPT and press ENTER.
The program will give you the option:

Table 9.4k. Sample F Reliability Checks. F. Table 8 Number 5—Gypsum Spring 5 gpm

Reliability check	Attention value	Analysis value	Conclusion	
$\frac{(C - A)}{(C + A)}$ %	>5%	1.0%		
Hardness $- \frac{\text{Entered} - \text{Calc}}{\text{Entered}}$	>5%	***		
$\frac{\text{Entered TDS} - \text{TDSC}}{\text{Entered TDS}}$	>5%	0%		
$\frac{\text{Entered TDS} - \text{TDS 180}}{\text{Entered TDS 180}}$	>5%	3%		
$\frac{\text{Entered TDS}}{\text{Conductivity}}$	<0.5 and >0.75	0.99	*High	
$\frac{\text{TDS calc}}{\text{Conductivity}}$	<0.5 and >0.75	0.99	*High	
$\frac{\text{Conductivity}}{\text{sum MEQ cations}}$	<90 and >110	69	*Low	
Carbonate	0.2 (calc)	0.0		
$\frac{K}{K + Na}$	>0.2	0.37	High	
$\frac{Mg}{Mg + Ca}$	>0.4	0.10		
$\frac{Ca}{Ca + SO_4}$	<0.5	0.49		
$\frac{Na}{Na + Cl}$	<0.5	0.52		
Conclusion	Analysis acceptable		Yes	No

*Conductivity possibly low.

a. of running an existing WATEQ4F.DAT file.
b. entering data to create a new WATEQ4F.DAT file, or
c. converting a WATEVAL.H20 to a WATEQ4F.DAT file.

Examining output files — The WATEQ4F program was written for a 132-character-wide printer.

a. If you are using a dot matrix printer it may be set to print in compressed mode. For a hard copy set line printer to 132 characters and enter PRINT WATEQ4F.PRN and press ENTER. A listing of the various WATEQ4F files is given in Table 9.5.
b. If you are using a laser printer, the file to be printed is read into a word-processing program and reformatted to fit the page. This is most readily done by changing font size.
c. If you just wish to look at the data the simplest option is to use the DOS Edit program. To accomplish this type EDIT WATEQ4F.PRN and use page up, etc., as shown by the program.

BRIEF DESCRIPTION OF FILES AND OPERATION

An outline flow chart of the various files is shown in Figure 9.3.

Input files

WQ4FINPT.EXE is an interactive compiled QuickBASIC program. It is a preprocessor for the compiled WATEQ4F.EXE FORTRAN program. It is necessary because of the complex

Table 9.4l. Sample F Source Rock Evaluation. F. Table 8 Number 5—Gypsum Spring 5 gpm

Parameter	Value	Conclusion
SiO_2 (mmol/l)	0.48	
$\frac{HCO_3}{SiO_2}$	4.86	Silicate weathering
$\frac{SiO_2}{Na + K - Cl}$	0.97	Cation exchange
$\frac{Na + K - Cl}{Na + K - Cl + Ca}$	0.03	Plagioclase weathering unlikely
$\frac{Na}{Na + Cl}$	0.52	Albite or ion exchange
$\frac{Mg}{Mg + Ca}$	0.10	Granitic weathering
$\frac{Ca}{Ca + SO_4}$	0.49	Gypsum dissolution
$\frac{Ca + Mg}{SO_4}$	1.1	Dedolomitization likely
TDS calculated (mg/l)	2479	Carbonate weathering, brine, evaporites, or seawater
$\frac{Cl}{\text{sum anions}}$	0.02	Silicate or carbonate weathering
$\frac{HCO_3}{\text{sum anions}}$	0.07	Seawater, brine, or evaporites
Langelier index		
Conclusion	Aquifer mineralogy	Gypsum with minor dolomite
Conclusion	Reactions	Some ion exchange and possibly dedolomitization

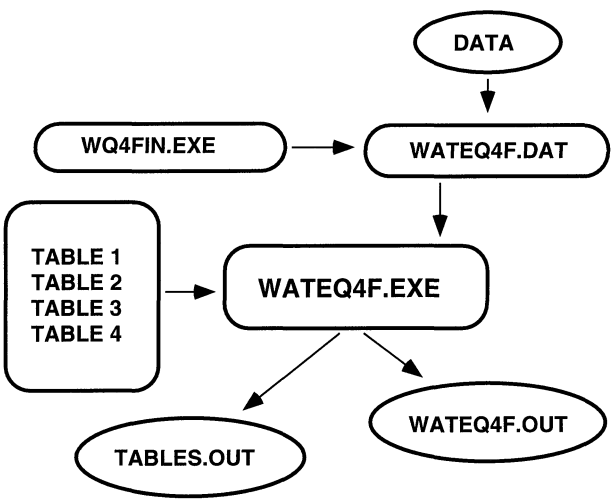


Figure 9.3. Outline of WATEQ4F program and files.

formating common to most FORTRAN programs. The data are saved to a file called WATEQ4F.DAT. This file must be renamed if you wish to keep it, as it will be overwritten when the program is run again.

WQ4FINPT.EXE accepts your analytical data and prepares a file WATEQ4F.DAT, which is read by the main WATEQ4F.EXE program. WATEQ4F.EXE also reads in the thermody-

Table 9.4m. Sample G Reliability Checks G. Seawater

Reliability check	Attention value	Analysis value	Conclusion
$\frac{(C - A)}{(C + A)}$ %	>5%	1.0%	
Hardness $-\frac{\text{Entered} - \text{Calc}}{\text{Entered}}$	>5%	***	
$\frac{\text{Entered TDS} - \text{TDSC}}{\text{Entered TDS}}$	>5%	−3%	
$\frac{\text{Entered TDS} - \text{TDS 180}}{\text{Entered TDS 180}}$	>5%	−3%	
$\frac{\text{Entered TDS}}{\text{Conductivity}}$	<0.5 and >0.75	***	
$\frac{\text{TDS calc}}{\text{Conductivity}}$	<0.5 and >0.75	***	
$\frac{\text{Conductivity}}{\text{sum MEQ cations}}$	<90 and >110	***	
Carbonate	0.2 (calc)	0.0	
$\frac{K}{K + Na}$	>0.2	***	
$\frac{Mg}{Mg + Ca}$	>0.4	0.84	High
$\frac{Ca}{Ca + SO_4}$	<0.5	0.27	Low
$\frac{Na}{Na + Cl}$	<0.5	0.47	Low
Conclusion	Analysis acceptable		Yes No

namic data files TABLE1, TABLE2, TABLE3, and TABLE4. Another option allows the input of data from a WATEVAL *.H2O file.

The parameters that may be input are conductivity, total dissolved solids (TDS), temperature, pH, Eh, dissolved organic carbon (DOC), dissolved oxygen (DO), Ca, Mg, Na, K, Cl, SO_4, HCO_3, Fe, H_2S, CO_3, SiO_2, NH_4, B total, PO_4, Al, F, and NO_3. In addition, the following trace elements or ions may be entered: Fe^{2+}, Fe^{3+}, Cs, Li, Sr, Ba, Rb, I, Br, Mn, Cu, Zn, Cd, Pb, NO_2^-, Ni, Ag, As total, As^{3+}, As^{5+}, Fulvate, and Humate.

Several samples may be entered at a time; however, with a floppy disk system the output file may be too large to save.

The main program WATEQ4F.EXE is compiled for use with a math coprocessor.

WATEQ4F OUTPUT FILES

Two files are output from WATEQ4F.EXE. These are

1. TABLES.OUT - Listing of thermodynamic data used with the analyses.
2. WATEQ4F.OUT - Data output file - includes FORTRAN page prompts.

The WQ4FINPT program changes printer to compressed-print mode, which is 132 characters wide (IBM dot matrix printers only) and changes the printer back to 80-character width (IBM dot matrix printers only). The preprocessor WQ4FINPT will call the main program WATEQ4F. If a WATEVAL *.H20 is used for input the output file is *.WQ4. It must be

Table 9.4n. Sample G Source-Rock Evaluation. G. Seawater

Parameter	Value	Conclusion
SiO_2 (mmol/l)	0.05	
$\frac{HCO_3}{SiO_2}$	45.96	Carbonate weathering
$\frac{SiO_2}{Na + K - Cl}$	Cl > (Na + K)	
$\frac{Na + K - Cl}{Na + K - Cl + Ca}$	Cl > (Na + K)	
$\frac{Na}{Na + Cl}$	0.47	Reverse softening, seawater
$\frac{Mg}{Mg + Ca}$	0.84	Dolomite dissolution and calcite precipitation or seawater
$\frac{Ca}{Ca + SO_4}$	0.27	Ca removal, ion exchange, or calcite precipitation
$\frac{Ca + Mg}{SO_4}$	2.3	Dedolomitization unlikely
TDS calculated (mg/l)	35,490	Carbonate weathering, brine, evaporites, or seawater
$\frac{Cl}{\text{sum anions}}$	0.90	Seawater, brine, or evaporites possible
$\frac{HCO_3}{\text{sum anions}}$	0.00	Seawater, brine, or evaporites
Langelier index	−0.67	Undersaturated with respect to calcite
Conclusion	Aquifer mineralogy	Typical seawater parameters
Conclusion	Reactions	Calcite precipitation

noted that each time the program is run both the input and output data files are overwritten. A step by step discussion of the output is shown in Tables 9.6a to 9.6h.

ECOPLUS

ECOPLUS is an ecosystem distribution program written) by A. W. Hounslow and Kelly D. Goff. ECOPLUS consists of four interrelated and integrated programs:

1. Obtains distribution parameters from a variety of input data using a series of estimation techniques.
2. Allows the calculation of half-life estimates from specific laboratory or field data.
3. Calculates solute concentrations at a specific point after a specified period of time in a groundwater system.
4. Calculates the distribution of a solute in a specified ecosystem using the technique of McCall et al. (1983). The compartments of the ecosystem used are shown in Figure 9.4 (see page 346).

Running ECOPLUS — To run ECOPLUS type ECOPLUS and press ENTER. At the next prompt press ENTER or "E" for EGA graphics or "H" for no graphics. To examine the behavior of a particular chemical in the environment enter the parameters listed under 'Parameter Estimation' below using the new data option from the main menu. After editing and evaluation the distribution parameters that have been calculated may be stored in a disk file. They are also available to all parts of the program as one moves from one part to

Table 9.4o. Sample H Reliability Checks. H. Table 12 Number 2—Oil Field Brine 4952.

Reliablity check	Attention value	Analysis value	Conclusion
$\frac{(C - A)}{(C + A)}$ %	>5%	−0.3%	
Hardness $-\frac{\text{Entered} - \text{Calc}}{\text{Entered}}$	>5%	***	
$\frac{\text{Entered TDS} - \text{TDSC}}{\text{Entered TDS}}$	>5%	0%	
$\frac{\text{Entered TDS} - \text{TDS 180}}{\text{Entered TDS 180}}$	>5%	2%	
$\frac{\text{Entered TDS}}{\text{Conductivity}}$	<0.5 and >0.75	0.66	
$\frac{\text{TDS calc}}{\text{Conductivity}}$	<0.5 and >0.75	0.66	
$\frac{\text{Conductivity}}{\text{sum MEQ cations}}$	<90 and >110	90	
Carbonate	0.2 (calc)	0.0	
$\frac{K}{K + Na}$	>0.2	0.01	
$\frac{Mg}{Mg + Ca}$	>0.4	0.34	
$\frac{Ca}{Ca + SO_4}$	<0.5	1.00	
$\frac{Na}{Na + Cl}$	<0.5	0.48	Typical of oil-field brine
Conclusion	Analysis acceptable		Yes No

another. The program outline is shown in Figure 9.5 (see page 346). The main menu options are shown in Table 9.7. If the chemical is in the unevaluated database provided (CHEM.ECO) the parameters may be read in directly.

PARAMETER ESTIMATION

The information that may be entered for the parameter estimation routine includes:

a. Solute name.
b. Molecular weight (or molecular formula).
c. Melting point (°C).
d. Boiling point (°C).
e. Vapor pressure (maximum of five values). Units may be:
    i. atmos
    ii. mm Hg (Torr)
    iii. kilo Pascals
    iv. bars
    v. psi or psia
f. Solubility (maximum of five values). Units may be:
    i. mg/l or ppm
    ii. mmol/l or mol/m^3
    iii. mmol/l
    iv. mole fraction
g. K_{ow} (maximum of five values). Units may be:
    i. K_{ow}
    ii. log K_{ow}

Table 9.4p. Sample H Source-Rock Evaluation. H. Table 12 Number 2—Oil Field Brine 4952.

Parameter	Value	Conclusion
SiO_2 (mmol/l)	0.79	Volcanic glass or hydrothermal water possible
$\frac{HCO_3}{SiO_2}$	11.21	Carbonate weathering
$\frac{SiO_2}{Na + K - Cl}$	Cl > (Na + K)	
$\frac{Na + K - Cl}{Na + K - Cl + Ca}$	Cl > (Na + K)	
$\frac{Na}{Na + Cl}$	0.48	Reverse softening, seawater
$\frac{Mg}{Mg + Ca}$	0.34	Limestone-dolomite weathering
$\frac{Ca}{Ca + SO_4}$	1.00	Ca source other than gypsum, carbonates, or silicates
$\frac{Ca + Mg}{SO_4}$	842.7	Dedolomitization unlikely
TDS calculated (mg/l)	17,015	Carbonate weathering, brine, evaporites, or seawater
$\frac{Cl}{\text{sum anions}}$	0.97	Seawater, brine, or evaporites possible
$\frac{HCO_3}{\text{sum anions}}$	0.03	Seawater, brine, or evaporites
Langelier index	1.17	Oversaturated with respect to calcite
Conclusion	Aquifer mineralogy	Typical oil-field brine analysis
Conclusion	Reactions	

Table 9.5. WATEQ4F Files

WATEQ4F files	Description
WQ4FIN.EXE	QuickBASIC input program
TABLE1	Thermodynamic database
TABLE2	Thermodynamic database
TABLE3	Thermodynamic database
TABLE4	Thermodynamic database
WATEQ4F.EXE	FORTRAN water equilibrium program
WATEQ4F.DAT	Input file from WQ4FIN.EXE
WATEQ4F.OUT	Output file from WATEQ4F.EXE
WATEQ4F.PRN	Data output file includes FORTRAN page prompts
TABLES.OUT	Listing of thermodynamic data used with the analyses

h. H or KH (Henry's law constant) (maximum of five values). Units may be:
   i. atmos m^3/mole
   ii. unitless
   iii. atmos-m^3 air/m^3 water
   iv. 1/KH unitless

i. K_{oc} or K_{som} (maximum of five values). Units may be:
   i. K_{oc}
   ii. log K_{oc}
   iii. K_{som}
   iv. log K_{som}

Table 9.6a. WATEQ4F Output File Explained

		03T06 Limestone Spring 71000 gpd	
			Comments
TEMP	=	23.900000	Temperature °C
PH	=	7.700000	pH
EHM	=	9.999000	True Eh of the solution Not used if value >9.0
DOC	=	000000	Dissolved organic carbon
DOX	=	.000000	Dissolved oxygen content mg/l
CORALK	=	0	Carbon index = 0 alkalinity not corrected for Si, B, etc. = 1 above corrections made = 2 total carbon and not alkalinity entered
FLG	=	MG/L	Units index mmol/l, meq/l, mg/l, ppm, molality
DENS	=	1.000000	Density g/cc
PRNT	=	0	Output options set in program
PUNCH	=	1	Not used
EHOPT	=	0	Use Fe^{2+}/Fe^{3+} if there is no measured Eh
EMPOX	=	0	Dissolved oxygen treatment
TDS	=	.000000	Analytical TDS—ppm
COND	=	287.000000	Specific conductance—$\mu s\ cm^{-2}$ at 25°C
SIGMDO	=	.000000	Standard deviation dissolved oxygen —not used
SIGMEH	=	.000000	Standard deviation Eh—not used
SIGMPH	=	.000000	Standard deviation pH—not used

Table 9.6b. WATEQ4F Output File Explained

Species	Index no	Input concentration
Ca	0	48.01000000
Mg	1	5.80000000
Na	2	4.00000000
K	3	.70000000
Cl	4	4.80000000
SO_4	5	6.40000000
HCO_3	6	168.03420000
Fe total	16	.00000000
H_2Saq	13	.00000000
CO_3	17	.00000000
SiO_2 tot	34	8.90180000
NH_4	38	.00000000
B tot	86	.00000000
PO_4	44	.00000000
Al	50	.00000000
F	61	.00000000
NO_3	84	.00000000

Table 9.6c. WATEQ4F Output File Explained

		Results of iterations—not used		
ITER	S1-AnalCO3	S2-AnalSO4	S3-AnalF	S4-AnalPO4
1	5.563277E−05	1.036079E−05	0.000000E+00	0.000000E+00
2	3.315557E−07	7.858685E−08	0.000000E+00	0.000000E+00
3	−5.608808E−09	−1.597885E−09	0.000000E+00	0.000000E+00
ITER	S5-AnalCL	S6-AnalH2S	S7-AnalFULV	S8-AnalHUM
1	0.000000E+00	0.000000E+00	0.000000E+00	0.000000E+00
2	0.000000E+00	0.000000E+00	0.000000E+00	0.000000E+00
3	0.000000E+00	0.000000E+00	0.000000E+00	0.000000E+00

Table 9.6d. WATEQ4F Output File Explained

03T06 LIMESTONE SPRING 71000 gpd Date = 1/24/94 13:36

DOX =	.0000	
DOC =	.0	
INPUT TDS =	.0	
Anal Cond =	287.0	
Calc Cond =	292.1	conductivity calculated by program
Anal EPMCAT =	3.0655	
Anal EPMAN =	3.0237	
Percent difference in input cation/anion balance =	1.3723	
Calc EPMCAT =	2.9940	Equivalents/million calculated by program after speciation calculations.
Calc EPMAN =	2.9518	
Percent difference in calc cation/anion balance =	1.4203	
Total Ionic Strength (T.I.S.) from input data =	.00455	
Effective Ionic Strength (E.I.S.) from speciation =	.00442	

Eh = 9.9 or pe = 100 imply no calculations were made.

	Input	Sigma	Fe3/Fe2	Sigma	Sato H2O2/O2	Sigma	NO3/NO2	Sigma
Eh	9.999	.000	9.900	.000	9.900	.000	.000	.000
pE	100.000	.000	100.000	.000	100.000	.000	100.000	.000

	NO3/NH4	Sigma	Calc H2O2/O2	Sigma	SO4/S=	Sigma	As5/As3	Sigma
Eh	9.900	.000	9.900	.000	9.900	.000	9.900	.000
pE	100.000	.000	100.000	.000	100.000	.000	100.000	.000

Entered parameters

T	pH	TDS ppm
23.90	7.700	246.6

Various parameters calculated by the program

Effective Ionic Str	pO2 Atm	pCO Atm	pCH4 Atm	CO2 Tot	Uncom CO2 ppm	Uncom CO2	Ncrb Alk*	aH2O
.00442	0.00E+00	3.23E−03	0.00E+00	.00285	2.70E−03	1.19E+02	1.38E−06	.9999

*Noncarbonate alkalinity.

j. Bioconcentration factor (BCF) (maximum of five values). Units may be:
   i. BCF
   ii. log BCF

Details of the conversion equations are given in Table 9.8.

ECOPLUS PARAMETER EVALUATION

A literature search for partition parameters usually leads to the acquisition of a set of parameters. These are frequently expressed in different units. After conversion to a chosen unit they often have widely variable values. The derivation of an internally consistent set of partition parameters from these data is accomplished in several stages.

1. Convert each parameter to the same units so that direct comparisons may be made. The units used in ECOPLUS are

Table 9.6e. WATEQ4F Output File Explained

03T06 LIMESTONE SPRING 71000 gpd

Speciation Table

1	Species		Anal ppm	Calc ppm	Anal Molal	Calc Molal	Activity	Act Coeff	−Log Act
0	Ca	2	48.010	46.195	1.198E−03	1.153E−03	8.722E−04	.7565	3.059
28	CaOH	1		.000616		1.080E−08	1.005E−08	0.9311	7.998
31	CaSO4aq	0		1.041		7.648E−06	7.656E−06	1.0010	5.116
81	CaHSO4	1		.000000		9.201E−13	8.567E−13	.9311	12.067
29	CaHCO3	1		2.972		2.941E−05	2.738E−05	.9311	4.563
30	CaCO3aq	0		.823		8.222E−06	8.230E−06	1.0010	5.085
1	Mg	2	5.800	5.612	2.386E−04	2.309E−04	1.752E−04	.7589	3.756
18	MgOH	1		.000568		1.375E−08	1.281E−08	.9311	7.893
22	MgSO4aq	0		.161		1.342E−06	1.343E−06	1.0010	5.872
21	MgHCO3	1		.464		5.443E−06	5.068E−06	.9311	5.295
20	MgCO3aq	0		.080		9.454E−07	9.463E−07	1.0010	6.024
2	Na	1	4.000	3.993	1.740E−04	1.738E−04	1.619E−04	.9316	3.791
43	NaSO4	−1		.004479		3.763E−08	3.504E−08	.9311	7.455
42	NaHCO3aq	0		.019		2.277E−07	2.279E−07	1.0010	6.642
41	NaCO3	−1		.001456		1.754E−08	1.633E−08	.9311	7.787
3	K	1	.700	.700	1.791E−05	1.790E−05	1.665E−05	.9304	4.778
45	KSO4	−1		.000725		5.363E−09	4.993E−09	.9311	8.302
63	H	1		.000021		2.129E−08	1.995E−08	.9370	7.700
26	CH	−1		.008441		4.965E−07	4.622E−07	.9311	6.335
17	CO3	−2		.456		7.604E−06	5.756E−06	.7569	5.240
6	HCO3	−1	168.034	163.760	2.755E−03	2.685E−03	2.504E−03	.9327	2.601
85	H2CO3aq	0		7.054		1.138E−04	1.139E−04	1.0011	3.944
5	SO4	−2	6.400	5.532	6.664E−05	5.761E−05	4.349E−05	.7550	4.362
62	HSO4	−1		.000009		8.775E−11	8.170E−11	.9311	10.088
4	Cl	−1	4.800	4.800	1.354E−04	1.354E−04	1.260E−04	.9304	3.900
34	SiO2 tot	0	8.902		1.482E−04				
23	H4SiO4aq	0		14.155		1.473E−04	1.475E−04	1.0010	3.831
24	H3SiO4	−1		.084		8.843E−07	8.233E−07	.9311	6.084
25	H2SiO4	−2		.000009		9.890E−11	7.432E−11	.7515	10.129

03T06 LIMESTONE SPRING 71000 gpd
Mole ratios from analytical molality-log activity ratios

H1 = $[H^+]$		H2 = $[H^+]^2$	H3 = $[H^+]^3$		K2 = $[K^+]^2$
Cl/Ca	=	1.1303E−01	Log (Ca/H2)	=	12.3406
Cl/Mg	=	5.6752E−01	Log (Mg/H2)	=	11.6436
Cl/Na	=	7.7815E−01	Log (Na/H1)	=	3.9092
Cl/K	=	7.5629E+00	Log (K/H1)	=	2.9215
Cl/Al	=	0.0000E+00	Log (Al/H3)	=	.0000
Cl/Fe	=	0.0000E+00	Log (Fe/H2)	=	.0000
Cl/SO4	=	2.0322E+00	Log (Ca/Mg)	=	.6970
CL/HCO3	=	4.9164E−02	Log (Na/K)	=	.9876
Ca/Mg	=	5.0211E+00	Log (Ca/K2)	=	6.4975
Na/K	=	9.7191E+00	Log (Diss Fe/H2)	=	15.4000

a.	Vapor pressure	mm Hg
b.	Solubility	mg/l
c.	K_{ow}	log K_{ow}
d.	K_{oc}	log K_{oc}
e.	BCF	log BCF
f.	Henry's law constant	Dimensionless

The conversion factors used in ECOPLUS are listed in Table 9.8.

2. Compare each value with others in the set and note outliers.
3. Use regression equations to calculate parameters from other parameters. Typically, one can calculate:

Table 9.6f. WATEQ4F Output File Explained

Notes on table containing ion activity products, solubility products, and saturation indices

(1) Index number of mineral species

(2) Name of mineral species

(3) $\text{Log} \dfrac{\text{activity product}}{\text{solubility product}} = \text{Saturation Index}$

(4) Standard deviation of analytical data—not used.

(5) Standard deviation of thermodynamic data.

(6) $\text{Log} \dfrac{\text{activity product}}{\text{maximum solubility product}}$

(7) $\text{Log} \dfrac{\text{activity product}}{\text{minimum solubility product}}$

(8) Log (activity product)

(9) Log (average solubility product)

(10) Log (minimum solubility product)

(11) Log (maximum solubility product)

Table 9.6g. WATEQ4F Output File Explained

03T06 Limestone Spring 71000 gpd

Ion activity products, solubility products and saturation indices

(1)	(2) Phase	(3) Log AP/KT	(4) Sigma (A)	(5) Sigma (T)	(6) Log AP /MinKT	(7) Log AP /MaxKT	(8) Log AP	(9 Log KT	(10) Log MinKT	(11) Log MaxKT
17	Anhydrite	−2.794					−7.421	−4.627		
21	Aragonite	.030		.020			−8.299	−8.329		
150	Artinite	−5.637					4.041	9.678		
19	Brucite	−5.220					−16.427	−11.206		
12	Calcite	.174		.020	.254		−8.299	−8.474	−8.553	
97	Chalcedony	−.296					−3.831	−3.536		
20	Chrysotile	−5.068					−56.943	−51.875		
29	Clinoenstite	−3.582			−3.216	−3.876	−20.258	−16.676	−17.042	−16.382
99	Cristobalite	−.229					−3.831	−3.602		
28	Diopside	−3.656					−39.819	−36.163		
11	Dolomite	−.318					−17.296	−16.977		
340	Epsomite	−5.971					−8.118	−2.148		
27	Forsterite	−8.977					−36.685	−27.707		
18	Gypsum	−2.820					−7.421	−4.601		
64	Halite	−9.270					−7.690	1.580		
117	Huntite	−5.390					−35.288	−29.898		
38	Hydrmag-nesit*	−15.720					−52.412	−36.693		
98	Magadiite	−9.598					−23.898	−14.300		
10	Magnesite	−.984			−.734	−1.234	−8.996	−8.012	−8.262	−7.762
66	Mirabilite	−10.778					−11.944	−1.166		
58	Nahcolite	−5.834					−6.392	−.558		
60	Natron	−11.468					−12.822	−1.354		
149	Nesquehonite	−3.391			−3.879	−4.466	−8.996	−5.605	−5.117	−4.530
101	Quartz	.192					−3.831	−4.023		
36	Sepiolite(c)	−3.644					11.793	15.437		
153	Sepiolite(a)	−6.867					11.793	18.660		
100	SiO2 (a,L)	−.801					−3.831	−3.030		
395	SiO2 (a,M)	−1.111					−3.831	−2.721		
37	Talc	−1.919		2.000	249	−3.667	19.605	21.525	19.357	23.273
65	Thenardite	−11.766					−11.943	−.177		
61	Thermonatr*	−12.954					−12.822	.133		
31	Tremolite	−4.572					−144.243	−139.671		
59	Trona	−18.468					−19.214	−.746		

* Some names are truncated in the program printout.

Table 9.6h. WATEQ4F Output File Explained

Interpretation of Speciation Table

Consider the calcium species from the table above. The calculated ppm is the concentration of each species in ppm. The amount of calcium in each species equals:

$$\frac{\text{calculated ppm}}{\text{molecular weight of species}} * \text{atomic weight of calcium}$$

The values then total the entered analytical ppm of calcium. Values are shown in the table below.

		Anal ppm	Calc ppm	Molecular Wt of species	Equivalent Ca
Ca	2	48.010	46.195	40.08	46.195
CaOH	1		.000616	57.09	0.0004
CaSO4 aq	0		1.041	136.14	0.306
CaHSO4	1		.000000	137.15	0.000
CaHCO3	1		2.972	101.10	1.178
CaCO3 aq	0		.823	100.09	0.330
Total		48.010			48.009

Interpretation of Saturation Index Table

	Phase	Log AP/KT	Sigma (A)	Sigma (T)	Log AP /MinKT	Log AP /MaxKT	Log AP	Log KT	Log MinKT	Log MaxKT
17	Anhydrite	−2.794					−7.421	−4.627		
21	Aragonite	**.030**		.020			−8.299	−8.329		
12	Calcite	**.174**		.020	.254		−8.299	−8.474	−8.553	
97	Chalcedony	−.296					−3.831	−3.536		
11	Dolomite	−.318					−17.296	−16.977		
18	Gypsum	−2.820					−7.421	−4.601		
64	Halite	−9.270					−7.690	1.580		
101	Quartz	**.192**					**−3.831**	**−4.023**		

Note: The highlighted values of the saturation index, log AP/KT, that are positive are those where the solution is oversaturated with respect to the designated phase. This includes aragonite, calcite, and quartz. In the case of calcite the saturation index may also be considered as the difference in pH between the solution and the pH of a solution with which the calcite is in equilibrium, that is, where the saturation index is zero.

a.	Vapor pressure	From boiling point, and melting point
b.	Solubility	From K_{ow}
c.	BCF	From K_{ow}
d.	K_{ow}	From K_{oc}
e.	K_{oc}	From solubility
f.	Henry's law constant	From vapor pressure and solubility

A listing of those used in ECOPLUS is given in Table 9.9.

4. The evaluation procedure suggested is to examine first the parameter that is dependent on the maximum number of other parameters. The order usually followed is
   a. Examine the entered Henry's law values and those calculated from all combinations of solubility and vapor pressure. Identify outliers and possibly delete them.
   b. Similarly, the entered values of K_{oc} and those derived from three different solubility equations and six different K_{ow} equations are compared and again outliers noted and possibly deleted. The range of values for each set of regression equations also gives an indication of the extent of the possible uncertainty in the values.
   c. Less useful minor comparisons may be made between:
      (i) reported and estimated vapor pressure
      (ii) reported solubility and solubility estimated from K_{ow}. This estimated value is usually significantly higher than the reported solubility.
      (iii) reported BCF and BCF estimated from K_{ow}

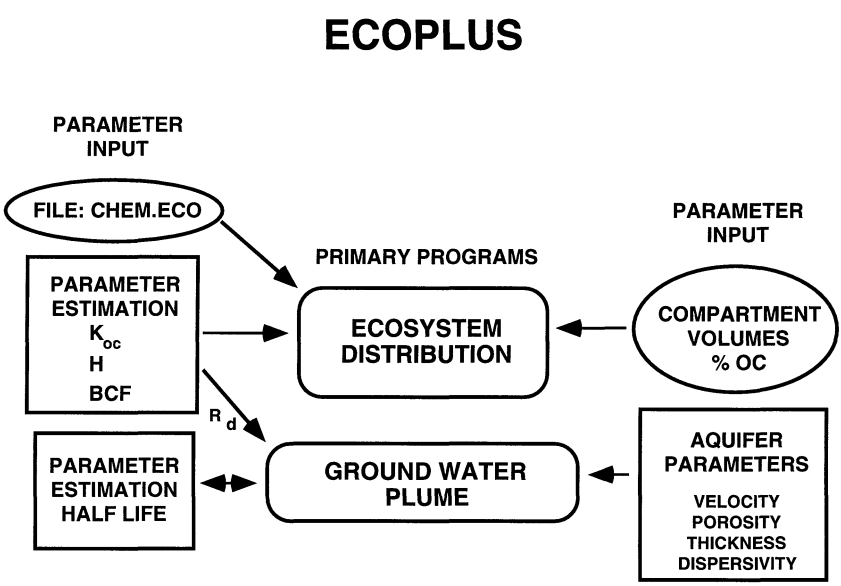


Figure 9.4. Environmental compartments available in the ECOPLUS program.

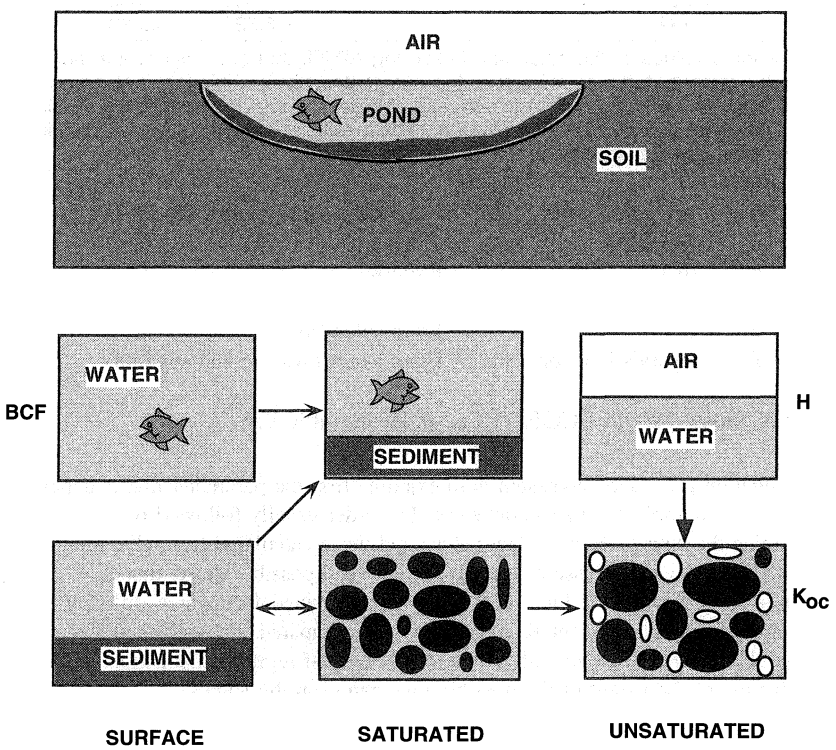


Figure 9.5. Outline of ECOPLUS computer program.

Table 9.7. ECOPLUS Main Menu Options

-- MAIN MENU --

1. NEW DATA AND RETARDATION
   This allows:
   a. the entry of new data for parameter estimation
      (this is the main option—see below for details),
   b. the direct input of K_{oc}, BCF, H, and half-life
      (calculation of log K_{oc} from connectivity can be done here—Sabijic, 1987),
      and the calculation of the retardation coefficient
      (used in groundwater calculations below, the R_d value is transferred to that part of the program), and
   c. editing previous multiple-parameter entries.

2. CHEM.ECO FILE ENTRY
   This is a file containing about 60 organic chemicals with K_{oc}, BCF, and H data. The data set was derived primarily from Mercer et al., 1990 (EPA 600/8–90/003).

3. HALF-LIFE CALCULATION
   This routine allows the direct entry of half-life or rate constant as well as enables the estimation of half-life from BOD, surface water data, or groundwater data. The possible options are
   a. direct input of half-life—units may be years, days, hours, minutes, seconds,
   b. direct input of rate constant—per day,
   c. estimate half-life from BOD—ThOD may be entered or calculated,
   d. estimate half-life from surface water data,
   e. estimate from groundwater calculation, or
   f. calculate concentration using half-life.

4. GROUNDWATER CALCULATION
   This routine calculates the solute concentration at point (x,y) after time t days. It is essentially a one-point mass transport model.
   The aquifer data required includes:
   a. groundwater velocity (ft/day),
   b. longitudinal dispersivity (ft)—usually 70
   c. transverse dispersivity (ft)—usually 14 or 1/5 of b.
   d. effective porosity (<1)—usually about 0.2, and
   e. aquifer thickness (ft).
   The retardation and half-life values are calculated in the program.
   The source data include:
   a. number of sources, and
   b. loading, either as
   mass-injection rate (lb/day) or
   recharge rate (gal/day) and concentration of solute (mg/l).
   The x,y and time parameters are entered as
   a. distance from source downgradient (ft),
   b. distance from source across gradient (ft), and
   c. time for plume migration (days) or
      the entry of two dates from which the program calculates the days.

5. ECO-SYSTEM EXAMINATION
   In order to calculate the distribution of a solute in a soil-water-air-fish ecosystem the K_{oc}, BCF, and H must be known. These may be calculated or entered in other parts of the program. They are always displayed in the upper part of each screen. The ecosystem as defined by McCall et al. (1983) is used as a default, although it may be changed to suit the user. The compartments are shown in Figure 9.5.

6. ADD TO CHEM.ECO FILE
   After entering and evaluating parameter data the final average values of K_{oc}, BCF, H, and $t_{1/2}$ may be saved to this file.

7. EXIT PROGRAM

-- END OF MAIN MENU --

Table 9.8. Parameter Conversions

	Conversion Factors
Pressure	
1 mm Hg	= 1 Torr (vacuum technology)
	= atmos. * 760
	= kPa (kilo Pascals) * 7.501
	= psia * 51.72
	= bars * 750.1
Temperature	
°C	$= \frac{(F - 32) * 5}{9}$
K	= °C + 273.15
log x	$= \frac{\ln x}{\ln 10}$
Henry's Law Constant	
H (dimensionless)	$= \frac{H'}{R * T}$ with R in similar units to H′
R	= 0.082054 liter-atm/deg/mol
R	= 8.20562E−05 atm-m^3/deg/mol
K_{oc}	= Ksom * 1.724
Solubility	
mg/l	= ppm for dilute solutions
micromoles/l	$= \text{mg/l} * \frac{1000}{\text{molecular weight}}$
mole/l	= micromoles/l/10^6
mole fraction	$= \frac{\text{moles/l}}{\text{(mole/l)} + 55.51}$
mole/$meter^3$	= mmol/l
D_s	= (1 − porosity) * 2.65 (S.G. quartz)
K_d	$= K_{oc} * \frac{\%\ \text{organic carbon}}{100}$
R_d	$= 1 + K_d * \frac{\text{bulk density}}{\text{porosity}}$

5. The final selected value of each parameter is a weighted average of those reported values and estimates remaining. The weighting factor is an arbitrary estimate of the reliability of the estimation procedure. Reported values are given the highest weight. As an example, reported K_{oc} is given a weighting of 5, K_{oc} derived from K_{ow} a weighting of 4, and K_{oc} derived from solubility a weighting of 1. The weighting factor may be changed by the user.

EXAMPLE OF THE USE OF ECOPLUS

Question: for *methylchloroform* (1,1,1-TCA or 1,1,1-trichloroethane) obtain the best estimates for log K_{oc}, log BCF, and K_H. Give your reasons for this selection. Discuss the distribution of methylchloroform in the ecosystem. Use McCall's ecosystem parameters. How would the compound distribute itself in an aquifer? An intensive literature search turned up the following parameters. Enter these into the ECOPLUS program and discuss the results. Note only one answer is possible for the molecular weight! What is the correct molecular weight? These data are given in Table 9.10.

Table 9.9. Parameter Estimation Equations

	Estimated boiling point—T_b		
1.	$\log T_b = 3 - \frac{4}{5} * \sqrt{M}$	T_b = boiling point in K, M = molecular weight, for M > 200	Banks, 1939
	Estimated melting point—T_m		
2.	$T_m = 0.5839\ T_b$	T_m = melting point in K	Gold and Ogle, 1969
	Vapor pressure—P		
3.	$\ln P = -(4.4 + \ln T_b)^* \left[1.803 * \left(\frac{T_b}{T} - 1\right) - 0.803 * \ln \frac{T_b}{T}\right] - 6.8 * \left(\frac{T_m}{T} - 1\right)$	P = vapor pressure in atmospheres, T_b = boiling point (K), T_m = melting point (K), If $T_m > T$ ignore last term	Mackay et al., 1982b
	Solubility		
4.	$\log S = -\log K_{ow} + 0.76 - 0.01 * T_m$	S = solubility in mole/liter, T_m = melting point in °C, for liquids T_m = 25°C	Yalkowsky et al., 1983
	Henry's law constant (dimensionless)		
5.	$H = 16.04 * Po * M/T * S$	Po = vapor pressure of pure compound (mm Hg), S = solubility in mg/l (maximum solubility 1 mol/l), M = molecular weight, T = temperature K, Not used for miscible solutes.	Dilling, 1977
	Henry's law constant (atm m^3/mol)		
6.	$H = 10.6 * \left[1 - \frac{T_b}{T}\right] + 6.8 * \left[1 - \frac{T_m}{T}\right] + 0.0318 * (T_b - 273) - 5.15$	T_b = boiling point (K), T_m = melting point (K) solids	Mackay et al., 1982a
	K_{oc}		
7.	$\log K_{oc} = -0.55 * \log S + 3.64$	S in mg/l	Kenaga and Goring, 1980
8.	$\log K_{oc} = -0.54 * \log S + 0.44$	S in mole fraction	Karickhoff et al., 1979
9.	$\log K_{oc} = -0.557 * \log S + 4.277$	S in micromoles/l	Chiou et al., 1979
10.	$\log K_{oc} = 0.544 * \log K_{ow} + 1.377$		Kenaga and Goring, 1980
11.	$\log K_{oc} = 0.937 * \log K_{ow} - 0.006$		Brown and Flagg, 1981
12.	$\log K_{oc} = 1.00 * \log K_{ow} - 0.21$		Karickhoff et al., 1979
13.	$\log K_{oc} = 0.94 * \log K_{ow} + 0.02$		Brown, 1979
14.	$\log K_{oc} = 1.029 * \log K_{ow} - 0.18$		Rao and Davidson, 1980
15.	$\log K_{oc} = 0.524 * \log K_{ow} + 0.855$		Briggs, 1973
	Bioconcentration factor		
16.	$\ln BCF = 0.935 * \ln K_{ow} - 3.443$		Kenaga and Goring, 1980
17.	$\log BCF = 0.935 * \log K_{ow} - 1.495$		

Table 9.10. Example Illustrating the Use of ECOPLUS Program

	Methylchloroform. (1.1.1-trichloroethane) $CH_3—CCl_3$				
	1	2	3	4	5
Molecular weight	**133.4***	123.4			
Melting point	−32.5°C				
Boiling point	74.1°C				
Vapor pressure	0.163 atmos	100 mm Hg	0.13 atmos	2 psi	
Solubility	1334 mg/l	950 ppm	7.5 mmol/l		
Octanol/water partition coefficient	K_{ow} = 300	log K_{ow} = 2.48			
Distribution coefficient	Log K_{oc} = 2.11	K_{oc} = 150			
Bioconcentration factor	BCF = 9	BCF = 12			
Henry's law constant	1.63E−1 atmos − m^3/mol	1.8E−2 atmos −m^3/mol	1.60E−2 atmos m^3/mol	7.7E−1 (unitless)	220 atmos − m^3/m^3

*The true molecular weight may either be calculated by hand or by using the ECOPLUS routine.

Table 9.11a. Henry's Law Constants—All Data

		Henry's Law Constant (Dimensionless)				
Entered Henry's law values		**6.663 Solubility 1 1334 mg/l**	**0.736 Solubility 2 950 mg/l**	**0.654 Solubility 3 1000 mg/l**	**0.770**	**0.162**
Vapor pressure 1	124 mm Hg	**0.666**	**0.936**	**0.889**		
Vapor pressure 2	100 mm Hg	**0.538**	**0.755**	**0.717**		
Vapor pressure 3	99 mm Hg	**0.532**	**0.746**	**0.709**		
Vapor pressure 4	103 mm Hg	**0.556**	**0.781**	**0.742**		

Table 9.11b. Henry's Law Constants—Selected Data

Entered Henry's law values		**6.663 Solubility 1 1334 mg/l**	**0.736 Solubility 2 950 mg/l**	**0.654 Solubility 3 1000 mg/l**	**0.770**	**0.162**
Vapor pressure 1	124 mm Hg	0.666	0.936	0.889		
Vapor pressure 2	100 mm Hg	0.538	**0.755**	**0.717**		
Vapor pressure 3	99 mm Hg	0.532	**0.746**	**0.709**		
Vapor pressure 4	103 mm Hg	0.556	**0.781**	**0.742**		

Table 9.11c. Log K_{oc}—All Data

		log K_{oc}						
Entered log K_{oc} values		**2.110**	**2.176**					**Average 2.143**
		Equation 7	***Equation 8***	***Equation 9***				
Solubility 1 1334 mg/l		**1.921**	**2.462**	**2.049**				2.144
Solubility 2 950 mg/l		**2.002**	**2.542**	**2.131**				2.225
Solubility 3 1000 mg/l		**1.990**	**2.529**	**2.119**				2.213
		Equation 10	***Equation 11***	***Equation 12***	***Equation 13***	***Equation 14***	***Equation 15***	
log K_{ow} 1	2.477	**2.725**	**2.315**	**2.267**	**2.348**	**2.369**	**2.153**	2.363
log K_{ow} 2	2.400	**2.726**	**2.318**	**2.270**	**2.351**	**2.372**	**2.155**	2.365

Table 9.11d. Solubility—All Data

	Solubility mg/l		
Entered solubility	**1334**	**950**	**1000**
		Equation 4	
log K_{ow} 1	2.477	**1439**	
log K_{ow} 2	2.400	**1429**	

Table 9.12. Partitioning of 1,1,1-TCA into Ecosystem

1,1,1-Trichloroethane	H = 0.59		$\log K_{oc}$ = 2.18	log BCF = 0.84
	Air	**Water**	**Soil/sediment**	**Fish**
Full ecosystem	99.9	0.1	0.01	Negligible
Terrestrial	3.5	6.0	90.5	
Pond		92.9	7.1	Negligible

Table 9.13. Analyses for WATEVAL Exercise (Values in mg/l)

	1	**2**	**3**	**4**	**5**
Na^+	9.5	0.2	24.0	3.5	76.0
K^+	1.4	0.0	.0	1.7	3.5
Ca^{2+}	27.0	2.5	74.0	28	178.0
Mg^{2+}	6.2	7.7	9.5	72	86.0
HCO_3^-	93.0	44.0	277.0	398	285.0
SO_4^{2-}	32.0	0.0	19.0	28	707.0
Cl	5.2	0.7	24.0	5	11.0
SiO_2	39.0	16.0	11.0	11	14.0
pH	6.6	8.5	7.0	7.6	7.4
T°C	6	—	—	13.3	15.0
TDS				579	
Cond. umho	258	—	570	663	1510

Analyses from U.S. Geological Survey Professional Paper 440-F.

Table 9.14. Analyses for Exercise 2—G-Site (Analyses in mg/l)

	MW 4S	**MW 4M**	**MW 4D**	**PW 01**
Sodium	5.0	4.8	8.3	5.4
Potassium	0.5	1.1	0.9	1.2
Calcium	0.6	19.0	33	1.5
Magnesium	0.5	0.9	1.5	0.6
Chloride	8	9	10	7
Sulfate	4	5	4	4
Alkalinity	2	47	85	7
Silicon	1.8	3.3	3.4	2.4
pH	6	6	6	6

Parameter Estimation — 1. Each of the Henry's Law constants was converted to its dimensionless form by ECOPLUS. The values derived from the various solubilities and vapor pressures were also calculated and are presented in tabular form below. Henry's law constant calculated from all possible data are shown in Table 9.11a.

Considering first the entered values obtained from the literature, it is apparent that the first value is off by an order of magnitude, possibly because of a decimal place error. The last value is also considerably less than the other values. Examination of the calculated values suggests that a vapor pressure of 124 mm Hg leads to H values that are possibly too high and that a solubility of 1334 lead to H values that are too low. The selected H values are shown highlighted in Table 9.11b after deletion of those suspect values.

2. Both literature values are converted to log K_{oc} and are very close, so there is no reason to delete either. The K_{oc} values calculated from both solubility and log K_{ow} are also similar enough that no reason exists to delete any. The solubility value (1334 mg/l) suspect in the

Table 9.15. Benzene Data for ECOPLUS Exercise

	Benzene C_6H_6				
Molecular weight					
Melting point	42°F				
Boiling point	80.1°C				
Vapor pressure	75 mm Hg (20°C)	0.1 atm (20°C)	125E − 3 atm		
Solubility	0.82 g/l (20°C)	22.4 mol/m3 (20°C)	1780 ppm	1780 ppm	log mole fraction = −3.39
Octanol/water partition coefficient	log K_{ow} = 2.14	K_{ow} = 135	log K_{ow} = 2.11		
Distribution coefficient	K_{oc} = 83	log K_{oc} = 1.78			
Bioconcentration factor					
Henry's law constant	4.39E−3 atm m^3/mol (20°C)	240 atm − m^3 water/m^3 air	0.241 E−3 m^3 − atm/mol		

Table 9.16. Data for ECOPLUS Groundwater Exercise

	Aquifer data	
125 ft. thick	0.2 porosity	0.04% organic carbon
Dispersivity	70 ft longitudinal	14 ft/transverse
	Groundwater data	
1.5 ft/day velocity		
	Chemical data	
3-Chlorotoluene	M. Wt = 126.59 log K_{oc} = 3.08	80 lb. spill (1 day) (36.3 kg)

Table 9.17. Data for ECOPLUS Ecosystem Distribution Exercise

	H (unitless)	log K_{oc}	log BCF
1,1,1-Trichloroethane	0.59	2.18	0.84
Pentachlorophenol	0.0001	4.72	3.18
2,4-Dichlorophenol	0.0001	2.58	1.22

H calculation does not give results for K_{oc} sufficiently different to delete it here. Log K_{oc} values calculated from all possible equations are given in Table 9.11c.

3. Comparision of the entered solubility values and those estimated from K_{ow} (Table 9.11d are also relatively similar, so that deleting any cannot be supported. Those solubilities calculated from K_{ow} are always considerably higher than the literature solubility values.

Parameter partitioning — The difference in partitioning behavior between the full ecosystem and the mini ecosystems is tabulated in Table 9.12.

With a large air compartment the 1,1,1-TCA partitions into the air. If the air volume is minimal as in the terrestrial soil model, most of the 1,1,1-TCA partitions into the solid phase. If water predominates as in the pond model, partitioning into the water occurs. In the pond and full ecosystem models the 1,1,1-TCA bioconcentrates into the fish to the same extent as it does into the sediment or soil.

EXERCISES

WATEVAL Exercises

1. Interpret the origin of the waters listed in Table 9.13. (From White et al. 1963.)

Table 9.18a. WATEVAL Sample 1 Reliability Checks. Sample No 1. Table 1 Number 9—Groundwater (28′ Well), Granite, MD

Reliability check	Attention value	Analysis value	Conclusion
$\frac{(C - A)}{(C + A)}$ %	>5%	−0.7%	
Hardness $- \frac{\text{Entered} - \text{Calc}}{\text{Entered}}$	>5%	***	
$\frac{\text{Entered TDS} - \text{TDSC}}{\text{Entered TDS}}$	>5%	***	
$\frac{\text{Entered TDS} - \text{TDS 180}}{\text{Entered TDS 180}}$	>5%	***	
$\frac{\text{Entered TDS}}{\text{Conductivity}}$	<0.5 and >0.75	***	
$\frac{\text{TDS calc}}{\text{Conductivity}}$	<0.5 and >0.75	0.83	
$\frac{\text{Conductivity}}{\text{sum MEQ cations}}$	<90 and >110	112	
Carbonate	0.2 (calc)	0.0	
$\frac{K}{K + Na}$	>0.2	0.08	
$\frac{Mg}{Mg + Ca}$	>0.4	0.27	
$\frac{Ca}{Ca + SO_4}$	<0.5	0.67	
$\frac{Na}{Na + Cl}$	<0.5	0.74	
Conclusion	Analysis acceptable		Yes No

2. Case History—"G" Site. (From Geiger Superfund Site, 1987.)

These data refer to a pumping well PW01 and a monitoring well MW4 having three sampling depths—shallow, medium, and deep. The wells are 190 ft apart and the pumping well is screened from the water table to its full depth of 35 ft. Is there evidence of mixing? What conclusions can be drawn from the plot? Analyses are listed in Table 9.14.

Data problems:

1. Si is given and not SiO_2
2. Alkalinity is undefined. Is it bicarbonate, or has it been converted to $CaCO_3$? Use analysis with the highest alkalinity to establish units. If conversion is required the equivalent weight of $CaCO_3$ is the molecular weight/2. You may also use the Edit conversion function in WATEVAL.

The alkalinity question, whether $CaCO_3$ or HCO_3^-, may be resolved by looking at the anion-cation balance of the water with the highest value (MW 4D).

ECOPLUS Exercises

Parameter Estimation

For benzene using the data in Table 9.15 obtain the best estimates for log K_{oc}, log BCF, and K_H. Give your reasons for the selection.

Table 9.18b. WATEVAL Sample 1 Source-Rock Evaluation. Sample No 1. Table 1 Number 9—Groundwater (28′ Well), Granite, MD

Parameter	Value	Conclusion
SiO_2 (mmol/l)	0.65	Volcanic glass or hydrothermal water possible
$\frac{HCO_3}{SiO_2}$	2.35	Silicate weathering
$\frac{SiO_2}{Na + K - Cl}$	2.15	Ferromagnesian minerals
$\frac{Na + K - Cl}{Na + K - Cl + Ca}$	0.31	Plagioclase weathering possible
$\frac{Na}{Na + Cl}$	0.74	Albite or ion exchange
$\frac{Mg}{Mg + Ca}$	0.27	Granitic weathering
$\frac{Ca}{Ca + SO_4}$	0.67	Ca source other than gypsum, carbonates, or silicates
$\frac{Ca + Mg}{SO_4}$	2.8	Dedolomitization unlikely
TDS calculated (mg/l)	213	Silicate weathering possible
$\frac{Cl}{\text{sum anions}}$	0.06	Silicate or carbonate weathering
$\frac{HCO_3}{\text{sum anions}}$	0.65	
Langelier index	−1.67	Undersaturated with respect to calcite
Conclusion	Aquifer mineralogy	Pyritic andesite
Conclusion	Reactions	

Groundwater Exercise

Use the data tabulated in Table 9.16.

a) Assuming a retardation factor of 1 and the direct entry of the chemical into the groundwater system, calculate the maximum concentration that would occur in a well 1500 ft directly downgradient from the spill. How long after the spill would this occur?

b) Calculate the retardation factor for 3-chlorotoluene and recalculate a) above.

Ecosystem Distribution

Discuss the distribution of 1,1,1-trichloroethane, pentachlorophenol, and 2,4-dichlorophenol in McCall's ecosystems using the data in Table 9.17. Discuss the difference in partitioning behavior between the full ecosystem and the mini ecosystems. Finally, compare the behavior of all three compounds.

ANSWERS TO EXERCISES

WATEVAL Exercises
Analyses in Table 9.13

1. Table 1 Number 9—Groundwater (28′ well), Granite, MD—Table 9.18a and b

Analysis acceptable.

Source-rock deduction

Table 9.18c. WATEVAL Sample 2 Reliability Checks. Sample No 2. Table 2 Number 5—Groundwater (250′ Well) Peridotite, NC

Reliability check	Attention value	Analysis value	Conclusion
$\frac{(C - A)}{(C + A)}$ %	>5%	1.7%	
Hardness $-\frac{\text{Entered} - \text{Calc}}{\text{Entered}}$	>5%	***	
$\frac{\text{Entered TDS} - \text{TDSC}}{\text{Entered TDS}}$	>5%	***	
$\frac{\text{Entered TDS} - \text{TDS 180}}{\text{Entered TDS 180}}$	>5%	***	
$\frac{\text{Entered TDS}}{\text{Conductivity}}$	<0.5 and >0.75	***	
$\frac{\text{TDS calc}}{\text{Conductivity}}$	<0.5 and >0.75	***	
$\frac{\text{Conductivity}}{\text{sum MEQ cations}}$	<90 and >110	***	
Carbonate	0.2(calc)		
$\frac{K}{K + Na}$	>0.2	***	
$\frac{Mg}{Mg + Ca}$	>0.4	0.84	
$\frac{Ca}{Ca + SO_4}$	<0.5	***	
$\frac{Na}{Na + Cl}$	<0.5	0.31	
Conclusion	Analysis acceptable		Yes No

Bicarbonate/silica = 2.35 (<< 10), indicates silicate weathering.
TDS = 213 mg/l (relatively low), supports silicate weathering.
5 mg/l chloride (very low) probably from precipitation.
Excess Na (Na + K = Cl) probably from albite weathering.
Potassium (1.4 mg/l) possibly low for a granite.
Silica > twice excess sodium, indicates ferromagnesian minerals present.
Sulfate (32 mg/l) unusually high for granitic rock, possibly from pyrite oxidation.
pH of 6.6 indicates sulfuric acid neutralized, presumably by calcite because $Ca^{2+} > SO_4^{2-}$.
Na/Ca suggests intermediate plagioclase.
The high silica suggests volcanic glass or hydrothermal waters and therefore andesite rather than a granodiorite.

Conclusion: most of the deductions would support a pyritic andesite source. This is at variance with the described origin.

2. Table 2 Number 5—Groundwater (250′ well) Peridotite, NC—Table 9.18c and d

Analysis acceptable
Source-rock deduction

Very low chloride (0.7 mg/l) and sodium (0.2 mg/l) would suggest these ions were derived from rain water.
Bicarbonate/silica = 2.71 (<<10), indicates silicate weathering.

Table 9.18d. WATEVAL Sample 2 Source-Rock Evaluation. Sample No 2. Table 2 Number 5—Groundwater (250′ Well) Peridotite, NC

Parameter	Value	Conclusion
SiO_2 (mmol/l)	0.27	
$\frac{HCO_3}{SiO_2}$	2.71	Silicate weathering
$\frac{SiO_2}{Na + K - Cl}$	Cl > (Na + K)	
$\frac{Na + K - Cl}{Na + K - Cl + Ca}$	Cl > (Na + K)	
$\frac{Na}{Na + Cl}$	0.31	
$\frac{Mg}{Mg + Ca}$	0.84	Ferromagnesian minerals
$\frac{Ca}{Ca + SO_4}$	1.00	Ca source other than gypsum, carbonates, or silicates
$\frac{Ca + Mg}{SO_4}$		
TDS calculated (mg/l)	71 mg/l	Silicate weathering possible
$\frac{Cl}{\text{sum anions}}$	0.03	Silicate or carbonate weathering
$\frac{HCO_3}{\text{sum anions}}$	0.97	Silicate or carbonate weathering
Langelier index	−1.17	Undersaturated with respect to calcite
Conclusion	Aquifer mineralogy	Peridotite
Conclusion	Reactions	

TDS of 71 mg/l is low, supporting silicate weathering.
The main cations are magnesium, followed by calcium where (Mg > Ca), ferromagnesian silicate weathering.

Conclusion: the data suggest mafic rock such as peridotite.

3. Table 6 Number 8—Groundwater (350′ well), Limestone, TX—Table 9.18e and f

Analysis acceptable. Reported TDS is sum of ions.
Source-rock deduction

Bicarbonate/silica = 24.8 (>>10), indicating carbonate weathering.
Chloride and sulfate moderately low (24 and 19 mg/l, respectively), indicating little if any evaporite solution.
TDS moderate (446 mg/l) moderate, supporting carbonate weathering.
Mg/(Mg + Ca) = 17%, suggesting dominant limestone and some dolomite.
Excess sodium over chloride suggests cation exchange.

Conclusion: Dolomitic limestone with cation exchange is suggested.

Table 9.18e. WATEVAL Sample 3 Reliability Checks. Sample No 3. Table 6 Number 8—Groundwater (350′ Well), Limestone, TX

Reliability check	Attention value	Analysis value	Conclusion
$\frac{(C - A)}{(C + A)}$ %	>5%	0.7%	
Hardness $- \frac{\text{Entered} - \text{Calc}}{\text{Entered}}$	>5%	***	
$\frac{\text{Entered TDS} - \text{TDSC}}{\text{Entered TDS}}$	>5%	***	
$\frac{\text{Entered TDS} - \text{TDS 180}}{\text{Entered TDS 180}}$	>5%	***	
$\frac{\text{Entered TDS}}{\text{Conductivity}}$	<0.5 and >0.75	***	
$\frac{\text{TDS calc}}{\text{Conductivity}}$	<0.5 and >0.75	0.78	
$\frac{\text{Conductivity}}{\text{sum MEQ cations}}$	<90 and >110	100	
Carbonate	0.2 (calc)	0.0	
$\frac{K}{K + Na}$	>0.2	0.15	
$\frac{Mg}{Mg + Ca}$	>0.4	0.17	
$\frac{Ca}{Ca + SO_4}$	<0.5	0.90	
$\frac{Na}{Na + Cl}$	<0.5	0.61	
Conclusion	Analysis acceptable		Yes No

4. Table 7 Number 5—Dolomite well 95′—Table 9.18g and h

Analysis acceptable
Source-rock deduction

Bicarbonate/silica = 35.6 (>>10), suggesting a carbonate origin.
Bicarbonate is the dominant anion, also suggesting carbonate origin.
Langelier index of 0.1 indicates saturation with respect to carbonate.
TDS (547 mg/l) is moderate and supports carbonate origin.
Mg/(Mg + Ca) = 80.9%, very high for dolomite (which should be 50%).
Na, K, and Cl low, probably from precipitation.
$Ca^{2+} > SO_4^{2-}$, suggesting some gypsum solution in addition to carbonate.
$Mg^{2+} > Ca^{2+}$ indicates removal of calcite—supported by the saturation with respect to calcite.
$Ca^{2+} + Mg^{2+}/SO_4^{2-} = 12.5$, not close to one, so dedolomitization is unlikely using this criteria.
Na is only slightly greater than Cl; therefore, cation exchange is unlikely.

Conclusion: dolomite weathering coupled with calcite precipitation is the most likely origin of this water.

5. Table 7 Number 6—Groundwater (208′ well), Dolomite, OH—Table 9.18i and j

Analysis acceptable
Source-rock deduction

Bicarbonate/silica = 26 (>>10), suggesting carbonate weathering.

Table 9.18f. WATEVAL Sample 3 Source-Rock Evaluation. Sample No 3. Table 6 Number 8—Groundwater (350′ Well), Limestone, TX

Parameter	Value	Conclusion
SiO_2 (mmol/l)	0.18	
$\frac{HCO_3}{SiO_2}$	24.80	Carbonate weathering
$\frac{SiO_2}{Na + K - Cl}$	0.34	Cation exchange
$\frac{Na + K - Cl}{Na + K - Cl + Ca}$	0.23	Plagioclase weathering possible
$\frac{Na}{Na + Cl}$	0.61	Albite or ion exchange
$\frac{Mg}{Mg + Ca}$	0.17	Limestone-dolomite weathering
$\frac{Ca}{Ca + SO_4}$	0.90	Ca source other than gypsum, carbonates, or silicates
$\frac{Ca + Mg}{SO_4}$	11.3	Dedolomitization unlikely
TDS calculated (mg/l)	446	Silicate weathering possible
$\frac{Cl}{\text{sum anions}}$	0.12	Silicate or carbonate weathering
$\frac{HCO_3}{\text{sum anions}}$	0.81	Silicate or carbonate weathering
Langelier index	−0.51	Undersaturated with respect to calcite
Conclusion	Aquifer mineralogy	Dolomitic limestone
Conclusion	Reactions	Cation exchange

Table 9.18g. WATEVAL Sample 4 Reliability Checks. Sample No 4. Table 7 Number 5—Dolomite Well 95′

Reliability check	Attention value	Analysis value	Conclusion
$\frac{(C - A)}{(C + A)}\%$	>5%	1.8%	
$\text{Hardness} - \frac{\text{Entered} - \text{Calc}}{\text{Entered}}$	>5%	***	
$\frac{\text{Entered TDS} - \text{TDSC}}{\text{Entered TDS}}$	>5%	5%	Reported TDS is sum of ions
$\frac{\text{Entered TDS} - \text{TDS 180}}{\text{Entered TDS 180}}$	>5%	40%	
$\frac{\text{Entered TDS}}{\text{Conductivity}}$	<0.5 and >0.75	0.87	
$\frac{\text{TDS calc}}{\text{Conductivity}}$	<0.5 and >0.75	0.83	
$\frac{\text{Conductivity}}{\text{sum MEQ cations}}$	<90 and >110	88	
Carbonate	0.2 (calc)	0.0	
$\frac{K}{K + Na}$	>0.2	0.22	
$\frac{Mg}{Mg + Ca}$	>0.4	0.81	High
$\frac{Ca}{Ca + SO_4}$	<0.5	0.71	
$\frac{Na}{Na + Cl}$	<0.5	0.52	
Conclusion	Analysis acceptable		Yes No

Table 9.18h. WATEVAL Sample 4 Source-Rock Evaluation. Sample No 4. Table 7 Number 5—Dolomite Well 95′

Parameter	Value	Conclusion
SiO_2 (mmol/l)	0.18	
$\frac{HCO_3}{SiO_2}$	35.63	Carbonate weathering
$\frac{SiO_2}{Na + K - Cl}$	3.35	Ferromagnesian minerals
$\frac{Na + K - Cl}{Na + K - Cl + Ca}$	0.07	Plagioclase weathering unlikely
$\frac{Na}{Na + Cl}$	0.52	Albite or ion exchange
$\frac{Mg}{Mg + Ca}$	0.81	Dolomite dissoln and calcite pptn or seawater
$\frac{Ca}{Ca + SO_4}$	0.71	Ca source other than gypsum, carbonates, or silicates
$\frac{Ca + Mg}{SO_4}$	12.6	Dedolomitization unlikely
TDS calculated (mg/l)	547	Carbonate weathering, brine, evaporites, or seawater
$\frac{Cl}{\text{sum anions}}$	0.02	Silicate or carbonate weathering
$\frac{HCO_3}{\text{sum anions}}$	0.90	Silicate or carbonate weathering
Langelier index	0.01	Near saturation with respect to calcite
Conclusion	Aquifer mineralogy	Dolomite
Conclusion	Reactions	Calcite precipitation

Table 9.18i. WATEVAL Sample 5 Reliability Checks. Sample No 5. Table 7 Number 6—Groundwater (208′ Well), Dolomite, OH

Reliability check	Attention value	Analysis value	Conclusion
$\frac{(C - A)}{(C + A)}$ %	>5%	0.9%	
Hardness $- \frac{\text{Entered} - \text{Calc}}{\text{Entered}}$	>5%	***	
$\frac{\text{Entered TDS} - \text{TDSC}}{\text{Entered TDS}}$	>5%	***	
$\frac{\text{Entered TDS} - \text{TDS 180}}{\text{Entered TDS 180}}$	>5%	***	
$\frac{\text{Entered TDS}}{\text{Conductivity}}$	<0.5 and >0.75	***	
$\frac{\text{TDS calc}}{\text{Conductivity}}$	<0.5 and >0.75	0.90	
$\frac{\text{Conductivity}}{\text{sum MEQ cations}}$	<90 and >110	78	
Carbonate	0.2 (calc)	0.0	
$\frac{K}{K + Na}$	>0.2	0.03	
$\frac{Mg}{Mg + Ca}$	>0.4	0.44	
$\frac{Ca}{Ca + SO_4}$	<0.5	0.38	
$\frac{Na}{Na + Cl}$	<0.5	0.91	
Conclusion	Analysis acceptable		Yes No

Table 9.18j. WATEVAL Sample 5 Source-Rock Evaluation. Sample No 5. Table 7 Number 6—Groundwater (208′ Well), Dolomite, OH

Parameter	Value	Conclusion
SiO_2 (mmol/l)	0.23	
$\frac{HCO_3}{SiO_2}$	20.05	Carbonate weathering
$\frac{SiO_2}{Na + K - Cl}$	0.08	Cation exchange
$\frac{Na + K - Cl}{Na + K - Cl + Ca}$	0.41	Plagioclase weathering possible
$\frac{Na}{Na + Cl}$	0.91	Albite or ion exchange
$\frac{Mg}{Mg + Ca}$	0.44	Limestone-dolomite weathering
$\frac{Ca}{Ca + SO_4}$	0.38	Ca removal, ion exchange, or calcite precipitation
$\frac{Ca + Mg}{SO_4}$	1.1	Dedolomitization likely
TDS calculated (mg/l)	1361	Carbonate weathering, brine, evaporites, or seawater
$\frac{Cl}{\text{sum anions}}$	0.02	Silicate or carbonate weathering
$\frac{HCO_3}{\text{sum anions}}$	0.24	
Langelier index	0.37	Oversaturated with respect to calcite
Conclusion	Aquifer mineralogy	Dolomite and gypsum
Conclusion	Reactions	Dedolomitization and cation exchange

TDS 1361 mg/l is very high, supports extensive carbonate weathering.
The positive Langelier index suggests saturation or oversaturation with respect to calcite.
Sulfate is very high (707 mg/l), suggesting gypsum solution.
Calcium is < sulfate and sodium > chloride, which suggests ion exchange.
Mg/(Mg + Ca) = 44%, suggesting dolomite solution.
The excess Na (over Cl) is still less than the deficiency of calcium (relative to SO_4^{2-}), which suggest calcium must have been removed by means other than cation exchange.
This information together with the ratio of $Ca^{2+} + Mg^{2+}/SO_4^{2-}$ of 1.1 strongly suggests dedolomitization.

Conclusion: dolomite weathering coupled with gypsum solution led to dedolomitization. Ion exchange is also suggested.

CASE HISTORY—"G" SITE

The best balance is obtained assuming that the alkalinity is as $CaCO_3$.

Two possible hypotheses are possible from the given data.

1. There are two aquifers, a deep one and a shallow one, or an upper aquifer being diluted with infiltrating rain water. The shallow water is dilute, but has a sodium chloride composition that indicates rain water. The deeper water contains some dissolved NaCl, but also calcium bicarbonate, which may be indicative of calcite solution.

2. The second hypothesis, suggested by the fact that the analyses lie on a straight line pointing to the Ca and HCO_3^- corners of the Piper diagram, is that this is a recharge area and as the water infiltrates downgradient there is progressive solution of the calcium carbonate from the aquifer.

ECOPLUS EXERCISES

Parameter Estimation

When the values were converted to similar units, it was apparent that the solubility of 0.82 g/l or 820 mg/l was too low, half the other solubility values. The H calculated using this solubility was twice that of the other values, and the K_{oc} calculated from it was 0.2 log units higher that the other values. Also the Henry's law constant of 0.24E-3 m^3-atmos/mol recalculated to 0.01 (dimensionless), which is about $^1/_{10}$th that of the other values. If these values are omitted, the final parameters are: log K_{oc} = 1.951, log BCF = 0.494, and H (dimensionless) = 0.192.

GROUNDWATER Exercise

a. A maximum concentration of 0.09 mg/l will be observed after 900 days.

b. The retardation factor for 3-chlorotoluene is 6.1. A maximum concentration of 0.015 mg/l will be observed after 5460 days.

Ecosystem Distribution

The distribution of 1,1,1-TCA in the ecosystem is given in Table 9.19a. With a large air compartment the 1,1,1-TCA partitions into the air. If the air volume is minimal as in the terrestrial soil model most of the 1,1,1-TCA partitions into the solid phase. If water predominates as in the pond model the partitioning into the water occurs. In the pond and full ecosystem models the 1,1,1-TCA bioconcentrates into the fish to the same extent as it does into the sediment or soil.

The distribution of pentachlorophenol in the ecosystem is given in Table 9.19b. The extremely low Henry's law constant precludes any more than a trace of pentachlorophenol from entering the atmosphere. The extremely high K_{oc} value means that almost all of the pentachlorophenol partitions into the solid soil or sediment phases. In the pond system there is major bioconcentration into the fish.

Table 9.19a. Ecosystem Distribution for 1,1,1-TCA

1,1,1-Trichloroethane	H = 0.59		log K_{oc} = 2.18	log BCF = 0.84
	Air	**Water**	**Soil/sediment**	**Fish**
Full ecosystem	99.9	0.1	0.01	Negligible
Terrestrial	3.5	6.0	90.5	
Pond		92.9	7.1	Negligible

Table 9.19b. Ecosystem Distribution for Pentachlorophenol

Pentachlorophenol	H = 0.0001		log K_{oc} = 4.72	log BCF = 3.18
	Air	**Water**	**Soil/sediment**	**Fish**
Full ecosystem	0.7	2.0	97.3	0.003
Terrestrial		0.02	99.98	
Pond		3.6	96.3	0.006

The distribution of 2,4-dichlorophenol in the ecosystem is given in Table 9.19c. Only a small amount of 2,4-dichlorophenol will partition into the air, even considering the huge volume of this compartment because of the very low Henry's law constant. The relative quantities that are distributed between the water and the solid phases depends on the relative sizes of the two compartments. In the soil model, most will partition into the solid, whereas in the pond model most of the 2,4-dichlorophenol is in the water. Significant bioconcentration occurs although concentrations in the sediment are similar to that in the fish.

The distribution of the three compounds in the full ecosystem are shown in Table 9.19d. Most 1,1,1-trichloroethane partitions into the air, whereas much smaller amounts of 2,4-dichlorophenol do so, and almost none of the pentachlorophenol enters the air. Most of the pentachlorophenol partitions into the solid phase, whereas 2,4-dichlorophenol is concentrated in the water.

Table 9.19c. Ecosystem Distribution for 2,4-Dichlorophenol

2,4-Dichlorophenol	H = 0.0001		$\log K_{oc}$ = 2.58	log BCF = 1.22
	Air	**Water**	**Soil/sediment**	**Fish**
Full ecosystem	21.6	57.9	20.5	0.001
Terrestrial		2.6	97.4	
Pond		84.0	16.0	0.0001

Table 9.19d. Ecosystem Distribution Comparison for Three Compounds

Full ecosystem	**Air**	**Water**	**Soil/sediment**	**Fish**
1,1,1-Trichloroethane	99.9	0.1	0.01	Negligible
Pentachlorophenol	0.7	2.0	97.3	0.003
2,4-Dichlorophenol	21.6	57.9	20.5	0.001

Glossary

Abiotic does not involve living organisms

Accuracy the closeness of the analysis value to the true value

Acetaldehyde ethanal

Acetamide ethanamide

Acetic acid ethanoic acid

Acetone propanone

Acetylene ethyne

Acidity capacity of a solution to neutralize a strong base

Activity (thermodynamic) effective concentration

Activity coefficient ratio of activity to concentration

Acyclic open-chain compounds

Addition reaction addition to both sides of a double or triple bond

Adsorbate solute

Adsorbent material on which solute is adsorbed

Adsorption adherence of ions or molecules in solution to the surface of solids

Adsorption isotherm graph relating the concentration of a solute in water to its concentration in a solid

Advection solutes move with same velocity as the water

Albite $NaAlSi_3O_8$ plagioclase end member

Aldose sugar containing an aldehyde group

Aliphatic straight or branched hydrocarbons

Alkali metals elements with one electron in the s orbital, and an oxidation number of I

Alkaline earth metals elements with two electrons in the s orbital, and an oxidation number of II

Alkalinity capacity of a solution to react with strong acid, usually reported in terms of equivalent amount of calcium carbonate

Amino acid carboxylic acids with amino group on second carbon

Amorphous without crystalline structure

Amphibole ferromagnesian silicate with hydroxyl ions

Amphibolite non-foliated metamorphic rock consisting primarily of amphibole

Amyl- old term for pentyl-

Andesite fine-grained volcanic equivalent of diorite

Anhydrite $CaSO_4$

Aniline aminobenzene

Anion exchange anions in clays that may be replaced by other anions

Anion-cation balance the difference between the sum of the cations and the sum of the anions over the sum of all ions expressed as a percent

Anorthite $CaAl_2Si_2O_8$ plagioclase end member

Anthracene three ring condensed hydrocarbon (straight)

Anthroposphere man's effect on the other geochemical spheres

Aragonite $CaCO_3$

Aromatic group of organic chemicals containing one or more benzene rings

Aromatic ring planar, unsaturated, cyclic hydrocarbon s, and some heterocyclics (such as thiophene and pyridine) with overlapping π electrons.

Atmosphere the air surrounding the planet

Atom smallest particle of an element that possesses the properties of that element

Attenuation dilution of solute away from its source

Augite variety of pyroxene

Barite $BaSO_4$

Basalt fine-grained volcanic equivalent of gabbro

Bauxite AlOOH

BCF bioconcentration factor

Benzoic acid benzenecarboxylic acid

Benzyl- prefix or radical name of toluene

Bioconcentration a measure of the degree to which a solute dissolved in water is partitioned into the fat of some living organism, usually a fish

Biodegradation decomposition by microorganisms

Biosphere living organisms on and around the earth

Biotic involves living organisms

Biotite dark colored ferromagnesian mica

Biphenyl two benzene rings joined by one C-C bond

Bitterns residual seawater remaining after halite has precipitated out

Brine a water containing a high concentration of dissolved salts, usually sodium chloride

Bromoform tribromomethane

Brownian random motion of molecules in liquids and gases

BTEX benzene, toluene, ethylbenzene, xylenes

Buffer a solution resistant to change in pH when hydroxyl or hydrogen ions are added

Butane four carbon hydrocarbon

Butyric acid butanoic acid

Calcite $CaCO_3$

Caliche a layer of secondary calcium carbonate precipitated from the soil solution

Carbohydrate polyhydroxyl aldehydes or ketones (sugars)

Carbolic acid old name for phenol

Carbonate hardness temporary hardness

Carboxylic organic acid

CAS No. Chemical Abstracts Service registry number

Cation exchange capacity (CEC) milliequivalents of exchangeable cations per 100 gram of dried sample

CFC chlorofluorocarbons

Chloroform trichloromethane

Chromatography differential solute movement resulting from the movement of a solution through a porous solid

Clastic fragments of other rocks

Clay fine-grained, hydrous aluminum silicate

Clay adsorption	process whereby ions or molecules are held on the surface of the clay particles
Clay minerals	fine-grained hydrous aluminosilicates
Clay size fraction	very fine-grained sediment having particle diameters less than 4 microns
Colloid	a very fine-grained constituent, such as a clay, dispersed in water
Condensation reaction	an organic reaction releasing water such as the reaction of alcohol and carboxylic acid to form an ester
Conductivity	the reciprocal of the resistance in ohms between the opposite faces of a 1 cm cube of an aqueous solution
Conglomerate	coarse-grained clastic sedimentary rock
Contaminant	a constituent that changes natural water quality
—COOH	representing a carboxylic acid
Correlation coefficient	a measure of the degree to which two variables vary together
Crystalline (minerals)	a regular internal arrangement in atoms in a mineral
Crystalline (rocks)	rock in which the minerals form an interlocking meshwork of grains
Cs	concentration in soil
Cw	concentration in water
Cyclic	closed-chain compounds
Darcy's law	an equation used to compute the velocity of water flowing through porous medium
Decomposition	breakdown
Dedolomitization	replacement of dolomite by calcite, initiated by a high calcium concentration, usually derived from gypsum solution
Degradation	breakdown
Denitrification	microbial reduction of nitrate to nitrogen gas and/or nitrous oxide
Desorption	reverse of adsorption
Diffusion	dilution by spreading
Dilution	render less concentrated
Dimensionless	without units
Dimer	molecule composed of two identical molecules
Diorite	coarse-grained igneous rock consisting of plagioclase and amphibole
Dioxane	1,4-diethylene dioxide
Dioxin	three cycle six atom rings with the center ring having 2 oxygens in para positions
Dispersion	spreading of solute by a non-uniform movement in porous media, effecting all solutes equally
Dispersivity	dispersion divided by velocity
Dolomite	$CaMg(CO_3)_2$
Dolomitization	the formation of the mineral dolomite
Dolostone	sedimentary rock composed primarily of dolomite
Ecosystem	an interactive system of a biologic community and its non-living environment
Effluent	a discharge of pollutants into the environment, generally liquid
Eh	potential of a reaction relative to that of a hydrogen electrode
Electron	a negatively charged subatomic particle surrounding the nucleus

Electronegativity a measure of an atom's ability to attract shared electrons in a structure

Element matter that is composed of only one kind of atom

Elimination reaction an organic reaction where two groups on adjacent carbon atoms of a saturated chain are removed

Elution removal of an adsorbed solute

Emulsions colloidal particles of one liquid dispersed in another liquid

Enthalpy the chemical energy stored in a substance at constant temperature and pressure

Entropy measure of organization or order within a system

Environment the sum of all external conditions influencing the life and survival of an organism

EPA The United States Environmental Protection Agency

epm equivalents per million (meq/kg solution)

Equilibrium constant ratio of the forward and reverse rates of a reaction

Equivalents number of moles of cationic or anionic charges

Erg unit of work and energy

Ethane saturated two carbon hydrocarbon

Ethene unsaturated two carbon hydrocarbon

Ethylene ethene

Evaporates relatively soluble salts that accumulate in oceans and later form evaporites

Evaporites chemical sediments that have been precipitated from water

Exchangeable cations cations in clays that may be replaced by other cations

Exponent power to which a number is raised

Exponential raising to a power

Fat ester of glycerol and fatty acids—triglycerides

Fatty acid carboxylic acid with even number of carbon atoms (2–22)

Feldspars Na, K, and/or Ca aluminum silicates

Ferromagnesian minerals minerals (usually silicates) containing varying amounts of iron and magnesium in solid solution

Fluorite CaF_2

Formaldehyde methanal

Formality moles of solute per kilogram of solution

Formic acid methanoic acid

Free energy energy available for chemical reactions

Freundlich isotherm equation relating the concentration of a solute on a solid phase with its concentration in the liquid phase

Fulvic acid soil colloid soluble in both acids and alkalis

Fused ring (organic chem) a ring with one or more sides in common with another ring

Gabbro coarse-grained igneous rock containing plagioclase and pyroxene

Garnet iron aluminum silicate common in metamorphic rocks

Gaussian a normal distribution in statistics (gives bell-shaped curve)

Geometric isomer substituents on same or opposite sides of a double bond or ring

Geothermometry using element ratios (whose concentrations are dependent on temperature) to estimate the temperature of a solution

Gley Soil soil developed under conditions of poor drainage resulting in the reduction of iron and other elements

Glycerin glycerol

Glycerol 1,2,3-propanetriol, trihydric alcohol or triol

Gneiss coarse-grained metamorphic rock with foliation resulting from alternating layers of light and dark minerals

Goethite FeOOH

Granite coarse-grained igneous rock consisting of quartz and potash feldspar

Gypsum $CaSO_4.2H_2O$

Half-life time required for the concentration of a solute to be reduced to half of its initial concentration

Halite NaCl

Halogens elements with 5 electrons in the p orbital, and an oxidation number of $-I$ except when combined with oxygen

Hardness sum of calcium and magnesium expressed in terms of mg/l of calcium carbonate

Hematite Fe_2O_3

Henry's law relationship of the concentration of a solute in water to its partial pressure

Heterocyclic contains one or more non-carbon atoms in a ring

Heterogeneities nonhomogeneous parts

Hexose six carbon sugar

Hornblende variety of amphibole

Hornfels very fine-grained non-foliated metamorphic rock

Humic soil colloid soluble in alkali but not acid

Humin soil colloid insoluble in both acids and alkalis

Hydraulic involving the movement of water

Hydrocarbons organic compounds containing only carbon and hydrogen

Hydrolysates secondary products of the chemical breakdown of aluminosilicates such as feldspar

Hydrophilic chemical compounds which concentrate in water

Hydrophobic chemical compounds which concentrate in lipids (fats)—water repellent

Hydrosphere distribution of water on the planet

Hydrothermal natural hot water

Igneous rock formed by cooling and solidification of molten silicates

Illite mica-like potassium clay mineral with two tetrahedral layers separated by one octahedral layer with some potassium held tightly between the layers

Immiscible liquids that do not mix

Inertial resistance to a change of state or motion

Insecticides used to kill insects

Insoluble does not dissolve in

Inverse reciprocal of

Iodine number grams of iodine combining with 100 g of fat

Isomer same molecular formula but different structure

Isoprene 2-methyl-1,3-butadiene (monomer of natural rubber)

Isotope forms of an element composed of atoms with the same atomic number, but different mass numbers

Kaolinite a clay mineral with one tetrahedral layer and one octahedral layer

K_d distribution coefficient of solute between water and solid phase

Ketose sugar containing ketone group

K_{oc} distribution coefficient of solute between water and organic carbon

K_{ow} distribution coefficient of solute between n-octanol and water

Laminar fluid flow that is smooth and straight (no mixing)

Langelier index saturation index for calcite

Laterite highly weathered tropical soil

Limestone sedimentary rock composed primarily of calcite.

Limonite same as goethite

Lipid natural products soluble in water-immiscible solvents but insoluble in water

Lithosphere distribution of rocks on the planet

ln abbreviation for $\log_e$

log abbreviation for $\log_{10}$

Marble non-foliated metamorphic rock consisting primarily of calcite

Mass balance sum of original material plus whatever entered the system, minus whatever left the system

MEK methyl ethyl ketone, butanone

Membrane filtration natural reverse osmosis where shale acts as a semipermeable membrane

Metamorphic rock rock derived from pre-existing rocks by solid state changes in response to changes in temperature, pressure, and stress

Methane one carbon hydrocarbon

Micas layered aluminosilicates with potassium held tightly between the layers—often with lesser amounts of iron and magnesium

Micromoles one millionth of a mole

Microorganisms includes bacteria, fungi and viruses, and microscopic protozoa, nematodes and arthropods

Milliequivalents a thousandth of an equivalent

Mixing waters of two or more origins mixing

Monomer the small molecules or building blocks of polymers

Molality (m) moles of solute per kilogram of water

Molarity (M) moles of solute per liter of solution

Mole $6.02 * 10^{23}$ atoms or molecules of a compound, equals one gram formula weight of that material

Mole fraction ratio of the number of moles of a given constituent to the total number of moles of all constituents

Montmorillonite a clay mineral with two tetrahedral layers separated by one octahedral layer with some exchangeable calcium, sodium, and water held between the layers—type of clays that have a high cation exchange capacity

Multiphase more than one phase, not miscible

Muscovite light colored potassium mica

n-Octanol straight chain alcohol with eight carbon atoms

Naphthalene two ring condensed hydrocarbon

Natural softening adsorption of calcium and magnesium from water by Na-clay (usually montmorillonite) and the release of sodium to the water

Neutron an electrical neutral subatomic particle found in the nucleus

—NH_2 representing an amine group

Noncarbonate hardness same as permanent hardness

Nonionic does not ionize or break up into positive and negative particles (ions)

Normalized a parameter related to a fixed quantity of another parameter, e.g., K_{oc} is normalized to 1% of organic carbon

Octanol-water two immiscible liquids used to determine partitioning coefficients

—OH representing an alcohol or phenolic group

Optical isomer isomers are mirror images of one another

Organic compounds of carbon excluding oxides and carbonates

Oxalic acid ethanedioic acid

Oxidates products formed by the oxidation of iron and manganese

Oxidation number the charge that an atom would have if both of the electrons in each bond were assigned to the more electronegative element

PAH polyaromatic hydrocarbons

Partial analysis a situation where a major ion has not been analyzed thus precluding an anion-cation balance check

Partition distribution of solute between two immiscible phases

PCB polychlorinated biphenyls

PCE perchloroethylene, tetrachloroethene

pe negative log of the electron concentration

Pentose five carbon sugar

Perchloro- all hydrogen atoms replaced by chlorines

Peridotite coarse-grained igneous rock consisting of olivine and pyroxene

Permanent hardness the amount of hardness greater than temporary hardness

Pesticides used to kill insects, fungi, weeds, rodents, algae, and micro-organisms

pH negative log of the hydrogen ion concentration in mol/l

Phenanthrene aromatic three ring condensed hydrocarbon

Phenol hydroxybenzene — aromatic alcohol

Phenyl- prefix or radical name of benzene

Phthalic acid o-benzene dicarboxylic acid

Picric acid 2,4,6-trinitrophenol — yellow explosive

Piper diagram a diagram in which the anion and cations are plotted in separate triangles on either size of a diamond where each analysis is plotted as a circle whose area is proportional to the TDS

Plagioclase Na, Ca feldspar

Plume distribution of a solute in groundwater, surface water, or air, usually from a point source

PNA polynuclear aromatics — polyaromatic hydrocarbons

Podzol soil formed in cool humid climates under coniferous forests characterized by a highly leached A horizon

Pollutant an introduced material that makes a resource, such as a water supply, unfit for a specific purpose

Polyaromatic aromatic compound containing more than one benzene ring joined by the sides

Polyester polymer of a dihydric alcohol (ethylene glycol) and terephthalic acid

Polymer a very large molecule composed of repeating units

Polynuclear aromatic polyaromatic hydrocarbons

Polysaccharide sugar polymers

Porosity the ratio of void spaces to the total volume of a rock, sediment, or soil

Potash feldspar (orthoclase) $KAlSi_3O_8$

ppb abbreviation for parts per billion (wt/wt basis)—μg/Kg

ppm abbreviation for parts per million (wt/wt basis)—mg/Kg

Precision the spread around the mean of a set of replicates

Propane saturated three carbon hydrocarbon

Propionic acid propanoic acid

Protein polyamide polymer of natural amino acids

Proton a positively charged subatomic particle found in a nucleus

Pyridine nitrogen atom replacing a carbon in a benzene ring

Pyrite FeS_2

Pyrite oxidation microbial oxidation of pyrite to sulfuric acid

Pyroxene ferromagnesian silicate

Quartz SiO_2

Quartzite non-foliated metamorphic rock consisting primarily of quartz

R_d retardation coefficient

Recharge surface water infiltration into groundwater

Reciprocal one over the number

Redox the oxidation-reduction environment of water

Reduzates organic material and sedimentary sulfides

Regression graph showing correlation of one variable with another

Resistates minerals resistant to chemical and mechanical breakdown

Retardation velocity of solute relative to that of water

Reverse ion exchange the release of calcium (and magnesium) from a clay (usually montmorillonite) and the adsorption of sodium by that clay

Reynolds number number used to determine if flow is laminar or turbulent

Rhyolite fine-grained volcanic equivalent of granite

Rock salt coarse-grained sedimentary rock consisting primarily of halite

Roughness describing the degree of friction between a fluid and its bounding container

Salicylic acid 2-hydroxybenzenecarboxylic acid

Saline Soil soil containing an accumulation of soluble salts

Salinity ($^0/_{00}$) parts of solute (mass) per thousand parts of solution (mass)

Sandstone medium-grained clastic sedimentary rock

Saponification hydrolysis of a fat with alkali yielding glycerol and soap

Saturated (hydrogeology) voids between particles filled with liquid

Saturated (organic chem) no double or triple bonds

Saturation (chemistry) a solution containing the maximum quantity of solute at that temperature

Saturation index log of ion activity product over solubility product

Schist medium- to coarse-grained metamorphic rock with foliation caused by the parallel arrangement of platy minerals

Sediment transported and deposited particles derived from rocks, soils, or biological materials

Sedimentary rock rock resulting from the consolidation of loose sediment, or by precipitation from solution, or from the accumulation of the remains of plants and animals

Shale compacted fine-grained clastic sedimentary rock

Slate fine-grained metamorphic rock with slaty cleavage

Smectite an older name for montmorillonite

Soap sodium or potassium salt of fatty acid

Sodium adsorption ratio (SAR) measures the degree to which sodium in irrigation water replaces the adsorbed calcium and magnesium in soil clays

Soil unconsolidated earth material subjected to environmental and biologic parameters over a period of time — the products of chemical weathering dependent on climate, biological activity, parent material, topography, and time

Solubility measure of the amount of a solute dissolved in a liquid at a specified temperature

Soluble qualitative term indicating a high degree of solubility

Solute the material dissolved in a liquid

Solution the result of dissolving a solute in a solvent

Solvent the liquid in which a solute dissolves

SOM soil organic matter

Sorption term often used instead of adsorption

Sorting separation of clastic sedimentary grains into different size fractions

Source rock deduction aquifer mineralogy and rock-water reactions deduced from the water composition

Speciation the ratio of different species of an element in water

Species (chemistry) the different ions and complexes in which an element may exist

Steroid polycyclic compounds closely related to terpenes

Stiff diagram a plotting technique using four parallel horizontal axes — each analysis plots as distinctive pattern

STORET the United States Environmental Protection Agencies Water Quality Data Base

Streamlines the path of a liquid under laminar flow conditions

Stripping (hydrogeology) removal of a solute by passing air through an aqueous solution so that it partitions into the air

Structural isomer group of organic chemicals including chain, position, and functional group isomers

Subsurface a general term used to designate the material beneath the surface of the earth

Sugar polyhydroxyl aldehydes or ketones

Sulfate reduction microbial reduction of sulfate resulting in H_2S and bicarbonate

Suspended insoluble particles remaining dispersed in a liquid

System	a combination of parts organized into a unified whole
Tailing	departure from a normal curve
TCE	trichloroethene
Temporary hardness	equals alkalinity if alkalinity is less than total hardness
Terpene	dimer of isoprene
TNT	trinitrotoluene—explosive
TOC	total organic carbon
Toluene	methylbenzene
Total dissolved solids (TDS)	mass of ions plus silica
TOX	total organic halogen
Toxic	poisonous or harmful to plant or animal life
Trace	constituents found in minute quantities
Transverse	across
Trilinear	a term used to describe plotting data on a triangular diagram
Turbulence	fluid particles moving along very irregular paths
Unequivocal	without question
Unitless	without units
Unsaturated (chem)	contains double or triple bonds
Unsaturated (hydro)	zone of aeration
Vapor	gaseous form of a material
Velocity	distance traveled in a unit of time
Vermiculite	clay mineral closely related to chlorite and montmorillonite
Vinyl-	prefix or radical name of ethene—ethenyl
Volatile	vaporizes or changes to a gaseous state readily
Volcanic	rock formed by extrusion at the surface of the earth
WATSTORE	the United States Geological Survey Water Quality Data Base
Wax	ester of fatty acid and long-chain alcohol
Xylene	dimethylbenzene

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