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Fourth Edition

ENVIRONMENTAL CHEMISTRY

A GLOBAL PERSPECTIVE

Gary W. vanLoon
& Stephen J. Duffy

Environmental Chemistry
a global perspective

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A GLOBAL PERSPECTIVE

Fourth Edition

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Preface to First Edition

During the past decade, environmental chemistry has come into its own as a respected sub-discipline in the field of chemical science—a subject that occupies an important place in both teaching and research activities of many academic institutions.[1] In its early phases, environmental chemistry was essentially a catalogue or description of chemical properties of the natural world and of concentrations of contaminants. As the subject matured, however, it has come to encompass challenging studies of highly complex systems, and not just in a static way. Current research focuses on the processes that operate within and between various environmental compartments and the ways in which human activities interact with the natural processes. Studies in environmental chemistry use information from all the traditional sub-disciplines, building on this and contributing new knowledge in highly specific ways. Beyond the specialized research, environmental chemistry also involves attempts to integrate the particular ideas into a comprehensive picture of how the natural environment functions and responds to stresses. In this book, we have tried to introduce the basic concepts of the subject and to capture its vitality and relevance to key issues of global concern.

In preparing *Environmental Chemistry—A Global Perspective*, we have kept several ideas in mind.

- The book deals with *chemical principles* operating in the natural and altered environment.
- It builds on the fundamentals of physical, organic and inorganic chemistry. As such, it is directed toward students at the second- or third-year level in an undergraduate chemistry programme.
- It presents a descriptive approach to the most important topics within the overall subject of environmental chemistry; at the same time, we give an introduction to some basic quantitative calculations.
- The subject is considered in a global context. Examples are chosen from all the continents, emphasizing the world-wide interconnectedness of all environmental issues.

The writing of the book builds on many years of research and teaching (for both of us) within the broad areas of environmental chemistry. We are indebted to students who have asked questions and to students who have found answers through their involvement in research projects. We also acknowledge support from colleagues in the Department of Chemistry and the School of Environmental Studies at Queen's University, as well as at Brock University. Finally, and most important, we wish to offer thanks to our family members for their support of our work over many years.

It is hoped that, in a small way, this book may contribute to understanding that is needed to maintain and restore this good Earth.

> '... and God saw everything that he had made, and it was very good ...'
>
> Genesis 1.31a

December 1999

Gary W. vanLoon
Stephen J. Duffy

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[1] Glaze, W.H., Environmental chemistry comes of age, *Environ. Sci. Technol.*, **28** (1994), 169A.

Preface to Fourth Edition

Studies in chemistry of the environment maintain an important position in the undergraduate and graduate curricula of chemistry, applied science, and environmental studies. At the same time, the subject continues to be one of rich research activity. To the public as well, environmental issues where chemistry plays a central role remain strongly in focus.

- The reality of global warming and the impact of human activity are now increasingly accepted as fact supported by a growing body of data. NASA calculated that July 2016 was 0.84 degrees Celsius warmer than the 1950–1980 global average. In the same month, the level of carbon dioxide in the atmosphere passed the 400 ppmv mark.[1] This compares with a value of 365 ppmv at the time of the first edition of this book—almost a 10% increase over the past 16 years.
- Local air quality too is a growing concern, especially in major urban centres like Beijing and New Delhi, but also increasingly in much broader areas beyond the present hot spots. In 2016, the UNEP reported that almost one quarter of deaths globally are due to environmental effects—many of these associated with air pollution.
- Water quantity and quality issues remain critical. Around the world, one person in five has no access to safe drinking water. Polluted water from industrial, agricultural, and domestic sources affects the health of 1.2 billion people every year, and contributes to the death of 15 million children less than 5 years of age every year.
- Healthy soils provide numerous environmental services, interacting directly with water and air. And importantly, healthy soils are the foundation of the food system. The FAO (Food and Agriculture Organization of the United Nations) reports that about one third of the Earth's agricultural soils have been degraded due to various factors. Maintenance and restoration of soil quality is a global challenge directly linked to providing safe and nutritious food for growing populations around the world.

Energy use is central to all these issues, with its importance in terms of industrial and agricultural production and the role it plays in trade, travel, heating and cooling. Accompanying its use, there are consequent multiple impacts on the environment. Energy consumption has continued to rise, reaching its highest level ever in 2016.

Responding in part to the environmental concerns associated with these critical life-support components, 190 world leaders in 2015 committed to 17 sustainable development goals established by the United Nations. Solutions for most of these goals will involve a significant input of what can broadly be called environmental chemistry.

All these factors were in our mind as we prepared the Fourth Edition of *Environmental Chemistry*. We have modified and updated many areas in the book and briefly introduced several new subjects that have gained in importance during the past several years. At the same time, the book continues to focus on the chemical foundations that are needed in order to understand and respond to subjects both old and new that are relevant in all areas of the world.

We again acknowledge the support of students and colleagues, especially those at Queen's and Mount Allison Universities.

September 2017

Gary vanLoon
Stephen Duffy

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[1] Notably, the concentration reported at the time of reading the proofs for this book was 407.7 ppmv, an unusually large increase over the past 10 months. (https://www.esrl.noaa.gov/gmd/ccgg/trends/)

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The complete worked solutions to the end of chapter problems are available for lecturers as PDF files on the book's companion web site: www.oup.com/uk/vanloon4e/

Abbreviations

AcE	acetylcholinesterase enzyme
AGGI	annual greenhouse gas index
Anammox	anaerobic ammonium oxidation
ANC	acid neutralizing capacity
AQI	air quality index
AROTEL	airborne Raman, ozone, temperature, and aerosol lidar (also see Lidar)
ASP	activated sludge process
BC	black carbon
BCF	bioconcentration factor
BLM	biotic ligand model
BOC	biodegradable organic carbon
BOD	biological (or biochemical) oxygen demand
BOM	biodegradable organic matter
BOQ	Bay of Quinte
BTU	British thermal unit
CB	chlorobenzene
CCF	chemical concentration factor
CEC	cation exchange capacity
CFC	chlorinated fluorocarbon (or chlorofluorocarbon)
COD	chemical oxygen demand
COH	coefficient of haze
CP	chlorophenol
DDD	dichlorodiphenyldichloroethane
DDE	dichlorodiphenyldichloroethene
DDT	dichlorodiphenyltrichloroethane
DIAL	differential absorption lidar (also see Lidar)
DOC	dissolved organic carbon
DOM	dissolved organic matter
DTPA	diethylenetriaminepentaacetate
DU	Dobson unit
EC	electrical conductivity
EDTA	ethylenediaminetetraacetic acid
en	electronegativity
EPA	(US) Environmental Protection Agency
ERF	effective radiative forcing
ESP	exchangeable sodium percentage
FA	fulvic acid
FBC	fluidized-bed combustion
GAC	granular activated charcoal
GHG	greenhouse gas
GUS	groundwater ubiquity score
GWP	global warming potential
HA	humic acid
HCFC	hydrochlorofluorocarbon
HFC	hydrofluorocarbon
HM	humic material

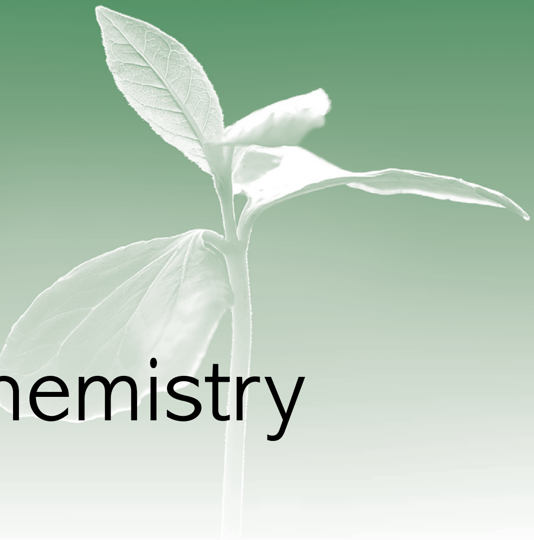
HNLC	high nitrate, low chlorophyll
Hu	humin
IP	inhalable particulates
IPC	isopropyl *N*-phenylcarbamate
IPCC	Intergovernmental Panel on Climate Change
IR	infrared
K_d	distribution coefficient
K_{OC}	organic carbon–water partition coefficient ($K_{OC} = 1.7 \times K_{OM}$)
K_{OM}	organic matter–water partition coefficient
K_{OW}	octanol–water partition coefficient
LC_{50}	lethal concentration 50 (concentration that would be lethal to 50% of an infinitely large population of the test organism over a given time period)
LD_{50}	lethal dose 50 (dose that would be lethal to 50% of an infinitely large population of the test organism over a given time period)
Lidar	light detection and ranging
LPG	liquefied petroleum gas
MAMC	Metropolitan Area of Mexico City
MAS	magic angle spinning (in NMR)
MIC	methyl isocyanate
MMT	methylcyclopentadienyl manganese tricarbonyl
MPI	multi-pollution index
MSW	municipal solid waste
MTBE	methyl tertiary-butyl ether
NMHC	non-methane hydrocarbon
NMR	nuclear magnetic resonance
NOAA	(US) National Oceanic and Atmospheric Administration
NOAEL	no observable adverse effects level (also called LD_0 or LC_0)
NOM	natural organic matter
NTA	nitrilotriacetic acid
ODP	ozone depletion potential
OM	organic matter
OMI	ozone monitoring instrument
PAH	polyaromatic hydrocarbon
PAN	peroxyacetic nitric anhydride
PAR	photosynthetically active radiation
PBDE	polybrominated diphenyl ether
PCB	polychlorinated biphenyl
PCDD	polychlorinated dibenzo-*p*-dioxin
PCDF	polychlorinated dibenzofuran
PCP	pentachlorophenol
PET	poly(ethylene terephthalate)
PM	particulate matter ($PM_{2.5}$—fraction of fine particles smaller than 2.5 µm)
POC	particulate organic carbon
POM	particulate organic matter
POP	persistent organic pollutant
ppbv	parts per billion by volume
ppm	parts per million
ppmv	parts per million by volume
PPN	peroxypropionic nitric anhydride
PSC	polar stratospheric clouds
PTFE	polytetrafluoroethene

PVC	polyvinyl chloride
pzc	point of zero charge (pH_0)
R_f	retardation factor
RF	radiative forcing
RIRF	relative instantaneous radiative forcing (index)
RPP	reductive pentose phosphate (cycle)
RSP	respirable suspended particulates
RVP	Reid vapour pressure
SAR	sodium adsorption ratio
SOLVE	Sage III ozone loss and validation experiment
SOF	soluble organic fraction (of diesel fuel)
SPF	sun protection factor
SPM	suspended particulate matter
SS	suspended solids
TCE	trichloroethylene
TCE	tonnes of coal equivalent
TDF	total dustfall
TN	total nitrogen
TOC	total organic matter
TOE	tonnes of oil equivalent
TOMS	total ozone mapping system
TP	total phosphate
TS	total solids
TSP	total suspended particulate
TSS	total suspended solids
TVA	total volatile acids
UF	urea–formaldehyde (polymer)
UNEP	United Nations Environment Programme
VOC	volatile organic compound
WHO	World Health Organization
zpc	zero point of charge (pH_0)

Environmental Chemistry

a global perspective

> We have to visualize the Earth as a small, rather crowded spaceship, destination unknown, in which humans have to find a slender thread of a way of life in the midst of a continually repeatable cycle of material transformations. In a spaceship, there can be no inputs or outputs. The water must circulate through the kidneys and the algae, the food likewise, the air likewise. . . . In a spaceship there can be no sewers and no imports.
>
> Up to now the human population has been small enough so that we have not had to regard the Earth as a spaceship. We have been able to regard the atmosphere and the oceans and even the soil as inexhaustible reservoirs, from which we can draw at will and which we can pollute at will. There is writing on the wall, however. . . . Even now we may be doing irreversible damage to this precious little spaceship.
>
> *K.E. Boulding, 1966*



Chapter 1

Environmental chemistry

The history of the Earth can be said to have begun more than 4.6 billion years ago.

For largely unexplained reasons, a cloud of molecular particles—mostly hydrogen—rotating through the galaxy began to contract and spin with increasing velocity. As the gravitational energy increased, contraction continued to accelerate and massive amounts of heat were generated. Initially, the heat was radiated out into space, but eventually it became trapped within the confines of the central body—the *protostar*—and its core became extremely dense and hot. The massive energy release caused hydrogen within the hottest regions to become ionized. The hydrogen nuclei became fuel for self-sustaining thermonuclear fusion reactions that maintained an interior temperature far in excess of 1 000 000 K.

The luminous sphere of gas that formed in this way could have been any typical star; this particular one is known to us as the Sun. The rapidly rotating core of matter that had contracted to form the Sun left on its periphery other matter that took the shape of a disc, known as the *solar nebula*. As nebula particles remote from the Sun cooled, gases in that part of the solar system began to interact to form compounds. Some atoms and molecules condensed to form more particles, and collisions amongst them, over time, gradually drew them together into solid bodies known as planetesimals. Eventually, with further coalescence, the small planetesimals grew to such a size, now planets, that they could retain an atmosphere. Reactions occurred within and between the atmosphere and the solid/liquid phases of the young planets. The elements that were present, and the changing affinities between these elements as the system cooled, determined the molecular species that were created.

One of these planets was the Earth.

Early Earth history

In this earliest period of the Earth's life, the solid materials present in its core consisted of iron and alloys of iron, while the mantle and crust of the Earth were in large part made up of oxides and silicates of metals. The major gases in the primeval atmosphere were dihydrogen, dinitrogen, carbon monoxide, and carbon dioxide. Over time, much of the atmosphere was lost into space, whereas continued volcanism brought gases to the surface where they reacted to form other new gas species. Oxygen was abundant but there was no free dioxygen gas. In its entirety, this element was present in combined form—associated with metals or in the atmosphere as carbon dioxide.

Very early in the Earth's history, water was formed most likely by reactions such as

$$4H_2 + CO_2 \rightarrow CH_4 + 2H_2O \qquad (1.1)$$

$$H_2 + CO_2 \rightarrow CO + H_2O \qquad (1.2)$$

To occur to any significant extent, the two reactions require the presence of catalysts and these were available in the form of metal oxides on the surface of the primordial Earth.

Water making up the early seas may have been acidic due in part to dissolved carbon dioxide as well as to hydrochloric acid and sulfur species that were trace components of the early atmosphere. The acids, thought to be concentrated enough to generate an aqueous pH of about 2, and the warm temperatures of the early oceans were sufficient to cause significant dissolution of components in the associated rocks. Dissolution is a neutralizing process and the pH of the seas rose to a value (pH ~ 8) near that of the present-day oceans. At the same time, concentrations of metals in the water increased, sometimes exceeding the solubility products of secondary minerals. For example, the presence of dissolved aqueous carbonate species led to the formation of early sedimentary deposits of calcite ($CaCO_3$) and other carbonate minerals.

$$Ca^{2+} + CO_3^{2-} \rightarrow CaCO_3 \tag{1.3}$$

Also significantly affecting oceanic chemistry were continued underwater releases of gases and volcanic eruptions.

Volcanic activity, folding and uplift of rocks under pressure from the movement of tectonic plates, chemical and physical erosion, and sedimentation all changed the nature of the crust of the Earth over long periods of the Earth's early history.

The beginnings of life

Because there was no free oxygen in the atmosphere, no ozone could be formed. The atmosphere was then transparent to a broad flux of solar radiation, including a large input of ultraviolet (UV) light. This highly energetic radiation and the presence of catalysts made it possible for simple organic compounds like methanol and formaldehyde to be synthesized.

$$CO + 2H_2 \rightarrow CH_3OH \tag{1.4}$$

$$CO + H_2 \rightarrow HCHO \tag{1.5}$$

Very early in the Earth's history these and other species—including HCN, NH_3, H_2S, and many others—were formed. Some of the small molecules reacted further to produce more complex compounds, even including amino acids and simple peptides.

Very primitive forms of life are known to have developed as early as 4 billion years ago. The first cells used simple inorganic molecules as starting material for their synthesis and they, of course, lived in an environment devoid of free oxygen. With increasing complexity, around 3.5 billion years ago, some cells developed an ability to carry out photosynthesis—a reaction that released oxygen into the atmosphere.

$$CO_2 + H_2O \rightarrow \{CH_2O\} + O_2 \tag{1.6}$$

At first, as quickly as it formed, the free oxygen was removed by reaction with terrestrial materials. As the amount of aquatic plant life increased, however, free oxygen began to build up and by about 2 billion years ago the environment at the Earth's surface could be described as essentially oxidizing. Carbon dioxide gradually became a minor gas in the atmosphere. The presence of free oxygen led to the synthesis of ozone, which acted to partially shield the highly energetic components of solar radiation from reaching the Earth's surface. This opened the possibility for terrestrial life to emerge.

The recent Earth

It was the development of life and an oxidizing atmosphere that dominated the change from the primitive to the present environment, and in the past billion years many features of the Earth's composition have remained relatively constant. Yet we should not leave the impression that geological and life processes were static during that period. On the contrary, the Earth is a dynamic system where processes such as volcanism, movement of tectonic plates, weathering,

Table 1.1 Some important physical properties of the present-day Earth.[a]

Mass / kg	5.98×10^{24}		
Radius / m	6.38×10^{6}		
Density / kg m^{-3}	5520		
Distance from Sun / km	1.5×10^{8}		
Surface temperature / K	290		
	Atmosphere	**Oceans**	**Land**
Mass / kg	5.27×10^{18}	1.37×10^{21}	
Surface area / m^2		3.61×10^{14}	1.48×10^{14}
Approximate density / kg m^{-3}	1.3 (at Earth's surface, 0°C)	1030	2700 (surface rocks)
Major components	N_2, O_2, H_2O, Ar	H_2O, dissolved species Na^+, Cl^-, SO_4^{2-}, Mg^{2+}	Si, O, Al, Fe, Ca (as silicates, oxides, carbonates, etc.)

[a] Additional data regarding the nature of the Earth are provided in Appendices A.1–A.3.

erosion, sedimentation, and the continuing evolution of life interact to provide the environment in which we now live. As changes occur in one compartment—through interactions and feedback—changes occur over the Earth as a whole.

Nevertheless, from about 1 billion years ago to the present, the average composition of the atmosphere, the oceans, and the land, in their major components, has remained relatively constant. Table 1.1 lists some important physical features of our present-day Earth.

1.1 Environmental chemistry

Systems and surroundings in environmental chemistry

In the terminology of thermodynamics, we define the *universe* as consisting of a *system* and its *surroundings*. The system is that portion of the universe under direct investigation while the surroundings comprise everything beyond the system. We can apply this concept, for example, to consider an industrial chemical process such as the production of the wood preservative pentachlorophenol (PCP). The system—essentially what goes on in the factory reactor—is subject to investigation by chemists who develop and optimize appropriate synthetic reactions and by engineers who design and set up the manufacturing facility itself. Historically, much effort has been expended on examining the properties of systems but, increasingly, there is concern about surroundings.

In our example, when scientists move outside the factory and focus attention on the impact of the industrial process on its surroundings—such as release of the product PCP or by-products like dioxins—then the subject becomes one of environmental chemistry.

We may continue our example by moving away from manufacturing to the other end of the scientific spectrum where we examine mechanisms by which chemicals such as dioxins enter a living organism, the biochemical transformations they undergo, their molecular mode of action, and their elimination. The target organism has then become the system and is a subject for study by biologists, biochemists, and toxicologists.

What goes on in the surroundings outside the organism—transport of dioxins, associative reactions with soil and water, degradation process, etc.—is the subject matter of environmental chemistry. To express it simply, environmental chemistry is the chemistry of surroundings—the universe minus the system.

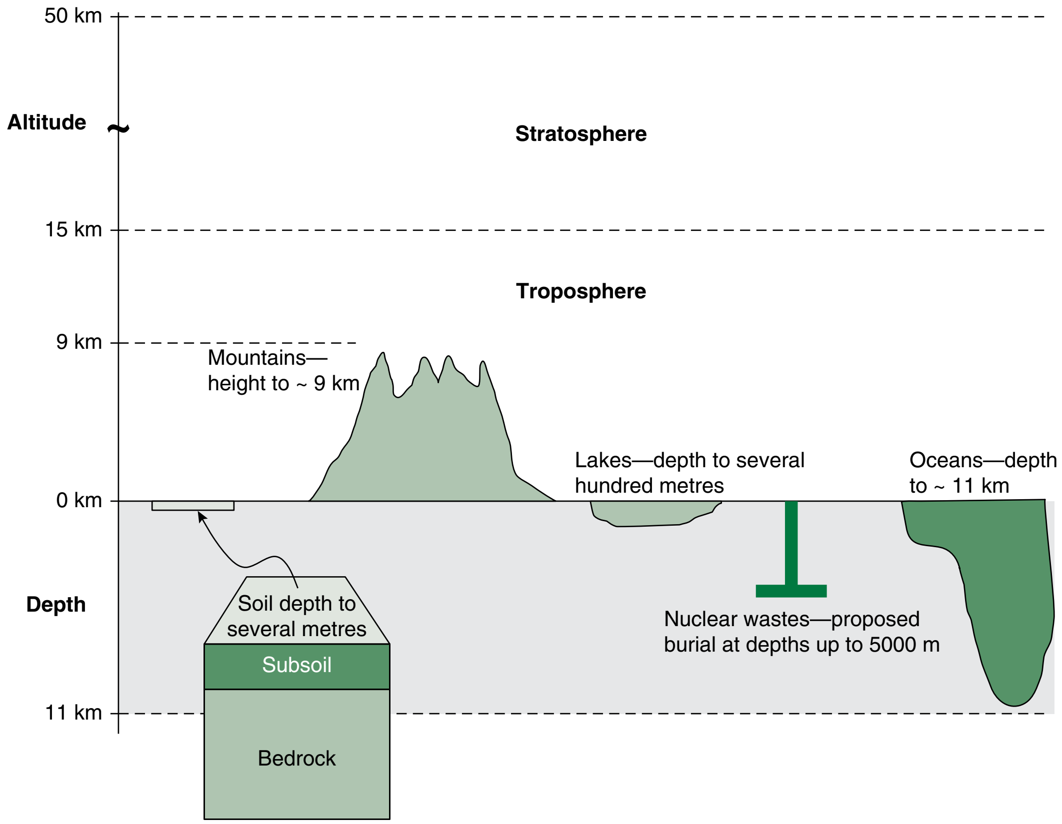


Fig. 1.1 The environment near the surface of the Earth.

Given this very broad concept of environmental chemistry, we must be clear about the physical extent of these surroundings. Beginning where humans live, we can move inward toward the centre of the Earth. We will find that, below a relatively thin layer of the Earth's crust, few chemical processes affect the environment, at least over a time-scale of years or even thousands of years. The layer may be as thin as a metre when considering many soil processes, ranging to tens of metres for lakes or a few kilometres for oceans and when considering the disposal of nuclear wastes. Even at its greatest, the layer is only a very small fraction of the 6380 km radius of the Earth (Fig. 1.1).

Moving outward into the atmosphere above the Earth's surface, there occur complex processes supported by and supporting Earth-bound reactions. Many of these processes take place at low altitudes but we know that chemical reactions at heights of 30 km or higher are critical to maintaining the Earth as it is.

Therefore, out of the total surroundings of the vast universe, a thin shell, perhaps 50 km in thickness, on and above the Earth's surface is the subject for most of what we say on the theme of environmental chemistry. Even these specified surroundings are very large and very complex—especially compared with the small, controlled systems with which chemists are usually involved in a laboratory. We will therefore frequently zero in on a more limited, defined portion such as the atmosphere of a building, water in a small lake, or a particular layer of soil, but when we do this we are really turning that part of the surroundings into a new system. We should never lose sight of the fact that each small part of the environment is connected with other parts and together they make an interrelated whole.

What this book is about

The book has been written to provide the chemical basis for understanding our surroundings, the global environment. Emphasis will be on the composition of the natural environment, the processes that take place within it, and the kinds of changes that come about as a result of human activities. Many examples will be used to illustrate the principles being described and these will be chosen from situations throughout the world, because environmental chemistry is indeed a global subject. Nevertheless, there are many important specific types of problems that, inevitably, will not be mentioned. It is not the goal of this book to provide a complete collection of all environmental issues, but our objective is to give a chemical background so that one can have a basis for understanding such issues.

Having said this, we must point out that there are several important subjects that the book will *not* cover in detail.

The book is not about *environmental analysis*, though almost every environmental topic discussed is based on information obtained by analysis. Often the quality of the discussion depends on the quality of the available data. For this reason, analytical chemistry is central to our understanding of the environment. And analysis is by no means straightforward. Determining ozone or nitrogen oxides in the stratosphere at an altitude of 25 km requires sophisticated instrumentation and interpretation. Finding the concentration of mercury that is available for uptake by fish in a body of water requires careful measurement and elegant reasoning related to the significance of the results. Environmental analytical chemistry is a large subject in its own right; it will be mentioned in examples and is the focus of some of our *literature links* (see later), but not as a separate subject in this book.

The book is not about *environmental toxicology*. One of the reasons—but by no means the only one—why twenty-first-century inhabitants of the Earth are so concerned about the environment is that its contamination and degradation inevitably have effects on human beings. The direct toxicological effects, the mechanisms by which they occur, and the quantitative aspects defining conditions under which organisms, particularly the human organism, are influenced by chemicals are the subjects of toxicology. In general, this book will be concerned with chemical behaviour external to specific organisms, although in several places we provide a brief discussion of basic toxicological principles, including factors affecting uptake and methods of assessing toxicity in the biosphere.

The book is not about *environmental control*—about detailed technologies for preventing or eliminating pollution, including important initiatives in 'green chemistry',[1] or about standards and laws that set guidelines and limits on levels of contaminants. These, too, are essential subjects for consideration if environmental science is to be more than a theoretical study. Where appropriate, we will document some important environmental guidelines and discuss technologies to achieve them. But for the most part, we will be concerned with the chemistry that underlies regulatory decisions and engineering design for control of pollution.

And, finally, the book is not about *environmental science* in its broadest sense. Books on environmental science attempt to cover the whole range of a topic, and they call on a large body of material from the sciences of climatology, geology, biology, and so on. To put any subject in context, we will open up some of the geographical, biological and historical perspectives but we will not dwell on them, important though they are.

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[1] Green chemistry is an important branch of chemistry and engineering that considers design of industrial chemical processes in the context of their environmental impacts. As such, it includes subjects like the use of benign materials in production, minimizing energy consumption, finding uses for by-products, and integrating processes, often in a cyclical manner. The goal of green chemistry is to carry out industrial activities in a way that reduces, even eliminates, adverse impacts of production on the environment.

1.2 Environmental composition

In learning about the chemistry of a particular element or compound in the environment, we usually begin by observing where it is found and measuring the concentrations that are present. Several questions must be considered. With what materials is the chemical associated? Are its concentrations normal or unusually high or low? Is it toxic? Then, if there are places where there are environmental problems due to high concentrations, we investigate the source of these elevated levels. Thallium provides an interesting example.

In the last decade, some considerable interest has developed around the environmental chemistry of thallium. This element has been described as enigmatic because of its somewhat surprising 'chemical personality'. While it is the heaviest element in group 13 of the periodic table, its most common oxidation state is thallium(I) and in many ways its chemistry is similar to that of the alkali metals. The environmental interest arises in part because it is toxic to aquatic organisms, humans, and other mammals. Being similar in behaviour to the alkali metals, it substitutes for potassium and causes metabolic disturbances by inhibiting the activity of important enzymes and coenzymes. Actually, in part because of its toxicity and also because it is colourless and tasteless, it has been considered to be 'the perfect poison'.

All this means that it is important to know about the occurrence of thallium: *what are normal levels in air, water, and soil, and where and why is it present in greater abundance in certain locations and situations?*

Thallium is a surprisingly common element, being widely and relatively evenly distributed in the natural environment with a global average in the Earth's crust of approximately 0.7 mg kg^{-1}. In the aqueous environment, the mobile thallium(I) is present in varying concentrations, but in uncontaminated sites the values are typically around 10 ng L^{-1} or less. With these 'background concentrations', areas that are subject to elevated levels can be identified. And this is what has been done in some instances:[2]

- Near coal mining operations in Nova Scotia, Canada, water levels of 20 µg L^{-1} and higher have been observed.
- Tailings from an abandoned gold mine in the same area have thallium concentrations up to 3.5 mg kg^{-1}.
- Soil concentrations averaging 20 mg kg^{-1} have been measured in the south-west of Guizhou Province, China in areas of thallium-rich minerals.

Measuring concentrations such as these is only the beginning of an environmental chemistry study, but it is often an essential beginning—one that forms the basis for deeper studies of processes and effects.

Species distribution

In many cases, it is helpful to go beyond measuring the total concentration of a particular element or compound in an environmental sample. Most substances can exist in more than one form, and a description of the species distribution for such substances is an important aspect of describing composition. In some instances, sophisticated analytical methods are used to distinguish between species in environmental samples. It is also possible to make use of distribution diagrams, of which there is a large variety of types, as an aid to evaluating species distribution. Figures 1.2 and 1.3 give examples of such diagrams for carbonate species and mercury in water.

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[2] Cheam, V., Thallium contamination of water in Canada, *Water Qual. Res. J. Canada*, **36** (2001), 851–77; Wong, H.K.T., A. Gauthier, and J.O. Nriagu, Dispersion and toxicity of metals from abandoned gold mine tailings at Goldenville, Nova Scotia, Canada, *Sci. Total Environ.*, **228** (1999), 35–47; Zhang, Z., B. Zhang, J. Long, X. Zhang, and G. Chen, Thallium pollution associated with mining of thallium deposits, *Sci. China* (Series D), **41** (1998), 75–81.

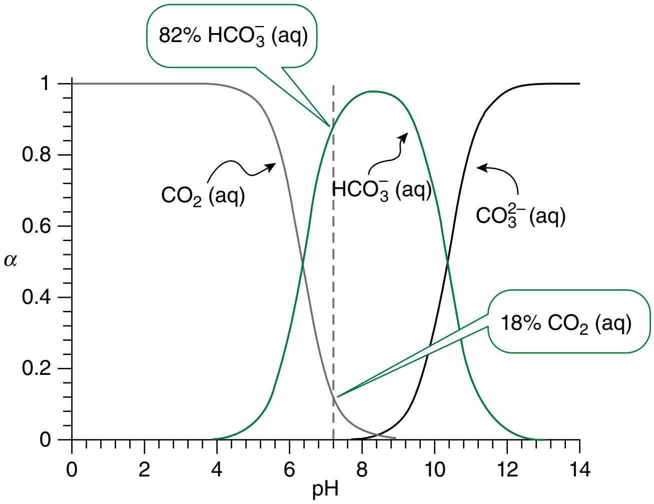

Fig. 1.2 Distribution of carbonate species as a function of pH. The α value is the fraction of a particular species, $\alpha = \frac{[\text{individual species}]}{[\text{sum of all species}]}$.

In the case of the carbonate system, the distribution is plotted as a function of pH of the water, while for mercury its composition is plotted against the chloride ion concentration. The diagrams are therefore limited by the variables that are chosen for their calculation.

Distribution diagrams are based in part on analytical data, both for concentrations of particular species in environmental samples and also for thermodynamic equilibrium constants of a variety of types. The carbonate diagram, for example, depends on knowing the association constant for aqueous carbon dioxide and water, as well as the acid dissociation constants for carbonic acid. The validity of a distribution diagram therefore depends on the availability and quality of appropriate thermodynamic data, and also on the very important (and problematic) assumption that a particular natural system is at thermodynamic equilibrium.

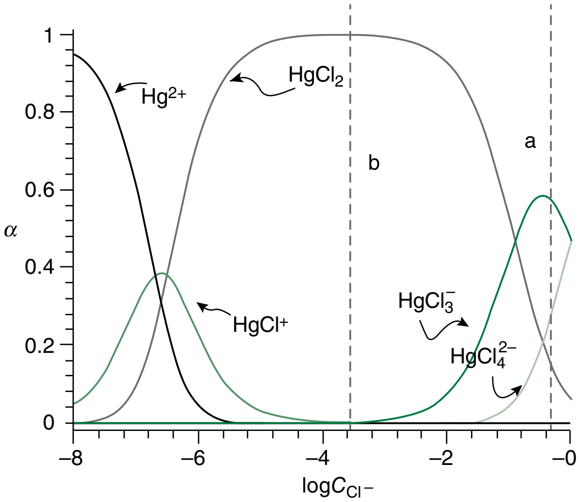

Fig. 1.3 Distribution of mercury chloro species in water as a function of chloride ion concentration, C_{Cl^-} (mol L^{-1}). The α value is the fraction of mercury in the form of a particular complex.

We can use these diagrams to estimate the fraction of individual species under particular conditions such as at a given pH. On Fig. 1.2, calculations show that the vertical line drawn at pH 7 intersects the carbon dioxide curve at $\alpha = 0.18$ and the hydrogen carbonate curve at $\alpha = 0.82$. At this pH, therefore, aqueous carbon dioxide makes up about 18% of all carbonate species, hydrogen carbonate about 82%, while carbonate is a negligible fraction.

The vertical line (a) on Fig. 1.3 refers to the oceans, which have a total chloride concentration of 0.56 mol L^{-1}. The $HgCl_4^{2-}$ is seen to make up 28% of mercury species, with $HgCl_3^-$ at 56% and $HgCl_2$ at 16%. Line (b) corresponds to well water with a chloride ion concentration of 9.5 ppm, where the only significant species of mercury is $HgCl_2$.

The species distribution of an element controls its behaviour in the environment and may be a major factor affecting biological availability. With thallium, in water its most common species is the soluble and mobile thallium(I) ion but, if it is oxidized to thallium(III), it is found mostly as insoluble colloidal species from which a portion may settle into the sediment.

In the case of mercury, in the aqueous environment it exists as inorganic species in the 0, +1, and +2 oxidation states depending on redox and other conditions. However, the major species found in fish is partially methylated mercury, CH_3Hg^+, which is produced in sediments by a variety of microbiological processes. This species is toxic both to the fish and to other animals (including humans) that may consume the fish. It is clearly important, then, to be aware not only of how much mercury is present in a sample, but also of the distribution of forms of the element in that sample.

1.3 Chemical processes

Knowledge of the composition of a particular compartment of the environment is a starting point for a description of environmental chemistry. However, if we stop there, we imply that the system is static, which, of course, is not true. There are many processes—physical, chemical, and biological—that operate within and connect the various components. The processes may be completely 'natural' and, in fact, over the geological time-scale, it is such processes that have contributed to making the Earth the way it is. Therefore, a second phase of developing understanding of environmental chemistry is to learn about the chemical reactions that are a part of the environmental processes.

In order to summarize the broad features of reactions involving environmental species, we will find it useful to think of the environment in terms of four principal compartments—the atmosphere (the gaseous environment), the hydrosphere (the liquid, essentially aqueous environment), the terrestrial (solid) environment, and the biosphere (the living environment). At first glance, these categories appear to be quite clear-cut; however, it will become evident that there are many overlapping areas. For example, we usually think of soil as part of the terrestrial environment, but the chemical behaviour of soil solutions and soil gases plays a major role in determining the environmental characteristics of soil itself. Concerning the compartments, we can then describe chemical processes within each, and also reactions that bring about transitions from one to the other.

Figure 1.4 shows a simple diagrammatic representation of the global water system and its relation to the various compartments.[3] Strictly speaking, most of the processes shown in this example are physical in that they involve phase changes, not chemical reactions, but the form of the diagram is similar to those constructed to show environmental chemical relationships.

The figure allows us to obtain an overview of the relations between the various forms of the substance. It also shows the cyclic nature of many natural processes. In the steady state, the parts of the cycle are balanced so that concentrations remain constant. This enables us to calculate residence times. In the water cycle, the total mass of water at any time in the atmosphere is approximately 1.3×10^{16} kg. The inward flux is 4.23×10^{17} and 7.29×10^{16} kg y^{-1} by

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[3] The form of this diagram will be used for other systems. For an example, see Fig. 14.11.

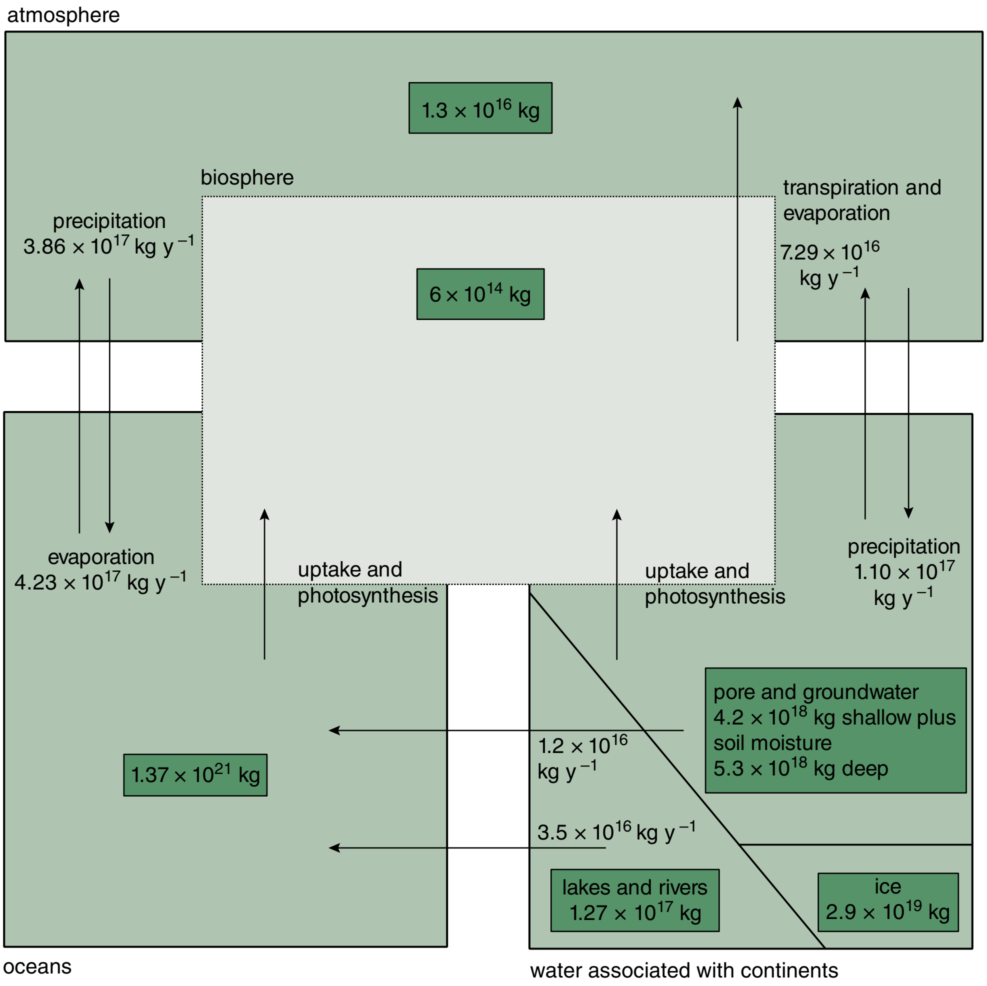


Fig. 1.4 The water cycle. Boxed values in kg are total amounts in the given compartment. Values in kg y^{-1} are fluxes or movement from one compartment to another. (Values taken from a number of sources and reported in Berner, E.K. and R.A. Berner, *The global water cycle*, Prentice Hall, Inc., New Jersey; 1987.)

evaporation from oceans and land-based water, respectively. This is balanced by outward fluxes of 3.86×10^{17} and 1.10×10^{17} kg y^{-1} precipitation onto the ocean and land. Therefore the total inward and outward flux is 4.96×10^{17} kg y^{-1} and the residence time of water in the atmosphere is determined as shown in Example 1.1.

Example 1.1 **Calculation of residence time**

$$\tau = \text{residence time} = \frac{\text{steady state amount}}{\text{flux (in or out)}}$$

$$= \frac{1.3 \times 10^{16}\,\text{kg}}{4.96 \times 10^{17}\,\text{kg}\,\text{y}^{-1}} = 0.0262\,\text{y} = 9.6\text{ days}$$

This is the average time that a molecule of water spends in the atmosphere.

The box model cycle illustrated in Fig. 1.4 provides an overview of the major processes interconnecting compartments of the global water ecosystem, and may also allow for identification of important reactions within a single compartment. But there are many details involving

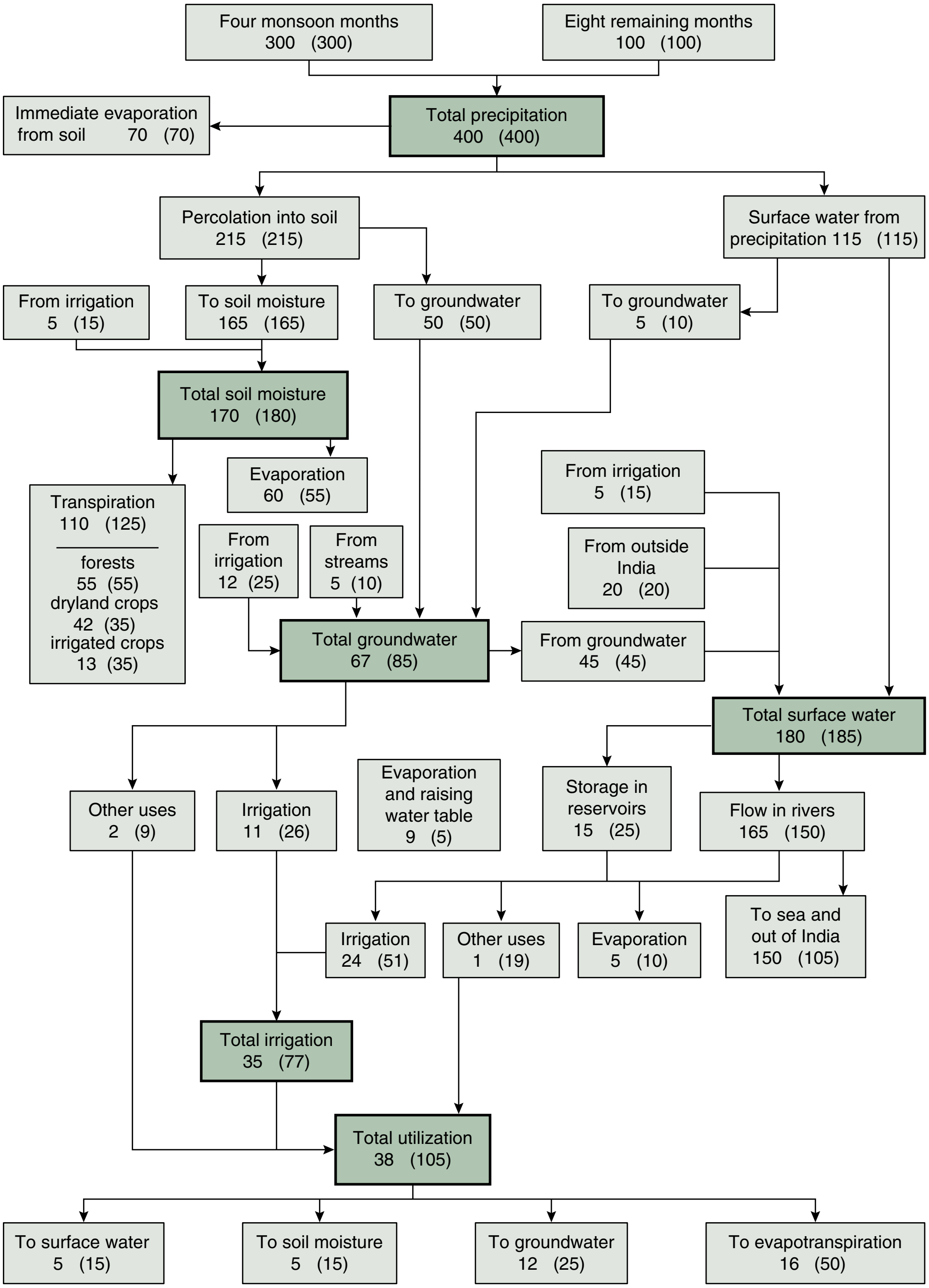


Fig. 1.5 Water resource flux in India. Values given are in million hectare metres—a hectare metre is the volume of water required to cover 1 ha (10 000 m^2) to a depth of 1 m. This is a volume of 10^4 m^3 or a mass of approximately 10^7 kg. The first numerical figure of each pair is a value for 1974; the second, in parentheses, is an estimate for 2025. (Centre for Science and Environment, *The state of India's environment: a citizen's report*, India; 1978.)

specific reactions that are essential to completing the picture. As an example, a comprehensive description of water resource distribution in India is provided in Fig. 1.5. This shows details of the fate of water supplied by precipitation each year in that part of the subcontinent.

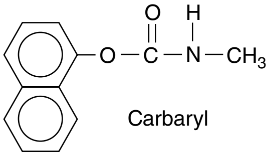
The information contained in such a diagram along with appropriate chemical data could be used, for example, in developing a complete picture of water used for irrigation. We shall see later that irrigation is the major consumer of water on a global scale. The combined qualitative and quantitative data allow for estimating fluxes of individual chemicals—a requirement for evaluating sustainability of the water resource in agriculture. With reference to Fig. 1.5, there are two terms, *source* and *sink*, that are important and relevant to this and other environmental discussions. The *source* of all water in India is rainfall as is shown at the top of the diagram. There are several *sinks*, that is, the 'final' fate of the water after it has gone through a variety of processes. In this case, the sinks are identified as surface water, groundwater, soil moisture, and evapotranspiration.

Generating a valid description of environmental processes involves moving back and forth between the general, broad picture with its global context, and the particular detailed delineation of specific chemical reactions. Studies in both these areas contribute to our knowledge of the subject. One of the challenges of environmental chemistry is to bring together the general and the particular.

1.4 Anthropogenic effects

A third aspect of a study of environmental chemistry is to examine the effects of human (anthropogenic) activities on the natural processes which are always ongoing. The anthropogenic effects may be catastrophic, usually in a localized area, and are then referred to as disasters. A tragic example was the uncontrolled release of toxic methyl isocyanate (MIC) gas near Bhopal, in central India in 1984.

In the early morning of 3 December 1984 just outside the city of Bhopal in central India, there was a massive release of four tonnes of MIC (CH_3–N=C=O) gas from a storage tank at the Union Carbide plant where the chemical had been manufactured since 1980. The dense gas floated across the surrounding landscape killing more than 3800 persons and leaving at least 300 000 affected by exposure—some severely.



Carbaryl

MIC is a starting material for the manufacture of the widely used carbamate pesticide, carbaryl, and was stored under refrigeration in an underground tank at the Bhopal plant site. A combination of technological problems—failure of the cooling unit, leakage of water into the tank, loss of nitrogen pressure above the MIC, and failure of several safety devices—was the immediate cause of the accident. But there were political, organizational, and human factors that provided a setting in which the multiple failures could occur simultaneously.[4] This tragic event is not unique but fortunately no spills or releases with such massive and deadly consequences have occurred in more recent years. In part this is due to adoption of voluntary programmes of *responsible care* by some members of the chemical industry.

Other environmental perturbations are more gradual and the effects may show up only in the medium or long term. This does not imply that the consequences are any less serious. For example, the possibility of global warming due to build-up of greenhouse gases in the troposphere

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[4] A detailed account of the story of this, the worst industrial crisis in history, is given in Shrivastava, P., *Bhopal, anatomy of a crisis*, Ballinger Publishing Co., Cambridge, Massachusetts; 1987.

is of great concern with respect to life throughout the planet in the twenty-first century. Should adverse consequences due to global warming become a reality, its reversal, even if possible, could take as long a period of time as its advent.

In considering the potential effects of anthropogenic inputs into the environment, we make use of our knowledge of both the composition and the process data.

An example comes from consideration of the possible problems associated with the use of sewage sludge from municipal wastewater-treatment facilities as an amendment/fertilizer on soils used for agricultural purposes. This is a widely followed practice that has beneficial aspects as it supplies organic matter and small amounts of major and minor nutrients to the soil. One of the concerns regarding the practice is that potentially toxic concentrations of certain metals that are present in the sludge can be taken up by plants and incorporated in the food chain. Cadmium is one element of interest in this regard. Soils have a range of natural cadmium concentrations with a typical value being approximately 0.8 $\mu g\ g^{-1}$. Of the cadmium, it is thought that most is present as inorganic mineral species associated with the clay mineral phase of the soil. Sewage sludge is a variable and heterogeneous material but a typical cadmium concentration is 80 $\mu g\ g^{-1}$, some one hundred times greater than that of the soil itself. In considering whether additions of sludge to soil initiate a cadmium toxicity problem, the amount of sludge added becomes an issue as it will define the final concentration. Consideration of the form of cadmium in the sludge—it will probably be bound with the organic matrix—is also important. Finally, the geochemical and biochemical reactions that the added cadmium must undergo will be considered. These will include interconversions between various inorganic and organic species of the element in the soil, leaching of soluble forms, immobilization by ion exchange or other adsorption processes on the solid soil phases, and biological uptake by micro- or macro-organisms (Fig. 1.6).

The ultimate fate of the added cadmium depends on the extent of the individual reactions, how each process affects the others, and the ways in which a changing environment can alter the balance.

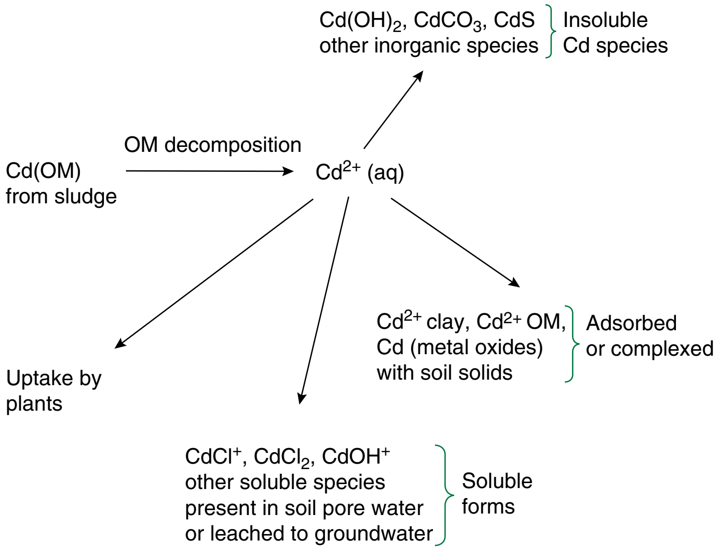

Fig. 1.6 Cadmium biogeochemical reactions in soil after addition as a trace component in sewage sludge. OM, Organic matter.

1.5 Content of the chapters

Basic principles and examples

This book is divided into three main sections: the atmosphere—the air that we breathe; the hydrosphere—the water that supports all manner of life; and the terrestrial environment—the land that is the source of so many resources. But, it is important to remember that these are all part of the one, integrated global environment; features within each part overlap and dynamic interactions within and among the various compartments are always ongoing. For this reason, you will find, for example, that many issues discussed in the hydrosphere section (especially Chapters 12, 14, and 15) are equally relevant to the terrestrial environment. There are many other cases where material in one section or chapter applies equally to other parts of the book. Keep the overlapping connections in mind as you work your way through the book. To assist in doing this, when you are only part way through your reading, it may be good to read the final chapter (Chapter 21). This will help you to see how all these ideas fit into the global picture.

Literature links

In all the chapters, there are descriptive material, data, and example problems from around the world, along with other resource suggestions and problems to solve. In addition, in each chapter we have also chosen to highlight and summarize a recent research investigation in environmental chemistry; these investigations come from research groups all around the world. Each description, which we call a *Literature link*, is based on a paper that has been published in a readily accessible research journal since 2005. The subject of environmental chemistry is a very active one and we encourage you to delve into the original papers; this will give you a sense of the exciting challenges that are encountered in this field of science—challenges in obtaining data, in interpreting it in the context of the specific area studied, and in fitting the information and interpretation into the global picture of how the Earth's environment functions. As you read each link, also think about how the research relates to the principles introduced in that chapter.

Think about this

Scattered throughout the chapters are a number of boxes entitled *Think about this*, where we make a brief statement or pose a question related to the subject being discussed. In some cases we provide suggestions or hints to guide your thinking, or an answer to the question. But usually we leave things in an open-ended way, seeking to encourage you to search elsewhere or come up with your own ideas. For example, we might have asked you, in considering Figure 1.3, to think about how the form of mercury dissolved in a river might change as the river flowed into the ocean. You would know that the key feature here is that chloride levels would change from a very low level to the concentration found in sea water (0.561 mol L^{-1}, see Appendix B.1). Therefore, the mercury species change might correspond to moving from line b (fresh water) to line a (sea water) on the figure, so the principal species would change from $HgCl_2$ to a mixture of $HgCl_3^-$, $HgCl_4^{2-}$, and $HgCl_2$.

Fermi questions

Throughout the book, you will also encounter what are called *Fermi questions*.[5] These are questions that are unlike the calculations in the examples or the problems given at the end of each chapter, which are ones that usually require very specific and well-known procedures,

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[5] Fermi questions receive their name from Enrico Fermi, an Italian physicist who was instrumental in the development of quantum theory. Fermi questions make use of fundamental general knowledge, estimation and quantitative reasoning, communicating in simple mathematics, and questioning skills. Fermi questions encourage the use of different, sometimes non-traditional, approaches and emphasize the problem-solving process rather than the answer.

information or data in order to determine a result. A Fermi question requires a different approach. For Fermi questions, 'back-of-the-envelope' type calculations make use of rough estimates of background information along with intuition and reasoning to come up with a very approximate but reasonable suggested conclusion. There is no 'correct answer' and a discussion is always necessary in order to make clear one's thinking and strategy. Below is our first Fermi question. As an example, we provide a suggested answer in this initial case.

Fermi question

What volume of fuel would be consumed during the morning 'rush hour' of a typical large-sized North American city? What impacts would this have on the local environment? How would this situation compare to that in a city of similar size in Africa?

- We begin by choosing a reasonable 'large size'—say 2 million. Of this total population, about 40% could be either very young or older and retired and therefore unlikely to be driving during rush hour.
- We could estimate that half of the other 60% might be driving during rush hour—to work, transporting children to school, or for other purposes. In addition, there will be trucks and other commercial vehicles—say 100 000. Therefore, the total number of vehicles on the road $= 2 \times 0.6 \times 0.5 = 0.6$ million cars $+ 0.1$ million others.
- A reasonable, but perhaps low, estimate of a one-way commute would be 15 km. Total distance driven $= 0.7 \times 15$ km $= 10.5$ million km.
- An average fuel mileage (mixture of car sizes) might be 10 km per L. Total fuel = 1 100 000 L, around one million litres.

Emission of particulates and several gases from the exhaust of all vehicles contributes to poor air quality in the local environment. These will be described in detail in Chapter 4.

In Africa, in most cases the number of vehicles and distances travelled are much smaller, but there will be major differences between cities. For example, Cairo has a large population of cars while the number in Kinshasa is much smaller. Other features that will affect air quality are the climate and the type of vehicles, engines, and fuel. All of these are significantly different in most parts of Africa from the situation in the USA.

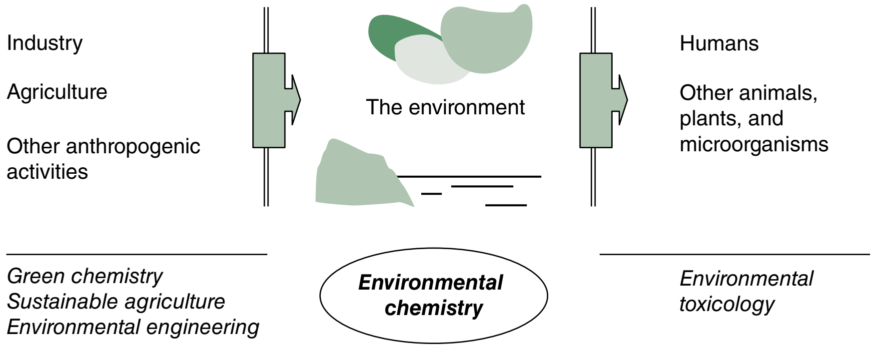

Fig. 1.7 Environmental chemistry, in the centre of the diagram, is concerned with the chemical nature, processes, and anthropogenic influences that take place in the atmosphere, the hydrosphere, and the terrestrial environment. Other branches of environmental science are directed more specifically toward the control and regulation of potentially harmful agents or to understanding how these agents affect living organisms.

Environmental chemistry

In summary, the subject matter in this book covers the chemistry of surroundings, the environment on and near the Earth's surface. These surroundings include air (the atmosphere), water (the hydrosphere), and land (the terrestrial environment), all filled with life of many kinds, and we will deal with them in that order.

In considering particular environmental subjects, we focus on the basic chemistry and to do this it is necessary to examine some or all of the three factors—composition, chemical processes, and perturbations caused by natural or anthropogenic activities—that we have discussed above (Fig. 1.7). Although a systematic approach requires that individual topics be studied in isolation, the overlap, the connections, and the interdependence must always be kept in mind. Perhaps most important, as citizens of the Earth, while we are studying this vast subject, we should remember that we share together a single global environment.

ADDITIONAL RESOURCES

1. Baird, C. and M. Cann, *Environmental chemistry*, 4th edn., W.H. Freeman and Co., Salt Lake City, Utah; 2008.
2. Eby, G.N., *Principles of environmental geochemistry*, Brooks/Cole-Thomson Learning, Pacific Grove, California; 2004.
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4. Spiro, T.G. and W.M. Stigliani, *Chemistry of the environment*, 2nd edn., Prentice Hall, Upper Saddle River, New Jersey; 2003.
5. Sawyer, C.N., P.L. McCarty, and G.F. Parkin, *Chemistry for environmental engineering and science*, 5th edn., McGraw Hill Companies, New York; 2002.
6. The United Nations Environment Programme, *UNEP Yearbook 2009*, EARTHPRINT Ltd, Stevenage, UK; 2009.
7. The United Nations Environment Programme, *Global Environment Outlook 6 (GEO-6):* http://web.unep.org/geo/, accessed November 2016.

   The following two resources are online materials (course notes, videos etc.) provided for courses on environmental chemistry given at two American universities.
8. Chemistry Department, *Environmental Chemistry CH390*, Oregon State University, http://oregonstate.edu/instruct/ch390/, accessed August 2016.
9. Foust, R. *Environmental chemistry*, Northern Arizona University, 2007, http://www2.nau.edu/~doetqp-p/courses/env440/env440-2/index.htm, accessed August 2016.

Part A

The Earth's atmosphere

When you understand all about the Sun
and all about the atmosphere
and all about the rotation of the Earth
you may still miss the radiance of the sunset.
A. N. Whitehead, 1926

Chapter 2

The Earth's atmosphere

The focus of this chapter is on the fundamental concepts needed to understand chemical processes that occur in the atmosphere—processes that will be examined in more detail over the next several chapters. We will accomplish this by:

- describing the physical nature of the atmosphere, its structure and composition, and the important role played by solar radiation in defining these features;
- providing basic concepts that will be used in later chapters to describe important chemical processes related to ozone, smog, acid precipitation chemistry, atmospheric aerosols, urban and indoor air, and global climate;
- reviewing fundamental physical chemistry properties of gases;
- introducing gas-phase reactions along with related thermodynamic and kinetic calculations, and including photochemical reactions as well as the extremely important category of free radical reactions.

2.1 The Earth's atmosphere—the air we breathe

Of the planets in the solar system Mercury, nearest the Sun, has almost no atmosphere. The next three planets, Venus, Earth, and Mars, lost whatever gases were present at their formation and the atmospheres they now possess arise from gases released from their interiors and reactions that these have undergone. The atmosphere of each planet is unique. The outer planets have extremely dense atmospheres made up mostly of hydrogen and helium, little changed from the original composition at the time of formation.

The Earth's atmosphere is a thin shell of gases surrounding the globe. The thinness becomes clear when we realize that the part of the atmosphere in which all human activity takes place adds less than 0.3% to the radius of the Earth. Its unique chemistry, including compounds such as oxygen (molecular oxygen or dioxygen) and carbon dioxide that support the processes upon which all forms of life depend, distinguishes this atmosphere from that of other planets in the solar system. Table 2.1(a) shows the relative amounts of the four most abundant gases in the dry atmosphere. The trace gases are shown in Table 2.1(b).

The mixing ratios (concentrations, see Section 2.3) of the major gases remain relatively constant up to an altitude of about 80 km. The constancy arises because the kinetic energy of these molecules is sufficient to overcome any gravitational forces that would lead to settling. Because the mixing ratios of the major components are constant, the average molar mass, $\overline{M}_a$, of the atmosphere can be calculated.

Table 2.1(a) Major components of the atmosphere near the surface of the Earth.[a]

Component	Mixing ratio / %	/ ppmv
Nitrogen	78.08	780 800
Oxygen	20.95	209 500
Argon	0.93	9300
Carbon dioxide[b]	0.0402	402

[a] Concentrations (mixing ratios, a term that is defined in Section 2.3) are calculated on a dry atmosphere basis. The water content is a fifth major component, but its concentration is variable, ranging from <0.5 to 3.5%.
[b] https://www.co2.earth/, accessed September 2016.

Table 2.1(b) Minor components of the atmosphere near the surface of the Earth.[a]

Component	Mixing ratio / %	/ ppmv
Neon	0.0018	18
Helium	0.0005	5
Methane	0.000183	1.83
Hydrogen	0.000053	0.53
Nitrous oxide	0.0000328	0.328

Example 2.1 The average molar mass of air in the lower atmosphere

$$\bar{M}_a = M_{N_2} \times f_{N_2} + M_{O_2} \times f_{O_2} + M_{Ar} \times f_{Ar} + M_{CO_2} \times f_{CO_2} \qquad (2.1)$$

where M and f refer to the molar mass and fractional abundance, respectively, of each component. Applied to the regions below 80 km of the Earth's dry atmosphere,

$$\begin{aligned}\bar{M}_a &= 28.01\,\mathrm{g\,mol^{-1}} \times 0.7808 + 32.00\,\mathrm{g\,mol^{-1}} \times 0.2095 + 39.95\,\mathrm{g\,mol^{-1}} \\ &\quad \times 0.0093 + 44.01\,\mathrm{g\,mol^{-1}} \times 0.000402 \\ &= 28.96\,\mathrm{g\,mol^{-1}}\end{aligned}$$

It should not be surprising that the molar mass is close to, but somewhat greater than, that of pure N_2.

Above about 80 km altitude, the concentrations of the major species do begin to change significantly due to photochemical processes that cause dinitrogen and especially dioxygen to dissociate. These processes will be discussed later in this chapter.

In contrast to the major species of gases in the troposphere, the concentrations of some trace gases vary considerably. Reactive gases such as NO_2 and SO_2, the precursor compounds for acid precipitation (Chapter 5) persist for only hours to days and their tropospheric mixing ratios (in the ppbv range) are not constant as they are dependent on local sources. Other trace gases such as volatile organic compounds (VOCs) or volatile/semi-volatile persistent organic pollutants (POPs) (Chapter 4) vary within a hemisphere due to their sources, distribution by air currents, and oxidative removal processes. Finally trace gases such as CH_4, N_2O (Table 2.1b), and chlorofluorocarbons (CFCs) have long atmospheric lifetimes and therefore show relatively constant compositions around the globe. More will be discussed about these gases in Chapter 8 along with carbon dioxide.

Regions of the atmosphere

The atmosphere can be conveniently divided into four sections based on the direction of temperature change as one proceeds from lower to higher altitudes. The pattern is clearly shown as the zigzag line on Fig. 2.1. Beginning at the Earth's surface where the temporally and spatially averaged temperature is approximately 17°C (290 K), the atmospheric temperature falls steadily to a value of about –60°C (213 K) at an altitude of approximately 15 km. This part of the atmosphere closest to the Earth's surface, in which humans live and most biological activity occurs, is called the troposphere.

Regions of the Earth's atmosphere...		**'with increase in altitude...'**
• Troposphere	~ 0–15 km	Temperature decreases
• Stratosphere	~ 15–50 km	Temperature **increases**
• Mesosphere	~ 50–85 km	Temperature decreases
• Thermosphere	~ 85–500 km	Temperature **increases**

The troposphere, a region of intense convective mixing, contains approximately 85% by mass of the entire atmosphere. The upper boundary of the troposphere, the tropopause, marks the altitude at which the direction of temperature change reverses. Above this, the next region is called the stratosphere where increasing altitude brings increasing temperature up to approximately –2°C (271 K) at 50 km, the stratopause; such a temperature profile is called an inversion. Due to the rising temperature and decreasing density with increasing altitude, there is little convective mixing and the stratosphere is a relatively stable region. At the stratopause, there is a second reversal in temperature and in the mesosphere, the region above, temperature decreases with altitude to –90°C (183 K) at 85 km, the mesopause. Continuing above this height, the temperature once more begins to increase in a region called the thermosphere, reaching a value of about 1200°C (1473 K) at 500 km. These and other features of the atmosphere are shown in Fig. 2.1.

In rarefied atmospheres it is important to be aware that we are referring to *thermodynamic* temperatures, which are measures of the kinetic energy of molecules in the atmosphere. At high altitudes, if we were to use a conventional mercury thermometer to measure temperature, the reading would be much lower than 1200°C (1473 K) as the number of (highly energetic) collisions of gas molecules with the thermometer would be very small under the near-vacuum conditions.

Atmospheric pressure

Atmospheric pressure, P°, is measured by the force of gravity acting on the atmosphere, divided by the total area of the Earth's surface, as calculated by eqn 2.2,

$$P^\circ = \frac{M_{\text{atm}}\, g}{4\pi r^2} \tag{2.2}$$

where P° is the pressure at the Earth's surface (sea level) = 101 325 Pa, M_{atm} is the mass (in kg) of the atmosphere, g is the acceleration due to gravity = 9.81 m s^{-2} (this is approximately constant since most of the atmosphere is near the Earth's surface), and r is the radius of the Earth = 6.37×10^6 m.

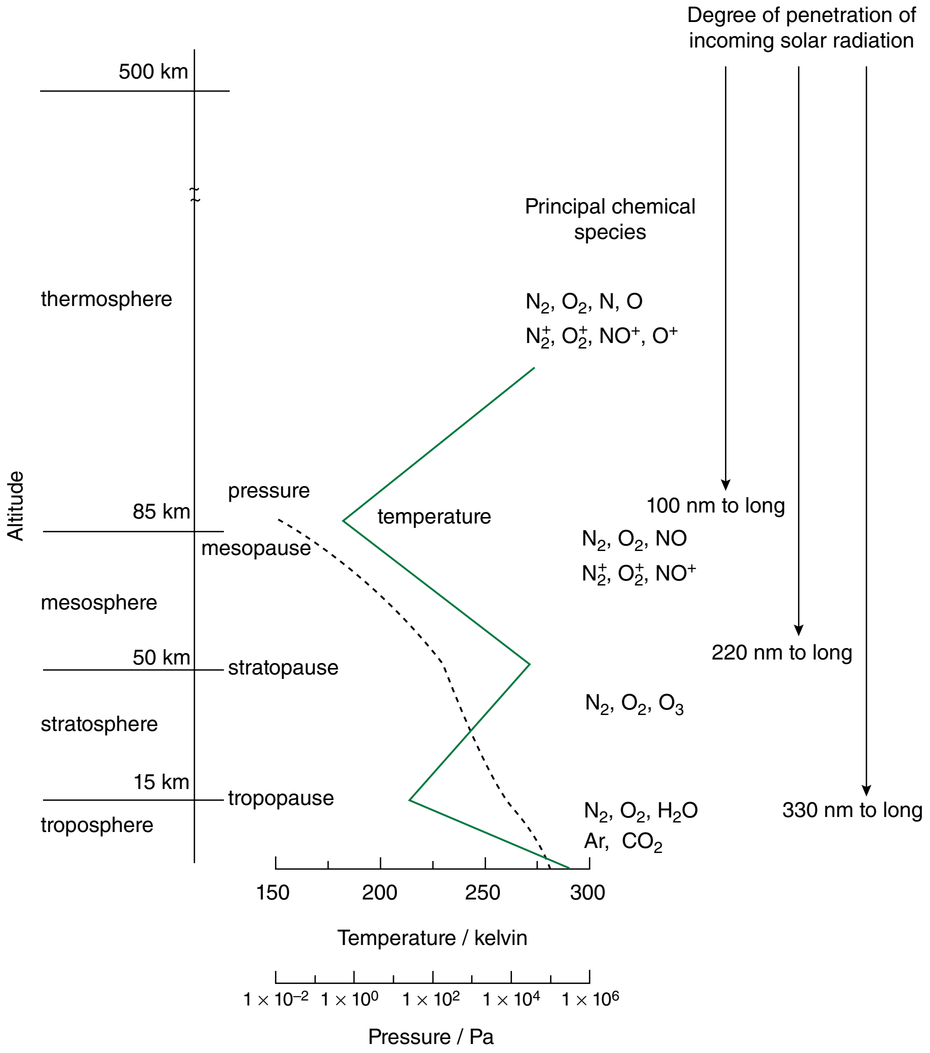

Fig. 2.1 The regions of the atmosphere showing temperature and pressure variations, principal chemical species, and penetration of incoming solar radiation. Solid line, temperature; dashed line, pressure. 0°C = 273 K.

Equation 2.2 can then be rearranged to calculate the total mass of the atmosphere:

Pa = kg $\text{m}^{-1}\ \text{s}^{-2}$

$$M_{\text{atm}} = 101\,325\ \text{Pa} \times 4 \times 3.14 \times (6.37 \times 10^{6}\ \text{m})^{2}/9.81\ \text{m s}^{-2}$$

$$M_{\text{atm}} = 5.27 \times 10^{18}\ \text{kg}$$

Solving, we obtain a mass of 5.27×10^{18} kg for the atmosphere. We will make frequent use of this value.

Think about this
What is the total mass of air in the room where you are now located?

Like temperature, pressure also changes with altitude but it undergoes a nearly steady decrease described by the equation

0.0290 kg mol^{-1} (or 29.0 g mol^{-1} if height is in km)

all units in exponential term cancel

$$P_h = P^\circ e^{-\overline{M}_a g h / RT} \qquad (2.3)$$

height in m (or km if M is in g mol^{-1})

where, in this equation, P_h = pressure at given altitude / Pa, P° = pressure at sea level = 101 325 Pa, h = altitude / m, g = acceleration due to gravity = 9.81 m s^{-2}, $\overline{M}_a$ = average molar mass of atmospheric molecules = 0.0290 kg mol^{-1}, R = gas constant = 8.314 J mol^{-1} K^{-1}, and T = temperature / K. Note that an identical numerical result would be obtained if, simultaneously, altitude is expressed in km and molar mass in g mol^{-1}.

Knowing pressure means that with a defined volume we are able to calculate total moles (or individual moles of particular species) at any altitude using the ideal gas law ($PV = nRT$).

Think about this

What is the atmospheric pressure at the tropopause (~15 km) and how many grams of oxygen are in 1 m^3, compared with that at the Earth's surface?

$$\text{P}_\text{h} = 101\,325 \text{ Pa} \times e^{-29.0 \times 9.81 \times 15/8.314 \times 213} = 9103 \text{ Pa}$$

$$n = PV / RT$$

$$n = 9103 \text{ Pa} \times 1 \text{ m}^3/8.314 \text{ J mol}^{-1}\text{K}^{-1} \times 213 \text{ K} = 5.14 \text{ mol (total)}$$

$$\text{moles of O}_2 = 0.2095 \times 5.14 \text{ mol} = 1.077 \text{ mol O}_2$$

$$\text{mass of O}_2 = 1.077 \text{ mol} \times 32.00 \text{ g mol}^{-1} = 34.5 \text{ g O}_2 \text{(in 1 m}^3 \text{ at 15 km)}$$

The atmospheric pressure at the tropopause is about one eleventh the pressure at the surface of the Earth and there is only 34.5 g/m^3 of oxygen compared with 279 g/m^3 (at 20°C) at the Earth's surface.

Because temperature appears in the denominator of the exponential term, there are small changes in slope of the pressure *versus* altitude curve within the different regions of the atmosphere and this is shown graphically in Fig. 2.1.

Main point 2.1 On the basis of the direction of temperature change with increasing altitude, the atmosphere is divided conceptually into four regions—the troposphere, stratosphere, mesosphere, and thermosphere. The relative amounts of the major gases remain constant for the first 80 km but, as indicated by the decreasing pressure with increasing altitude, the absolute amount of each gas decreases.

2.2 Solar influence on the chemical composition of the atmosphere

In order to understand the chemical composition of regions in the atmosphere it is convenient to begin with the thermosphere and proceed in a direction toward the Earth. At high altitudes, there is a near vacuum: at an altitude of 100 km (in the lower thermosphere), the pressure is approximately 0.025 Pa. This means that the concentration (molecules per unit volume) of all chemical species is only about one four-millionth of that at the Earth's surface (101 325 Pa / 0.025 Pa). As this region is on the outer fringe of the atmosphere, atoms and molecules are exposed to a full solar spectrum, including radiation in the ultraviolet (UV) region. This is high-energy radiation; for example, radiation of wavelength 100 nm, has associated energies calculated as follows.

Example 2.2 **Energy of 100 nm electromagnetic radiation**

For one photon,

speed of light

$$E = h\nu = \frac{hc}{\lambda} = \frac{6.6\times10^{-34}\,\mathrm{J\,s}\times3.0\times10^{8}\,\mathrm{m\,s^{-1}}}{100\times10^{-9}\,\mathrm{m}} \qquad (2.4)$$

$$= 2.0\times10^{-18}\,\mathrm{J\ per\ photon}$$

and thus, for 1 mol of photons,

sufficient to break N_2 triple bond

$$E = 2.0\times10^{-18}\times6.0\times10^{23} = 1200\ \mathrm{kJ\ mol^{-1}}$$

1200 kJ mol^{-1} of energy is associated with radiation having a 100 nm wavelength.

Note: the notation $h\nu$ is used to represent energy (E), at a specified wavelength (λ), associated with a single photon in a photochemical reaction, (Planck's constant (h) multiplied by frequency (ν)). When multiplied by Avogadro's number, as shown in the calculation above and used below in various reactions, $h\nu$ then represents one mole of photons.

Such high energies are capable of bringing about dissociation of dinitrogen and dioxygen into their constituent atoms, and this occurs to a large extent in the thermosphere.

$$N_2 + h\nu\ (\lambda \le 126\,\mathrm{nm}) \rightarrow 2N \qquad \Delta H^\circ \ge 945\,\mathrm{kJ\ mol^{-1}} \qquad (2.5)$$

$$O_2 + h\nu\ (\lambda \le 240\,\mathrm{nm}) \rightarrow 2O \qquad \Delta H^\circ \ge 498\,\mathrm{kJ\ mol^{-1}} \qquad (2.6)$$

As shown, the energy required for dissociation in these two cases corresponds to electromagnetic radiation with $\lambda \le 126$ nm and $\lambda \le 240$ nm, respectively. Some dissociated atoms remain in the atomic form while others recombine, and new species such as NO are also produced in the thermosphere. The relative proportion of atoms to molecules increases with altitude and at 120 km the concentration of oxygen atoms approximately equals that of dioxygen molecules. A substantial portion of nitrogen, but less than that of oxygen, is also present as atoms. Because much of the oxygen and nitrogen gases are in the atomic form, the average molar mass, $\bar{M}_a$, becomes smaller than the value of 28.96 g mol^{-1} that obtains in the lower atmosphere.

Besides breaking bonds, solar energy is also capable of ionizing both molecules and atoms (reactions 2.7 and 2.8). For this reason, the region above the mesopause is alternatively referred to as the ionosphere.

$$N_2 + h\nu\ (\lambda \le 80\,\mathrm{nm}) \rightarrow N_2^+ + e^- \qquad \Delta H^\circ \ge 1500\,\mathrm{kJ\,mol^{-1}} \qquad (2.7)$$

$$O + h\nu\ (\lambda \le 91\,\mathrm{nm}) \rightarrow O^+ + e^- \qquad \Delta H^\circ \ge 1310\,\mathrm{kJ\,mol^{-1}} \qquad (2.8)$$

Note the use of standard enthalpy rather than free energy to describe the energetics of atmospheric gas-phase reactions. This is convenient because temperature and pressure have less influence on enthalpy compared with free energy changes. Also, it allows for description of the energetics of bond breaking and formation aside from statistical considerations of the bulk system.

In regions of the atmosphere where energy is absorbed causing ionization, the reverse exothermic electron-capture reactions also occur to some extent, releasing energy as kinetic energy. This is the reason for the high thermodynamic temperatures in the thermosphere. Proceeding closer to the Earth's surface but still in this region, there is a smaller flux of less highly energetic radiation to be absorbed and so the temperature and the population of atoms and ions decrease.

In the mesosphere, solar radiation begins to encounter new types of chemical species. Ozone (O_3), which has a relatively high concentration in the stratosphere, is also present to some extent above the stratopause and is capable of absorbing solar radiation of lower energy than that required for the dissociation and ionization of more stable species. This absorption of longer wavelength radiation leads to an increase in temperature when moving to lower altitudes in the mesosphere.

The absorption of radiation by ozone causes it to dissociate producing an oxygen molecule and atom, which are both in an electronically excited state, as indicated by the asterisk shown below, for absorption of radiation in the UV:

excited oxygen species
(higher energy)

$$O_3 + h\nu \ (\lambda \leq 325\,\text{nm}) \rightarrow O_2^* + O^* \qquad (2.9)$$

The temperature decline, as one moves down through the stratosphere, is explained in the same way as the decline in the thermosphere. Radiation within the energy range of ozone absorption has already been removed in the higher regions, producing elevated temperatures there; it therefore cannot penetrate further.

Little additional radiation is absorbed as solar photons pass through the troposphere. However, when the remaining spectrum of radiation strikes the Earth's surface it is partly absorbed by land and water and then re-emitted as lower energy infrared (IR) radiation. Some of the IR radiation is absorbed by certain gases in the troposphere—the two principal ones being water vapour and carbon dioxide. Absorption causes heating near the Earth's surface, an effect that declines with increasing altitude as there is less radiation remaining to be absorbed and the concentration of absorbing gases is also declining. The heating of the Earth's lower atmosphere in this manner is the well-known 'greenhouse effect'. It is a key factor in supporting life as we know it on Earth, but anthropogenic perturbations could seriously alter the present balance. Much more will be said about this topic in Chapter 8.

It is important to be aware that the chemical composition of Earth's atmosphere is not an equilibrium system. If that were so, then all of the oxygen would exist combined with other elements, and none would be free to support life. Ultimately, the Sun provides energy for many otherwise energetically unfavourable processes, including photosynthesis that allows plants to make use of carbon dioxide and produce oxygen.

The constant supply of energy from the Sun is either absorbed, stored by chemical reactions, or reflected back into space by the Earth. The combination of these factors maintains the energy relations of the Earth in delicate balance.

The troposphere

Most of the material concerning atmospheric chemistry discussed in this book relates to the troposphere, a region of intense air movement, so that gases of both natural and anthropogenic origin are constantly being mixed in vertical as well as lateral dimensions.

When the atmosphere becomes heated near the Earth's surface, the lighter, warmer air rises into regions of lower pressure. As the pressure declines, the upward-moving air parcel expands, a process that requires the gas molecules to do work. Work done means a loss of kinetic energy

Table 2.2 Comparison of tropospheric atmospheres from various regions.

Location	Atmospheric characteristic
Oceans	Sea salt aerosol (sodium, calcium, magnesium, chloride, sulfate, and minor elements)
Land (dry)	Airborne dust (soil-related, plant pollens, etc.)
Urban	High levels of pollutants may be present (smoke, dust, primary and secondary smog chemicals)
Arid tropics	Low humidity, intense solar radiation
Humid tropics	High humidity, natural volatile organics, intense solar radiation
Arctic	Sunlight period variable on a yearly cycle, Arctic haze (see Chapter 6) is present (containing sulfate aerosols, soot, and metals)

and a lower temperature (which is the average kinetic energy of the molecules in that portion of the air). This process by which there is a decrease in temperature without any transfer of heat outside the air parcel is called *adiabatic cooling*. The rate at which temperature decreases is called the *adiabatic lapse rate* which for dry air is approximately 10°C for every 1000 m gain in altitude. For moist air, the rate is somewhat reduced by processes of condensation of water vapour into clouds in the cooler atmosphere. The combination of factors leads to the temperature of –60°C at an altitude of 15 km at the tropopause.

The upward movement of air is also one cause among several others that leads to convective mixing within the troposphere. A molecule released at the Earth's surface would typically be swept up to the top of the troposphere in one or two days. Lateral mixing also occurs, but at a slower rate. Within each hemisphere, good mixing on the spatial scale requires approximately one month. Therefore, any gaseous matter that has a long residence time is well mixed, making the overall composition of the troposphere homogeneous with respect to these species. This includes all the major gases listed in Table 2.1. Local variations in concentration are characteristic of physically or chemically reactive species—water vapour and many trace species being good examples. Because of their reactivity, such gases are not stable for a sufficiently long time to become well mixed and homogeneous in composition.

Other examples of how the components of tropospheric air depend on location including over the open ocean, over large continental areas, urban areas, the tropics, and the Arctic are given in Table 2.2.

Main point 2.2 Temperature and compositional changes in the regions of the atmosphere are related to reactions that are determined by the energy of solar radiation at various altitudes. In the troposphere, the temperature profile is such that the atmosphere is usually well mixed and the chemical composition is relatively constant throughout, except for short-lived species.

2.3 Reactions and calculations in atmospheric chemistry

Measures of atmospheric concentration

Some of the methods used to measure concentration of gases in the atmosphere may not be familiar to many people. For gases that make up a large proportion of the atmosphere, fractional or percentage concentrations are used but, in contrast to solids and liquids, these are usually expressed on a molar, not mass, basis. The Avogadro relationship then defines that molar ratios would also be equivalent to a volume ratio or a ratio of partial pressures. A general term used to express atmospheric concentration is 'mixing ratio' (see Table 2.1). As an example, the mixing ratio for nitrogen in the dry troposphere, expressed as a fraction, is 0.7808 or 78.08%. This means that, for every 100 mol of all gases except water, 78.08 mol are nitrogen. It also means that, at atmospheric pressure ($P° = 101\ 325$ Pa), the partial pressure of nitrogen can be calculated as

$$\overbrace{0.7808}^{\text{mixing ratio}} \times \underbrace{101\,325\,\text{Pa}}_{\text{total atmospheric pressure}} = \overbrace{7.911 \times 10^{4}\,\text{Pa}}^{\text{partial pressure}}$$

For gases present at low concentrations, the *parts per . . .* family of units is frequently used to express mixing ratios. As with the fractional and percentage concentrations, equivalent calculations are done on a molar, pressure, or volume basis. The term used to express concentrations is, for example, parts per million by volume for which the symbol is ppmv. The mixing ratio of methane in the dry troposphere is approximately 1.83 ppmv. This means that there are 1.83 µmol of methane for every 1.0 mol of the components of air. It also means that a fraction, 1.83 millionths, of the total pressure is due to methane.

$$(\overbrace{1.83\ \text{ppmv}}^{\text{mixing ratio}}\ \underbrace{/\ 10^{6}}_{\text{factor to convert ppmv to fraction}}) \times 101\,325\ \text{Pa} = 0.19\ \text{Pa}$$

Note that ppmv is again different from the meaning of ppm applied to solids or liquids. We can, of course, do the conversion. Using an average molar mass of air of 29 g mol^{-1}, a 1.83 ppmv concentration is the same as 1.01 ppm by mass. The latter concentration unit is rarely used in atmospheric studies.

Units of mass per volume, moles per volume, or molecules per volume are other frequently used ways of expressing concentration of gases and particles in the atmosphere. Example 2.3 illustrates a simple conversion between mixing ratio and concentration for oxygen.

Example 2.3 **Conversion of units used in measuring of atmospheric concentrations of gases**

What is the concentration of oxygen in the atmosphere (0°C and 1 atm pressure) using units of g L^{-1}?

At 0°C and 101.3 kPa, the molar volume of a gas is 22.4 L. Therefore, 1 L of air contains 1/22.4 = 0.0446 mol of all gases, of which the mixing ratio of oxygen is 20.95%. The concentration of O_2 is then

$$0.0446\ \text{mol L}^{-1} \times 20.95\ \% / 100 = 9.35 \times 10^{-3}\,\text{mol L}^{-1}$$

In mass terms, this is equivalent to $32.0\ \text{g mol}^{-1} \times 9.35 \times 10^{-3}\ \text{mol L}^{-1} = 0.299\ \text{g L}^{-1}$, since 1 mol of oxygen has a mass of 32.0 g.

The mixing ratio units for oxygen have been converted to mass per volume (upon defining volume).

A related set of units giving molecules per volume is commonly used for some important atmospheric species that are present in very small concentrations. For atmospheric aerosols, solid or liquid particles in air, it is necessary to use mass per volume units to measure concentration. This is because there is no single molar mass for heterogeneous particles like dust or smoke.

Types of atmospheric reactions

A more detailed look at the chemistry involved in the troposphere and stratosphere will follow in subsequent chapters. Before beginning, we will examine some common features of atmospheric chemical reactions and introduce the types of calculations used in a quantitative description of the reactions. The discussion will make use of specific examples in order to illustrate important general principles, but the principles apply to all types of atmospheric reactions including 'natural' processes such as ozone creation and destruction in the stratosphere and also anthropogenic ones where a particular pollutant generated by human activity interacts with other atmospheric components.

Think about this

Many of the reactions that take place in the atmosphere depend on the time of day. Why?

Some reactions involve major gases and occur on a global scale, while others deal with trace species in a localized setting. In discussing the composition of the troposphere, we made note of the variability in mixing ratios of reactive minor components. While these gases are present in very small concentrations, many of them have short residence times, which is a reflection of their high reactivity. Frequently, a study of atmospheric chemistry then centres on the reactions in which the trace species are involved.

To illustrate types of reactions and basic calculations used, we have selected examples of production and degradation of some oxides of nitrogen, frequently referred to as NO_x. Later chapters will present more systematic discussions of these and other important reactions in the atmosphere.

Atmospheric reactions where thermodynamic calculations are appropriate

In some situations, thermodynamic calculations are appropriate for estimating concentrations of species produced in gas-phase reactions. For example, nitric oxide (NO) is generated during every combustion reaction including in forest fires, lightning discharges, industrial and domestic heating, and internal combustion engines, as a result of the combination of nitrogen and oxygen from the air.

$$N_2(g) + O_2(g) \rightarrow 2NO\ (g) \tag{2.10}$$

This reaction has a *positive free energy* of formation at 25°C that can readily be calculated, as shown in Example 2.4. The positive free energy indicates that the equilibrium of reaction 2.10 lies to the left.

Example 2.4 The calculation of free energy of formation for NO(g) at 25°C

From reaction 2.10,

$$\begin{aligned} \Delta G^\circ_{rxn} &= 2\Delta G^\circ_f(NO) - \Delta G^\circ_f(N_2) - \Delta G^\circ_f(O_2) \\ &= 2\ \text{mol} \times 86.55\ \text{kJ mol}^{-1} - 0 - 0 \\ &= +173.1\ \text{kJ}\quad \text{(per mol of reaction)} \end{aligned}$$

The ΔG°_f values for NO, N_2, and O_2 were obtained from Appendix B.2.

At ambient temperatures, therefore, nitric oxide is not formed to a significant extent. However, the reaction also has a positive entropy change as seen in the calculation below. As the temperature increases, therefore, the positive $\Delta G°$ value becomes smaller. At the very high temperatures associated with combustion, it is sufficiently small that significant quantities of nitric oxide can be produced.

For example, in a cylinder of an internal combustion engine at the time of ignition the temperature may reach approximately 2500°C (= 2773 K). In order to calculate the free energy change at the elevated temperature, we begin with data for the standard enthalpies of formation and absolute entropies, ΔH_f° and $S°$, respectively (consult Appendix B.2). The standard values are obtained at 25°C (= 298 K) and we assume that the ΔH_f° values are unaffected by temperature. The values of ΔH_f° for nitrogen and oxygen in the standard state are, by definition, zero.

Example 2.5 **The free energy and equilibrium constant for formation of NO(g) at 2773 K for reaction 2.10**

ΔG_{2773}° is determined by

$$\begin{aligned}\Delta G_{2773}^\circ &= \Delta H_{f(NO)}^\circ - T(2S_{NO}^\circ - S_{N_2}^\circ - S_{O_2}^\circ)\\ &= 2\times 90.25\,\mathrm{kJ\,mol^{-1}} - 2773\,\mathrm{K}\times(2\times 0.211 - 0.192 - 0.205)\,\mathrm{kJ\,mol^{-1}\,K^{-1}}\\ &= 111.2\ \mathrm{kJ\,mol^{-1}}\end{aligned}$$

From this final value of 111.2 kJ mol^{-1}, the equilibrium constant is then readily calculated.

$$\Delta G_T^\circ = -RT\ln K_p$$

$$\ln(K_p) = \frac{-\Delta G_T^\circ}{RT}$$

note the unit of J, **not kJ** here

$$\ln K_p = \frac{-111\,200\,\mathrm{J\,mol^{-1}}}{8.314\,\mathrm{J\,mol^{-1}\,K^{-1}}\times 2773\,\mathrm{K}} = -4.82$$

$$K_p = e^{-4.82} = 0.0081$$

The partial pressure of nitric oxide in the exhaust gases produced under these conditions is evaluated assuming the equilibrium condition

$$K_p = \frac{(P_{NO}/P°)^2}{(P_{N_2}/P°)(P_{O_2}/P°)}$$

In this equation, note that all pressures are relative to $P°$, 101 325 Pa.

While the equilibrium constant is still small, it is now large enough at this elevated temperature that some NO is produced, as we shall see in Example 2.6.

Example 2.6 **The mixing ratio of NO produced during combustion in the cylinder of an internal combustion engine**

Consider a situation where most of the oxygen has reacted with the fuel and the pressure of the residual oxygen is reduced to 1.0 kPa. Nitrogen does not take part in the combustion and its pressure in the compressed cylinder is 650 kPa. The temperature is 2773 K, and $P°$ is 101.3 kPa.

The residual O_2 reacts with N_2 to produce NO. After reaction, assume each has lost partial pressure of x kPa; According to reaction 2.10, P_{NO} will then be $2x$ kPa.

Using the equation for K_p above and the conditions described,

$$\frac{(2x/101.3)^2}{((650-x)/101.3)((1.0-x)/101.3)} = 0.0081$$

Because the pressures in this equation are relative to the standard pressure $P°$, all the fractions are dimensionless.

$$\frac{4x^2}{(650-x)(1.0-x)} = 0.0081$$

Assume $x << 650$ kPa and thus

$$\frac{4x^2}{650(1.0-x)} = 0.0081$$

giving the quadratic

$$4x^2 + 5.27x - 5.27 = 0$$

$$x = \frac{-5.27 \pm \sqrt{(5.27)^2 - 4(4)(-5.27)}}{2(4)} = 0.66$$

The assumption that $x << 650$ kPa is valid and

$$P_{\text{NO}} = 2x = 1.32 \text{ kPa}$$

The nitric oxide mixing ratio in the hot compressed cylinder is then

$$1.32 \text{ kPa} \div 650 \text{ kPa} \times 10^6 \text{ ppmv} = 2030 \text{ ppmv}$$

Assuming no catalytic decomposition of nitric oxide in the exhaust system, the nitric oxide would be released to the atmosphere along with the other combustion products.

Concentrations of this order have been observed in the exhaust of older automobiles built without emission control.[1] For example, measurements on the exhaust of a 1966 Valiant (Chrysler Corporation) V8 mid-size car running at 2000 rpm showed 1200 ppmv nitric oxide under no-load conditions and 2500 ppmv when the engine was operating with a 50 horsepower load. Fortunately, most cars that are built at present have efficient 'catalytic converters' that facilitate the conversion of nitric oxide and other undesirable combustion products into harmless gases. The chemistry of these processes will be described in Chapter 4.

We can attempt to go further with calculations concerning nitric oxide by determining what its concentration would be when the gases are cooled and diluted after exiting the exhaust system. The positive ΔG for reaction 2.10 suggests that at equilibrium, most of the NO will revert back to N_2 and O_2. The question we are asking then is 'How much of the nitric oxide remains in the atmosphere?' To answer this question, we begin with another equilibrium calculation.

Example 2.7 **Equilibrium concentration of NO in the atmosphere at 25°C**

Suppose nitric oxide present in the exhaust gases at an approximate mixing ratio of 2030 ppmv becomes diluted in the open air by a factor of 20 000, giving an atmospheric concentration of 0.100 ppmv or 100 ppbv. Assume that the ambient temperature is 25°C. Using a similar

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[1] Gould, R.F., (ed.), *Catalysts for the control of automotive pollutants*, Advances in Chemistry Symposium Series, no. 143, Chairman, J.E. McEvoy, American Chemical Society, Washington DC; 1975.

method (Example 2.5) of calculation for K_p we obtain a new equilibrium concentration of nitric oxide for the lower temperature

all units (not shown) cancel

$$\ln(K_p) = \frac{-173\,100}{8.314 \times 298}$$

$$K_p = 4.54 \times 10^{-31}$$

Again, we use the K_p expression

$$K_p = \frac{(P_{NO} / P°)^2}{(P_{N_2} / P°)(P_{O_2} / P°)}$$

The atmospheric pressures of nitrogen and oxygen are extremely large compared to the 100 ppbv NO and even with reaction 2.10 going from right to left, this will not significantly alter the partial pressures of 79 and 21 kPa, respectively. In the calculation below, let x be the partial pressure of nitrogen (and oxygen) produced as reaction 2.10 goes from right to left

$$4.54 \times 10^{-31} = \frac{((1.01 \times 10^{-5} - 2x)/101.3)^2}{((79 + x)/101.3)((21 + x)/101.3)}$$

Making assumptions that $x << 79$ and $x << 21$ for N_2 and O_2, respectively, and therefore ignoring x in the denominator, the equation is readily solved.

$$x = 5.05 \times 10^{-6}$$

Clearly, the assumptions of nearly constant partial pressure values for N_2 and O_2 were valid. Using these assumptions and returning to the original K_p expression, the very small equilibrium partial pressure expected for NO can be calculated.

$$4.54 \times 10^{-31} = \frac{(P_{NO} / 101.3)^2}{(79 / 101.3) \times (21/101.3)}$$

$$P_{NO} = 2.7 \times 10^{-14}\,\text{kPa}$$

Converting the calculated partial pressure into a mixing ratio, we would estimate the ambient atmospheric concentration of nitric oxide near a combustion source to be extremely small.

$$(2.7 \times 10^{-14}\,\text{kPa}/101.3\,\text{kPa}) \times 10^9 = 3 \times 10^{-7}\ \text{ppbv}$$

In summary, the mixing ratios of nitric oxide that we have calculated are as follows:

• in the exhaust gases	~2030 ppmv
• in the atmosphere after reaction to equilibrium	~3 × 10^{-7} ppbv

Clearly, our calculation has indicated that an almost negligible concentration of nitric oxide should remain in the atmosphere. In fact, this is not what is observed. Small but significant amounts are frequently found (e.g. ~100 ppbv, as in Fig. 4.2(b)) near combustion sources. The actual mixing ratios are then about one billion times higher than the calculated equilibrium values.

The reason for the huge difference arises from the use of thermodynamics, which assumes an equilibrium situation. In the engine cylinder, the temperature is high, reactions are very fast, and equilibrium is quickly attained, meaning that thermodynamic calculations are valid. In the ambient atmosphere, however, under moderate temperature conditions, reaction rates are slower and an equilibrium situation is never reached. As a consequence, the thermodynamic calculation gives a completely erroneous result for the concentration of nitric oxide at ambient temperatures.

Reactions where kinetic issues are important

The major discrepancy is therefore due to the fact that the reverse of reaction 2.10 is *extremely slow* at ambient temperatures. During combustion, there is sufficient thermal energy that equilibrium is rapidly established but, when cooling occurs, reactants and products are retained near levels corresponding to the high temperature equilibrium. Sometimes the term 'frozen' is used to describe a situation where thermodynamically unstable products do not react due to slow kinetics. The following calculation clearly shows this.

The second-order rate constant for the reaction (reverse of reaction 2.10)

$$2\mathrm{NO(g)} \rightarrow \mathrm{N_2(g)} + \mathrm{O_2(g)} \tag{2.11}$$

is given by

$$k_2 = 2.6 \times 10^6 \mathrm{e}^{-\left(3.21\times10^4\right)/T}\ \mathrm{m^3\ mol^{-1}\ s^{-1}}$$

where T = temperature / K. At 25°C, the value of k_2 is therefore $4.3 \times 10^{-41}\ \mathrm{m^3\ mol^{-1}\ s^{-1}}$. Using these kinetic data allows us to calculate the rate of decomposition of nitric oxide by the simple reaction.

Example 2.8 **Rate of conversion of nitric oxide to nitrogen and oxygen**

The first step is to convert the mixing ratio of 100 ppbv estimated above for nitric oxide to a concentration $[\mathrm{NO}]_i$ in mol m^{-3}:

$$[\mathrm{NO}]_i = \frac{n}{V} = \frac{P}{R\times T} = \frac{100\times10^{-9}\times 101\ 325\,\mathrm{Pa}}{8.314\,\mathrm{J\,mol^{-1}\,K^{-1}}\times 298\,\mathrm{K}}$$
$$= 4.1\times10^{-6}\ \mathrm{mol\,m^{-3}}$$

The rate of decomposition can now be estimated:

$$\mathrm{Rate} = k_2[\mathrm{NO}]_i^2$$
$$= 7.2\times10^{-52}\ \mathrm{mol\,m^{-3}\,s^{-1}}$$

The reaction is clearly very slow and the half-life is given by[2]

$$t_{1/2} = \frac{1}{k[\mathrm{NO}]_i}$$

$$t_{1/2} = \frac{1}{4.3\times10^{-41}\ \mathrm{m^3\ mol^{-1}\,s^{-1}}\times 4.1\times10^{-6}\ \mathrm{mol\,m^{-3}}}$$
$$= 5.7\times10^{45}\,\mathrm{s}$$
$$= 1.8\times10^{38}\,\mathrm{y}$$

The value of 1.8×10^{38} y is more than 10^{28} times as long as the age of the Earth. It is obvious that the nitric oxide generated during combustion is *thermodynamically unstable*, but it is *kinetically extremely inert* at 25°C with respect to reaction 2.11.

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[2] The half-life for first-order reactions is given by $t_{1/2} = \ln 2/k$ and for second-order reactions, $t_{1/2} = 1/k[\mathrm{reactant}]_{\mathrm{initial}}$.

In this example of nitric oxide discharged into the atmosphere after being produced in an engine, thermodynamics predicted complete reversion of nitric oxide to dinitrogen and dioxygen. A kinetic evaluation for the same reaction predicted essentially the opposite result—the nitric oxide remains completely stable with respect to these two products. Experimental observations indicate that actual atmospheric nitric oxide concentrations fall between these two extremes (see Table 5.2).

The observations imply that other reactions must be involved in controlling the atmospheric concentration of this gas and we must consider these simultaneously with reaction 2.11. The most important is the oxidation of nitric oxide to produce nitrogen dioxide. With dioxygen as oxidant (reaction 2.12), once again it can be shown that thermodynamics fails us, as a simple calculation shows that the ratio P_{NO_2} / P_{NO} should always be greater than 10^6.

$$2NO(g) + O_2(g) \rightarrow 2NO_2(g) \tag{2.12}$$

This is much greater than ratios normally found in the natural atmosphere. Once again, kinetics predicts that the oxidation should proceed slowly.

Consider the situation in a polluted urban atmosphere where the nitric oxide concentration in the morning might be approximately 150 ppbv (0.15 ppmv = 1.5×10^{-5} kPa, or 6.1×10^{-6} mol m^{-3} calculated in the same way as shown in the first step of Example 2.8; also see Fig. 4.2(b)). Assuming reaction 2.12 to be an elementary process, the rate is equal to $k_3(P_{NO})^2(P_{O_2})$. The third-order rate constant k_3 has been evaluated to be 1.4×10^{-2} (mol $m^{-3})^{-2}$ s^{-1} (or 2.3×10^{-3} kPa^{-2} s^{-1}) at 25°C. In Example 2.9, the partial pressures of the gases are provided in the familiar units of kPa. In doing the calculation, then, the uncommon kPa^{-2} s^{-1} unit for the rate constant is convenient. Using this information, we can calculate the initial rate of oxidation of nitric oxide.

Example 2.9 **Calculation of the rate of oxidation of NO by O_2**

Assume that oxygen has its normal partial pressure of approximately 21 kPa.

$$\begin{aligned} \text{Rate} &= 2.3 \times 10^{-3}\ \text{kPa}^{-2}\text{s}^{-1}(1.5 \times 10^{-5}\ \text{kPa})^2\,(21\ \text{kPa}) \\ &= 1.1 \times 10^{-11}\ \text{kPa}\,\text{s}^{-1} \\ &= \frac{1.1 \times 10^{-11} \times 10^9}{101.3} \times \overset{\text{s h}^{-1}}{3600} \times \underset{\text{h day}^{-1}}{24} \\ &= 9.3\ \text{ppbv day}^{-1} \end{aligned}$$

This initial rate of oxidation is slow compared with the known concentration and cannot explain the rapid build-up of nitrogen dioxide observed during a smog event (see Fig. 4.2(a) and (b)). We shall see in Chapter 4 that dioxygen is not the most important oxidant in this reaction. Rather it is a combination of ozone (O_3) and peroxy radicals (ROO•)—also present in a tropospheric smog—that has the major effect on oxidizing nitric oxide. A general form of the reaction with peroxy radical species is

$$ROO\bullet + NO \rightarrow RO\bullet + NO_2 \tag{2.13}$$

Unfortunately, detailed calculations for this general reaction are difficult because of the variety of peroxy and oxy radical species and their variable and frequently unknown atmospheric concentrations. Free radical chemistry will be introduced later in this chapter.

Main point 2.3 For any given atmospheric chemical process, either thermodynamic or kinetic control is possible, with the latter being frequently the case. Therefore, thermodynamic calculations alone often lead to erroneous predictions about concentrations, at least in the short term.

Photochemical reactions

If we now consider the means by which nitrogen dioxide is decomposed and reverts to nitric oxide we encounter another feature characteristic of atmospheric reactions—the fact that many of these reactions have a photochemical component. By this we mean that the absorption of (usually solar) electromagnetic energy by species in the atmosphere is required to stimulate certain reactions. The reactant is excited to a higher energy state, thus enhancing bond-breaking or bond-making processes. The first step in a photochemical reaction is

$$XY + h\nu \rightarrow XY^* \qquad \text{Absorption} \tag{2.14}$$

The asterisk here and elsewhere is used to denote an excited state species. Absorption of energy is followed by further reactions that may take a variety of pathways such as

$$XY^* \rightarrow X + Y \qquad \text{Decomposition} \tag{2.15}$$

or

$$XY^* + \text{other reactant(s)} \rightarrow \text{products} \tag{2.16}$$

The magnitude of the rate constant for a photochemical reaction, symbolized as *f* to distinguish it from the thermal rate constant *k*, is determined by several factors (eqn 2.17).

$$\overset{\text{photochemical rate constant}}{f} = \int_{\lambda_1}^{\lambda_2} \underset{\text{radiative flux}}{J_\lambda}\, \overset{\text{absorption cross-section}}{\sigma_\lambda}\, \underset{\text{quantum yield}}{\Phi_\lambda}\, d\lambda \tag{2.17}$$

In this expression, λ_1 and λ_2 are the wavelength 'limits' of the solar radiation being considered. For example, at the Earth's surface the values would be approximately 300 and 800 nm, respectively, while the range would extend to shorter wavelengths in the stratosphere. The other terms in the expression all depend on the range of wavelengths under consideration. J is the radiative flux, σ is the absorption cross-section, which is a measure of the ability of the molecule of interest to absorb radiation of the type being considered, and Φ is the quantum yield, which is the ratio of the number of molecules undergoing the specific reaction of types such as reactions 2.15 and 2.16 to number of quanta of radiation absorbed.

When every absorption event leads to the particular reaction of interest, Φ has a value of unity. However, what happens far more frequently is that the excited species is deactivated by (i) 'quenching' through collisions with other gases (M) (reaction 2.18) or (ii) by transferring energy to other molecules leading to their excitation (reaction 2.19), and Φ is very small.

$$XY^* + M \rightarrow XY + M + \text{kinetic energy} \qquad \text{Quenching} \tag{2.18}$$

$$XY^* + AB \rightarrow XY + AB^* \qquad \text{Intermolecular transfer} \tag{2.19}$$

As another extreme, the quantum yield is greater than one when a single activated molecule sets off a chain of events leading to a sequence of reactions.

As an example of a photochemical reaction we can again consider a case from tropospheric NO_x chemistry—the decomposition of nitrogen dioxide:

$$NO_2 + h\nu \rightarrow NO + O \tag{2.20}$$

The atomic oxygen produced in this reaction is in the ground state ($O(^3P)$) and, as an aside, it can be mentioned that $O(^3P)$ reacts with molecular dioxygen to generate ozone—the only significant pathway to produce ozone in the lower troposphere. The photolytic quantum yield for reaction 2.20 depends on the wavelength of the electromagnetic radiation and is near 1 for $\lambda < 360$ nm (near the high-energy end of the visible region of the spectrum) but falls off to 0 at about $\lambda > 440$ nm. It is commonly said that the minimum energy required to effect the process is associated with radiation of 400 nm. The rate of the reaction is given by

$$\text{Rate} = f_1[NO_2]$$

As usual, the photochemical first-order rate constant, f_1, depends on the intensity and wavelength of the incident radiation. For nitrogen dioxide photolysis, values of f_1 range from about $5.6 \times 10^{-3}\ s^{-1}$ in intense sunlight to zero at night.

Example 2.10 **Half-life of nitrogen dioxide in intense sunlight**

For the first-order reaction,

$$t_{1/2} = \ln 2/f_1$$
$$t_{1/2} = 0.693/5.6 \times 10^{-3}\,s^{-1}$$
$$t_{1/2} = 124\,s$$

In sunlight, therefore, nitrogen dioxide would have a half-life of ~120 s, indicating that the photolysis is rapid.

Decomposition of nitrogen dioxide is offset by synthesis, as shown above in reaction 2.13, also a kinetically rapid process. The steady-state situation established between decomposition and synthesis is known as a photostationary state and is described by equating the rates of the production and consumption reactions:

$$\text{production (reaction 2.13)} = \text{consumption (reaction 2.20)}$$

$$k_2[ROO\bullet][NO] = f_1[NO_2]$$

Therefore,

$$\frac{[NO_2]}{[NO]} = \frac{k_2[ROO\bullet]}{f_1}$$

(Note that ROO• is a composite of several species including ozone and k_2 is a composite rate constant.) In any case, the final equation determines the ratio of nitrogen dioxide to nitric oxide, a ratio that is established quickly and may vary from a small value in bright sunlight when f_1 is large to a higher night-time value.

The example we have used to illustrate the importance of photochemistry in atmospheric reactions is one that occurs in the troposphere. There are many other reactions and, as we move upward in altitude to the stratosphere and above, we find that photochemistry becomes even more important. Obviously, this is because of the availability of previously unabsorbed higher energy radiation in the rarefied upper atmosphere. There, photolysis of high binding-energy molecules like dioxygen and dinitrogen becomes possible as well as ionization of molecules and atoms that are 'normally' stable.

As we have noted, where kinetic properties determine the behaviour of chemical species in the atmosphere, we frequently use the term half-life, $t_{1/2}$, to describe the progress of the reaction. A similar, alternative description is given by the term residence time, τ (tau, also called atmospheric lifetime or residence time), which we defined in Chapter 1. Whereas $t_{1/2}$ represents the time taken for half of the reaction to occur, τ (the average lifetime) is the time during which the original concentration decreases to 37% (1/e) of its original value. For a first-order or pseudo first-order reaction, $t_{1/2}$ is equal to $\ln 2/k_1$ (or $\ln 2/f_1$) while τ is equal to $1/k_1$ (or $1/f_1$).

Main point 2.4 In addition to standard 'thermal reactions' there are important atmospheric processes that are, partly or completely, photochemical processes. The energy of solar radiation increases with increasing altitude so that photochemistry becomes even more important in the upper atmosphere.

Free radical reactions

A second key feature regarding chemical processes that occur in the atmosphere is the way in which free radicals[3] take part in many reactions. We will encounter a variety of radical species, but none is more important than the hydroxyl free radical (•OH), a species that will appear again and again in our study of atmospheric chemistry reactions. The neutral *hydroxyl radical* (not to be confused with the negatively charged *hydroxide ion*, OH^-, that is so pivotal in aqueous solution chemistry) is formed in the troposphere by a variety of means but the most important is a four-step process (including two photochemical steps).

$$NO_2 + h\nu \rightarrow NO + O \tag{2.20}$$

$$O + O_2 + M \rightarrow O_3 + M \tag{2.21}$$

In the second step, the combining of O and O_2 takes place as a result of an additional collision and an instantaneous energy-transfer process to another atmospheric molecule, a so-called 'third body', represented as M in reaction 2.21. Since dinitrogen and dioxygen are the most common species throughout the Earth's atmosphere, the third body is usually one of these molecules.

$$O_3 + h\nu \rightarrow O_2^* + O^* \tag{2.22}$$

$$O^* + H_2O \rightarrow 2{\bullet}OH \tag{2.23}$$

The atomic oxygen produced in reaction 2.20 is ground-state or triplet ($O(^3P)$) oxygen, while that in reaction 2.22 is in the excited state or singlet ($O(^1D)$) oxygen. For the former reaction, radiation in the visible region supplies sufficient energy to give a large value for the photochemical rate constant, f_1, while for the latter higher-energy ($\lambda < 325$ nm) UV radiation is required. Excited state oxygen atoms are essential in order to form hydroxyl by reaction with atmospheric (gaseous) water according to reaction 2.23. In competition with this reaction are quenching processes of the type

$$O^* + M \rightarrow O + M + \text{kinetic energy} \tag{2.24}$$

Because of the availability of many M species (O_2, N_2, etc.) in air, reaction 2.24 proceeds readily and this results in a low quantum yield, Φ, for the combined reactions 2.22 and 2.23.

Because of its low concentration and highly reactive nature, it is extremely difficult to measure[4] concentrations of hydroxyl radicals but, in many situations, levels have been estimated to be

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[3] Free radicals are atoms or molecules that have one or more unpaired electrons. They are usually highly reactive species. In most cases, we will denote radicals using a dot (•) beside or above the radical species. While some compounds containing nitrogen (like NO_2) or chlorine (like ClO) atoms have an unpaired electron, we make an exception and will not usually show the unpaired electron in such compounds, unless some other radical species is involved in the reaction.

[4] Elsele, F.L. and J.K. Bradshaw, The elusive hydroxyl radical: measuring OH in the atmosphere, *Anal. Chem.*, **65** (1993), 927A–39A.

between 1 × 10^4 and 2.5 × 10^6 molecules per cm^3 in the troposphere, with values being higher at low altitudes and latitudes, in daytime, and in areas of heavy pollution. The global average tropospheric concentration has been estimated to be 8.1 × 10^5 molecules per cm^3 while, in the tropics, an average concentration of 2 × 10^6 molecules per cm^3 may be a reasonable estimate. The factors determining actual concentrations of the hydroxyl radical relate to reactions 2.20 to 2.24.

We will later encounter a number of varied atmospheric reactions in which hydroxyl radicals take part. However, in a quantitative sense, the two most important are

$$\bullet OH + CO \rightarrow \underset{\text{hydrogen radical}}{\bullet H} + CO_2 \qquad (2.25)$$

$$\bullet OH + CH_4 \rightarrow \underset{\text{methyl radical}}{\bullet CH_3} + H_2O \qquad (2.26)$$

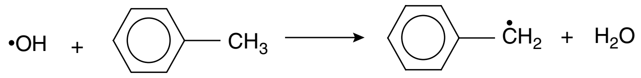
Reactions with carbon monoxide and methane account for approximately 70% and 30%, respectively, of all reactions involving hydroxyl radical in an unpolluted atmosphere. In the course of both reactions, other highly reactive radical species (the hydrogen and methyl radicals) are formed and these, in turn, react further:

$$\bullet H + O_2 + M \rightarrow \underset{\text{hydroperoxyl radical}}{HOO\bullet} + M \qquad (2.27)$$

$$\bullet CH_3 + O_2 + M \rightarrow \underset{\text{peroxymethyl radical}}{CH_3OO\bullet} + M \qquad (2.28)$$

The peroxy radical products are important oxidants as we have seen in the case of oxidation of nitric oxide (reaction 2.13).

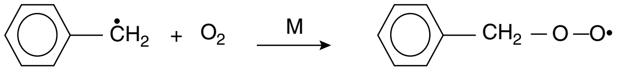
In regions affected by either natural or anthropogenic gaseous emissions, other processes frequently contribute significantly to the loss of the hydroxyl radical. Most of the reactions may be classified into two categories. The first category is hydrogen abstraction as in the reactions with toluene (reaction 2.29) and formaldehyde (reaction 2.30).



(2.29)

$$\bullet OH + HCHO \longrightarrow H\dot{C}{=}O + H_2O \qquad (2.30)$$

Similarly to the reaction with methane, in reactions 2.29 and 2.30 new highly reactive radical species are produced and they too react further with oxygen as in reactions 2.31 and 2.32, forming peroxy radical species.

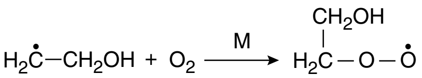


(2.31)

$$H\dot{C}{=}O + O_2 \longrightarrow HOO\bullet + CO \qquad (2.32)$$

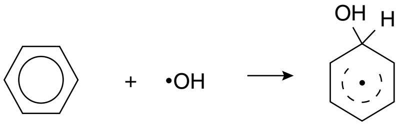
The second category of reactions is usually an addition across a multiple bond as illustrated by the reactions with ethene (reaction 2.33) and benzene (reaction 2.35). Dimethyl sulfide (DMS) is an exception to this, reacting through both an abstraction and addition route. Again, new highly reactive species are produced and these typically begin a further reaction sequence by adding oxygen (reactions 2.34 and 2.36).

$$\bullet OH + H_2C{=}CH_2 \longrightarrow H_2\dot{C}{-}CH_2OH \qquad (2.33)$$

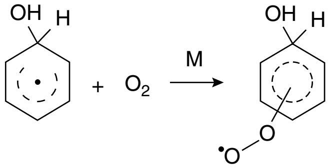


$$H_2\dot{C}{-}CH_2OH + O_2 \xrightarrow{M} H_2\overset{\overset{\displaystyle CH_2OH}{|}}{C}{-}O{-}\dot{O}$$

(2.34)



(2.35)



(2.36)

There is a great variety of organic species present in the atmosphere at low concentrations. These include ones of biogenic origin emitted by living or decomposing organisms and the multitude of chemicals released to the atmosphere from combustion of fossil fuels and from many industrial processes. Even present in buildings, organic species are given off by the diverse natural and synthetic materials used in construction. The possible chemical reactions with which these chemicals are involved are also limitless, but a surprising number are initiated and propagated by hydroxyl or other radical species. In many cases, the first step of these reactions is well understood, often involving principles such as those just shown; rate constants are also available so that the rate of destruction can be calculated. Frequently, the subsequent reaction steps are less clear and the mechanisms leading to ultimate destruction are not known.

Main point 2.5 Free radicals play a dominant role in many atmospheric reactions and the hydroxyl radical is especially prominent in this regard.

Literature link The hydroxyl radical factor

We cannot overestimate the importance of the role played by free radical species, especially the hydroxyl radical, in atmospheric chemistry. This will become evident as we proceed through later chapters of this book. A recent paper, *The cleansing capacity of the atmosphere,* by Prinn, R.G., *Annu. Rev. Environ. Resour.,* **28** (2003), 29–57, describes a wide range of processes by which trace gases in the atmosphere, many of human origin, are oxidized ***via*** radical-mediated processes. The ability of the atmosphere to destroy such compounds, thus cleansing itself, is referred to as its oxidation capacity.

The author points out important atmospheric conditions that affect the concentration of hydroxyl in the troposphere, and therefore the atmosphere's oxidation capacity. The concentration is lower at night-time, in winter, under cloudy conditions, in areas where nitric oxide emissions are reduced, in dry atmospheres and where the stratospheric ozone layer is especially thick. From what has been said in this chapter, you should be able to understand the reasons for each of these effects.

The most important anthropogenic factors affecting the concentration of hydroxyl are the emissions of carbon monoxide, hydrocarbons, and nitrogen oxides. As we have seen, elevated emission rates of the former two compounds accelerate the consumption of hydroxyl and, if this were significant, would lead to a reduction in its abundance. On the other hand, increased amounts of nitrogen oxides will favour greater production of additional hydroxyl. It is interesting that carbon monoxide and nitrogen oxides are both products of combustion, so one is left with the question: 'Over time, will hydroxyl levels increase or decrease?' Most models described in the paper referenced above indicate that a decrease in the range 10–20% is likely over time.

The word *sink* is used frequently to indicate a route by which chemical species are removed from the atmosphere. Radical reactions are an important sink for destroying undesirable species like VOCs, sulfur dioxide, and nitrogen dioxide. But there are other sinks as well. For example, another removal mechanism for sulfur dioxide and nitrogen dioxide is by having these dissolve in water droplets in clouds, and then being rained out of the atmosphere.