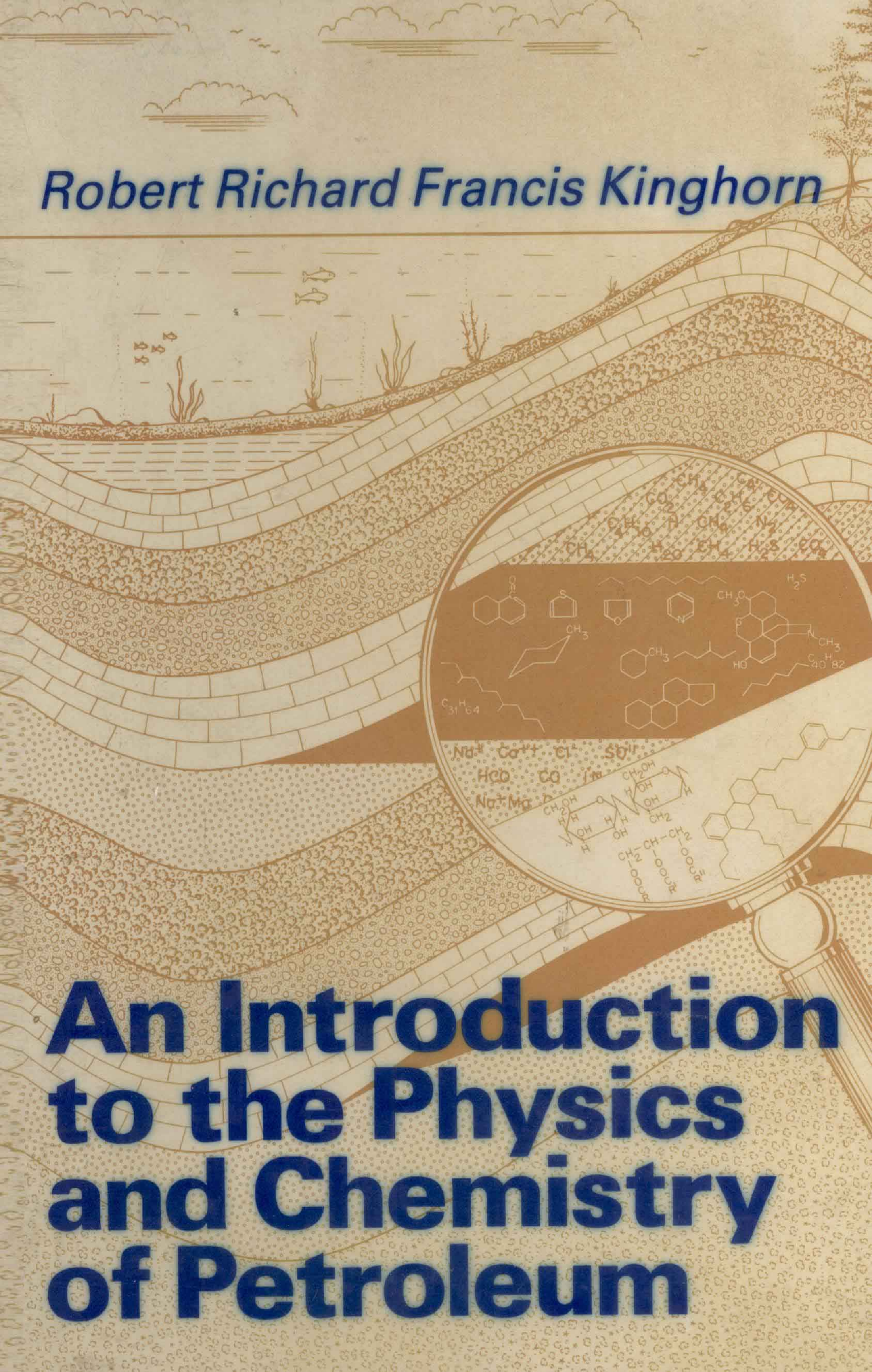
Robert Richard Francis Kinghorn

# An Introduction to the Physics and Chemistry of Petroleum



# *An Introduction to the Physics and Chemistry of Petroleum*

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geochemists are akin to the British and American peoples who have been described as two races separated by a common language.

I am grateful to all those authors whose work I have quoted. The amount of literature on petroleum, organic geochemistry, and related studies is growing at what is nearly an exponential rate, and it is impossible but to quote only a fraction of the published and relevant work. I have tried to quote a representative sample of the most important papers. The omission of reference to any particular work probably reflects more on this author than on those omitted. I would like to express my very special gratitude to all those who have assisted me in this work, especially Jenny Curtis for the excellent typing, Tony Brown, Haraldo Cantanhede and Ella Ng Chieng Hin for the drafting of the diagrams, Mokhles Rahman for the photographs of the organic matter, and for the many long and helpful discussions, Gill Davies; and last, but by no means least, my two best friends, one for the present of the pen with which this book was written and without whose encouragement and support it would probably be unfinished and the other, Caesar, for giving up many walks and sitting patiently at my feet whilst I was working.

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# Chapter 1

# Introduction and Basic Concepts

## INTRODUCTION

This book is primarily concerned with petroleum, liquid, gaseous, and solid concentrated accumulations of organic matter which can be extracted from the earth and used as sources of fuel and as raw materials. Hydrocarbon occurrences have been known for centuries and they have been used in various ways by the inhabitants local to these occurrences. At first there was no conscious effort made to discover the source of these hydrocarbons, which were normally present on the surface as seeps, to discover more seeps, or even to trade in these materials. Later reports indicate that some trade developed and that some production was from hand-dug pits and wells, but nothing was recorded as to the necessity or means of discovering new, especially underground, sources.

The relatively small world population had a need for oil products, mainly for illumination and lubrication, which could be met from animals and plants. It was realization that the distillation of mineral oils could provide products which were superior to those obtained from vegetable and animal sources that was the encouragement for prospectors to look for hitherto unknown sources of petroleum. The demand for hydrocarbon products has increased as the population of the world has increased and as the means of discovering and producing oil have improved. Oil has progressed from principally being a source of illumination to being a major contributor to the world's energy supplies and a source of raw materials for the chemical industry. Thus the changing and increasing uses of petroleum products, together with an ever-growing world population which expects continually increasing standards of living, means that the search for oil and gas is more urgent than ever.

Petroleum exploration is a very expensive business and it is a high-risk venture with very large amounts of money having to be expended with no guarantee of a return. Although a large number of preliminary tests and examinations can be made, the only way to ascertain whether or not there is oil in a particular region is to drill a well or wells. The preliminary work will serve to locate the prospect and minimize the risks as far as possible, but only the drilling of wells will provide the answer as to whether or not oil is present and if so in what quantity and of what quality. Drilling on shore is expensive but many of the world's on-land prospects have already been evaluated and explored, so that the search is being extended to continental shelves. The cost of operating off shore, especially where the weather can be bad for long periods, is greater by several orders of magnitude than drilling on land. On-shore exploration is still taking place, but is confined either to locating small accumulations in already known petroleum provinces or to exploration in the more remote regions of the world. The former offers small returns and the latter requires very large capital investment, and thus every technique which can improve the chances of successful exploration is a worthwhile investment.

In the early days of petroleum exploration the preferred drilling location was on top of an anticline. Experience has shewn that anticlines are not the only geological formation in which petroleum can occur. Geologists nowadays have to have a much wider understanding of the geological environment which is conducive to the formation, migration, accumulation, preservation, and production of oil and gas. The methods which have been used by geologist and his associates to obtain this understanding have increased. For instance, geophysics is a widely used exploration tool, but its benefits are maximized when used in conjunction with other methods. Geochemistry is now becoming one of the very important exploration facilities because it enables petroleum geologists to assess the chances that hydrocarbons have been generated and to indicate of what type and in what quantity those hydrocarbons will be. The location of a porous and permeable reservoir is essential for the discovery of oil but for that reservoir to be of any value it must contain hydrocarbons. Organic geochemistry can indicate whether or not a suitable source of hydrocarbons exists and can thus enable the petroleum geologist to fit another piece in to the exploration puzzle. Geochemistry is an extra source of information which, together with all the others, allows the petroleum geologist to make a better and more valuable judgement of the petroleum prospects of an area. This can result in the saving of large sums of money. There will be no point in drilling into a reservoir sand if there is no source of organic matter with which to fill that reservoir. Organic geochemical investigations will be continued until the completion of the exploration and development. Initial analyses may involve surface samples from the edge of the basin, but later investigations involve material obtained from wells. Each well will provide more material which will allow a greater insight in the organic geochemistry of that basin.

Unfortunately, very few geologists have been taught the organic chemistry or the physical properties of the organic components of sedimentary rocks. Most geology courses include instruction in the chemistry and physics of the inorganic mineral constituents of rocks. Whilst those are of importance to petroleum geologists, petroleum is an organic substance, normally fluid, and it is a knowledge of organic chemistry and the physical properties of organic compounds which are of greater value to the petroleum geologist. Thus many geologists enter the petroleum industry to find their colleagues talking in a different language about subjects of which they are ignorant. In spite of this, many important recommendations and decisions have to be made based upon organic geochemical reports by geologists whose chemical knowledge is very limited.

'Petroleum' is a name derived from the Latin words *petra* (rock) and *oleum* (oil) and it is a general term used to describe mixtures of organic compounds, whether liquid, gaseous, or solid, which occur within the earth and which can be extracted. One of the principal components of petroleum is the hydrocarbon fraction which contains compounds composed solely of hydrogen and carbon. These compounds have great commercial value as they can be used as various types of fuel and as feedstock for the petrochemical industry. The word petroleum can be used to describe all three phases of extractable organic compounds found in the earth although the three phases can each have separate names. Gaseous petroleum is normally called natural gas; strictly speaking it should be called natural hydrocarbon gas as inorganic gases also occur in the ground. Natural gas is 'associated' if it occurs with liquid petroleum whilst 'non-associated' gas is that which does not overlie oil. Liquid petroleum, as extracted, is known as crude oil so as to distinguish it from the refined oil which is derived from crude oil. The semi-solid and solid forms of petroleum are called asphalts, tars, bitumens, pitches, or localized names such as Albertite or Gilsonite. The name petroleum is only applied to secondary organic matter, that is matter which has been produced by the thermal breakdown of kerogen. Thus oil shale would never be referred to as petroleum, but an oil or tar sand would be so described. The oil shale contains unmatured organic matter in an insoluble solid form and the action of heat is required to convert it to fluid products. An oil or tar sand contains material which has been produced by the thermal breakdown of organic matter similar to that found in an oil shale. It is relatively soluble in organic solvents and can be a fluid, even if a viscous fluid, when warmed.

In most cases these occurrences of petroleum are associated with aqueous solutions of inorganic salts. These brines are the fluids which filled the pore spaces when the sediments were deposited, and although much water is lost during compaction and at the same time the composition of the brine alters, the pores will still be filled with water. This water has to be displaced by the oil when the oil fills the reservoir. Because of the association of oil and water, a description of the character of oilfield brines is included in this book. In addition, the application of oilfield brine analysis, especially in exploration, is discussed.

Because very little organic chemistry has been taught in geology courses, the remainder of this chapter will be devoted to chemistry. There will be a description of the bonding in carbon compounds and this will be followed by an outline description of the types of compounds to be discussed in this book, the optical activity of organic compounds and the biosynthesis of organic carbon compounds.

The majority of this chemistry is organic chemistry, i.e. the chemistry of carbon, because carbon is unique among the earth's elements in that it can form compounds in which there are long chains of atoms. No other element can form chains of the length of those formed by carbon.

## STRUCTURE OF THE ATOM

Matter is composed of molecules and molecules are composed of atoms, which are the basic building units of matter. Every atom consists of protons, neutrons, and electrons and the number of the protons and electrons determines the chemical properties of that atom. Protons and neutrons are of almost identical mass, whereas electrons are 1/1850 the mass of a proton. Protons have a unit positive charge and electrons carry a unit negative charge (Table 1.1).

**Table 1.1**

| Particle | Mass (atomic mass units)* | Charge† |
|---|---|---|
| Proton | 1.00732 | +1 |
| Electron | 0.00055 | −1 |
| Neutron | 1.00866 | 0 |

*1 a.m.u. is $^1/_{16}$ of the mass of an oxygen atom. The absolute weight of an electron is $9.1 \times 10^{-28}$ g and that of a proton is $1.67 \times 10^{-24}$ g.
†unit electron charge $-1.60 \times 10^{-19}$ coulomb

An atom is made up of a nucleus which contains protons and neutrons, in approximately equal numbers for the light elements, but with an excess of up to 50% of neutrons for the heavy elements, and the nucleus is surrounded by sufficient electrons to make the whole atom electrically neutral. The atomic number of an element is the number of protons or electrons in one atom of that element. All atoms of the same element have the same number of protons and electrons and they thus have the same chemical properties, as these properties are determined by the arrangement of the electrons. If two atoms have the same atomic number but different atomic weights it is because the number of neutrons in the nucleus varies. For instance, chlorine has atomic number 17 (i.e. it contains 17 protons and 17 electrons) but a chlorine atom normally contains either 18 or 20 neutrons. The natural occurrences of chlorine atoms with atomic weights 35 and 37 are such that the average atomic weight of chlorine is 35.46.

Experiments have shewn that atoms have diameters about $10^5$ as great as their nuclei. Thus an atom has a compact, dense nucleus surrounded at some distance by electrons. These electrons are believed to be in motion around their nucleus and were once considered to circle their nucleus like planets around a sun. As they have the opposite electrical charge to the nucleus they should, according to classical physics, be attracted to the nucleus, but because they do not collapse into the nucleus some agency must prevent this. In 1913 Niels Bohr, a Danish physicist, suggested that the total energy of an electron is quantized, that is restricted to certain values, and thus an electron cannot have any energy but only particular energy levels. Thus there is a minimum energy level for electrons around atoms and this keeps an electron in the lowest orbit around an atom.

The electrons in an atom are not all of the same energy and the energy levels in an atom are discrete, limited, and only able to contain a specified number of electrons. The number of electrons a level or shell can hold depends upon the particular level. The maximum electron population of any energy level is $2n^2$, where $n$ is the number of the level. ($n$ has whole-number values: 1, 2, 3, etc., and electrons in the lowest energy level of $n = 1$ are referred to as being in the $K$ shell or orbit. These electrons are the most tightly bound. The higher shells are lettered $L$, $M$, $N$, etc., corresponding to $n = 2,3,4$, etc.) Thus the first shell can contain only two electrons, the second shell can hold up to eight, and so on. Not all the electrons within a shell may have the same energy, as energy sub-levels or sub-shells within a main shell is from zero to $n$ (where $n$ is the principal quantum number). The lowest sub-shell within a main shell is designated $s$, the second sub-level is $p$, etc. An $s$ sub-shell can contain two electrons and a $p$ sub-shells six electrons. These are the only sub-levels that concern organic chemistry

From the above discussion it will be seen that in the $K$ shell there can be a maximum of two electrons and these will be in the $s$ sub-level, while in the $L$ shell there can be up to eight electrons and these can be in the $s$ and $p$ sub-levels. These are known as the $2s$ and $2p$ electrons, respectively. Table 1.2 shews the electronic configuration of the common elements referred to within this book.

**Table 1.2** Electronic configuration of common elements

| Element | | H | C | N | O | S | Na | Mg | Cl |
|---|---|---|---|---|---|---|---|---|---|
| *K* | | 1 | 2 | 2 | 2 | 2 | 2 | 2 | 2 |
| *L* | *s* | | 2 | 2 | 2 | 2 | 2 | 2 | 2 |
| | *p* | | 2 | 3 | 4 | 6 | 6 | 6 | 6 |
| *M* | *s* | | | | | 2 | 1 | 2 | 2 |
| | *p* | | | | | 4 | | | 5 |

The electrons are considered to be in pairs in orbitals within a sub-level. Thus, the two $1s$ electrons will be in one orbital and the two $2s$ electrons in another similar orbit but with higher energy. The six $2p$ electrons will be in the three orbitals all of the same energy but higher than that of the $2s$ orbitals. The Pauli exclusion principle states that only two electrons can be in one orbital and that these electrons will have opposite spins. When this occurs the electrons are said to be paired. Where electrons occupy equivalent orbitals singly, they will have parallel spins and such elements will have a resultant magnetic field. Such elements are weakly attracted to magnets and are called paramagnetic. This phenomenon should be compared with those solids, such as iron, which are strongly attracted to magnets and are