

THE CHEMISTRY OF RIVER WATERS

with special reference to  
the rivers of Natal

by

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## C O N T E N T S

	<u>Page</u>
SUMMARY	i
LIST OF SYMBOLS	iv
PART I THEORETICAL BASIS	
1. <u>General introduction</u>	1
2. <u>Solutes of river waters</u>	2
Origin of river waters. Carbonates. Sulphate. Chloride. Silica. Calcium. Magnesium. Sodium. Potassium. Minor mineral solutes. Pollution. Total dissolved solids.	
3. <u>Fundamental ionic relations</u>	13
Outline of the theoretical treatment. Solutes and ions of natural waters. The strong electrolytes. Calcium and magnesium hydroxides. Titration curves. General equations for hydrion concentration.	
4. <u>Activity coefficients</u>	29
Successive approximations. Activity coefficient as a function of TDS. Waters of high TDS.	
5. <u>Probable errors</u>	37
Errors in dissociation constants. Errors in activity coefficients. Errors due to pH measurements. Summary.	
PART II APPLICATION TO SPECIAL TOPICS	
6. <u>Solubility products</u>	42
Carbon dioxide. Calcium and magnesium hydroxides and carbonates.	
7. <u>Alkalinity</u>	49
Definition of total alkalinity. Determination of total alkalinity. Analytical checks. The three forms of alkalinity. Notation. Reformulation of the ionic balance.	
8. <u>Carbonic acid</u>	64
Calculation of the total carbonic acid. Determination of the total carbonic acid. Free carbonic acid. Unbound carbonic acid. Comparison of theory and experiment. Carbonic acid in Natal rivers. Carbonic acid in rain and sea water.	



9.	<u>The titration curve</u>	75
	General characteristics. Changes in carbonic acid content. Changes in TDS. Changes in water composition.	
10.	<u>Corrosivity and the pH<sub>s</sub></u>	81
	Saturation pH value. An approximate pH <sub>s</sub> equation. Corrosivity and the pH <sub>s</sub> . Notes on anti-corrosion water treatment.	
11.	<u>Hardness</u>	92
	Terminology. Determination of temporary hardness. Calculation of the temporary and permanent hardnesses. Hardness in Natal rivers. Errors of the calculations. Variation of hardness with TDS. Note on the cold lime-soda process.	
PART III	RIVERS OF NATAL	
12.	<u>The physiography of rivers</u>	106
	Physiographic zonation. Climate and river flow. Climate and TDS. Correlations between TDS, flow and conductivity. TDS and chemical composition.	
13.	<u>The standardisation of water analyses</u>	118
	Possible procedures. Molar percentages. Examples. Variations of the molar percentages. Design of sampling programmes. Minor comments.	
14.	<u>A graphical representation of water analyses</u>	131
	Possible schemes. The molar percentage spectrum. Illustrations.	
15.	<u>Water series</u>	135
	General characteristics of Natal river waters. The series of chlorided waters. The series of sulphated waters. General characteristics of the two water series.	
16.	<u>Chemical classification of river waters</u>	144
	General. Water quality. Oxygen relationships in rivers. Scheme of classification.	
17.	<u>Some particular Natal rivers</u>	155
	Introduction. The Illovo river. The Nonoti river. The Umfolozi river. Small coastal rivers. General summary of water quality in Natal.	



APPENDIX A SUMMARY OF ANALYTICAL CALCULATIONS

APPENDIX B TABLES OF NUMERICAL DATA

APPENDIX C TABLES OF EXPERIMENTAL DATA

APPENDIX D SOME EXPERIMENTAL TESTS

REFERENCES

## S U M M A R Y

In Part I is presented the theoretical basis of the whole work. After a brief introduction (chapter 1), an account is given of the principal solutes present in river waters (chapter 2). By applying Ricci's treatment of ionic relations in aqueous solutions, general equations governing the pH values of river waters are derived and discussed (chapters 3 - 5).

The advantage of this particular treatment is that it does not proceed by making any approximations initially and so enables theoretically exact equations to be readily derived. Only in the final stages need approximations be introduced to simplify the calculations, and this results in the solution to a given problem being obtained as a set of relatively simple equations each of which is valid over a particular and well-defined range of values of the variables. Procedures which introduce approximations at too early a stage, on the other hand, are liable to give erroneous results, and at best they involve arguments which are not convincing.

The hydrogen ion concentration of a natural water in the range  $3.7 < \text{pH} < 9.7$  is given by equation (3.43) under ideal conditions, and corrections for non-ideality are readily made. This equation is not new but its derivation is. It comes directly from an application of Ricci's concepts and its range of validity is clear. Moreover, its derivation in this way involves an unambiguous definition of the total alkalinity of a water in terms of quantities which are directly measurable, in contrast with the usual textbook definition in terms of the hydroxyl, bicarbonate and carbonate ion concentrations which cannot be measured but which must be inferred from other quantities. The new definition enables it clearly to be seen just how the alkalinity and pH value of a water are affected by changes in chemical composition.

In Part II various special topics are considered, using the theoretical treatment just considered. These include certain solubility products (chapter 6), the alkalinity and carbonic acid content of natural waters (chapters 7 and 8), titration curves and buffer capacity (chapter 9).



It is demonstrated that the bicarbonate, carbonate and hydroxide alkalinities of a water (the "three forms of alkalinity") are indeed close approximations to the bicarbonate, carbonate and hydroxyl ion concentrations in the normal pH range (as most other texts assume but without adequate justification), although this breaks down at about pH 9 and above. Similarly, it is confirmed that the free or undissociated carbonic acid concentration is closely approximated by the stoichiometric excess of total carbonic acid over the total alkalinity. The discussion of alkalinity also enables the ionic balance, used as a check on the accuracy of a water analysis, to be formulated in a newer and simpler way.

The discussion of carbonic acid leads to a very simple expression for the percentage saturation of a natural water with carbonic acid at ordinary temperatures and atmospheric pressure, and from the data presented it is concluded that unpolluted river waters are virtually in equilibrium with atmospheric carbon dioxide. This in turn leads to a new criterion for the detection of some types of pollution.

Solubility products find an application in considering the saturation pH value ( $\text{pH}_s$ ), i.e. the pH value at which a given water is in equilibrium with solid calcium carbonate, and in chapter 10 an expression for  $\text{pH}_s$  is derived which differs slightly from the expression originally obtained by Langelier in 1936. Comparison of the pH and  $\text{pH}_s$  enables scale-forming and scale-dissolving waters to be distinguished, as is well known, but doubts are expressed as to the importance of this with regard to the corrosion of metals, even though it is now common water-works practice to adjust the pH and  $\text{pH}_s$  of waters in an attempt to minimise corrosivity. That the aggressiveness of waters towards cement and concrete is governed by the  $\text{pH}_s$  cannot be doubted, however. Some comments are made on the methods that can be used to adjust the  $\text{pH}_s$  values of waters. One limiting factor is the buffer capacity of the water, which makes waters of TDS less than 100 ppm very difficult to treat.

The hardness of waters is discussed in chapter 11. Although hardness was originally defined in terms of the soap-destroying powers of the water, this definition appears to have become disregarded in recent years and a confusing terminology has developed. After defining terms logically, a scheme for the approximate calculation of the temporary and permanent hardnesses of a water is presented. This is the first time any such calculations appear to have been attempted. Surface waters in Natal



are thereby found to fall into two groups, according as to whether their TDS is greater or less than 100 ppm.

In Part III the rivers of Natal are then discussed more specifically. A brief account of the physiography of rivers (chapter 12) indicates the necessity for a means of standardising water analyses so that they can be compared one with another. A suitable means of standardisation is proposed (chapter 13) and then utilised (chapter 14) in formulating a graphical representation of water analyses. It then appears that two major series of natural waters may be recognised and distinguished chemically (chapter 15), most waters belonging to the one series or the other and a few being of mixed type. The technological properties of each series are discussed (soda alkalinity, hardness, corrosivity,  $\text{pH}_s$  and buffer capacity) and it is concluded that, in each case, the TDS is of much greater importance than is chemical composition.

This simplifying conclusion is utilised to design a chemical classification of river waters according to quality and potential water use (chapter 16), although in so doing it is necessary also to take into account the content of organic material and dissolved oxygen of the water. Finally, brief accounts are given of the chemistry of some particular rivers of Natal (chapter 17) to illustrate the application of some of the matters considered earlier, and a concise summary of water quality throughout the Province as revealed by the results of extensive river surveys is provided.

The various calculations that may be applied to a given water analysis to determine the values of important derived parameters are summarised in Appendix A. Tables of numerical data required in these calculations are given in Appendix B. In Appendix C are listed various analyses and numerical results referred to in the text, while in Appendix D are described some experiments with artificial waters designed to test some of the theoretical equations.

# LIST OF SYMBOLS

See also note on barred symbols, p.61.

A	Total alkalinity as ppm of $\text{CaCO}_3$
a	Molar concentration of carbonic acid (total)
$a_1$	Molar concentration of bicarbonate ions $\text{HCO}_3^-$
$a_2$	Molar concentration of carbonate ions, $\text{CO}_3^{2-}$
$a_s$	Value of a for water in equilibrium with atmospheric carbon dioxide
B	Buffer capacity
C	Electrical conductivity in micromho at $20^\circ\text{C}$
c	Molar concentration of calcium hydroxide (total)
$c_1$	Molar concentration of monovalent $\text{Ca}(\text{OH})^+$ ions
$c_2$	Molar concentration of divalent $\text{Ca}^{2+}$ ions
$c_r$	Molar concentration of the r th ionic species
e	Total alkalinity in equivalents per litre, defined by equation (3.42)
$\bar{e}_c$	Total alkalinity in meq/litre calculated from equation (3.42)
$\bar{e}_t$	Total alkalinity in meq/litre determined by titration
F	Free (non-ionised) carbonic acid concentration as ppm of $\text{CO}_2$
f	Molar concentration of free (non-ionised) carbonic acid
G	Ratio of total millimolar concentration of acids and bases to the TDS in ppm
H	Molar concentration of hydrions
$H_*$	The product $H\gamma$ , equal under the appropriate conditions to the hydrion activity
h	Molar concentration of hydrochloric acid
I	Total hardness as ppm of $\text{CaCO}_3$
i	Total hardness in equivalents per litre, defined by equation (11.1)



j	Molar concentration of silica
$K_1$	First dissociation constant of carbonic acid
$K_2$	Second dissociation constant of carbonic acid
$K_c$	Second dissociation constant of calcium hydroxide
$K_m$	Second dissociation constant of magnesium hydroxide
$K_s$	Second dissociation constant of sulphuric acid
$k_a$	Solubility product of carbonic acid
$k_c$	Solubility product of calcium hydroxide
$k_{ca}$	Solubility product of calcium carbonate
$k_m$	Solubility product of magnesium hydroxide
$k_{ma}$	Solubility product of magnesium carbonate
$k_w$	Ionic product of water
m	Molar concentration of magnesium hydroxide (total)
$m_1$	Molar concentration of monovalent $Mg(OH)^+$ ions
$m_2$	Molar concentration of divalent $Mg^{2+}$ ions
n	Molar concentration of sodium hydroxide
OH	Molar concentration of hydroxyl ions
P	Equivalents of acid to attain phenolphthalein end-point
$P_h$	Permanent hardness as ppm of $CaCO_3$
$P(pH, \gamma)$	Ratio $F/e$ defined by equation (8.11)
p	Molar concentration of potassium hydroxide
pH	Defined, under the conditions supposed, as $-\log H_*$
$pH_s$	Saturation pH value
$P_h$	Permanent hardness in equivalents per litre
$Q(pH, \gamma)$	Ratio $a/e$ defined by equation (8.5)
S	Percentage saturation with carbonic acid
s	Molar concentration of sulphuric acid (total)



$s_1$	Molar concentration of bisulphate ions $\text{HSO}_4^-$
$s_2$	Molar concentration of sulphate ions $\text{SO}_4^{2-}$
R	Corrosion ratio
T	Equivalents of acid to attain methyl orange end-point
$T_h$	Temporary hardness as ppm of $\text{CaCO}_3$
$T_s$	Total dissolved solids in ppm
Z	Soda alkalinity as ppm of $\text{CaCO}_3$
z	Soda alkalinity in equivalents per litre, defined by equation (11.5)
$\beta$	Charge coefficient of acid or base
$\gamma$	Activity coefficient of univalent ions
$\mu$	Ionic strength
$v_r$	Valency of r th ionic species.

# THE CHEMISTRY OF RIVER WATERS

with special reference to  
THE RIVERS OF NATAL

## PART I THEORETICAL BASIS

### 1. GENERAL INTRODUCTION

The original intention of the present work was to establish some rational classification of river waters, according to their chemical composition, which could be used in assessing water quality and potential water use. It was soon found, however, that it was first necessary to re-examine the theoretical foundations of many of the concepts of water chemistry already in common use, since much of the existing literature was often vague and misleading.

The reason for this lack of clarity arises directly from the fact that the chemical characteristics of any natural water depend upon a whole set of interrelated ionisation and hydrolysis equilibria. For mathematical convenience, theoretical studies of these equilibria usually involve the introduction at an early stage of extensive approximations, with the result that there is often much doubt as to the strict validity of the final conclusions. In extreme cases, indeed, those conclusions may be quite fallacious.

A considerable simplification has been introduced to this field of study by Ricci (1952) which goes far to remove such defects. By utilising his concepts and methods of calculation it is possible to place water chemistry upon a surer and more rational foundation. Accordingly the present work became divided into three fairly distinct sections. In Part I the theoretical basis of the whole is described. In Part II various more specific topics are discussed in detail, These include the behaviour of natural waters towards carbon dioxide and calcium carbonate, the alkalinity of waters, their titration curves and the hardness of waters. Finally, in Part III it is then possible to consider river waters more generally and to take up the question of their chemical classification.

Throughout, an attempt is made at full generalisation, but with emphasis upon the river waters of South Africa and particularly of Natal.



## 2. SOLUTES OF RIVER WATERS

### Origin of river waters

It is generally accepted that very little of the water which flows as rivers or streams over the earth's surface is of primary origin (Mason, 1952). Almost the whole of their flow in fact originates as rain.

Once it has reached the ground, rainwater either flows over the surface and collects together to form streams (the run-off), following depressions and channels in the surface, or it seeps downwards (the run-in) through porous rocks and soils or through cracks and fissures. If the depth of penetration is not great, the run-in fairly rapidly reappears on the surface as a small intermittent spring or as seepage from the side of a channel, valley or depression. If the depth of penetration is more extensive the water may spend a considerable time underground, but it will still eventually reappear as a spring, perhaps many miles from its point of entry; such springs are usually of perennial type.

The concentration of total dissolved solids (TDS) in rain water is remarkably low (10 ppm or less), but rain contains much carbonic acid dissolved from the atmosphere and this is necessarily in a "free" or chemically uncombined form. Hence rainwater is very active in promoting the chemical decomposition of rocks and minerals, and in so doing it takes soluble materials into solution. Evidently the longer the water stays in contact with the rocks, the greater its TDS will become. Consequently run-off water is usually still of very low TDS, seepage water and that from shallow springs shows a higher level, and the water of springs fed from deep underground may often have a TDS exceeding 1000 ppm.

Since rivers contain water from all possible sources in intermixture, the TDS of river water may be anything from about 10 to 1000 ppm or more. We shall see that, in Natal at least, values greater than about 500 ppm usually arise through pollution, i.e. the addition of material of any kind to the river by human agency.

### Carbonates

In view of the above remarks it is only to be expected that carbonates and bicarbonates are the principal salts in most river waters.



Clarke (1924 A) states that these constitute about 50% of the dissolved solids in the average fresh water.

Limestones and dolomites are particularly susceptible to attack by water containing carbonic acid, the carbonates being converted to soluble bicarbonates. The feldspars present in many igneous rocks are also readily attacked in this way, being leached of lime and alkalies to leave a residue of clay.

Carbonates are also generated by the oxidation of the organic matter present in most natural waters and originating either by the decay of plant and animal material entering by natural means or from the inflow of sewage and similar effluents. Such organic material may be of almost any type, but it commonly includes a group of ill-defined colloidal substances often collectively termed "humus" and similar to peat in composition. According to figures collected by Clarke (1924 B), the highest concentrations of organic matter (excluding cases of pollution) are found in rivers of the tropical regions.

The waters from peats, recent or ancient, are characterised by a low TDS and a high proportion of carbonates derived from the oxidation of organic materials (Wilson, 1947). These waters are also low in sulphates, which become reduced to sulphides by bacteria in the peat (the sulphur subsequently being evolved as hydrogen sulphide), but usually high in sodium because of its replacement in the water for calcium and magnesium by base-exchange processes.

Wilcox (1962) has shown that the proportion of carbonates in water that has been used for irrigation may be materially decreased through precipitation of calcium carbonate in the soil, the calcium carbonate lost being roughly balanced by the uptake of an equivalent amount of sodium chloride. Evapotranspiration causes the TDS of the drainage water to become from 2 to 10 times greater than its initial level.

#### Sulphate

Normally sulphates rank next in preponderance to carbonates in river waters. They are derived principally from the oxidation of pyrite, which is widely disseminated in igneous rocks, and of some less common sulphides. The crystals of gypsum commonly occurring in clay deposits arise in this way (Vendl and Almasy, 1952). Underground water thus usually contains calcium sulphate in solution, and rivers may take up sulphates by passing over beds of gypsum.



The soils in arid regions commonly contain alkali sulphates, drawn upwards in solution by capillary action and crystallising as the solution evaporates at the ground surface. The occasional heavy rains of such regions redissolve these salts and wash them into rivers.

Sulphates also find their way into rivers through industrial pollution (especially where this comprises drainage from coal mines since pyrite usually accompanies the coal) and from agricultural fertilizers.

In the absence of pollution, South African rivers do not usually contain more than a few ppm of sulphate. Beauchamp (1953) has noted that streams flowing into East African lakes are generally low in sulphate, and an analysis of the Nile near Cairo given by Clarke (1924 B) also shows a low proportion of sulphate (about 4% of the TDS). A low sulphate content thus seems a widespread characteristic of surface waters of the African continent, although quite the reverse is the case in coalfield areas (Kemp, 1962).

#### Chloride

Although large quantities of chloride are liberated in the gaseous emanations from magmas (Mason, 1952) and sometimes appear in underground waters as a consequence of past magmatic activity (Lindgren, 1932; Bond, 1946), only a very small part of the chlorides of river waters can be traced to an origin in igneous rocks (Clarke, 1924 A). Sedimentary rocks usually contain traces of chloride, and those of marine origin are likely still to contain sea water in their pores which is released as the rock weathers or as underground water moves through it. In arid regions chlorides, like sulphates, occur in the soil and may become washed into rivers. In rare cases chlorides in a river may be derived from beds of rock salt or from brines such as those found in association with petroleum.

Chlorides derived from sea spray may be contained in the rain of coastal regions, and high proportions of chloride might arise from this source in coastal rivers (see discussion of sodium, below).

Chlorides also enter rivers as pollution from various sources, e.g. irrigation water (discussed above) and sewage effluents (sewage contains approximately 60 ppm of chloride).

#### Silica

The silica content of natural waters may be derived from the decomposition of almost any rock-forming silicate except those contained

in shales and slates. Hence only waters originating in and draining areas composed of shales, slates, quartzitic sandstones and ancient well-leached soils (all of which contain minerals representing the end-products of the aqueous decomposition of rocks) may be expected to be relatively low in silica content. It is not clear, however, whether this expectation is in fact valid, since the concentration of silica in waters presents several puzzling features.

The chief source of silica in natural waters is probably the feldspars. Clarke (1924 A) gives the percentage compositions of these minerals as follows:

	<u>Albite</u>	<u>Orthoclase</u>	<u>Anorthite</u>
$\text{SiO}_2$	68.7	64.7	43.2
$\text{Al}_2\text{O}_3$	19.5	18.4	36.7
$\text{CaO}$	-	-	20.1
$\text{Na}_2\text{O}$	11.8	-	-
$\text{K}_2\text{O}$	-	16.9	-

From these he deduces that albite and orthoclase will contribute more silica to percolating waters than will anorthite, and that whilst the first two will also contribute sodium and potassium, the third will yield calcium. Hence he supposes that when a water has an exceptionally high silica content, the content of alkalies will probably exceed that of lime.

Although the quartz grains of a sandstone would not be expected to yield much silica to water in contact with them it must be noted that, since the grains may be cemented together by a variety of materials (e.g. calcite, gypsum, silica itself, iron compounds), the compositions of waters from sandstones may vary accordingly (Bray, 1946). In fact, the cementing material is generally the source of most of the dissolved materials of waters associated with sandstones (Hem, 1959).

There is controversy concerning the state in which silica is held in solution in natural waters. Roy (1945) concluded that, though most geologists consider silica to occur in colloidal form, colorimetric tests have shown, as most chemists have assumed, that it is present in true solution, probably as the ion  $\text{SiO}_3^{2-}$ . However, other evidence quite contrary to this view has been published (Iwasaki, Katsura and Tarutani, 1951). Consequently Hem (1959) concluded that the silica of most waters is present as particles of sub-colloidal size, probably in a readily disturbed equilibrium with simple monosilicate ions.



In Table 2.1 are given the analyses (major solutes only) of 22 Natal rivers which are known to be unpolluted or polluted to only a very slight degree. These analyses will be used as examples throughout most of the present work, but for the moment it need only be noted that, unlike many of the other solutes, silica clearly does not vary systematically with the TDS. In fact, the concentration of silica appears to be scattered at random about a mean of 16.3 ppm.

Nordell (1951) has listed the analyses of 98 American rivers, and these show just the same characteristics, being randomly scattered about precisely the same mean of 16.3 ppm.

Neither the Natal nor the American rivers show any correlation between silica content and pH value, even though the solubility of silica increases markedly with pH (Iler, 1955).

A detailed review of present knowledge concerning dissolved silica and silicates has been given by Iler (1955), from which it appears that, in solutions of dilution comparable to that of natural waters, dissolved silica exists as mono- and disilicate ions  $\text{HSiO}_3^-$ ,  $\text{SiO}_3^{2-}$ ,  $\text{HSi}_2\text{O}_5^-$ ,  $\text{Si}_2\text{O}_5^{2-}$  and  $\text{HSi}_2\text{O}_6^-$ , together with the non-ionised monomeric acid  $\text{H}_2\text{SiO}_3$ . Evidence is cited for the occurrence of various equilibria between these ions and hydrions and the non-ionised acid. Yet the fact remains that in neither the American nor the Natal rivers is it normally necessary to include silica when calculating an ion balance; the total equivalent concentration of the cations is always substantially equal to that of the anions without the inclusion of silica. The same applies to all the analyses of Natal rivers presented in the present work, while the work of many survey teams, such as Inerfield et al (1960), in America have confirmed this finding for many other American rivers. Indeed it is usual American analytical practice (American Public Health Association, 1965) to regard silica as occurring in the ionic form  $\text{SiO}_3^{2-}$  only if the water is alkaline and the silica concentration high; otherwise it is considered non-ionic. (Many old analyses often show ionic silica, but usually it is clear that this is only a device to obtain a satisfactory ion balance and has no real justification; such analyses must be viewed with caution as they usually contain appreciable errors).

However, it is not invariably true that silica is ionic only when at high concentration in alkaline waters. According to data published by Taylor (1958), British rivers show quite different behaviour in that their silica concentrations are very much lower (ranging from



Table 2.1

## Chemical analyses of some Natal rivers

R i v e r	TDS in ppm	Conductivity in micromho	pH value	Ca, ppm	Mg, ppm	Na, ppm	K, ppm	Total alkalinity, as ppm CaCO <sub>3</sub>	SO <sub>4</sub> , ppm	Cl, ppm	SiO <sub>2</sub> , ppm
Sterk near Ambleside	41	53	7.4	3.1	2.2	4.7	0.7	23.2	Nil	4.5	11.5
Illovo above Richmond	41	66	8.1	5.2	1.8	4.2	0.1	27.2	Nil	0.8	13.0
Mooi above Mooi River	42	41	7.1	5.0	1.8	2.8	0.7	21.7	8.2	0.9	6.7
Karkloof at Shafton	42	43	7.7	3.5	1.7	4.2	0.5	23.8	Nil	1.7	16.5
Ingagane above Alcockspruit	49	58	8.4	5.0	2.0	4.3	3.6	34.8	3.0	0.9	6.7
Lions near Lidgetton	59	66	7.3	6.6	3.5	5.5	1.2	39.1	1.7	0.1	16.9
Nungwana near Nungwana Falls	60	98	8.4	3.9	2.5	7.0	0.1	20.6	Nil	15.2	14.7
Umgeni at Nagle Dam	69	91	7.1	6.5	3.0	7.9	1.0	38.3	1.4	8.9	14.7
Umgegu at Umfula	77	107	7.9	5.6	3.9	13.4	1.3	42.6	Nil	11.7	19.0
White Umfolozi near Vryheid	78	100	7.2	9.8	2.9	1.2	6.2	46.6	2.3	2.1	17.5
Lenjane's at Lenjane's Drift	81	100	7.8	12.6	5.7	6.5	3.0	58.6	2.3	2.3	13.0
Tugela at Colenso	85	121	8.0	12.9	5.9	6.4	0.7	68.6	1.8	1.2	15.1
Sundays near Newcastle	95	127	8.2	11.1	7.2	8.2	1.5	79.2	3.2	0.1	16.4
Gogoshi near Mtunzini	108	163	7.8	2.5	1.0	29.3	0.8	17.3	Nil	45.6	15.2
Unvoti at Bitakona	116	174	8.0	10.2	5.1	18.5	1.1	65.2	7.3	13.5	20.8
Umfolozi at Mtubatuba	136	243	7.8	14.6	9.0	24.8	1.5	94.5	Nil	19.3	15.6
Umzinkulwana at Baboons Castle	143	248	8.7	11.5	9.6	27.7	1.1	68.6	7.3	35.7	9.1
Bloukrans near Colenso	191	292	8.4	29.7	14.1	20.3	1.7	166.8	4.3	3.9	16.6
Umhlanga at Trenance	213	418	7.5	9.9	12.4	46.5	1.6	78.2	8.0	76.5	11.5
Umzinyatshana near Dundee	232	319	8.6	26.6	20.8	23.7	1.3	182.5	7.4	4.6	43.3
Isipingo near Inwabi	320	510	8.0	13.5	15.8	73.5	2.7	61.3	13.8	140.8	16.4
Mpushini near Pietermaritzburg	332	403	7.5	30.7	19.3	56.0	1.1	178.5	4.7	77.5	29.0

These analyses were obtained by the author during his work on the Natal rivers. This applies to all data cited in the text without reference.



about 1 to 15 ppm) and show a direct correlation with the TDS. In these rivers the silica appears to be ionic, or partly so.

### Calcium

The calcium in natural waters is principally derived from limestones and, to a lesser degree, from gypsum. However, limestones and gypsum deposits are relatively scarce in South Africa. In Natal, metamorphosed limestone occurs at the Marble Delta (the confluence of the Umzimkulu and Umzimkulwana rivers) near Port Shepstone, while gypsum is found in the Tugela valley near Ngobevu and appears to cause increases in the sulphate content of the Tugela river there.

The lime feldspar, anorthite, also forms an important source of calcium in igneous rocks, with hornblendes, pyroxenes and apatite as minor sources.

The loss of calcium carbonate from waters used for irrigation has already been mentioned.

### Magnesium

The major sources of magnesium are magnesian limestones and dolomites (not of much importance in South Africa), with amphiboles, pyroxenes and olivine as minor sources. Some magnesium also appears to be derived directly from sea spray (Bertrand, 1943, 1945).

In most waters of low to moderate TDS the magnesium content is usually less than that of calcium. Higher magnesium can occur on occasion, e.g. where magnesium minerals predominate in the rocks or where admixture with sea water occurs (Hem, 1959).

Schmassmann (1947), in a study of the underground water from limestones of the eastern Jura mountains, found that increasing concentrations of magnesium were accompanied by decreasing amounts of dissolved oxygen. This was traced to the oxidation of the ferrous iron occurring in dolomite in isomorphous replacement of the magnesium.

### Sodium

The sodium found in natural waters may often be derived (together with chloride) partly from the connate sea water of rocks of marine origin and partly from sea spray. Sea salts can in fact be carried a surprisingly great distance inland before becoming washed out of the atmosphere by falling rain, and many natural waters owe a large proportion of their dissolved salts to this origin. For example Gorham (1957) concluded that

70% of the salts in the waters of the English Lake District originate in this way, and about 50% of the salts in rivers of Galway.

The distance to which sea salts may be carried depends upon the strength and direction of the prevailing wind and also upon the rainfall in the region concerned. They are likely to travel further in arid regions where the precipitation is low. It is probable that the evaporation of droplets of sea water results in a mechanical separation of the various sea salts so that the composition of rain water, allowing for dilution, is not necessarily the same as that of the sea, nor is it necessarily invariable. Published information concerning this is scanty but has been summarised by Gorham (1955 A).

In arid regions much sodium may enter the rivers from the salts deposited by evaporation in the soil.

Sodium is also derived from the decomposition of the alkali feldspar albite, and some may be obtained from nepheline syenites (Clarke, 1924 A). Waters from coastal alluvium, though invariably high in chloride, may not necessarily be correspondingly as high in sodium. This is probably due to base-exchange processes occurring in the alluvium (Wilson, 1947).

Sodium is a very common constituent of polluting effluents of many kinds.

#### Potassium

The main source of potassium in natural waters is the alkali feldspar orthoclase, and in addition some may be derived from leucite rocks (Clarke, 1924 A). Agricultural fertilizers may also contribute much potassium to rivers.

However, potassium is of minor importance in natural waters and is rarely present in concentrations of more than a few ppm. It is less readily dissolved from rocks than is sodium (Hem, 1959) and is more readily removed from waters by base-exchange processes.

#### Minor mineral solutes

Unpolluted natural waters contain many other mineral solutes than those considered above, but usually in only very small concentrations.

Thus iron and aluminium are almost invariably present in river waters, but rarely in large amounts. Indeed Clarke (1924 A) stated that when more than a trace of either of these is found to be present it is most likely that small amounts of suspended silt have not been completely



removed from the sample before analysis. Pollution may give rise to abnormally high concentrations, however. In particular, where rivers receive drainage from coal mines or from natural coal outcrops they are likely to contain high concentrations of these elements (Braley, 1954), the iron being derived from the oxidation of pyrite contained in the coal seams and associated strata and the aluminium coming from local rocks and soils by the action of the acidic substances formed by that oxidation. In Natal, the drainage from disused and working coal mines is a pollution problem of particular concern (Kemp, 1962). However, the iron and aluminium contents of unpolluted rivers are usually less than 1 ppm (Hem, 1959).

Lead, zinc, copper and other metals have been found in waters in regions where their ores are mined. Manganese is also found occasionally but rarely exceeds 1 ppm unless the water has been polluted or has an acidic reaction (Hem, 1959).

Traces of phosphate may be taken up from sedimentary rocks and from the apatite of igneous rocks, and larger concentrations may be found where the water traverses phosphate rock. In Natal the phosphate concentration in unpolluted rivers is always small, not usually exceeding about 0.3 ppm as  $\text{PO}_4^{3-}$ . Higher concentrations may occur where agricultural fertilizers are used and where sewage or similar effluents are present, phosphates often being present in soap preparations and synthetic detergents.

Traces of fluoride and of borate are often encountered in water draining certain igneous and metamorphic rocks, especially those containing apatite and tourmaline (Hem, 1959). Fluoride concentrations greater than about 1 ppm are usually considered objectionable in water to be used for domestic supply.

Except for some mineral springs, natural waters normally contain only small concentrations of nitrates, leached from soils where decay processes or the biological fixation of nitrogen are occurring. Larger quantities are usually indicative of organic pollution. The nitrate content of unpolluted Natal rivers does not usually exceed 1.5 ppm as nitrogen, although it shows a fairly great variability. Whenever cases of excessive algal growth have been investigated here it has usually been found that an increased nitrate content has been the cause.

Pollution can also give rise to the presence of ammonia, but Ingols and Navarre (1952) have found that some granites contain ammonium



chloride which is leached out as the rock weathers.

### Pollution

Polluted waters may, of course, contain almost any substance at all in solution or suspension, and detailed discussions have been given by many authors, e.g. Klein (1957).

Pollution of an inorganic nature usually involves an increase in the TDS. This can lead to the destruction of organisms inhabiting a river through the action of osmotic effects, particularly if the TDS exceeds about 2000 ppm. Changes in the pH value may also be caused and few organisms can resist large changes in this parameter, most being adapted to living in a single restricted pH range. In addition, some dissolved salts may have a direct toxic action.

An increase in the amount of suspended matter in the water can bring about biological changes. Too much silt, in fact, can destroy practically the whole fauna of a river - breathing tubes become clogged, burrows become silted up, the character of the river bed may be changed, and so on. Algae can also be destroyed, since a high silt content will reduce the intensity of light below the water surface and so hinder photosynthetic processes. In some cases large volumes of pollution may change the temperature of the water (boiler effluents, cooling waters, etc) and this also will cause changes in the riverine flora and fauna.

Organic pollution may give rise to any of the above effects and in addition produces effects of its own, invariably resulting in a change of the fauna and flora through interference with the ecological balance. Changes in the habitats of the animal population may also be induced (the interstices between stones may be blocked by deposits of slime, the marginal vegetation may become fouled, sludge banks may be formed on the river bed, and so on) and these invariably lead to changes in the population itself.

The amount of oxygen contained in solution in the water is always decreased by organic pollution since decay processes (invariably oxidative) are initiated (some inorganic pollutants, e.g. ferrous iron, may have a similar effect). Unpolluted natural waters free from organic matter are almost saturated with dissolved oxygen and thus present a reasonably clean appearance, are free from odour and maintain a normal animal and plant population. With a moderate amount of organic pollution, however, the growth of algae may be promoted owing to the presence of nutrient



substances such as ammonia, nitrates and phosphates, which may be present initially in the pollution (hence purely inorganic pollution can also have a similar effect) or may be formed by decomposition processes instigated by the action of bacteria. The so-called "sewage fungus" may appear, excessive developments of the sheathed filamentous bacterium Sphaerotilus natans or of the aquatic fungus Leptomitius lactens (Harrison and Heukelekian, 1958). Protozoa (which prey upon bacteria) and algal feeders (insect larvae, small crustaceans, snails and some fish) may also proliferate, while the growth of worms is usually encouraged.

If the pollutorial load is very large it may well exhaust the dissolved oxygen of the water completely so that conditions become anaerobic. The water then becomes black, unsightly and malodorous and its normal fauna and flora are completely destroyed. Under such conditions fermentation processes, again instigated by bacteria, convert the organic materials to soluble substances (pyruvic acid, indole, skatole, mercaptan, cadaverine, putrescine, etc) which are ultimately removed (as hydrogen sulphide, methane etc) but by different routes than under aerobic conditions. Even if the water does not actually become anaerobic, suspended solids may be deposited on the river bed and, under appropriate conditions, build deep sludge banks within which anaerobic conditions may arise.

One way of assessing the organic content of a water is to determine the biochemical oxygen demand (BOD), and this will be discussed more fully in chapter 16.

#### Total dissolved solids

Since any river continually picks up soluble matter from the rocks and soils that it drains (for river water is never more than an extremely dilute solution which seldom approaches saturation with any dissolved salt) and continually receives detritus of all kinds that falls into it, its TDS usually increases progressively from source to mouth, even in the absence of any effluent flows that may enter the water. This general rule may be set aside, however, if the river has tributaries which carry water of very low TDS.

Clarke (1924 A) and Conway (1942) have considered the effects of geology upon the TDS of rivers and concluded that streams issuing from and draining igneous or metamorphic rocks show a low TDS, usually 50 ppm or less. Where there are shales and sandstones the TDS can rise to

100 ppm, but where limestones occur it may reach 200 ppm or more. Higher values than this (and values exceeding 1000 ppm may be encountered) may be due to drainage from arid regions where saline soils occur, or else to pollution.

The TDS of a river water is, however, highly variable and is influenced by many factors other than geology. Some of these will be considered in a later chapter.



### 3. FUNDAMENTAL IONIC RELATIONS

#### Outline of the theoretical treatment

Ricci's treatment (1952) is based on the concept that any aqueous solution of electrolytes can be regarded as a solution of the corresponding free acids and bases, utilising the simple definitions that an acid is a chemical compound (i.e. not an ion) which provides hydrions when in aqueous solution and a base is one which similarly provides hydroxyl ions. These acids and bases will be ionised to a greater or lesser degree.

In the majority of cases the resulting ions do not chemically react with one another by processes other than the ionisation reactions themselves or their converses. Consequently the various acids and bases present may be regarded as quite independent. Cases do occur wherein other reactions take place between ions, e.g. the polymerisation of simple monosilicate ions, but even these can be treated by the same mathematical principles. Ricci calls such cases complex, and the mathematical relationships involved are indeed more complicated. Complex solutes, however, are rarely of importance in natural waters.

Each molecule of acid or base in an aqueous solution gives rise to a certain number of charged species. The number of equivalents of charge (other than due to hydrogen or hydroxyl ions) derived from one mole of the acid or base is defined as its charge coefficient,  $\beta$ . This can be expressed as a function of the ionisation constants and the hydrion concentration as the only required parameters. Thus for a polybasic acid  $H_zX$  under ideal conditions:

$$\beta = \frac{1 + 2 K_2/H + 3 K_2 K_3/H^2 + \dots + z K_2 K_3 \dots K_z/H^{z-1}}{1 + H/K_1 + K_2/H + K_2 K_3/H^2 + \dots + K_2 K_3 \dots K_z/H^{z-1}} \quad (3.1)$$

where  $H$  is the molar hydrion concentration and the  $K$ 's are the ionisation constants of the acid. A similar expression holds for a polyacidic base  $M(OH)_z$ , but containing the molar hydroxyl concentration  $OH$  in place of  $H$ . Where a dissociation is strong, the corresponding constant is considered infinite.

The electroneutrality condition is then:

$$H - OH = \sum_a \beta_a t_a - \sum_b \beta_b t_b \quad (3.2)$$

where the suffixes a and b refer to acids and bases respectively and  $t_a$  or  $t_b$  denotes the total (analytical) molar concentration of the corresponding acid or base.

Since the ionic product of water is constant, under ideal conditions it may be represented as:

$$k_w = H \times OH \quad (3.3)$$

The electroneutrality condition (3.2), after substitution of the appropriate expressions for the  $\beta$ 's, can thus always be expanded to a polynomial of degree n in H:

$$A_n H^n + A_{n-1} H^{n-1} + \dots + A_1 H + A_0 = 0 \quad (3.4)$$

Here the coefficients of H are functions of the molar concentrations and ionisation constants of the acids and bases, while n is equal to the number of ionisation constants (including  $k_w$ ) plus one.

This polynomial may be accurately solved for H by numerical methods, or an approximate solution may be obtained by solving the quadratic:

$$a H^2 + b H + c = 0 \quad (3.5)$$

obtained by rejecting from the polynomial all but the three successive largest terms. The success of this approximation depends upon the fact that the successive coefficients  $A_r$  of (3.4) involve progressively more of the ionisation constants in products with a progressively greater number of factors, so that  $A_r$  falls in magnitude as r increases. The terms  $A_r H^r$  therefore numerically increase, for a given value of H, and then decrease again as r increases. The three largest terms therefore always occur together.

Each approximate solution obtained in this way will be valid over a specific range of H or of the other concentrations, and the approximation procedure therefore has the advantage that it provides, not a single value for H, but an algebraic expression giving H in terms of some of the constants and concentrations. For example, the Henderson and similar simple equations result automatically from this procedure. The accuracy of such an approximate algebraic solution is extremely great under the appropriate conditions, and these conditions can always be specified precisely in terms of the coefficients of the general polynomial



(3.4) and hence in terms of the ionisation constants and concentrations.

In general form, the required solution of the quadratic (3.5) may be written as:

$$H = -\frac{b}{2a} + \sqrt{\left(\frac{b}{2a}\right)^2 - \frac{c}{a}} \quad (3.6)$$

since the negative root is physically meaningless. If  $c/a$  is small in comparison with  $(b/2a)^2$  this further approximates to:

$$H = -c/b \quad (3.7)$$

and if  $c$  is small in comparison with both  $a$  and  $b$ :

$$H = -b/a \quad (3.8)$$

Corrections for non-ideality are made by introducing activity coefficients, which can be done at any stage of the working. Provided the solution is sufficiently dilute we can utilise the Debye-Huckel limiting law and take  $\gamma$  as the activity coefficient of any univalent ion in the solution,  $\gamma^4$  as that of any divalent ion,  $\gamma^9$  as that of any trivalent ion, and so on. Moreover, under the condition supposed the value of  $\gamma$  can be equated with the mean activity coefficient  $\gamma_{\pm}$  of a strong uni-univalent electrolyte at the same ionic strength. This results in the following replacements finally appearing:

$$\begin{aligned} k_w & \text{ replaced by } k_w/\gamma^2 \\ K_1 & \text{ replaced by } K_1/\gamma^2 \\ K_2 & \text{ replaced by } K_2/\gamma^4 \\ K_3 & \text{ replaced by } K_3/\gamma^9 \\ & \text{and so on.} \end{aligned}$$

Thus  $\gamma$  occurs always as a square or higher power and in combination with concentration terms in such a fashion that the objection that single-ion activity coefficients are of no physical significance (Guggenheim, 1933) does not apply.

This procedure will certainly be satisfactory over the concentration range of main interest in the present work (up to a TDS of 1000 ppm), but it cannot be relied upon outside that range since the mean activity coefficients of uni-univalent electrolytes can then no longer be supposed equal (Lewis and Randall, 1923).

The actual values of  $\gamma$  will be discussed in a later chapter.

Under ideal conditions, the pH value of an electrolyte solution is simply and unambiguously defined in terms of decadic logarithms:

$$\text{pH} = - \log H \quad (3.9)$$

but under non-ideal conditions this must be replaced by:

$$\text{pH} = - \log \gamma H \quad (3.10)$$

This no longer avoids the objections concerning single-ion activity coefficients, but since the whole concept of pH is theoretically uncertain (Kemp, 1950) this last equation must be regarded as purely empirical. It is completely justified by experimental results.

Other symbols and functions will be introduced and explained during the course of this text. In general the scheme is followed of using lower case Roman letters (with suffixes if necessary) for molar concentrations, K with suffixes for the ionisation constants of acids and bases, and lower case k with suffixes to denote ionic products. Temperature variations are not considered in the present work, it being assumed that the temperature is constant at a standard 25°C. Valuable contributions to the study of temperature effects have been made by Langelier (1946) and by Dye (1952). For ready reference, the values used for commonly occurring constants are given in Table 1B of Appendix B.

#### Solutes and ions of natural waters

From chapter 2 it is seen that the major inorganic solutes of natural waters (excluding mineral springs, which often depart from normal in composition) are the carbonates, bicarbonates, sulphates and chlorides of calcium, magnesium, sodium and potassium, together with silica usually in non-ionic form. Other cations and anions may also be present, but usually in amounts too small to be of importance in the discussion of pH values.

Following Ricci (1952), a natural water may thus be regarded in the first instance as containing carbonic, sulphuric and hydrochloric acids together with calcium, magnesium, sodium and potassium hydroxides, as well as non-ionic silica. The TDS, as has been stated, may be anything from about 10 to 1000 ppm or more, although values greater than about 500 ppm in ordinary surface waters in Natal at least usually arise through pollution. For sea water, estuarine waters and underground waters with higher TDS values than 1000 ppm there is usually insufficient data available to establish valid activity corrections. For example, it



appears that in sea water  $\gamma$  should be of the order of 0.66, but it can no longer be taken as the same for all uni-univalent salts and for purposes of pH calculation (which in this case depends almost entirely upon bicarbonates) we shall find that a much lower value must be used. The same theoretical principles still apply to such waters, however.

The concentrations of all the important solutes in a water may be determined unambiguously by suitable analytical methods, although few if any water chemists ever undertake the determination of carbonic acid as a routine measure. The total carbonic acid, as will be shown, is one of the most important parameters in water chemistry since it is one of the factors governing the precise shape of the titration curve, but fortunately, in the absence of its direct determination, it is possible to calculate it fairly accurately from other data. The calculation is often made by means of a number of assumptions and approximate relationships which may not be theoretically well founded, but a rigid treatment is relatively easy to devise (see chapter 8).

Each of the major solutes of natural waters will now be considered in turn.

#### The strong electrolytes

Sodium hydroxide, potassium hydroxide and hydrochloric acid are strong uni-univalent electrolytes, completely ionised at all concentrations. This means that, in each case,  $\beta = 1$ . Discussion of these cases illustrates the general method of working, although they are of trivial nature.

Hence for hydrochloric acid in water under ideal conditions, equation (3.2) becomes simply:

$$H - OH = h \quad (3.11)$$

where  $h$  is the molar concentration of the acid (equal to the molar concentration of chloride ions). Using (3.3) this gives:

$$H - k_w/H = h \quad (3.12)$$

which rearranges to the quadratic:

$$H^2 - hH - k_w = 0 \quad (3.13)$$

By (3.6) the exact solution of this is:

$$H = \frac{h}{2} + \sqrt{\frac{h^2}{4} + k_w} \quad (3.14)$$

which may be written:

$$H = \frac{1}{2}h + \frac{1}{2} \sqrt{(h^2 + 4k_w)} \quad (3.15)$$

The value of  $k_w$  at  $25^\circ\text{C}$  is  $1.01 \times 10^{-14}$  (Harned and Owen, 1950) so that for all practical purposes (3.15) reduces to:

$$H = h \quad (3.16)$$

Alternatively, this same result could be obtained by applying equation (3.8). The introduction of activity corrections for the non-ideal case leaves (3.16) unchanged.

For sodium hydroxide at molar concentration  $n$  we similarly have:

$$H - OH = -n \quad (3.17)$$

Using (3.3) to eliminate  $OH$  finally gives the quadratic:

$$H^2 + nH - k_w = 0 \quad (3.18)$$

This may be solved directly by (2.6):

$$H = \frac{-n}{2} + \frac{1}{2} \sqrt{(n^2 + 4k_w)} \quad (3.19)$$

which is fully accurate. But since  $4k_w$  is negligible in comparison with  $n^2$  in practical cases, it appears that (3.19) gives zero as the corresponding approximate value for  $H$ . Physically this is not acceptable, but it must be realised that the result only means that  $H$  is negligible in comparison with  $n^2$  and hence is a perfectly valid result. To obtain a more useful value for  $H$ , we may apply equation (3.7), which gives:

$$H = k_w/n \quad (3.20)$$

Applying activity correction, this becomes:

$$H = k_w/n \gamma^2 \quad (3.21)$$

It is interesting to note, however, that using (3.3) in (3.20) gives:

$$H = H.OH/n \quad \text{or} \quad OH = n \quad (3.22)$$

and this is unchanged in the non-ideal case.

Exactly similar results are obtained for potassium hydroxide.

#### Calcium and magnesium hydroxides

The hydroxides of calcium and magnesium,  $\text{Ca(OH)}_2$  and  $\text{Mg(OH)}_2$ , are diacidic bases, strong in the first dissociation but weak in the second (Bell, 1954; Prue, 1966; Stock and Davies, 1948). In aqueous



solutions they thus give rise to the ions  $\text{Ca(OH)}^+$ ,  $\text{Ca}^{2+}$ ,  $\text{Mg(OH)}^+$  and  $\text{Mg}^{2+}$ , but non-ionised molecules are never present.

To consider calcium hydroxide first, let the total (analytical) molar concentration be  $c$ . Then if  $c_1$  is the molar concentration of the univalent ion and  $c_2$  that of the divalent ion:

$$c = c_1 + c_2 \quad (3.23)$$

Under ideal conditions, the second dissociation constant  $K_2$  is given by:

$$K_c = \frac{k_w c_2}{c_1 H} \quad (3.24)$$

its numerical value being  $3.1 \times 10^{-2}$  (Vogel, 1951).

From these two equations follow the relations:

$$\begin{aligned} c_1/c &= k_w / (k_w + K_c H) \\ c_2/c &= K_c H / (k_w + K_c H) \end{aligned} \quad (3.25)$$

for the ionisation fractions. Correcting these for non-ideality gives:

$$\begin{aligned} c_1/c &= k_w \gamma^2 / (k_w \gamma^2 + K_c H) \\ c_2/c &= K_c H / (k_w \gamma^2 + K_c H) \end{aligned} \quad (3.26)$$

By the base analogue of (3.1), the charge coefficient of this hydroxide is ideally:

$$\beta = \frac{k_w + 2 K_c H}{k_w + K_c H} \quad (3.27)$$

Magnesium hydroxide gives rise to equations of identical form. We shall denote its total molar concentrations by  $m$ , those of the uni- and divalent ions by  $m_1$  and  $m_2$ , and let  $K_m$  stand for the second dissociation constant. The value of  $K_m$  is  $2.6 \times 10^{-3}$  (Vogel, 1951).

The values of the ionisation fractions for the two hydroxides under ideal conditions for various values of pH are as shown in Figure 3.1. It will be seen that the univalent ion  $\text{Ca(OH)}^+$  is of little or no importance below about pH 11 while the univalent ion  $\text{Mg(OH)}^+$  is of little or no importance below about pH 10, i.e. it exists in appreciable proportions down to a rather lower pH than is the case for the calcium hydroxide system.

If Figure 3.1 (and similar diagrams such as Figures 3.2 and 3.3) are redrawn using a logarithmic scale on the vertical axis, the sloping

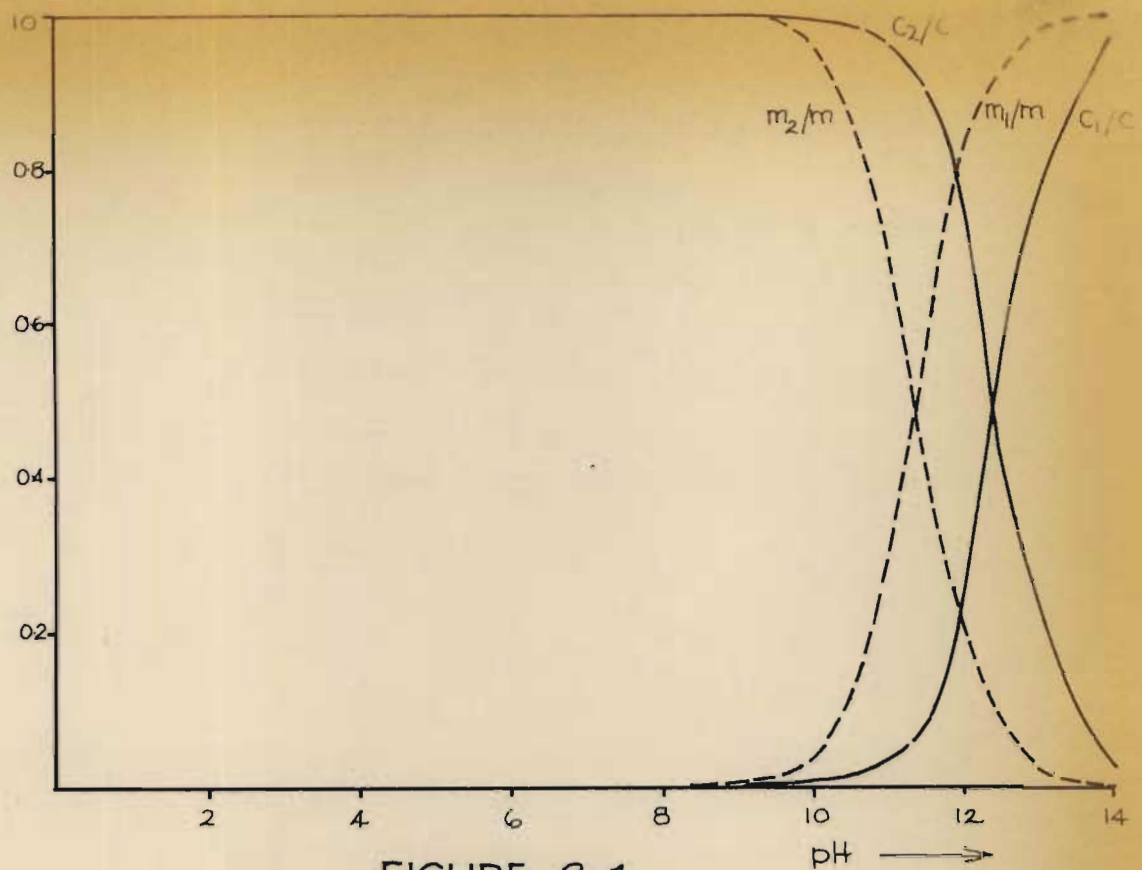


FIGURE 3.1

Ideal ionisation fractions for calcium hydroxide (—) and magnesium hydroxide (---) at different pH values

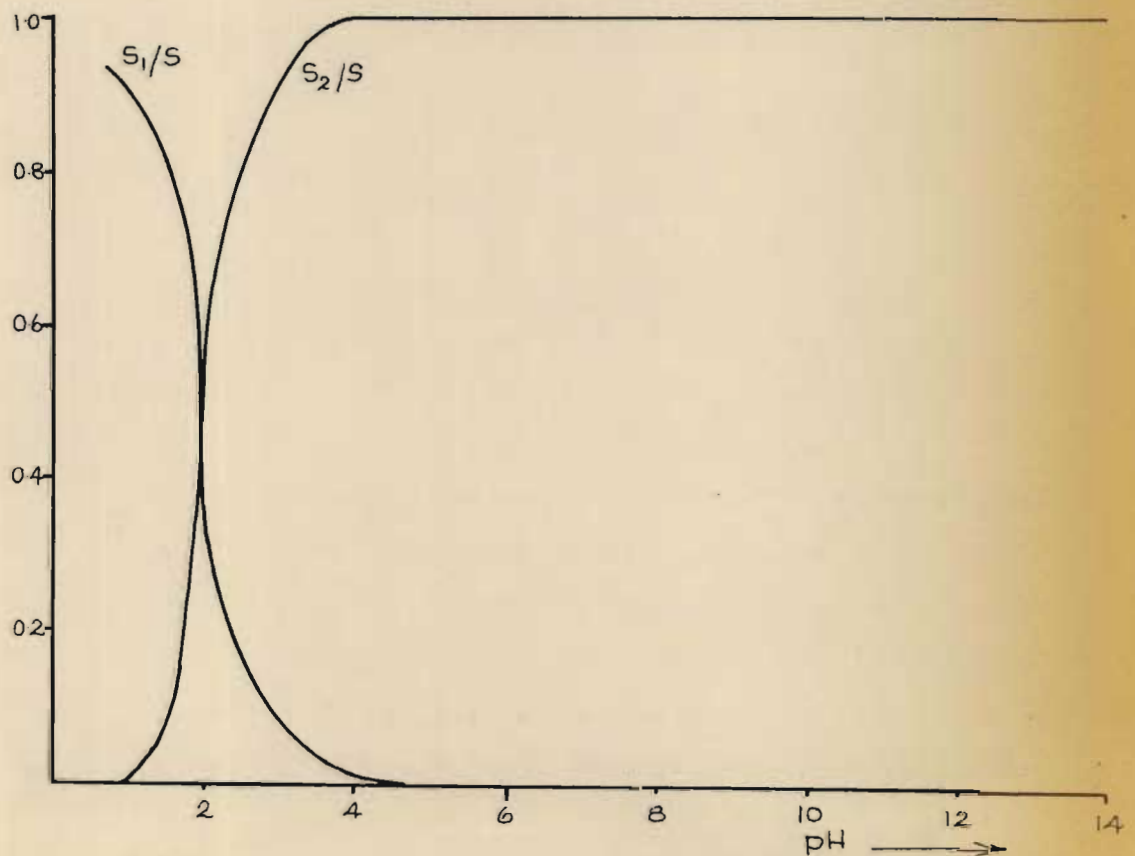


FIGURE 3.2

Ideal ionisation fractions for sulphuric acid at different pH values



curved portions of the graphs will become virtually straight lines. Apart from a scale factor, the diagrams will then be identical with the versatile logarithmic diagrams that have been used extensively by Scandinavian chemists for representing chemical equilibria (Lee and Sillen, 1959).

### Sulphuric acid

Sulphuric acid,  $\text{H}_2\text{SO}_4$ , is a dibasic acid, strong in its first dissociation but weak in its second. In aqueous solutions it thus gives rise to the bisulphate and sulphate ions,  $\text{HSO}_4^-$  and  $\text{SO}_4^{2-}$ , but non-ionised molecules are never present.

Denoting the total (analytical) molar concentration by  $s$  and those of the bisulphate and sulphate ions respectively by  $s_1$  and  $s_2$ , it follows that:

$$s = s_1 + s_2 \quad (3.28)$$

Under ideal conditions, the second dissociation constant  $K_s$  is defined by:

$$K_s = \frac{s_2 H}{s_1} \quad (3.29)$$

its numerical value being about  $1 \times 10^{-2}$  (Vogel, 1951; Glasstone, 1942).

From these relations it follows that:

$$\begin{aligned} s_1/s &= H/(H + K_s) \\ s_2/s &= K_s/(H + K_s) \end{aligned} \quad (3.30)$$

which enable the ionisation fractions  $s_1/s$  and  $s_2/s$  to be calculated as functions of the pH. The calculated ideal values are shown in Figure 3.2, from which it is seen that only the sulphate ions are of any significance, except at pH values below about 4.

By equation (3.1), the charge coefficient of sulphuric acid is ideally:

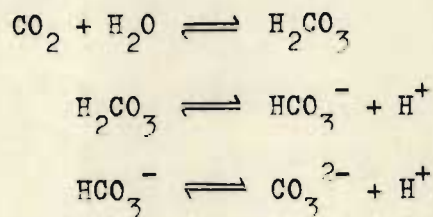
$$\beta = \frac{H + 2 K_s}{H + K_s} \quad (3.31)$$

### Carbonic acid

Carbonic acid,  $\text{H}_2\text{CO}_3$ , is dibasic, giving rise to bicarbonate and carbonate ions,  $\text{HCO}_3^-$  and  $\text{CO}_3^{2-}$ . Both dissociations are weak, so that non-ionised molecules are always present in aqueous solutions.

Values of the first dissociation constant,  $K_1$ , at 25°C have been given as  $4.54 \times 10^{-7}$  (MacInnes and Belcher, 1933),  $4.323 \times 10^{-7}$  (Shedlovsky and MacInnes, 1935) and  $4.45 \times 10^{-7}$  (Harned and Davis, 1943). A mean value of  $4.43 \times 10^{-7}$  is there<sup>fore</sup> adopted in the present work. The value of the second dissociation constant,  $K_2$ , at 25°C was determined as  $4.69 \times 10^{-11}$  by Harned and Scholes (1941).

It should be noted that when carbon dioxide is dissolved in water the following equilibria are established:



The constant here denoted by  $K_1$  is in fact defined as:

$$K_1 = \frac{[\text{H}^+][\text{H}_2\text{CO}_3^-]}{[\text{CO}_2 + \text{H}_2\text{CO}_3]}$$

where the brackets denote molar concentrations. A review of the carbon dioxide - water system has been given by Bell (1959), who showed that the ratio  $[\text{H}_2\text{CO}_3] / [\text{CO}_2]$  at 25°C is about 0.0037. Consequently the true first dissociation constant of carbonic acid, defined as

$[\text{H}^+][\text{HCO}_3^-] / [\text{H}_2\text{CO}_3]$ , has the value  $K_1$  (0.0037/1.0037). However, if (as is done in the present work) we agree to make no distinction between "free carbonic acid", "free carbon dioxide" and "non-ionised carbonic acid" but include them all in the value of the term  $[\text{H}_2\text{CO}_3]$ , we can satisfactorily and much more simply operate with  $K_1$  defined as:

$$K_1 = \frac{[\text{H}^+][\text{HCO}_3^-]}{[\text{H}_2\text{CO}_3]}$$

Let  $a$ ,  $f$ ,  $a_1$  and  $a_2$  respectively denote the molar concentrations of total carbonic acid, free (non-ionised) carbonic acid, bicarbonate ions and carbonate ions. Then, under ideal conditions, the dissociation constants are given by:

$$\begin{aligned} K_1 &= \frac{a_1^{\text{H}}}{f} \\ K_2 &= \frac{a_2^{\text{H}}}{a_1} \end{aligned} \tag{3.32}$$



while the four concentrations are related by:

$$a = f + a_1 + a_2 \quad (3.33)$$

From these relations it follows that:

$$\begin{aligned} a_1/a &= K_1 H / (H^2 + K_1 H + K_1 K_2) \\ a_2/a &= K_1 K_2 / (H^2 + K_1 H + K_1 K_2) \\ f/a &= H^2 / (H^2 + K_1 H + K_1 K_2) \end{aligned} \quad (3.34)$$

Applying the activity corrections for the non-ideal case, these become:

$$\begin{aligned} a_1/a &= K_1 H \gamma^4 / (H^2 \gamma^6 + K_1 H \gamma^4 + K_1 K_2) \\ a_2/a &= K_1 K_2 / (H^2 \gamma^6 + K_1 H \gamma^4 + K_1 K_2) \\ f/a &= H^2 \gamma^6 / (H^2 \gamma^6 + K_1 H \gamma^4 + K_1 K_2) \end{aligned} \quad (3.35)$$

Assuming ideality, the values of these ionisation fractions can readily be found from (3.34) for various values of pH. The results obtained by such calculations are shown in Figure 3.3. Evidently at pH values between about 6 and 9 bicarbonate ions predominate, but in more alkaline solutions carbonate ions become important whilst in more acidic ones free carbonate acid is present in appreciable proportions. It is readily shown that the maximum value of  $a_1/a$  occurs at an (ideal) pH of 8.34, corresponding to  $H = \sqrt{K_1 K_2}$ .

By (3.1), the value of the charge coefficient of carbonic acid in aqueous solution is (ideally) given by:

$$\beta = \frac{K_1 H + 2 K_1 K_2}{H^2 + K_1 H + K_1 K_2} \quad (3.36)$$

### Titration curves

We shall in this work be concerned only with the titration of dissolved substances with strong monobasic acid or strong monoacidic base. Consequently whenever we refer to a titration curve it is to be understood that reference is always made to a curve obtained in that way.

Let  $y$  be the molar concentration of any acid or base, and suppose that it is titrated as described. For simplicity, we assume ideal conditions and also suppose that the volume of the solution being titrated does not alter significantly during the process.

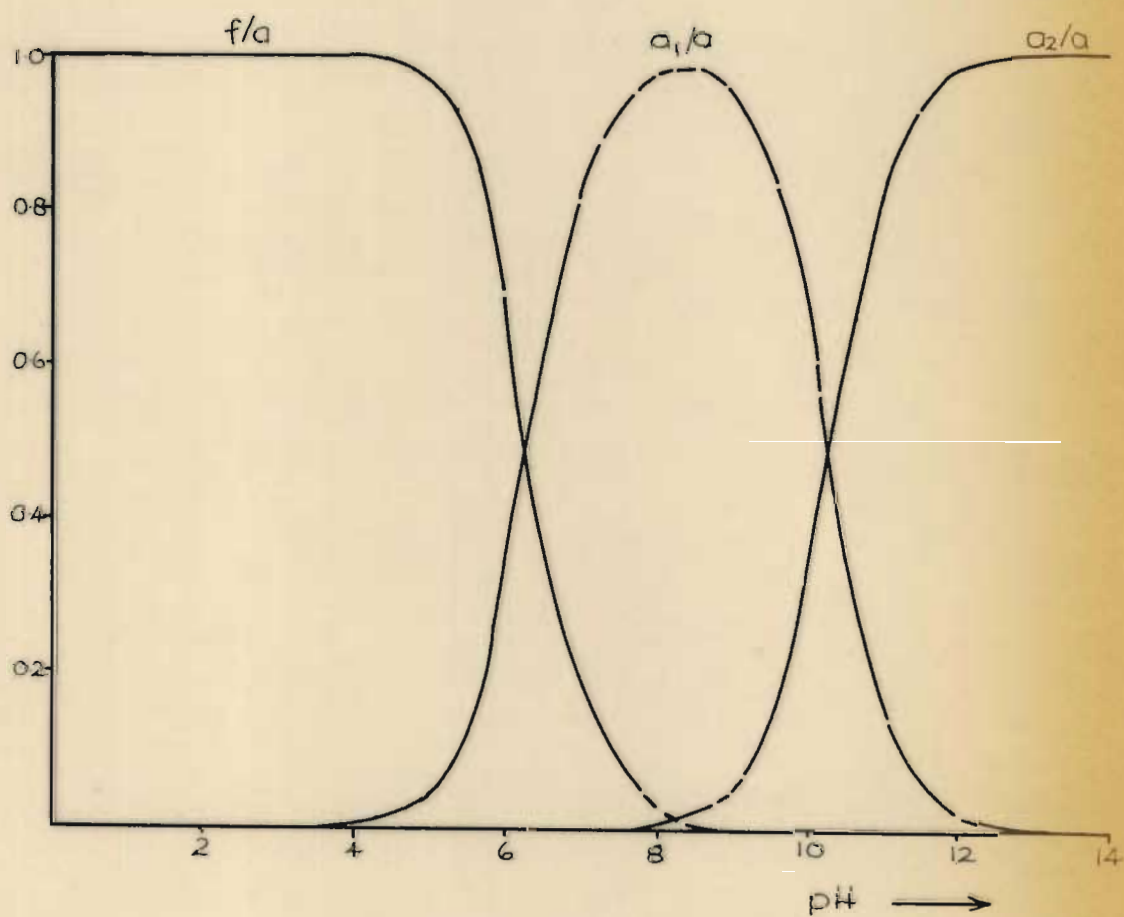


FIGURE 3.3

Ideal ionisation fractions for carbonic acid at different pH values



The charge coefficient of the strong acid or base is unity (see above), while that of the acid or base being titrated is  $\beta$  and given by the correct form of equation (3.1). For the titration of an acid we therefore have, by equation (3.2):

$$H - OH = \beta y + x \quad (3.37)$$

and for the titration of a base:

$$H - OH = -\beta y + x \quad (3.38)$$

where  $x$  denotes the molar concentration of strong acid at any instant or, if  $x$  is negative, the molar concentration of strong base. These equations may be expanded to polynomials like (3.4). By solving for  $H$  and plotting the values of  $pH = -\log H$  against the corresponding values of  $x$  we can thus draw the required titration curve.

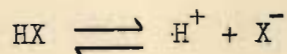
The properties of such curves have been considered in detail by Ricci (1952). For present purposes we need only note a few of the salient points.

If the curve relates to a polyacidic base  $M(OH)_z$  or a polybasic acid  $H_zX$  with  $z$  stages of dissociation, its equation will be of degree  $z + 2$  in  $H$  or, if the first dissociation is strong,  $z + 1$ . For example, sodium hydroxide and hydrochloric acid provide quadratics in  $H$ , calcium hydroxide and sulphuric acid provide cubics, and carbonic acid gives an equation of the 4th degree.

Each titration curve will show one or more "end-point" inflections where the  $pH$  changes very greatly for small additions of strong acid or base. For a strong acid or base there will be one such inflection, occurring at the point of stoichiometric neutralisation. For a weak acid or base there will be one inflection occurring at the same point but becoming less marked with lower values of the dissociation constant, and another occurring at  $x = 0$  but usually so vague as to be of no practical use. For a dibasic acid there will in general be three such inflections: one occurring at  $x = 0$ , one at  $x = y$  and one at  $x = 2y$ , but not all of these need be sufficiently pronounced to be experimentally detectable, the governing factors being the values of the two dissociation constants. Thus for sulphuric acid, strong in its first dissociation, only the end-point  $x = 2y$  appears; for carbonic acid only the end-points  $x = 0$  and  $x = y$  are detectable. Similarly, a diacidic base in general shows end-points at  $x = 0$ ,  $x = -y$  and  $x = -2y$ , but for calcium and magnesium

hydroxides only the third of these is detectable.

The reciprocal of the gradient of the titration curve is a measure of the buffer capacity of the solution being titrated, i.e. of the degree to which the solution resists pH changes when acids and bases are added to it. Buffering action arises from the existence of equilibria of the form:



which follow the Le Chatelier principle. Near an end-point inflection of any kind the gradient is high and hence the buffer capacity low. Between two such inflections the gradient is low so that the buffer capacity is high; moreover it here becomes higher as the concentration increases. The concept of buffer capacity has application in some problems of water treatment, as we shall show.

The titration curve of carbonic acid is particularly important in the study of natural waters. The equation of this curve, under ideal conditions and the other restrictions supposed, is:

$$\text{H} - \text{OH} = \frac{a (K_1\text{H} + 2 K_1K_2)}{\text{H}^2 + K_1\text{H} + K_1K_2} + x \quad (3.39)$$

where  $a$  is the molar concentration, and for  $a = 10^{-2}$  the curve is as shown in Figure 3.4. The two end-points occur at pH 4.18 with  $x = 0$  and 8.34 with  $x = a$ . The former is commonly known as the "methyl orange" end-point, the latter as the "phenolphthalein" one, since these two indicators are often used for their detection. The exact pH value of each end-point depends on the value of  $a$ ; the methyl orange end-point may occur anywhere between pH 4 and 5, the phenolphthalein between pH 7 and 9. The greatest buffer capacity occurs between  $x = 0$  and  $x = a$ , especially at high concentrations.

#### General equations for hydron concentration

From equation (3.2), using also (3.3) and inserting the proper expressions for the charge coefficients, the general equation for the hydron concentration, under ideal conditions, of a water containing carbonic, sulphuric and hydrochloric acids together with calcium, magnesium, sodium and potassium hydroxides at molar concentrations  $a$ ,  $s$ ,  $h$ ,  $c$ ,  $m$ ,  $n$  and  $p$  respectively is:



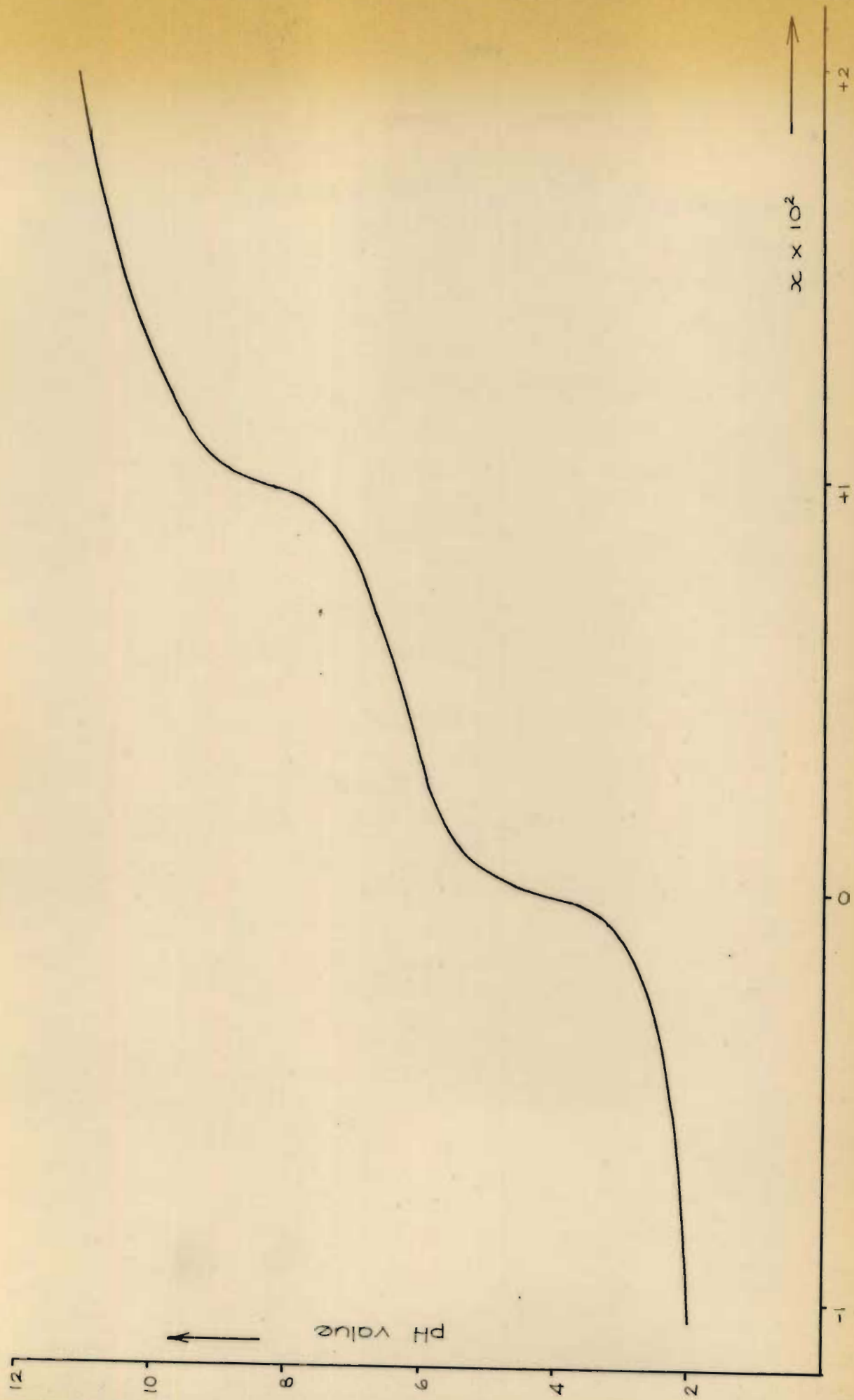


FIGURE 3.4

Ideal titration curve of carbonic acid at molar concentration  $10^{-2}$

$$\begin{aligned}
 H - \frac{k_w}{H} = & \frac{a (K_1 H + 2 K_1 K_2)}{(H^2 + K_1 H + K_1 K_2)} + \frac{s (H + 2 K_s)}{(H + K_s)} \\
 & - \frac{c (k_w + 2 K_c H)}{(k_w + K_c H)} - \frac{m (k_w + 2 K_m H)}{(k_w + K_m H)} \quad (3.40) \\
 & + h - n - p
 \end{aligned}$$

The same equation will also apply to waters which in addition contain non-ionised silica, since this solute can evidently play no part in the ionic equilibria governing the pH, i.e. the equation will apply to most natural waters.

The coefficient of  $s$  will be indistinguishable from 2 (working to a precision of 1%) if  $\text{pH} > 3.69$ . The coefficient of  $c$  will likewise be indistinguishable from 2 if  $\text{pH} < 10.80$ . Similarly the coefficient of  $m$  will be indistinguishable from 2 if  $\text{pH} < 9.72$ .

Consequently, in the range  $3.7 < \text{pH} < 9.7$  the general equation reduces to:

$$H - \frac{k_w}{H} = \frac{a (K_1 H + 2 K_1 K_2)}{(H^2 + K_1 H + K_1 K_2)} + h + 2s - 2c - 2m - n - p \quad (3.41)$$

For convenience we may write:

$$e = 2c + 2m + n + p - 2s - h \quad (3.42)$$

and (3.41) then becomes:

$$H - \frac{k_w}{H} = \frac{a (K_1 H + 2 K_1 K_2)}{(H^2 + K_1 H + K_1 K_2)} - e \quad (3.43)$$

This last equation should apply to most natural waters under ideal conditions, since their pH values usually lie in the range 6 to 9. Waters with pH down to 4.5 and up to 10.3 sometimes occur, but these are relatively rare.

The titration curve of a water to which (3.43) applies will be given by:

$$H - \frac{k_w}{H} = \frac{a (K_1 H + 2 K_1 K_2)}{(H^2 + K_1 H + K_1 K_2)} - e + x \quad (3.44)$$

and clearly this will show two end-point inflections just like the curve



for carbonic acid: a "methyl orange" end-point at a pH of about 4 or 5 with  $-e + x = 0$  or  $x = e$ , and a "phenolphthalein" end-point at a pH of about 7 or 8 with  $-e + x = a$  or  $x = e + a$ .

The quantity  $e$  defined by (3.42) is the total alkalinity of the water. It is usually expressed in practice as ppm of  $\text{CaCO}_3$ , and if its value in these units is denoted by  $A$ , it follows that:

$$A = 5 \times 10^4 e \quad (3.45)$$

since the equivalent weight of calcium carbonate is almost exactly 50.

On expansion (3.43) yields an equation of the 4th degree in  $H$ :

$$\begin{aligned} H^4 + (K_1 + e)H^3 - \left[ (k_w - K_1K_2) + K_1(a - e) \right] H^2 \\ - K_1 \left[ k_w + K_2(2a - e) \right] H - K_1K_2k_w = 0 \end{aligned} \quad (3.46)$$

According to the relative values of  $a$  and  $e$  various particular solutions of this equation arise and can be established by the general principles outlined at the beginning of this chapter - a full discussion has been given by Ricci (1952). The forms taken by these particular solutions are conditioned by the relative values of the constants  $K_1$ ,  $K_2$  and  $k_w$  and the values of  $a$  and  $e$  that are normally encountered.

(a)  $e < 0$

Under this condition the water will possess, not alkalinity, but acidity (equal to  $-e$ ). The pH will be low, anything below about 4 or 5 depending on the value of  $a$ , and the hydron concentration will be given by:

$$H = -e \quad (3.47)$$

This result will ideally hold down to a pH of about 3.7, and only to lower values if the sulphate concentration is negligibly small.

(b)  $e = 0$

Here the water has no appreciable acidity nor alkalinity. We obtain:

$$H = -\frac{1}{2}K_1 + \frac{1}{2}\sqrt{(K_1^2 + 4k_w + 4K_1a)} \quad (3.48)$$

corresponding to a pH of about 4 or 5, depending on the value of  $a$ . During the titration of a water sample with strong monoacidic base or strong monobasic acid, the total alkalinity will become zero at the methyl orange end-point, so this equation gives the pH value of that end-point.

(c)  $0 < e < a$

This is the most common case encountered in natural waters and leads to:

$$H = K_1 (a - e - K_2 - k_w/K_1)/(e + K_1) \quad (3.49)$$

This holds in the region between the methyl orange and phenolphthalein end-points, i.e. from an ideal pH of about 4 or 5 to one of 7 or 8 depending on the value of  $a$ .

(d)  $e = a$

This leads to:

$$H = \sqrt{K_1 (K_2 + k_w/a)} \quad (3.50)$$

and corresponds to an ideal pH of 7 or 8 depending on the value of  $a$ . This corresponds to the phenolphthalein end-point.

(e)  $a < e < 2a$

This condition leads to:

$$H = \frac{K_2 (2a - e + k_w/K_2)}{K_2 + (e - a) - k_w/K_1} \quad (3.51)$$

and holds from an ideal pH of about 7 or 8 to one of 8 or 11 depending on the value of  $a$ , provided the calcium and magnesium concentrations are negligibly small.

(f)  $e = 2a$

Equation (3.43) remains applicable only if the calcium and magnesium concentrations are negligibly small, and now leads to:

$$H = \frac{1}{2a} \left[ k_w + \sqrt{(k_w^2 + 4a K_2 k_w)} \right] \quad (3.52)$$

which corresponds to an ideal pH of about 8 or 11 depending on the value of  $a$ . This equation gives the pH of a pure ideal solution of sodium or potassium carbonate.

(g)  $e > 2a$

Again (3.43) is only valid now for negligibly small concentrations of calcium and magnesium, but then leads to:

$$H = k_w/(e - 2a - k_w/K_2) \quad (3.53)$$

which corresponds to very high pH values.



Although each of these equations applies only under ideal conditions, it may be readily corrected for non-ideality by the method already described.

Some further approximations are possible if  $a$  and  $e$  are sufficiently large. Under such circumstances equation (3.49) becomes:

$$H = K_1 (a - e)/e \quad (3.54)$$

while (3.51) becomes:

$$H = K_2 (2a - e)/(e - a) \quad (3.55)$$

These are the well-known Henderson equations. Similarly equation (3.53) becomes:

$$H = k_w/(e - 2a) \quad (3.56)$$

In practice, it will be found that equation (3.51) does not give such a close approximation to the solution of the general equation (3.46) as does (3.49), particularly at higher pH values. This is of little practical consequence, however, since the general equation itself breaks down at high pH values in any case. The main application of the particular equations (3.47) - (3.53) is the calculation of titration curves (e.g. for purposes of anti-corrosion water treatment, as described in chapter 10), and investigation of the upper pH ranges is rarely of any interest in this connection.

A few simplifications of the general equation (3.40) are possible for other pH ranges beyond the limits of 3.7 and 9.7, but they all give rise to expansions of the 5th, 6th or 7th degree in  $H$  and particular solutions resembling (3.47) - (3.53) cannot be written for them owing to mathematical complexity. These equations are of so little practical use that it is not necessary to consider them further.

#### 4. ACTIVITY COEFFICIENTS

##### Successive approximations

The equations developed so far have all assumed ideality. As pointed out in chapter 3, corrections for non-ideality may be introduced by using the activity coefficient  $\gamma$  in the appropriate manner.

The value of  $\gamma$  can be calculated if the ionic strength,  $\mu$ , of the water or solution is known. As is well known, the value of  $\mu$  depends upon the concentrations of the various ions present, according to the relation.

$$\mu = \frac{1}{2} \sum_r v_r^2 c_r \quad (4.1)$$

where  $v_r$  is the valency and  $c_r$  the molar concentration of the  $r$ th ionic species (strictly,  $\mu$  is defined in molal rather than molar concentrations, but in dilute solutions the difference is insignificant).

For values of TDS up to 1000 ppm, which is the range of greatest interest in the present work,  $\gamma$  can be found from the Debye-Huckel equation which, taking the mean value of the ionic diameters concerned to be  $4 \times 10^{-8}$  cm at  $25^\circ\text{C}$  becomes:

$$-\log \gamma = \frac{0.509 \sqrt{\mu}}{1 + 1.32 \sqrt{\mu}} \quad (4.2)$$

The temperature variations of the constants in this equation are so small that they may be disregarded for present purposes (if  $\gamma = 0.950$  at  $25^\circ\text{C}$ , its value will be 0.952 at  $0^\circ\text{C}$  and 0.948 at  $40^\circ\text{C}$ ).

In the absence of any further information, it is necessary to find the value of  $\gamma$  by a series of successive approximations. On the assumption that  $\gamma = 1.000$ , the values of  $H$  and all other ionic concentrations dependent upon  $H$  may be calculated and hence a value of  $\mu$  found from (4.1) and of  $\gamma$  from (4.2). Using this value of  $\gamma$ ,  $H$  and the other ionic concentrations can be recalculated, so that a new value of  $\mu$  and hence another value of  $\gamma$  is obtained. The process is continued until a stage is reached where  $\gamma$  remains unchanged by recalculation, and this unchanged value is taken as the required value of  $\gamma$ . The success of the process depends on the fact that, by equation (4.2),  $\gamma$  is insensitive to small changes in  $\mu$ .

As an illustration, consider a water whose analysis is as follows:



Ca	16.9	ppm
Mg	8.8	ppm
Na	16.7	ppm
K	2.3	ppm
SO <sub>4</sub>	4.5	ppm
Cl	18.0	ppm
Total alkalinity	91.5	ppm CaCO <sub>3</sub>
TDS	138	ppm
pH	7.00	ppm

The analysis is first expressed in terms of the molar concentrations of acids and bases present. This is accomplished by dividing the observed (total) concentration of each solute by its molecular weight and multiplying by a factor of  $10^{-3}$  (which itself converts ppm or mg/l to g/l). It is sufficiently accurate for this purpose to use the rounded-off molecular weights:

Ca	=	40	SO <sub>4</sub>	=	96
Mg	=	24	Cl	=	35.5
Na	=	23			
K	=	39			

and in general all calculations may be taken to three significant figures. The results are:

$$\begin{array}{ll}
 c = 4.23 \times 10^{-4} & s = 4.69 \times 10^{-5} \\
 m = 3.67 \times 10^{-4} & h = 5.07 \times 10^{-4} \\
 n = 7.26 \times 10^{-4} & e = 1.83 \times 10^{-3} \\
 p = 5.90 \times 10^{-5} &
 \end{array}$$

where the value of e is obtained from equation (3.45) or:

$$e = 2 A \times 10^{-5} = \frac{A}{50} \times 10^{-3} \quad (4.3)$$

In order to calculate the bicarbonate and carbonate ion concentrations it is necessary to know the total concentration of carbonic acid, a. As already pointed out, although this concentration can be determined by the proper experimental technique, the determination is generally not undertaken as a routine measure by water chemists. Consequently the value of a must usually be found by a theoretical calculation. In practice, this is only possible if the water concerned is such that equation (3.43) in its non-ideal form remains valid, i.e. if the pH value

lies between about 3.7 and 9.7, for outside this range more complicated equations hold instead and these do not admit of ready solution.

The pH of the water of the present example being 7.00, equation (3.43) is valid, and on assuming  $\gamma = 1.000$  the value of  $a$  may be found by rearranging the equation to the explicit form:

$$a = \frac{H^2 + K_1 H + K_1 K_2}{K_1 H + 2 K_1 K_2} (H - k_w/H + e) \quad (4.4)$$

The value so obtained is:

$$a = 2.24 \times 10^{-3}$$

since the value of  $H$ , from (3.9), is:

$$H = 1.00 \times 10^{-7}$$

Equations (3.34) now give values for  $a_1$  and  $a_2$ , whilst that of  $OH$  comes directly from (3.3). The various ionic concentrations (in molar units) are thus:

$Ca^{2+} = c = 4.23 \times 10^{-4}$	$SO_4^{2-} = s = 4.69 \times 10^{-5}$
$Mg^{2+} = m = 3.67 \times 10^{-4}$	$Cl^- = h = 5.07 \times 10^{-4}$
$Na^+ = n = 7.26 \times 10^{-4}$	$HCO_3^- = a_1 = 1.83 \times 10^{-3}$
$K^+ = p = 5.90 \times 10^{-5}$	$CO_3^{2-} = a_2 = 8.59 \times 10^{-7}$
$H^+ = H = 1.00 \times 10^{-7}$	$OH^- = k_w/H = 1.01 \times 10^{-7}$

Using these results in (4.1) now gives:

$$\mu = 3.24 \times 10^{-3}$$

and setting this in (4.2) yields:

$$\gamma = 0.940$$

The calculation of  $a$  is now repeated, using this value of  $\gamma$  in the corrected form of (4.4), which may be written:

$$a = \frac{H^2 \gamma^6 + K_1 H \gamma^4 + K_1 K_2}{K_1 H \gamma^4 + 2 K_1 K_2} (H - k_w/H \gamma^2 + e) \quad (4.5)$$

The value of  $H$ , however, must first be found from (3.10) instead of (3.9), and the values of  $a_1$  and  $a_2$  from (3.35) instead of (3.34), while  $OH$  is now  $k_w/H \gamma^2$ .



The values of some of the ionic concentrations thus become changed a little:

$$\begin{array}{ll} \text{H}^+ = 1.06 \times 10^{-7} & \text{HCO}_3^- = 1.83 \times 10^{-3} \\ \text{OH}^- = 1.07 \times 10^{-7} & \text{CO}_3^{2-} = 1.03 \times 10^{-6} \end{array}$$

From (4.1) we have, using these values:

$$\mu = 3.24 \times 10^{-3}$$

precisely as before, so that (4.2) again gives  $\gamma = 0.940$ .

The value of  $\gamma$  being the same as that from the previous step, this is the required final value.

It may be noted that the further the pH departs from 7.00, the greater the number of steps necessary to obtain the final result for  $\gamma$ , since recalculation causes H and OH to alter more markedly. Often the arithmetical work required in a given case may be enormous. However, it will later be shown that  $\gamma$  need not be known with extreme accuracy, and a more rapid means can thus be developed for determining its value with sufficient accuracy for most purposes.

#### Activity coefficient as a function of TDS

The TDS of a water is determined by evaporating a known volume of it to dryness and then heating it further to dehydrate the crystallised salts. Disregarding the various inherent errors of this procedure (which will be discussed subsequently), it will be realised that the process converts bicarbonates and free hydroxides to normal carbonates if it is carried out properly. The whole of the total alkalinity thus appears in the dried residue as carbonates under normal circumstances, and since the alkalinity of the original sample was A ppm of  $\text{CaCO}_3$ , the "concentration" of carbonate ion in the residue is thus 0.6 A ppm, i.e. it would have this concentration if the residue were redissolved in the original volume of pure water without any hydrolysis occurring.

Consequently if  $T_s$  is the TDS in ppm, we can write:

$$T_s = \text{Ca} + \text{Mg} + \text{Na} + \text{K} + \text{SO}_4 + \text{Cl} + \text{SiO}_2 + 0.6 A \quad (4.6)$$

where Ca, Mg, etc, denote the analytical ppm concentrations of the corresponding solutes in the original water.

This equation may also be written in terms of the molar concentrations:

$$T_s = (40c + 24m + 23n + 39p + 96s + 35.5h + 60j + 30e) \times 10^3 \quad (4.7)$$

where  $j$  denotes the molar concentration of  $\text{SiO}_2$ . From this equation we may further eliminate  $e$  by means of (3.42):

$$T_s = (100c + 84m + 53n + 69p + 36s + 5.5h + 60j) \times 10^3 \quad (4.8)$$

and the result may be written:

$$T_s \times 10^{-3} - (5.5h + 60j) = 100c + 84m + 53n + 69p + 36s \quad (4.9)$$

Now from (4.1), the full expression for  $\mu$  is:

$$\mu = 2c + 2m + \frac{1}{2}n + \frac{1}{2}p + 2s + \frac{1}{2}h + \frac{1}{2}a_1 + 2a_2 + \frac{1}{2}H + \frac{1}{2}OH \quad (4.10)$$

Provided  $5 < \text{pH} < 9$ , the terms  $\frac{1}{2}H$  and  $\frac{1}{2}OH$  can normally be ignored in comparison with the other terms on the right. Figure 3.3 also shows that, under this condition,  $2a_2$  is small in comparison with  $\frac{1}{2}a_1$ . Thus (4.10) approximates to:

$$\mu = 2c + 2m + \frac{1}{2}n + \frac{1}{2}p + 2s + \frac{1}{2}h + \frac{1}{2}a_1 \quad (4.11)$$

Furthermore, under the same condition  $a_1$  is approximately equal to  $e$ , and on accepting this and applying (3.42) we obtain:

$$\mu = 3c + 3m + n + p + s \quad (4.12)$$

Comparison with (4.9) therefore suggests that we may, as a fair approximation, put:

$$T_s \times 10^{-3} - (5.5h + 60j) = X \mu \quad (4.13)$$

where  $X$  is a constant. Taking the terms in  $c$ ,  $m$ ,  $n$ ,  $p$  and  $s$  in succession gives, individually, values of  $X$  equal to  $100/3$ ,  $84/3$ ,  $53$ ,  $69$  and  $36$ . The mean of these is about  $40$ , and since  $60j$  is approximately equal to  $16.3 \times 10^{-3}$  (see chapter 2) while  $5.5h$  is usually small in comparison, (4.13) may be approximated to:

$$T_s \times 10^{-3} - 20 \times 10^{-3} = 40 \mu \quad (4.14)$$

and rearranged to the form:

$$\mu = 2.5 (T - 20) \times 10^{-5} \quad (4.15)$$

This relation is very similar to the equation:

$$\mu = 2.5 T \times 10^{-5}$$

proposed by Langelier (1936) on the supposition that in most natural waters the total concentration of monovalent ions was about equal to that of divalent ions. This supposition is generally true in view of the pH values of the waters, but Langelier did not take the presence of non-ionic silica



into account. Equation (4.15) does not make this omission, but it tends to break down if  $5.5h$  is not small. However, under that circumstance the TDS must be high and non-ionic silica becomes of little importance. Langelier's equation will then give results very little different from those of (4.15). The two equations diverge at low TDS values.

Values of  $\gamma$  calculated by (4.15) for various values of  $T_s$  are given in Table 2B (in Appendix B). From these, the water analysis used above as an example gives  $\gamma = 0.942$ , in very good agreement with the value 0.940 found by successive approximation. It is worth noting that the use of Table 2B in this case gave the value of  $\gamma$  in just 5 seconds, whilst the calculation by successive approximations required about an hour before the final result was obtained.

Although the approximations involved in (4.15) are extensive, the insensitivity of  $\gamma$  to changes in  $\mu$  ensures that the results are not highly erroneous.

#### Waters of high TDS

In chapter 3 it was stated that the theoretical equations could not be applied to waters of TDS greater than 1000 ppm because assumptions concerning activity coefficients broke down above this limit. An empirical approach may be possible, however, even in such cases, though only in a restricted sense.

Harvey (1928) has given results for the direct determination of the total carbonic acid in sea water and its variation with the pH and total alkalinity. From these it can be deduced that, at the well-established mean value of 120.3 ppm of  $\text{CaCO}_3$  for the total alkalinity of sea water (see Sverdrup et al, 1942) and a pH of 7.90, the molar concentration  $a$  is  $2.11 \times 10^{-3}$ . It is then possible to use equations (3.10) and (4.5) to calculate a value of  $\gamma$ . The result is  $\gamma = 0.297$  and this value, when used with other values of pH and total alkalinity, reproduces the other results given by Harvey to within 0.2%.

This value  $\gamma = 0.297$  is thus an empirical value which can be used with confidence to find values of  $a$  in samples of sea water of known  $e$  and pH, or to find pH given  $e$  and  $a$ . There is no warrant for using it for any other purpose, e.g. it is not legitimate to use it for the computation of values of  $a_1$ ,  $a_2$  and  $f$ , nor is it legitimate to interpret the value of  $H$  given by (3.10) as the true hydrion concentration in such a case. This  $H$  can only be regarded in such instances as a mathematical



parameter related to the experimental pH and giving valid results when combined with the empirical value of  $\gamma$  in equation (4.5). The value  $\gamma = 0.297$  is clearly some kind of average value of activity coefficients which has no physical meaning although it is mathematically useful.

A fuller account of the relations between pH,  $a$ ,  $e$ , etc. in sea water has been given by Strickland and Parsons (1960). Their treatment is also purely empirical, proceeding on the principles of selecting the values of various coefficients so that the equations which contain them are bound to remain valid. Thus, full as it is, the account by these authors does not add anything to our knowledge of fundamental parameters.

The average TDS of sea water being 35,320 ppm, equations (4.15) and (4.2) lead to  $\gamma = 0.612$ . This is very near the correct value for the mean activity coefficient of sodium chloride at the same ionic strength, but far different from the above value of 0.297. This illustrates the dangers likely to be encountered if any attempt is made to extrapolate the data of Table 2B much beyond 1000 ppm TDS. Probably little error (about 1%) will be involved if extrapolation is made up to about 2000 ppm, but beyond this point the basic principles of the theoretical treatment begin to fail.

In Figure 4.1 the continuous line shows the value of  $\gamma$  plotted against the TDS (represented on a logarithmic scale) according to equation (4.15) up to 1000 ppm. The circled point represents the value  $\gamma = 0.297$  calculated above for sea water. The dotted line linking this point to the continuous curve has been drawn by eye and will doubtless give with fair accuracy the values of  $\gamma$  for diluted sea waters - some such values are given in the extension of Table 2B in Appendix B. It may be supposed that waters of other types will also be approximately represented by this line, but this is only an assumption that may be utilised as a first approximation in the absence of any other information.

To summarise, equations (4.15) and (4.2) may be reliably used to determine  $\gamma$  for most waters up to a TDS of 1000 ppm, and the value so determined may be used in all ionic calculations. In the TDS range 1000 - 2000 ppm the same procedure may be used, but the  $\gamma$  value and the whole theoretical treatment begins to become unsound so that the results are necessarily only approximate. Above 2000 ppm TDS, Figure 4.1 may be used to obtain estimated  $\gamma$  values which will be reasonably reliable for waters of the sea water type but may be much in error for waters of other type. But these values may only be used in calculations involving  $e$ ,



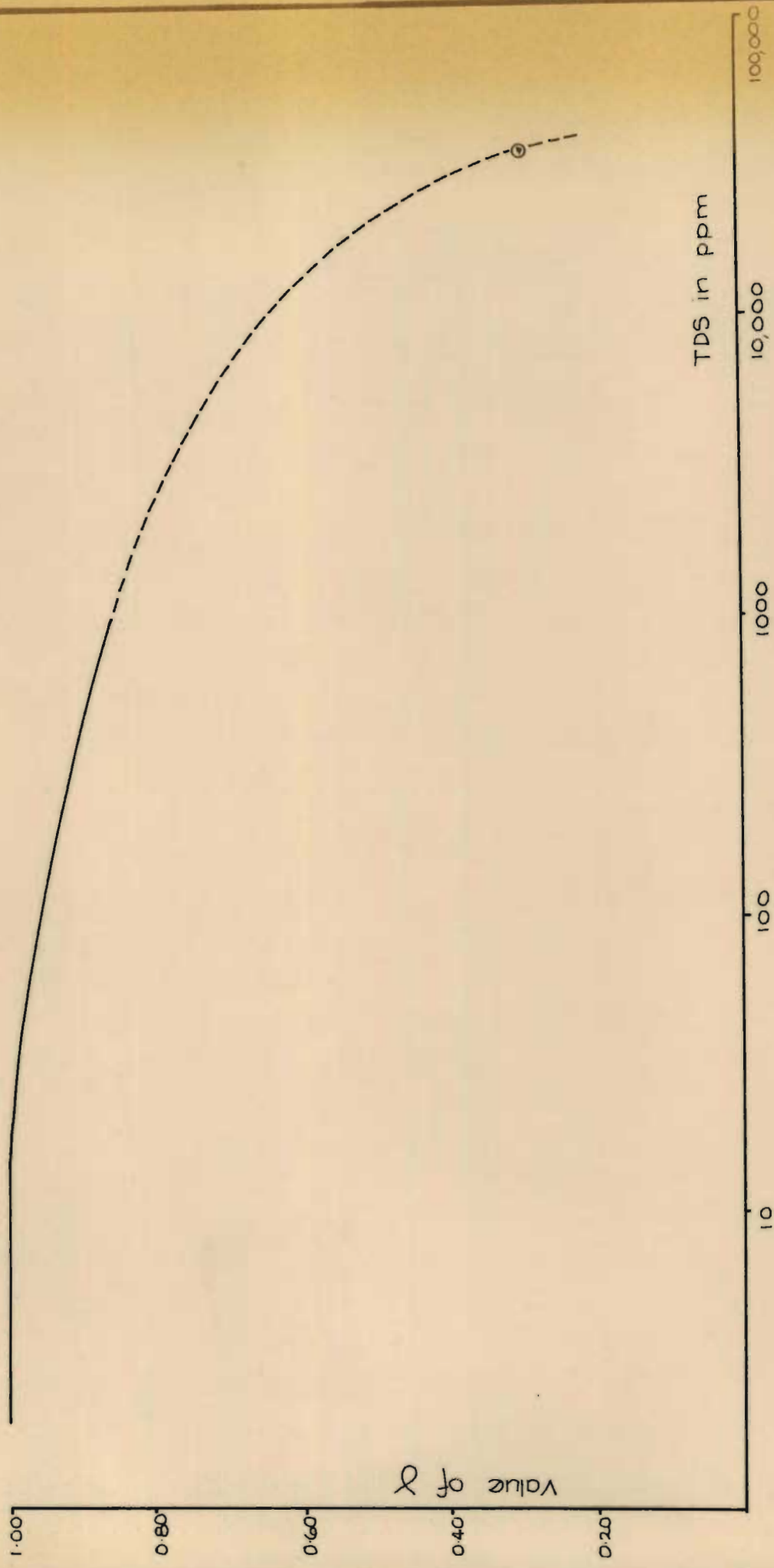


FIGURE 4.1

Probable values of  $\chi$  for waters of high TDS

a and pH, not in any calculations involving  $a_1$ ,  $a_2$ , f, H and OH except those based on equation (3.10) as an intermediate step in finding e, a or pH.



## 5. PROBABLE ERRORS

### Errors in dissociation constants

Three dissociation constants ( $k_w$ ,  $K_1$  and  $K_2$ ) are involved in equation (3.43) and its associated forms. The values of these can only be determined experimentally, and since the values which have been accepted for use in the present work may be slightly in error they may lead to errors when the theoretical equations are applied to specific cases.

The value of  $k_w$  seems very well established and hence possible errors in this instance need not be considered in much detail. Taking (3.43) in the form (4.5), i.e. explicit for  $a$  and corrected for non-ideality, it is evident that  $k_w$  has very little effect upon the calculated value of  $a$  except at high pH values (pH 10 and above for all normal values of  $e > 10^{-4}$ ). As will be seen, other probable errors are much more important.

The error in the accepted value of  $K_1 = 4.43 \times 10^{-7}$  would appear to be of the order of  $10^{-8}$ . To study the effects of this we may take equation (3.43) in its ideal form and rearranged to be explicit for  $a$ , i.e. take (4.4). By differentiation we find:

$$\frac{\partial a}{\partial K_1} = - \frac{a H^2}{K_1 (H^2 + K_1 H + K_1 K_2)} \quad (5.1)$$

Consequently if  $\Delta K_1$  is a small error in  $K_1$  and  $\Delta a$  the corresponding small error in  $a$ :

$$\Delta a = \frac{\partial a}{\partial K_1} \Delta K_1 \quad (5.2)$$

and we can write:

$$\frac{\Delta a}{a} = - \frac{H^2}{H^2 + K_1 H + K_1 K_2} \cdot \frac{\Delta K_1}{K_1} \quad (5.3)$$

Similarly, from the ideal equations (3.34) it follows that:

$$\left. \begin{aligned} \frac{\Delta a_1}{a_1} &= 0 \\ \frac{\Delta a_2}{a_2} &= 0 \\ \frac{\Delta f}{f} &= - \frac{\Delta K_1}{K_1} \end{aligned} \right\} \quad (5.4)$$

If  $\Delta K_1$  is of the order of  $10^{-8}$ , we may take  $\Delta K_1/K_1$  as  $2.26 \times 10^{-2}$ . Equations (5.3) and (5.4) then show that the corresponding errors in  $a_1$  and  $a_2$  are zero, the percentage error in  $f$  (i.e.  $100 \Delta f/f$ ) is uniformly 2.26 and the percentage error in  $a$  depends upon pH but reaches its highest value of 2.26 at low pH values ( $\text{pH} \ll 4$ ).

It therefore appears that any probable error in the value of  $K_1$  is of relative insignificance.

However, the accepted value of  $K_2 = 4.69 \times 10^{-11}$  may be in error by as much as 10% ( $\Delta K_2$  of order  $5 \times 10^{-12}$ ), and this has much more serious consequences.

Proceeding as before we now find:

$$\left. \begin{aligned} \frac{\Delta a}{a} &= - \frac{H K_2 (K_1 + 2H)}{(H^2 + K_1 H + K_1 K_2) (H + 2K_2)} \cdot \frac{\Delta K_2}{K_2} \\ \frac{\Delta a_1}{a_1} &= - \frac{2K_2}{H + 2K_2} \cdot \frac{\Delta K_2}{K_2} \\ \frac{\Delta a_2}{a_2} &= \frac{H}{H + 2K_2} \cdot \frac{\Delta K_2}{K_2} \\ \frac{\Delta f}{f} &= - \frac{2K_2}{H + 2K_2} \cdot \frac{\Delta K_2}{K_2} \end{aligned} \right\} \quad (5.5)$$

For various values of pH, the percentage errors in these four concentrations due to an error of 10% in  $K_2$  are thus as shown in Table 5.1. There is an appreciable error in  $a$  in the range  $9 < \text{pH} < 11$  which amounts to a maximum of about 2%. The error in  $a_1$  is negligible below pH 8, becomes about 5% at pH 10 and then increases with pH to a limit of 10%. However,  $a_1$  is relatively small above pH 12 so that large errors in this range are of no practical importance. Hence the errors in  $a_1$  may be counted serious only in the range  $10 < \text{pH} < 12$ . By similar arguments, the error in  $a_2$  is of no practical importance except in this same pH range, whilst the error in  $f$  is negligible at all pH values.

It therefore appears that the theoretical equations will give values accurate enough for most practical purposes for  $a$ ,  $a_1$  and  $f$  at all pH values, but they cannot be relied upon to give accurate values of  $a_2$  in



the range  $10 < \text{pH} < 12$  unless the value of  $K_2$  can be shown to be highly accurate.

Table 5.1  
Probable percentage errors due to a  
10% error in  $K_2$

pH	Error in a	Error in $a_1$ or f	Error in $a_2$
1	$9.38 \times 10^{-9}$	$9.38 \times 10^{-9}$	10.0
2	$9.38 \times 10^{-8}$	$9.38 \times 10^{-8}$	10.0
3	$9.38 \times 10^{-7}$	$9.38 \times 10^{-7}$	10.0
4	$9.38 \times 10^{-6}$	$9.38 \times 10^{-6}$	10.0
5	$9.21 \times 10^{-5}$	$9.38 \times 10^{-5}$	10.0
6	$7.95 \times 10^{-4}$	$9.38 \times 10^{-4}$	10.0
7	$5.55 \times 10^{-3}$	$9.38 \times 10^{-3}$	10.0
8	$4.73 \times 10^{-2}$	$9.29 \times 10^{-2}$	9.90
9	$4.15 \times 10^{-1}$	$8.61 \times 10^{-1}$	8.76
10	1.65	4.84	5.15
11	$7.97 \times 10^{-1}$	9.02	$4.84 \times 10^{-1}$
12	$1.02 \times 10^{-1}$	9.90	$1.05 \times 10^{-1}$
13	$1.06 \times 10^{-2}$	4.99	$1.07 \times 10^{-2}$
14	$1.07 \times 10^{-3}$	10.0	$1.07 \times 10^{-3}$

#### Errors in activity coefficients

Although all the equations can readily be corrected for non-ideality by the insertion of  $\gamma$  in the proper manner, it is very difficult to formulate the precise mathematical dependence of errors upon the probable error in  $\gamma$ .

However, from the special solutions (3.53), (3.54) and (3.55) it appears that we may generally put:

$$H = R \gamma^{-r} \quad (5.6)$$

where  $R$  has a fixed value for any particular instance and  $r$  may be anything from 2 to 4. This being so we can write:

$$\partial H / \partial \gamma = -r R \gamma^{-(r+1)} \quad (5.7)$$

so that the error  $\Delta H$  consequent upon a small error  $\Delta \gamma$  in  $\gamma$  may be formulated as:

$$\frac{\Delta H}{H} = -r \frac{\Delta \gamma}{\gamma} \quad (5.8)$$

If the error in  $\gamma$  is 1%, then the error in  $H$  will usually be about 2%, since the value of  $r$  for most natural waters is 2, but may reach 4% at high pH values.

It follows from equations (3.34) that the errors in  $a_2$  and  $f$  will always be negligible if  $\gamma$  is in error by this extent, that the error in  $a$  may be about 2% below pH 8 but negligible above, and that the error in  $a_1$  will show much the same variation as that in  $a$ .

Equation (4.15) is considered to give  $\gamma$  to about  $\pm 1\%$ , whilst even less error should arise when  $\gamma$  is found by the method of successive approximation.

#### Errors due to pH measurements

At low values ( $< 7$ ) of pH, equation (4.4) approximates to:

$$a = H^2 / K_1 \quad (5.9)$$

from which we find:

$$\frac{\Delta a}{a} = 2 \frac{\Delta H}{H} \quad (5.10)$$

At high ( $> 10$ ) pH values, (4.4) approximates to:

$$a = \frac{1}{2} (c - k_w/H) \quad (5.11)$$

which leads to:

$$\frac{\Delta a}{a} = \frac{k_w}{2 a H} \cdot \frac{\Delta H}{H} \quad (5.12)$$

At middle pH values  $a$  becomes approximately equal to  $c$  and so virtually independent of  $H$ .

Consequently an error of 1% in  $H$  will give rise to an error of about 2% in  $a$  with  $pH < 7$ , virtually no error in  $a$  with  $7 < pH < 10$ , but may cause very great errors in  $a$  in the range  $pH > 10$ .

Ideally, pH is a function of  $H$  only, by (3.9):

$$pH = -\log H$$

and from this we have:

$$\Delta pH = -\frac{1}{2.303} \cdot \frac{\Delta H}{H} \quad (5.13)$$

It follows that an error of about 0.05 in the pH value will make an error of about 2% in  $H$ , and from the above it is seen that the resulting error



in a will be:

pH < 7	about 4%
7 < pH < 10	very small
pH > 10	from zero to very great.

A pH value cannot be accurately measured to less than  $\pm 0.05$  without extremely good instrumentation and a refined experimental technique. The above errors in a are therefore likely to be encountered with normal careful working in the laboratory when a is deduced from the pH. Measurements of pH in the field, however, will certainly not be accurate to closer than  $\pm 0.1$  and may even be in error by more than  $\pm 0.5$ . This means that any value of a based on a field pH measurement on a water of pH much below 7 or greater than 10 is probably worthless, but that in the range  $7 < \text{pH} < 10$  the error in a will still be virtually negligible. Fortunately the latter is the range most commonly encountered in natural waters.

It follows that if the pH of a natural water is measured with ordinary care, the errors in a and  $a_1$  may be estimated at about 5% or less and the errors in  $a_2$  and f will be insignificant. But for other waters the theoretical equations will break down completely at pH values much greater than 10 just because of the impossibility of obtaining pH measurements of sufficient accuracy.

### Summary

By summing all the probable errors (the equations being too complicated to permit any more detailed treatment), it appears that, provided the pH is measured with ordinary care, for most natural waters in the middle pH range we may expect negligible errors in  $a_2$ , errors of about 5% in a and  $a_1$  and of about 2% in f, whilst the errors in the calculated values of H and OH for such waters will be very small.

Errors due to temperature have not been discussed. They will become effective through changes in the values of the constants  $k_w$ ,  $K_1$  and  $K_2$ , but under normal circumstances the consequences cannot be very marked.

The breakdown of equation (3.43) below pH 3.7 and above pH 9.7 due to sulphates or calcium and magnesium salts has already been discussed in chapter 3.

Finally, if the theoretical equations are used in reverse to calculate values of pH from other observations, independently made, errors of calculation will be well within experimental error and hence may be considered negligible.

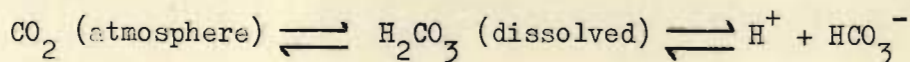
## PART II    APPLICATION TO SPECIAL TOPICS

### 6.    SOLUBILITY PRODUCTS

#### Carbon dioxide

All natural waters, and most other waters during some stage of their life history, are in contact with the atmosphere. Since this contains carbon dioxide in small but perceptible concentration (0.03% by volume) most waters will therefore contain carbonic acid in solution. In addition the respiratory activities of the organisms inhabiting the water ensure a continual supply of carbon dioxide to the water, especially where there is dissolved or suspended organic matter arising from enrichment or pollution, and unless this can be rapidly removed by some process or other, relatively high concentrations of carbonic acid may arise.

When pure water is in equilibrium with carbon dioxide the following equilibria will exist:



and in consequence we may write:

$$k_a = H a_1 \gamma^2 \quad (6.1)$$

where  $k_a$  is a constant and  $H$ ,  $a_1$  and  $\gamma$  are as already defined. The constant  $k_a$  may be termed the solubility product of carbonic acid since any increase of  $H$  or of  $a_1$  which would make  $k_a$  exceed its constant value will result in carbon dioxide gas coming out of solution, and conversely any such changes tending to cause  $k_a$  to take on a lower value will result in carbon dioxide being dissolved into the water from the atmosphere. Evidently the value of  $k_a$  depends upon temperature and the partial pressure of carbon dioxide over the water, but we shall consider its value only at 25°C and  $3 \times 10^{-4}$  atmosphere, i.e. for water in equilibrium with atmospheric carbon dioxide.

The solubility of carbon dioxide in water at 25°C and 1 atmosphere pressure is 1.45 g/l (Handbook of Chemistry and Physics, 1950), which is  $3.30 \times 10^{-2}$  molar. It cannot be assumed, by Henry's law, that the solubility at  $3 \times 10^{-4}$  atmosphere will be decreased in proportion, since this law applies only to the undissociated species and allowance must be made for the disturbance of the dissociation equilibrium because of the



reduced concentration. The calculation may therefore be carried out as follows:

For the case of 1 atmosphere pressure,  $a = 3.30 \times 10^{-2}$  and the hydron concentration is given by equation (3.48) in non-ideal form, which may be written:

$$H = -K_1/2\gamma^2 + \sqrt{(K_1^2/4\gamma^4 + k_w/\gamma^2 + K_1a/\gamma^2)} \quad (6.2)$$

The concentration  $a_1$  of bicarbonate ions will be given by equation (3.35), whilst those of carbonate and hydroxyl ions will be negligibly small.

Using the method of successive approximation to find  $\gamma$ , we thus obtain:

$$\begin{aligned} \gamma &= 0.987 \\ H &= 1.23 \times 10^{-4} \\ a_1 &= 1.23 \times 10^{-4} \end{aligned}$$

and then by equation (3.35) we find  $f = 3.28 \times 10^{-2}$ . By Henry's law, the value of  $f$  at  $3 \times 10^{-4}$  atmosphere is thus  $9.84 \times 10^{-6}$ . From the equation (3.35), or directly from the corrected form of (3.32), we have:

$$f/a_1 = H\gamma^2/K_1$$

and since  $a_1 = H$  this may be written:

$$H = \sqrt{(f K_1)}/\gamma$$

Using the above small value of  $f$  we then find, by the method of successive approximation:

$$\begin{aligned} \gamma &= 0.998 \\ H &= 2.09 \times 10^{-6} \\ a_1 &= 2.09 \times 10^{-6} \end{aligned}$$

so that, finally:

$$a = f + a_1 = 1.19 \times 10^{-5}$$

which is the required solubility at  $25^\circ\text{C}$  and  $3 \times 10^{-4}$  atmosphere.

Equation (6.1) then gives:

$$k_a = 4.36 \times 10^{-12}$$

For water with alkalinity  $e$  equivalents/litre the general equation (3.43) will hold under ideal conditions (within its own limits, of course). If this water is to be in equilibrium with atmospheric

carbon dioxide, (6.1) must also be satisfied. Ideally this becomes:

$$k_a = H a_1 \quad (6.3)$$

and by using (3.34) to eliminate  $a_1$  may be written:

$$k_a = K_1 H^2 a / (H^2 + K_1 H + K_1 K_2) \quad (6.4)$$

Substituting in (3.43) thus yields:

$$H - \frac{k_w}{H} = \frac{k_a (K_1 H + 2 K_1 K_2)}{K_1 H^2} - e \quad (6.5)$$

which expands to a cubic in H:

$$H^3 + e H^2 - (k_w + k_a) H - 2 k_a K_2 = 0 \quad (6.6)$$

Provided  $H^3 > 2 k_a K_2$ , which corresponds to  $pH < 7.13$ , an approximate solution of this is obtainable from:

$$H^2 + e H - (k_w + k_a) = 0 \quad (6.7)$$

which, by (3.8) yields:

$$H = -e \quad (6.8)$$

and hence applies to acidic waters in which  $e < 0$ . Substituting this result in (6.4) and rearranging gives:

$$a = \frac{k_a (e^2 - K_1 e + K_1 K_2)}{K_1 e^2} \quad (6.9)$$

which gives the concentration of carbonic acid in any acidic water of alkalinity  $e < 0$  in equilibrium with the atmosphere. Whatever the value of  $e$  within ordinary limits (i.e. from about  $10^{-6}$  to  $10^{-12}$ ), clearly  $a$  will be approximately equal to  $k_a/K_1$  whose value is  $9.84 \times 10^{-6}$ , about 20% lower than the value of  $a$  for  $e = 0$ , as would be expected.

If however  $pH > 7.13$ , the approximate solution of (6.6) is obtainable from:

$$e H^2 - (k_w + k_a) H - 2 k_a K_1 = 0 \quad (6.10)$$

and by (3.8) takes the form:

$$H = \frac{k_w + k_a}{e} \quad (6.11)$$



which approximates further to:

$$H = k_a / e \quad (6.12)$$

With  $e = 10^{-3}$  (which we shall find to be the order of magnitude in most Natal rivers), this gives  $H = 4.36 \times 10^{-9}$ , corresponding to an ideal pH of 8.36.

Substituting (6.12) in (6.4) and rearranging gives an expression for the ratio  $a/e$  for such a water in equilibrium with the atmosphere:

$$\frac{a}{e} = \frac{K_1 K_2 e^2 + k_a K_1 e + k_a^2}{k_a K_1 e} \quad (6.13)$$

This equation applies over a limited range ( $7.13 < \text{pH} < 9.7$ ). An equation of wider application ( $3.7 < \text{pH} < 9.7$ ) is obtainable directly from (6.4) and (6.6).

#### Calcium and magnesium hydroxides and carbonates

Theoretical discussions of the hardness and corrosivity of waters hinge upon the conditions for the precipitation of the hydroxides and carbonates of calcium and magnesium. It is convenient in the present chapter to derive equations for and numerical values of the corresponding four solubility products.

The solubility product of calcium hydroxide is defined as:

$$k_c = (\text{Ca}^{2+}) (\text{OH}^-)^2 \quad (6.14)$$

where the parentheses denote activities. Since

$$(\text{OH}^-) = k_w / (\text{H}^+) \quad (6.15)$$

this may be written:

$$k_c = (\text{Ca}^{2+}) k_w^2 / (\text{H}^+)^2 \quad (6.16)$$

In terms of concentrations, using our usual notation:

$$\left. \begin{aligned} (\text{Ca}^{2+}) &= c_2 \gamma^4 \\ (\text{H}^+) &= H \gamma \end{aligned} \right\} \quad (6.17)$$

so that we have:

$$k_c = c_2 k_w^2 \gamma^2 / H^2 \quad (6.18)$$

From equation (3.40), the hydrion concentration of an ideal solution of calcium hydroxide is given by:

$$H - \frac{k_w}{H} = - \frac{c (k_w + 2 K_c H)}{k_w + K_c H} \quad (6.19)$$

which may be expanded to a cubic in H:

$$K_c H^3 + (k_w + 2c K_c)H^2 - k_w (K_c - c)H - k_w^2 = 0 \quad (6.20)$$

The solubility of calcium hydroxide being 1.59 g/litre at 25°C (Handbook of Chemistry and Physics, 1960), we have  $c = 2.15 \times 10^{-2}$  so that  $k_w \ll 2c K_c$ . Hence 6.20 may be written:

$$K_c H^3 + 2c K_c H^2 - k_w (K_c - c)H - k_w^2 = 0 \quad (6.21)$$

By the principles outlined in chapter 3, the value of H which satisfies this is given very closely by solving the quadratic:

$$2c K_c H^2 - k_w (K_c - c)H - k_w^2 = 0 \quad (6.22)$$

and, after correcting for non-ideality, is:

$$H = \frac{k_w (K_c - c \gamma^4)}{4c K_c \gamma^2} + \sqrt{\left[ \frac{k_w^2 (K_c - c \gamma^4)^2}{16c^2 K_c^2 \gamma^4} + \frac{k_w^2}{2c K_c} \right]} \quad (6.23)$$

Using equations (3.26) to find  $c_1$  and  $c_2$ , the value of  $\gamma$  may be found by the method of successive approximation. The results are:

$$\gamma = 0.817 \quad \text{and} \quad H = 4.24 \times 10^{-13}$$

so that we finally obtain:

$$K_c = 5.38 \times 10^{-6}$$

The case of magnesium hydroxide may be treated in precisely the same way. Published values (Handbook of Chemistry and Physics, 1950; Nordell, 1951; Thorne and Roberts, 1948) of the solubility at 25°C vary somewhat, but a fair estimate seems to be 0.0096 g/litre. This corresponds to  $m = 1.7 \times 10^{-4}$ . The solubility product is defined as:

$$K_m = m_2 \frac{k_w^2 \gamma^2}{H^2} \quad (6.24)$$

where  $m_1$  and  $m_2$  can be found from the magnesium analogues of equations



(3.26). Successive approximation gives:

$$\gamma = 0.975 \quad \text{and} \quad H = 3.29 \times 10^{-11}$$

whence we obtain:

$$k_m = 1.38 \times 10^{-11}$$

For calcium carbonate the solubility product is defined as:

$$k_{ca} = c_2 a_2 \gamma^8 \quad (6.25)$$

and for an ideal solution of calcium carbonate in water equation (3.40) gives:

$$H - \frac{k_w}{H} = \frac{a (K_1 H + 2 K_1 K_2)}{H^2 + K_1 H + K_1 K_2} - \frac{a (k_w + 2 K_c H)}{k_w + K_c H} \quad (6.26)$$

which expands to an equation of the 5th degree in H. Taking the solubility at 25°C as 0.014 g/litre (Handbook by Chemistry and Physics, 1950), so that  $c = a = 1.4 \times 10^{-4}$ , and then neglecting terms in the coefficients of H which are small in comparison with others, the 5th degree equation reduces to:

$$\begin{aligned} & K_c H^5 + 2 a K_c H^4 + a K_1 K_c H^3 - K_1 K_c k_w H^2 \\ & - k_w K_1 (k_w + K_2 K_c + a K_2) H - K_1 K_2 k_w^2 = 0 \end{aligned} \quad (6.27)$$

The solution of this equation for H is obtained by solving the quadratic:

$$a K_c H^2 - K_c k_w H - k_w (k_w + K_2 K_c + a K_2) = 0 \quad (6.28)$$

Correcting for non-ideality, the required solution is:

$$H = \frac{k_w}{2 a \gamma^2} + \sqrt{\left[ \frac{k_w^2}{4 a^2 \gamma^4} + \frac{k_w (k_w \gamma^6 + K_2 K_c + a K_2 \gamma^4)}{a K_2 \gamma^6} \right]} \quad (6.29)$$

Employing (3.35) to find  $a_1$  and  $a_2$  and (3.26) to find  $c_1$  and  $c_2$ , the value of  $\gamma$  is obtainable by the method of successive approximation:

$$\gamma = 0.976 \quad \text{and} \quad H = 1.11 \times 10^{-10}$$

so that we finally obtain:

$$k_{ca} = 5.12 \times 10^{-9}$$

For magnesium carbonate precisely the same procedure may be followed. Again published values (Handbook of Chemistry and Physics, 1950; Nordell, 1951; Thorne and Roberts, 1948) of the solubility at 25°C vary somewhat (Nordell's value is out of line by a factor of 10, presumably a misprint), but 0.80 g/litre appears to be a fair estimate. This corresponds to  $m = a = 9.5 \times 10^{-3}$ . The solubility product is defined as:

$$k_{ma} = m_2 a_2 \gamma^8 \quad (6.30)$$

where  $m_1$  and  $m_2$  can be found from the magnesium analogues of equation (3.26). Successive approximation gives:

$$\gamma = 0.840 \quad \text{and} \quad H = 2.10 \times 10^{-11}$$

whence we obtain:

$$k_{ma} = 1.62 \times 10^{-5}$$

For convenience, these four solubility product values are included in the list of constants in Table 1B of Appendix B. Values given in the literature, for reasons adduced by Lewin (1960), show a wide scatter beyond the range of reasonable experimental error, but it is encouraging to note that Fair and Geyer (1954) have given  $k_{ca} = 4.82 \times 10^{-9}$  and  $k_{ma} = 1 \times 10^{-5}$ , while the Handbook of Chemistry and Physics (1950) lists  $k_m = 1.2 \times 10^{-11}$ , values fairly close to those just calculated.

Note that the solubility product of calcium hydroxide is about three orders of magnitude greater than that of magnesium hydroxide so that normally it will not precipitate even if the pH is high enough to cause precipitation of the magnesium compound. Similarly, that the solubility product of magnesium carbonate is about four orders of magnitude greater than that of calcium carbonate so that normally it will not precipitate even if conditions are such as to cause precipitation of the calcium compound.



## 7. ALKALINITY

### Definition of total alkalinity

The total alkalinity of a water has been defined above by equation (3.42):

$$e = 2c + 2m + n + p - 2s - h \quad (7.1)$$

and this definition will be valid for most natural waters (it can be modified so as to apply to any water at all by the addition of extra terms of appropriate sign on the right to account for ionic solutes not already included).

Many textbooks of water chemistry give an apparently quite different definition which, in our notation, may be written:

$$e = OH + a_1 + 2a_2 - H \quad (7.2)$$

In virtue of the electroneutrality condition (3.2) this is, however, strictly equivalent to (7.1) and merely constitutes an alternative way of regarding the same phenomenon.

Unfortunately not one of the quantities appearing on the right of (7.2) can be directly determined for any water sample.  $H$  can be found only by means of a pH measurement and requires that  $\gamma$  is already known,  $OH$  must be calculated from the non-ideal form of equation (3.3), while  $a_1$  and  $a_2$  must be obtained from equation (3.35) which in turn requires prior knowledge of the total carbonic acid concentration,  $a$ . If acid or base is added to the water, it is necessary first to know how  $\gamma$  and pH are affected and then to carry through calculations based on the above equations before  $e$  can be calculated from (7.2). In practice, therefore, equation (7.2) is very often quite useless.

On the other hand, every term on the right of (7.1) can be determined for every water by direct chemical analysis, and if acid or base is added this same equation shows immediately just how  $e$  is changed.

The use of (7.1) rather than (7.2) to define the total alkalinity thus has all the merits of logic, precision, lack of ambiguity and practical convenience. Equation (7.2), which can often lead to considerable confusion of thought, would be best disregarded altogether.

### Determination of total alkalinity

Equation (3.44) has shown that the total alkalinity of a water may be determined by titrating it with strong acid to the "methyl orange" end-point.

The ideal pH value of that end-point is given by (3.48) which, corrected for non-ideality, becomes:

$$H = -K_1/2 \gamma^2 + \sqrt{(K_1^2/4 \gamma^4 + k_w/\gamma^2 + K_1 a/\gamma^2)} \quad (7.3)$$

Since  $a$  is commonly of the order of  $10^{-3}$ , the end-point pH will usually be around 4.7 but will depend on the precise value of  $a$ . Transferring the term  $K_1/2 \gamma^2$  to the left of (7.3) and squaring, we obtain after some rearrangement:

$$\gamma^2 H^2 = \frac{k_w + K_1 a}{1 + K_1/\gamma^2 H}$$

and since  $K_1/\gamma^2 H \ll 1$  at the methyl orange end-point, this approximates to:

$$\gamma^2 H^2 = k_w + K_1 a$$

and then further to:

$$\gamma^2 H^2 = K_1 a$$

Hence by using equation (3.10) we may write approximately:

$$pH = \frac{1}{2} \log K_1 - \frac{1}{2} \log a = 3.18 - \frac{1}{2} \log a \quad (7.4)$$

We note from this that changes in the chemical composition and TDS of the sample during the titration will ordinarily have little or no effect upon the end-point pH. Such will be the case usually when a 100 ml sample is taken and titrated with 0.02 N-hydrochloric acid. If for any reason a diluted sample is taken for titration, allowance for a different end-point pH consequent upon a materially altered value of  $a$  will need to be made.

Methyl orange indicator is often used to detect the end-point, but this is not wholly satisfactory since the colour change is often not sharp simply because the water under examination is no more than an extremely dilute solution (a graphic illustration of this was provided by Harris (1958) who pointed out that the water in a silt-free river running at a TDS of 200 ppm is 99.98% pure, of higher quality in fact than some



of the chemical reagents commonly used in the laboratory). Moreover the colour change of methyl orange occurs over the pH range 3.1 - 4.4 (Tomicek, 1951) and we shall see that this does not cover the correct value of the end-point, which occurs in the pH range of 4.1 - 5.2.

The only accurate way of determining the total alkalinity is thus by electrometric titration. Since the value of  $a$  is usually not known at the time, this really means that the titration curve of each water should be plotted during the titration and the correct end-point selected from the curve. This is a time-consuming procedure, clearly not suitable as a routine technique when many samples have to be analysed. Under such circumstances it is more expeditious to titrate to a predetermined pH value.

Since the buffering power of the sample is very low in the vicinity of the end-point, it is evident that small discrepancies (smaller than those arising from the use of methyl orange - see Figure 3.4) in the selected pH value will have a negligible effect on the accuracy of the titration. Therefore any procedure that allows a reasonable estimate of the value of  $a$  to be made in advance can be used to calculate an end-point pH that will be adequate for most practical purposes.

Such a procedure may be established by making use of the detailed unpublished analytical results obtained by Oliff during a survey of the Tugela river system of Natal, which includes streams of a wide variety of water types common in South Africa (see Oliff, 1960). The relevant details for various samples taken from these rivers are given in Table 1C of Appendix C. For these samples there is a correlation between  $a$  and the electrical conductivity (correlation coefficient = 0.872 with 173 degrees of freedom, corresponding to a probability far less than 0.001). This may be expressed in the form of a regression equation:

$$a = 7.63 \times 10^{-6} C \quad (7.5)$$

where  $C$  is the conductivity in micromho.

Using this relation in (7.4) gives:

$$\text{pH} = 5.74 - \frac{1}{2} \log C \quad (7.6)$$

which allows the end-point pH of the total alkalinity titration to be estimated from the conductivity of the water (a property very readily and rapidly measured). The values so calculated for various values of the conductivity are given in Table 5B of Appendix B.

A similar treatment can be given for the "phenolphthalein" end-point at higher pH upon which certain other determinations depend. By (3.50), correcting for non-ideality, at this end-point:

$$H = \frac{1}{\gamma^3} \sqrt{K_1 (K_2 + k_w \gamma^2/a)} \quad (7.7)$$

Hence we can write:

$$pH = 2 \log \gamma - \frac{1}{2} \log K_1 - \frac{1}{2} \log (K_2 + k_w \gamma^2/a) \quad (7.8)$$

Inserting the numerical values of  $K_1$ ,  $K_2$  and  $k_w$  and using the regression (7.5) to replace  $a$  by  $C$  then gives:

$$pH = 8.32 - \frac{1}{2} \log (1 + 28.2 \gamma^2/C) + 2 \log \gamma \quad (7.9)$$

Now  $C$  is approximately equal to  $T/0.68$  where  $T$  is the TDS in ppm (as discussed in a later chapter). Hence by means of Table 2B we can find a value of  $\gamma$  for each value of  $C$  and so, using (7.9), calculate the appropriate pH. Values so obtained are also given in Table 5B of Appendix B.

It may be noted that the American Public Health Association (1965) in its manual "Standard Methods" suggests using a pH for the methyl orange end-point which varies according to the alkalinity. On the assumption that  $a = e$  (which is roughly true for many natural waters), it is possible to compare these values with those from Table 5B:

<u>Total alkalinity,</u> <u>ppm CaCO<sub>3</sub></u>	<u>End-point pH,</u> <u>"Standard Methods"</u>	<u>End-point pH,</u> <u>Table 5B</u>
30	5.1	4.8
150	4.8	4.4
500	4.5	4.2

Similarly, the manual gives 8.3 uniformly for the pH of the phenolphthalein end-point, whereas Table 5B gives 8.2. The agreement in each case is quite good.

Equations (7.6) and (7.9) only hold for normal surface waters, because the regression (7.5) only applies to waters of this type. If a water of abnormal type is to be analysed (e.g. a highly polluted water) it is preferable not to rely upon Table 5B but rather to make a preliminary total alkalinity titration to an end-point pH of 4.6, i.e. an average value not likely to lead to gross errors in most cases. From this an approximate value of  $e$  can be found, and hence an approximate value of  $a$



(by the methods described in chapter 8) which can then be used in (7.4) to obtain a more reliable pH. This can then be used for an accurate titration. Such a procedure will still usually be more rapid than to plot out the titration curve.

Although most natural waters contain appreciable total carbonic acid concentrations, abnormal waters and artificial waters (trade effluents, etc) may be encountered which do not. In such cases, the determination of total alkalinity and the interpretation of the result obtained must be approached with caution. For example, a solution of sodium sulphate could easily be titrated to an end-point pH of about 4.6, but the result would not give the total alkalinity of the solution since the correct value of this is zero. A careful study of the ion balance of the analysis must be made in such cases, and qualitative tests on the water sample itself or the residue on evaporation may also be required. Sometimes (as in the case of the sodium sulphate solution) a determination of the full titration curve will be of assistance (but not invariably - e.g. a mercuric chloride solution can give a titration curve exactly similar to that of carbonic acid).

A further factor influencing the accuracy of total alkalinity determinations and of numerical values calculated from their results is, of course, the possibility of changes occurring in the sample after sampling but before analysis. Correct experimental technique will minimise such changes, but difficulties may arise if the pH value measured subsequently in the laboratory is found to be different from what it was in the field at the time of sampling, as often does occur. It might seem correct, having determined the total alkalinity, to utilise this together with the field pH for further calculations rather than to combine it with the laboratory pH, on the grounds that one is concerned primarily with what was in the original water body instead of with what is now in the sample bottle. However, it must be borne in mind that the major part of the difference between the field and laboratory pH values is likely to consist of experimental error, occasioned simply by the use of the pH meter under rugged field conditions. Thus in most cases there is nothing at all to be gained by using field pH results (except, for example, as approximate on-the-spot guides for tracing a particular source of pollution), provided that the water being sampled is not one which is likely to undergo radical pH changes before it can be brought to the laboratory (for example, a mine drainage water containing ferrous sulphate which becomes rapidly oxidised



and precipitated by bacterial action). On the contrary, it is usually far preferable to utilise in calculations the results of accurate pH determinations made in the laboratory rather than those of more or less crude field determinations, and no attempt should be made to "correct" the laboratory results to field conditions. The results of an analysis will thus relate to the sample in the bottle at the time the analysis was undertaken, and in this respect they will be accurate. For them also to relate accurately to the water body concerned at the time it was sampled it is necessary that adequate precautions concerning the storage and preservation of the sample are taken.

#### Analytical checks

Since every chemical determination necessarily involves some degree of experimental error, and since large errors may at any time be unwittingly made during the course of a chemical analysis, some check on analytical accuracy is desirable.

The replication of determinations is an obvious step that might be taken in this direction, but this is not always possible. It increases the labour involved in an analysis by at least 100% and presupposes that the analyst has an ample amount of sample at his disposal (usually it is his complaint that he has not been given enough!) In any case, replication will not reveal errors due to any form of consistent bias (reiterated arithmetical slips, systematic errors in calibration constants, etc).

An easy check that has already been mentioned and which can often be applied with little added labour is the comparison of the experimental TDS (if this has been determined) with the value obtained by calculation from equation (4.6). That equation assumed that such things as nitrate, phosphate, iron, aluminium, fluoride, etc were absent, although cases often occur where these are present in appreciable concentration. Not only will they then affect the TDS, but they may also need to be taken into account in other connections so that theoretical equations need to be modified slightly in such cases. Equation (4.6) may be written more generally as:

$$T = Ca + Mg + Na + K + SO_4 + Cl + SiO_2 + 0.6 A + z \quad (7.10)$$

where  $z$  is an additional term representing the contribution of solutes other than those specifically shown in the equation. Sometimes such additional solutes are not accurately determinable, so that the check



then breaks down (e.g. organic matter may be present, but unless it is known to be some one particular compound its true amount cannot usually be assessed).

A second easy check involves the comparison of the experimental or calculated TDS with the electrical conductivity of the sample. In its simplest form this will be further discussed in a later chapter. Again, it is not universally applicable. More complex forms of this check have been suggested (see American Public Health Association, 1965) as well as quite different checks based upon independent determinations of total anions or cations using the ion-exchange resins. All these checks suffer from the defect that they involve additional experimental manipulation and hence introduce additional sources of error, and for this reason they may be considered unsatisfactory.

A form of check that is of great utility and which avoids such difficulties arises from the fact that, in any solution of electrolytes, the total equivalent concentration of the cations must be equal to that of the anions. Because of the presence of inherent errors, very few analyses will ever show an exact ion balance, but it is possible to lay down limits which the observed anion - cation concentration difference should not normally exceed.

The limits in general use at the present time (see American Public Health Association, 1965) are derived from the work of Greenberg and Navone (1958) who undertook a statistical analysis of almost 1000 routine water analyses made in two laboratories over a period of three years. They found that the standard deviation of the difference between the total anion and total cation concentrations, both expressed in milliequivalents per litre, varied with the value of the total anion concentration itself, their actual values being shown by the circled points in Figure 7.1. From these results they derived the relation:

$$\left| \sum \text{anions} - \sum \text{cations} \right| = 0.1065 + 0.01055 \sum \text{anions} \quad (7.11)$$

for the standard deviation and suggested that any analysis should be rejected if it gave an anion-cation difference numerically greater than this.

There are two points involved here to which objections may be raised.

In the first place, the choice of one standard deviation as the criterion for rejecting an analysis is illogical. An error of this

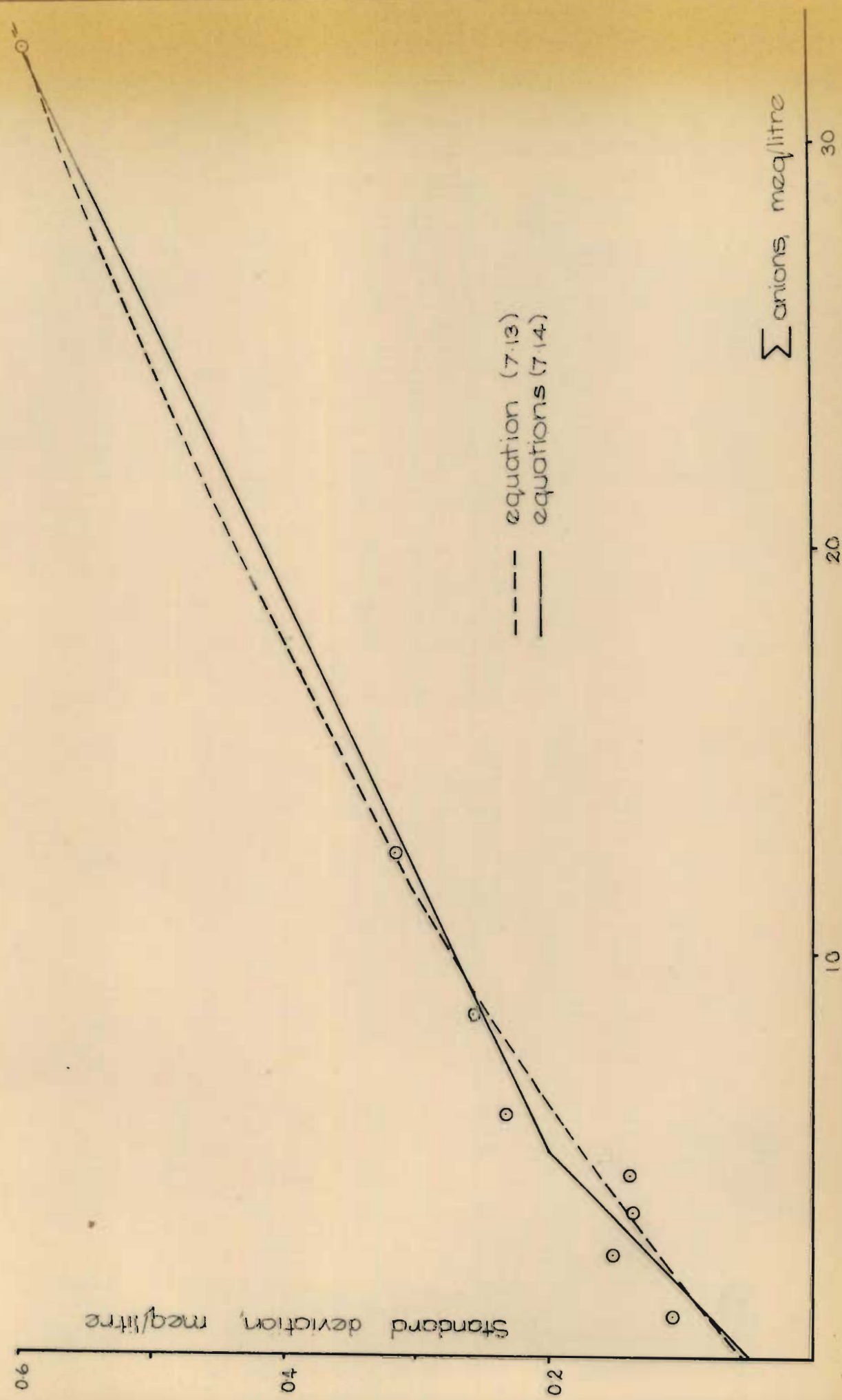


FIGURE 7.1 Standard deviations of the anion-cation differences



magnitude, by chance alone, is likely to arise about 32 times in 100 analyses and is of no statistical significance. To use the proposed criterion in the manner suggested means that some 32% of all analyses made must be repeated without necessarily obtaining any gain in accuracy. If a repeat analysis by chance does not violate the proposed criterion, this means only that it contains different errors from the original analysis but not necessarily smaller ones. It may quite well happen that one of the repeated determinations involves some much larger error than the original but such that the ion-cation difference is numerically reduced; the new analysis might then be regarded as acceptable even though it is in fact more in error than the original. The net result of taking one standard deviation as the criterion of rejection is thus to increase the analytical work unnecessarily by more than 32% and to introduce a bias in the final results such that the anion-cation differences reported are abnormally low. It does not necessarily lead to increased accuracy.

It is a violation of the fundamental concepts of statistics in this particular problem to select as criterion any level of the anion-cation difference that is not a statistically significant one. The selected level must correspond to at least two standard deviations before it can be counted statistically significant, for in that case the criterion would be violated by chance not more than 5 times out of 100 analyses. An analysis which violated the criterion would then be considered significantly in error and hence worth repeating.

Two standard deviations is in fact a convenient limit to set, so that (7.11) should be amended to read:

$$\left| \sum \text{anions} - \sum \text{cations} \right| = 0.2130 + 0.0310 \sum \text{anions} \quad (7.12)$$

If an analysis violates this limit (or any other acceptable limit that may be set) it should be independently repeated, redetermining all the solutes and not just checking one or two (though in practice the very first step should be to check all the calculations since an arithmetical slip may easily be the cause of an apparent violation). The result will be that about 5% of all analyses made will have to be repeated and that no bias will arise in the anion-cation differences finally reported. If consistently more than 5% of the analyses have to be repeated, there is something wrong with the analytical techniques, and the same applies if consistently less than 5% need repetition. In most cases the repeat analysis will prove acceptable, but if not this is a sign either that



consistent analytical errors are being made (e.g. a standard solution is of incorrect composition, a reagent is impure, interference effects are occurring, etc), or that the analysis is not complete, i.e. one or more solutes are present in addition to those that have been actually determined. On the other hand, compensating errors may result in an ion balance being obtained when it should not, so that although the ion balance is a useful check on analytical accuracy it is not an absolute one.

The second objection to the proposals of Greenberg and Navone is that equation (7.11) is too great an approximation. The experimental results shown in Figure 7.1 indicate that the standard deviation of the anion-cation difference is best represented, not by a straight line as is assumed in equation (7.11), but by a curve which is concave downwards, i.e. the standard deviation is disproportionately less at lower concentrations so that in this range (7.11) leads to a limit criterion which is too lax. The experimental results are in fact much better represented by the curve:

$$\left| \Sigma \text{ anions} - \Sigma \text{ cations} \right| = -0.3515 + \sqrt{0.1639 + 0.0227 \Sigma \text{ anions}} \quad (7.13)$$

although such a relation is too cumbersome to be of much practical use.

A better approximation than (7.11) is obtained if two straight lines are employed, one holding up to a value of 5 meq/litre for total anions and the other, of lower gradient, holding for concentrations greater than this, as shown in Figure 7.1. The equations of these lines are:

$$\left| \Sigma \text{ anions} - \Sigma \text{ cations} \right| = \begin{cases} 0.0500 + 0.0300 \Sigma \text{ anions} & (\Sigma \leq 5) \\ 0.1280 + 0.0144 \Sigma \text{ anions} & (\Sigma > 5) \end{cases} \quad (7.14)$$

Hence it is proposed that the critical value for the ion balance should be taken as two standard deviations based on the equations:

$$\left| \Sigma \text{ anions} - \Sigma \text{ cations} \right| = \begin{cases} 0.1000 + 0.0600 \Sigma \text{ anions} & (\Sigma \leq 5) \\ 0.2560 + 0.0288 \Sigma \text{ anions} & (\Sigma > 5) \end{cases} \quad (7.15)$$

These limits (which will be formulated rather differently later in this chapter) strictly apply only to the range of water samples considered by Greenberg and Navone, and it is only an interim measure, in the absence of additional data, to apply them to all water samples. Indeed, it is the present author's belief that equations (7.15) are too rigid at high concentrations (TDS greater than about 2000 ppm) when applied to surface waters in South Africa, although the supporting evidence for this is too



scanty to warrant detailed discussion.

It should be mentioned here that some caution should be used in applying any such balance criterion to the analysis of a sample in which chemical changes have occurred between the times of sampling and analysis. It is not always possible or desirable to arrest all such changes, and this can give rise to apparent discrepancies. For example, most samples of surface water will deposit iron compounds on storage, probably as a result of bacterial action. It is most convenient to carry out the main part of the analysis on a filtered portion of the stored sample (since any attempt to stabilise the iron, e.g. by adding acid, will interfere with some of the other determinations) but to determine the total iron (usually not more than 1 ppm) on a second portion suitably treated to bring the deposited iron back into solution. In such a case it is not legitimate to include the iron in the ion balance (though an abnormally high iron concentration may seem to contribute appreciably to the total cation concentration) since the analytical result for total iron relates to a different sample than used for the other determinations.

#### The three forms of alkalinity

Consider a solution possessing total alkalinity  $e$  but no carbonic acid. All the alkalinity must necessarily be in the form of free hydroxide. Suppose carbonic acid is now progressively introduced. At first this will combine with the hydroxides to produce normal carbonates, and when the molar carbonic acid concentration  $a$  has risen so that  $a = \frac{1}{2} e$  there will no longer be free hydroxides. Further introduction of carbonic acid will convert the carbonate to bicarbonate, and when  $a = e$  this process also will be complete. The addition of any more carbonic acid will then result in a solution containing bicarbonates and uncombined carbonic acid.

At any stage of the process, the sum of the equivalent concentrations of hydroxide, carbonate and bicarbonate will be equal to  $e$ , the total alkalinity, which remains unchanged in value. These three equivalent concentrations are referred to as the hydroxide, carbonate and bicarbonate alkalinities respectively and collectively constitute the three forms of alkalinity. Their values can evidently be obtained from the following scheme for any case where  $a$  and  $e$  are known.

	Equivalents per litre		
	Bicarbonate alkalinity	Carbonate alkalinity	Hydroxide alkalinity
$a = 0$	0	0	0
$0 < a < \frac{1}{2} e$	0	$2a$	$e - 2a$
$a = \frac{1}{2} e$	0	$e$	0
$\frac{1}{2} e < a < e$	$2a - e$	$2(e - a)$	0
$a = e$	$e$	0	0
$a > e$	$e$	0	0

This scheme is readily established when it is recognised that:

for  $x$  equivalents/litre of hydroxide,  $e = x$  and  $a = 0$   
 for  $y$  equivalents/litre of carbonate,  $e = y$  and  $a = \frac{1}{2} y$   
 for  $z$  equivalents/litre of bicarbonate,  $e = z$  and  $a = z$

Now suppose we take a water sample and divide it into two portions which we each titrate with strong acid, one to the phenolphthalein end-point (if possible) and the other to the methyl orange end-point. This will require  $P$  and  $T$  equivalents of acid respectively. Various cases now arise:

- If the pH value of the water is less than or equal to that of the phenolphthalein end-point, it is clear from chapter 3 that  $e \leq a$ . Titration to that end-point with acid is then not possible and we may take  $P = 0$  in this case. Titration to the methyl orange end-point will, however, give  $T = e$  as usual.
- If  $0 < a < e$ , titration to the methyl orange end-point will again give  $T = e$ , but since the methyl orange and phenolphthalein end-points on the titration curve are separated by  $a$  equivalents of acid, we also have  $T - P = a$ .
- If  $a = 0$ , again we shall have  $T = e$ , but now the titration curve reduces to that of a hydroxide solution and shows but a single end-point inflection. We shall find approximately that  $P = T$ .

Using these results, the above scheme for the three forms of alkalinity may be presented in an alternative form, as shown below.

These two schemes are almost, but not fully, identical. The



first is rigidly correct as a matter of definition, but the second is only an approximation when the water contains hydroxide alkalinity alone, the condition  $P = T$  being strictly true if the concentration (i.e. the TDS) is sufficiently large. In practice, however, this case is a rare one; it certainly never occurs in natural waters and is unlikely to be met in other waters.

	Equivalents per litre		
	Bicarbonate alkalinity	Carbonate alkalinity	Hydroxide alkalinity
$P = T$	0	0	T
$\frac{1}{2} T < P < T$	0	$2 (T - P)$	$2 P - T$
$P = \frac{1}{2} T$	0	T	0
$0 < P < \frac{1}{2} T$	$T - 2P$	$2P$	0
$P = 0$	T	0	0

This division of the total alkalinity into its three specialised forms is clearly based upon stoichiometric considerations and makes no direct reference to ionic concentrations. Consideration of the titration curve of carbonic acid (Figure 3.4) and of the ionisation fractions in a carbonic acid solution (Figure 3.3) suggests, however, that there should be some relationship between the forms of alkalinity and the concentrations of the corresponding ions, and indeed most textbooks of water chemistry present arguments, based on such diagrams, to show that the alkalinities and the ionic concentrations are virtually identical. These arguments are not usually convincing, however, and it is worthwhile to investigate the matter further.

The molar concentrations of bicarbonate, carbonate and hydroxyl ions existing in ideal 0.01 molar carbonic acid solutions at different pH values (supposed obtained by the addition of appropriate amounts of strong acid or base) can be calculated from equations (3.3), (3.9) and (3.34). The equivalent concentrations are readily obtained from these. By calculating the titration curve (Figure 3.4) of the solution and applying the rigid (first) scheme given above, the equivalent concentrations of the three forms of alkalinity may also be obtained.

Figure 7.2 shows how these equivalent concentrations vary with the pH, the continuous lines representing the ions and the broken ones the

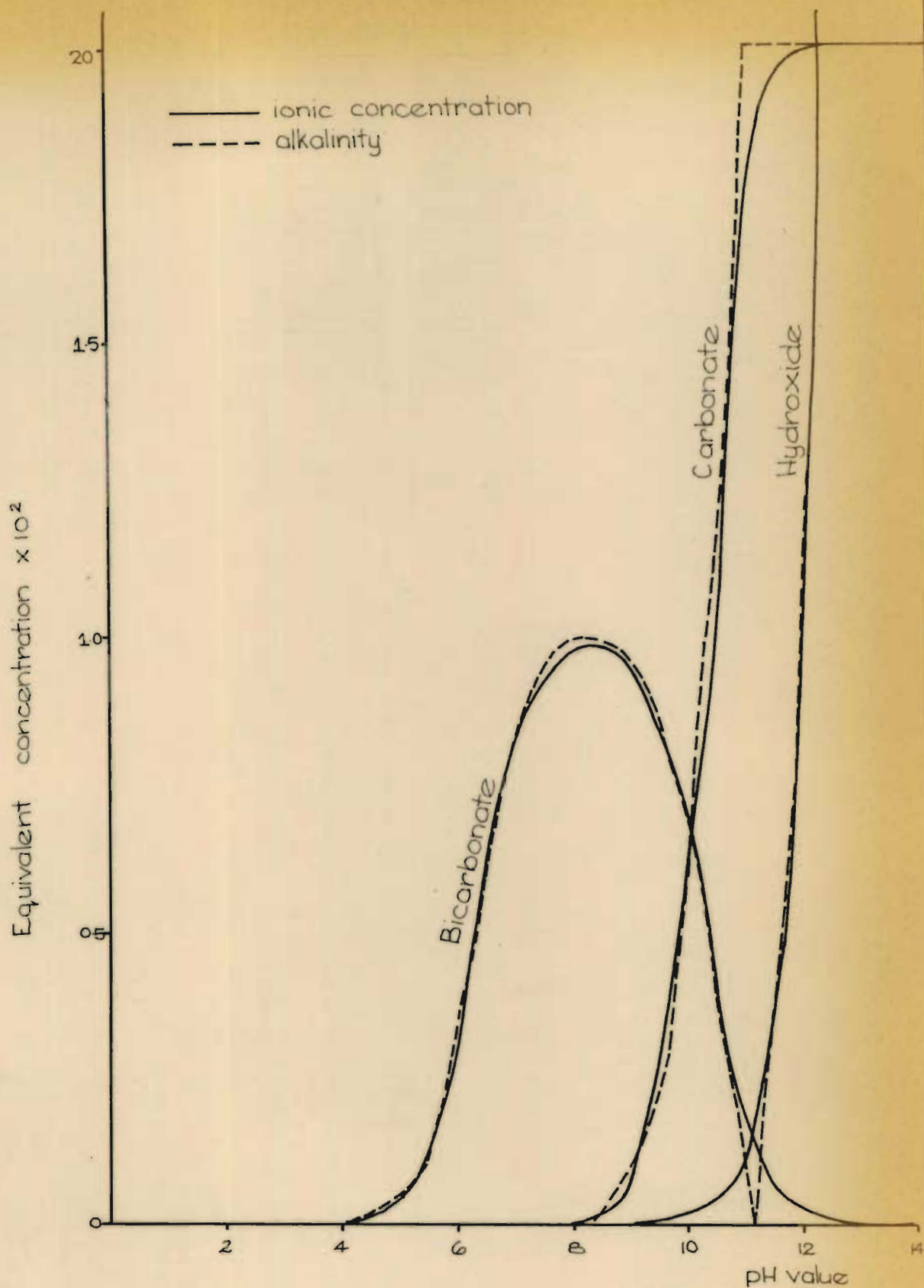


FIGURE 7.2

Comparison of alkalinities and ionic contrations in ideal  $10^{-2}$  molar carbonic acid solutions



alkalinities. It is seen that the concentrations of the alkalinities are very close indeed to those of the corresponding ions. The greatest discrepancies appear in the vicinity of pH 11 where the carbonate alkalinity is somewhat greater and the bicarbonate and hydroxide alkalinities lower than the corresponding ionic concentrations.

For real solutions the agreement cannot be quite so good, for the ionic curves will shift slightly because of non-ideality effects while the alkalinity curves will shift similarly but to a smaller extent because real and ideal pH values will not be quite identical. However, it is clear that, in the pH range of most frequent interest (pH 5 to 10) and for solutions of not too great TDS (not exceeding 1000 ppm), the values of the alkalinities very closely approximate to those of the corresponding ionic concentrations.

Therefore, for most practical purposes determinations of alkalinity are equivalent to determinations of ionic concentrations. This is a most useful conclusion and has enabled schemes of mathematical relationships to be set up by some workers, e.g. Dye (1958), which can often be of great service. Applications of such schemes must be made with some caution, however, for although one or more of the forms of alkalinity may be zero in a given case, the corresponding ionic concentration can never be zero although it may certainly be minute.

### Notation

Before proceeding further it is convenient to introduce a modification of our existing notation.

So far, most of the theoretical equations have been expressed in terms of molar concentrations. This, however, is an inconvenient choice of units for practical use on account of the small magnitudes of the solute concentrations in waters. It is much better to work in terms of millimolar concentrations, so we shall henceforth use a barred symbol such as  $\bar{a}$  and  $\bar{c}$  to denote a concentration in millimoles per litre, whilst the corresponding symbol without the bar (e.g.  $a$  and  $c$ ) will continue to denote the same concentration in molar units.

Similarly the symbol  $e$  will continue to denote the total alkalinity in equivalents per litre, but  $\bar{e}$  will be used to denote the same concentration in milliequivalents per litre.

In other words, the bar functions as an operator signifying multiplication by 1000 and we have:

$$\begin{aligned}\bar{e} &= e \times 10^3 \\ \bar{a} &= a \times 10^3 \\ \bar{c} &= c \times 10^3\end{aligned}$$

and so on. The result will be greatly to simplify the tabulation and practical handling of data.

### Reformulation of the ionic balance

One immediate application of our discussion of the three forms of alkalinity arises in connection with the ionic balance discussed previously.

Equations (7.15) as they stand present the practical difficulty that, before the value of the term  $\Sigma$  anions can be calculated, the concentrations of the bicarbonate and carbonate ions must be evaluated. Disregarding the hydrogen and hydroxyl ions whose concentrations are usually negligible (correction for this at extreme pH values can easily be introduced if required), we have, in our modified notation:

$$\Sigma \text{ cations} = 2 \bar{c} + 2 \bar{m} + \bar{n} + \bar{p} \quad (7.16)$$

$$\Sigma \text{ anions} = 2 \bar{s} + \bar{h} + \bar{a}_1 + 2 \bar{a}_2 \quad (7.17)$$

But under the conditions supposed, for all practical purposes  $\bar{a}_1$  is the bicarbonate alkalinity,  $2\bar{a}_2$  the carbonate alkalinity and their sum is the total alkalinity. Since the two alkalinities would be separately found by titration, we may take their sum as the total alkalinity obtained by direct titration. Denoting this by  $\bar{e}_t$ , we can thus replace (7.17) by:

$$\Sigma \text{ anions} = 2 \bar{s} + \bar{h} + \bar{e}_t \quad (7.18)$$

In consequence we have, from (7.16) and (7.18):

$$\Sigma \text{ anions} - \Sigma \text{ cations} = \bar{e}_t - (2 \bar{c} + 2 \bar{m} + \bar{n} + \bar{p} - 2 \bar{s} - \bar{h}) \quad (7.19)$$

Here the bracketed expression is also equal to the total alkalinity as defined by (3.42) and as would be found by calculation from the rest of the analysis. Denoting this by  $\bar{e}_c$  we thus have:

$$\Sigma \text{ anions} - \Sigma \text{ cations} = \bar{e}_t - \bar{e}_c \quad (7.20)$$

If the analysis is free from error, obviously  $\bar{e}_t$  and  $\bar{e}_c$  should be equal. Equation (7.20) therefore suggests that  $\left| \bar{e}_t - \bar{e}_c \right|$  may be



taken as an indicator of analytical balance equally as well as  $\left| \sum \text{anions} - \sum \text{cations} \right|$  and that the same numerical limit may be placed upon its possible range of values.

Combining (7.20) and (7.18) with (7.15) we thus obtain equations giving the permissible (two standard deviations) limit for  $\left| \bar{e}_t - \bar{e}_c \right|$  :

$$\left| \bar{e}_t - \bar{e}_c \right| = \begin{cases} 0.1000 + 0.0600 (2 \bar{s} + \bar{h} + \bar{e}_t) & (\text{For values} \leq 5) \\ 0.2560 + 0.0288 (2 \bar{s} + \bar{h} + \bar{e}_t) & (\text{For values} > 5) \end{cases} \quad (7.21)$$

Here the final inequality in each case refers to the term  $(2 \bar{s} + \bar{h} + \bar{e}_t)$ . These equations may be used in place of (7.15), to which they are exactly equivalent, as a criterion of accuracy to 95% confidence, i.e. it may be expected that 95 analyses out of 100 will fulfill the balance defined by these equations and hence an unbalanced analysis by this criterion should be considered erroneous. Their application in any given case involves only simple arithmetic.

If necessary, the concentrations of ions other than those explicitly named in the equations can readily be introduced by simple and obvious modifications.

Since the balance will seldom, if ever, be exact, we shall in every analysis have two different values of  $\bar{e}$ , namely  $\bar{e}_t$  found by direct titration and  $\bar{e}_c$  found by calculation. Usually there will be no reason to favour one of these any more than the other, so the value of  $\bar{e}$  may be taken as the mean of  $\bar{e}_t$  and  $\bar{e}_c$  when further calculations are to be made. Occasionally, however, it may be clear that either  $\bar{e}_t$  or  $\bar{e}_c$  is the more reliable, and in such cases the appropriate one should be selected as giving the better value for the true total alkalinity.

8. CARBONIC ACIDCalculation of the total carbonic acid

It has already been pointed out that, despite the fundamental importance of this parameter, the total carbonic acid content of a water is not usually determined as a routine procedure by water chemists. Consequently it is in most cases necessary to calculate its value from the results of other determinations.

For this purpose we may utilise equation (4.5), provided it is applicable:

$$a = \frac{H^2 \gamma^6 + K_1 H \gamma^4 + K_1 K_2}{K_1 H \gamma^4 + 2 K_1 K_2} (H - k_w/H \gamma^2 + e) \quad (8.1)$$

As a mathematical convenience we may define a quantity  $H_*$  by the relation:

$$H_* = H \gamma \quad (8.2)$$

so that, by equation (3.10), we can put:

$$pH = -\log H_* \quad (8.3)$$

$H_*$  is, of course, the hydrogen ion activity under the general conditions supposed (see chapter 3).

Using (8.2) in (8.1) gives:

$$a = \frac{H_*^2 \gamma^4 + K_1 H_* \gamma^3 + K_1 K_2}{K_1 H_* \gamma^3 + 2 K_1 K_2} (H_*/\gamma - k_w/H_* \gamma + e) \quad (8.4)$$

If the terms  $H_*/\gamma$  and  $k_w/H_* \gamma$  are negligibly small in comparison with  $e$ , this may be simplified to:

$$a = \frac{H_*^2 \gamma^4 + K_1 H_* \gamma^3 + K_1 K_2}{K_1 H_* \gamma^3 + 2 K_1 K_2} \cdot e \quad (8.5)$$

This last equation will hold to within 1% for the range  $5 < pH < 9$  if  $e \geq 10^{-3}$  (which is usually the case) or for the range  $6 < pH < 8$  if  $e \geq 10^{-4}$ . It may be written symbolically as:

$$a = Q(pH, \gamma) \cdot e \quad (8.6)$$

and multiplying each side by  $10^3$  gives:

$$\bar{a} = Q(pH, \gamma) \cdot \bar{e} \quad (8.7)$$



Values of  $Q$  for various values of  $pH$  and  $\gamma$  are given in Table 3 B of Appendix B and enable  $\bar{a}$  to be found very easily from the values of  $pH$  and  $\bar{e}$  in most practical cases where no direct determination of  $\bar{a}$  has been undertaken. Instances where this procedure fails will be of rare occurrence (at least, as far as South African waters are concerned), and in such cases recourse must be made to the full equation (8.1).

#### Determination of the total carbonic acid

The direct determination of the total carbonic acid depends on the fact (see chapter 3) that the methyl orange and phenolphthalein end-points on the titration curve of a water sample are separated by a equivalents. The values of both  $a$  and  $e$  can therefore be found for any water by suitable titration with strong monobasic acid and strong monoacidic base, thus:

(a)  $pH < \text{methyl orange end-point}$

Titrate with strong base first to the methyl orange end-point (requiring  $x$  moles of base) and then to the phenolphthalein end-point (requiring  $y$  moles of base from the original starting point). Then:

$$e \propto x \quad \text{and} \quad a \propto y - x$$

(b)  $pH > \text{phenolphthalein end-point}$

Titrate with strong acid first to the phenolphthalein end-point (requiring  $x$  moles of acid) and then to the methyl orange end-point (requiring  $y$  moles of acid from the original starting point). Then:

$$e \propto y \quad \text{and} \quad a \propto y - x$$

(c) Intermediate  $pH$

Titrate with strong acid to the methyl orange end-point (requiring  $x$  moles of acid) and then, using a second sample of the water concerned, titrate with strong base to the phenolphthalein end-point (requiring  $y$  moles of base). Then:

$$e \propto x \quad \text{and} \quad a \propto x + y$$

If the samples used are 100 ml in volume and the strong acid and base are 0.02 N, the variables  $x$  and  $y$  may be taken as the volumes (in ml)

required for the titrations and the value of the proportionality constant in each case will then be  $2 \times 10^{-4}$  or, if the results are to be expressed as ppm of  $\text{CaCO}_3$ , it will be 10.

In practice, the titration will be best carried out electrometrically to the end-point pH values given by Table 5B. The solution of strong base must evidently be carbonate free, however, and this requirement often makes for difficulties and errors under routine laboratory conditions. Some experimental results, which show that the total carbonic acid concentration as determined in this way and as calculated by equation (8.7) are in good agreement, are given in Appendix D.

### Free carbonic acid

The concentration of free (non-ionised or molecular) carbonic acid in a water can be found by a method of calculation very similar to that just described for the total carbonic acid.

By equation (3.35) we have:

$$f = \frac{H^2 \gamma^6 a}{H^2 \gamma^6 + K_1 H \gamma^4 + K_1 K_2} \quad (8.8)$$

On substituting (8.2) in this and eliminating  $a$  by (8.5) we obtain:

$$f = \frac{H_*^2 \gamma^4}{K_1 H_* \gamma^3 + 2 K_1 K_2} \cdot e \quad (8.9)$$

as an approximation valid for the same conditions and with the same limits of accuracy as (8.5) itself.

Multiplying through by  $10^3$  gives:

$$\bar{f} = \frac{H_*^2 \gamma^4}{K_1 H_* \gamma^3 + 2 K_1 K_2} \cdot \bar{e} \quad (8.10)$$

and we can further convert this to:

$$F = \frac{44 H_*^2 \gamma^4}{K_1 H_* \gamma^3 + 2 K_1 K_2} \cdot \bar{e} \quad (8.11)$$

where  $F$  is the free carbonic acid expressed in ppm of  $\text{CO}_2$ .

This may be symbolically written as:

$$F = 44 P(\text{pH}, \gamma) \cdot \bar{e} \quad (8.12)$$



and values of  $P$  for various values of  $pH$  and  $\gamma$  are given in Table 4B of Appendix B to facilitate rapid calculation of  $F$  in most practical cases. In the rare cases where (8.12) no longer holds, recourse must be made to the full equation (8.8).

Similar tabulations of values to enable the bicarbonate and carbonate ion concentrations to be easily calculated could also be drawn up, but these will not often be required in practice and hence need not be considered here.

#### Unbound carbonic acid

Whenever a water containing carbonates has a  $pH$  above that of the methyl orange end-point, it must possess a total alkalinity  $e > 0$ , and conversely. On the other hand, when the  $pH$  is less than this limiting value then  $e < 0$  and it is logically consistent to say that the water has an acidity equal to  $-e$ .

We have seen that, if the  $pH$  lies between that of the methyl orange and phenolphthalein end-points, then  $0 < e < a$  and the water has a bicarbonate alkalinity equal to  $e$ . This at once indicates that not all of the total carbonic acid is stoichiometrically bound as bicarbonates - there are, in fact,  $(a - e)$  moles per litre of carbonic acid in an unbound state. It is often said that such a water also possesses an "acidity" (due to the unbound carbonic acid), but this is a most unfortunate choice of nomenclature since it leads to the idea that the water possesses both alkalinity and "acidity" simultaneously.

We shall therefore refer to the  $(a - e)$  moles per litre of carbonic acid in such a water as the unbound carbonic acid, and clearly distinguish this from the free (non-ionised or molecular) carbonic acid. Evidently if  $e \leq 0$  all the carbonic acid present must be unbound, and if  $e \geq a$  the unbound carbonic acid is zero.

Just as there is a close relationship between the three forms of alkalinity and the bicarbonate, carbonate and hydroxyl ion concentrations, so we may expect there to be a similar relationship between the free and unbound carbonic acid.

The molar concentration of free carbonic acid in an ideal 0.01 molar carbonic acid solution at different  $pH$  values (supposed obtained by the addition of appropriate amounts of strong acid or base) can be calculated from equations (3.9) and (3.34). The calculated titration curve of the solution (Figure 3.4) enables  $e$  to be found for any  $pH$ , and

since  $a = 10^{-2}$  we readily have the corresponding value  $(a - e)$  of the unbound carbonic acid.

Figure 8.1 shows how both the free (continuous line) and unbound (broken line) carbonic acid vary with the pH. It is seen that the two curves are virtually indistinguishable, and consequently the unbound carbonic acid may for all practical purposes be taken as equivalent to the free carbonic acid. As in the case of the similar conclusion concerning the forms of alkalinity, this has been used to establish useful mathematical relationships, e.g. Dye (1958). It must be noted, however, that although the unbound carbonic acid is always zero when the pH is above that of the phenolphthalein end-point, the free carbonic acid in a carbonate solution is never exactly zero.

#### Comparison of theory and experiment

The ideal equations (3.34) and (3.43) for  $a_1$ ,  $a_2$  and  $f$  and for  $a$  respectively are not new. Instead of deriving them by Ricci's method by way of the charge coefficient of carbonic acid, they may be obtained directly from the equations (3.3) and (3.32), which define  $k_w$ ,  $K_1$  and  $K_2$ , together with the stoichiometric relation (3.33) and the alternative definition of total alkalinity (7.2). This derivation, however, does not lead to any precise assessment of the range of validity of equation (3.43) and hence of the other relations that depend upon it.

De Martini (1938) published equations obtained by this alternative route which are identical with those given in the present work, though algebraically rearranged. Moore (1939) expressed them in numerical form, using the value  $k_w = 10^{-14}$  and taking the values  $K_1 = 4.54 \times 10^{-7}$  and  $K_2 = 5.61 \times 10^{-11}$  at  $25^\circ\text{C}$  from MacInnes and Belcher (1933). In this form the equations appear as:

$$\left. \begin{aligned} (\text{OH}^-) &= \frac{5 \times 10^{-10}}{H} \\ (\text{CO}_2) &= \frac{9.70 \times 10^{10} H}{1 + \frac{11.22 \times 10^{-11}}{H}} \left( \frac{A}{50,000} + H - \frac{10^{-14}}{H} \right) \\ (\text{HCO}_3^-) &= \frac{50,000}{1 + \frac{11.22 \times 10^{-11}}{H}} \left( \frac{A}{50,000} + H - \frac{10^{-14}}{H} \right) \\ (\text{CO}_3^{2-}) &= \frac{5.61 \times 10^{-6}/H}{1 + \frac{11.22 \times 10^{-11}}{H}} \left( \frac{A}{50,000} + H - \frac{10^{-14}}{H} \right) \end{aligned} \right\} \quad (8.13)$$



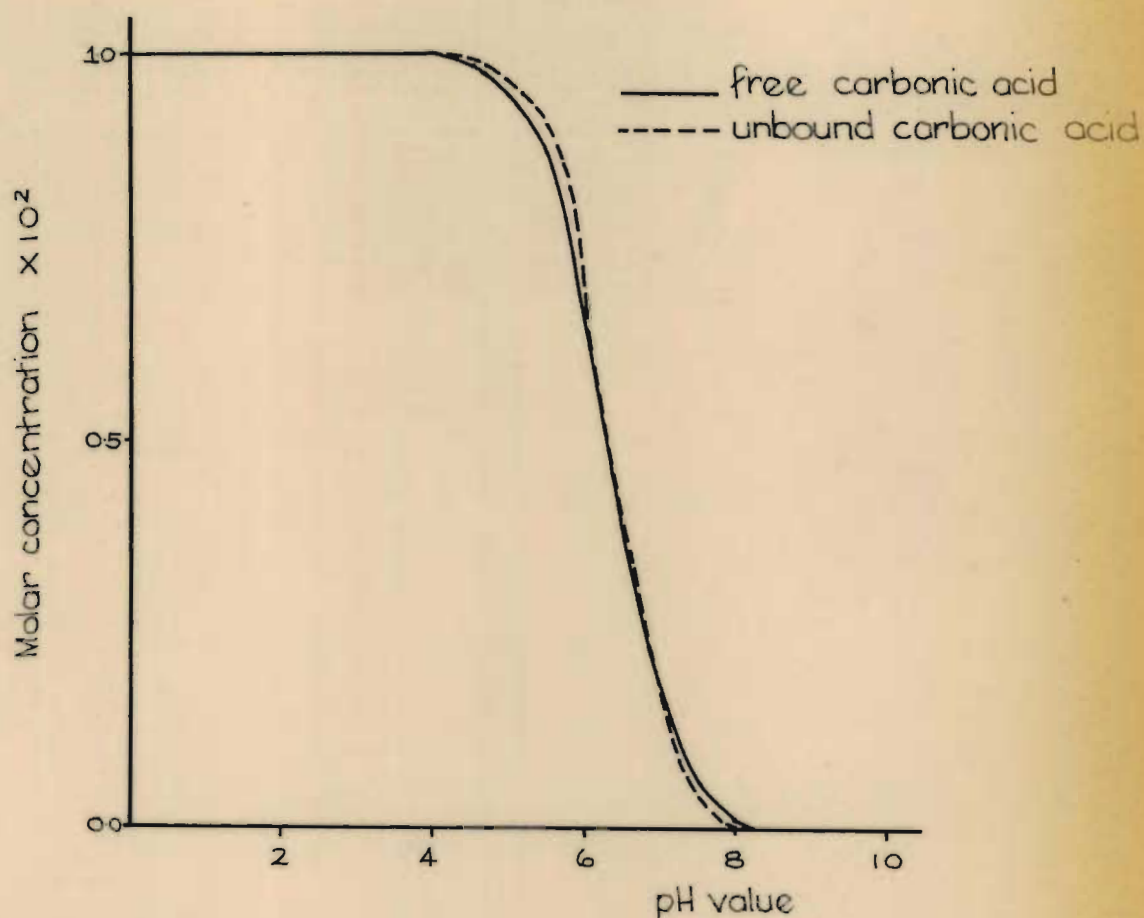


FIGURE 8.1

Comparison of free and unbound carbonic acid concentrations in ideal  $10^{-2}$  molar carbonic acid solutions

Here A is the total alkalinity in ppm of  $\text{CaCO}_3$ ;  $(\text{OH}^-)$ ,  $(\text{HCO}_3^-)$  and  $(\text{CO}_3^{2-})$  are the concentrations of the hydroxyl, bicarbonate and carbonate ions, expressed as ppm of  $\text{CaCO}_3$ ;  $(\text{CO}_2)$  is the concentration of free carbonic acid, expressed as ppm of  $\text{CO}_2$ ; and H is obtained from the ideal relation (3.9) defining pH as  $-\log H$ . Moore discussed the possibility of correcting these equations for non-ideality and for temperature, but since such corrections have opposing results he concluded that all such corrections could usually be neglected.

He himself made careful measurements on synthetic solutions (presumably made from sodium salts) and compared the calculated results for ionic concentrations with the experimental alkalinity values, supposing alkalinities and corresponding ionic concentrations to be identical. However, as discussed above, ionic concentrations and alkalinities are not strictly identical, so a more reliable comparison procedure would be to calculate  $e$  and  $a$  from the titration results, from these compute the alkalinities, and then compare the calculated and experimental alkalinities.

Table 8.1 shows, firstly, the pH value and total alkalinity (as ppm  $\text{CaCO}_3$ ) as determined electrometrically by Moore for nine such synthetic solutions, and the value of  $\gamma$  obtained for each solution by the method of successive approximation. Later rows of the table show the values of the bicarbonate, carbonate and hydroxide alkalinities obtained by Moore by electrometric titration, in each case expressed as ppm  $\text{CaCO}_3$ , the theoretical values of these obtained by using the non-ideal equation (4.5) for  $a$  and then the scheme set out on p. 59, and the theoretical values obtained by applying equations (8.13) and (3.33) to find  $a$  and then using the scheme on p. 59.

It will be seen that the theoretical equations of the present work, corrected for non-ideality, give far better alkalinity results than do Moore's equations. The latter, in most of the tabulated cases, give a quite false picture of the alkalinity components of the solutions. Our own equations fall off in accuracy as the pH increases, the errors at a pH above about 9.8 becoming too large for the results to be at all reliable. This is what would be expected in view of the discussion in chapter 5, and indicates that our accepted value of  $K_2$  must be slightly in error. The complete breakdown of Moore's equations may be mainly attributed to the use of an even more erroneous value for  $K_2$ , for we have seen that errors in  $\gamma$  (which he took as uniformly 1.000) do not affect



Table 8.1

### Moore's experimental results compared with theory

[illegible]

the final results very much.

Therefore it appears that our equations, in the absence of calcium and magnesium salts, are reliable up to a pH of about 9.8. This is rather better than the discussion of chapter 5 might suggest.

The literature contains very few records of experimentally determined unbound carbonic acid determinations, probably because accurate determination is not easy and calculation usually gives results adequate for most purposes. Where actual determinations have been reported (e.g. Rudolfs and Wong, 1939) it is often clear, from internal evidence, that the experimental errors were relatively large.

However, Moore (1939) has cited some very careful analytical results due to Wagner and Enslow (1922) and used them as a check upon his own calculations. We may use the same figures for a similar purpose, bearing in mind that, although Moore refers to the results as determinations of "free carbonic acid", they are in fact determinations of what we term unbound carbonic acid. Unfortunately the cited data do not include TDS values for the determination of  $\gamma$ , but if it is assumed that the total alkalinity is proportional to the TDS and is equal to 65.3 ppm as  $\text{CaCO}_3$  at a TDS of 119 ppm (these being the average values from Table 2.1), values of  $\gamma$  can be deduced which cannot be too much in error. Values of  $a$  are then calculated from equation (4.5), and the unbound carbonic acid as ppm  $\text{CO}_2$  is then equal to  $44(a - e)$ .

The experimental and calculated values are given in Table 8.2. It will be seen that the agreement between the experimental values and those calculated by our equation is very good, the differences probably being of no practical significance and about equal to the experimental error. The results calculated by Moore's equations do not differ significantly from ours. This might have been expected, since we have seen that possible errors in  $K_2$  do not materially affect  $f$  or  $a_1$  and that errors in  $\gamma$  have little effect either.

It therefore appears that the theoretical equations developed here, with their non-ideality corrections, are in general superior to Moore's uncorrected equations and may be trusted to agree with experiment up to about pH = 9.8. For reasons already explained, they do not apply much outside the range  $3.7 < \text{pH} < 9.7$  if sulphates (at low pH) or calcium and magnesium salts (at high pH) are present, unless special corrections developed for such cases are employed.



Table 8.2

Experimental and calculated values  
for unbound carbonic acid

Sample	pH	Total alkalinity, ppm $\text{CaCO}_3$	$\gamma$	Unbound carbonic acid as ppm $\text{CO}_2$		
				Observed	Theoretical	Moore
1	6.80	11.0	1.000	4.0	3.5	3.3
2	6.60	10.0	1.000	6.0	5.0	4.9
3	6.45	10.0	1.000	7.0	7.0	6.9
4	6.55	80.0	0.941	44.0	42.2	43.7
5	6.60	70.0	0.944	36.0	33.0	34.1
6	6.40	60.0	0.949	46.0	44.9	46.3
7	7.55	22.0	0.975	1.5	1.1	0.8
8	6.45	10.0	1.000	7.0	7.0	6.9
9	6.65	12.0	0.996	5.0	5.3	5.1
10	7.00	15.0	0.987	3.0	2.9	2.8
11	6.00	3.0	1.000	7.0	5.9	5.9
12	6.00	3.0	1.000	7.0	5.9	5.9
13	7.30	31.0	0.967	3.0	2.9	2.7
14	6.70	22.0	0.975	9.0	8.4	8.4
15	6.70	23.0	0.974	8.0	8.9	8.7
16	6.95	25.0	0.972	4.0	5.4	5.3
17	6.60	21.0	0.976	9.0	10.2	10.3
18	6.60	20.0	0.978	8.0	9.7	9.8
19	7.35	23.0	0.974	4.0	1.9	1.7
20	6.50	16.0	0.984	8.0	9.9	9.8
21	7.35	33.5	0.965	1.5	2.8	2.4

### Carbonic acid in Natal rivers

In Table 8.3 are shown the millimolar concentrations of the major solutes of the 22 unpolluted Natal rivers whose analyses are given in Table 2.1, together with the values of  $\gamma$  and the function  $Q$  defined by equation (8.6). The analyses all fulfil the ionic balance, and the value given for  $\bar{e}$  in each case is the mean of  $\bar{e}_t$  and  $\bar{e}_c$ . For future reference, a summary of the scheme of calculation is given in Appendix A.

For a water in equilibrium with atmospheric carbon dioxide, the total carbonic acid concentration in moles per litre will be  $a_s$ , and from equation (6.13) we have, correcting for non-ideality:

$$a_s = \frac{K_1 K_2 e^2 + k_a K_1 \gamma^2 e + k_a^2 \gamma^2}{k_a K_1 \gamma^2} \quad (8.14)$$

In view of the numerical values of the various constants in this equation, it is clear that in most cases this reduced very closely to

$$a_s = e \quad (8.15)$$

If  $a$  is the total concentration of carbonic acid actually present, the percentage saturation of the water with carbonic acid is clearly:

$$S = \frac{100 a}{a_s} \quad (8.16)$$

and from (8.15) this becomes closely approximated by:

$$S = \frac{100 a}{e} \quad (8.17)$$

Further, using (8.6) this may be written:

$$S = 100 Q \quad (8.18)$$

The function  $Q$  is thus a direct measure of the percentage saturation, provided the conditions for (8.5) to be valid are fulfilled (i.e.  $5 < \text{pH} < 9$  if  $e \geq 10^{-3}$  or  $6 < \text{pH} < 8$  if  $e \geq 10^{-4}$ ). In other cases the full, more complicated expression for  $S$  must be used:

$$S = \frac{100 k_a K_1 \gamma^2 (H^2 \gamma^6 + K_1 H \gamma^4 + K_1 K_2)}{(K_1 H \gamma^4 + 2 K_1 K_2) (K_1 K_2 e^2 + k_a K_1 \gamma^2 e + k_a^2 \gamma^2)} (H - k_w / H \gamma^2 + e) \quad (8.19)$$

It is clear that (8.15) is independent of temperature variation in the normal ambient temperature range because  $e$  is temperature



Table 8.3

Millimolar concentrations, etc. calculated from the analyses of Table 2.1

River	$\gamma$	$\bar{e}^*$	$\bar{c}$	$\bar{m}$	$\bar{n}$	$\bar{p}$	$\bar{a}$	$\bar{s}$	$\bar{h}$	Q
Sterk near Ambleside	0.975	0.449	0.0775	0.0917	0.204	0.0180	0.489	Nil	0.127	1.09
Illovo above Richmond	0.975	0.559	0.130	0.0750	0.183	0.0026	0.565	Nil	0.0225	1.01
Mooi above Mooi River	0.974	0.389	0.125	0.0750	0.122	0.0180	0.459	0.0854	0.0254	1.18
Karkloof at Shafton	0.974	0.471	0.0875	0.0708	0.183	0.0128	0.490	Nil	0.0479	1.04
Ingagane above Alcockspruit	0.970	0.652	0.125	0.0833	0.187	0.0923	0.647	0.0313	0.0254	0.993
Lions near Lidgetton	0.965	0.818	0.165	0.146	0.239	0.0307	0.908	0.0177	0.0028	1.11
Nungwana near Nungwana Falls	0.965	0.347	0.0975	0.104	0.304	0.0026	0.345	Nil	0.428	0.993
Umgeni at Nagle Dam	0.961	0.716	0.163	0.125	0.344	0.0256	0.838	0.0146	0.251	1.17
Umgegu at Umfula	0.959	0.872	0.140	0.163	0.583	0.0333	0.889	Nil	0.330	1.02
White Umfolozi near Vryheid	0.959	0.88	0.245	0.121	0.0522	0.159	1.01	0.0240	0.0592	1.14
Lenjane's at Lenjane's Drift	0.958	1.26	0.315	0.238	0.283	0.0769	1.30	0.0240	0.0648	1.03
Tugela at Colenso	0.957	1.37	0.323	0.246	0.278	0.0180	1.40	0.0188	0.0338	1.02
Sundays near Newcastle	0.954	1.53	0.278	0.300	0.357	0.0386	1.53	0.0333	0.0028	1.00
Gogoshi near Mtunzini	0.949	0.282	0.0625	0.0417	1.28	0.0205	0.290	Nil	1.28	1.03
Unvoti at Bitakona	0.947	1.27	0.255	0.213	0.804	0.0282	1.30	0.0760	0.380	1.02
Umfolozi at Mtubatuba	0.943	1.98	0.365	0.375	1.08	0.0386	2.04	Nil	0.544	1.03
Umzimkulwana at Baboons Castle	0.941	1.41	0.288	0.400	1.20	0.0282	1.38	0.0760	1.01	0.977
Bloukrans near Colenso	0.932	3.36	0.743	0.588	0.883	0.0436	3.34	0.0448	0.110	0.993
Umhlanga at Trenance	0.929	1.41	0.248	0.517	2.02	0.0410	1.49	0.0833	2.16	1.06
Umzinyatshana near Dundee	0.927	3.75	0.665	0.867	1.03	0.0333	3.68	0.0771	0.130	0.982
Isipingo near Inwabi	0.918	1.12	0.338	0.659	3.20	0.0692	1.13	0.144	3.97	1.01
Mpushini near Pietermaritzburg	0.916	3.46	0.768	0.804	2.44	0.0282	3.67	0.0490	2.18	1.06

\*  $\bar{e}$  is taken as the mean of  $\bar{e}_t$  and  $\bar{e}_c$



invariant. Hence also must be (8.18), i.e.  $Q$  must be virtually independent of temperature in this range. Therefore here is some justification for disregarding temperature effects in the present work (see chapter 5).

From the values of  $Q$  given in Table 8.3 it is clear that the percentage saturation in the 22 Natal rivers ranges from about 98 to 118% with a mean of 104%. It therefore appears as a general rule that unpolluted river waters in Natal (and indeed most other river waters also, according to the data published in the literature) are virtually in equilibrium with atmospheric carbon dioxide. The fact that there is a small bias to values rather more than 100% indicates a slight tendency to supersaturation, suggesting that those processes occurring within rivers to generate carbon dioxide (mainly the respiration of aquatic organisms) take place a little more rapidly than the diffusion of carbon dioxide to the atmosphere through the air-water interface.

Moreover, on the basis of these results it appears that the composition of a river water may be regarded as anomalous (i.e. probably affected by pollution) if the percentage saturation with carbon dioxide lies outside the range 95 - 120.

In Table 8.4 are shown the calculated concentrations of free carbonic acid, as ppm of  $\text{CO}_2$ , in the same 22 rivers (obtained from equation (8.12)). The values range from 0.1 to 10.1 ppm with a mean of 2.1 ppm, and it is readily seen that 95% of the values are less than 6 ppm. On this basis, it may therefore be supposed that, with 95% confidence, a river water may be regarded as anomalous (i.e. probably affected by pollution) if the free carbonic acid exceeds 6 ppm. This is in agreement with the conclusions of Ellis (1937) that more than 6 ppm of free carbonic acid in rivers of the U.S.A. is usually indicative of pollution. But the fact that the unpolluted Mpushini river shows 10.1 ppm and yet only 106% saturation indicates that the percentage saturation is more significant than the concentration.

This conclusion is also reached by considering that the saturation will always be high in a stream of low pH but that the free carbonic acid will only be high if the alkalinity is high, and conversely that at moderate or high pH the saturation may not be significantly high although the free carbonic acid may be high if the alkalinity is sufficiently great (as in the Mpushini).

The values of  $Q$  given in Table 3B of Appendix B show that any water in contact with the atmosphere is saturated with carbon dioxide



Table 8.4

Free carbonic acid in unpolluted Natal rivers

River	Free CO <sub>2</sub> , ppm
Sterk near Ambleside	1.7
Illovo above Richmond	0.4
Mooi above Mooi River	3.0
Karkloof at Shafton	0.9
Ingagane above Alcockspruit	0.3
Lions near Lidgetton	3.9
Nungwana near Nungwana Falls	0.1
Umgeni at Nagle Dam	5.4
Umgega at Umfula	1.0
White Unfolozi near Vryheid	4.2
Lenjane's at Lenjane's Drift	1.9
Tugela at Colenso	1.3
Sundays near Newcastle	0.9
Gogoshi near Mtunzini	0.4
Umvoti at Bitakona	1.2
Unfolozi at Mtubatuba	2.9
Unzinkulwana at Baboons Castle	0.2
Bloukrans near Colenso	1.2
Umhlanga at Trenance	4.1
Umzinyatshana near Dundee	0.8
Isipingo near Inwabi	1.0
Mpushini near Pietermaritzburg	10.1

when its pH value is that of the phenolphthalein end-point, i.e. when its total alkalinity is stoichiometrically in the form of bicarbonate and there is no unbound carbonic acid so that  $a = e$ . Equation (8.15) also shows this. At lower pH values the water will be supersaturated and tend to evolve carbon dioxide to the atmosphere, at higher pH values it will be under-saturated and tend to absorb carbon dioxide from the air.

#### Carbonic acid in rain and sea water

Analyses of rain and sea water are given in Table 8.5. The former is the mean of five soot-free samples from the English Lake District (Gorham, 1955B). The latter is a mean analysis taken from Sverdrup et al (1942).

For the rain water we have  $\bar{e}_t = 0.040$  and  $\bar{e}_c = -0.0042$ . The former does not accord with the pH value (the total alkalinity would be zero at a pH of 5.2, so that at the tabulated pH the sample must have a total acidity, not alkalinity). The latter is likely to be erroneous since it contains all the accumulated analytical errors, which are probably great in view of the low concentrations even though the analysis fulfils the ionic balance. However, by equation (6.8) the pH value corresponds to  $\bar{e} = -0.013$ . Using this, the total carbonic acid concentration is given by (4.5) as  $1.51 \times 10^{-5}$  molar, which corresponds to about 150% saturation. Supersaturation can be accounted for by the fact that rain is formed by condensation in regions of the atmosphere where the temperature is low and the solubility of carbon dioxide in water correspondingly high (e.g. at  $0^\circ\text{C}$  the equilibrium concentration is  $2.4 \times 10^{-5}$  molar, instead of  $1.00 \times 10^{-5}$  molar at  $25^\circ\text{C}$ ). All the carbonic acid is in the unbound state and will be able to act chemically upon minerals, rocks and soils, so it is easily appreciated why rain plays such an important part in geological weathering processes. Rivers being, as we have seen, almost in equilibrium with atmospheric carbon dioxide, the weathering processes evidently consume almost all the aggressive (unbound) carbonic acid of rain water that does not return unchanged to the atmosphere.

For the sea water  $\bar{e}_t = 2.41$  and  $\bar{e}_c = 5$ , although the analysis gives an ionic balance. We take  $\bar{e} = \bar{e}_t$  since the alkalinity of sea water has been determined with great accuracy by many workers. From (4.5), using the value  $\gamma = 0.297$  adopted in chapter 4, the total carbonic acid  $a = 2.16 \times 10^{-3}$ . If however, equation (8.14) is applied with this same value of  $\gamma$ , the percentage saturation with carbon dioxide works out to



about 66%. Yet it is clear that, since the pH of sea water is very close to that of the phenolphthalein end-point, there must be almost equilibrium between the carbon dioxide dissolved in the oceans and that of the atmosphere, i.e. the saturation is approximately 100%. Harvey (1928) has suggested that sea water may be undersaturated with carbon dioxide, but later work (summarised by Defant, 1961) has shown that, although slight local undersaturation or supersaturation can occur, on the whole there is a fairly steady equilibrium state. The apparent value of 66% saturation is in fact a false result, consequent upon using the empirical value  $\gamma = 0.297$  in an equation to which it was never intended to apply. The incorrectness of such a procedure was pointed out at the end of chapter 4. There is no means of determining from the available data what value of  $\gamma$  may be adopted for use in equation (8.14).

Table 8.5

Analyses of rain and sea water

	Rain water	Sea water
pH	4.9	7.9
TDS, ppm	13	35,320
Total alkalinity, ppm $\text{CaCO}_3$	2.0	120.3
Ca, ppm	0.2	410
Mg, ppm	0.3	1,303
Na, ppm	3.1	10,818
K, ppm	0.2	389
$\text{SO}_4$ , ppm	1.7	2,713
Cl, ppm	5.1	19,441
$\text{SiO}_2$ , ppm	-	0.1

## 9. THE TITRATION CURVE

### General characteristics

At this stage it will be useful to consider in more detail the titration curve of a normal (carbonated) natural water.

Figure 9.1 shows the ideal titration curve of a typical water for which  $a = 10^{-2}$ , plotted with pH as ordinate and total alkalinity during titration as abscissa. The two end-point inflections occur at  $e = 0$  and  $e = a$  so that the horizontal separation between them is equal to the total carbonic acid concentration,  $a$ , in this case  $10^{-2}$ . The actual total alkalinity of the water in its initial state at the commencement of titration is represented by some particular point on the curve such as the point X.

The horizontal distance between this initial point X and the methyl orange end-point is equal to the total alkalinity,  $e$ , of the water. Figure 9.1(a) shows the situation when  $0 < e < a$ , Figure 9.1(b) when  $e > a$  and Figure 9.2(c) when  $e < 0$ .

These three diagrams also show that, when the total alkalinity of the water changes, its (ideal) titration curve remains unaltered. The only difference in the diagram is that the point X denoting the initial state of the water is displaced in the appropriate direction along the curve.

The reciprocal of the gradient of the curve at the initial point X is a measure of the buffer capacity of the water, and this is clearly low in the vicinity of the two end-point inflections but relatively high elsewhere.

### Changes in carbonic acid content

If the total carbonic acid content of the water becomes changed, the titration curve itself becomes altered.

In Figure 9.2 are shown the ideal titration curves of waters with  $a = 10^{-2}$ ,  $5 \times 10^{-3}$ ,  $2 \times 10^{-3}$ ,  $10^{-3}$  and  $10^{-4}$ . It is seen that, as  $a$  decreases, the pH for a given value of  $e$  increases, the phenolphthalein moves closer to the methyl orange end-point inflection, while the buffer capacity in the range  $0 < e < a$  (reciprocal gradient of the curve) progressively decreases. Eventually the two end-point inflections become indistinguishable, the curve then resembling that of a strong



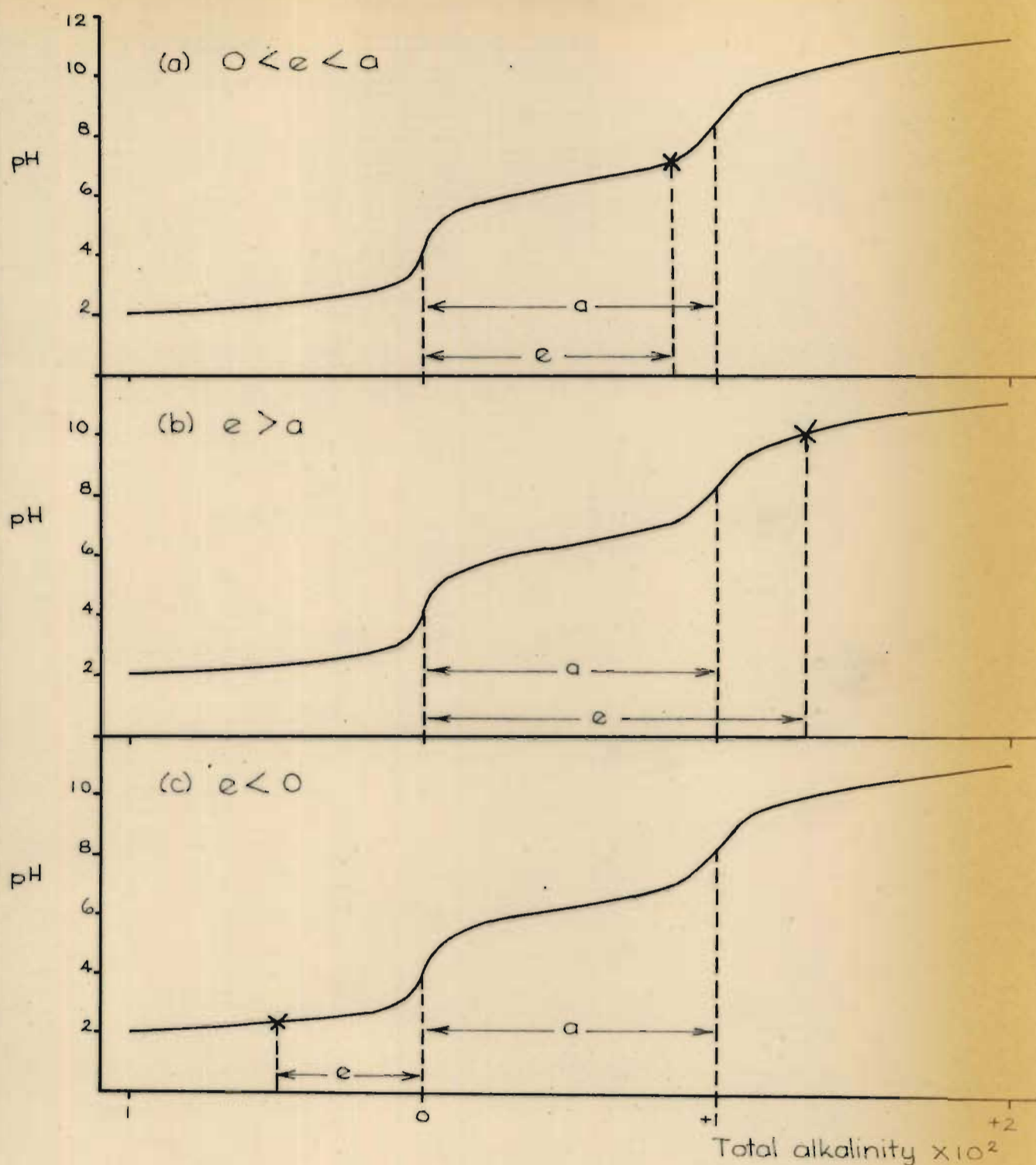


FIGURE 9.1

Ideal titration curves of a water which is  $10^{-2}$  molar in carbonic acid

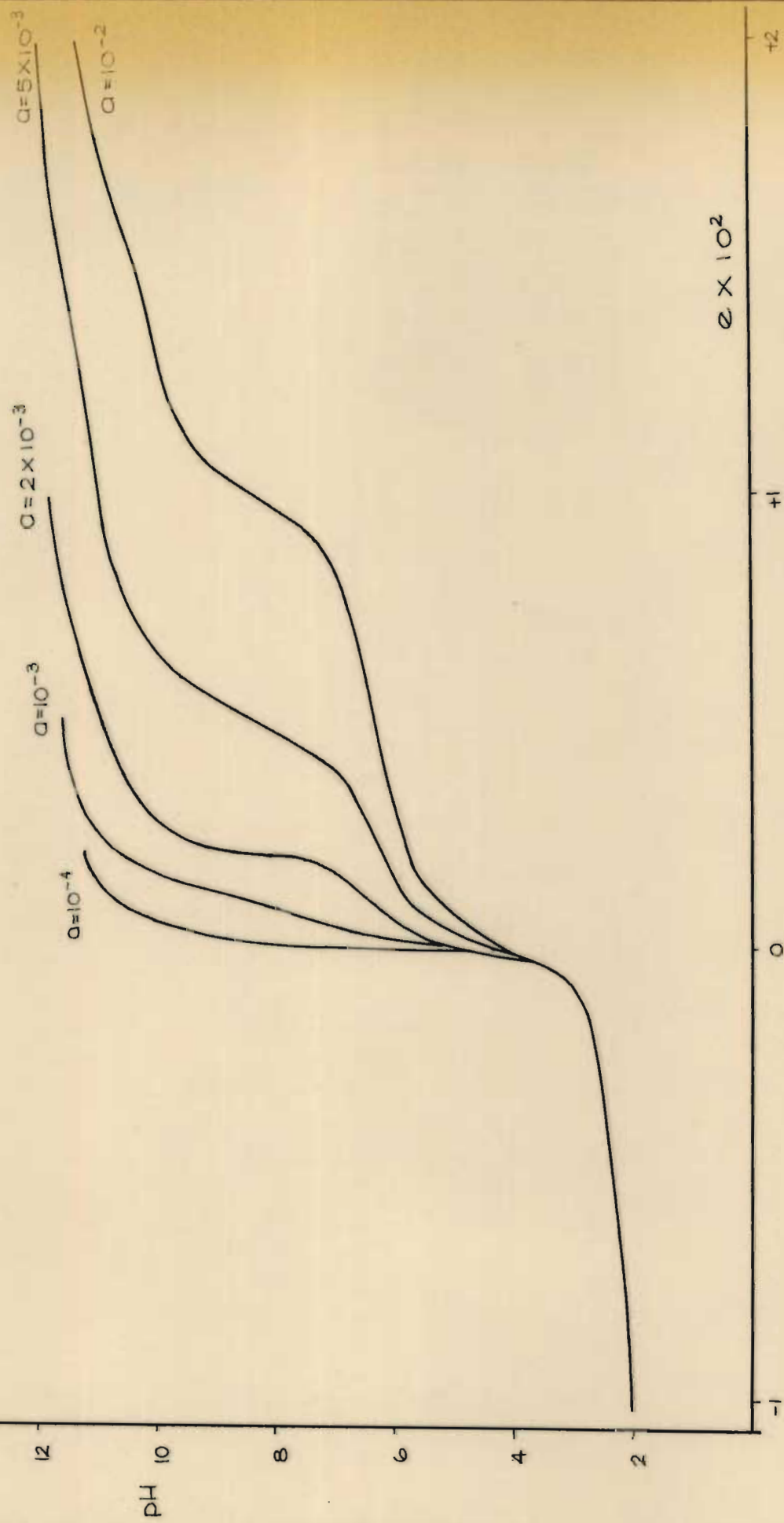


FIGURE 9.2

Ideal titration curves of carbonic acid solutions of different molar concentration



acid. In the range  $e < 0$ , however, the curve remains unaltered.

The buffer capacity,  $B$ , is defined as:

$$B = \frac{de}{dpH} \quad (9.1)$$

and since, in the ideal case, the pH is equal to  $-\log H$  this may be written:

$$B = -2.303 H \frac{de}{dH} \quad (9.2)$$

From equation (3.43) it follows that in the range  $3.7 < pH < 9.7$  we have:

$$B = 2.303 \left[ \frac{a K_1 H (H^2 + 4 K_2 H + K_1 K_2)}{(H^2 + K_1 H + K_1 K_2)^2} + H + \frac{k_w}{H} \right] \quad (9.3)$$

Here  $B$  is expressed as equivalents per litre per pH unit. For practical purposes it is more convenient to express the buffer capacity as meq per litre per pH unit. Denoting this by  $\bar{B}$  we can write:

$$\bar{B} = U_1 \bar{a} + U_2 \quad (9.4)$$

where:

$$U_1 = \frac{2.303 K_1 H (H^2 + 4 K_2 H + K_1 K_2)}{(H^2 + K_1 H + K_1 K_2)^2} \quad (9.5)$$

$$U_2 = 2303 (H + k_w/H)$$

Values of  $U_1$  and  $U_2$  for various pH values in the range 4.0 to 9.0 are given in Table 6B of Appendix B. Activity corrections may readily be introduced to these equations, but for the application it is intended to make here this is unnecessary.

Table (9.1) shows the values of  $\bar{B}$  for the 22 Natal rivers of Tables 2.1 and 8.3. They show little correlation with any other property of the water, but have a tendency to increase as the TDS increases.

According to McKee and Wolf (1963) a water is considered as being adequately buffered to support healthy aquatic life if its pH is between 7 and 8 and its total alkalinity at least 100 ppm as  $CaCO_3$ . This corresponds to a value of  $\bar{B}$  of at least 0.12. In the following chapter we shall see that Natal river waters should have  $\bar{B}$  at least 0.10 if they are to be successfully treated to eliminate corrosivity. The value  $\bar{B} = 0.10$  therefore appears to be a significant one.

Kleijn (1965) has given a discussion of buffer capacity, though he has used approximations that are dubious, water analyses that are not in ionic balance, and assumptions as to the saturation of waters with carbon dioxide which do not seem valid.

Table 9.1

Buffer capacities of Natal river waters

R i v e r	Buffer capacity $\bar{B}$ in millimolar units
Sterk near Ambleside	0.09
Illovo above Richmond	0.03
Mooi above Mooi River	0.14
Karkloof at Shafton	0.05
Ingagane above Alcockspruit	0.04
Lions near Lidgetton	0.20
Nungwana near Nungwana Falls	0.02
Umgeni at Nagle Dam	0.25
Umgega at Umfula	0.07
White Umfolozi near Vryheid	0.26
Lenjane's at Lenjane's Drift	0.11
Tugela at Colenso	0.09
Sundays near Newcastle	0.08
Gogoshi near Mtunzini	0.03
Umvoti at Bitakona	0.08
Umfolozi at Mtubatuba	0.17
Umzimkulwana at Baboons Castle	0.10
Bloukrans near Colenso	0.19
Umhlanga at Trenance	0.22
Umzinyatshana near Dundee	0.21
Isipingo near Inwabi	0.07
Mpushini near Pietermaritzburg	0.55

Changes in TDS

In Table 9.2 are shown the calculated pH values of a  $10^{-3}$  molar solution of carbonic acid for various values of the total alkalinity under both ideal and real conditions, in the latter case assuming  $\gamma = 0.800$ ,



i.e. supposing the TDS to be about 2500 ppm.

Below  $e = a$  the real pH is a little higher than the ideal, above  $e = a$  it is a little lower. However, the two sets of values are only slightly different (not more than 0.3 units), so that in most practical cases the pH may be calculated accurately enough by assuming ideality. Differences between the ideal and real hydron concentrations may nevertheless be appreciable (e.g. at  $e = 5 \times 10^{-4}$  in the present case the ideal value of H is  $4.6 \times 10^{-7}$ , the real value  $2.9 \times 10^{-7}$ ), and hence also must be those between the real and ideal values of other ionic concentrations.

#### Changes in water composition

The effects upon the titration curve of changing the composition of the water in any way may readily be deduced from the above discussion, and may be summarised as follows:

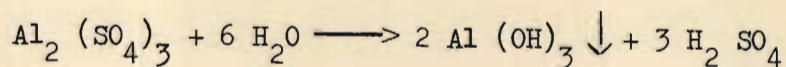
- (a) the addition of neutral non-carbonated salts such as sodium chloride or magnesium sulphate (provided the general equation (3.41) remains valid) has only a second order effect on the titration curve consequent upon the change induced in the activity coefficient  $\gamma$ .
- (b) the addition of strong base or acid changes the value of the total alkalinity  $e$  and causes the point X representing the chemical state of the water to move along the titration curve to the right (base) or left (acid) without materially changing the shape of the curve.
- (c) the addition of carbonic acid in general lowers the pH and causes the titration curve to change its shape in the manner shown in Figure 9.2, although the point X representing the chemical state of the water remains on the curve at the same value of  $e$ .
- (d) the addition of a carbonate or bicarbonate (each of which may be regarded as a mixture of base and carbonic acid) will change the shape of the titration curve as in (c) and will also cause the point X representing the chemical state of the water to move to the right, towards larger values of  $e$ .

In general, any solute which is added to the water may, according to Ricci's (1952) concepts be regarded as the equivalent mixture of acid and base, so that the effects on the titration curve can always be worked out from the above principles. One special case is the addition of aluminium sulphate, commonly used in water treatment processes, for at the usual pH values encountered in surface waters this becomes hydrolysed to

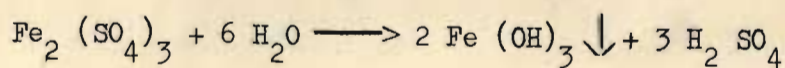
Table 9.2  
Real and ideal pH values for  $10^{-3}$   
molar carbonic acid solutions

$e \times 10^3$	Ideal pH $\gamma = 1.000$	Real pH $\gamma = 0.800$
- 1.00	3.00	3.10
- 0.50	3.30	3.40
- 0.30	3.52	3.62
- 0.20	3.70	3.80
- 0.10	4.00	4.10
0.00	4.68	4.70
+ 0.10	5.40	5.69
+ 0.20	5.75	6.04
+ 0.30	5.99	6.27
+ 0.50	6.35	6.64
+ 0.70	6.72	7.01
+ 0.80	6.96	7.25
+ 0.90	7.31	7.60
+ 1.00	8.30	8.12
+ 1.10	9.28	9.08
+ 1.20	9.62	9.44
+ 1.30	9.84	9.67
+ 1.50	10.17	10.04
+ 1.80	10.43	10.40
+ 2.00	10.56	10.59

insoluble aluminium hydroxide and free sulphuric acid:

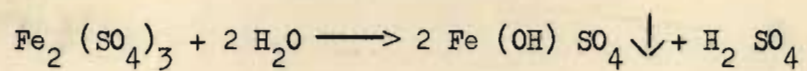


The addition of 1 mole of the salt therefore has the same effect as the addition of 3 moles of sulphuric acid. Ferric sulphate may behave in the same way:





but it may alternatively give a basic precipitate:



in which case the liberated sulphuric acid will be less than 3 moles.

## 10. CORROSIVITY AND THE $pH_s$

### Saturation pH value

The saturation pH value ( $pH_s$ ) of a water is defined as the pH value that results when, by addition or removal of carbonic acid but by no other chemical change, the water is brought into equilibrium with solid calcium carbonate.

This parameter was first introduced by Langelier (1936) in connection with the corrosivity of water supplies. His theoretical equation for the calculation of its value may be regarded as a first approximation, since its derivation rested upon an assumption (that H and OH were negligibly small in comparison with other ionic concentrations) that is not necessarily true and which was introduced at too early a stage of the working.

A more rigid expression for  $pH_s$  is obtainable from equation (3.43) for a water containing carbonic acid and alkalinity under ideal conditions. Using (3.34) this may be written:

$$H - \frac{k_w}{H} = \frac{a_2 (K_1 H + 2 K_1 K_2)}{K_1 K_2} - e \quad (10.1)$$

The ideal condition for the water to be in equilibrium with solid calcium carbonate is the ideal form of (6.25):

$$k_{ca} = c_2 a_2 \quad (10.2)$$

But (3.43) is valid only in the range  $3.7 < pH < 9.7$  and in this range  $c_2$  is indistinguishable from  $c$  (see Figure 3.1). Hence (10.2) may be written:

$$k_{ca} = c a_2 \quad (10.3)$$

and insertion of this in (10.1) gives:

$$H - \frac{k_w}{H} = \frac{k_{ca} (K_1 H + 2 K_1 K_2)}{c K_1 K_2} - e \quad (10.4)$$

This equation expands to a quadratic in H:

$$(k_{ca} - c K_2) H^2 - K_2 (ec - 2 k_{ca}) H + c K_2 k_w = 0 \quad (10.5)$$

and will have a real root only if:



$$K_2^2 (ec - 2 k_{ca})^2 > 4 c K_2 k_w (k_{ca} - c K_2) \quad (10.6)$$

This condition is not always satisfied. Provided  $e > 0$ , it will certainly be satisfied if:

$$K_2^2 (ec)^2 > 4 c K_2 k_w k_{ca} \quad (10.7)$$

$$\text{i.e.} \quad e^2 > 4 k_w k_{ca} / c K_2 \quad (10.8)$$

so that there may be no solution to (10.5) if  $|e|$  and  $c$  are small in value. In practice, this is likely to happen if the total alkalinity is less than 5 ppm as  $\text{CaCO}_3$  and the calcium concentration less than 4 ppm as Ca, i.e. with rain water and surface waters of extremely low TDS.

Provided the condition (10.6) is satisfied, then for all ordinary values of  $e$  and  $c$  the root of (10.5) is, by (3.8):

$$H = \frac{K_2 (ec - 2 k_{ca})}{k_{ca} - c K_2} \quad (10.9)$$

and since  $c K_2$  is always negligibly small in comparison with  $k_{ca}$  this further reduces to:

$$H = \frac{K_2 (ec - 2 k_{ca})}{k_{ca}} \quad (10.10)$$

Evidently this is only of physical significance if  $ec > 2 k_{ca}$  for otherwise it becomes negative in sign. In particular this requires  $e > 0$ , so that no water with a pH of less than about 4 can ever be in equilibrium with calcium carbonate. If  $e > 0$  but is small in value, equilibrium is only possible if the condition (10.6) is fulfilled, as we have seen. On the other hand, if the product  $ec$  is too large, equation (10.10) will lead to a value of  $H$  so great that it is outside the range of validity of (3.43), i.e.  $\text{pH} < 3.7$ , and the above theoretical treatment will fail. However, (10.10) shows that this will only occur if  $ec$  exceeds about  $2 \times 10^{-5}$ , which corresponds to the product  $A \cdot \text{Ca}$  exceeding about 40,000,  $A$  being the total alkalinity as ppm of  $\text{CaCO}_3$  and  $\text{Ca}$  the calcium concentration as ppm of Ca. The treatment is therefore valid for most ordinary cases encountered in practice, since such high values are rare.

Denoting the value of  $H$  given by (10.10) as  $H_s$  and correcting

for non-ideality gives:

$$H_s = \frac{K_2 (e c \gamma^8 - 2 k_{ca})}{k_{ca} \gamma^4} \quad (10.11)$$

and if  $pH_s$  is defined as  $-\log H_s$  we obtain:

$$pH_s = \log k_{ca} - \log K_2 + 3 \log \gamma - \log (e c \gamma^8 - 2 k_{ca}) \quad (10.12)$$

This may be written in numerical form by inserting the values of  $k_{ca}$  and  $K_2$  and replacing  $e$  and  $c$  by the practical values  $A$  and  $Ca$ :

$$pH_s = 11.34 + 3 \log \gamma - \log (A.Ca \gamma^8 - 20.5) \quad (10.13)$$

The equation developed by Langelier (1936), whose derivation we have criticised, gives results almost indistinguishable from those of (10.13) in the ideal case, except that whereas (10.13) leaves  $pH_s$  undefined if  $A.Ca \gamma^8 < 20.5$ , i.e. such a water cannot be in equilibrium with calcium carbonate, Langelier's equation always gives a definite value. Langelier attempted to introduce non-ideality corrections, although in this he was not very successful, better results being obtained later by Larson and Buswell (1942) which numerically agree very closely with the corrections in (10.13).

#### An approximate $pH_s$ equation

If it is assumed that the alkalinity and calcium contents of a natural water are proportional to the TDS, we can write:

$$A.Ca = \alpha T^2 \quad (10.14)$$

where  $\alpha$  is a constant and  $T$  is the TDS in ppm. Using the average values  $A = 65.3$ ,  $Ca = 10.9$  and  $T = 119$  (so that  $\gamma = 0.946$ ) from Table 2.1, we have  $\alpha = 5.03 \times 10^{-2}$ . If  $T$  is further assumed to be approximately equal to two-thirds the electrical conductivity in micromho (see chapter 12 below), then after inserting (10.14) in (10.13), using the above value of  $\gamma$  and neglecting the term 20.5, we obtain:

$$pH_s = 13.12 - 2 \log C \quad (10.15)$$

where  $C$  is the electrical conductivity in micromho at  $20^\circ C$ .

In Table 10.1 are given the  $pH$  and  $pH_s$  values for the Natal rivers of Table 2.1. The  $pH_s$  was obtained from equation (10.13) using the



Ca values of Table 2.1 but values of A corresponding to  $\bar{e}$  in Table 8.3 instead of the original alkalinities (which have already been stated to contain errors). In column 5 of Table 10.1 are given the  $\text{pH}_s$  values calculated from the approximate relation (10.15).

It is evident that (10.15), though a crude approximation, gives surprisingly good results (apart from the anomalous case of the Gogoshi). The root mean square error of the calculated values is 0.61, so that the 95% confidence limits of accuracy for (10.15) can be set at about  $\pm 1.2$ . These limits are too wide for the equation to be of direct practical use.

On the basis of equation (10.15) it might be supposed that, for any particular natural water, a regression equation of the form:

$$\text{pH}_s = X - Y \log C \quad (10.16)$$

would exist, where X and Y are constants. Such relationships do indeed exist, the following being examples calculated from data recorded during some South African river surveys:

- (a) Tugela river system of Natal (Oliff, 1960):

$$\text{pH}_s = 10.40 - 0.943 \log C$$

Standard error of estimate = 0.41

- (b) Umgeni river system of Natal (Schoonbee and Kemp, 1965):

$$\text{pH}_s = 11.64 - 1.37 \log C$$

Standard error of estimate = 0.46

- (c) Great Berg river system of the Cape (Harrison and Elsworth, 1958):

$$\text{pH}_s = 13.30 - 1.85 \log C$$

Standard error of estimate = 0.20

- (d) Jukskei river of the Transvaal (Allanson, 1961):

$$\text{pH}_s = 9.16 - 0.478 \log C$$

Standard error of estimate = 0.17

However, these equations are clearly of little practical use.

Table 10.1

Saturation pH values of Natal river waters

	pH	pH <sub>s</sub>	Saturation index	Approx. pH <sub>s</sub> by equation (10.15)	R
Sterk near Ambleside	7.4	9.75	- 2.4	9.67	0.28
Illovo above Richmond	8.1	9.32	- 1.2	9.48	0.04
Mooi above Mooi River	7.1	9.54	- 2.4	9.86	0.50
Karkloof at Shafton	7.7	9.64	- 1.9	9.85	0.10
Ingagane above Alcockspruit	8.4	9.27	- 0.9	9.59	0.14
Lions near Lidgetton	7.3	9.13	- 1.8	9.48	0.05
Nungwana near Nungwana Falls	8.4	9.81	- 1.4	9.14	1.23
Umgeni at Nagle Dam	7.1	9.12	- 2.0	9.20	0.39
Umgegu at Umfula	7.9	9.10	- 1.2	9.06	0.38
White Umfolozi near Vryheid	7.2	8.83	- 1.7	9.12	0.12
Lenjane's at Lenjane's Drift	7.8	8.55	- 0.8	9.12	0.09
Tugela at Colenso	8.0	8.50	- 0.5	8.95	0.05
Sundays near Newcastle	8.2	8.53	- 0.3	8.91	0.05
Gogoshi near Mtunzini	7.8	10.84	- 3.0	8.70	4.54
Umvoti at Bitakona	8.0	8.67	- 0.7	8.64	0.42
Umfolozi at Mtubatuba	7.8	8.31	- 0.5	8.35	0.28
Umzimkulwana at Baboons Castle	8.7	8.58	+ 0.1	8.33	0.82
Bloukrans near Colenso	8.4	7.80	+ 0.6	8.19	0.06
Umhlanga at Trenance	7.5	8.68	- 1.2	7.88	1.65
Umzinyatshana near Dundee	8.6	7.81	+ 0.8	8.11	0.08
Isipingo near Inwabi	8.0	8.67	- 0.7	7.70	3.80
Mpushini near Pietermaritzburg	7.5	7.81	- 0.3	7.91	0.66

Corrosivity and the pH<sub>s</sub>

It is evident that if the pH<sub>s</sub> of a water exceeds its actual pH value, that water will tend to dissolve calcium carbonate when it has the opportunity. Conversely, if the pH exceeds the pH<sub>s</sub> the water is super-saturated with calcium carbonate and will tend to deposit it out of solution.

Langelier (1936) took the view that any water will corrode



metals, particularly iron, but that a water supersaturated with calcium carbonate would deposit a scale of calcite upon metallic surfaces in contact with it and so protect them from its corrosive action. He defined the saturation index of a water as equal to  $(\text{pH} - \text{pH}_s)$ , so that a water with a negative index would be potentially corrosive whilst one with a positive index would be scale-forming and hence not corrosive. To minimise the corrosivity of a water, on this view, it was essential to treat the water so that its saturation index would be just on the positive side of zero (a markedly scale-forming water being undesirable since it would eventually, not corrode, but block pipes and fittings). Treatment would involve changing the pH or  $\text{pH}_s$  or both by suitable addition of lime, soda ash, etc.

It will be seen from Table 10.1 that the waters of most Natal rivers, according to these principles, should be counted as corrosive (negative saturation index). The  $\text{pH}_s$  tends to decrease as the TDS (or conductivity) decreases, as equation (10.15) predicts.

Ryznar (1944) suggested the use of the stability index, defined as  $(2 \text{pH}_s - \text{pH})$ , as a more quantitative parameter for measuring the corrosive or scale-forming properties of waters, but this suggestion appears to be not well founded and his observational data have been questioned. For example, Stumm (1960) has discussed the importance of organic acids, oxygen, chlorides, nitrates, redox potentials and other factors which can influence corrosivity.

In this connection it is relevant to refer again to Lewin's (1960) observation that, in precipitation reactions, it is often necessary for the relevant ionic product to be between  $10^3$  and  $10^5$  times greater than the normal solubility product value before precipitation actually occurs. This means that the effective value of  $k_{ca}$  must be, not  $5.12 \times 10^{-9}$ , but between  $5 \times 10^{-6}$  and  $5 \times 10^{-4}$  so that, according to equation (10.13), the effective  $\text{pH}_s$  values of most waters will be from 3 to 5 units higher than the normal calculated values, i.e. most river waters should have very great potential corrosivity.

In place of Ryznar's stability index, Dye (1958) introduced the momentary excess of calcium carbonate, that amount by which the calcium carbonate concentration in an aqueous solution exceeds the theoretical maximum as measured by the stability product. Similarly McCauley (1960A) introduced the driving force index, the ratio of the calcium carbonate concentration to that of the solubility product. Both these indices



appear to be more useful than Ryznar's index (McCauley, 1960B; Dye, 1964) and the driving force index in particular takes some account of Lewin's comment.

However, even if the basic postulate that the deposition of calcite makes for protection from corrosion is correct, it by no means follows that a positive saturation index (or corresponding values of the other indices) indicates that a protective scale will necessarily be formed. The deposited solid phase could easily remain in suspension as a turbidity or settle as a loose and non-protecting sludge. The practical importance of  $pH_s$  in regard to the corrosion of metals seems, in fact, to have become greatly over-stressed in recent years. It does not seem to be really such a fundamentally useful parameter in this connection as is generally supposed, and clear and convincing experimental evidence of its utility has never been produced. The fact that Langelier (1936) himself only claimed that his saturation index denoted a potentiality appears to have become disregarded by later workers. There are many waters in Natal with large negative saturation indices which yet are used in public and private water supplies without any especial anti-corrosion treatment but without the appearance of any very exceptionally heavy corrosion in pipes and fittings, so that one suspects that the connection between  $pH_s$  and the corrosion of metals is largely illusory. Indeed, in Natal it seems often more reasonable to attribute cases of high corrosivity to high chloride content rather than to  $pH_s$ . However, the importance of  $pH_s$  with regard to the corrosion by waters of cement, concrete and asbestos cement seems to be unchallengeable.

More recently (Larson and Skold, 1958; American Public Health Association, 1965) an entirely different index of corrosivity has been suggested. This is defined as:

$$R = \frac{2s + h}{e} = \frac{2\bar{s} + \bar{h}}{\bar{e}} \quad (10.17)$$

In the neutral pH range and in presence of dissolved oxygen, values of this index less than about 0.2 are said to indicate general freedom from corrosion to metals, whereas increasingly higher values are indicative of more corrosive waters. The value of this index R for each of the rivers concerned (calculated from the data of Table 8.3 is shown in the last column of Table 10.1. Using this criterion, 10 of the 22 rivers may be counted free from corrosivity, although this bears very little relation



to the indications of the saturation index.

### Notes on anti-corrosion water treatment

Although we have expressed doubts as to the real worth of the  $\text{pH}_s$  in connection with corrosivity, the fact remains that anti-corrosion water treatment based on control of the  $\text{pH}_s$  is very widely practised. It is of interest, therefore, to consider the application of our theoretical equations to this problem.

First of all, we note that the rivers of Table 2.1 show the following average values: total alkalinity 65.3 ppm as  $\text{CaCO}_3$ , calcium 10.9 ppm as Ca, pH value 7.85 and TDS 119 ppm (the latter corresponding to  $\gamma = 0.946$ ). From these values it is readily seen that  $Q = 1.03$ ,  $\bar{e} = 1.31$  and  $\bar{a} = 1.35$ . If the TDS of this average water is supposed to become changed by simple dilution or concentration, the variation with the TDS of the pH can be found from equation (3.49) in its non-ideal form and that of the  $\text{pH}_s$  from equation (10.13). Figure 10.1 shows how these two parameters change with the TDS under the conditions supposed, and Figure 10.2 similarly shows the corresponding changes in the saturation index. The value of the corrosion index R defined by (10.17), however, remains constant as the TDS changes, its average value being 0.46.

These variations may be taken as typical for Natal river waters (although, of course, waters of composition different from the average will behave somewhat differently). It is seen that the  $\text{pH}_s$  progressively decreases as the TDS rises, the pH is almost unchanged, while the saturation index has negative values at low TDS and rises to approach the value + 1.0 at high TDS, becoming zero at a TDS of about 300 ppm, i.e. according to the Langelier hypothesis the water is potentially corrosive at low TDS but scale-forming at high TDS. This of course does not mean that the saturation index of a water may be raised merely by increasing the TDS (e.g. by adding sodium chloride), for the addition of salts in this way would so change the chemical composition of the water that Figures 10.1 and 10.2 would no longer apply.

Clearly a scale-forming water can be made stable, i.e. zero saturation index, by any treatment that will reduce the pH and/or increase the  $\text{pH}_s$ . Both these effects may be achieved by the addition of acids, and in practice the water can be stabilised by gassing it with carbon dioxide or by dosing it with sulphuric or hydrochloric acid. Since most river waters of Natal (at least, most of those used as water supplies) have

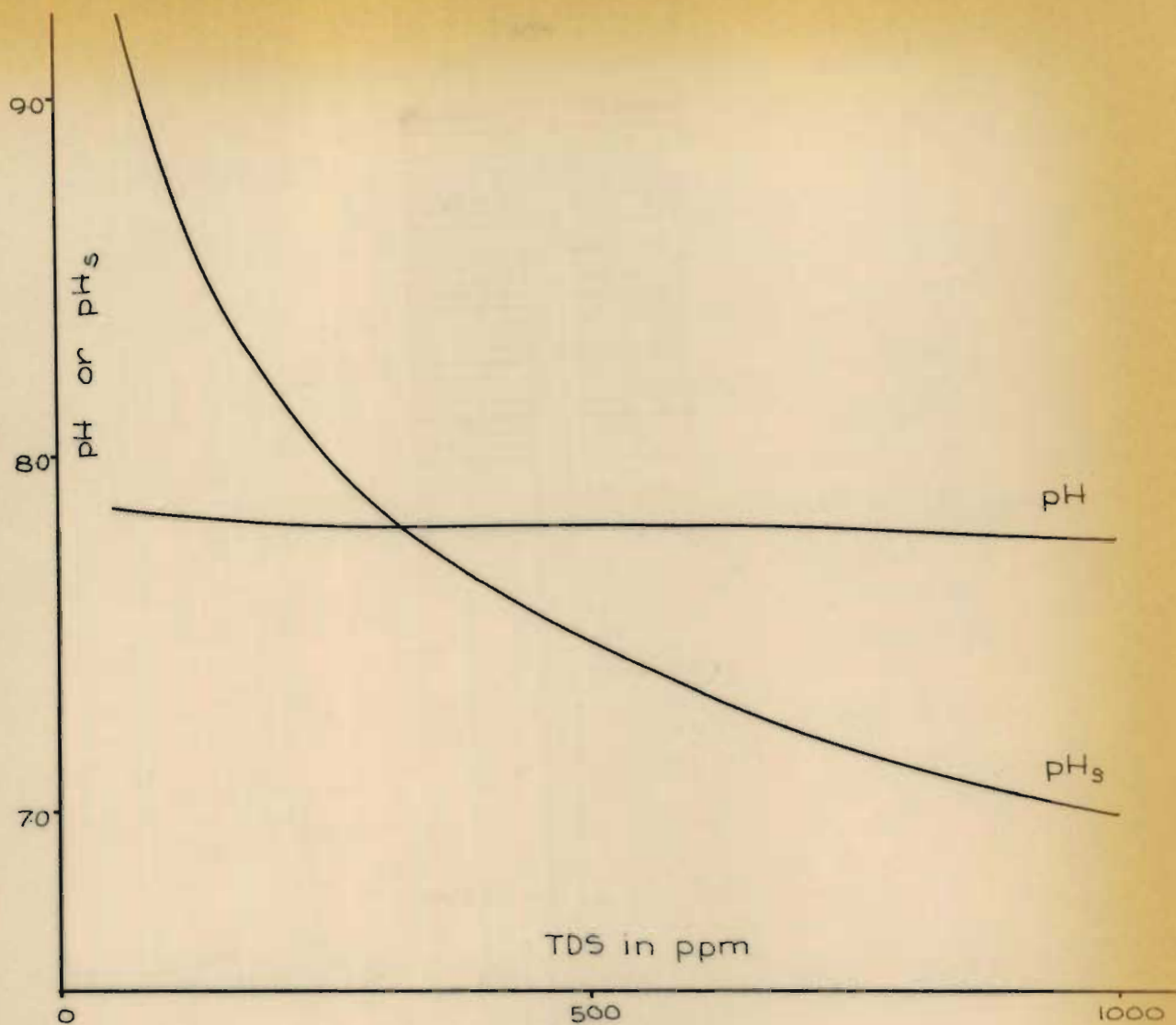


FIGURE 10.1

Variation of pH and pH<sub>s</sub> for average Natal river water

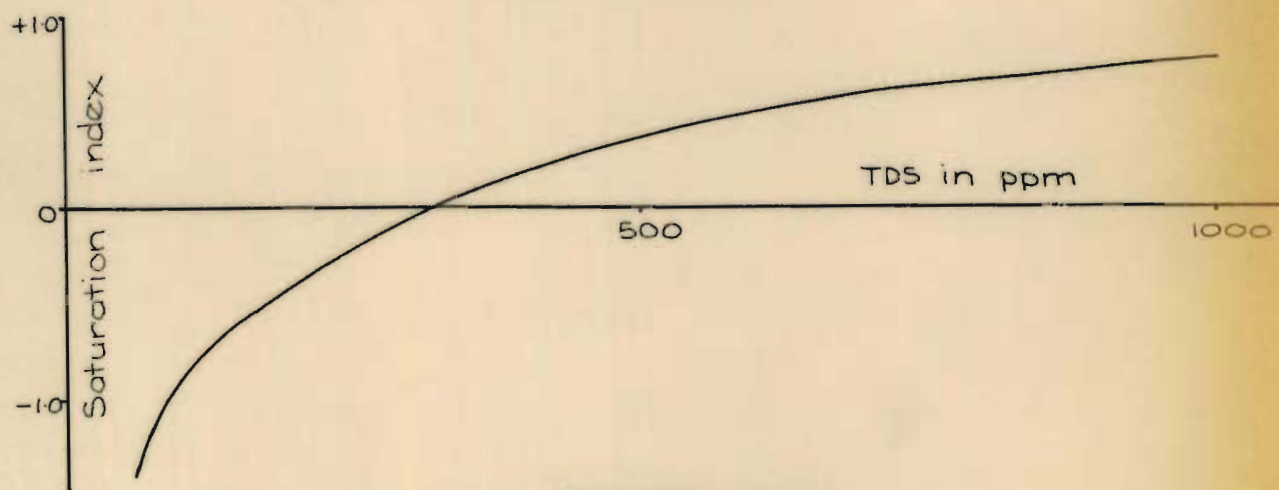


FIGURE 10.2

Variation of saturation index with TDS for average Natal river water



negative saturation indices, as shown by Table 10.1, this problem does not usually arise in this Province.

The more common waters with negative saturation index can similarly be stabilised by any treatment that will raise the pH and/or decrease the  $\text{pH}_s$ . Dosing with bases or soluble carbonates or bicarbonates will have the desired effect, but the most efficient treatment is dosing with lime (calcium hydroxide,  $\text{Ca}(\text{OH})_2$ ) since this increases the pH and lowers the  $\text{pH}_s$  by a double action (increase of alkalinity and of calcium content - see equation (10.13)).

A useful technique (Hoover, 1938; Cox, 1964) in working out a possible treatment is to stir excess powdered calcium carbonate into a sample of the raw water until equilibrium is attained (this normally is a matter of a few minutes, and can be checked by analysis since at equilibrium the pH and  $\text{pH}_s$  must be equal). The required lime dose will be approximately that which is necessary to produce in the raw water the same total alkalinity or the same pH as after the calcium carbonate treatment (the addition of calcium carbonate necessarily changes the total carbonic acid content of the water whilst the addition of lime does not so that the lime dose is only approximated by this technique, but the discrepancy cannot be great unless the lime dose is large). The actual dose can therefore be established by trial or obtained from the simple relation:

$$\text{Lime dose (ppm)} = (A_t - A_r) \times 0.74 \quad (10.18)$$

where  $A_t$  is the alkalinity of the sample after calcium carbonate and  $A_r$  that of the raw water, both expressed as ppm of  $\text{CaCO}_3$ . Where  $A_r$  exceeds  $A_t$  the raw water is scale-forming and can be dosed with sulphuric acid, the approximate dose being obtained in similar fashion:

$$\text{Sulphuric acid dose (ppm)} = (A_r - A_t) \quad (10.19)$$

The theoretical calculation of the lime dose necessary for a water with a negative saturation index is not simple because of the complicated mathematical forms of the equations involved. In outline, it may be accomplished approximately, as follows. Let  $x$  ppm be the amount of lime added. The alkalinity of the treated water then becomes  $(A + 1.35 x)$  ppm  $\text{CaCO}_3$  and the calcium content  $(Ca + 0.541 x)$  ppm, where  $A$  and  $Ca$  are the values in the raw water. On the assumption that the dosing does not materially change the TDS and hence leaves  $\gamma$  at its raw water value, the



$pH_s$  of the treated water can be found from equation (10.13) and the pH value from the non-ideal form of the relevant one of equations (3.49) - (3.51). If these results for various values of  $x$  are plotted, the value of  $x$  for which  $pH = pH_s$  can be found and will be the required lime dose. The value of the pH at this value will be that of the treated water.

When this procedure is applied to the "average Natal river water" discussed above it is found that the pH at which, by treatment with lime, the water is stabilised varies with the TDS as shown in Figure 10.3. Clearly, waters of low TDS are only stabilised at high pH levels.

This gives rise to practical difficulties. Accepted standards for drinking water (World Health Organisation, 1963) specify that the pH value should not exceed 8.5, while Figure 10.3 shows that, in general, a raw water with a TDS less than about 100 ppm cannot be stabilised with lime and meet this standard. Similar calculations show that the use of soda ash instead of lime gives almost identical results. Further, the use of a calcium salt, such as calcium chloride, instead of lime can be shown to require such extremely large doses as to be quite impracticable.

Evidently the difficulty with low TDS water arises from their low buffering power, which means that the pH value becomes raised by the addition of lime or soda ash to a much greater extent than the  $pH_s$  becomes lowered. It is readily shown that, at a TDS of 100 ppm the average Natal river water has a buffer capacity  $\bar{B}$  of 0.10, as has already been mentioned in chapter 9.

There appears to be only one means of stabilising a water of low TDS and yet leaving its pH reasonably low. This is by adding excess lime to bring the  $pH_s$  to below 8.5 and then adding sulphuric acid or gassing with carbon dioxide until the pH is reduced to the same level as the  $pH_s$ . The second stage of this process will cause a small increase in the  $pH_s$ , and this should be allowed for in the initial lime dose. But even this treatment may well fail if the TDS is too low.

The lime dose required to produce a given  $pH_s$  in this lime-acid treatment can be obtained approximately from equation (10.13). Assuming  $\gamma$  to have the average value 0.946, letting  $A$  and  $Ca$  denote their values in the raw water and  $pH_s$  the desired value after adding  $x$  ppm of lime, that equation may be written first as:

$$pH_s = 11.46 - \log (A + 1.35 x) (Ca + 0.541 x) \quad (10.20)$$



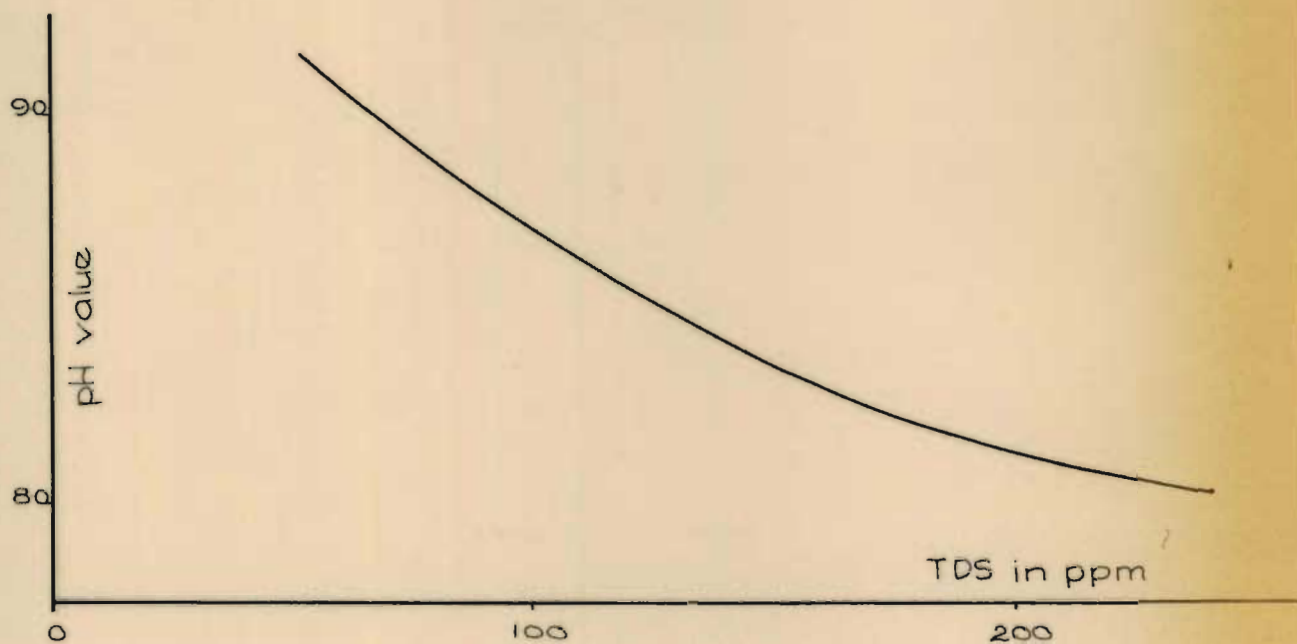


FIGURE 10.3

pH of average Natal river water after  
stabilisation with lime

and then as:

$$(A + 1.35 x) (Ca + 0.541 x) = \text{antilog} (11.46 - pH_s) = X \quad (10.21)$$

This is a simple quadratic in  $x$  whose solution, after introducing some numerical approximations which do not materially affect the result, may be written:

$$x = \sqrt{\left[ \frac{1}{2} (0.5 A + 1.4 Ca)^2 - 1.4 (A Ca - X) \right]} - \frac{2}{3} (0.5 A + 1.4 Ca) \quad (10.22)$$

If sulphuric acid is used in the second stage of the process, the necessary dose may be found by trial or obtained from the calculated (ideal) titration curve of the limed water. A considerable simplification<sup>\*</sup> arises if the final values of  $pH = pH_s$  can be chosen equal to the initial  $pH$  of the raw water. The necessary sulphuric acid dose is then given very closely by:

$$\text{Sulphuric acid dose (ppm)} = 1.35 x \quad (10.23)$$

It should be remembered that most raw waters need treatment to remove suspended solids. This commonly entails flocculation by the addition of aluminium sulphate and lime, and the treatment will always have some effect on the  $pH$  and  $pH_s$ . The "raw water" considered in the design of  $pH_s$  correction treatments should therefore be taken as the water after the addition of the flocculation reagents. Often the two processes, flocculation and  $pH_s$  correction, can be combined into one.

In view of the considerable expense of any form of  $pH_s$  correction, it is clear that the whole subject of  $pH_s$  and corrosivity needs further fundamental investigation in order that its many doubtful aspects can be clarified.

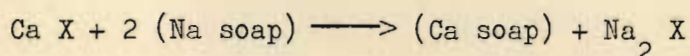
\* Alternatively, if  $pH = pH_s$  is chosen equal to 8.3, the sulphuric acid dose will be that needed to reduce the value of  $\bar{e}$  for the limed water to equal its value of  $\bar{a}$ .



## 11. HARDNESS

### Terminology

Historically, the hardness of a water was a parameter designed to measure the soap-destroying powers of the water and was early shown to be related to the calcium and magnesium concentrations. It is a matter of elementary chemistry that dissolved calcium and magnesium salts react with the soluble sodium (or potassium) compounds that constitute soap to form insoluble substances by a simple process of double decomposition:



and the detergent powers of the soap are not manifest until such reactions have first removed most of the dissolved calcium and magnesium salts.

Total hardness may therefore be unambiguously defined as the sum of the calcium and magnesium concentrations in the water, expressed in any convenient units.

Metals such as iron, aluminium, manganese, strontium and zinc can also give rise to the precipitation of soap, but these do not usually occur in appreciable concentrations in natural waters and so need not be considered here.

Heating any water where  $0 < e < 2a$  expels carbonic acid, converts dissolved bicarbonates to carbonates and causes the pH to rise. Some or all of the total hardness may thereby be caused to precipitate as a sludge or scale of insoluble calcium and magnesium compounds. The total hardness will thus be reduced, and that part of it which is so removable by heating is termed the temporary hardness. The remainder, which is not removable in this way, is termed the permanent hardness.

Confining our attention to dissolved calcium and magnesium only, if the total hardness in equivalents per litre is denoted by  $i$  it is clear that:

$$i = 2 (c + m) \tag{11.1}$$

In practical units the total hardness is usually expressed as ppm of  $\text{CaCO}_3$ . If  $I$  is the total hardness in these units, then:

$$I = 10^5 (c + m) = 100 (\bar{c} + \bar{m}) \tag{11.2}$$

Since the total alkalinity of the water in equivalents per litre is

defined by (3.42) as:

$$e = 2c + 2m + n + p - 2s - h \quad (11.3)$$

we can write:

$$e = i + z \quad (11.4)$$

where  $z$  is defined as:

$$z = n + p - 2s - h \quad (11.5)$$

The quantity  $z$  may be termed the soda alkalinity of the water. In practical units of ppm  $\text{CaCO}_3$  its value will be:

$$Z = A - I \quad (11.6)$$

Clearly two distinct possibilities arise:

(a)  $z > 0$

The soda alkalinity will be a true net alkalinity, and in an ordinary water containing carbonic acid it will be stoichiometrically combined to form bicarbonates or carbonates. When carbonic acid is driven off from such a water, the bicarbonates will be converted to carbonates and the pH raised so that calcium and magnesium compounds may be precipitated. The precipitation will not necessarily be complete because of the small but definite solubilities of the precipitated substances, e.g. Taylor (1958) states that, on an average, about 20 ppm of the total hardness expressed as  $\text{CaCO}_3$  remains in solution. Conversely, if the initial calcium and magnesium concentrations are less than these values, no precipitation can occur at all. In general, then, waters of this type will have temporary hardness and a small permanent hardness, but there will be some instances (mainly waters of low TDS) where the hardness must be counted as wholly permanent.

(b)  $z < 0$

The soda alkalinity now has a negative value and is strictly a net acidity. Any calcium and magnesium that are present will therefore be combined partly with this net acidity as sulphates and chlorides, and partly with the carbonic acid as bicarbonates and carbonates. It is therefore possible to distinguish between non-carbonic hardness and carbonic hardness. The former will be equal to  $-z$  equivalents per litre or  $(I - A)$  ppm of  $\text{CaCO}_3$ , the latter will be equal to



$i + z = e$  equivalents per litre or A ppm of  $\text{CaCO}_3$  (for a water where  $z > 0$ , the total hardness will be wholly of the carbonic type and the non-carbonic hardness will be zero). A water with  $z < 0$  will also increase in pH when carbonic acid is removed from it, and the precipitation of calcium and magnesium compounds may therefore occur just as in the previous case, i.e. the water will usually show temporary hardness and will always show permanent hardness. However, the proportion of combined carbonic acid in this water is necessarily less, relative to the total hardness. It would therefore be expected that the loss of carbonic acid would not have such extensive consequences, i.e. the water of this type would in general have a greater permanent hardness.

What we have above termed the "carbonic hardness" is referred to by other authors, e.g. Nordell (1951), as the "bicarbonate" or "carbonate" hardness, or even the "temporary" hardness. Similarly what we have termed the "non-carbonic hardness" is alternatively termed the "non-carbonate" or even "permanent" hardness. The terms "bicarbonate", "carbonate" and "non-carbonate" are confusing when so used, while it is clear that to define "temporary" and "permanent" hardness in this way bears no relation to the original meaning of these terms. In the present work, for the sake of logic and consistency, we shall adhere to the original meanings of temporary and permanent hardness and use the additional names as we have introduced them above, viz:

soda alkalinity	$z = e - i$ or $Z = A - I$
carbonic hardness	$i$ or $I$ provided $z > 0$ ; otherwise the balance of the hardness
non-carbonic hardness	$-z = i - e$ or $-Z = I - A$ provided $z < 0$ ; otherwise zero.

#### Determination of temporary hardness

The analytical procedure for the determination of temporary hardness (see Vogel, 1951) is simple in principle. A sample of the water is boiled, taking care to minimise evaporation losses, allowed to cool, and filtered. The total hardness of the filtrate is then determined, e.g. by versenate titration. The result is the permanent hardness of the water. The temporary hardness is then found by subtracting this value from the separately determined total hardness of the original water.



The procedure is liable to many errors, arising for example from evaporation losses, uptake of carbon dioxide during cooling and lack of equilibrium between the solid and aqueous phases at the time of filtration. Also it seems doubtful whether the results can have much direct practical application since the physical conditions of the determination are not very closely related to those of practical water engineering, e.g. the conditions within a domestic water heater where the possible deposition of scale could present problems of major importance. Filtering the boiled sample while hot would give rather different analytical results and would be more closely relevant to many practical applications, although it would probably introduce additional experimental errors.

It seems to be because of objections of this kind that the analytical determination of temporary hardness, according to its original definition, is largely omitted nowadays as a routine procedure.

#### Calculation of the temporary and permanent hardnesses

To attempt the theoretical calculation of the temporary and permanent hardnesses of a water, as defined above, is an extremely difficult task which, as far as is known, has not been attempted hitherto.

The fact that the analytical determination of temporary hardness involves the cold filtration of the boiled water sample means that, for purposes of calculation, we need only know the values of the various dissociation and solubility constants at room temperature. Otherwise, in the absence of knowledge of their values near the boiling point, calculation would not be possible.

Although the water is boiled during the experimental procedure, this serves only to remove excess carbonic acid. In a theoretical treatment we may picture the removal as proceeding at room temperature, i.e. we merely suppose the concentration  $a$  to decrease progressively until bicarbonates are converted to carbonates so that  $a = \frac{1}{2} e$ . The pH is thereby increased.

The hydrion concentration at  $a = \frac{1}{2} e$  is given ideally by equation (3.52) provided the calcium and magnesium concentrations are not appreciable. This condition is most probably not satisfied closely enough for the application we are now attempting and for accurate results we should therefore use, not (3.52) which is itself a special solution of (3.41), but a form of the more general equation (3.40). This, however, is too cumbersome for easy manipulation and we have no choice



but to use (3.52). Our treatment cannot therefore be very accurate, but it should certainly provide a correct qualitative picture of the hardness properties of ordinary waters.

Since the results will not be quantitatively exact, we may further simplify matters by assuming ideal conditions ( $\gamma = 1.000$ ).

When  $a = \frac{1}{2} e$ , the water may deposit magnesium and calcium hydroxides and carbonates, provided certain conditions are fulfilled. These conditions arise from the solubility product relations (6.18), (6.24), (6.25) and (6.30) and, by the use of (3.25) and (3.24), may be written:

$$\text{for Mg(OH)}_2 \quad m > \frac{k_m H (k_w + K_m H)}{k_w^2 K_m} \quad (11.7)$$

$$\text{for Ca(OH)}_2 \quad c > \frac{k_c H (k_w + K_c H)}{k_w^2 K_c} \quad (11.8)$$

$$\text{for MgCO}_3 \quad m > \frac{k_{ma} (k_w + K_m H) (H^2 + K_1 H + K_1 K_2)}{a K_1 K_2 K_m H} \quad (11.9)$$

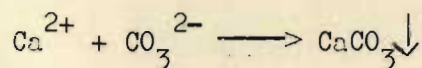
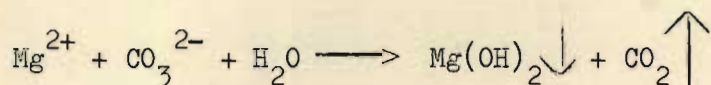
$$\text{for CaCO}_3 \quad c > \frac{k_{ca} (k_w + K_c H) (H^2 + K_1 H + K_1 K_2)}{a K_1 K_2 K_c H} \quad (11.10)$$

The calculated limiting values which must be exceeded before these compounds precipitate are therefore as shown in Table 11.1 for various values of  $a$ . From these results it may be deduced that magnesium hydroxide will be precipitated from most waters, calcium hydroxide will not usually be precipitated, magnesium carbonate may be precipitated from waters of very high TDS (above about 2000 ppm) and calcium carbonate will be precipitated from most waters.

Hence, if we consider normal surface waters with TDS below 2000 ppm, we need only be concerned with the precipitation of magnesium hydroxide and calcium carbonate.

We therefore suppose that such a water is changed in composition in two stages. First, carbonic acid is removed until  $a = \frac{1}{2} e$ . Second, the precipitation of magnesium hydroxide and/or calcium carbonate occurs until equilibrium is established. In this second stage, each mole of

precipitate that is formed corresponds to one additional mole of carbonic acid becoming lost, either to the atmosphere as carbon dioxide or to the solid phase in chemical combination:



At the same time there is a corresponding decrease in the total alkalinity, so that the condition  $a = \frac{1}{2} e$  is always maintained during this stage of the process. As precipitation occurs the pH must fall, consequent upon the simultaneous decrease in  $a$ , as shown in Table 11.1, and this will continue until the equilibrium values of  $m$  and  $c$  are reached. The whole process will then stop.

Table 11.1

Limiting values of  $m$  and  $c$  at  
various values of  $a$

$a$	pH	$m$ for $\text{Mg}(\text{OH})_2$	$c$ for $\text{Ca}(\text{OH})_2$	$m$ for $\text{MgCO}_3$	$c$ for $\text{CaCO}_3$
$10^{-2}$	11.13	$1.13 \times 10^{-5}$	3.03	$2.87 \times 10^{-3}$	$6.20 \times 10^{-7}$
$10^{-3}$	10.56	$1.17 \times 10^{-4}$	$4.05 \times 10$	$2.94 \times 10^{-2}$	$8.23 \times 10^{-5}$
$10^{-4}$	9.87	$2.58 \times 10^{-3}$	$9.62 \times 10^2$	$6.50 \times 10^{-1}$	$2.00 \times 10^{-4}$
$10^{-5}$	8.98	$1.50 \times 10^{-1}$	$5.78 \times 10^4$	$3.81 \times 10$	$1.20 \times 10^{-2}$
$10^{-6}$	8.00	$1.33 \times 10$	$5.26 \times 10^6$	$3.52 \times 10^3$	1.11

Three cases in general are possible:

- (a) Both  $\text{Mg}(\text{OH})_2$  and  $\text{CaCO}_3$  are precipitated

Let  $e'$  be the final alkalinity of the water. The final concentration of total carbonic acid is then  $a' = \frac{1}{2} e'$  and the final concentration of hydrions is given by equation (3.52). The final magnesium and calcium concentrations are then, from (11.7) and (11.10):

$$m' = \frac{k_m H (k_w + K_m H)}{k_w^2 K_m} \quad (11.11)$$

$$c' = \frac{2 k_{ca} (k_w + K_c H) (H^2 + K_1 H + K_1 K_2)}{e' K_1 K_2 K_c H} \quad (11.12)$$



These relations yield the values shown in Table 11.2 over the range of  $e'$  of greatest interest.

Table 11.2  
Equilibrium concentrations as functions of  $e'$

$e'$	$m'$	$c'$	H	pH
$10^{-2}$	$2.14 \times 10^{-5}$	$1.30 \times 10^{-6}$	$1.08 \times 10^{-11}$	10.97
$8 \times 10^{-3}$	$2.66 \times 10^{-5}$	$1.66 \times 10^{-6}$	$1.22 \times 10^{-11}$	10.91
$6 \times 10^{-3}$	$3.55 \times 10^{-5}$	$2.25 \times 10^{-6}$	$1.44 \times 10^{-11}$	10.84
$4 \times 10^{-3}$	$5.40 \times 10^{-5}$	$3.61 \times 10^{-6}$	$1.81 \times 10^{-11}$	10.74
$2 \times 10^{-3}$	$1.16 \times 10^{-4}$	$8.21 \times 10^{-6}$	$2.74 \times 10^{-11}$	10.56
$10^{-3}$	$2.67 \times 10^{-4}$	$1.98 \times 10^{-5}$	$4.25 \times 10^{-11}$	10.37
$8 \times 10^{-4}$	$3.55 \times 10^{-4}$	$2.64 \times 10^{-5}$	$4.93 \times 10^{-11}$	10.31
$6 \times 10^{-4}$	$5.19 \times 10^{-4}$	$3.91 \times 10^{-5}$	$6.00 \times 10^{-11}$	10.22
$4 \times 10^{-4}$	$9.14 \times 10^{-4}$	$6.96 \times 10^{-5}$	$8.01 \times 10^{-11}$	10.10
$2 \times 10^{-4}$	$2.57 \times 10^{-3}$	$2.00 \times 10^{-4}$	$1.36 \times 10^{-10}$	9.87
$10^{-4}$	$8.01 \times 10^{-3}$	$6.31 \times 10^{-4}$	$2.41 \times 10^{-10}$	9.62

In this range, it is found that  $\log m'$ ,  $\log c'$  and  $\log H$  can be represented very closely as linear functions of  $\log e'$ , thus:

$$\log m' = - 7.5667 - \frac{4}{3} \log e' \quad (11.13)$$

$$\log c' = - 8.5499 - \frac{4}{3} \log e' \quad (11.14)$$

$$\log H = - 12.4539 - \frac{2}{3} \log e' \quad (11.15)$$

By subtraction, it is readily found from these relations that:

$$m' = 9.62 c' \quad (11.16)$$

From (11.3) and (11.5):

$$e' = 2 c' + 2 m' + z \quad (11.17)$$

where  $z$  is the soda alkalinity, positive or negative and the same in the final as in the initial state. Inserting (11.16):

$$e' = 21.2 c' + z \quad (11.18)$$

and on substituting this in (11.14) we obtain:

$$\log c' = - 8.5499 - \frac{4}{3} \log (21.2 c' + z) \quad (11.19)$$

which, in terms of millimolar units, may be written:

$$\log \bar{c}' = -1.5499 - \frac{4}{3} \log (21.2 \bar{c}' + \bar{z}) \quad (11.20)$$

Values of  $\bar{c}'$  which satisfy this for various values of  $\bar{z}$  (found by a graphical solution) are as in Table 11.3. By plotting these values of  $\bar{c}'$  against  $\bar{z}$  as independent variable, the value of  $\bar{c}'$  for any particular case can be read off and the corresponding value of  $\bar{m}'$  may be found from (11.16) in the form:

$$\bar{m}' = 9.62 \bar{c}' \quad (11.21)$$

The permanent hardness of the water will thus be, in milliequivalents per litre:

$$\bar{p}_h = \bar{c}' + \bar{m}' = 10.62 \bar{c}' \quad (11.22)$$

or, in ppm of  $\text{CaCO}_3$ :

$$P_h = 1062 \bar{c}' \quad (11.23)$$

and the temporary hardness, as ppm of  $\text{CaCO}_3$  will be:

$$T_h = I - P_h \quad (11.24)$$

(b) Only  $\text{CaCO}_3$  is precipitated

When the working for the previous case (a) is applied to a water which precipitates calcium carbonate but not magnesium hydroxide, it necessarily ensues that the value calculated for  $\bar{m}'$  exceeds the value of  $\bar{m}$  in the original water. In such a case the final alkalinity of the water must be, not that given by (11.17), but rather:

$$e' = 2 c' + 2 m + z \quad (11.25)$$

Equation (11.19) must therefore now be replaced by:

$$\log c' = -8.5499 - \frac{4}{3} \log (2c' + 2m + z) \quad (11.26)$$

which may be written:

$$\log \bar{c}' = -1.5499 - \frac{4}{3} \log (2 \bar{c}' + 2 \bar{m} + \bar{z}) \quad (11.27)$$

Values of  $\bar{c}'$  which satisfy this for various values of  $(2 \bar{m} + \bar{z})$ , again obtained by graphical solution, are as in Table 11.4, and a plot of these against  $(2 \bar{m} + \bar{z})$  may be used to find the value of  $\bar{c}'$  in any given case.



The permanent hardness, in ppm of  $\text{CaCO}_3$  will now be:

$$P_h = 100 (\bar{c}' + \bar{m}) \quad (11.28)$$

and the temporary hardness is obtainable as before from (11.24).

Table 11.3

Solutions of equation (11.20)

$\bar{z}$	$\bar{c}'$
+ 2.0	0.0098
+ 1.0	0.0183
0.0	0.0380
- 1.0	0.0700
- 2.0	0.1112

Table 11.4

Solutions of equation (11.27)

$(2 \bar{m} + \bar{z})$	$\bar{c}'$
+ 2.0	0.0105
+ 1.0	0.0258
0.0	0.1458
- 1.0	0.5530
- 2.0	1.0338

(c) No precipitation

In this case, not only will  $\bar{m}'$  as calculated in (a) exceed  $\bar{m}$ , but also  $\bar{c}'$  as calculated in (b) will exceed  $\bar{c}$ . The permanent hardness is now equal to the total hardness and there is no temporary hardness.

Hardness in Natal rivers

It is convenient at this stage to consider the hardnesses of the Natal rivers of Table 2.1. Out of these 22 rivers, 3 have non-carbonic hardness (Nungwana, Umhlanga and Isipingo) and 4 have no temporary hardness (Sterk, Karkloof, Nungwana and Gogoshi), as shown by the calculated results given in Table 11.5 which are obtained by the procedure described

Table 11.5

Results of hardness calculations for the rivers of Table 2.1

R i v e r	TDS, in ppm	ppm of $\text{CaCO}_3$					Substance precipitated		I as % of TDS	$T_h$ as % of I	Final pH
		Total alkalinity* A	Total hardness I	Soda alkalinity Z	Permanent hardness $P_h$	Temporary hardness $T_h$	$\text{CaCO}_3$	$\text{Mg(OH)}_2$			
Sterk	41	23	17	6	17	0	-	-	42	0	10.23
Illovo	41	28	21	7	17	4	+	-	51	19	10.24
Mooi	42	20	20	0	19	1	+	-	48	5	10.17
Karkloof	42	24	16	8	16	0	-	-	38	0	10.24
Ingagane	49	33	21	12	16	5	+	-	43	24	10.28
Lions	59	41	31	10	22	9	+	-	53	29	10.32
Nungwana	60	17	20	- 3	20	0	-	-	33	0	10.14
Ungeni	69	36	29	7	21	8	+	-	42	28	10.28
Umgegu	77	44	30	14	22	8	+	-	39	27	10.36
White Umfolozi	78	44	37	7	21	16	+	-	47	43	10.28
Lenjane's	81	63	55	8	29	26	+	-	68	47	10.37
Tugela	85	69	57	12	29	28	+	-	67	49	10.40
Sundays	95	77	58	19	32	26	+	+	61	45	10.46
Gogoshi	108	14	10	4	10	0	-	-	93	0	10.08
Umvoti	116	64	47	17	26	21	+	-	41	45	10.41
Umfolozi	136	99	74	25	29	45	+	+	54	61	10.47
Unzinkulwana	143	71	69	2	39	30	+	+	48	44	10.40
Bloukrans	191	168	133	35	25	108	+	+	70	81	10.51
Umhlanga	213	71	76	- 5	43	33	+	+	36	43	10.37
Umzinyatshana	232	188	153	35	25	128	+	+	66	84	10.51
Isipingo	320	66	99	-33	60	39	+	+	31	39	10.27
Mpushini	332	173	157	16	33	124	+	+	47	79	10.45

\* Accords with the value of  $\bar{e}$  in Table 8.3.



above. The absence of temporary hardness from the Gogoshi is clearly due to its anomalous chemical composition, most of its TDS comprising sodium chloride; in the other instances it is a result of the low TDS. The fallacy involved in taking the non-carbonic hardness (zero except in the three named cases) as representing the permanent hardness is clearly shown by the tabulated data.

The total hardnesses range from 10 to 157 ppm as  $\text{CaCO}_3$  or from 31 to 93% of the TDS, but in no systematic manner. No water with TDS less than 95 ppm shows temporary hardness due to the precipitation of magnesium hydroxide, and no water with TDS less than this shows a temporary hardness exceeding 28 ppm as  $\text{CaCO}_3$  or 49% of the total hardness. At higher levels of TDS, however, temporary hardnesses up to 84% of the total hardness occur, although it is notable that the two rivers in this TDS range with non-carbonic hardness (Umhlanga and Isipingo) each have a temporary hardness of only 30 - 40% of the total, i.e. much lower than the other rivers of about the same TDS.

A classification of waters according to total hardness has been given by the British Ministry of Health and is quoted by Klein (1957):

<u>Total hardness as</u> <u>ppm <math>\text{CaCO}_3</math></u>	<u>Description</u>
0 - 50	Soft
50 - 100	Moderately soft
100 - 150	Slightly hard
150 - 200	Moderately hard
200 - 300	Hard
> 300	Very hard

The waters of Table 11.5 mostly fall in the soft to slightly hard groups.

Taking these rivers as representative of Natal rivers in general, it therefore appears that we can divide their waters into two main groups:

- (a) those with TDS below about 100 ppm, which usually are soft to moderately soft, do not have temporary hardness due to magnesium hydroxide and whose temporary hardnesses never exceed 50% of the total hardness or 30 ppm as  $\text{CaCO}_3$ ; often the temporary hardness in this group is zero.
- (b) those with TDS above 100 ppm, which are usually slightly to very hard, may show temporary hardnesses exceeding 50% of the total (unless

they possess non-carbonic hardness) and usually have temporary hardness due to both calcium carbonate and magnesium hydroxide.

It is interesting that the 100 ppm limit for TDS is the same value that we have suggested as "critical" in relation to buffer capacity (chapter 9) and anti-corrosion water treatment (chapter 10).

For any water, the pH value after precipitation of the temporary hardness by removal of carbonic acid is given approximately by equation (11.15) in the form:

$$\text{pH} = 9.32 + \frac{2}{3} \log A' \quad (11.29)$$

where  $A'$  is the final alkalinity in ppm of  $\text{CaCO}_3$  and is equal to  $(Z + P_h)$ . For the 22 Natal rivers these final pH values are shown in the last column of Table 11.5 and range from about 10.1 to 10.5, but experience shows that they are not reliable, being 1 - 2 units too high.

#### Errors of the calculations

Errors in the theoretical treatment given above arise from two sources: (a) the assumption of ideality and (b) the use of a form of equation (3.41) probably outside its pH range of applicability. It is virtually impossible to estimate quantitatively the effects of these two, except to say that (b) cannot be very important since the coefficients of  $c$  and  $m$  in the most general equation (3.40) do not depart greatly from 2.00 except at relatively high pH values.

In Appendix D are given some results which show that the ideal calculations are fairly well confirmed by actual experiment. Discrepancies appear to arise, however, for waters of very high magnesium content (50 ppm and more). Since such waters are not common, in Natal at least, whenever the TDS is reasonably low, it therefore appears that the calculations can satisfactorily be applied to most waters which have any potential domestic or industrial use, i.e. to most waters for which the calculations are ever likely to be of importance.

#### Variation of hardness with TDS

It is clear that a water can show no temporary hardness if its TDS is too low, since the calcium and magnesium concentrations will be less than their equilibrium values at  $a = \frac{1}{2} e$  and no precipitation will ensue. It is also clear, since the molar equilibrium concentration of magnesium is about ten times that of calcium although the molar magnesium



and calcium concentrations in most surface waters are of the same order of magnitude (see Table 2.1), that the deposition of temporary hardness always involves the precipitation of calcium carbonate but only that of magnesium hydroxide if the TDS of the water is sufficiently great.

If a water is supposed to increase steadily in TDS through simple concentration, without any other change of chemical composition, the variation of the temporary and permanent hardnesses will show some interesting features. There are three cases to consider:

(a)  $Z = 0$

In this case the data of Table 11.3 show that, once the TDS is sufficiently high for both calcium carbonate and magnesium hydroxide to precipitate together, the permanent hardness remains constant at 38 ppm of  $\text{CaCO}_3$ . This behaviour is shown schematically in Figure 11.1(a).. The temporary hardness, at increasing TDS, approaches 100% of the total hardness, but can never actually attain this level because of the persisting 38 ppm of permanent hardness.

(b)  $Z > 0$

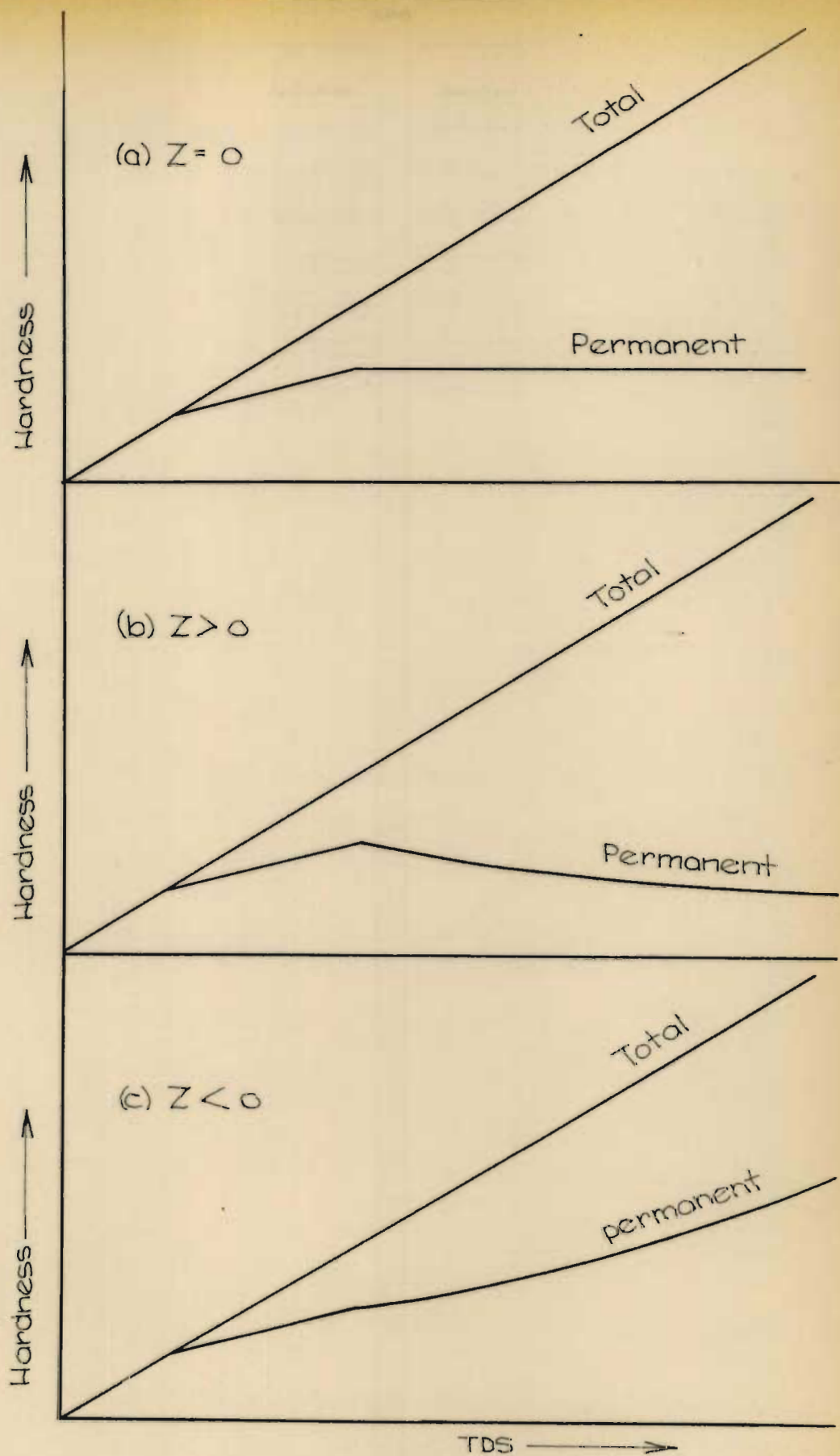
Here, once the TDS is sufficiently high, the permanent hardness decreases as the TDS increases, as in Figure 11.1(b). The temporary hardness, as a percentage of the total, therefore climbs more rapidly than in the preceeding case as the TDS continues to rise and earlier approaches more closely to the 100% level.

(c)  $Z < 0$

The permanent hardness now increases as the TDS increases, as in Figure 11.1(c). As a percentage of the total, the temporary hardness rises very slowly with increasing TDS (it may even show a maximum under certain circumstances) and eventually tends to a limit well below 100%.

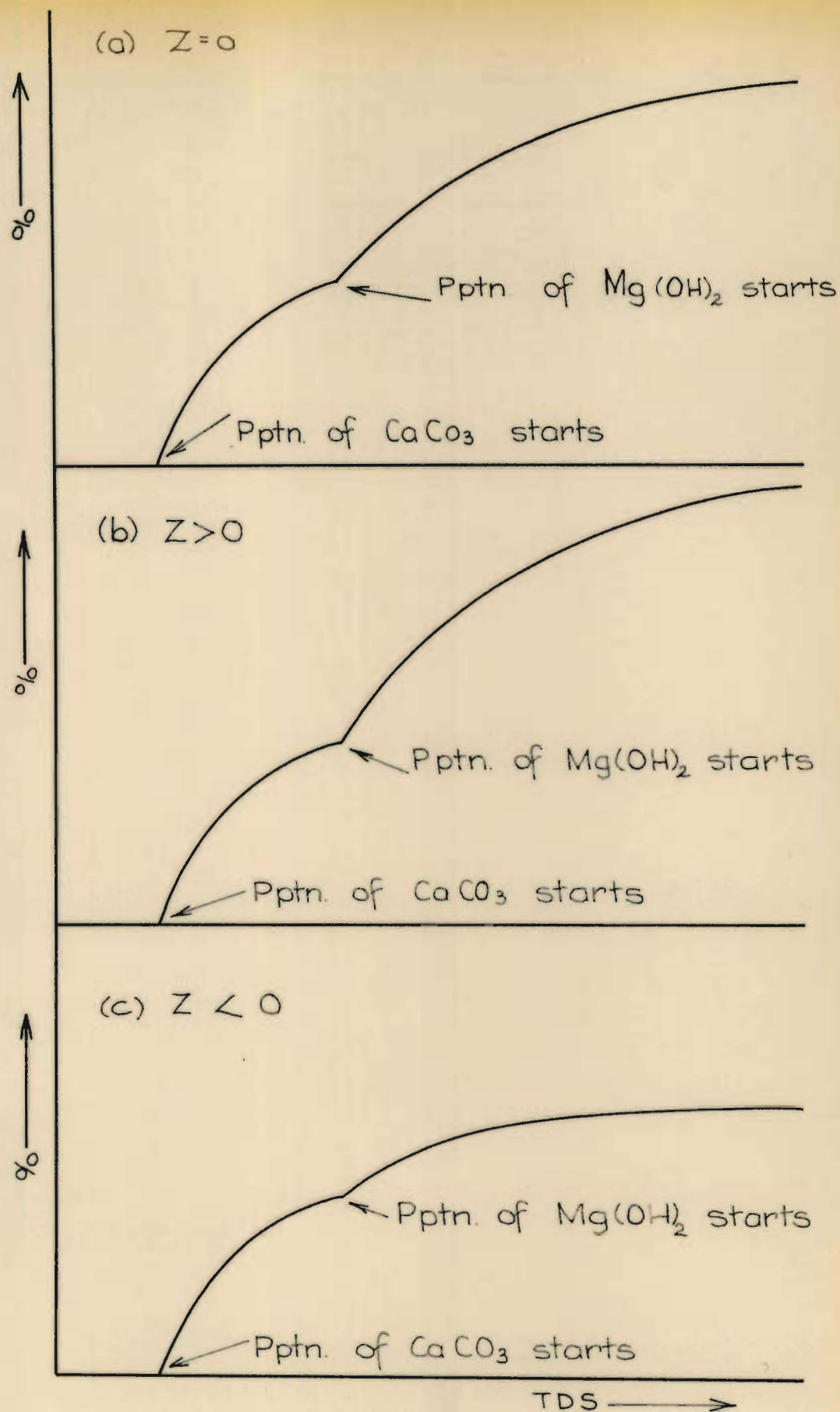
Figure 11.2 shows the three corresponding forms of the variation with TDS of the temporary hardness as percent of the total. Note that in each case there is a range of TDS where the temporary hardness is zero, then a range over which only calcium carbonate is precipitated. Each curve then shows a discontinuity and continues with a different gradient as magnesium hydroxide commences to deposit as well.

The anomalous characteristics of the waters of the Umhlanga and Isipingo rivers, noted above, are now understandable as a consequence of their possessing non-carbonic hardness (case (c),  $Z < 0$ ).



Variation of FIGURE 11.1 hardness with TDS



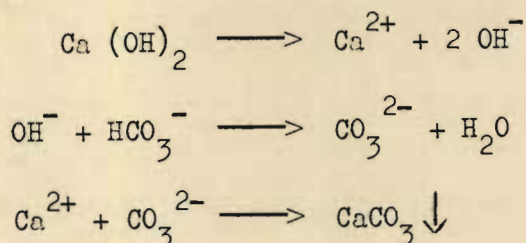


**FIGURE 11.2**

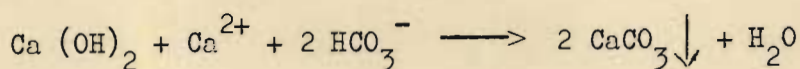
Temporary hardness as percent of total hardness

Note on the cold lime-soda process

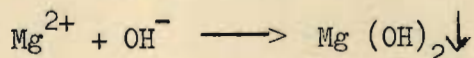
One extensively used method of water softening which depends upon the above theoretical principles (although textbooks often give a quite inadequate theoretical explanation) is the cold lime-soda process. This consists of the addition of lime (calcium hydroxide) to the water being treated so that the pH is raised and the following reactions are induced:



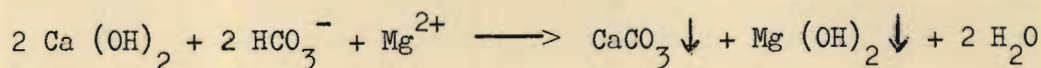
The net result of these is:



so that most of the calcium already present as well as all that added in the lime can usually be precipitated. Addition of still more lime then causes the pH to rise still further until the additional reaction:



is also induced. The net result of all four induced reactions is then:



so that most of the original magnesium may now be removed without increase of the calcium content. The addition of lime thus results in a decrease of the total hardness.

When sufficient lime has been added, dosing with soda ash (sodium carbonate) may follow, if considered necessary. This supplies further carbonate ions so that a further precipitation of calcium carbonate may result.

The final product is a clear water with a reduced total hardness (silt, organic matter, iron and manganese also being removed, as well as many bacteria) and a pH of anything up to about 11 (which can later be reduced if necessary by carbonation). In principle the doses required and the composition of the treated water can be calculated approximately by theoretical methods similar to those used above for hardness calculations, but in practice the process is prone to involve delayed or partial



precipitation so that an empirical approach is always necessary.

Details of the technology of the process have been given by Nordell (1951), Taylor (1958) and the American Water Works Association (1951) among others, including consideration of various after-treatment processes designed to correct the final high pH and to prevent the slow subsequent formation of precipitates from supersaturated solutions. It appears that, by using a lime dose chemically equivalent to about  $1\frac{1}{2}$  times the carbonic hardness (i.e. 106 ppm of lime per 100 ppm of carbonic hardness as  $\text{CaCO}_3$ ), this form of hardness may be reduced to about 30 ppm as  $\text{CaCO}_3$ . About 10% of the magnesium will be precipitated, the rest of the reduction being due to precipitation of calcium carbonate. By using a soda ash dose chemically equivalent to about half the non-carbonic hardness (i.e. 53 ppm of soda ash per 100 ppm of non-carbonic hardness as  $\text{CaCO}_3$ ), this form of hardness may also be appreciably reduced. These are empirical findings which must be experimentally checked in every case, and it must be borne in mind that results obtained on the works scale may, because of supersaturation and delayed precipitation, be quite different from those obtained in the laboratory.

PART III     RIVERS OF NATAL

12.     THE PHYSIOGRAPHY OF RIVERS

Physiographic zonation

The course of any river is mainly controlled by the topography of the country over which it flows, since it will usually follow the path of steepest descent from its source to the sea (the exceptions to this comprise those cases where the course was initiated by an ancient topography which has subsequently changed). However, as soon as it starts to flow the river commences to erode the soil or rock over which it passes, rapidly cutting a bed or channel for itself and, in the course of geological time, even causing marked alterations in the topography of its catchment area. The moving water carries with it a certain amount of solid matter, either small rock particles in suspension or larger bodies (sand grains, pebbles or even boulders) which it rolls along the river bed. Where the water runs rapidly, the load of solid material that it transports is large and acts as a rasp to erode the bed still more. Where the water runs slowly the load of solids is small and instead of erosion there is a deposition of the surplus solid matter which the water can no longer carry, so that pebble beds, sand banks, etc. are built up.

Usually the source of the river lies in mountainous or hilly country where the topography is one of steep slopes. Though streams here may not be large in size, the current speeds are great so that erosion proceeds apace.

Often, before reaching the sea, the river flows across a coastal plain of almost level country. Here, though the river may be of major size, its current speed will be low so that much solid material is deposited and that in such a way as to divert the water and cause it to meander in a slowly changing course across a flat flood plain.

The curve which results when the distance of each point along the course of the river from its source is plotted against altitude is the profile of the river, and the river is said to be of a certain age according to the characteristics of its profile.

The profile of a typical mature river is shown in Figure 12.1. It is convenient to divide this into four zones, each of which has different



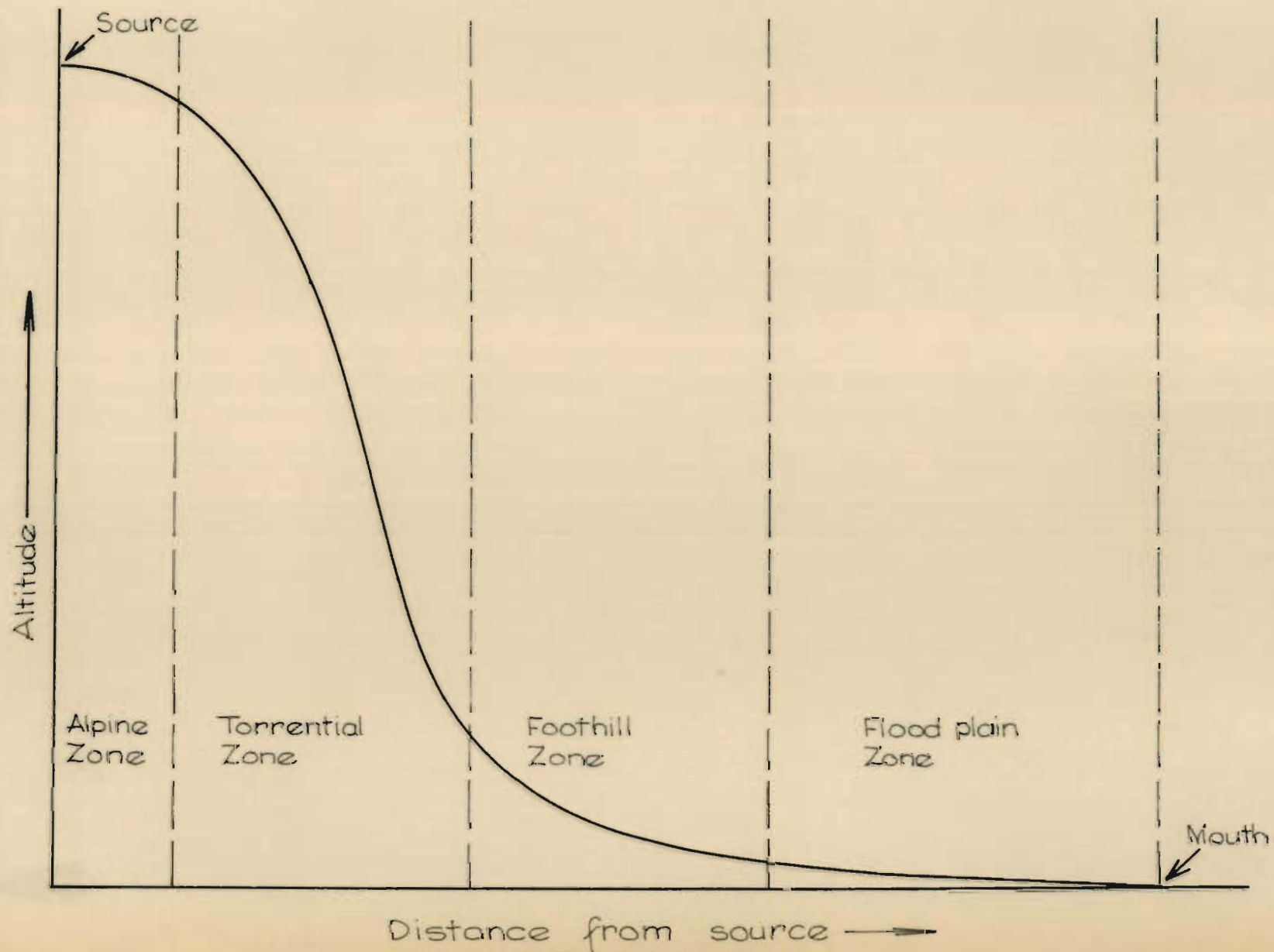


FIGURE 12.1

Typical profile of a mature river

physiographic characteristics from the others. Close to the source is the alpine zone or region of mountain streams, and this is followed by the torrential zone or region of most rapid descent. Erosion occurs predominantly in these zones. As the descent becomes less rapid the foothill zone occurs and here, where the current speed is less, there is a balance between erosion and deposition. Following this comes the floodplain zone, the region of slowest descent where the water is no longer confined between banks and deposition occurs predominantly. The lowest reaches of this zone, where the water level rises and falls with the tide and where the freshwater of the river becomes mixed with the salt water of the sea, constitute the estuary.

With a young river, the floodplain and perhaps the foothill zone is missing and over the whole course erosion proceeds rapidly. As the river comes to maturity a floodplain zone develops and grows, and as it passes into old age the alpine and then the torrential zone becomes smaller and disappears as erosion scours away the mountains and levels the topography.

Differential movements of the sea and land surfaces in geological time can cause changes in the profile so that an old river can become rejuvenated or a young one prematurely aged. Again, a river may show a repetition of some of its zones, e.g. the foothill zone may lie on an elevated plateau and hence be followed by another torrential zone as the water runs over the edge of the plateau.

The zonation of a river is usually regarded as of particular importance to the hydrobiologist since differences of altitude (hence of temperature), current speed, load of solids and nature of the river bed presumably markedly influence the flora and fauna of the water so that the species inhabiting one zone are quite different from those found in another. However, results obtained by Schoonbee (1964) during a hydrobiological study of the Umgeni river have suggested that these effects are sometimes not so pronounced as is often supposed.

River zonation in Natal is usually more complex than elsewhere. The Province is bounded inland by the Drakensberg escarpment, and from there the ground falls away to the coast in a series of erosion terraces. Most of the rivers that reach the sea course through narrow gorge-like valleys cut into rugged country in their lower portions, although higher up they flow with low gradient over open rolling country and there show ox-bows and meanders. This is a consequence of the Natal Monocline, an



extensive downwards flexure towards the coast of the otherwise almost horizontally bedded rock strata, along an axis running roughly parallel to the coast (King, 1951). The rivers have thus been rejuvenated - the floodplain zones are not extensive and "drowned estuaries" are common. Moreover the occurrence of falls or rapids as the water passes down from one erosion terrace to the next causes some zones to be repeated.

In general, the actual catchment area of a river can also be divided into zones which correspond to those of the river profile, as shown in Figure 12.2. These catchment zones possess different potentialities of development and use (Whitmore, 1961) so that the development of any catchment for agriculture and industry usually follows one uniform pattern. The alpine zone is generally left undeveloped since it is often not readily accessible. The first permanent agricultural settlement usually occurs in the torrential and foothill zones, where dryland farming is practised on account of the high rainfall that these zones usually experience, and the torrential zone usually remains as the grazed, cultivated or forested uplands of the catchment. Usually the rainfall in the floodplain zone is relatively small so that here irrigation farming must be practised once agriculture in the upper zones of the catchment has been established. Diversion and storage works in the foothill zone therefore become necessary to ensure a stable supply of water, and consequently a competition for water between the floodplain and foothill zones commences. Urban and industrial development usually commences in the floodplain zone, and with this problems of river pollution begin to rise. The water supply must now satisfy, not a stable, but a progressively increasing demand. Once the demand for water equals the available supply, further economic development of the catchment will cease. Consequently in a fully developed catchment water storage must be very carefully planned, the upper zones of the catchment must be skilfully managed so as to ensure a stabilised run-off, pollution abatement and re-use of water must be practised, and all other sources of water must be exploited to the full.

In Natal, this development pattern has been followed closely. The Province is still primarily an agricultural one. Cattle are raised over its whole area, and also sheep (except in the extreme north coastal region). Maize (but not wheat) is grown extensively but especially in the northern areas (again except in the extreme north coastal region) and citrus orchards are established in a belt extending from Mooi River to Durban (principally naartjies, with lemons and some oranges and



FIGURE 12.2

Zonation of a river catchment



grapefruit). Pineapples are grown along the coast to the north, sugar is cultivated along the whole coastal belt except for its northern end, and forrestries are developed along the coast and in the Natal Midlands.

The population of Natal is concentrated around Durban and Pietermaritzburg, one quarter of the total population (all races) being found in this region. Here live most of the Europeans. Bantu dwell all over the Province, but are concentrated in and near the middle and lower Tugela basin and in a broad region along the coast and in the south - the coastal belt is in fact separated from the higher region of the Midlands by an almost continuous belt of Bantu reserves occupying the rugged country just inland from the coast. Coloureds and Asiatics are found predominantly in the coastal belt, especially to the south of Durban. There are no large cities apart from Durban and Pietermaritzburg, and according to the 1960 census there were then only 38 towns each with a population of more than 2000. In the rural areas the density of the European population is of the order of 1 per square mile, whilst that of the Bantu population on European farms is of the order of 100 per square mile. In the Bantu reserves, however, it rises in places to around 300 per square mile. The density of the rural Asiatic population is negligible, people of this race being limited to the town and villages.

Some of the inland towns are industrial centres on a relatively small scale, but mostly the land surface of Natal is given over to European farms and Bantu reserves, areas of other types (the coal mines of Northern Natal, the sugar growing areas, forrestries, nature reserves) being few in number and making up only a small fraction (just over 5%) of the total land area. Consequently it is apparent that most of the river catchments in Natal are at present in an early stage of development while only very few (including the Umgeni catchment in which stand both of the two major cities) have reached the stage of urbanisation and industrialisation, and of these only the Umgeni catchment is approaching the stage where water supply and demand are balanced.

#### Climate and river flow

The flow of a river is almost wholly derived from the run-off in its catchment. This in turn depends primarily upon the rainfall but is also affected by such factors as topography, geology, pedology and land use. Moreover, since the area of the ground surface which contributes the run-off is extremely large in comparison with the actual bed of the



river, there is a magnifying effect which makes the flow very sensitive to changes in run-off.

The river flow thus shows a marked seasonal variation, parallel to the seasonal variation of rainfall. Where there are well-marked dry and rainy seasons, there will be corresponding times of low and high river flow. In high latitudes where freezing conditions occur during one period of the year and where the precipitation then occurs as snow, the time of highest river flow will be when the annual thaw sets in, and a similar effect will occur anywhere else if sufficiently heavy snowfalls are experienced.

Superimposed on the seasonal variation will be variations of flow of shorter period, representing the day-to-day variation of precipitation over the catchment.

The effects of climate upon river flow in South Africa are particularly marked. In the summer months (November to May) anticyclones are established over the Indian and Atlantic Oceans and favour an influx of warm moist air on the eastern side of the country. During this period 86% of the Republic receives the bulk of its annual rainfall. In winter (June to September) a prominent anticyclone arises over the centre of the country so that the flow of air from the east is prevented. Rain is then confined to the southern and western parts of the Cape Province, the rest of the country experiencing drought conditions. Over the whole country the mean annual rainfall is about 17.5 inches and is highest in the east (about 45 inches), lowest in the west (1 - 2 inches or less). Prolonged heavy rains occur at times over wide areas, especially in the south and south-east of the Cape Province, but the summer rainfall of most of the country occurs with thunderstorms which reach their maximum frequency in February. The rainfall can then be very intense for short periods (3.5 - 4 inches per hour in parts of the Transvaal), often accompanied by hail.

During summer, maximum temperatures of 90 - 95°F are fairly common and, since the greater portion of South Africa has an elevation of over 3000 feet, the evaporation rate is high. Hot winds (berg winds) are experienced in the coastal districts and dust storms can occur over the inland regions. In winter, temperatures below freezing may occur inland, but frosts sufficient to freeze water are rare along the coast. Snowfalls are confined to mountainous districts and occur most often (average 5 times per year) on the Drakensberg escarpment.



The annual rainfall of Natal ranges from less than 25 inches at places inland to 45 inches or more at the coast and in the vicinity of the Drakensberg, of which some 70 - 80% falls in summer. Because of the high temperatures and low humidities inland, many of the smaller streams there dry up completely during the winter (dry season) months, although all the major rivers maintain steady but much reduced flows (this behaviour in fact prevails throughout the summer rainfall areas of South Africa). Near the coast, rivers and streams are fed by the seepage of underground water working down from areas of higher altitude. For example, it is estimated from figures quoted by Thomas (1951) that about half the average dry season flow of 200 cusecs in the lower Umgeni river is due to underground water.

The steep contours and river gradients as well as the heavy summer rains make summer floods frequent. In the smaller streams irregular flash floods often occur during which the flow may rise to at least 300 times the seasonal average. Describing the occurrence of floods in the tributaries of the Tugela river, Oliff (1960) speaks of "a wall of muddy water 3 - 5 feet high advancing downstream bearing trees, animals and detritus".

The silt concentrations in the Natal rivers, because of such circumstances, are naturally high. Thus, as much as 2.78% of suspended solids has been recorded in the Tugela at Bergville (Middleton and Oliff, 1961), the average concentration at this station being about 0.1%. Values of the order of 10% have been found in the Umkomaas river. Although the river waters are usually fairly clear during the dry season, the silt contents and turbidities rise to maximum values during the early stages of each flood, only to fall again as the flood continues even though the level of the water remains high. High silt loads and turbidities are troublesome in water storage and purification works, but on the other hand the summer floods scour out the river beds and prevent the accumulation of detritus that could otherwise give rise to conditions of gross pollution.

The occurrence of brief periods of very high flow complicates statistical calculations concerning river flows, since a bias towards high values is thus introduced into means. By using a logarithmic transformation of the data, however, this bias can be largely eliminated.



Climate and TDS

Clarke (1924 A) points out that where rainfall is abundant, so also is vegetation. Organic matter then accumulates in the soil and provides a source of carbonic acid which serves to break down rocks. Abundant rainfall (giving rise to large volumes of run-off which tend to dilute surface waters) and active rock decomposition (tending to produce greater amounts of soluble salts) thus have opposed effects on the TDS, which remains moderate in value.

In the colder parts of the temperate zone, alternations of freezing and thawing help to disintegrate the rocks and make them more accessible to the action of percolating water, thus increasing the TDS. But where winters are long and severe the soil remains frozen during a large part of the year and the solvent action of water is then very slight so that the TDS of a river is generally low. In hot and arid regions, on the other hand, the TDS tends to be high owing to evaporation.

Other factors can act so as to modify climatic effects very considerably. Pervious soils which can soak up a large proportion of the precipitation, releasing it only slowly by seepage to the rivers of the region, will serve to even out variations in flow, and because the percolating water has a larger contact time with soluble materials the TDS will tend to lie above the level that would otherwise be considered normal for the region concerned. Conversely, impervious soils which retain only a small fraction of the precipitation will lead to extreme variations in the flow and cause the TDS at times of flood to fall to abnormally low values. The formation of hard-pan in a soil, resulting in almost the whole of the precipitation appearing as run-off, is one way in which this may occur.

Now the South African climate is not sufficiently humid nor is the general relief of the country sufficiently low to favour the accumulation of vegetable decomposition products and the formation of humus soils, except in a few alluvial valleys. In fact, because of the fairly high diurnal temperature range and the strongly contrasted seasons over most of the country, mechanical weathering of surface rocks is favoured. The episodic nature of the rainfall aids in the removal of freshly formed rock fragments, so that no very great depths of soil are formed and plant growth has little opportunity to establish itself and exercise a protective effect. In consequence soil erosion is active. The absence of a soil cover of any extensive thickness over the underlying rocks means that the run-off is



relatively high in comparison with the run-in. Hence the flow of South African rivers varies very greatly and the TDS during floods can fall to very low values.

Early in the rainy season changes of TDS of 40 ppm or more can occur in a very short time (less than a day) owing to the rise and fall of floods, fluctuations of the daily rainfall over the catchment, etc. Minimum TDS values occur with no definite periodicity and are usually accompanied by high turbidities. As the season progresses the soils of the catchment become more waterlogged, thus increasing the ratio of run-off to run-in, and the TDS tends to fall to a fairly steady seasonal minimum while the flow climbs to a maximum.

As the dry season commences the TDS begins to increase and the flow to drop. These trends are usually interrupted by the occurrence of occasional rains but are resumed after each interruption so that a seasonal maximum TDS is eventually attained at the same time as a minimum flow. The onset of the first rains, however, immediately causes departure from this state of affairs.

Generally, the rainy season average TDS is of the order of 0.5 times the annual average, while the dry season average is of the order of 1.5 times the annual average, i.e. about 3 times the rainy season average.

#### Correlations between TDS, flow and conductivity

Since the TDS of natural waters is due mainly to mineral salts, an indication of the value of the TDS is provided by the electrical conductivity of the water. It is usual to determine the conductivity, in micromho, of a 1 cm cube of the water and reduce the result to a standard temperature of 20°C.

The conductivity is generally proportional to the TDS:

$$\text{Conductivity (micromho)} \times \text{Factor} = \text{TDS (ppm)}$$

and this relationship is a useful check upon TDS determinations. The value of the factor usually lies in the range 0.55 to 0.70, and in many cases can be taken as approximately 0.67.

Because of the high mobilities of the hydrogen and hydroxyl ions, the factor may be much lower than 0.55 if the water is exceptionally acidic or alkaline. Because of the effects of interionic attraction, the factor may be greater than 0.70 if the TDS of the water is high. Also, if the water contains organic matter this will contribute to the TDS but not

usually to the conductivity (since it will be largely colloidal and non-ionic) and the proportionality factor will then be high. Taylor (1958) states that, out of a number of waters examined in this way, the higher values of the factor were given by peaty waters - one of these gave a value as great as 1.25.

Illustrations of this relationship are provided by statistical examination of the results obtained from various river surveys in South Africa, using in each case the method of least squares to calculate the value of the proportionality factor after imposing the boundary condition that the conductivity and TDS approach zero together:

- (a) From the results obtained by Oliff (1960) during a survey of the Tugela river system of Natal:

$$\text{TDS} = 0.657 \times \text{conductivity}$$

valid up to 1120 micromho and associated with a standard error of estimate of 40.3 ppm in the TDS. This is an example of a normal river with a factor close to 0.67.

- (b) From the results obtained by Schoonbee and Kemo (1965) during a survey of the Umgeni river system of Natal:

$$\text{TDS} = 0.661 \times \text{conductivity}$$

valid up to 978 micromho and associated with a standard error of estimate of TDS of 18.9 ppm. This closely resembles the Tugela result.

- (c) The results obtained by Harrison and Elsworth (1958) during their survey of the Great Berg river of the Western Cape gave:

$$\text{TDS} = 1.105 \times \text{conductivity}$$

valid up to about 1000 micromho and associated with a standard error of estimate of TDS of 13.6 ppm. The water of this river contains organic matter, often sufficient to give it a distinct colour, and the high value of the proportionality factor is attributable to this.

- (d) The Jukskei river of the Witwatersrand, according to the results of Allanson (1961), gave the relation:

$$\text{TDS} = 0.589 \times \text{conductivity}$$

This river is highly polluted and during the survey gave conductivity values of high order, ranging from 406 to 6218 micromho.



It might be expected that an inverse correlation would exist between the conductivity of a river at a given point (or the TDS, since these variables are correlated) and its flow. Any relation between conductivity and flow would not be expected to be linear in form, since at high flow the conductivity should approach, not zero, but a minimum value of the order of that of rain water and at low flow it could become very high. The expected form is therefore hyperbolic, but would become approximately linear if both variables were logarithmically transformed:

$$\log \text{Flow} = A - B \log \text{conductivity}$$

where A and B are constants.

Such relations do exist (but not at any point on a river below a dam which artificially regulates the flow). For example, Hem (1959) gives data for the flow and conductivity of the San Francisco river at Clifton, Arizona, which lead to the relationship:

$$\log \text{Flow (cusecs)} = 4.56 - 0.932 \log \text{Conductivity (micromho)}$$

with a standard error of estimate of 0.20. This standard error is relatively high. It corresponds to a value of - 0.682 for the coefficient of correlation between the logarithms of flow and conductivity which, with 194 degrees of freedom, is of high statistical significance though of relatively low value. The relation therefore does not provide any accurate estimate of the flow from measurement of the conductivity.

Similarly for the Tugela river of Natal, measured at Colenso, there is a statistically significant correlation (correlation coefficient - 0.316 with 85 degrees of freedom), and also for the Umgeni river just above Nagle Dam, the only dam on the river at that time (correlation coefficient - 0.609 with 25 degrees of freedom). In neither case is the correlation close enough to be of any practical use.

The absence of a close correlation between conductivity and flow may arise from two main causes. It may be due to the occurrence of intermittent pollution. It may otherwise be due to the occurrence of sudden floods in the river, the first waters of a flood being often of higher conductivity than the later waters (Hem, 1959) because (a) the early run-off can itself be highly saline, (b) the early flood water can pick up salts left in the river channel by evaporation, and (c) the first water of the flood consists of water that was in transit in the channel before the rise of the river. Since South African rivers in general are subject to

sudden floods, they would not be expected to show close correlations of the nature discussed, although the seasonal variations of flow and TDS (or conductivity) do go hand-in-hand simply because floods are rare in the dry season.

It is worth noting here that the apparent flow of a stream does not necessarily bear any relation to its real total flow. Streams on sandy beds, for example, may appear completely dry and yet still be flowing at 20 cusecs or more within the sand of the bed. Consequently accurate flow measurements are far more difficult to obtain than might be supposed, and it is only under very special circumstances that a flow figure of any reliability is provided by superficial measurements.

#### TDS and chemical composition

It is clear from the above discussion that there is some relation between the flow of a river past a given point and the TDS of the water, even though that relation may not be a very definite one. But whether or not the chemical analysis of the water is also variable is not immediately apparent.

Conway (1942) has concluded that the concentrations of carbonate, calcium and magnesium in natural waters rise rapidly with the TDS until limiting values are reached at about 200 ppm. Higher TDS values are largely due to increases in the sodium sulphate and chloride contents.

Clarke (1924 B) observed that, although the waters from springs and wells may contain carbonates, sulphates or chlorides as their predominant salts, river waters mostly contain either carbonates or sulphates, the former being the most common. According to Conway (1942), chloride predominates over sulphate in the more dilute rivers, sulphate becoming predominant in the most concentrated ones.

Changes of flow may sometimes give rise to extensive changes of composition. Clarke (1924 A) cites the case of the river Chélif at Ksar-Boghari, Algeria, studied by Ville in 1857. During low flow sulphates predominated in the water of this river, although chlorides became predominant when the flow increased. This was attributed to the ready solubility of sodium chloride, which was thus considered to be the salt most rapidly leached from the soil during a flood.

The general trends discussed by Clarke and by Conway are not often observable in the waters of a single river since they relate to differences in magnitude of TDS which are of quite a different order from



those occurring in any one particular stream. On the other hand, it is well-known that there is often a correlation between the TDS and the concentrations of most of the major solutes of a river (Woxholt, 1959). This in turn implies that most of the composition changes shown by rivers (unless affected by pollution) are merely changes of dilution or concentration, such as will alter the TDS and the absolute magnitudes of the concentrations but leave the ratios between the different solute concentrations unchanged.

For this implication properly to be examined further, however, it is first necessary to have some standardised means of expressing analytical results which will eliminate simple dilution effects. Such a scheme of standardisation would have more practical application also since, from the above discussion, it is clear that the TDS values of rivers are so variable that it is not usually possible to make any immediate comparison between two different water samples.

### 13. THE STANDARDISATION OF WATER ANALYSES

#### Possible procedures

A widely used means of standardising analytical results is to express them, not in terms of concentrations, but as percentages of the TDS. This scheme, however, suffers from various defects.

The experimental determination of TDS (by evaporating a known volume of the clarified water to dryness and dehydrating and weighing the residue) is liable to relatively large errors. Traces of finely divided suspended matter, partial oxidation of organic material, volatilisation and decomposition of solid salts and incomplete removal of water of crystallisation all contribute to produce spurious experimental values. Often the dried residue is hygroscopic and difficult to weigh accurately. Different workers advocate different drying temperatures so that their results diverge somewhat. Even if all these difficulties are overcome, the fact remains that the solid material finally obtained does not coincide with the material originally present in solution (Hem, 1959). As an illustration of this last point, it may be noted that solutions of sodium bicarbonate and sodium carbonate containing 840 and 530 ppm respectively of the anhydrous salts both give experimental TDS values of 530 ppm because of the loss of carbon dioxide on evaporating the bicarbonate solution.

This last objection can still be valid if a calculated TDS is used in place of an experimental one. It certainly holds if the TDS is calculated according to equation (4.6), since the value given by this designedly relates to the solid residue, not to the original solution. A different basis for the calculation could meet this objection, but the others would still remain valid.

Even if the other solute concentrations vary roughly in proportion to the TDS, that of silica often does not (see chapter 2). In fact the behaviour of silica is often such that, if it is expressed as a percentage of the TDS, many rivers will show a decrease in silica percentage as their TDS rises, even though the percentages of the other solutes remain almost unchanged. In other words, just because the silica concentrations of many rivers show such little variation, the percentage of silica in the TDS would be merely another way of expressing the TDS itself and as such would not be independent of dilution effects at all.



No arithmetical procedure can be designed to correct for this effect because it exhibits no great regularity and is not of a fully general occurrence - rivers in some parts of the world do not behave in this way.

These considerations may be coupled with the conclusions of chapter 2 that silica in natural waters is often not ionic. Jointly they suggest that it would be expedient to omit silica altogether from the standardised analysis. If this is done, the individual solute concentrations could in most cases be expressed as percentages, not of an experimental or calculated TDS, but of the total ionisable solutes in the water.

However, there remains one practical defect of any method of standardisation based on concentrations, namely that it is not stoichiometric unless the concentration units are molar or normal. Unless such units are used, the analysis will never show in a solution of mixed salts, for example, that a particular cation is necessarily linked with a particular anion, and likewise if the concentration of one of the salts is increased or another is added it will never show the percentages of the corresponding cation and anions to increase by directly related amounts.

It therefore appears that a satisfactory way of standardising water analyses would be to utilise the equivalent or molar concentrations of all the ionic solutes, ignoring non-ionic ones, and to express each such concentration as a percentage of their total.

#### Molar percentages

Most of our theoretical work has been expressed in terms of molar (or millimolar) concentrations of the acids and bases present in the water (the Riccian solutes), the one exception being the total alkalinity. Yet although the latter is expressed in equivalents (or milliequivalents) its value is obtainable from an equation (3.42) in which the experimental concentrations appear in molar units. We have even expressed the ionic balance (7.21) in terms of molar units.

It would be possible to rewrite all the equations, replacing moles by equivalents. But this would give rise to a host of fractional coefficients, destroying the simplicity of many of the equations. It is therefore far preferable to keep to the molar units. This will only prove inconvenient, in fact, if ion-exchange processes are considered, and then it will be necessary to introduce other equations like (3.42). Such considerations are outside the scope of the present work.

Therefore we propose to express any water analysis in standardised form by summing the millimolar concentrations of the ionised acids and bases present in solution and expressing each such concentration as a percentage of that sum. The resulting percentages will be referred to as the molar percentages of the solutes in the water.

This automatically limits the standardisation to concern only the ionic solutes of the water and thus avoids any difficulties with silica. It can take into account the possible presence of organic and unusual inorganic acids and bases in polluted and abnormal waters, but it must be remembered that such substances will interfere both with the calculation and determination of the total carbonic acid concentration so that standardised analyses of these waters must be calculated and interpreted with suitable caution. From chapter 2 it is evident that only seven solutes (calcium, magnesium, sodium and potassium hydroxides together with carbonic, sulphuric and hydrochloric acids) need normally be considered in the standardisation calculations, since other solutes (excluding silica) rarely occur in concentrations of more than 1 ppm and their neglect will normally cause no appreciable error (especially so since analytical errors are usually of a larger order).

It may be pointed out that the checking of the ionic balance and the calculation of the total carbonic acid concentration require the molar concentrations to be calculated. The use of molar rather than any other form of percentages therefore does not add unduly to the arithmetical work.

### Examples

To illustrate the molar percentage concept we may use the analyses of rain and sea water given in Table 8.5, to which may be added the following figures given by Clarke (1924 B) as representing a world average river whose pH is about 7.5:

TDS, ppm	100
Total alkalinity, ppm $\text{CaCO}_3$	60.8
Ca, ppm	21.2
Mg, ppm	3.5
Na, ppm	6.0
K, ppm	2.2
$\text{SO}_4$ , ppm	12.6
Cl, ppm	5.9
$\text{SiO}_2$ , ppm	12.1



Each analysis fulfills the ionic balance, but we have seen (chapter 8) that we must take  $\bar{e} = -0.013$  for the rain water and  $\bar{e} = \bar{e}_t$  for the sea water. For the river water we may take  $\bar{e}$  as the mean of  $\bar{e}_c$  and  $\bar{e}_t$  in the usual way. In Table 13.1 are given the results of recalculating these analyses in terms of millimolar concentrations, according to the methods of Appendix A.

In Table 13.2 are given the molar percentages for these waters. From these, since concentration differences have been eliminated, some interesting comparisons can be made. The high molar percentages of sodium hydroxide and hydrochloric acid in sea water are, of course, only to be expected. More worthy of comment is the extremely low molar percentage of carbonic acid and the fact that the molar percentage of magnesium hydroxide is over five times that of calcium hydroxide. The rain water shows a closely similar composition, although with a negative value of  $e$  (see chapter 8). Evidently the dissolved substances in this sample have been derived largely from the sea (see chapter 2). The river water differs markedly from the others. Carbonic acid is the predominant acid, the molar percentage of calcium hydroxide exceeds that of magnesium hydroxide and the proportions of sodium hydroxide and hydrochloric acid are greatly reduced. The value of  $e$  is positive again.

Further examples are provided by the analyses of Natal rivers given in Tables 2.1 and 8.3. The molar percentages corresponding to these are shown in Table 13.3 and it will be seen that many of the irregularities previously apparent have now disappeared. The last column of the Table shows the total millimolar concentration of ionised solutes in these waters.

Table 13.1

Molar concentrations of rain, sea and river water

	Rain water	Sea water	River water
$\gamma$	1.000	0.297	0.952
$e$	-0.013	2.41	1.23
$c$	0.005	10.3	0.530
$m$	0.0125	54.3	0.146
$n$	0.135	470	0.261
$p$	0.0051	9.97	0.0564
$a$	0.0151	2.16	1.32
$s$	0.0177	28.3	0.131
$h$	0.144	548	0.166

Table 13.2

Molar percentages of rain, sea and river water

	Rain water	Sea water	River water
$\text{Ca(OH)}_2$	1.5	0.9	20.3
$\text{Mg(OH)}_2$	3.7	4.8	5.6
$\text{NaOH}$	40.4	41.9	10.0
$\text{KOH}$	1.5	0.9	2.2
$\text{H}_2\text{CO}_3$	4.5	0.2	50.5
$\text{H}_2\text{SO}_4$	5.3	2.5	5.0
$\text{HCl}$	43.1	48.8	6.4

Variation of the molar percentages

It is a logical consequence of the mathematical form of the molar percentages that they must succeed in eliminating dilution or concentration effects from the analysis in the desired manner. However, we must now enquire as to the constancy of the percentages in any given case.

Since any water analysis necessarily contains errors, it is evident that a series of analyses for samples from the same point on a given river will show a random variation from this cause, and this must be properly allowed for when comparing the molar percentages. Yet there is but little firm information available on analytical errors. The American Public Health Association (1965) have included some data in their manual of standard methods, but it is not very clear just what the figures measure. The present author has carried out 10 replicate analyses of a solution containing 30 ppm of calcium, 15 ppm of magnesium, 100 ppm of sodium, 140 ppm of sulphate and 80 ppm of chloride, with a total alkalinity of 80 ppm as  $\text{CaCO}_3$ , and obtained the following standard deviations:

Ca	0.80
Mg	0.57
Na	4.51
$\text{SO}_4$	3.24
Cl	3.79
Alkalinity	0.66

These do not accord with the above published data. Moreover, if an analysis is checked by an ion balance technique, the errors in the results finally



Table 13.3

Molar percentages calculated from the analyses of Table 2.1

R i v e r	TDS, ppm	Molar percentages							Total millimoles/litre of ionised solutes
		Ca(OH) <sub>2</sub>	Mg(OH) <sub>2</sub>	NaOH	KOH	H <sub>2</sub> CO <sub>3</sub>	H <sub>2</sub> SO <sub>4</sub>	HCl	
Sterk near Ambleside	41	7.7	9.1	20.3	1.8	48.5	0.0	12.6	1.007
Illovo above Richmond	41	13.3	7.7	18.7	0.3	57.7	0.0	2.3	0.978
Mooi above Mooi River	42	13.7	8.2	13.4	2.0	50.5	9.4	2.8	0.910
Karkloof at Shafton	42	9.8	7.9	20.5	1.4	55.0	0.0	5.4	0.892
Ingagane above Alcockspruit	49	10.5	7.0	15.7	7.7	54.4	2.6	2.1	1.191
Lions near Lidgetton	59	10.9	9.7	15.8	2.0	60.2	1.2	0.2	1.509
Nungwana near Nungwana Falls	60	7.6	8.1	23.7	0.2	27.0	0.0	33.4	1.281
Umgeni at Nagle Dam	69	9.3	7.1	19.5	1.5	47.5	0.8	14.3	1.761
Umgega at Umfula	77	6.5	7.6	27.3	1.6	41.6	0.0	15.4	2.138
White Umfolozi near Vryheid	78	14.7	7.2	3.1	9.5	60.6	1.4	3.5	1.670
Lenjane's at Lenjane's Drift	81	13.7	10.3	12.3	3.3	56.6	1.0	2.8	2.302
Tugela at Colenso	85	13.9	10.6	12.0	0.8	60.4	0.8	1.5	2.318
Sundays near Newcastle	95	11.0	11.8	14.0	1.5	60.3	1.3	0.1	2.540
Gogoshi near Mtunzini	108	2.1	1.4	43.0	0.7	9.8	0.0	43.0	2.975
Umvoti at Bitakona	116	8.3	7.0	26.3	0.9	42.6	2.5	12.4	3.056
Umfolozi at Mtubatuba	136	8.2	8.4	24.3	0.9	46.0	0.0	12.2	4.443
Unzinkulwana at Baboons Castle	143	6.6	9.1	27.4	0.6	31.6	1.7	23.0	4.382
Bloukrans near Colenso	191	12.9	10.2	15.3	0.8	58.1	0.8	1.9	5.752
Umhlanga at Trenance	213	3.8	7.9	30.8	0.6	22.7	1.3	32.9	6.559
Umzinyatshana near Dundee	232	10.3	13.4	15.9	0.5	56.7	1.2	2.0	6.482
Isipingo near Inwabi	320	3.6	6.9	33.7	0.7	11.9	1.5	41.7	9.510
Mpushini near Pietermaritzburg	332	7.7	8.1	24.5	0.3	37.0	0.5	21.9	9.939
M e a n	119	9.4	8.4	20.8	1.8	45.2	1.3	13.1	-

reported will not be the same as those determined for simple replications. Consequently all that can be done under the circumstances is to give a rough estimate of the magnitude of analytical errors, and it is proposed to take the standard deviation of each determination as 5% of the true result. This at least appears of about the right order of magnitude.

Now if  $x_i$  is the molar concentration of any solute, the corresponding molar percentage will be:

$$p_i = 100 x_i / \sum_i x_i \quad (13.1)$$

where the summation extends over all the ionised solutes considered in calculating the percentages. Assuming that, owing to compensating effects, the errors in  $\sum_i x_i$  are negligible, the variance of  $p_i$  is given by:

$$\text{var } p_i = \left( \frac{100}{\sum_i x_i} \right)^2 \text{var } x_i \quad (13.2)$$

By a familiar theorem of statistics, if  $u$  and  $v$  are two independent variates:

$$\text{var } (u - v) = \text{var } u + \text{var } v \quad (13.3)$$

Hence if  $\Delta_i$  denotes the difference between two independent determinations of  $p_i$ :

$$\text{var } \Delta_i = 2 \text{var } p_i = 2 \left( \frac{100}{\sum_i x_i} \right)^2 \text{var } x_i \quad (13.4)$$

Taking the standard deviation of  $x_i$  as 5% of  $x_i$  (see above), we have:

$$\text{var } x_i = (0.05 x_i)^2 \quad (13.5)$$

so that:

$$\text{var } \Delta_i = 2 \left( \frac{5 x_i}{\sum_i x_i} \right)^2 \quad (13.6)$$

which, using (13.1) may be written:

$$\text{var } \Delta_i = 2 (p_i/20)^2 \quad (13.7)$$

and the standard deviation of  $\Delta_i$  is thus  $p_i/20$ ,



This suggests that we can be 95% confident that, due to analytical error alone,  $\Delta_i$  (which is clearly distributed about a zero mean) will not exceed  $p_i\sqrt{2/10}$ , i.e. two standard deviations. In other words, two values of  $p_i$  observed on different occasions should not differ more than 5 times out of 100 occasions by more than about  $p_i/7$ .

In Table 2 C of Appendix C are given the analyses of two different snap samples from each of 14 unpolluted rivers of Natal, each pair of samples having been taken at different times from one sampling point. Each analysis fulfils the ionic balance, and the calculated molar percentages are given in Table 3 C. If  $p_i$  is taken as the mean of each pair of values, it is found that out of all 98 pairs, 51 differ by more than  $p_i/7$ .

This suggests that the differences between the percentages are due to factors additional to analytical error, and that these rivers show real chemical variations beyond those due to simple dilution or concentration.

Such chemical variations could arise in any river from several causes. Water rising to the surface from underground in the form of springs or seepage water draining from soil strata several feet in thickness would be expected to be of fairly high TDS and quite different in composition from surface run-off which has had very little contact time with the ground surface and hence is usually of low TDS. The composition of the river water would thus depend upon the proportions in which these two components are mixed into it, and this could vary from time to time. Similarly, rainfall can cause soluble materials accumulated on the ground surface to be washed into the river and so change the chemical composition of its water. This would be particularly marked with the first rains after a fairly long dry period.

In addition, the water which passes a given point along the course of a river is usually gathered from a set of large and small tributaries. If the total catchment area is large, rain may on occasion fall over the catchment of one tributary but not over those of others. The water will require a certain period of time after it has reached the ground surface before it passes the given point, and this period will be different for all the tributary catchments. Thus the water at the point concerned is likely to consist of a succession of different water masses, each derived from a different tributary catchment. There is evidence to support this hypothesis in that different types of suspended silt, each derived from its own particular catchment, are known to arrive at a given



station along a river at different times, according to the distribution of recent rainfall, and each type of silt must necessarily move with the water in which it originally became suspended. Each of these water masses, since it has a different place of origin, has had a different history and is of a different age from those adjacent to it, is thus likely to have different chemical characteristics. There will be no sharp line of demarcation between one water mass and the next because of diffusion and turbulent mixing, but the result will be to produce perceptible differences in the analyses of samples taken from the same place but at different times.

A fourth possible cause of chemical variation in a river arises when it receives effluents of any kind. Most effluents are quite different in composition from river water and hence cause composition changes in the river. Since effluent flows can vary quite independently of the river flow, the composition of the river water below the point of entry of an effluent is likely to vary in a quite complex manner.

Of interest in this connection are the detailed results obtained by Malan (1959) during his investigation of the Wilge river of the Orange Free State. In the course of this work samples were taken daily at various sampling points over a period of a year (from 1957 to 1958). Where two or more successive samples did not differ in conductivity by more than 10 micromho they were combined in equal proportions to form a composite sample, and in this way the samples from the Wilge at Frankfort for the whole year were reduced to 59 in number. Several of these did not fulfill the ionic balance, and on eliminating these there remain 44 analyses for the river at that point. These analyses are given in Table 4 C of Appendix C and the calculated molar percentages in Table 5 C.

Inspection of these results suggests that there is some systematic variation of the molar percentages with the conductivity, and in fact each molar percentage shows a highly significant degree of correlation with conductivity. In Table 13.4 are given, for each solute, the value of the coefficient of correlation between molar percentage and conductivity and the probability P that this value might arise by purely random effects. In each case the probability is exceedingly small.

The values of the correlation coefficients are too low to be of any practical utility, but they show that, on an average, the molar percentages of calcium and magnesium hydroxides and the carbonic acid tend to increase as the conductivity increases whilst those of sodium and potassium hydroxides and sulphuric and hydrochloric acids tend to decrease,



and it cannot be doubted that these variations are real.

Hence it is clear that, although the molar percentages are necessarily independent of simple dilution effects, in any particular river they may still show a fairly wide degree of variation because of real chemical variations which occur in the water.

#### Design of sampling programmes

The above discussion has immediate application to the design of sampling programmes for the conduct of river surveys.

The extent of the chemical variation will evidently vary from one river to another so that it is not possible to say in advance for a given case what that extent will be. If any accurate and detailed knowledge is required of the mean and extreme chemical compositions of the water of a particular river, regular and very frequent sampling for at least a full year (to cover the complete river regime) is thus necessary. The data of Table 3 C suggests that often over 100 samples may be needed.

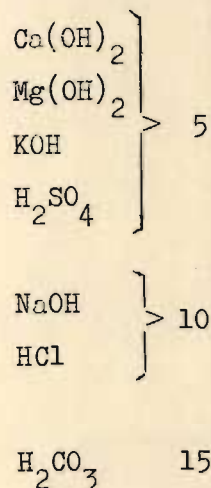
Table 13.4

Correlation of molar percentage and conductivity  
for the Wilge river

Solute	Correlation coefficient between molar percentage and conductivity	P
$\text{Ca(OH)}_2$	+ 0.606	< 0.001
$\text{Mg(OH)}_2$	+ 0.557	< 0.001
NaOH	- 0.596	< 0.001
KOH	- 0.786	< 0.001
$\text{H}_2\text{CO}_3$	+ 0.726	< 0.001
$\text{H}_2\text{SO}_4$	- 0.421	0.001
HCl	- 0.663	< 0.001

However, from the practical point of view of water technology such details are not usually necessary. Such parameters as the buffer capacity, pH,  $\text{pH}_s$  and hardness are not much affected by relatively extensive changes in the molar percentages, as can be appreciated from the contents of earlier chapters, and it is only these chemical parameters together with the TDS that are usually of technological interest (excluding the investigation of water pollution). Hence a very good idea of the average and

extreme values of technological interest can be obtained from a mere two samples, taken at the height of the dry and rainy seasons so as to cover virtually the full range of variation. Working according to this scheme means sacrificing more detailed information on grounds of economy, but it would be advisable to take some additional samples if the two analyses are found to differ markedly as shown by their molar percentages. As a working criterion, we may take the extreme values of the differences between pairs in Table 3 C, conveniently rounded off, and regard molar percentages as disagreeing if they differ by more than the following amounts:



Only 4 of the 14 rivers of Table 3 C show greater differences than these; the Mooi, Mpushini and Umvoti only just exceed one or two of the limits (HCl in each case, and  $\text{H}_2\text{SO}_4$  for the Mooi) but the Ingagane shows quite large differences for NaOH, KOH,  $\text{H}_2\text{CO}_3$  and  $\text{H}_2\text{SO}_4$ .

Two samples should also normally suffice for the detection of pollution by chemical means, judging this not only from the samples from a single station but also from those from higher and lower stations used as controls. Studies of the amount and degree of pollution in a particular case, however, constitutes a detailed investigation for which a large number of samples is necessary.

If, instead of comparing the analyses of samples taken at different times from a single station (as in Tables 2 C and 3 C), we compare those of samples taken at almost the same time (within a few hours) from stations several miles apart, the variation of the molar percentages is of a much smaller degree (excluding, of course, cases where a major tributary of quite different composition or a large load of polluting material enters the river between the two stations). This is illustrated by the data of Tables 6 C and 7 C, which respectively give the normal analyses and the molar percentages for each of two different stations on a



set of eight unpolluted Natal rivers. In no case do the two members of any pair of the percentages differ by more than the amounts listed above.

On the other hand, where effluent streams enter the river between the two stations, these critical values are often exceeded. Table 8 C gives the normal analyses and Table 9 C the molar percentages for each of two stations, one above and one below an effluent, on a set of four Natal rivers. The Umbogintwini receives the treated sewage effluent from the African Explosives and Chemical Industries factory (the effluent also containing the outflow from laboratory sinks, drainage from the factory area, etc); only the sodium and potassium hydroxide percentages are virtually unchanged. The Umzinyatshana receives sewage effluent from Dundee via the Steenkoolspruit but it also collects the drainage from coal mines (mostly disused) and dumps in its catchment; there is a marked increase in its carbonic acid percentage and a corresponding increase in the proportion of sulphuric acid. Similarly the Ingagane collects drainage from both active and disused coal mines, and although this is not sufficient to cause any very marked deterioration in the quality of its water, it results in a rather large increase in the molar percentage of sulphuric acid. The Mooi receives domestic and industrial effluents from Mooi River town, and these cause an increase in its molar percentage of sodium hydroxide (this would not by itself be considered as evidence of pollution, but becomes significant when considered in conjunction with the pH, conductivity, TDS and other chemical parameters).

Results such as these fully justify the usual technique of river surveys for the detection (but not assessment) of pollution by comparing the analyses for adjacent sampling stations.

#### Minor comments

Applications of the molar percentages will be further considered in the following chapters, but before coming to these there are three minor points which should be mentioned.

Firstly, it may to some seem objectionable to speak of the molar percentages of acids and bases in waters which are virtually neutral in reaction and contain in solution, not acids and bases, but salts. However, this is only a mode of expression and is really no more misleading than, for example, the widely used method of reporting a magnesium concentration as "ppm of  $\text{CaCO}_3$ ". Indeed, Nordell (1951) went so far as to report all analytical results (except pH) in  $\text{CaCO}_3$  units, even if the water should



have no calcium or carbonic acid at all. In most natural waters the molar concentration of an acid or base, i.e. of any Riccian solute, is in fact identical with that of some single ion, except in the case of carbonic acid. Were it not for this exception, an analysis could be expressed indifferently and with numerical identity in terms of either ions or acids and bases, but in practice, because of the invariable presence of carbonic acid, no such alternative mode of expression is possible unless some form of arbitrary convention is separately introduced. Anyone unfamiliar with the convention would then find analyses reported in terms of it just as confusing (if not more so) as analyses expressed in terms of Riccian solutes. Therefore no attempt is made here to establish such a convention.

Secondly, it will be noted from the Tables of molar values already given that the sum of the molar concentrations or percentages of the bases is rarely equal to that of the acids. This is because of the different valencies of the ions concerned as well as the fact that carbonic acid may be present in non-ionised form. The acid and base sums would be more nearly equal if equivalent rather than molar units were used, but the equality would still not be exact in waters of low pH because of the non-ionised carbonic acid (at extreme pH values, high or low, hydrogen or hydroxyl ions would also have to be taken into account). Therefore this is not an additional argument for using equivalent units (see above). But neither is the inequality of the acid and base sums a sign of an erroneous analysis.

Thirdly, an admitted defect of the molar percentages is that, once they are calculated, it is not possible to convert them back to ppm concentrations at a given TDS because the total molar concentration of the solutes involved has disappeared during the course of the percentage calculations. Fortunately it is only rarely that such reversed calculations are ever needed, and in the few cases that are encountered a fairly crude approximation will usually suffice. Evidently, for a given water:

$$\begin{aligned} &\text{Total molar concentrations (millimoles/litre)} \\ &= G \times \text{TDS (ppm)} \end{aligned} \quad (13.8)$$

where G is a constant. From the last column of Table 13.3 it is readily verified that, for the 22 Natal rivers concerned, the value of G ranges from 0.0212 to 0.0327 with an average of 0.0266. Hence we can put:

$$\text{concentration (millimoles/litre)} = \frac{0.0266 \times \text{molar \%} \times \text{TDS (ppm)}}{100} \quad (13.9)$$



from which the approximate ppm concentration is readily found (by multiplying by the appropriate molecular or ionic weight).

#### 14. A GRAPHICAL REPRESENTATION OF WATER ANALYSES

##### Possible schemes

It is often not easy to compare analyses one with another and hence deduce general trends because a mass of numerical data can have a masking effect. Particularly if several parameters vary simultaneously, the analytical figures can even cause some confusion so that no clear picture of the overall variation is obtainable. Moreover, a set of figures is not particularly memorisable. But if the data can be represented by some kind of diagram then comparisons of all kinds are greatly facilitated and, with a proper graphical system, analytical results can become better retained in the mind.

The molar percentages introduced in the previous chapter are well suited to form the basis of a graphical means of displaying most of the inorganic results of a water analysis because, as has been discussed, dilution effects of a more or less accidental nature have been eliminated from them. They may be utilised graphically in many different ways (polygonal diagrams, bar charts of histogram form, pie charts, diagrams of circular form, etc.), but in most cases some objection which renders the scheme of limited utility can always be raised. For example, diagrams such as polygons with a fixed number of axes or vertices are not sufficiently elastic in that they can represent only a fixed number of solutes, bar charts are similarly objectionable, pie charts are not comparable one with another because the sector representing a particular solute never keeps the same orientation from one case to the next, and diagrams built of concentric circles always look very much alike.

After trials with many possible systems, the one described below proved to be the simplest and the most satisfactory.

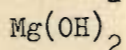
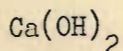
##### The molar percentage spectrum

The data needed for this particular technique consists of the molar percentages, the TDS in ppm and the pH value.

The molar percentages are to be arranged in a particular order (in fact, essentially the same order as has been used in the tabulations already presented). It is most important that this order should never be varied, for alteration will utterly confuse the final diagram. The particular conventional order, to be invariably retained, is the



following:



Any other bases, in order of molecular weight



Any other acids, in order of molecular weight



The diagram is obtained directly from the molar percentages in the above order.

First a rectangle is drawn with its long sides horizontal and of any convenient length but scaled to represent 100%. For most purposes a scale of 1 cm = 10% will be suitable. The width of the rectangle should be about one-tenth of the length, otherwise the interpretation of the diagram becomes less easy.

The left hand side of the rectangle represents zero percent. At a distance to the right of this proportional to the molar percentage of calcium hydroxide, a vertical line is drawn. At a distance to the right of this line proportional to the molar percentage of magnesium hydroxide, a second vertical line is drawn. Then to the right of this, at a distance proportional to the molar percentage of the next solute in order from the above list, another vertical line is drawn. Continuing in this way, working progressively to the right and taking the molar percentages in strict order from the above list, the last vertical line to be drawn will represent hydrochloric acid and will, of course, coincide with the right hand edge of the rectangle.

In drawing the vertical lines it is convenient to use broken lines for the additional acids and bases (if any) not specifically named in the list, e.g. for silicic acid if this need be considered, for ferrous and ferric hydroxides, for nitric or hydrofluoric acids, and so on. This will emphasise that the molar percentage concerned relates to an unusual solute and will prevent it being confused with the more common solutes.

The rectangle will then appear as in Figure 14.1. Each line in it (except the first) represents a solute, and the molar percentage of that solute will be proportional to the distance of the line from that on its

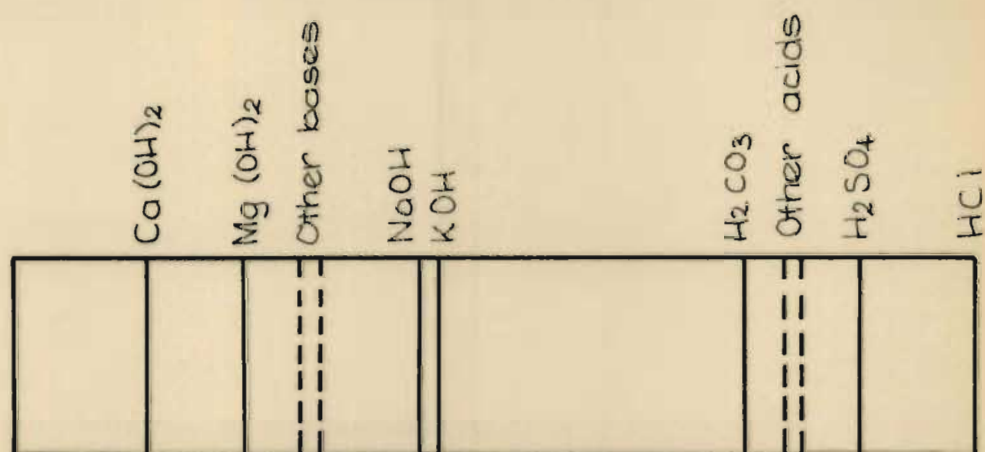


FIGURE 14.1

General appearance of molar percentage spectra



immediate left. The whole diagram will in fact resemble a line spectrum, and it is convenient to refer to it as the molar percentage spectrum of the water concerned (though, of course, it is not really a spectrum).

To complete the representation, the TDS in ppm may be written numerically to the left of the spectrum. Since the spectrum itself makes no reference to the TDS (TDS values cover too great a range to permit any direct graphical representation), this allows waters to be compared whose only difference is one of TDS. Often it may be more convenient to use conductivity instead of TDS. Similarly the pH value may be written numerically to the right of the spectrum.

The spectrum, with its associated numerical data, contains all the basic information needed to characterise the water it represents, at least as far as the inorganic solutes are concerned. If the molar percentages are subsequently read from the spectrum (with the aid of a ruler), the millimolar concentrations can be approximately obtained from the TDS by means of the relation (13.9), and from these approximate values of the ppm concentrations can be found. The total alkalinity is approximately obtained by substituting these approximate millimolar concentrations in equation (3.42) and is expressible in ppm of  $\text{CaCO}_3$  by multiplying by 50. Estimates of the hardness and soda alkalinity may then be obtained. By substituting the molar percentages themselves in equation (3.42) and dividing the result into the molar percentage of carbonic acid we have an approximate value for the  $a/e$  ratio which, under the appropriate conditions (see chapter 8) provides an estimate (after multiplying by 100) of the percentage saturation with carbon dioxide. Knowing  $\bar{e}$  and  $\bar{a}/\bar{e}$  gives  $\bar{a}$ . Approximate values of the forms of alkalinity (chapter 7) and free carbonic acid (chapter 8) may then be found, and if desired, since  $\gamma$  can be found from the TDS in the usual way, a value for  $\text{pH}_s$  can be obtained from equation (10.13).

In most cases the molar percentage spectrum will show features which, provided the above list of solutes is memorised in correct order, enable the individual lines to be readily identified without the necessity of actually labelling them on the diagram. For example, the molar percentage of potassium hydroxide is usually quite small so that this and the sodium hydroxide line form a doublet which can readily be picked out. The line to the right of this doublet will always represent carbonic acid, and this will usually be widely separated from the doublet since the molar percentage of this solute is usually relatively large. The extreme



right hand edge of the spectrum always represents hydrochloric acid. These particular lines therefore act as signposts for the identification of others. It is because of consequences such as this that the list of solutes is arranged in the particular order given above, and it is because these direct identifications will otherwise break down that the stated order must never be varied.

### Illustrations

Familiarity with molar percentage spectra can only be acquired by the study of some examples.

In Figure 14.2 are shown the molar percentage spectra of the rain, sea and world average river waters of Table 13.2 as well as of the average Natal river water (which is taken to have the composition of the mean of the 22 Natal rivers of Table 2.1, expressed in molar percentage form in Table 13.3). The differences between these spectra are very striking. The high molar percentages of sodium hydroxide and hydrochloric acid in the rain and sea water are clearly apparent, as also is the great similarity between the two waters despite the large differences in TDS and pH. Similarities between the two river analyses can also be seen, although the Natal average shows more sodium hydroxide and hydrochloric acid but less calcium hydroxide and carbonic acid than the world average. The NaOH - KOH doublets in these two spectra can be clearly seen.

The twenty-two spectra shown in Figure 14.3 relate to the Natal rivers of Tables 2.1, 8.3 and 13.3. That many of these rivers show various similarities can be seen at a glance, while the few exceptional cases (e.g. the Gogoshi) also stand out. It is interesting to note that there is some tendency for the percentage of sodium hydroxide and hydrochloric acid to be increased in the waters of higher TDS, while the percentage of carbonic acid is decreased. Clearly, however, there are many exceptions to this.

In Figure 14.4 are shown the spectra of the four rivers of Tables 8 C and 9 C, each sampled above and below sources of pollution. These plainly show the features already indicated in the previous chapter.



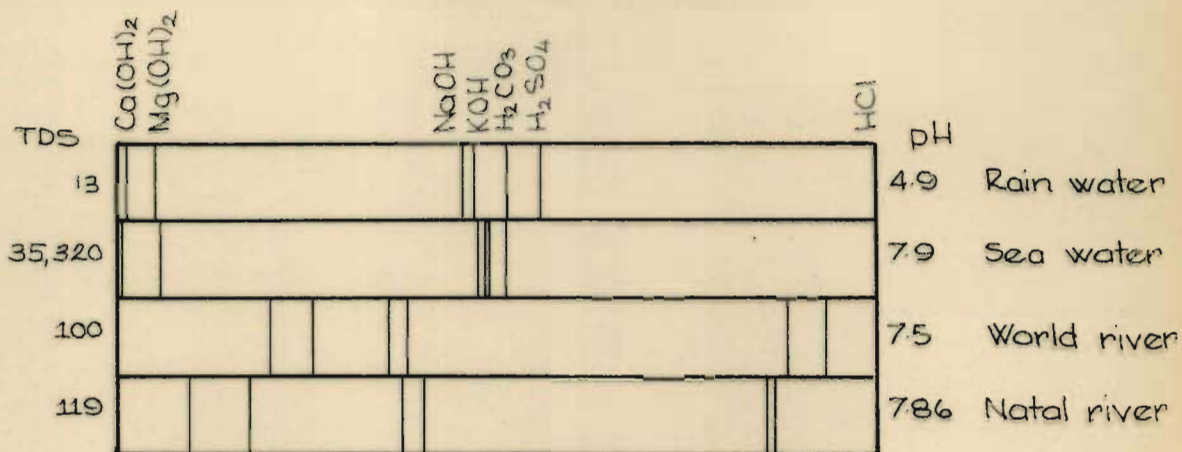


FIGURE 14.2

Spectra of rain, sea and river waters

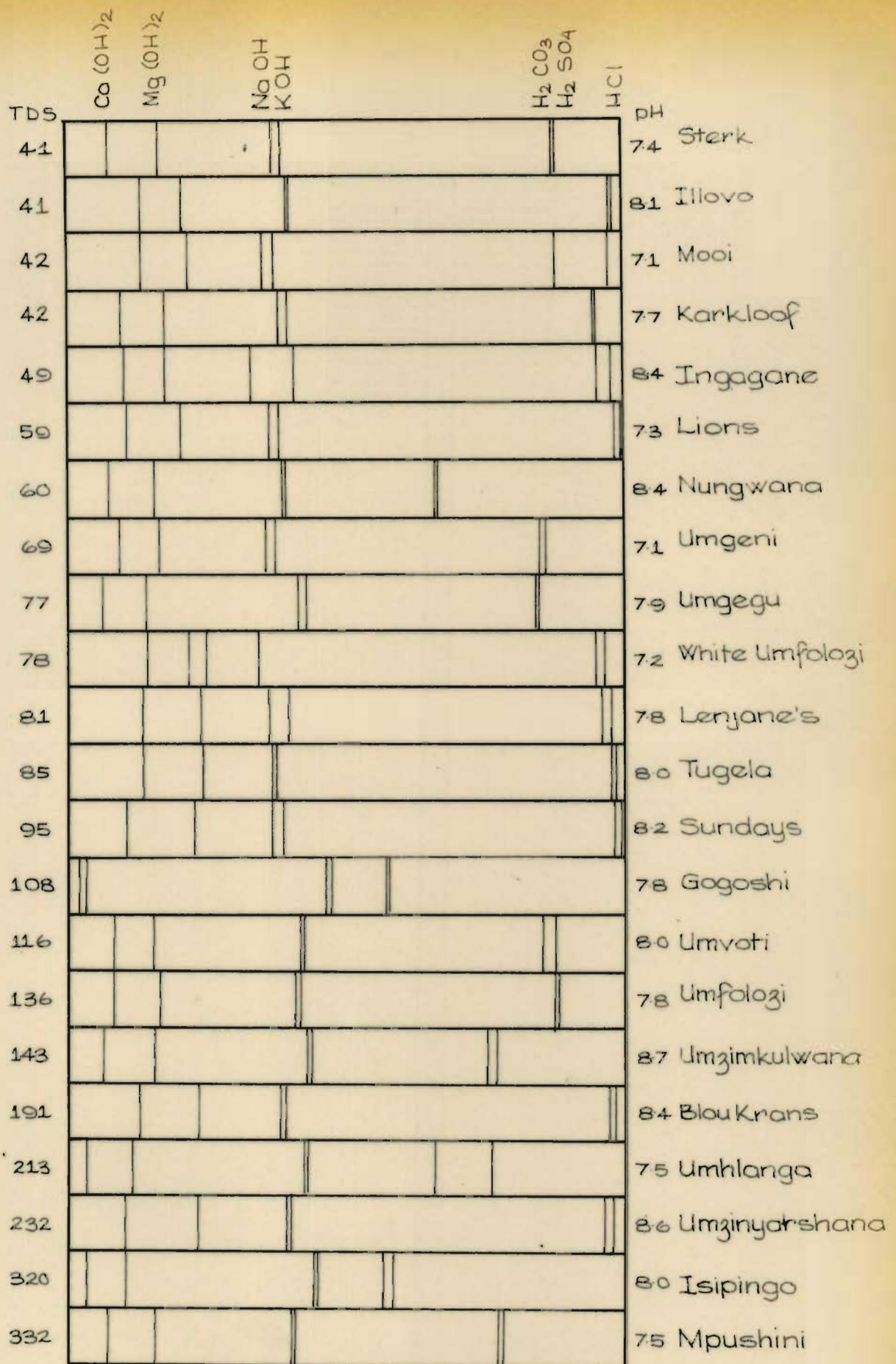


FIGURE 14.3

Spectra of Natal rivers (Table 2.1)



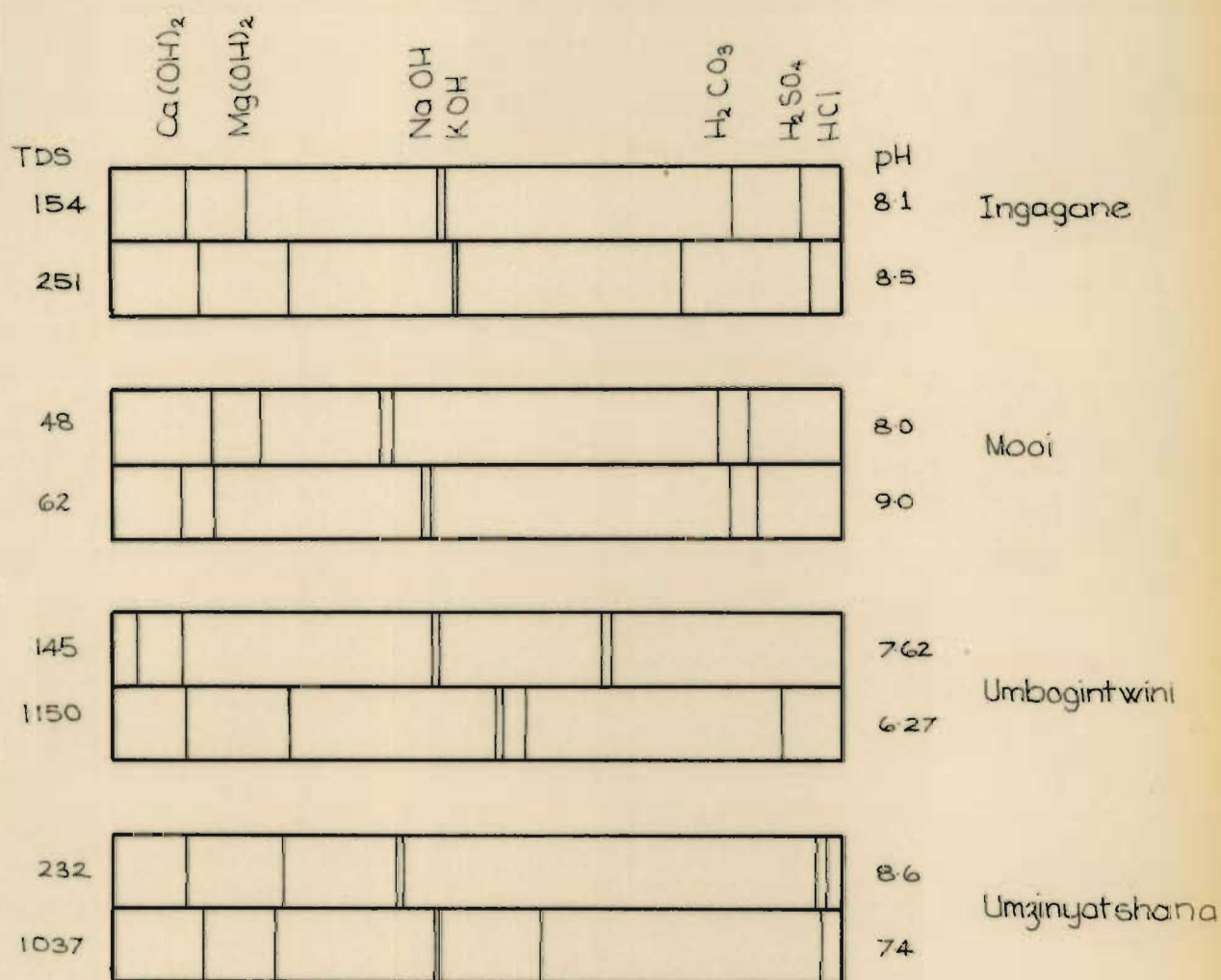


FIGURE 14.4

Spectra of rivers above and below sources of pollution

## 15. WATER SERIES

### General characteristics of Natal river waters

It is clear from the material presented in chapter 2 that the composition of a river water, i.e. the nature and amount of the substances dissolved in it, must be to some degree influenced by the geology of its catchment area, although other factors (such as climate and pedology) must be of influence also. From the information already summarised it is possible to make some brief comment on the observed compositions of the Natal rivers, and for this purpose we take Clarke's (1924 B) world average river as a standard for comparison even though this average is to some extent conjectural. The figures available to Clarke were by no means comprehensive (in particular he lacked results for rivers of Asia and Southern Africa) and he could only fill the gaps by making some assumptions. Against this world average we may set a Natal average, obtained from the data of Table 2.1 and assuming that the 22 rivers listed there form a representative sample. These two averages have already been presented in molar percentage form, but the figures are repeated in Table 15.1 for easy reference.

Table 15.1

#### Average analyses of rivers

		World average	Natal average
pH value		7.5	7.86
TDS, ppm		100	119
Molar percentages	Ca(OH) <sub>2</sub>	20.3	9.4
	Mg(OH) <sub>2</sub>	5.6	8.4
	NaOH	10.0	20.8
	KOH	2.2	1.8
	H <sub>2</sub> CO <sub>3</sub>	50.5	45.2
	H <sub>2</sub> SO <sub>4</sub>	5.0	1.3
	HCl	6.4	13.1

The following comments may be made:

#### (a) TDS

The abundant summer rainfall and the winter aridity will have



opposing effects upon the average TDS of the Natal rivers (chapter 12). The fact that most of the surface rocks of the Province comprise ancient and well leached shales, slates and sandstones suggests that the average TDS should be about 100 ppm (see chapter 12), and this agrees well with the tabulated value of 119 ppm.

(b) Calcium

The absence of any widespread limestone formations in Natal suggests a relatively low value for the average molar percentage of calcium hydroxide. In fact, the figure for the Natal rivers is almost half that for the world average, in agreement with this.

(c) Magnesium

In view of the low average TDS, the molar percentage of magnesium hydroxide in the Natal rivers would be expected to be somewhat lower than that of calcium hydroxide (see chapter 2). This is indeed the case, although the effect is very slight, the proportion of magnesium hydroxide in the Natal rivers being in fact surprisingly high.

(d) Sodium

Unexpectedly, the molar percentage of sodium hydroxide in the Natal rivers is about double that of the world average. The fact that most of the sedimentary rocks of Natal were laid down under marine conditions (du Toit, 1954) and hence doubtless contain connate sea water might be relevant here. On the other hand, sea salts derived from the Indian Ocean may be carried far inland by the strong on-shore winds which frequently arise - Bond (1946) has suggested that sodium in Natal waters up to 180 miles from the coast might originate in this way. Either of these possibilities might also explain the high proportion of magnesium hydroxide in these waters, already noted, since in sea water this solute is present in greater concentrations than calcium hydroxide (see chapter 13).

(e) Chloride

Since sodium and chloride appear to go approximately together in river waters, it is not surprising that the molar percentage of hydrochloric acid in the Natal average is about twice that of the world average. In fact the ratio  $\text{NaOH}/\text{HCl}$  of the percentages is almost equal for the two cases (Natal 1.59, world 1.56) but different from that of sea water (equal to 0.86), which in turn suggests that

the rivers do not contain sodium and chloride derived entirely from the sea.

(f) Carbonic acid

Since the pH and TDS values are much the same in the world and Natal averages, both the concentration and the molar percentage of carbonic acid in these waters would be expected to be very similar (each being in equilibrium with atmospheric carbon dioxide). This is indeed the case.

(g) Sulphate

The molar percentage of sulphuric acid in the Natal average is low. A low sulphate content has already been noted (chapter 2) as apparently characteristic of surface waters on the African continent.

These comments are, of course, very general in nature. They do not take into account the quite striking differences that arise in the chemistry of individual Natal rivers, even in the absence of pollution (see Tables 2.1 and 13.3). It might seem that such differences would be due to the fact that the catchments of individual rivers lie upon quite different geological formations. Certainly Bond (1946) has shown that underground waters derived from similar rock formations in South Africa have similar chemical features and differ from those from different formations, although there are various inconsistencies in the data. Similarly Kemp (1963) has shown that there is a tendency for some surface streams draining catchments built from particular geological formations in Natal to show similar chemical features, differing from those of streams draining catchments which are geologically different. Indeed, an attempt has been made (Brand et al, 1967), based upon this data, to "predict" the composition of rivers at particular points from knowledge of the catchment geology. However, this attempt has not proved particularly successful, since it has been found that even unpolluted waters often show quite unexpected characteristics, e.g. the Gogoshi and Isipingo rivers (Table 13.3) contain high proportions of chloride which cannot be accounted for by the geological data, the TDS of the Isipingo is very much higher than would be expected, and other examples of similar discrepancies have been noted in the publications just cited. However, the differences arising between different river waters in Natal are by no means random in nature, as will now be shown.



The series of chlorided waters

The data of Table 13.3 for 22 unpolluted Natal river waters show at once that there is no relationship at all between the TDS of the water and the molar percentage of any solute. It clearly follows that any type of Natal surface water may occur at any dilution. The TDS gives no clue to the water chemistry, nor does the chemistry to the TDS.

The solute which shows the greatest range of variation in molar percentage is carbonic acid. Owing to the arithmetical properties of percentages, if one percentage increases progressively it is obvious that some other percentage or group of percentages must progressively decrease, and it is thus of interest to enquire how the other percentages change as the molar percentage of carbonic acid increases.

If each of the other percentages of Table 13.3 is plotted against the molar percentage of carbonic acid it is found that there are several systematic variations:

- (a) the percentages of potassium hydroxide and sulphuric acid remain almost constant (apart from statistical scatter).
- (b) the percentages of calcium and magnesium hydroxide each tend to increase (the former more rapidly) as the percentage of carbonic acid increases.
- (c) the percentages of sodium hydroxide and hydrochloric acid each decrease markedly as the percentage of carbonic acid increases, the latter decreasing much more rapidly and becoming almost zero when the carbonic acid reaches 60% while the former is reduced to only about 15% at this point.

The last of these is particularly interesting since it indicates that, as the proportion of carbonic acid increases, not only is the proportion of sodium chloride in the water reduced, but also that some of the sodium chloride becomes progressively replaced by sodium bicarbonate (or carbonate, depending on the pH).

No attempt has been made to calculate regression equations for these relationships, since the scatter is in each case too great for such equations to be of much reliability, but by visually fitting "best" straight lines to the plotted data and combining these lines in the appropriate fashion, the diagram of Figure 15.1 was obtained. This is equivalent to a display of molar percentage spectra stacked one above the other,

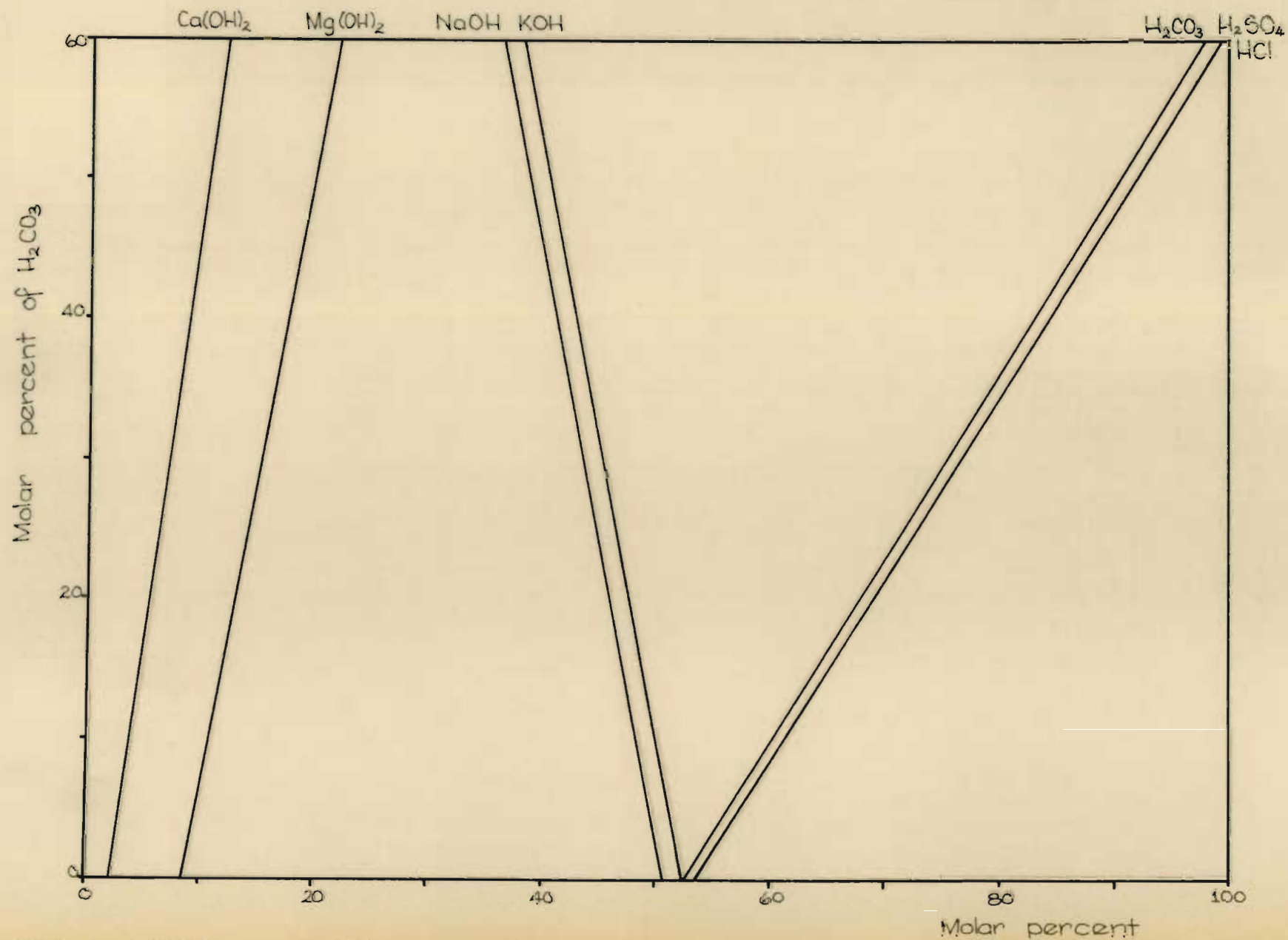


FIGURE 15.1

The series of chlorided waters



the upper ones relating to waters of high molar percentage of carbonic acid. Reading across the diagram horizontally for specific carbonic acid percentages enables the spectra to be drawn in the usual form, and in this way the spectra of Figure 15.2 have been obtained. These spectra match very closely with those shown in Figure 14.3.

In Table 10 C are given the analyses, expressed in terms of molar percentages, of 28 rivers of Natal selected from Brand et al (1967), the sole criteria of selection being that the rivers concerned should be unpolluted and their analyses fulfil the ionic balance. On comparing these with the values obtained from Figure 15.1 to match the observed molar percentage of carbonic acid, excellent agreement results and, using the usual criteria for comparing molar percentages (chapter 13), in only three instances (Umvunyama, Waschbank and Sinkwazi) is there any significant discrepancy.

It therefore seems that most Natal river waters are members of one great series of waters whose compositions are as represented by Figure 15.1, at least to a first approximation. In addition, the analyses of sea water (Table 13.2) with only 0.9% of carbonic acid and of rain water (Table 13.2) with 4.5% of carbonic acid also fit into this same series.

For convenience, this particular series of waters will be referred to as the series of chlorided waters.

#### The series of sulphated waters

It is clearly not to be considered that all surface waters should belong to the chlorided series, nor can it immediately be assumed that this series of waters exists outside Natal. It is therefore of great interest to examine the analyses of river waters from other regions.

Nordell (1951) has published the analyses of 98 river waters from the U.S.A. All this data are expressed in terms of ppm of  $\text{CaCO}_3$ , but recalculation to millimoles/litre is relatively simple. Unfortunately he does not itemise sodium and potassium separately, but it may be assumed for purposes of calculation that the molar percentage of potassium hydroxide is 1.8, as in Figure 15.1. Also, he omits to give pH values, so that accurate calculation of the total carbonic acid cannot be made, but it is clear from chapter 8 that there will be no very great error if we assume that  $e = a$  for these analyses. With these assumptions the molar percentages can be calculated, the results of the calculations being given in Table 11 C.

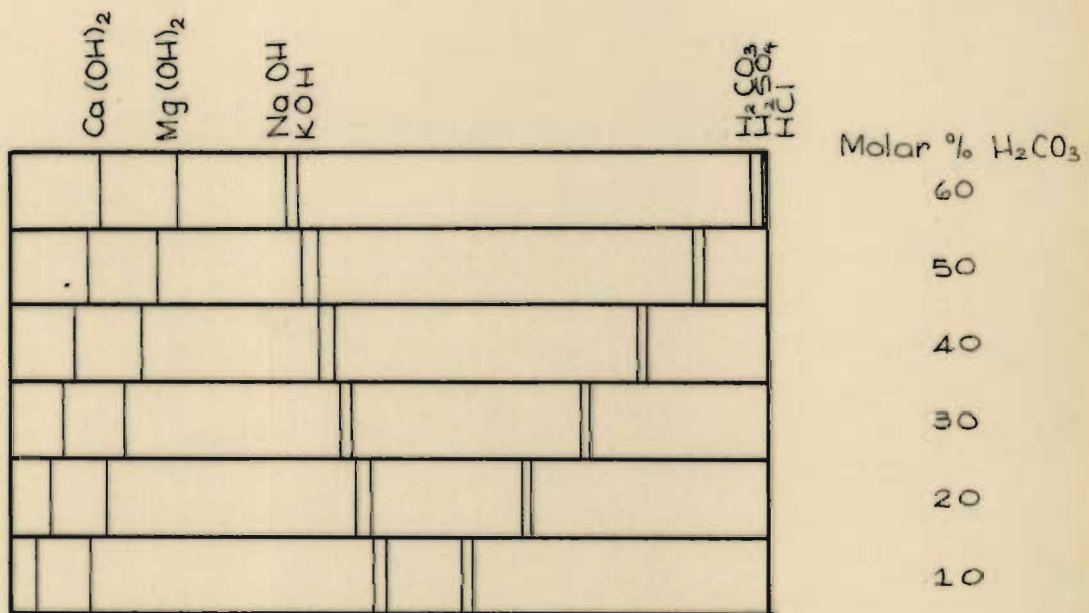


FIGURE 15.2

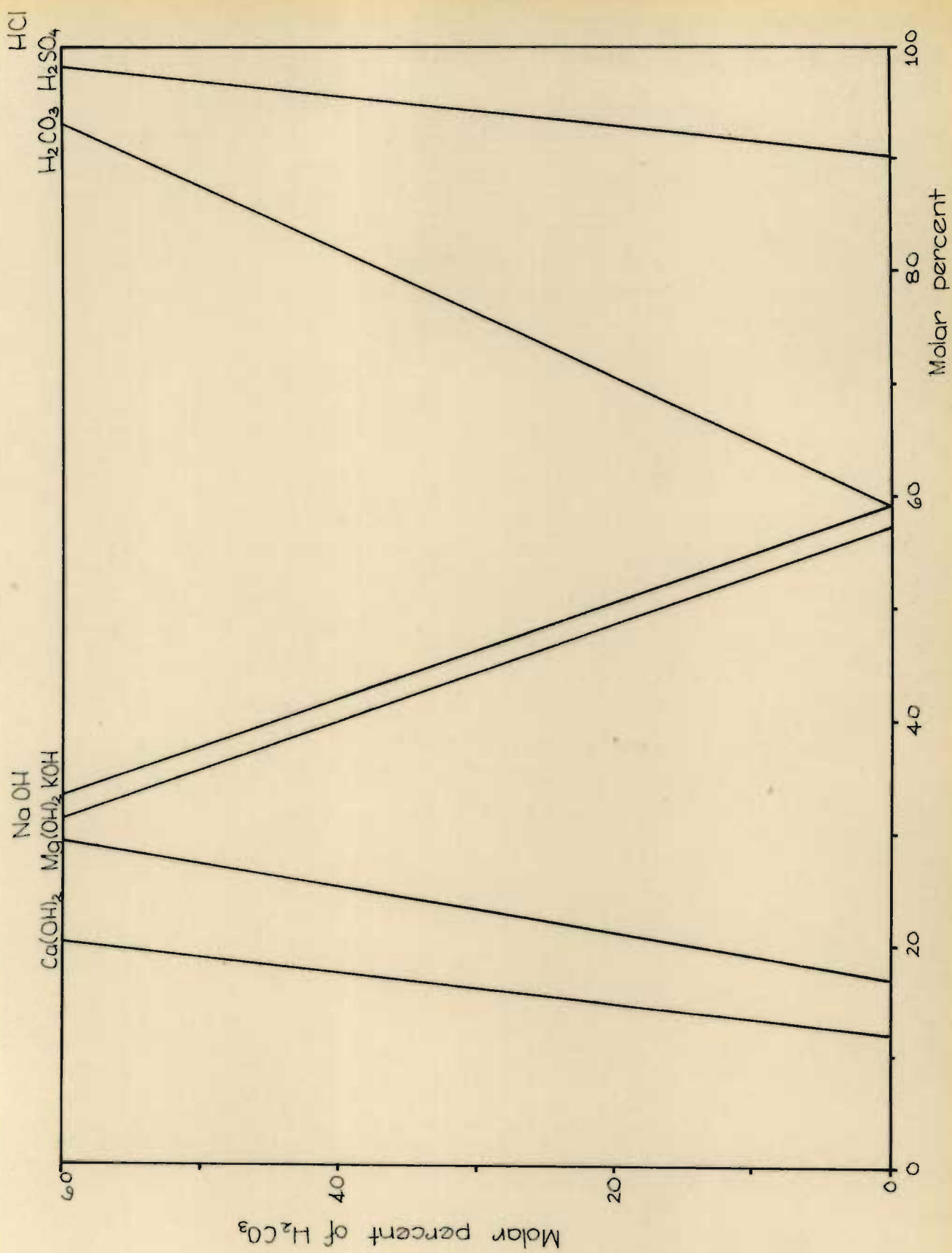
Typical chlorided molar percentage spectra



Examination of these results shows that in many instances the analyses can be fitted to Figure 15.1, i.e. waters of the chlorided series are common in America as well as in Natal. In some cases the fit is not very good, and in 40 cases there is clearly no agreement at all. These cases are marked with an asterisk in Table 11 C.

If the 40 discrepant cases are treated in precisely the same fashion as the 22 Natal rivers of Table 13.3, a diagram (Figure 15.3) can be constructed similarly to that of Figure 15.1, and this seems to represent a second series of waters which may conveniently be termed the series of sulphated waters since all its members contain greater molar percentages of sulphuric acid than in the previous case. The diagram shows that these waters (a) contain more calcium hydroxide than those of the chlorided series, (b) contain less hydrochloric acid, (c) have sodium sulphate and sodium chloride together showing the same behaviour as sodium chloride alone in the chlorided series as the molar percentage of carbonic acid decreases, and (d) contain less sodium, particularly at the higher levels of carbonic acid percentage.

It therefore appears that the sulphated waters constitute a second major series of the world's surface waters, and to seek confirmation we may now examine the data for 43 British rivers given by Taylor (1958). Taylor has expressed ~~his analyses~~ his analyses in terms of the concentrations of hypothetical dissolved salts, but recalculation is readily accomplished. Again pH values are missing from the data so that the assumption  $e = a$  must be invoked. Many of the analyses show relatively high concentrations of nitrates, but these have been disregarded in the calculations, the results of which are shown in Table 12 C. Comparing these with Figure 15.3 it is found that, except for one circumstance, 10 analyses (marked with an asterisk in Table 12 C) fit reasonably well into the chlorided series, 3 (marked with a double asterisk) are anomalous, while the remaining 31 fit reasonably well into the sulphated series. The exceptional circumstance is that in almost every case the calcium hydroxide percentage is much higher and the magnesium hydroxide percentage much lower than accords with Figure 15.3, but if only their total is considered (i.e. the total hardness) the fit is quite good. That these British rivers are anomalous as regards their silica content has already been noted (chapter 2), so it is perhaps not surprising that some other anomalies should appear as well.



**FIGURE 153** The series of sulphated waters



However, although it cannot be claimed that any really satisfactory proof has been given, these results strongly suggest that the series of sulphated waters exists and, like the chlorided series, is quite common throughout the world. It is of interest to note that the world average (Table 15.1) accords quite well with the sulphated but not with the chlorided series.

It is not possible to account for the origin of either of these two series of waters at the present time. However, it is of interest to note that, in Natal, rivers polluted by drainage from coal mines often approximate to the sulphated type. In addition, the clays of the temperate zone are known to contain much pyrite which yields sulphates on weathering, and this might explain why sulphated waters are relatively common in Britain and the U.S.A. Typical molar percentage spectra of the sulphated series, obtained from Figure 15.3, are shown in Figure 15.4.

Obviously it cannot be claimed that the chlorided and sulphated series are the only types of natural waters that exist, for Clarke (1924 B) has listed many other kinds of water. The two series do seem to represent the majority of river waters, however, and they bring together waters which Clarke separated as distinct types. It might be expected that waters of intermediate type, resulting from a mixture of waters of each series, would be fairly common, but out of all the analyses listed here only one in Table 12 C (Dee \*\*) appears to be of this nature.

#### General characteristics of the two water series

By roading off values from Figures 15.1 and 15.3 it is readily shown that all waters of the sulphated series should possess a negative soda alkalinity (chapter 11) while most waters of the chlorided series, i.e. those with a molar percentage of carbonic acid exceeding about 20, should show a positive soda alkalinity. The expected variation is shown in Figure 15.5, where the soda alkalinity has been calculated by applying equation (11.5) to the molar percentages. If the same calculation is applied to the chlorided waters listed in Tables 13.3 and 10 C, the soda alkalinity certainly shows a trend of the correct form (correlation coefficient + 0.717 with 45 degrees of freedom and hence statistically significant) but the scatter is too great for this to be of any practical utility. The existence of such a trend, however, shows that although the sulphated waters evidently have greater total hardness than chlorided waters of the same TDS, their temporary hardness will, on the whole,

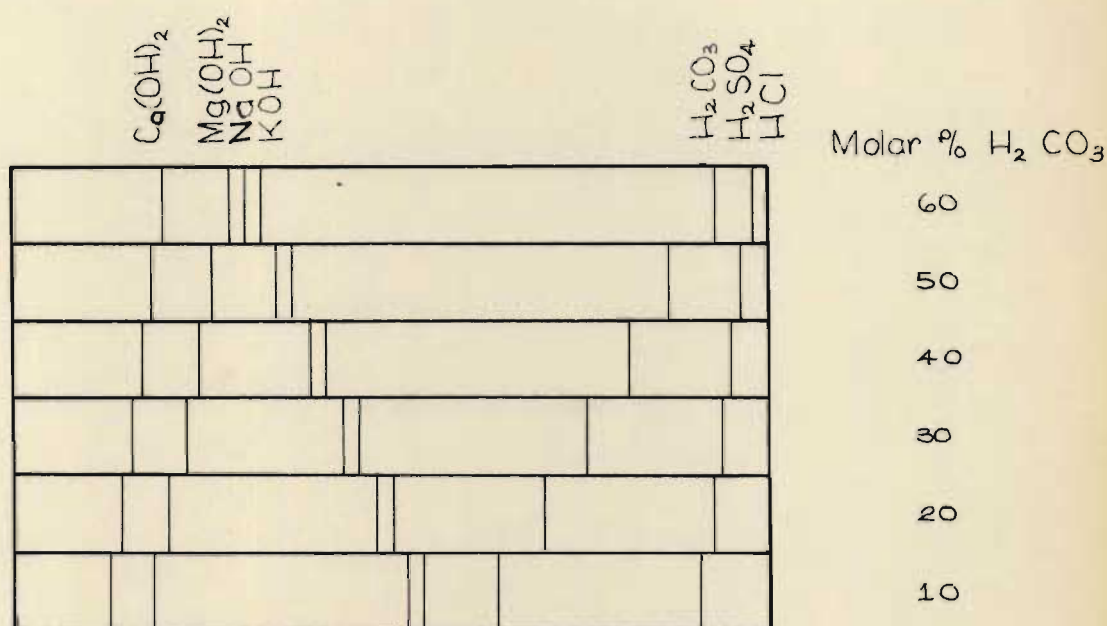
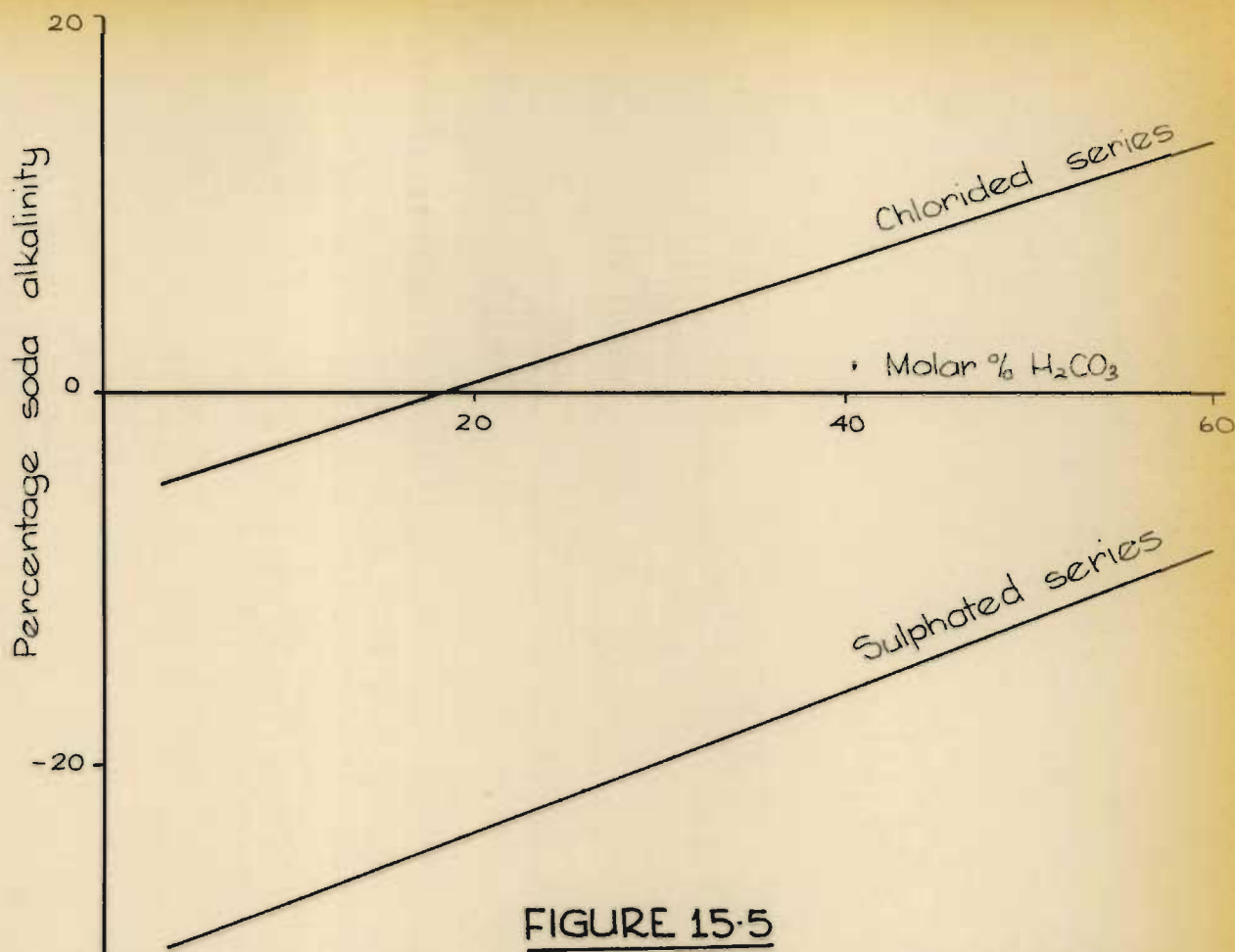


FIGURE 15.4

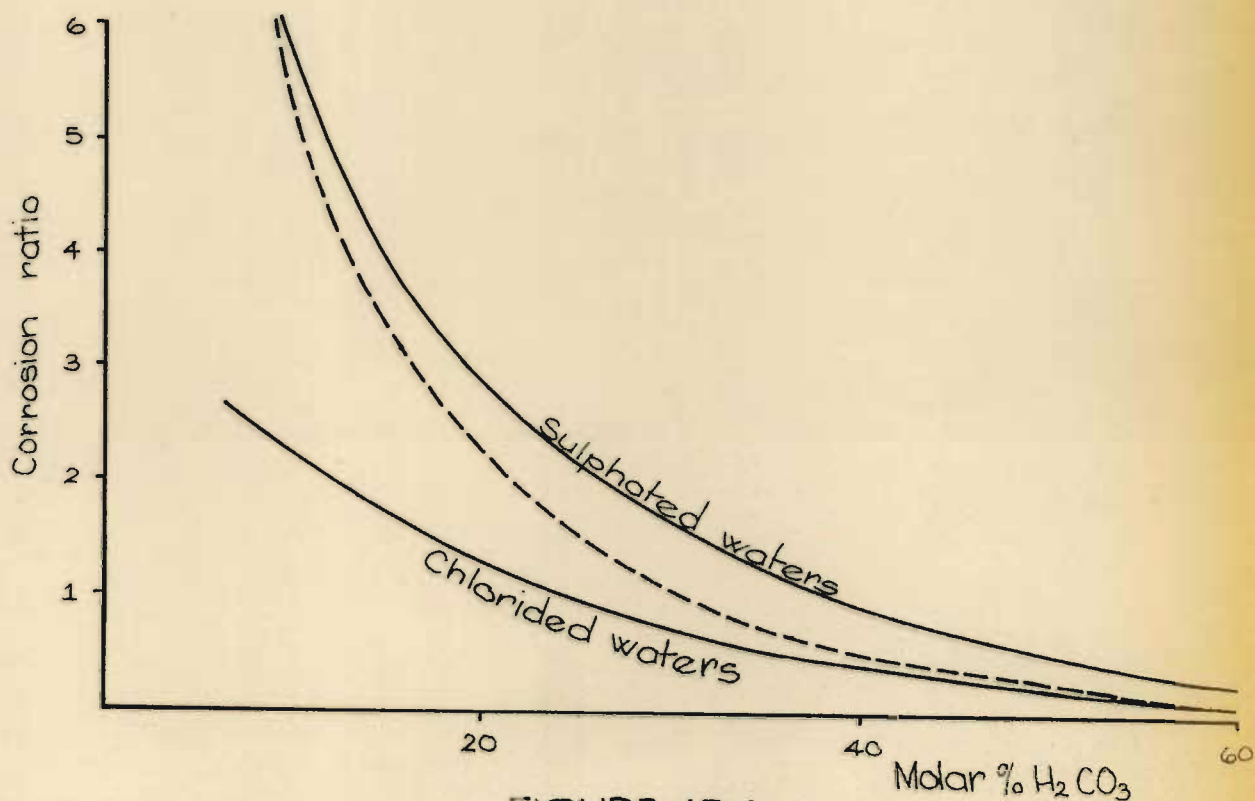
Typical sulphated molar percentage spectra





**FIGURE 15.5**

Variation of soda alkalinity with molar percentage of carbonic acid



**FIGURE 15.6**

Variation of corrosion ratio with molar percentage of carbonic acid

amount to a smaller percentage of the total hardness and hence, in absolute magnitude, may not suffer very much from that of the corresponding chlorided waters.

Since the corrosion ratio (chapter 10) is independent of the TDS (being a concentration ratio), it can be computed by applying equations (10.17) and (3.42) to the molar percentages. For each of the two series of waters, the value of the corrosion ratio then varies with the molar percentage of carbonic acid as in Figure 15.6. No water can have a molar percentage of carbonic acid much greater than 60 (for 66.7% corresponds to a pure calcium or magnesium bicarbonate solution), so that the sulphated waters, which show the higher values of R, will in general always be corrosive to metals while the chlorided waters will only be corrosive if their molar percentage of carbonic acid is less than about 50. This evidently means that most waters, of whatever series, will in fact be corrosive to metals. The chlorided waters of Tables 13.3 and 10 C in fact give values of R which lie closely on a curve intermediate between the two full curves of Figure 15.6, as shown by the broken line. The above conclusion is therefore valid.

If it is the case that a water contains 100 millimoles/litre of dissolved ionic substances, the molar percentages become identical with the millimolar concentrations. Concentrations in ppm can then be calculated and hence, using equation (4.6) and assuming an average of 16 ppm of silica (chapter 2), so also can the TDS. Concentrations at other TDS values can then be found with good accuracy by proportion, and in particular the calculated values of Ca and A can be used in equation (10.13), in conjunction with values of  $\gamma$  from Table 2 B, to find the saturation pH value,  $\text{pH}_s$ . The results of such calculations are summarised in Figure 15.7. It will be seen that the  $\text{pH}_s$  decreases with the molar percentage of carbonic acid but decreases as the TDS increases, and also that the  $\text{pH}_s$  values for chlorided and sulphated waters of the same TDS are very little different. Since most of these waters have pH values in the range 7.0 to 8.5, it is evident from Figure 15.7 that almost any water of either series with TDS less than 100 ppm will be under-saturated with calcium carbonate, whereas at higher levels of TDS the controlling factor will be the molar percentage of carbonic acid.

The buffer capacity,  $\bar{B}$ , at a given pH value will evidently show a linear dependence on both the TDS and the molar percentage of carbonic acid, and the relationship will be precisely the same for the chlorided



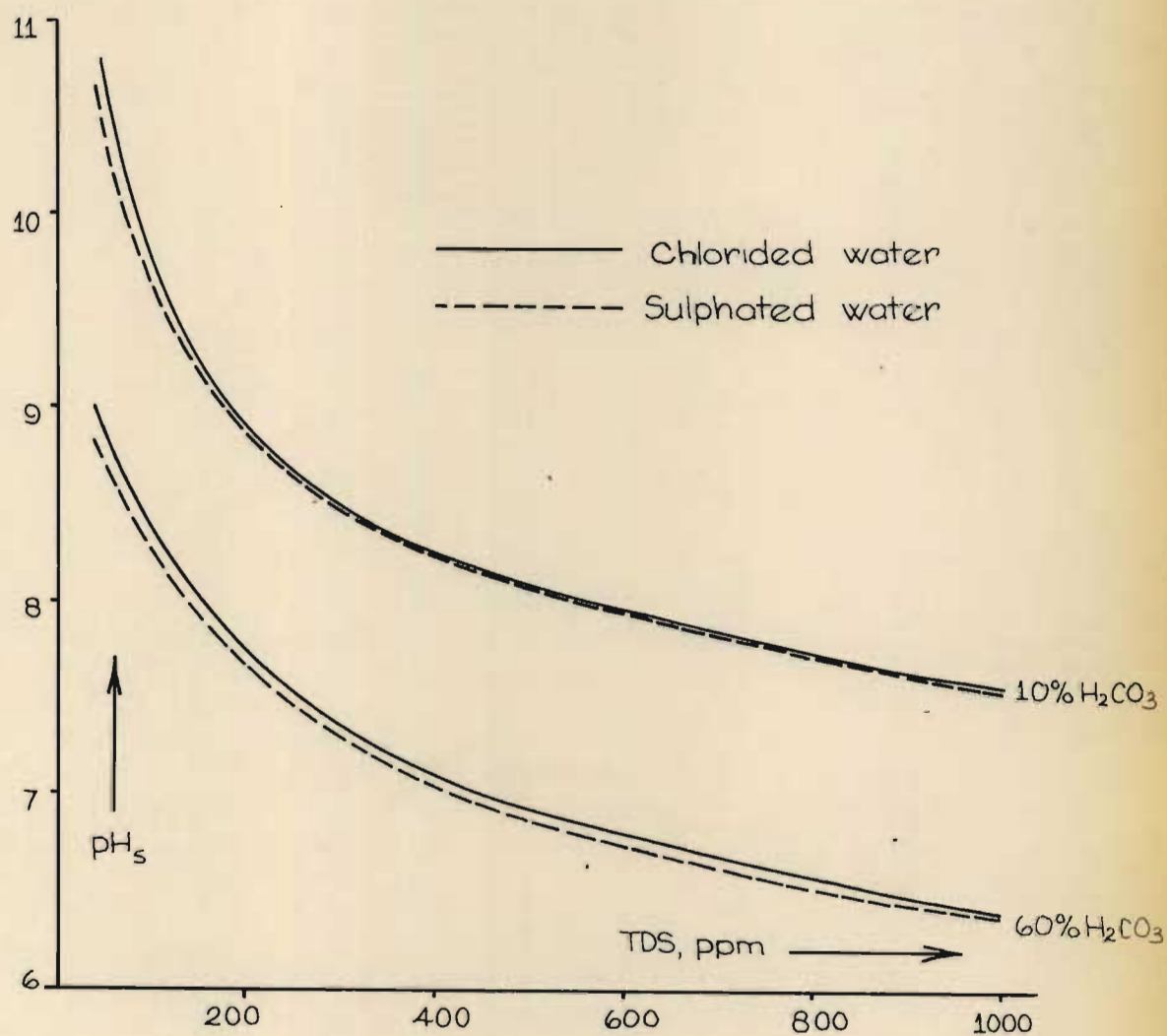


FIGURE 15.7  
Variation of  $pH_s$  with TDS

as for the sulphated series.

It is interesting to note that, taking the electrical conductivity to be proportional to the TDS, the curves of Figure 15.7 can be represented by an equation of the form (10.16), the constant  $X$  being a function of the molar percentage of carbonic acid. Taking this function to be linear, as a first approximation, the calculated values of Figure 15.7 can be represented by:

$$\text{pH}_s = 13.95 - 0.03 (\% \text{H}_2\text{CO}_3) - 1.85 \log C \quad (15.1)$$

where  $C$  is the electrical conductivity in micromho and is taken as 1.5 times the TDS in ppm. For the 22 rivers of Table 2.1, using the values of the carbonic acid percentage in Table 13.3 and comparing the  $\text{pH}_s$  values with those accurately calculated in Table 10.1, it is found that the above equation gives results with a root mean square error of 0.36. This is considerably less than that for equation (10.15), as was expected. However, the new equation is of no greater practical value since the percentage of carbonic acid cannot be known unless a full analysis has been carried out, and in that case it is evidently more satisfactory to calculate the  $\text{pH}_s$  accurately from equation (10.13).

Both chlorided and sulphated waters show very similar characteristics as regards those properties of technological interest (hardness, corrosion ratio, buffer capacity and  $\text{pH}_s$ ). This is because all these waters have a certain close similarity in chemical composition, although naturally this is not true if we consider waters of abnormal analysis such as caused by appreciable pollution or other agencies. However, previous chapters have shown that TDS is important to all these technological properties. Consequently it may be concluded in general that, provided the abnormal waters are not considered, these properties are governed principally by the TDS of the water.



## 16. CHEMICAL CLASSIFICATION OF RIVER WATERS

### General

We are now in a position to consider the classification of river waters on a chemical basis.

River waters can be classified in various different ways, depending on the application for which the classification is designed. Thus Clarke (1924 B) has established a classification according to the inorganic salts dissolved in the water, Kolkwitz and Marsson (1908, 1909) followed by later workers such as Liebmann (1951, 1955) have formulated classifications based on the oxygen chemistry of the water and its flora and fauna, Beak (1964) has used a purely hydrobiological classification, Klein (1957) quotes a classification due to the Royal Commission on Sewage Disposal and some variations of it which virtually consider only the presence of organic matter in the water, Horton (1965) classifies rivers by means of an index number based not only upon the water chemistry but also geographic knowledge of their catchments, and Wilcox (1948, 1955) and other workers (see references cited by McKee and Wolf, 1963) have classified waters for use in irrigation, confining their attention to the inorganic solutes. There is a distinct need, however, for a classification of general scope that gives an overall picture of water quality and relates directly to potential water use.

Unfortunately "water quality" is an ambiguous term which cannot be precisely defined without reference to some specific use of the water (Hoak, 1953). It is not synonymous with purity (distilled water is very pure but has corrosive and solvent properties which make it unsuitable for many uses) nor with freedom from pollution (a mineral spring may be unpolluted and yet be unsuitable for most uses because of its excessive content of dissolved salts). Moreover, different water uses have different water requirements, so that what is considered "good" quality for one purpose may be "poor" for another, e.g. McKee and Wolf (1963) quote specifications which require a total alkalinity of 80 - 150 ppm as  $\text{CaCO}_3$  for brewing dark beer, 75 - 80 ppm for brewing light beer, and not exceeding 60 ppm for laundering.

It is thus clear that any practical classification of river waters according to quality must be to some extent artificial. This is no real defect if the basis of the classification is sufficiently clear.

### Water quality

Evidently very many factors have to be taken into account in assessing the suitability of a given water for a particular use, and a scheme of classification which attempted to incorporate them all would be far too complicated for practical use. It is therefore a practical necessity to select a small number of parameters which are independently variable, each of them individually having a major bearing upon water use.

With the proper choice of parameters it will then be possible to make an assessment of the potential uses of the water (though other factors must be considered before any finality becomes possible), and water quality can then be defined in terms of broadness of potential water use. In particular, it follows that water which is suitable for drinking will automatically be regarded as of high quality, since such a water is also suitable for almost any other domestic, industrial, agricultural and recreational use.

From chapters 9, 11 and 15 it is clear that the TDS of the water must be of major importance in such a classification since it influences the hardness,  $\text{pH}_s$  and buffering power, which are themselves parameters of great practical interest. It is certainly of importance in connection with the suitability of the water for drinking, since it is generally considered (S.A. Bureau of Standards, 1951; World Health Organisation, 1961; Henzen and Stander, 1962; U.S. Public Health Service, 1962) that, because of the physiological effect of water containing a high proportion of dissolved salts, water of TDS exceeding 500 ppm is not suitable for drinking unless no other source of supply is available, and that water with more than 1000 ppm TDS is not suitable for drinking at all.

We have seen that natural waters, by and large, are all very similar in chemical composition. It follows that, provided the TDS is acceptably low, the actual analysis of the water has little relevance to its suitability for drinking (except for the possible presence of certain elements such as fluorine, zinc, copper, arsenic, etc. and toxic organic substances), nor does it have much influence on hardness,  $\text{pH}_s$  and buffering power. Further, if a water has been polluted by inorganic substances, this usually results in an increase of the TDS, and in general any resulting unacceptable values of pH, alkalinity, hardness, sulphate content, etc. are reflected in abnormally high TDS values.

Therefore the TDS is certainly one of the factors that must be



utilised in assessing potential water use and hence water quality.

In fact there are only two other factors, also of major importance but independent of the TDS, that need to be considered. These are the dissolved oxygen concentration and the content of organic matter. These are topics not yet discussed in the present work, which is mainly concerned with the inorganic chemistry of river waters, so some brief account of them must be given for the sake of completeness before proceeding further.

#### Oxygen relationships in rivers

Organic material in a river becomes oxidised in course of time and converted to simple mineral substances. Bacteria initiate this conversion and proliferate, utilising the organic materials as foodstuffs, but because the processes of breakdown require oxygen the result is to decrease the dissolved oxygen (DO) content of the water, even to the point where anaerobic conditions arise if there is sufficient organic material present. However, as the organic matter is consumed, the DO is eventually replenished from the atmosphere. Algae usually become established below the anaerobic zone, contribute to the oxygen replenishment by their photosynthetic activities (which can cause the DO at a particular point to follow a diurnal cycle of variation since photosynthesis changes its rate with the intensity of the incident light) and proceed to remove nitrates, phosphates and other essential plant nutrients from the water. Bacterial feeders, such as protozoa, which are prolific while the bacterial population remains high, are replaced by algal feeders (insects, crustaceans, snails and some fish) and the water eventually returns almost to its original condition. The TDS, however, usually shows some increase, for once mineral salts are formed in solution they remain.

These are the processes of self-purification. They respond to changes in temperature and also proceed more rapidly in shallow and turbulent streams because oxygen can be more readily taken up by turbulent water and there is increased opportunity for organic material to be brought into contact with the sides and bottom of the channel, the surfaces of rocks and debris and the leaves and stems of growing aquatic plants, all of which may become covered with a zoogloal slime in which intense biological activity can occur to promote the rapid removal of organic material from the water. In a country such as South Africa where water is often in scant supply and has a limiting effect on almost every form of economic



development, the self-purifying powers of the rivers rank as a national asset and merit very careful preservation (Stander, 1959). In some countries the rivers were at one time assumed to be a relatively simple and inexpensive means of disposing of wastes of all kinds, but the consequence was that the self-purifying powers of the water became completely over-taxed and pollution reached alarming proportions, the river waters being made unfit for any uses whatsoever and very complex problems of water supply and waste disposal being created. Some such problems are already appearing at some localities in South Africa.

The decomposable organic material in a water is indirectly measured by the biochemical oxygen demand (BOD), which is essentially the respiratory oxygen consumed under standard conditions (5 days at 20°C in the dark) by aerobic micro-organisms in or added to the water (American Public Health Association, 1965; Ministry of Housing and Local Government, 1956; Society for Analytical Chemistry, 1958). Though open to a number of objections, both theoretical and practical, the BOD provides a measurement more related to the conditions and processes occurring in organically enriched water than do other experimental quantities which involve chemical oxidation by means of permanganate or dichromate or by combustion. It provides a link between river chemistry and hydrobiology in that it gives values which are reasonably reproducible for surface waters and which relate quite closely to the composition and structure of the faunal population at the point of sampling.

Streeter and Phelps (1925), during a survey of the Ohio river, proposed a simple mathematical formulation linking the DO and BOD of an organically enriched or polluted river. This has given rise to a very extensive literature which need not be reviewed in detail here. The essential ideas involved are (a) that the BOD decays exponentially by a kinetically first order process governed by a rate constant  $k_1$ , (b) that removal of BOD entails the consumption of an equivalent amount of DO, and (c) that the DO of the water is replenished from the atmosphere by a first order process governed by a rate constant  $k_2$ . These lead to a differential equation which can readily be integrated to show the DO as a function of time or of distance downstream from the point of entry of the organic material, as in Figure 16.1. This shows a typical oxygen sag, the DO falling at first as demand exceeds supply, passing through a minimum and then rising as it is replenished from the atmosphere, while the BOD itself decreases exponentially.



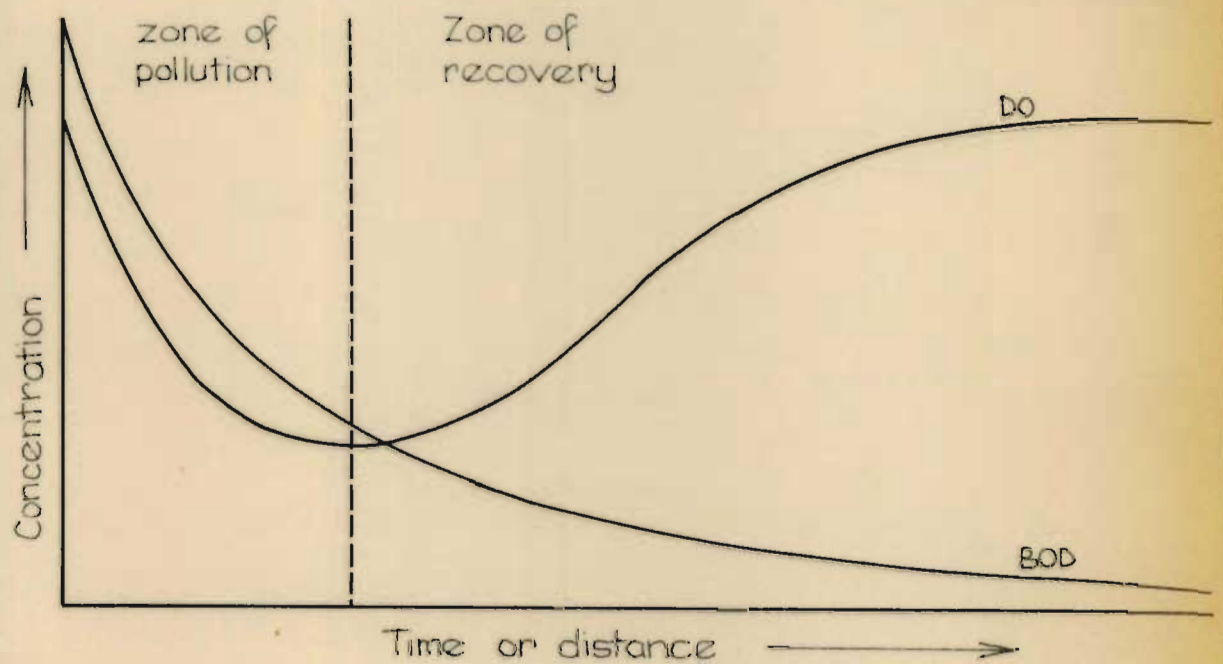


FIGURE 16.1

Typical oxygen sag curve and BOD profile

Streeter and Phelps (1925) found the rate constant  $k_1$  to have the value  $0.1 \text{ day}^{-1}$  (in terms of decadic logarithms) from experiments in the laboratory. Many workers have studied the value of the rate constant  $k_2$ , and among the more recent results may be mentioned those of Owens, Edwards and Gibbs (1964) who gave the equation:

$$k_2 = 9.4 U^{0.67} h^{-1.85} \text{ day}^{-1} \quad (16.1)$$

where  $U$  is the mean velocity of the stream in ft/sec and  $h$  the mean depth in feet ( $U$  in the range 0.1 - 5.0 ft/sec and  $h$  in the range 0.4 - 11.0 ft). When the theory is applied to rivers, however, rather different values of  $k_1$  are often found (Thomas, 1948). This is not surprising in view of the fact that the simple oxygen sag equation ignores the removal of BOD by deposition and adsorption (i.e. without consumption of DO), takes no account of the oxygen demand of sludge banks, does not consider the resuspension of deposited organic material and makes no attempt to allow for the generation of oxygen by photosynthesis (such matters have been included in a more complex formulation by Dobbins, 1964). Even the kinetic assumptions underlying the constant  $k_1$  have been called into question (Stones, 1963; Re Velle, Lynn and Rivera, 1965).

Although the quantitative aspects of the simple oxygen sag theory are therefore not well founded, it is clear that it does give a correct qualitative picture of the self-purification process. Below the entry of organic material a river shows a zone of pollution where the BOD remains relatively high while the DO decreases to a minimum. This is followed by a zone of recovery where the BOD decays to vanishing point while the DO rises again to its normal level. The later, more complex and more accurate theories of oxygen sag do not disturb this simple overall picture.

Very little work on oxygen sag has been undertaken so far in South Africa despite the importance of the subject to water supply and pollution control problems. It has been noted, during river surveys in Natal, that even grossly polluted rivers often recover within 10 miles, in contrast with the experience of various American workers who have usually observed that their larger and slower rivers require much larger distances. This appears to be due in part to the fact that the Natal rivers are shallow and flow swiftly and turbulently, thus exhibiting much larger values of the reaeration constant  $k_2$ . Some preliminary results



obtained by the writer at the start of a programme of investigation of oxygen sag in Natal have also shown that the rate of non-oxidative removal of BOD from the water can be extremely great, leading to apparent values of the BOD constant  $k_1$  up to ten times greater than the usual  $0.1 \text{ day}^{-1}$ . This also is probably a consequence of very turbulent flow (Velz and Gannon, 1963).

As regards water quality, it is evident that water with a relatively high BOD must be regarded as very poor. Such a water is likely to give rise to biological growths in reticulation systems, to develop a reduced DO on standing and to develop unpleasant tastes and odours (even if it does not become completely anaerobic). Usually it will require special treatment to render it suitable for domestic and industrial use. Moreover, a high BOD is not usually due to natural causes, and its presence therefore indicates that the water has most likely been polluted in some way and that its use as a source of water supply must necessarily be viewed with suspicion. Certainly a water of this nature will be quite unfit for drinking.

On the other hand, a water with a relatively low DO but without a high BOD might well possess taste and odour and be bacteriologically or otherwise unsuitable as a source of supply, but it should be regarded as of somewhat better quality since it will usually have come from the recovery zone of a river. It would not require such extensive treatment before use, biological growths should present less problems and pathogenic bacterial counts should generally be lower.

#### Scheme of classification

The above considerations lead to the recognition of various different types of natural waters, which may be distinguished as follows:

##### 1. According to TDS

- (a) SOFT waters with TDS less than 100 ppm.

These waters have very low hardness, possess scale-dissolving properties (relatively high  $\text{pH}_s$  and negative saturation index) and low buffering power so that they are difficult or uneconomic to treat by the usual methods of  $\text{pH}_s$  correction. They are all potentially suitable for drinking (i.e. provided they also fulfil accepted criteria independent of the TDS) and for all other uses.

- (b) NORMAL waters with TDS between 100 and 500 ppm.

These are soft to moderately hard waters, fairly well buffered and usually scale-dissolving, but they are readily treated by the usual methods of  $\text{pH}_s$  correction and again are potentially suitable for drinking and all other uses.

- (c) HARD waters with TDS between 500 and 1000 ppm.

These waters are not usually markedly scale-dissolving nor scale-forming. They have high hardness and are well buffered, and hence are not difficult to treat if necessary by the usual methods of  $\text{pH}_s$  correction, but they may require relatively high dosages. They are not considered potentially suitable for drinking or domestic use unless no other source of supply is available. They may not be suitable for agriculture (except perhaps irrigation) but are potentially usable for many industrial purposes.

- (d) MINERALISED waters with TDS exceeding 1000 ppm.

These are usually hard, scale-forming waters, not suitable for drinking or domestic use and probably not acceptable for agricultural or industrial use.

## 2. According to BOD

- (a) PURE waters with BOD less than 1.5 ppm.

The surface waters of highest quality fall in this class, and in Natal they are the completely undisturbed waters found in the mountain streams at the head of many of the rivers (Brand et al, 1967).

- (b) CLEAN waters with BOD between 1.5 and 3.0 ppm.

This group includes the majority of the river waters in Natal (Brand et al, 1967). These waters are all of quite good quality but not of such excellence as those of the Pure group.

- (c) POOR waters with BOD between 3.0 and 5.0 ppm.

In Natal these waters are usually polluted to a small degree (Brand et al, 1967), but not to the extent that they are unsuitable for a wide range of uses. A BOD exceeding 3.0 ppm may give rise to some difficulties in conventional water treatment plants (see references given by McKee and Wolf, 1963).

- (d) SULLIED waters with BOD between 5.0 and 15.0 ppm.

These are mostly polluted waters, liable to possess tastes and



odours and to show high bacterial counts, and streams carrying such waters invariably show a characteristic fauna. The waters will often be low in dissolved oxygen, although the majority of shallow, fast-flowing rivers in Natal will not become anaerobic at such a BOD level. These waters are not suitable for any use except perhaps irrigation.

- (e) FOUL waters with BOD exceeding 15.0 ppm.

These are all heavily polluted waters, not suitable for any use except perhaps irrigation, and are all very low in oxygen, often anaerobic.

### 3. According to DO

- (a) OXYGENATED waters with DO at least 60% of saturation.

These are acceptable, other things being equal, as sources of supply.

- (b) DEOXYGENATED waters with DO less than 60% of saturation.

These are not acceptable as sources of supply because they are liable to become anaerobic on standing in reservoirs, tanks and pipes, hence developing tastes and odours, as the oxidation of organic material occurs. Although it is fairly simple to raise the DO during treatment, a deoxygenated water has usually been polluted in some way and cannot be accepted as safe for many uses without further investigation.

The TDS, BOD and DO are thus the three parameters by means of which water use is to be assessed and hence water quality characterised. Since they can vary independently, taking all three parameters into account gives rise to 40 different water types. However, these are 40 different chemical types and do not immediately relate to water use; thus they are not to be taken as 40 different grades of water quality.

When the characteristics of each of these 40 types are considered separately, it can be seen that it is possible to combine them so as to form six larger classes according to their potential uses. This combination can be achieved through the following scheme:

		Pure	Clean	Poor	Sullied	Foul
Oxygenated	Soft	I	II		V	VI
	Normal					
	Hard	III				
	Mineralised	IV				
Deoxygenated	Soft					
	Normal					
	Hard					
	Mineralised					

From Class I to Class VI the potential uses of the waters become progressively restricted, so that according to definition the water quality progressively falls off. The six classes are thus classes of water quality, and their characteristics may be summarised as follows:

CLASS I Waters of the highest possible quality which should be preserved from any form of pollution. Potentially suitable for all uses. In Natal these are the waters of most mountain streams and river headwaters, and many are scheduled trout streams. Their class comprises the OXYGENATED SOFT PURE waters.

CLASS II Waters of good or reasonably good quality, potentially suitable for drinking and any other use after appropriate treatment. Generally the greater the degree of organic enrichment, the more extensive will be the treatment required. These waters make up the majority of the rivers of Natal. They comprise the OXYGENATED waters of the SOFT CLEAN and POOR groups and the NORMAL PURE, CLEAN and POOR groups.

CLASS III Waters which are not considered suitable for drinking or domestic



use unless no other source of supply is available. They may not be suitable for some agricultural uses but can be used for many industrial purposes. They are the OXYGENATED waters of the HARD PURE, CLEAN and POOR groups.

CLASS IV Waters which are not suitable for drinking or domestic use and which are probably not acceptable for industrial or agricultural use, except perhaps irrigation. These are the OXYGENATED MINERALISED waters of the PURE, CLEAN and POOR groups (not necessarily polluted waters) and all DEOXYGENATED waters of the same groups (most of which are polluted waters but not common in occurrence).

CLASS V Waters which are mostly polluted and which are not suitable for any use except perhaps irrigation. They comprise the SULLIED waters of any group, and active efforts should be made to improve their quality where possible so as to increase their potential usefulness.

CLASS VI Waters carrying heavy organic pollution, not suitable for any use except perhaps irrigation and which can constitute public health hazards or public nuisances. These are the FOUL waters of any group, and active efforts should be made as a matter of urgency to improve their quality.

It must be stressed that any such scheme of classification, because it can necessarily only deal in generalities, can only be taken as a guide and not as a final criterion. Thus, although waters of Classes I and II are described as potentially suitable for drinking, this potentiality will only be an actuality if the water fulfils other accepted standards for trace elements, bacteriology, etc. In other words, when a specific problem of water use is encountered the classification can be of considerable assistance but, in the last analysis, each case must be treated on its own merits.

There are still several matters that need to be considered before the proposed classification can be regarded as fully satisfactory. When it is applied to individual water samples there is no difficulty, for the scheme will unambiguously classify the quality of the water that is actually in the sample bottle. Difficulties arise when attempts are made to classify a river rather than individual samples of its water.

For example, the inherent variability of river waters means that a certain stream, normally providing water falling in, say, Class II, may occasionally carry water of Class III. If the necessary data were available (it would require a team of men working for several years), it might be possible to decide on such a rule as allocating the water at one particular point on a river to that class in which 80% of all the samples fall. But so far the necessary data is not available and, through shortage of man-power, rivers in South Africa have to be classified on the evidence of a very limited number of samples. At the present time it seems best to classify a river according to the worst water sample that it has provided, although admittedly this introduces a degree of bias into the final result.

Since a chemical sample reveals the condition of a river at a given point at the instant of sampling while samples of the flora and fauna of the river reveal the conditions prevailing during the immediate past, it is in principle possible to use biological samples to supplement chemical ones and so obtain some idea of the variability of some of the water quality parameters. This possibility is being investigated (S.J. Pretorius, private communication), but no final conclusion has yet been reached. Biological sampling presents its own characteristic difficulties, and a far greater knowledge of the ecology of the different species inhabiting rivers and river beds than hitherto exists is necessary before any of the results can be adequately interpreted.



## 17. SOME PARTICULAR NATAL RIVERS

### Introduction

To illustrate various points from the preceding chapters, some examples will now be given, drawn from the results of surveys that have been made of the rivers of Natal (Brand et al, 1967). Each example has been chosen as representative of many other streams of similar chemical characteristics. The examples comprise the Illovo river as typical of a clean Natal river, the Nonoti river as typical of a river receiving organic pollution, the Umfolozi river which in some parts contains highly mineralised water, and a set of small coastal rivers which exhibit certain characteristic peculiarities.

The chemical results cited will be confined to those relating to the topics that have been considered in the earlier chapters, since it is not the aim of the present work to give a detailed account of river pollution, i.e. details of the chemical composition of specific types of polluting effluents and their effects upon the receiving water. A brief account of the wider range of chemical determinations that are usually employed in river surveys has been given elsewhere (Kemp, 1967).

In conclusion, a brief general summary of river water quality in Natal is presented.

### The Illovo river

The Illovo river rises at an altitude of just over 5000 ft near Keerom, about 4 miles north-east of Byrne. It meanders markedly, but its course generally runs east south-east. After 4 miles it has dropped to 3500 ft and passes through Byrne and then, after a further 6 miles, through Richmond. The river then flows for some 38 miles before it enters a deep gorge-like valley cut into hilly country, the gradient steepening sharply so that the water drops about 500 ft over 2 miles of flow. After flowing a further 20 or more miles through this valley, it emerges on to the flatter country of the coastal region at about 600 ft and finally enters the Indian Ocean after a total length of flow of 82 miles. The catchment area amounts to 361 square miles.

In the upper part of the catchment, down to the vicinity of Mount Misery, about 15% of the total area is arable land, the rest being equally divided between natural veld or bush and forestry. The Umlazi

Location 4676 occupies the rest of the catchment to within a few miles of the coast. Finally the river crosses a narrow belt of sugar fields and passes a sugar mill before entering the urbanised coastal area in its lowest mile of flow.

Table 17.1 gives the chemical results obtained in the dry season of 1964 for seven sampling stations:

- (1) Above Byrne
- (2) Above Richmond
- (3) Below Richmond
- (4) Rosebank
- (5) Shiri
- (6) Above mill
- (7) Below mill

It is clear from the analyses that the water of this river down to station 5 is of Class I quality, just comes into Class II at station 6, and at station 7 it is degraded to Class VI on account of the very high BOD. The DO at this station is also low and the pH value decreased.

The molar percentage spectra are shown in Figure 17.1, and down to station 6 are those of typical chlorided waters, with markedly decreased proportions of carbonic acid at stations 5 and 6. Station 7, however, gives an anomalous spectrum out of line with the progressive downriver changes shown by the higher stations.

The values of various parameters calculated from the analyses are shown in Table 17.2. Both the free carbonic acid and the percentage saturation with carbon dioxide are significantly high at station 7 (exceeding 6 ppm and outside the range 95 - 120% respectively - see chapter 8). The  $pH_s$  is high at all stations and the saturation index is negative, but the corrosion index is fairly low down to station 5 so that corrosivity should not be much of a problem with the water of this river. The water is soft at all stations, the temporary hardness is low and the buffer capacity appreciable.

The Illovo is thus a river of high water quality, although it is heavily loaded with organic material in its last mile or so.

#### The Nonoti river

The Nonoti river rises at an altitude of about 1300 ft some 14 miles from the coast, about 4 miles west of the peak Nonoti. It



Table 17.1

Analyses of the Illovo river

Station No:	1	2	3	4	5	6	7
pH value	7.48	7.31	7.32	7.50	7.74	7.43	6.58
Conductivity, micromho	100	88	113	133	141	182	188
TDS, ppm	48	51	49	60	72	104	120
DO, ppm	10.8	9.2	9.7	10.6	11.0	8.5	3.1
DO, % saturation	102	90	92	104	101	106	44
BOD, ppm	0.4	0.3	1.0	1.0	1.0	1.2	38.1
Total alkalinity, as ppm $\text{CaCO}_3$	25.7	31.1	30.2	38.6	45.6	46.0	55.2
Ca, ppm	4.9	5.2	5.6	6.9	7.6	7.7	10.2
Mg, ppm	3.0	2.9	2.5	3.6	4.7	5.4	6.1
Na, ppm	5.0	6.0	6.2	8.8	11.7	22.2	23.6
K, ppm	0.5	0.8	0.7	0.7	0.8	1.4	2.7
$\text{SO}_4$ , ppm	Nil	Nil	Nil	Nil	Nil	1.3	1.9
Cl, ppm	5.5	3.4	4.1	6.2	12.0	29.5	30.4
$\text{SiO}_2$ , ppm	12.5	12.0	10.5	9.6	6.9	7.7	9.1
Flow, cusecs	1.5	6	6	6	7	25	10

Stn	TDS	$\text{Ca(OH)}_2$		$\text{Mg(OH)}_2$		$\text{NaOH}$ $\text{KOH}$		$\text{H}_2\text{CO}_3$ $\text{H}_2\text{SO}_4$		$\text{HCl}$	pH
1	48										7.48
2	51										7.31
3	49										7.32
4	60										7.50
5	72										7.74
6	104										7.43
7	120										6.58

FIGURE 17.1

Molar percentage spectra of the Illovo river

Stn	TDS	$\text{Ca(OH)}_2$ $\text{Mg(OH)}_2$		$\text{NaOH}$ $\text{KOH}$		$\text{H}_2\text{CO}_3$ $\text{H}_2\text{SO}_4$		$\text{HCl}$	pH
1	72								7.48
2	108								6.49
3	112								7.40
4	132								7.48

FIGURE 17.2

Molar percentage spectra of the Nonoti river



Table 17.2

Calculated parameters of the Illovo river

Station No:	Hardness as ppm $\text{CaCO}_3$			$\text{pH}_s$	Saturation index	Corrosion ratio	Free carbonic acid, as ppm of $\text{CO}_2$	$\text{CO}_2$ as % saturation	Buffer capacity $\bar{B}$
	Total	Permanent	Temporary						
1	25	22	3	9.44	- 1.96	0.29	1.7	107	0.09
2	25	20	5	9.30	- 1.99	0.15	3.0	111	0.15
3	24	19	5	9.29	- 1.97	0.18	2.9	111	0.21
4	33	22	11	9.19	- 1.69	0.21	2.4	107	0.13
5	39	26	13	8.94	- 1.20	0.36	1.6	104	0.10
6	42	28	14	8.97	- 1.54	0.90	3.3	108	0.17
7	51	30	21	8.75	- 2.17	0.77	33.4	164	1.04

traverses hilly country for the first few miles of its course and passes a sugar mill at Doringkop. The gradient steepens as the river then falls to about 500 ft, whereafter it traverses coastal lowlands, passes a second sugar mill at Darnall and finally enters the Indian Ocean after a total course of 19 miles. Together with its smaller tributaries, the Nonoti drains a catchment of 69 square miles, the whole of which is devoted to sugar cultivation.

Table 17.3 gives the chemical results, obtained during the dry season of 1963, for 4 stations on this river:

- (1) About 1 mile above the Doringkop mill
- (2) About 1 mile below the mill
- (3) Kearsney road bridge, about 4 miles below station 2
- (4) About 5 miles below station 3.

The analyses shows that the water is of Class I quality at station 1, but at station 2 it is degraded to Class VI because of the high BOD. The DO at this station is also very low and the pH value markedly reduced. At stations 3 and 4 the BOD is much reduced and allows the water to be assigned to Class II. In other words, over a distance of about 4 miles the river has virtually recovered from the heavy organic load at station 2.

The molar percentage spectra are shown in Figure 17.2, and these relate to typical chlorided waters.

Various calculated values are shown in Table 17.4. The free carbonic acid and the percentage saturation with carbonic acid are abnormally high at station 2, as would be expected as a consequence of rapid oxidation of organic matter (cf station 7 on the Illovo river). The  $\text{pH}_s$  is high at all stations, as also is the corrosion ratio, and the saturation index is negative. Corrosion is therefore likely to prove troublesome. The water at all stations is soft, but the total hardness at station 2 is about double that at station 1 and the temporary hardness shows a sharp increase. The buffer capacity is appreciable.

The Nonoti thus affords an example of a river showing recovery from a heavy organic load. The resemblances between the water at station 2 and that of the Illovo river at station 7 are notable since they show that this type of organic load has much the same effect upon any river.



Table 17.3

Analyses of the Nonoti river

Station No:	1	2	3	4
pH value	7.48	6.49	7.40	7.48
Conductivity, micromho	100	161	174	219
TDS, ppm	72	108	112	132
DO, ppm	9.5	0.8	9.4	9.9
DO, % saturation	90	8	91	94
BOD, ppm	0.8	37.5	3.9	1.6
Total alkalinity, as ppm $\text{CaCO}_3$	15.8	31.1	40.8	47.0
Ca, ppm	3.2	8.2	8.6	10.0
Mg, ppm	2.1	3.8	3.9	5.5
Na, ppm	16.9	17.4	20.8	29.1
K, ppm	1.3	7.1	5.1	4.0
$\text{SO}_4$ , ppm	1.0	1.3	0.6	3.7
Cl, ppm	21.9	30.2	29.6	39.8
$\text{SiO}_2$ , ppm	13.8	13.1	17.3	10.5
Flow, cusecs	1.8	1.8	2.2	2.6

Table 17.4

Calculated parameters of the Nonoti river

Station No:	Hardness as ppm $\text{CaCO}_3$			pHs	Saturation index	Corrosion ratio	Free carbonic acid, as ppm of $\text{CO}_2$	$\text{CO}_2$ as % saturation	Buffer capacity $\bar{B}$
	Total	Permanent	Temporary						
1	17	17	0	9.90	- 2.42	1.62	1.2	107	0.07
2	36	24	12	9.04	- 2.55	1.25	21.5	170	0.68
3	38	23	15	8.93	- 1.53	0.96	3.3	108	0.17
4	48	28	20	8.77	- 1.29	1.16	3.2	107	0.17



### The Umfolozi river

The Umfolozi river system comprises two major rivers, the Black Umfolozi to the north and the White Umfolozi to the south, which eventually combine to form one.

The White Umfolozi rises at 5200 ft on the Skurweberg, 13 miles west of Vryheid, and flows in a general south-easterly direction for 205 miles before joining with the Black Umfolozi. The latter rises at 4000 ft on the slopes of the Inyati and Ngwibi mountains in the Vryheid Coalfield and flows roughly parallel to the White Umfolozi for 90 miles before the two rivers join at 300 ft immediately below the Umfolozi Game Reserve. Their combined water then flows for a further 40 miles, passing just south of Mtubatuba to enter the Indian Ocean at St. Lucia estuary. The total catchment area of the whole river system is 4375 square miles of which the upper half comprises European farmlands, the central third comprises Bantu reserves, while the lower portion below the Game Reserve is again European farmland (principally devoted to sugar cultivation).

Table 17.5 gives the chemical results, obtained during the dry season of 1966, for 9 stations on the river system:

- (1) White Umfolozi near Vryheid
- (2) White Umfolozi at Welgevonden
- (3) White Umfolozi near Msizazwe
- (4) White Umfolozi above confluence
- (5) Black Umfolozi at Inyati
- (6) Black Umfolozi at Swartfolozi
- (7) Black Umfolozi near Embukodweni
- (8) Black Umfolozi above confluence
- (9) Umfolozi river below confluence

It was not possible to undertake BOD determinations on these samples (other rivers were being sampled simultaneously, which meant being away from the laboratory for several days at a time with no facilities for proper incubation). The oxygen absorbed from acidic permanganate (OA) was therefore determined instead. Since the results were uniformly low, and since there appear to be no sources of appreciable organic pollution near the rivers concerned, it is presumed that the BOD would in no case have exceeded 3 ppm. The water at most stations may therefore be confidently assigned to Class II, except at station 1 (where it could be of Class I quality) and at station 5 (where it is clearly Class III).

Table 17.5

Analyses of the Umfolozi river

Station No:	1	2	3	4	5	6	7	8	9
pH value	7.95	7.80	8.35	8.15	5.45	7.80	8.20	8.35	8.28
Conductivity, micromho	90	220	261	296	1095	259	168	332	490
TDS, ppm	63	137	174	179	847	172	121	198	303
DO, ppm	10.3	10.7	7.2	10.2	7.8	9.3	9.6	9.8	9.3
DO, % saturation	111	100	83	105	85	97	105	103	94
OA, ppm	0.8	1.8	0.4	0.4	0.4	0.4	2.4	0.1	1.1
Total alkalinity, as ppm $\text{CaCO}_3$	39.5	92.0	140.8	124.6	18.6	34.0	64.3	114.9	175.2
Ca, ppm	6.7	16.4	21.6	19.9	120.7	19.5	10.9	21.0	32.7
Mg, ppm	3.4	8.5	13.8	13.5	36.5	7.7	10.6	15.6	23.1
Na, ppm	5.2	17.8	21.1	25.8	82.5	20.3	14.8	27.8	43.5
K, ppm	0.7	1.3	1.3	1.3	5.8	1.3	0.9	1.5	1.9
$\text{SO}_4$ , ppm	1.0	3.3	1.8	1.0	575.0	80.5	20.7	14.6	22.5
Cl, ppm	5.0	17.5	12.2	25.2	Nil	4.6	7.3	31.7	56.9
Flow, cusecs	1.5	8	50	100	2	4	100	100	200



The Black Umfolozi rises in a deep valley between mountains through which run coal seams. Many adits have been driven into the mountainsides to win the coal, and numerous streams draining these and the associated spoil dumps descend to the valley floor and enter the headwaters of the river. The high TDS, low pH value and very large sulphate concentration in the water at station 5 are characteristic of streams traversing coal mining areas. The molar percentage spectra are shown in Figure 17.3 and clearly show the anomalous character of the water at station 5, with its low proportion of carbonic and high proportion of sulphuric acid. Station 6 shows similar features, less pronounced, while at station 7 the water is virtually of normal type. The whole of the White Umfolozi (stations 1 - 4), the Black Umfolozi above the confluence (station 8) and the combined river below this point (station 9) contain typical water of the chlorided series. At station 6 the Black Umfolozi has the typical composition of a water of the sulphated series, but at station 5 the proportion of sulphuric acid is too great for this while at station 7 the water is probably of mixed chlorided-sulphated type.

Among the calculated parameters shown in Table 17.6, the saturation index shows that the upper portion of the White Umfolozi (stations 1 and 2) is aggressive towards calcium carbonate while the lower portion (stations 3 and 4) carries scale-forming water. The values of the corrosion ratio, however, indicate that the water is not very corrosive to metals. The Black Umfolozi is also aggressive towards calcium carbonate in its higher reaches, scale-forming only at station 8. The corrosion ratio shows that the water is very corrosive to metals at stations 5 and 6, the corrosivity becoming less at the lower stations. At station 9 the combined water from the two rivers is both scale-forming and corrosive to metals.

The White Umfolozi (stations 1 - 4) carries soft to slightly hard water, the temporary hardness being appreciable except at the highest point (station 1). The Black Umfolozi at station 5 has very hard water, most of the hardness being permanent, but at lower stations the water is very much softer. Below the confluence (station 9) the water is moderately hard, some 75% of the total hardness being temporary.

Except at station 5, the free carbonic acid and percentage saturation with carbonic acid do not attain significant values. At station 5, however, the concentration of free carbonic acid is very high (a consequence of the low pH), yet the saturation is only 78%. Again except

Stn	TDS	Ca(OH) <sub>2</sub>	Mg(OH) <sub>2</sub>	NaOH	KOH	H <sub>2</sub> CO <sub>3</sub>	H <sub>2</sub> SO <sub>4</sub>	HCl	pH
1	63								7.95
2	137								7.80
3	174								8.35
4	179								8.15
5	847								5.45
6	172								7.80
7	121								8.20
8	198								8.35
9	303								8.28

**FIGURE 17.3**  
Molar percentage spectra of the Umfolozi river



Table 17.6

Calculated parameters of the Umfolozi river

Station No:	Hardness as ppm $\text{CaCO}_3$			pHs	Saturation index	Corrosion ratio	Free carbonic acid as ppm $\text{CO}_2$	$\text{CO}_2$ as % saturation	Buffer capacity $\bar{B}$
	Total	Permanent	Temporary						
1	31	23	8	9.07	- 1.12	0.22	0.8	102	0.05
2	76	35	41	8.30	- 0.50	0.31	2.6	103	0.16
3	112	28	84	8.01	+ 0.34	0.14	1.1	100	0.16
4	106	31	75	8.09	+ 0.06	0.29	1.7	101	0.13
5	454	414	40	8.10	- 2.65	19.78	111.9	78	0.67
6	81	52	29	8.67	- 0.87	2.57	1.0	103	0.06
7	72	40	32	8.61	- 0.41	0.46	0.8	100	0.07
8	118	39	79	8.12	+ 0.23	0.51	0.9	100	0.13
9	178	44	134	7.69	+ 0.59	0.60	1.7	100	0.18

at station 5, the Black Umfolozi is on the whole less well buffered than the White.

The Black Umfolozi furnishes a typical example of a river receiving drainage water from coal mines. The rapid improvement in quality which the river shows below station 5 is mostly due to dilution through the entry of unpolluted tributaries.

#### Small coastal rivers

Table 17.7 gives the analytical results for 10 small Natal coastal rivers, sampled in the dry seasons of 1964 and 1966:

Umzimbazi on the old South Coast Road

Emseleni near Hibberds

Little Amanzimtoti at Smithfield

Umgababa on the old South Coast Road

Umhlutuni near New Guelderland

Isipingo at Isipingo Rail

Umhlanga at Ottawa

Amanzimtoti near Adams Mission

Ingane on the old South Coast Road

Sinkwazi near Sinkwazi station

In each case the flow was less than 1 cusec. The molar percentage spectra, shown in Figure 17.4, are all of the chlorided series except that of the Sinkwazi river, which appears to be of mixed chlorided-sulphated type, and are all characterised by low to very low carbonic acid percentages. The TDS values tend to be high, although not every river of this group shows a high TDS. The calculated parameters shown in Table 17.8 indicate that these waters range from soft to very hard while their temporary hardnesses vary from 26% of the total hardness (Umhlutuni) to 91% (Amanzimtoti). The waters are aggressive to calcium carbonate (except for the Sinkwazi water, which is scale-forming) and show high values of the corrosion ratio. In many cases they have high concentrations of free carbonic acid, but in no instance is the percentage saturation with carbon dioxide abnormal - the high concentrations are mainly due to the relatively high total alkalinities of these waters and hence have little bearing on water quality (see chapter 8). For the same reason, the buffer capacities are also high. Some of these waters show high BOD values (see Table 17.7), that of the Ingane being outstanding, and many of them show



Table 17.7  
Analyses of small coastal rivers

	Umzimbazi	Emseleni	Little Amanzimtoti	Umgababa	Umhlutuni	Isipingo	Umhlanga	Amanzimtoti	Ingane	Sinkwazi
pH value	7.27	7.54	7.82	7.40	7.54	7.70	7.40	7.50	7.38	7.80
Conductivity, micromho	449	707	449	423	1100	650	550	298	2268	2701
TDS, ppm	218	423	224	215	651	326	255	161	1180	1893
DO, ppm	5.7	5.4	10.4	8.3	4.9	5.8	3.5	10.2	2.2	8.4
DO, % saturation	56	57	102	84	48	54	35	100	21	85
BOD, ppm	5.8	-	1.7	0.5	4.4	1.3	1.1	1.0	28.5	2.1
OA, ppm	-	4.9	-	-	-	-	-	-	-	-
Total alkalinity, as ppm CaCO <sub>3</sub>	86.0	155.0	80.0	77.3	229.1	116.4	80.0	35.9	215.5	213.8
Ca, ppm	10.4	22.4	11.2	14.1	48.0	14.6	12.9	5.1	44.2	178.7
Mg, ppm	12.5	22.1	12.7	11.0	24.6	18.1	15.0	7.0	61.1	69.7
Na, ppm	50.5	107.0	53.4	44.5	164.0	75.0	56.0	37.6	279.0	387.0
K, ppm	1.4	2.5	2.2	2.3	8.5	2.6	1.2	2.1	4.8	3.9
SO <sub>4</sub> , ppm	1.9	39.4	5.9	10.2	3.1	1.0	17.0	8.2	12.9	577.2
Cl, ppm	74.6	119.0	72.5	69.8	244.9	126.7	92.8	62.7	549.9	532.0
SiO <sub>2</sub> , ppm	12.3	-	14.0	13.1	18.2	15.5	12.0	13.6	8.0	14.2
Flow, cusecs	0.6	0.5	0.4	0.03	0.06	0.1	0.3	< 0.01	< 0.01	0.1

	TDS	Ca(OH) <sub>2</sub>	Mg(OH) <sub>2</sub>	NaOH	KOH	H <sub>2</sub> CO <sub>3</sub>	H <sub>2</sub> SO <sub>4</sub>	HCl	pH
Umzimbazi	218								7.27
Emseleni	423								7.54
Little Amangimtoti	224								7.82
Umgababa	215								7.40
Umhlutuni	651								7.54
Isipingo	326								7.70
Umhlanga	255								7.40
Amangimtoti	161								7.50
Ingone * *	1180								7.38
Sinkwazi	1893								7.80

FIGURE 17.4

Molar percentage spectra of small coastal rivers



Table 17.8

Calculated parameters of small coastal rivers

	Hardness as ppm $\text{CaCO}_3$			$\text{pH}_s$	Saturation index	Corrosion ratio	Free carbonic acid as ppm $\text{CO}_2$	$\text{CO}_2$ as % saturation	Buffer capacity, $\bar{B}$
	Total	Permanent	Temporary						
Umzimbazi	78	37	41	8.64	- 0.37	1.27	86.9	112	0.43
Emseleni	148	28	120	8.09	- 0.55	1.26	8.6	106	0.48
Little Amanzimtoti	81	35	46	8.68	- 0.86	1.26	2.4	103	0.14
Umgababa	81	45	36	8.56	- 1.16	1.46	5.5	108	0.29
Umhlutuni	123	32	91	7.67	- 0.13	1.48	12.0	106	0.69
Isipingo	112	47	65	8.41	- 0.71	1.66	3.9	104	0.23
Umhlanga	95	54	41	8.61	- 1.21	1.98	5.5	108	0.29
Amanzimtoti	42	38	4	9.41	- 1.91	2.96	1.9	107	0.11
Ingane	365	280	85	7.88	- 0.50	3.90	14.2	101	0.73
Sinkwazi	738	534	204	7.34	+ 0.46	6.06	5.7	94	0.38

low DO concentrations. In no case is there any known source of pollution above the sampling station concerned, yet the waters vary in quality from Class II to Class VI.

It appears, therefore, that small coastal rivers in Natal tend to exhibit high TDS, low molar percentage of carbonic acid, low DO and high BOD as characteristic features, although any given river may not show all these features. It seems unlikely that these characteristics are due to catchment geology, since the geological map of Natal shows that these particular streams drain a variety of geological formations.

Because these streams are all of low flow, in many cases their water is virtually stagnating. This would lead to a reduction of DO and an increase of BOD (accumulation of organic matter under quiescent conditions, such matter being derived from animal and vegetable debris), as well as increase of the TDS due to evaporation. Some of the features of these particular rivers could thus be accounted for quite simply.

Wilcox (1962) has presented analyses of the Rio Grande from seven sampling points along a 450 mile stretch, and these show that irrigation drainage water can have a remarkable effect upon a river. Unfortunately his analyses are incomplete (in particular he has not recorded the pH values so that the total carbonic acid cannot be accurately calculated) and they do not all fulfil the ionic balance. Their detailed interpretation is therefore not possible, but they do show that the TDS of the water is materially increased (by a factor of about 8), while the sodium and chloride concentrations are increased still more greatly and the calcium concentration and total alkalinity are increased to a smaller degree. It appears that the effect of irrigation drainage water is thus to increase the TDS, to cause calcium bicarbonate (or carbonate) to become replaced by sodium chloride and even to cause additional sodium chloride to enter the water, i.e. the water shows changes of much the same pattern as arise when passing from high to low molar percentages of carbonic acid in the series of chlorided waters together with an accompanying increase in TDS. Under such circumstances the corrosion ratio will tend to increase steadily, while the variation of  $\text{pH}_s$  with TDS will be less marked than represented by the curves of Figure 15.7, so that a water with an initially high  $\text{pH}_s$  and hence a negative saturation index will retain the negative index as the TDS increases. By contrast, equation (8.18) and Table 3 C show that simple evaporation will not give rise to any appreciable change in the carbonic acid saturation, but Figure 10.2 shows that



if the average Natal river water becomes increased in TDS by simple concentration to a level of about 300 ppm, its saturation index becomes positive, and this change must be followed by a spontaneous deposition of calcium carbonate so that the molar percentage of carbonic acid becomes decreased. The final result would thus be a water of high TDS with low molar percentages of calcium hydroxide and carbonic acid and a zero or positive saturation index. Since all but one of the waters of Table 17.7 show negative values of the saturation index, it appears that simple evaporation does not after all explain their characteristic features, whereas the entry of irrigation drainage water does. Irrigation drainage water may be expected to show high BOD values on occasion and often to have low DO (oxygen being removed by micro-organisms as the water percolates through the soil).

It may therefore be concluded that the small coastal rivers of Natal, most of which lie in regions where intense irrigation is practised, owe their anomalous characteristics mainly to the entry of irrigation drainage water (which will consist of seepage rather than direct run-off). Evaporation, if it is of any influence at all, can play only a minor role.

#### General summary of water quality in Natal

At the present time, river surveys have been conducted by the CSIR, on behalf of the Town and Regional Planning Commission, over the whole of Natal except the southernmost portion (the Umkomaas and the rivers to the south). The present writer has participated in most of the work, and many of the results obtained have now been published (Brand et al, 1967).

The published reports should be consulted for full details, but it is of interest to conclude the present work by giving a brief summary of water quality in Natal as revealed by these surveys.

Employing the purely chemical classification of water quality given in the preceding chapter, it has been found that the headwaters and upper reaches of most rivers of this Province, where pollution is minimal, contain waters of Classes I and II, their middle reaches usually contain waters of Class II and sometimes Class III, while as the rivers approach the coast (the last 10 - 15 miles of flow) the quality often falls off markedly, even right down to Class VI, mainly as a result of urban, industrial and sometimes agricultural pollution. The small coastal rivers

are mostly of poor water quality, often because they are affected by irrigation in their catchments but sometimes in consequence of their low flow.

On the whole water quality throughout Natal is very good. Pollution occurs, however, throughout the Natal Coalfields (mineralisation of the waters from the acidic effluents and drainage of coal mines and dumps) and below most of the sugar mills in the coastal region (organic materials in mill effluents causing high BOD and low DO values). Some other industries are also responsible for isolated cases of pollution, and water quality usually (often unavoidably) falls off to some extent below towns and cities.



APPENDIX A

SUMMARY OF ANALYTICAL CALCULATIONS

1. The analytical results that are necessary for the full consideration of a particular water are as listed in the following example:

Conductivity	760	micromho
pH	8.50	
TDS	511	ppm
Total alkalinity as $\text{CaCO}_3$	268	ppm
Ca	71.8	ppm
Mg	35.9	ppm
Na	58.0	ppm
K	3.7	ppm
$\text{SO}_4$	106	ppm
Cl	52.2	ppm
$\text{SiO}_2$	16.3	ppm
DO	7.1	ppm
BOD	0.7	ppm
Temperature (when sampled)	26.0	°C

as well as the concentrations of any other major solutes that may be present and of any other minor solutes (nitrate, phosphate, fluoride, etc) large enough to affect the ionic balance or influence the pH value. When particular problems of a specialised nature are involved, various other special determinations may also be required.

The pH value should be measured as accurately as possible in the laboratory at the time of the analysis and the total alkalinity should be determined by electrometric titration to an end-point pH corresponding to the conductivity (see Table 5 B), in the present example to pH 4.3. The titration curves of samples thought to be anomalous in that they contain little or no total carbonic acid should be investigated before the alkalinity determination is undertaken.

2. Check the TDS by summing the ppm concentrations of Ca, Mg, Na, K,  $\text{SO}_4$ , Cl,  $\text{SiO}_2$  and any other significant solutes and adding to the total 0.60 times the total alkalinity as ppm  $\text{CaCO}_3$ . Compare the result with the experimental TDS. Poor agreement may indicate errors or omissions in the analysis.

Where the agreement is good (to within 10%), the mean of the two values may be taken as the true TDS. Where agreement is poor but not



due to analytical errors or omissions, the calculated TDS should be taken for further calculation in preference to the experimental value (because the poor agreement is commonly due to organic substances which do not contribute to the ionic strength, or to error in the experimental TDS).

An additional check is sometimes afforded by comparing the calculated TDS in ppm with 0.67 times the electrical conductivity in micromho.

In the above example, the calculated TDS is 505 ppm. Hence the work is continued using 508 ppm, the mean of the calculated and experimental values. From the conductivity we have 509 ppm, in excellent agreement.

3. Calculate the millimolar concentrations of acids and bases. Use rounded molecular weights for this:

Ca = 40	SO <sub>4</sub> = 96
Mg = 24	Cl = 35.5
Na = 23	(SiO <sub>2</sub> = 60)
K = 39	etc.

and divide the analytical figure in ppm by the appropriate molecular weight, working to three significant figures. Calculate  $\bar{e}_t$  from the relation:

$$\bar{e}_t = 0.02 \times \text{Total alkalinity (ppm CaCO}_3\text{)}$$

For the example, the results are:

Ca(OH) <sub>2</sub> $\bar{c}$ = 1.80	H <sub>2</sub> SO <sub>4</sub> $\bar{s}$ = 1.10
Mg(OH) <sub>2</sub> $\bar{m}$ = 1.49	HCl $\bar{h}$ = 1.47
NaOH $\bar{n}$ = 2.52	(SiO <sub>2</sub> = 0.272)
KOH $\bar{p}$ = 0.0949	$\bar{e}_t$ = 5.36

4. Apply the ionic balance. Calculate the value of:

$$\bar{e}_c = (2 \bar{c} + 2 \bar{m} + \bar{n} + \bar{p}) - (2 \bar{s} + \bar{h}) \pm \bar{x}$$

where  $\bar{x}$  refers to other acids or bases that may be present in significant concentrations, and hence find the value of  $|\bar{e}_t - \bar{e}_c|$ . The value of this should not exceed:

$$\begin{aligned} &0.1000 + 0.0600 (2 \bar{s} + \bar{h} + \bar{e}_t) \quad (\text{for values} < 5) \\ \text{or} \quad &0.2560 + 0.0288 (2 \bar{s} + \bar{h} + \bar{e}_t) \quad (\text{for values} > 5) \end{aligned}$$

where the final inequality refers to the term  $(2 \bar{s} + \bar{h} + \bar{e}_t)$ . If these limits are exceeded, the analysis must be checked (see chapter 7).

When the ionic balance is satisfactory, the true value of  $\bar{e}$  for further calculations may be taken as the mean of  $\bar{e}_t$  and  $\bar{e}_c$  (unless there is good reason to choose one of these values as more accurate than the other).

In the example we have:

$$\begin{aligned}\bar{e}_c &= 5.52 \\ |\bar{e}_t - \bar{e}_c| &= 0.16 \\ 2 \bar{s} + \bar{h} + \bar{e}_t &= 9.03\end{aligned}$$

hence we use the second of the above limits, which works out to 0.5161. Since  $|\bar{e}_t - \bar{e}_c|$  is less than this, there is ionic balance and the analysis may be considered as satisfactory. The true value of  $\bar{e}$  is now taken as the mean, 5.44.

5. Determine the value of  $\gamma$ . Provided  $5 < \text{pH} < 9$ , a sufficiently accurate value is obtainable from Table 2 B if the TDS is less than 1000 ppm. For higher TDS values,  $\gamma$  may be found approximately from the extension of Table 2 B. For  $\text{pH} < 5$  or  $\text{pH} > 9$ ,  $\gamma$  must be found by the method of successive approximation, as described in chapter 4.

In the example, the pH being 8.50 and the TDS 508 ppm, Table 2 B gives  $\gamma = 0.893$ .

6. If it has not been experimentally determined, calculate the value of  $\bar{a}$ , the millimolar concentration of total carbonic acid:

- (a) Provided  $5 < \text{pH} < 9$  and  $\bar{e} \geq 1.00$ , use Table 3 B to find the appropriate value of  $Q$  (pH,  $\gamma$ ). Then:

$$\bar{a} = Q \bar{e}$$

- (b) Provided  $6 < \text{pH} < 8$  and  $\bar{e} \geq 0.100$ , use Table 3 B as described under (a) above.

- (c) Provided  $3.7 < \text{pH} < 9.7$ , the value of  $\bar{a}$  for most other cases can be found from the equation:

$$\bar{a} = \frac{1000 (H^2 \gamma^6 + K_1 H \gamma^4 + K_1 K_2)}{(K_1 H \gamma^4 + 2 K_1 K_2)} \left( H - k_w/H \gamma^2 + \frac{\bar{e}}{1000} \right)$$



where H is defined by the relation:

$$\text{pH} = -\log \gamma H$$

- (d) In all the remaining cases, an accurate value of  $\bar{a}$  is not obtainable by calculation, but an approximate value is provided by (c) above.

In the example, procedure (a) may be applied (the most common case). For  $\text{pH} = 8.50$  and  $\gamma = 0.893$ , Table 3 B gives  $Q = 0.990$  so that:

$$\bar{a} = 0.990 \times 5.44 = 5.38$$

7. Calculate the molar percentages by adding  $\bar{c}$ ,  $\bar{m}$ ,  $\bar{n}$ ,  $\bar{p}$ ,  $\bar{a}$ ,  $\bar{s}$ ,  $\bar{h}$  and any other significant millimolar concentrations and expressing each as a percentage of the sum. The molar percentage spectrum may then be drawn (see chapter 14) and, by comparison with Figures 15.1 and 15.3, it may be decided whether the water belongs to the chlorided or sulphated series, using the criteria of agreement given in chapter 13 (page 127).

In the example, the total of the millimolar concentrations is 13.85, so that molar percentages are as follows:

$\text{Ca(OH)}_2$	13.0
$\text{Mg(OH)}_2$	10.8
NaOH	18.2
KOH	0.6
$\text{H}_2\text{CO}_3$	38.9
$\text{H}_2\text{SO}_4$	7.9
HCl	10.6

Here the sulphuric acid is rather too high for the chlorided series, while the magnesium hydroxide is rather too low for the sulphated series. The water thus appears to be of mixed chlorided-sulphated type.

8. The DO concentration may be expressed in terms of percentage saturation according to the temperature at the time of sampling (Table 6 B), the result being suitably corrected for altitude (Table 7 B). The result, together with the TDS, BOD and pH, can be utilised in assigning the water to its proper quality classification by Table 16.1.

In the example, the DO concentration corresponds to 87% saturation (the altitude correction being negligible). The water is therefore of Class III quality.

9. Other derived quantities can be calculated from the analysis if required:

- (a) Buffer capacity by equation (9.4).
- (b)  $\text{pH}_s$  by equation (10.13), taking  $A = 50 \bar{e}$ .
- (c) Saturation index, equal to  $\text{pH} - \text{pH}_s$  (see chapter 10).
- (d) Corrosion ratio by equation (10.17).
- (e) Free carbonic acid by equation (8.12) or (8.8).
- (f) Percent saturation with carbonic acid by equations (8.18) or (8.19).
- (g) The forms of alkalinity, according to chapter 7 (scheme on page 59).
- (h) The total, permanent and temporary hardness, according to chapter 11.

The example analysis yields the following results:

- (a)  $\bar{B} = 0.30$
- (b)  $\text{pH}_s = 7.30$
- (c) Saturation index = + 1.20
- (d) Corrosion ratio  $R = 0.67$
- (e) Free carbonic acid  $F = 1.4 \text{ ppm as } \text{CO}_2$
- (f) Percent saturation with carbonic acid = 99%
- (g) Bicarbonate alkalinity = 266 ppm as  $\text{CaCO}_3$   
 Carbonate alkalinity = 6 ppm as  $\text{CaCO}_3$   
 Hydroxide alkalinity = Nil  
 Total alkalinity = 272 ppm as  $\text{CaCO}_3$
- (h) Total hardness  $I = 329 \text{ ppm as } \text{CaCO}_3$   
 Permanent hardness  $P_h = 75 \text{ ppm as } \text{CaCO}_3$   
 Temporary hardness  $T_h = 254 \text{ ppm as } \text{CaCO}_3$

The water is therefore well-buffered and scale-forming but corrosive to metals. It is also very hard and has a large temporary hardness (77% of the total). To correct the corrosivity, lime may be added, but this will increase the scale-forming powers and the hardness. Similarly, to reduce the scale-forming powers, acid may be added, but this will increase the corrosivity, although leaving the hardness unchanged. As it stands, this water is not recommended for domestic use unless no other source of supply is available, on account of its high TDS, but it would become acceptable if given a form of softening treatment. This might be uneconomic; according to chapter 11, the use of the cold lime soda process would require the addition of about 290 ppm of lime and 30 ppm of soda ash as well as some after treatment. Under the circumstances, it would probably be best to use no treatment at all (apart from disinfection) if the water must be used for domestic purposes, relying on the scale-forming properties to give protection from corrosion and accepting the high hardness.



APPENDIX B

TABLES OF NUMERICAL DATA

Table 1 B

Values of constants at 25°C

Constant	Symbol	Value
Ionic product of water	$k_w$	$1.01 \times 10^{-14}$
First dissociation constant of $H_2CO_3$	$K_1$	$4.43 \times 10^{-7}$
Second dissociation constant of $H_2CO_3$	$K_2$	$4.69 \times 10^{-11}$
Second dissociation constant of $H_2SO_4$	$K_s$	$1.00 \times 10^{-2}$
Second dissociation constant of $Ca(OH)_2$	$K_c$	$3.1 \times 10^{-2}$
Second dissociation constant of $Mg(OH)_2$	$K_m$	$2.6 \times 10^{-3}$
Solubility product of $H_2CO_3$	$k_a$	$4.36 \times 10^{-12}$
Solubility product of $CaCO_3$	$k_{ca}$	$5.12 \times 10^{-9}$
Solubility product of $Ca(OH)_2$	$k_c$	<b><math>5.38 \times 10^{-6}</math></b>
Solubility product of $MgCO_3$	$k_{ma}$	$1.62 \times 10^{-5}$
Solubility product of $Mg(OH)_2$	$k_m$	$1.38 \times 10^{-11}$



Table 2 B

Approximate activity coefficients  
valid for  $5 < \text{pH} < 9$

TDS, ppm	$\gamma$	TDS, ppm	$\gamma$	TDS, ppm	$\gamma$
		100	0.952	200	0.930
		110	0.949	300	0.922
20	1.000	120	0.946	400	0.904
30	0.982	130	0.944	500	0.894
40	0.975	140	0.942	600	0.885
50	0.970	150	0.940	700	0.878
60	0.965	160	0.938	800	0.871
70	0.961	170	0.936	900	0.865
80	0.958	180	0.934	1000	0.859
90	0.955	190	0.932		
100	0.952	200	0.930		

The following additional extrapolated values are based on Figure 4.1:

TDS, ppm	$\gamma$	TDS, ppm	$\gamma$
1,000	0.859	10,000	0.644
2,000	0.814	20,000	0.505
3,000	0.780	30,000	0.375
4,000	0.755	40,000	0.227
5,000	0.732		
6,000	0.712		
7,000	0.690		
8,000	0.675		
9,000	0.659		

Table 3 B

Values of  $Q$  (pH,  $\gamma$ ) for calculation of total carbonic acid

pH	Activity coefficient, $\gamma$							
	1.000	0.980	0.960	0.940	0.920	0.900	0.880	0.860
6.0	3.25	3.21	3.16	3.12	3.08	3.03	2.99	2.94
6.1	2.79	2.76	2.72	2.69	2.65	2.62	2.58	2.54
6.2	2.42	2.40	2.37	2.34	2.31	2.28	2.25	2.23
6.3	2.13	2.11	2.09	2.07	2.04	2.02	2.00	1.97
6.4	1.91	1.89	1.87	1.85	1.83	1.81	1.79	1.78
6.5	1.71	1.70	1.69	1.67	1.66	1.65	1.63	1.62
6.6	1.57	1.55	1.54	1.54	1.52	1.52	1.50	1.48
6.7	1.45	1.44	1.43	1.43	1.42	1.41	1.40	1.39
6.8	1.36	1.35	1.34	1.34	1.33	1.32	1.32	1.31
6.9	1.29	1.28	1.27	1.27	1.26	1.26	1.25	1.25
7.0	1.23	1.22	1.22	1.21	1.21	1.20	1.20	1.20
7.1	1.18	1.18	1.17	1.17	1.16	1.16	1.16	1.16
7.2	1.14	1.14	1.14	1.13	1.13	1.13	1.13	1.12
7.3	1.11	1.11	1.11	1.11	1.10	1.10	1.10	1.10
7.4	1.09	1.09	1.09	1.08	1.08	1.08	1.08	1.08
7.5	1.07	1.07	1.07	1.07	1.06	1.06	1.06	1.06
7.6	1.05	1.05	1.05	1.05	1.05	1.05	1.05	1.05
7.7	1.04	1.04	1.04	1.04	1.04	1.04	1.04	1.04
7.8	1.03	1.03	1.03	1.03	1.03	1.03	1.03	1.03
7.9	1.03	1.02	1.02	1.02	1.02	1.02	1.02	1.02
8.0	1.02	1.02	1.02	1.02	1.01	1.01	1.01	1.01
8.1	1.01	1.01	1.01	1.01	1.01	1.01	1.01	1.01
8.2	1.01	1.01	1.00	1.00	1.00	1.00	1.00	1.00
8.3	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00
8.4	1.00	0.993	0.993	0.993	0.993	0.992	0.992	0.991
8.5	0.993	0.993	0.992	0.992	0.991	0.991	0.988	0.987
8.6	0.983	0.983	0.983	0.983	0.982	0.980	0.979	0.976
8.7	0.982	0.981	0.978	0.977	0.975	0.974	0.971	0.969
8.8	0.977	0.973	0.971	0.970	0.968	0.966	0.964	0.959
8.9	0.968	0.965	0.965	0.960	0.958	0.955	0.953	0.950
9.0	0.959	0.957	0.953	0.951	0.948	0.945	0.942	0.939



Values of P (pH,  $\gamma$ ) for calculation of free carbonic acid

[illegible]

Table 5 B

Calculated end-point pH values for alkalinity titrations

Conductivity micromho	End-point pH values	
	"Methyl orange"	"Phenolphthalein"
10	5.2	8.0
20	5.1	8.1
40	4.9	8.2
60	4.8	8.2
80	4.8	8.2
100	4.7	8.2
200	4.6	8.2
400	4.4	8.2
600	4.3	8.2
800	4.3	8.2
1000	4.2	8.2
1200	4.2	8.2
1400	4.2	8.2
1600	4.1	8.2



Table 6 B  
Values of  $U_1$  and  $U_2$  for calculation  
of ideal buffer capacity

pH	$U_1$	$U_2$
4.0	0.010	0.230
4.2	0.016	0.145
4.4	0.025	0.092
4.6	0.031	0.058
4.8	0.061	0.037
5.0	0.094	0.023
5.2	0.142	0.015
5.4	0.208	0.009
5.6	0.293	0.006
5.8	0.393	0.004
6.0	0.490	0.002
6.2	0.558	0.001
6.4	0.575	0.001
6.6	0.532	0.001
6.8	0.449	0.001
7.0	0.347	0.000
7.2	0.253	0.001
7.4	0.177	0.001
7.6	0.121	0.001
7.8	0.084	0.002
8.0	0.061	0.002
8.2	0.049	0.004
8.4	0.055	0.006
8.6	0.054	0.009
8.8	0.073	0.015
9.0	0.104	0.023

Table 7 B

Dissolved oxygen concentration in water in equilibriumwith saturated air at 760 mm pressure

(from American Public Health Association, 1965)

Temperature, °C	DO, ppm	Temperature, °C	DO, ppm
0	14.6	26	8.2
1	14.2	27	8.1
2	13.8	28	7.9
3	13.5	29	7.8
4	13.1	30	7.6
5	12.8	31	7.5
6	12.5	32	7.4
7	12.2	33	7.3
8	11.9	34	7.2
9	11.6	35	7.1
10	11.3	36	7.0
11	11.1	37	6.9
12	10.8	38	6.8
13	10.6	39	6.7
14	10.4	40	6.6
15	10.2	41	6.5
16	10.0	42	6.4
17	9.7	43	6.3
18	9.5	44	6.2
19	9.4	45	6.1
20	9.2	46	6.0
21	9.0	47	5.9
22	8.8	48	5.8
23	8.7	49	5.7
24	8.5	50	5.6
25	8.4		



Table 8 B

Altitude correction factor for DO saturation

Altitude in feet	0	200	400	600	800
0	1.00	1.01	1.01	1.02	1.03
1000	1.04	1.04	1.05	1.06	1.07
2000	1.07	1.08	1.09	1.10	1.11
3000	1.11	1.12	1.13	1.14	1.15
4000	1.15	1.16	1.17	1.18	1.19
5000	1.19	1.20	1.21	1.22	1.23
6000	1.24	1.25	1.26	1.27	1.27
7000	1.28	1.29	1.30	1.31	1.32
8000	1.33	1.34	1.35	1.36	1.37
9000	1.38	1.39	1.40	1.41	1.42

The percentage saturation, obtained from the observed DO and the data of Table 7 B, is corrected for altitude by multiplying by the factor f from the above Table, where f is given by:

$$\log f = A/K$$

A being the altitude in feet and K a constant equal to  $221.1 t$  where t is the average air temperature up to the altitude concerned which may be taken as approximately  $293^{\circ}\text{K}$  (Berry, Bollay and Beers, 1945; Sutcliffe, 1946).

APPENDIX C

TABLES OF EXPERIMENTAL DATA



Table 1 C

Total carbonic acid in streams of the Tugela river system

Date of sample	pH	Conductivity, micromho	TDS, ppm	Total alkalinity as ppm $\text{CaCO}_3$	Total carbonic acid millimoles/litre
<u>Bergville</u>		<u>TUGELA RIVER</u>			
7/54	7.4	52	62	36	0.78
8/54	8.0	57	79	50	1.02
10/54	7.9	60	78	92	1.88
11/54	7.4	36	50	28	0.61
12/54	7.4	30	39	31	0.68
1/55	7.4	32	36	30	0.65
2/55	7.2	40	39	34	0.78
3/55	7.3	40	35	34	0.75
4/55	7.8	75	59	59	1.22
<u>Labuschagne's Kraal</u>					
11/54	7.6	50	68	36	0.76
12/54	7.5	39	41	32	0.68
1/55	7.5	40	35	28	0.60
2/55	7.2	29	52	28	0.64
3/55	7.3	50	42	36	0.80
4/55	7.6	106	78	52	1.09
<u>Colenso</u>					
11/53	7.6	96	115	54	1.13
7/54	7.5	72	71	50	1.07
8/54	7.8	90	53	56	1.15
9/54	8.0	102	85	74	1.51
10/54	7.9	105	71	65	1.33
11/54	7.3	54	48	48	1.07
12/54	7.6	37	41	34	0.71
1/55	7.5	48	57	39	0.83
2/55	7.5	40	44	34	0.79
3/55	7.3	52	49	58	1.29
4/55	7.6	78	71	65	1.37

Continued /.....

Table 1 C (continued)

Date of sample	pH	Conductivity, micromho	TDS, ppm	Total alkalinity, as ppm $\text{CaCO}_3$	Total carbonic acid millimoles/litre
<u>Below Nkasini</u>					
11/53	7.5	190	167	99	2.19
7/54	7.6	140	108	95	2.00
8/54	8.2	175	119	86	1.72
9/54	8.2	155	106	90	1.80
11/54	7.7	67	62	50	1.04
4/55	8.2	139	120	90	1.80
<u>Tugela Ferry</u>					
11/53	7.6	240	203	118	2.48
6/54	7.8	238	178	98	2.02
7/54	7.7	370	255	228	4.74
8/54	8.2	370	267	187	3.74
9/54	8.2	325	207	165	3.30
10/54	8.0	120	102	98	2.00
11/54	7.7	102	92	70	1.46
12/54	7.8	136	94	78	1.61
2/55	7.5	87	70	55	1.18
3/55	8.2	104	88	64	1.28
4/55	7.8	186	141	108	2.22
<u>Below Ngubevu</u>					
12/53	7.5	180	160	95	2.03
6/54	8.0	190	122	93	1.90
7/54	8.3	255	161	119	2.38
8/54	8.5	300	197	148	2.94
9/54	8.5	302	187	134	2.62
11/54	7.8	111	95	68	1.40
<u>Middledrift</u>					
10/53	7.3	170	165	81	1.80
8/54	8.4	251	177	124	2.46
9/54	8.3	300	188	126	2.52
11/54	7.4	120	107	78	1.70
12/54	7.9	110	90	75	1.53

Continued /.....



Table 1 C (continued)

Date of sample	pH	Conductivity, micromho	TDS, ppm	Total alkalinity as ppm $\text{CaCO}_3$	Total carbonic acid millimoles/litre
<u>Middledrift</u> (continued)					
2/55	7.8	112	94	64	1.32
3/55	7.6	143	104	89	1.87
4/55	8.1	182	120	116	2.34
<u>Mandini</u>					
10/53	7.4	165	144	81	1.75
6/54	8.2	190	114	91	1.82
7/54	8.1	235	151	106	2.14
8/54	8.2	268	173	121	2.42
9/54	8.6	290	175	114	2.24
12/54	7.9	102	94	66	1.35
2/55	7.8	130	109	60	1.24
3/55	7.6	157	120	98	2.06
4/55	8.3	205	160	118	2.36
<u>MAHAI STREAM</u>					
11/54	7.8	25	13	27	0.56
2/55	7.2	31	19	26	0.59
3/55	7.3	28	25	27	0.60
4/55	7.8	40	30	29	0.60
<u>SANDSPRUIT</u>					
4/54	6.9	95	66	61	1.55
6/54	6.8	124	51	106	2.86
7/54	6.8	125	118	98	2.63
8/54	6.7	150	132	82	2.35
9/54	6.7	140	163	94	2.69
10/54	7.4	90	155	70	1.51
11/54	7.2	67	148	46	1.04
12/54	6.6	73	94	64	1.97
1/55	7.0	71	98	57	1.39
2/55	7.3	80	92	63	1.40
3/55	7.1	82	93	90	2.11
4/55	8.0	138	99	93	1.90

Continued /.....

Table 1 C (continued)

Date of sample	pH	Conductivity, micromho	TDS, ppm	Total alkalinity, as ppm CaCO <sub>3</sub>	Total carbonic acid millimoles/litre
<u>LITTLE TUGELA</u>					
8/54	8.2	86	86	56	1.12
10/54	8.1	75	42	66	1.33
11/54	7.9	42	56	34	0.69
12/54	7.4	47	50	33	0.72
1/55	7.4	50	39	31	0.68
2/55	7.2	37	31	24	0.55
3/55	7.5	54	48	38	0.81
4/55	7.8	102	51	55	1.13
<u>BLOUKRANS</u>					
12/53	7.9	700	512	161	3.28
4/54	7.8	210	140	110	2.27
6/54	8.0	830	453	211	4.26
7/54	8.1	940	603	284	5.74
8/54	8.5	1020	677	230	4.54
9/54	8.4	1120	774	253	5.02
10/54	8.5	760	466	222	4.39
11/54	7.9	455	310	233	4.75
12/54	7.7	136	137	104	2.16
2/55	8.6	440	321	220	4.32
3/55	8.2	370	333	222	4.44
4/55	8.2	668	453	252	5.04
<u>BUSHMANS RIVER</u>					
<u>Above Estcourt</u>					
10/54	8.2	180	136	84	1.68
11/54	7.7	110	102	50	1.04
12/54	7.7	68	57	50	1.04
2/55	7.6	73	68	50	1.05
3/55	8.4	106	91	76	1.51
4/55	8.2	166	194	108	2.16
5/56	7.1	56	56	39	0.91
6/56	6.8	60	53	42	1.13

Continued /.....



Table 1 C (continued)

Date of sample	pH	Conductivity, micromho	TDS, ppm	Total alkalinity, as ppm $\text{CaCO}_3$	Total carbonic acid millimoles/litre
<u>Above Estcourt (continued)</u>					
7/56	7.3	74	60	46	1.02
9/56	7.5	76	60	56	1.20
11/56	7.3	63	67	44	0.98
2/57	7.5	61	67	32	0.68
<u>Below Estcourt</u>					
5/56	7.2	59	46	39	0.89
6/56	7.0	68	69	43	1.05
7/56	7.4	78	66	48	0.94
9/56	7.5	83	63	58	1.24
11/56	7.3	63	61	44	0.98
<u>5 miles below Estcourt</u>					
5/56	7.0	59	50	43	1.05
6/56	7.0	80	72	48	1.17
7/56	7.6	90	76	52	1.09
9/56	7.4	106	79	64	1.40
11/56	7.1	45	113	41	0.96
2/57	7.4	70	75	34	0.74
<u>Above Weenen</u>					
5/56	7.4	73	53	46	1.00
6/56	6.9	85	65	52	1.32
7/56	7.7	108	90	61	1.29
9/56	8.2	135	95	80	1.60
11/56	7.2	36	97	40	0.91
<u>15 miles below Weenen</u>					
4/54	7.9	160	110	99	2.02
6/54	7.8	150	99	71	1.46
7/54	7.6	153	111	106	2.23
8/54	8.3	190	124	103	2.06
9/54	8.5	268	171	146	2.90
10/54	8.2	180	136	84	1.68
11/54	7.7	110	102	50	1.04

Continued /.....

Table 1 C (continued)

Date of sample	pH	Conductivity, micromho	TDS, ppm	Total alkalinity, as ppm CaCO <sub>3</sub>	Total carbonic acid, millimoles/litre
<u>15 miles below Weenen (continued)</u>					
12/54	7.7	68	57	50	1.04
2/55	7.6	73	68	50	1.05
3/55	8.4	106	91	65	1.29
4/55	8.2	166	194	108	2.16
<u>LITTLE BUSHMANS RIVER</u>					
11/54	7.9	42	43	34	0.69
12/54	7.3	42	32	28	0.62
1/55	7.3	40	35	28	0.62
2/55	7.2	40	35	29	0.66
3/55	7.5	45	38	31	0.66
4/55	6.8	45	45	37	1.00
9/55	7.2	68	63	43	0.95
5/56	6.7	57	46	30	0.86
6/56	6.9	65	64	51	1.30
7/56	7.4	72	61	47	1.02
9/56	7.5	90	70	63	1.35
10/56	7.4	144	90	80	1.74
2/57	7.6	55	73	28	0.59
<u>SUNDAYS RIVER</u>					
12/53	7.4	250	195	91	1.97
6/54	7.4	500	190	100	2.16
7/54	7.9	450	302	154	3.14
8/54	8.3	440	307	111	2.22.
10/54	7.7	155	145	70	1.46
<u>MOOI RIVER</u>					
6/54	7.7	166	118	90	1.87
7/54	8.5	250	153	128	2.54
8/54	8.6	390	283	217	4.26
9/54	8.3	470	302	254	5.08
10/54	7.5	85	143	58	1.24

Continued /.....



Table 1 C (continued)

Date of sample	pH	Conductivity, micromho	TDS, ppm	Total alkalinity, as ppm $\text{CaCO}_3$	Total carbonic acid millimoles/litre
11/54	7.8	94	81	62	1.28
12/54	7.3	110	71	52	1.15
2/55	7.8	87	68	58	1.19
3/55	7.9	104	88	61	1.24
4/55	8.2	178	127	103	2.06
<u>BUFFALO RIVER</u>					
11/53	7.8	170	119	70	1.44
6/54	8.0	202	132	103	2.10
7/54	8.2	250	160	122	2.44
8/54	8.5	270	177	122	2.42
9/54	8.5	285	172	132	2.62
11/54	7.8	136	110	85	1.75

Table 2C

Analyses of unpolluted Natal rivers

River	pH value	Conductivity, micromho	TDS, ppm	Total alkalinity, as ppm $\text{CaCO}_3$	Ca, ppm	Mg, ppm	Na, ppm	K, ppm	$\text{SO}_4$ , ppm	Cl, ppm	$\text{SiO}_2$ , ppm
Illovo at	8.1	59	41	26.1	4.8	1.6	3.9	0.1	Nil	1.0	13.7
Byrne	7.8	65	41	23.7	3.9	3.1	5.2	0.6	3.2	2.1	11.6
Ingagane above	8.4	58	49	39.2	5.0	2.0	4.3	3.6	3.0	0.9	6.7
Alcockspruit	8.1	248	153	75.2	16.7	8.2	24.5	1.5	36.6	7.5	13.3
Karkloof at	7.7	43	42	23.8	3.5	1.7	4.2	0.5	Nil	1.7	16.5
Shafton	7.1	60	58	27.0	4.8	2.6	4.6	0.8	5.1	5.4	15.5
Lions near	7.4	51	51	33.6	3.7	2.8	4.6	0.8	Nil	1.1	18.0
Lidgetton	7.3	66	59	39.1	6.6	3.5	5.5	1.2	1.7	0.1	16.9
Mooi above	7.1	41	42	21.7	5.0	1.8	2.8	0.7	8.2	0.9	6.7
Mooi River	8.0	59	52	26.2	5.9	1.7	4.1	0.6	4.3	4.9	10.1
Mpushini near	8.4	375	252	179.4	27.4	16.1	45.5	1.7	Nil	32.4	21.3
Pietermaritzburg	7.5	403	332	178.0	30.7	19.3	56.0	1.1	4.7	77.5	29.0
Sterk near	8.1	48	36	25.2	2.5	2.2	3.4	0.5	Nil	3.2	9.4
Ambleside	7.4	53	41	23.2	3.1	2.2	4.7	0.7	Nil	4.5	11.5
Tongaat at	7.5	98	74	21.1	2.3	2.6	14.0	1.2	2.7	19.3	17.6
Sibutu	7.4	109	82	23.8	2.7	2.2	19.7	1.4	0.6	21.3	19.9
Umgegu at	7.9	107	81	42.6	5.6	3.9	13.4	1.3	Nil	11.7	19.0
Umfula	7.5	110	80	45.8	5.1	3.8	14.5	1.5	Nil	8.4	21.7
Ugoni at	8.2	54	47	28.1	4.0	2.1	3.5	0.6	Nil	2.5	15.0
Nagle Dam	7.1	91	69	38.2	6.5	3.0	7.9	1.0	1.4	8.9	14.7
Umhloti above	8.0	133	106	46.2	6.1	4.4	19.0	1.6	3.0	23.9	19.8
Verulam	7.7	151	104	43.1	6.1	4.3	21.2	1.3	0.6	20.0	22.5
Umvoti at	6.8	39	31	20.0	2.6	0.4	4.5	1.5	3.6	0.5	6.1
Bitakona	8.0	174	116	65.2	10.2	5.1	18.5	1.1	7.3	13.5	20.8
Umzimkulwana at	8.1	231	123	78.8	11.5	8.2	24.0	1.4	2.0	22.1	6.7
Baboons Castle	8.7	248	143	68.6	11.5	9.6	27.7	1.1	7.3	35.7	9.1
Umzinyatshana	8.5	308	223	165.2	25.7	15.8	25.6	1.7	9.0	6.2	40.0
near Dundee	8.6	319	232	182.6	26.6	20.8	23.7	1.3	7.4	4.6	43.3



Table 3C

Molar percentages for the rivers of Table 2C

River	Ca(OH) <sub>2</sub>	Mg(OH) <sub>2</sub>	NaOH	KOH	H <sub>2</sub> CO <sub>3</sub>	H <sub>2</sub> SO <sub>4</sub>	HCl
Illovo at	12.7	7.0	17.9	2.7	56.7	0.0	3.0
Byrne	8.9	11.8	20.6	1.4	48.9	3.0	5.4
Ingagane above	10.1	6.7	15.1	7.5	56.0	2.5	2.1
Alcockspruit	10.3	8.4	26.3	0.9	39.5	9.4	5.2
Karkloof at	9.8	7.9	20.5	1.4	55.0	0.0	5.4
Shafton	9.8	8.8	16.3	1.7	46.7	4.3	12.4
Lions near	8.0	10.1	17.3	1.8	60.1	0.0	2.7
Lidgetton	10.9	9.7	15.8	2.0	60.2	1.2	0.2
Mooi above	13.8	8.3	13.5	2.0	50.2	9.4	2.8
Mooi River	13.7	6.6	16.7	1.4	44.4	4.2	13.0
Mpushini near	8.6	8.4	24.8	0.5	46.3	0.0	11.4
Pietermaritzburg	7.7	8.1	24.5	0.3	36.9	0.5	22.0
Sterk near	7.3	10.7	17.3	1.5	52.7	0.0	10.5
Ambleside	7.7	9.1	20.2	1.8	48.5	0.0	12.6
Tonga at	3.2	6.0	33.8	1.7	23.5	1.6	30.2
Sibutu	3.0	4.1	38.2	1.6	26.1	0.3	26.7
Umgegu at	6.6	7.6	27.2	1.6	41.5	0.0	15.5
Umfula	5.8	7.1	28.3	1.7	46.4	0.0	10.7
Ungeni at	10.5	9.2	15.9	1.6	55.4	0.0	7.4
Nagle Dam	9.3	7.1	19.5	1.5	47.5	0.8	14.3
Umhloti above	5.5	6.6	29.6	1.5	31.6	1.1	24.1
Verulam	5.4	6.3	32.4	1.2	34.8	0.2	19.7
Umvoti at	7.7	2.0	23.2	4.6	56.4	4.4	1.7
Bitakona	8.4	7.0	26.3	0.9	42.5	2.5	12.4
Umzimkulwana	7.2	8.6	26.1	0.9	41.1	0.5	15.6
at Baboons Castle	6.6	9.1	27.5	0.6	31.5	1.7	23.0
Umzinyatshana	10.6	10.9	18.4	0.7	54.9	1.6	2.9
near Dundee	10.3	13.4	15.9	0.5	56.7	1.2	2.0

Table 4C

Analytical results for the Wilge  
river, OFS

Sample No.	pH value	Conductivity, micromho	TDS, ppm	Total alkalinity, as ppm $\text{CaCO}_3$	Ca, ppm	Mg, ppm	Na, ppm	K, ppm	$\text{SO}_4$ , ppm	Cl, ppm	$\text{SiO}_2$ , ppm
1	8.3	105	81	46.0	9.6	3.8	8.4	4.3	4.4	6.0	17.0
2	8.1	110	90	51.5	10.0	5.5	9.0	4.1	4.0	12.0	14.0
3	7.6	115	116	55.0	12.0	5.3	11.5	5.4	16.6	10.0	22.0
4	8.5	120	87	53.0	10.4	4.8	9.3	4.3	4.3	6.0	16.0
5	8.6	125	97	52.4	12.0	4.5	12.0	4.9	6.4	10.0	16.0
6	8.4	125	99	66.0	13.6	5.5	10.0	2.8	3.4	6.4	18.0
7	7.9	130	104	67.0	14.4	5.8	11.6	3.4	3.0	12.0	14.0
8	7.6	130	109	65.6	13.3	6.0	11.0	4.6	7.6	10.0	17.0
9	7.2	135	98	52.0	12.0	4.1	12.0	5.4	6.8	12.0	14.0
10	7.5	140	109	70.0	14.6	6.5	11.5	4.0	5.6	7.0	18.0
11	8.4	145	109	74.0	15.6	6.0	10.4	2.2	4.0	9.0	17.0
12	8.7	150	110	74.0	15.2	7.0	13.0	3.6	4.5	8.0	14.0
13	8.3	150	116	79.0	16.4	6.2	12.2	2.4	5.0	9.0	17.0
14	8.1	150	117	78.0	16.4	6.7	11.6	3.4	3.1	12.0	17.0
15	8.0	155	109	76.3	14.8	6.0	12.0	3.6	3.0	10.0	14.0
16	7.4	155	112	75.0	15.6	6.7	13.5	3.5	4.6	9.0	14.0
17	8.7	160	114	81.0	16.0	6.5	13.0	2.9	5.0	7.0	15.0
18	7.4	160	123	78.8	16.6	6.8	11.5	3.4	9.0	10.0	18.0
19	7.9	170	119	64.0	13.2	5.8	14.0	5.0	13.8	15.0	14.0
20	7.2	170	130	86.0	17.8	7.3	14.0	3.1	6.0	10.0	20.0
21	8.6	175	116	85.0	15.2	7.7	15.0	3.0	6.0	4.0	14.0
22	8.1	175	123	87.0	18.4	6.2	13.0	3.2	3.3	10.0	17.0
23	8.3	185	123	81.2	15.2	6.7	18.0	4.8	6.4	10.0	13.0
24	8.2	185	135	85.2	16.8	7.7	17.0	3.9	6.4	14.0	18.0
25	8.1	190	121	80.4	16.0	6.0	14.0	4.0	6.5	11.0	15.0
26	8.0	190	134	95.0	19.2	7.9	13.0	2.8	3.8	12.0	18.0
27	8.2	195	134	101.0	19.6	8.4	14.0	2.9	3.5	8.0	17.0
28	8.6	200	141	104.0	20.8	9.1	15.5	2.8	7.8	9.0	14.0
29	7.8	210	132	92.0	17.6	8.2	15.0	3.9	6.0	11.0	15.0

Continued / ...



Table 4C continued

Sample No.	pH value	Conductivity, micromho	TDS, ppm	Total alkalinity, as ppm $\text{CaCO}_3$	Ca, ppm	Mg, ppm	Na, ppm	K, ppm	$\text{SO}_4$ , ppm	Cl, pp	$\text{SiO}_2$ , ppm
30	8.1	210	139	106.4	22.4	9.6	14.0	2.7	4.8	9.0	13.0
31	8.2	210	145	108.0	21.6	8.4	15.5	2.9	3.8	10.0	18.0
32	8.2	215	140	99.0	19.1	8.8	16.0	3.5	6.0	12.0	15.0
33	8.4	225	150	109.2	20.5	10.0	18.0	3.4	7.0	12.0	14.0
34	8.3	225	150	117.2	24.5	10.0	14.0	2.6	5.6	9.6	13.0
35	7.6	230	150	112.4	23.2	10.3	16.0	3.0	7.3	10.0	13.0
36	8.3	235	157	124.0	25.6	11.5	14.8	2.5	5.2	10.0	13.0
37	8.4	240	155	117.6	21.6	10.8	19.0	2.9	7.0	10.0	13.0
38	8.3	250	165	132.0	27.3	11.9	15.5	2.5	5.2	10.0	13.0
39	8.3	270	175	141.0	29.0	12.4	17.2	2.7	6.0	10.0	13.0
40	8.3	280	185	149.6	30.0	13.7	18.6	2.9	6.0	11.0	13.0
41	8.4	290	192	158.0	31.9	14.6	18.6	2.6	6.8	10.0	13.0
42	7.7	305	197	162.4	32.7	14.7	19.0	2.9	6.0	10.0	14.0
43	7.9	305	201	165.2	34.0	14.4	20.0	2.7	6.4	10.0	14.0
44	7.8	320	206	170.4	34.8	15.2	20.0	2.9	6.8	10.0	14.0

Table 5C

Molar percentages for the Wilge river

Sample No.	Ca(OH) <sub>2</sub>	Mg(OH) <sub>2</sub>	NaOH	KOH	H <sub>2</sub> CO <sub>3</sub>	H <sub>2</sub> SO <sub>4</sub>	HCl
1	11.7	7.7	17.8	5.4	47.0	2.2	8.2
2	10.4	9.5	16.4	4.4	43.4	1.7	14.2
3	11.0	8.1	18.2	5.0	41.1	6.3	10.3
4	11.3	8.6	17.5	4.8	48.4	2.0	7.4
5	11.6	7.2	20.2	4.8	42.8	2.6	10.8
6	12.9	8.7	16.5	2.7	51.0	1.3	6.9
7	12.2	8.2	17.0	3.0	47.0	1.1	11.5
8	11.4	8.6	16.4	4.0	47.2	2.7	9.7
9	10.8	6.2	18.8	5.0	44.4	2.6	12.2
10	11.9	8.8	16.3	3.3	51.4	1.9	6.4
11	13.4	8.6	15.6	1.9	50.3	1.4	8.8
12	12.2	9.3	18.0	2.9	49.0	1.5	7.1
13	13.0	8.2	16.8	2.0	50.2	1.7	8.1
14	12.7	8.6	15.6	2.7	48.9	1.0	10.5
15	11.9	8.1	16.8	3.0	50.1	1.0	9.1
16	11.6	8.3	17.5	2.7	50.9	1.4	7.6
17	12.6	8.6	17.8	2.3	50.9	1.6	6.2
18	12.5	8.5	15.0	2.6	50.1	2.8	8.5
19	10.6	7.8	19.4	4.1	40.0	4.6	13.5
20	11.8	8.1	16.2	2.1	52.6	1.7	7.5
21	11.3	9.5	19.2	2.3	52.4	1.9	3.4
22	13.4	7.5	16.5	2.4	51.0	1.0	8.2
23	10.5	7.7	21.5	3.4	47.3	1.8	7.8
24	11.1	8.5	19.5	2.6	46.1	1.8	10.4
25	12.0	7.5	18.2	3.1	47.9	2.0	9.3
26	12.8	8.8	15.2	1.9	51.2	1.1	9.0
27	12.8	9.1	15.9	1.9	53.4	1.0	5.9
28	12.8	9.4	16.6	1.8	51.1	2.0	6.3
29	11.5	9.0	17.0	2.6	50.2	1.6	8.1
30	13.5	9.6	14.7	1.7	53.2	1.2	6.1
31	13.0	8.5	16.3	1.8	52.5	1.0	6.9
32	11.9	9.1	17.3	2.2	49.6	1.5	8.4

Continued / ...



Table 5C continued

Sample No.	$\text{Ca(OH)}_2$	$\text{Mg(OH)}_2$	$\text{NaOH}$	$\text{KOH}$	$\text{H}_2\text{CO}_3$	$\text{H}_2\text{SO}_4$	$\text{HCl}$
33	11.6	9.5	17.7	2.0	49.8	1.7	7.7
34	14.0	9.5	13.9	1.5	53.6	1.3	6.2
35	12.7	9.4	15.3	1.7	53.0	1.7	6.2
36	13.6	10.2	13.7	1.4	53.9	1.2	6.0
37	11.7	9.8	18.0	1.6	51.2	1.6	6.1
38	13.8	10.1	13.7	1.3	54.3	1.1	5.7
39	13.8	9.8	14.2	1.3	54.3	1.2	5.4
40	13.4	10.2	14.4	1.3	54.1	1.1	5.5
41	13.7	10.4	14.0	1.1	54.8	1.2	4.8
42	13.4	10.0	13.5	1.2	56.3	1.0	4.6
43	13.8	9.7	14.1	1.1	55.6	1.1	4.6
44	13.7	10.0	13.6	1.2	56.0	1.1	4.4

Table 6C

Analyses of Natal rivers sampled at different stations

River	Station	pH value	Conductivity, micromho	TDS, ppm	Total alkalinity, as ppm CaCO <sub>3</sub>	Ca, ppm	Mg, ppm	Na, ppm	K, ppm	SO <sub>4</sub> , ppm	Cl, ppm	SiO <sub>2</sub> , ppm
Illovo	Below Richmond Rosebank	7.32	113	49	30.2	5.6	2.5	6.2	0.7	Nil	4.1	10.5
		7.50	133	60	38.6	6.9	3.6	8.8	0.7	Nil	6.2	9.6
Isipingo	Near Inwabi Isipingo Rail	8.00	510	320	61.3	13.5	15.8	73.5	2.7	13.7	140.8	16.4
		7.30	387	248	60.6	7.9	11.8	59.0	2.9	15.5	86.0	25.0
Umgeni	Above Nagle Dam Natal Estates	7.10	102	71	47.4	6.8	3.4	9.8	0.9	3.7	4.3	13.4
		6.90	175	108	59.4	9.0	5.5	22.2	1.4	5.2	15.7	13.0
Umhlali	Hopewell Shakaskraal	7.03	167	118	13.7	4.2	5.2	22.5	1.3	14.5	36.0	18.6
		6.77	227	168	23.6	7.8	8.5	33.0	2.4	29.5	52.7	15.1
Umhlatuzana	Above Pinetown Mariannhill	6.98	112	65	17.0	2.8	1.1	14.1	1.5	1.3	18.7	14.2
		7.21	183	97	31.4	4.2	4.3	22.7	2.2	1.3	27.5	13.3
Umhloti	Ndwedwe Above Verulam	8.29	109	87	40.8	5.2	3.8	13.5	1.3	1.3	12.5	23.1
		8.03	133	106	46.2	6.1	4.4	19.0	1.6	3.0	23.9	19.8
Umvoti	Glenmill Aldinville	7.83	185	116	57.9	9.1	5.9	23.3	1.3	2.4	21.2	17.1
		7.80	185	114	53.5	8.9	5.5	22.5	1.5	1.9	23.9	16.1
Umzimkulwana	Celebini Baboons Castle	8.00	226	153	70.0	11.6	10.0	20.7	0.8	5.4	38.0	15.8
		8.70	248	144	76.6	11.5	9.6	27.7	1.1	7.3	35.7	9.1



Table 7C

Molar percentages from Table 6C

River	Station	Ca(OH) <sub>2</sub>	Mg(OH) <sub>2</sub>	NaOH	KOH	H <sub>2</sub> CO <sub>3</sub>	H <sub>2</sub> SO <sub>4</sub>	HCl
Illovo	Below Richmond	10.4	7.7	20.0	1.3	52.0	0.0	8.6
	Rosebank	9.7	8.4	21.5	1.0	49.6	0.0	9.8
Isipingo	Near Inwabi	3.6	6.9	33.7	0.7	11.9	1.5	41.7
	Isipingo Rail	2.7	6.8	35.2	1.0	18.7	2.2	33.4
Umgenei	Above Nagle Dam	8.5	7.1	21.4	1.2	53.8	1.9	6.1
	Natal Estates	6.3	6.4	27.1	1.0	45.3	1.5	12.4
Umhloti	Hopewell	3.7	7.6	34.0	1.2	12.8	5.3	35.4
	Shakaskraal	4.3	7.9	31.9	1.4	14.7	6.8	33.0
Umhlatuzana	Above Pinetown	4.0	2.6	35.1	2.2	25.2	0.8	30.1
	Mariannhill	3.6	6.1	33.7	1.9	27.7	0.5	26.5
Umhloti	Ndwedwe	6.2	7.5	28.0	1.6	39.2	0.6	16.9
	Above Verulam	5.5	6.6	29.7	1.5	31.4	1.1	24.2
Umvoti	Glenmill	6.6	7.2	29.4	1.0	37.7	0.7	17.4
	Aldinville	6.7	6.8	29.3	1.1	35.3	0.6	20.2
Umzimkulwana	Celebini	7.1	10.3	22.1	0.5	32.3	1.4	26.3
	Baboons Castle	6.2	8.6	25.8	0.6	35.4	1.6	21.8

Table 8C

Analyses of Natal rivers above and below  
sources of pollution

River	Station	pH value	Conductivity, micromho	TDS, ppm	Total alkalinity, as ppm $\text{CaCO}_3$	Ca, ppm	Mg, ppm	Na, ppm	K, ppm	$\text{SO}_4$ , ppm	Cl, ppm	$\text{SiO}_2$ , ppm
Ingagane	Above Alcockspruit	8.1	248	154	75.2	16.7	8.2	24.5	1.5	36.6	7.5	13.3
	Confluence with Incondu	8.5	396	251	88.9	29.4	17.6	31.2	2.0	102.5	9.0	10.4
Mooi	Above Mooi River	8.0	59	48	27.0	5.9	1.7	4.1	0.6	4.3	4.9	10.1
	Below Mooi River	9.0	86	62	37.0	6.0	1.9	10.3	0.8	5.4	6.9	8.0
Umbogintwini	Above factory	7.62	260	145	48.7	6.9	6.1	35.4	1.5	5.5	50.0	9.9
	Below factory	6.27	1321	1150	19.4	87.7	75.7	138.6	9.5	722.5	64.2	22.0
Umzinyatshana	Above St George	8.6	264	232	185.6	26.6	20.8	24.0	1.3	7.0	4.6	43.3
	Below Steenkoolspruit	7.4	1210	1037	128.0	94.6	45.1	96.0	2.3	697.0	20.0	4.5



Table 9C

Molar percentages from Table 8C

River	Station	Ca(OH) <sub>2</sub>	Mg(OH) <sub>2</sub>	NaOH	KOH	H <sub>2</sub> CO <sub>3</sub>	H <sub>2</sub> SO <sub>4</sub>	HCl
Ingagane	Above Alcockspruit	10.3	8.4	26.3	0.9	39.5	9.4	5.2
	Confluence with Incandu	12.2	12.1	22.5	0.8	30.5	17.7	4.2
Moci	Above Moci River	13.7	6.6	16.5	1.4	44.8	4.2	12.8
	Below Moci River	9.4	5.0	28.1	1.3	41.2	3.5	11.5
Umbogintwini	Above factory	3.9	5.7	34.4	0.9	22.2	1.3	31.6
	Below factory	10.1	14.6	27.9	1.1	3.0	34.9	8.4
Umzinyatshana	Above St. George	10.1	13.3	15.8	0.5	57.2	1.1	2.0
	Below Steenkool-spruit	12.5	9.9	22.1	0.3	13.9	38.3	3.0

Table 10C

Molar percentages of unpolluted Natal rivers

R i v e r	Molar percentages						
	Ca(OH) <sub>2</sub>	Mg(OH) <sub>2</sub>	NaOH	KOH	H <sub>2</sub> CO <sub>3</sub>	H <sub>2</sub> SO <sub>4</sub>	HCl
Dorps above Utrecht	14.4	10.0	12.3	1.3	59.8	1.6	0.6
Little Tugela at Winterton	11.4	7.8	17.8	1.8	58.8	0.0	2.4
Little Bushmans above Estcourt	10.4	9.7	15.1	1.7	57.2	0.8	5.1
Sandspruit at Bergville	8.7	7.4	19.8	0.9	57.2	2.0	4.0
Bushmans at Estcourt	10.8	7.9	17.1	2.4	56.4	1.0	4.4
Incandu above Newcastle	12.0	5.7	17.5	2.1	55.1	2.2	5.4
Slang at confluence	10.9	9.1	16.8	2.6	55.1	0.6	4.9
Nondweni near Barklieside	11.5	11.8	14.5	0.3	53.7	0.5	7.7
Ingogo at Poonges Kraal	12.3	12.3	10.7	1.9	53.4	3.3	6.1
Blood at confluence	14.0	9.3	13.8	2.0	51.8	2.0	7.1
White Unfolozi near Ulundi	10.2	10.9	17.3	0.6	51.7	0.4	8.9
Umvunyama near Barklieside	8.1	15.4	14.1	0.4	51.0	0.8	10.2
Buffalo at Vants Drift	15.3	7.1	15.8	2.4	50.9	1.0	7.5
Waschbank near Utrecht	12.9	8.3	21.1	1.2	48.9	6.7	0.9
Hlimbitwa at confluence	9.8	6.3	26.1	1.1	43.0	0.7	13.0
Umlaas at Thornwood	5.8	9.8	27.0	1.1	34.2	2.4	19.7
Bloukrans at confluence	10.5	11.4	18.8	0.9	33.5	5.5	19.4
Umhloti near Mt. Moreland	5.6	7.1	30.0	1.0	31.6	1.2	23.5
Illovo above Illovo	5.9	6.8	29.4	1.1	31.1	0.4	25.3
Umhlatuzana at Mariannhill	3.6	6.1	33.6	1.9	27.9	0.5	26.4
Little Amanzintoti at Smithfield	4.0	7.5	32.8	0.8	25.0	0.9	29.0
Umhlali at Shakaskraal	5.5	5.8	32.2	1.3	23.4	3.5	28.3
Umhlutuni near New Guelderland	4.0	8.1	31.4	0.5	22.8	2.2	31.0
Umbogintwini above factory	3.9	5.7	34.4	0.9	22.2	1.3	31.6
Umhlatuzi at River View	3.7	8.3	31.6	0.3	21.7	1.1	33.3
Etete near Shakaskraal	5.5	6.3	30.3	1.0	20.1	2.0	34.8
Amanzimtoti above town	2.7	6.3	35.1	1.2	15.0	1.8	37.9
Sinkwazi near station	9.0	5.8	33.7	0.2	9.2	12.0	30.1



Table 11 C

American rivers

R i v e r	Molar percentages						
	Ca(OH) <sub>2</sub>	Mg(OH) <sub>2</sub>	NaOH	KOH	H <sub>2</sub> CO <sub>3</sub>	H <sub>2</sub> SO <sub>4</sub>	HCl
Alabama	18	6	14	2	52	5	3
Allegheny	16	5	20	2	31	8	18
Arkansas	8	3	34	2	17	7	29
Big Blue	16	6	17	2	48	5	6
Brazos	10	5	33	2	11	9	30
Cache	14	8	18	2	46	6	6
Cahaba	16	5	18	2	51	5	3
Cedar	19	10	6	2	56	5	2
Chattahoochee	11	3	29	2	46	5	4
Chikaskia	17	5	16	2	51	4	5
Chippewa	15	9	15	2	50	7	2
Cimarron	5	3	38	2	13	4	35
Clackamas	19	9	10	2	48	6	6
Columbia	18	8	12	2	51	6	3
Columbia	21	9	6	2	55	6	1
Cottonwood	22	8	8	2	45	12	3
Crooked	10	7	25	2	49	3	4
Cumberland	21	5	12	2	54	4	2
Delaware	18	8	12	2	48	7	5
Deschutes	11	6	25	2	51	2	3
Des Moines	19	11	8	2	48	10	2
Embarrass	17	13	6	2	56	4	2
Fall	18	6	13	2	54	3	4
Flint	19	5	23	2	39	5	7
Fox	17	14	5	2	53	7	2
Grand	20	11	4	2	55	5	3
Grande Ronde	15	3	21	2	54	3	2
Hudson	20	6	11	2	50	6	5
Illinois	17	12	8	2	49	7	5
Iowa	18	10	7	2	55	6	2
James	18	6	14	2	55	4	3
Kalamazoo	20	11	3	2	59	4	1
Kankakee	20	12	5	2	53	6	2

Continued / ...

Table 11C continued

R i v e r		Molar percentages						
		Ca(OH) <sub>2</sub>	Mg(OH) <sub>2</sub>	NaOH	KOH	H <sub>2</sub> CO <sub>3</sub>	H <sub>2</sub> SO <sub>4</sub>	HCl
Kansas		16	6	18	2	42	6	10
Kaskaskia	*	17	13	7	2	53	5	3
Kentucky		21	6	10	2	55	4	2
Klickitat		13	9	18	2	52	5	1
Lehigh	*	17	11	13	2	35	15	7
Marmaton	*	23	4	10	2	55	4	2
Maumee	*	19	8	11	2	40	6	14
Medicine Lodge	*	18	8	19	2	19	21	13
Miami	*	19	13	3	2	56	5	2
Mississippi	*	17	9	14	2	46	8	4
Mississippi		18	11	6	2	58	4	1
Missouri	*	17	8	19	2	35	15	4
Monongahela	*	20	6	20	2	21	24	7
Muddy	*	14	11	18	2	30	17	8
Muskingum	*	18	6	15	2	33	7	19
Okanogan		19	7	12	2	53	6	1
Oostanaula		15	6	18	2	55	2	2
Osage		20	6	12	2	53	4	3
Oswegatchee		18	8	11	2	55	5	1
Pearl		13	4	26	2	43	5	7
Peedee		13	3	26	2	47	3	6
Platte	*	17	8	20	2	32	17	4
Platte, North	*	17	7	18	2	42	11	3
Potomac	*	23	7	14	2	24	23	7
Powder		12	6	24	2	47	5	4
Raritan	*	18	10	22	2	33	7	8
Red		13	5	26	2	20	10	24
Republican		15	5	20	2	46	5	7
Rock		16	14	4	2	59	3	2
Rogue		14	5	21	2	52	3	3
Sacramento		12	10	18	2	46	6	6
Salinas		12	9	20	2	40	8	9
Saluda		17	4	19	2	46	4	8
San Antonio		16	9	15	2	41	10	7
San Gabriel		19	8	11	2	53	5	2

Continued / ....



Table 11C continued

R i v e r	Molar percentages						
	Ca(OH) <sub>2</sub>	Mg(OH) <sub>2</sub>	NaOH	KOH	H <sub>2</sub> CO <sub>3</sub>	H <sub>2</sub> SO <sub>4</sub>	HCl
Sangamon	17	13	6	2	56	4	2
San Joaquin	9	8	26	2	24	7	24
Santa Ana	16	6	17	2	51	3	5
Shenandoah	20	9	6	2	59	2	2
Siletz	12	4	28	2	36	5	13
Skagit *	19	7	13	2	49	8	2
Smoky Hill *	13	4	28	2	18	11	24
Snake *	15	7	17	2	43	7	9
Solomon *	15	4	23	2	37	7	12
Spokane	17	9	12	2	54	5	1
Spring *	23	5	12	2	43	12	3
Susquehanna *	21	6	11	2	48	6	6
Tennessee	19	6	11	2	50	2	10
Tombigbee *	19	3	17	2	53	3	3
Umatilla	13	6	22	2	46	5	6
Umpqua	15	7	17	2	49	4	6
Ventura *	20	9	13	2	32	20	4
Verdigris	19	5	13	2	51	3	7
Vermillion *	16	14	7	2	51	8	2
Wabash	9	7	26	2	15	4	37
Wabash, Little	14	10	15	2	54	9	6
Wallowa *	25	2	10	2	54	6	1
Walnut *	21	7	11	2	47	8	4
Wateree	12	5	24	2	48	3	6
Wenatchee	14	9	16	2	50	7	2
White, E. Fork *	19	12	3	2	59	4	1
White, W. Fork *	15	9	14	2	38	5	17
Willamette	15	7	18	2	47	4	7
Wisconsin	14	12	13	2	50	7	2
Youghiogeny *	22	11	13	2	0	47	5
Yakima	14	9	20	2	42	8	5
Yukon	22	8	5	2	58	4	1

Table 12C

British rivers

River		Molar percentages						
		$\text{Ca}(\text{OH})_2$	$\text{Mg}(\text{OH})_2$	NaOH	KOH	$\text{H}_2\text{CO}_3$	$\text{H}_2\text{SO}_4$	HCl
Stone	*	2	15	25	-	35	3	20
Swancombe	*	3	15	24	-	36	2	20
Holyford	*	17	2	26	-	20	8	27
De Lank	**	13	13	12	-	24	1	37
Avon		21	10	10	-	42	12	5
Cork	*	10	3	32	-	22	4	29
Liffey		24	3	11	-	49	4	9
Nantybella	*	3	4	42	-	8	4	39
Cerlog	*	12	5	28	-	19	7	29
Dee	**	17	5	23	-	24	10	21
Dee		18	7	16	-	39	7	13
Taff		13	11	20	-	41	9	6
Avon		27	1	9	-	54	2	7
Itchen		29	0	8	-	54	1	8
Now		25	3	10	-	51	3	8
Thames		28	3	7	-	48	7	7
Thames		25	2	15	-	41	3	14
Thames	**	3	12	29	-	1	7	46
Lee		28	2	11	-	43	7	9
Lee		26	5	11	-	39	10	9
Chelmer		27	2	10	-	49	4	8
Blackwater		24	2	13	-	45	5	11
Stour		24	3	12	-	47	4	10
Stour		28	1	8	-	54	2	7
Witham		30	2	8	-	41	12	7
Welland		28	5	6	-	43	9	9
Bure		16	1	26	-	28	5	24
Ouse	*	26	3	11	-	45	7	8
Windrush		27	2	9	-	54	3	5
Severn		15	10	20	-	27	12	16
Wye		21	3	20	-	28	12	16
Worfe		22	5	14	-	39	9	11

Continued / ...



Table 12C continued

R i v e r	Molar percentages						
	$\text{Ca}(\text{OH})_2$	$\text{Mg}(\text{OH})_2$	NaOH	KOH	$\text{H}_2\text{CO}_3$	$\text{H}_2\text{SO}_4$	HCl
Chess	29	1	8	-	55	2	5
Newbourne	27	0	14	-	45	4	10
Mole	26	7	7	-	41	11	8
Caterham	29	3	6	-	45	4	13
Colne	29	1	8	-	52	3	7
Tees	18	15	9	-	37	12	9
Little Avon	29	2	8	-	49	6	6
Otter *	18	5	20	-	35	5	17
Usk *	23	2	14	-	50	2	9
Kennet	28	1	9	-	53	3	6
Roach *	9	5	33	-	27	8	18
Mullinger	29	2	6	-	55	4	4

APPENDIX D

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SOME EXPERIMENTAL TESTS



In order to obtain some experimental check on some of the equations presented, a set of solutions resembling natural waters was prepared from distilled water and laboratory reagents - calcium chloride, magnesium sulphate, sodium chloride, sodium carbonate, sodium bicarbonate, magnesium carbonate and calcium hydroxide. Stock solutions of these in distilled water were prepared, the solutions being gassed with carbon dioxide if necessary to convert insoluble compounds to soluble bicarbonates, and from the stock solutions fourteen samples were prepared whose analyses are given in Table 1 D. Their pH values were adjusted to lie within the desired range by gassing with carbon dioxide or with air (to remove excess carbon dioxide).

All the analyses showed a satisfactory ionic balance.

The values of the activity coefficient,  $\gamma$ , for these samples are not strictly obtainable from the TDS by Table 2 B, since that table really applies only to natural waters. The correct values of  $\gamma$  were therefore calculated from the ionic strengths, which were themselves obtained by taking the carbonate and bicarbonate ion concentrations as being closely equal to the corresponding alkalinities. The values so obtained are shown in Table 2 D, with those found from the TDS also given for comparison. The two sets of values differ only slightly, the greatest error in the values calculated from the TDS amounting to only 1.7% (for sample no. 5).

From the observed pH and the calculated value of  $\gamma$  from the ionic strength, the appropriate value of  $Q$  was obtained from Table 3 B. Taking the total alkalinity,  $\bar{e}$ , in meq/litre as the mean of  $\bar{e}_c$  and  $\bar{e}_t$  in the usual way, the total carbonic acid concentration,  $\bar{a}$ , in millimoles/litre was calculated. This was compared with the experimental value obtained by titrating with standard hydrochloric acid and sodium hydroxide, as shown in Table 3 D. The maximum error in the calculated value was 11.1% (for sample no. 1), and the signless mean error was 5.6%. In chapter 5 it was deduced that the error in the calculated value of  $\bar{a}$  would be about 5% due to errors in dissociation constants, activity coefficients and pH measurements. Since the experimental value will also carry an appreciable error, as do the results of all water analyses, the experimental and calculated values of  $\bar{a}$  could diverge easily by 10%. The agreement obtained between the two sets of values can thus be considered very good. They are compared graphically in Figure 1 D.



Alternatively, the calculation may be reversed and the pH value calculated from the experimental values of  $\bar{a}$  and  $\bar{e}$  (here taking  $\bar{e}$  as the directly measured experimental value  $\bar{e}_t$ ). This gives the results shown in Table 4 D and compared graphically in Figure 2 D. The greatest discrepancy amounts to 0.31 unit (for sample no. 5), the signless average being 0.17 unit.

These results clearly show that the relations between  $\bar{a}$ ,  $\bar{e}$  and pH are adequately represented by the equations concerned. Discrepancies are readily accounted for by analytical errors, which in fact constitute the greatest problem in water chemistry. It may also be noted that by assuming ideality ( $\gamma = 1.000$ ), the calculated pH values of Table 4 D are unchanged while the greatest error in the calculated values of  $\bar{a}$  of Table 3 D amounts to 4.5% (sample no. 4), confirming that activity corrections are not usually needed when considering normal surface waters.

For each of the samples, the permanent hardness was determined in the following manner. 100 ml of the sample in a 500 ml round-bottomed flask was boiled under reflux for 30 minutes and then, after removal from the heater, was allowed to cool for 30 minutes, the mouth of the flask during this time being covered by a watch glass. The sample was then filtered on a no. 42 paper, the first runnings being used to rinse out the receiver and then being rejected. The total hardness of the filtrate was finally determined by titration with EDTA. Subtraction from the original total hardness gave the temporary hardness of the sample. The results obtained are shown in Table 5 D, together with those calculated by the procedure described in chapter 11. The experimental and calculated values are compared graphically in Figures 3 D and 4 D.

On the whole, these results show that the calculated values represent the experimental values fairly well, despite the approximations involved on the one hand and the uncertainties in the experimental technique on the other. The exceptions are samples 5, 6 and 13, each of which gave a very much greater permanent hardness than the calculated value. These are the three samples of greatest magnesium content.

The pH values of the samples after filtration are given in the last column of Table 5 D. They range from 7.64 to 10.17 and do not at all accord with the values calculated from equation (11.29), which range from 9.99 to 10.67. This discrepancy was as expected.



Table 1 D

Analyses of water samples

Sample No:	pH value	Ca, ppm	Mg, ppm	Na, ppm	Total alkalinity, as ppm $\text{CaCO}_3$ *	$\text{SO}_4$ ppm	Cl, ppm	Total hardness, as ppm $\text{CaCO}_3$	Calcd. TDS, ppm
1	7.38	26.5	21.1	114.0	79.7	80.0	185.3	153.2	475
2	6.68	26.4	21.0	114.0	78.1	80.0	185.3	152.8	474
3	6.83	5.3	4.5	22.8	15.9	16.0	37.1	31.9	95
4	6.40	5.1	4.6	22.8	15.4	16.0	37.1	31.7	95
5	8.42	13.2	57.0	54.8	353.6	Nil	12.0	267.8	349
6	6.99	13.0	57.1	54.8	352.1	Nil	12.0	267.6	348
7	8.13	2.7	11.3	11.0	82.2	Nil	2.4	53.5	78
8	7.12	2.9	11.4	11.0	82.2	Nil	2.4	54.7	77
9	7.89	52.9	41.1	70.8	132.7	160.0	127.9	301.3	532
10	7.00	53.3	41.0	70.8	137.2	160.0	127.9	302.3	535
11	6.77	10.7	8.2	14.2	31.4	32.0	25.6	60.5	110
12	6.46	10.4	8.4	14.2	31.9	32.0	25.6	60.5	110
13	7.13	67.8	63.5	35.2	514.3	Nil	12.1	431.2	487
14	7.09	16.3	17.6	13.3	123.9	Nil	12.1	113.0	134

\* All bicarbonate alkalinity except for No. 5, which had carbonate alkalinity amounting to 19.5 ppm as  $\text{CaCO}_3$

Table 2 D

Values of activity coefficients,  $\gamma$

Sample No.	$\gamma$ calculated from ionic strength	$\gamma$ calculated from the TDS
1	0.900	0.896
2	0.900	0.897
3	0.950	0.953
4	0.950	0.953
5	0.899	0.913
6	0.900	0.913
7	0.950	0.959
8	0.950	0.959
9	0.887	0.891
10	0.887	0.891
11	0.943	0.949
12	0.943	0.949
13	0.885	0.895
14	0.934	0.943



Table 3 D

Total carbonic acid concentrations,  $\bar{a}$

Sample No.	Calculated value of $\bar{a}$	Experimental value of $\bar{a}$	% error in calculated value
1	1.485	1.670	- 11.1
2	1.933	2.032	- 4.9
3	0.378	0.374	+ 1.1
4	0.521	0.534	- 2.4
5	7.206	6.876	+ 4.8
6	8.698	7.850	+ 10.8
7	1.582	1.656	- 4.5
8	1.827	1.814	+ 0.7
9	2.483	2.710	- 8.4
10	2.981	3.102	- 3.9
11	0.726	0.816	- 11.0
12	0.949	0.938	+ 1.2
13	11.591	11.208	+ 3.4
14	3.024	2.742	- 10.3

Table 4 D

Observed and calculated pH values

Sample No.	Observed pH	Calculated pH
1	7.38	7.60
2	6.68	6.83
3	6.83	7.08
4	6.40	6.47
5	8.42	8.73
6	6.99	7.23
7	8.13	8.10
8	7.12	7.35
9	7.89	7.90
10	7.00	7.20
11	6.77	6.86
12	6.46	6.66
13	7.13	7.35
14	7.09	7.30



Table 5 D

Hardness determinations \*

Sample No.	Original total hardness	Permanent hardness		Temporary hardness		Final pH
		Experimental	Calculated	Experimental	Calculated	
1	153.2	113.3	94.6	36.9	58.6	8.68
2	152.8	111.6	96.5	41.2	56.3	8.68
3	31.9	31.7	29.7	0.2	2.2	7.64
4	31.7	32.1	29.7	- 0.4	2.0	7.67
5	267.8	60.4	11.4	207.4	256.4	9.61
6	267.6	90.5	11.5	177.1	256.1	9.44
7	53.5	24.9	28.6	28.6	24.9	9.58
8	54.7	25.7	29.0	29.0	35.7	9.57
9	301.3	184.0	191.9	117.3	109.4	8.83
10	302.3	183.2	190.6	119.1	111.7	8.85
11	60.5	53.5	49.0	7.0	11.5	8.88
12	60.5	54.1	49.2	5.9	11.3	8.73
13	431.2	85.3	15.3	345.9	415.9	10.17
14	113.0	37.6	35.1	75.4	77.9	9.80

\* All values as ppm of  $\text{CaCO}_3$  except in last column

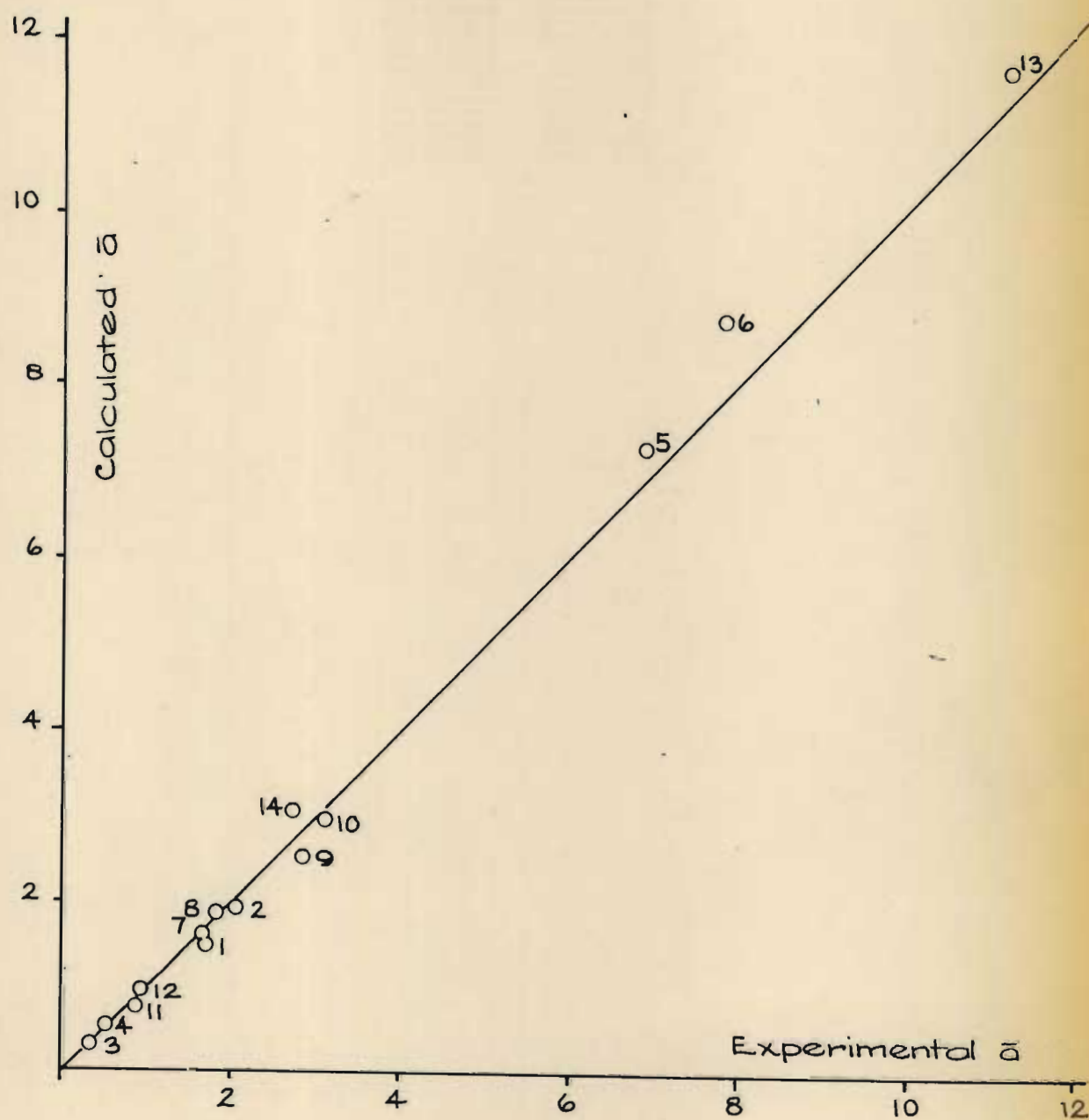


FIGURE 1D

Comparison of values of  $\bar{a}$



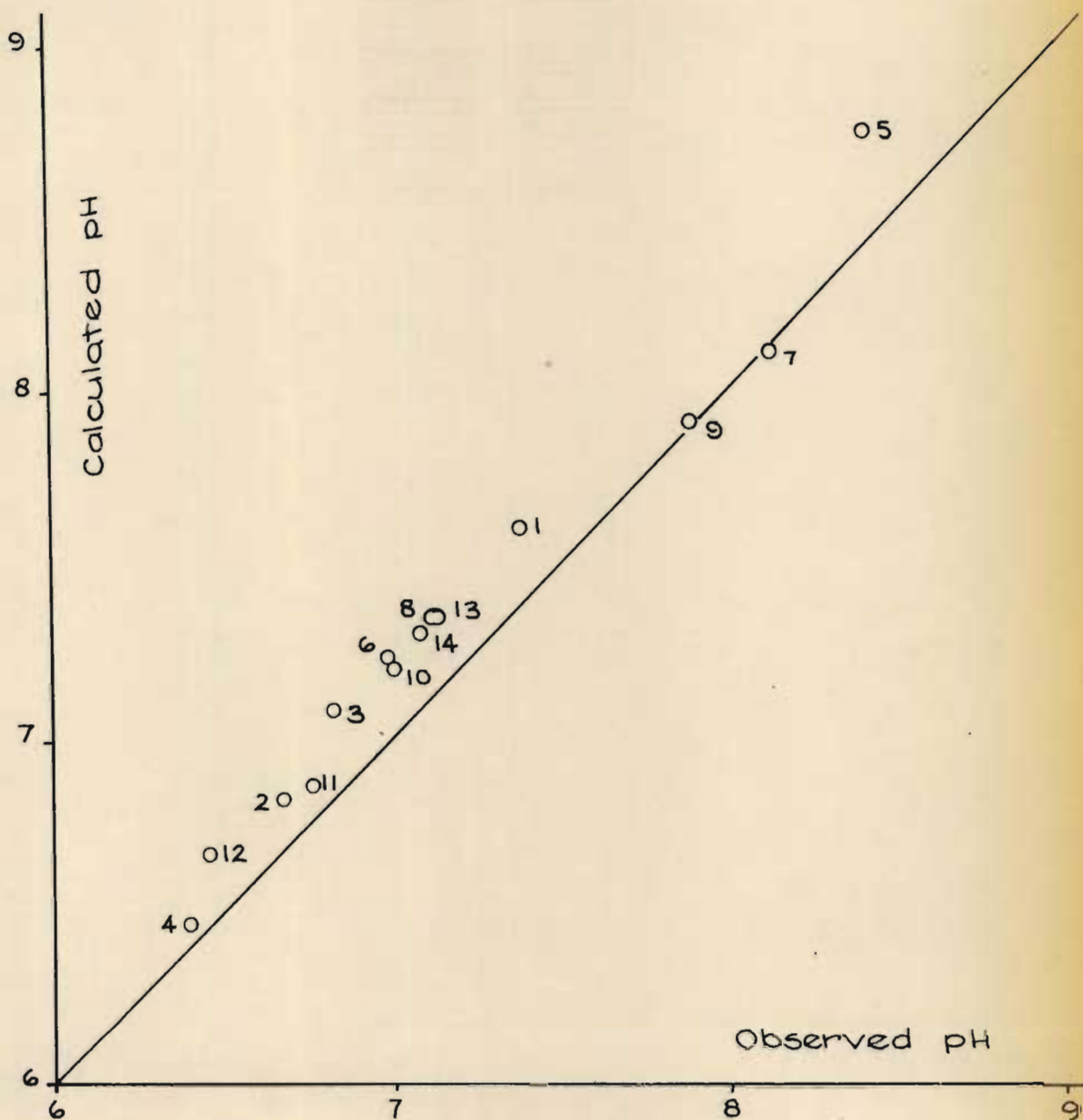


FIGURE 2D  
Comparison of pH values

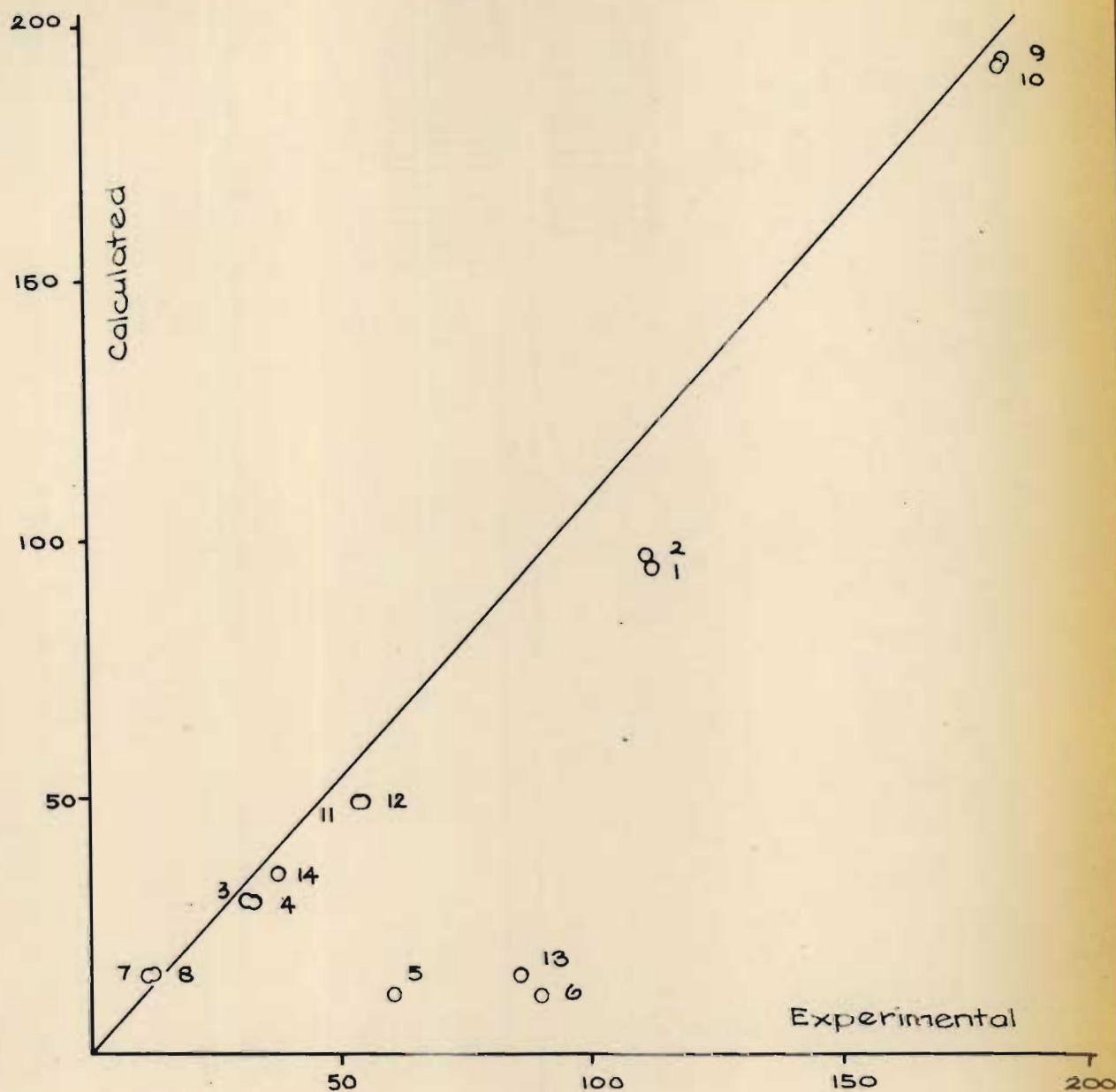


FIGURE 3D

Comparison of permanent hardness  
(as ppm of  $\text{CaCO}_3$ )



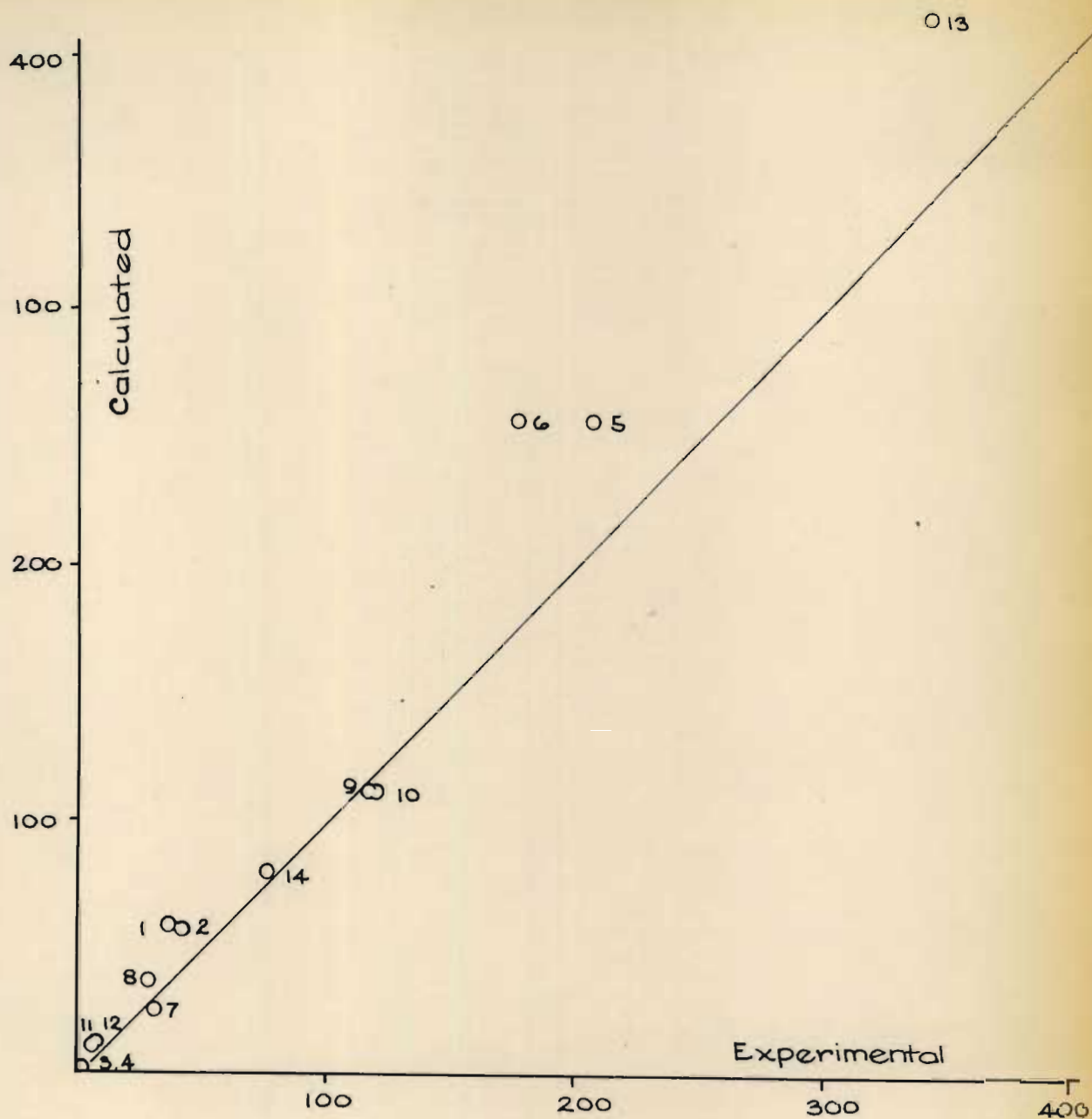


FIGURE 4D

Comparison of temporary hardnesses  
(as ppm of  $\text{CaCO}_3$ )

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