
HOW TO UNDERSTAND ACID-BASE

**A Quantitative Acid-Base Primer
for Biology and Medicine**

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INTRODUCTION

Acid-base chemistry is an important topic in biology, biochemistry, physiology, and clinical medicine, a topic that should be thoroughly understood by everyone in these fields. Despite this importance, the topic is usually approached in a piecemeal, qualitative, and confusing way, so that misunderstanding and disagreement seem to be much more common than the kind of useful quantitative understanding that is needed. The reason is partly that acid-base chemistry, like many topics in biology and medicine, can only be simplified down to a certain minimum level before serious errors and misinterpretations result. This minimum level is the elementary physical chemistry of aqueous solutions containing ions. Its major message is that we can only make sense of acid-base behavior of body fluids by taking into account how all the ions, not just hydrogen ions, participate in that behavior; hydrogen ions in body fluids cannot be understood as independent entities. Treating that elementary chemistry quantitatively, as we shall do in this book, not only enables us to understand hydrogen ion behavior clearly, it also relates that behavior to fluid and electrolyte balance in the whole organism in a direct and coherent way. Mastering the elementary chemistry is therefore well worth the minor effort involved.

We present the minimum necessary physical and chemical principles in Chapter 2. The rest of the book will then demonstrate their relevance and power by explaining the apparent complexities of acid-base phenomena in simple but thorough and quantitative terms. The treatment will progress from the simplest system, pure water, in Chapter 3, through

progressively more complex solutions and body fluids in succeeding chapters, to the final, surprisingly simple treatment of whole-body acid–base balance in Chapter 9.

Modern chemistry, even at the elementary level needed to understand hydrogen ion behavior, is largely understood in quantitative, and therefore mathematical, terms. Until recently, that mathematics has been avoided in acid–base chemistry for the sensible reason that it was not very much help before computers became available. Hydrogen ion concentration, the focus of acid–base chemistry, depends on severable variables, and the quantitative description of its behavior requires many simultaneous equations. Explicit analytical solutions for such sets of equations, when they can be written at all, are not usually regarded as useful because they are so unwieldy for practical calculations. Computers, including hand-held programmable calculators, have completely changed this situation; numerical values for the solutions to such equations are now easily and rapidly obtained by computer-implemented techniques of numerical analysis. As a result, computers have revolutionized our ability to analyze, understand, and predict the acid–base behavior of body fluids, or any solutions of biological or medical interest. This book is both an exposition, and an exploitation for its practical usefulness, of that revolution.

The treatment of acid–base chemistry and biology in this book is necessarily not at all like the treatments in current textbooks and research journals. References to previous literature are therefore sparse. There are so many differences in detail between the quantitative analytical treatment presented here and the conventional qualitative treatments that comparisons with even a few of the classical descriptions would have greatly increased the size of this book. It seemed more valuable in this introductory account to concentrate on the basic principles, and their important quantitative consequences, leaving to the reader the task of comparison and translation.

The nonmathematically oriented reader may ask at this point, how much of this new quantitative understanding of acid–base can be achieved without actually working through all the tedious details of the mathematics and the computer programs? The answer supplied by this book is that the minimum level of mathematical sophistication required is only that needed to appreciate what the relevant equations mean, why they must be true, and how they are related to each other. How they are to be solved can then be treated as an incidental technical problem. Most of the mathematical details therefore appear in appendices to the appropriate chapters rather than in the main text. They are there for those who want them, but for those who do not, they will not interrupt the flow of the main arguments. What we want to know is what the mathematics tells us about the behavior of all the variables in body fluids, especially hydrogen ion concentration, once we have specified the quantitative constraints on that

behavior that the laws of physics and chemistry require. Once calculated by the computer, that behavior is readily understood from computer-generated graphs and tables of values. These provide qualitative as well as quantitative pictures of the acid-base behavior of each solution.

In summary, this book presents a nontraditional treatment of acid-base behavior in body fluids. Its purpose is to help the reader work through the elementary physical chemistry of ionic solutions to the synthesis of a clear, quantitative, and practical understanding of how and why hydrogen ion concentration behaves as it does in those solutions and in the whole organism.

CHAPTER ONE

BODY FLUIDS

1.1. INTRODUCTION

The treatment in the following pages will focus on acid–base behavior in the fluids of the human body, but it should be clear that the method and the results are easily extended to any and all biological situations in which acid–base phenomena are important. The properties of human body fluids are of obvious clinical importance, and therefore provide a highly motivating as well as specific and concrete referent for our analyses.

The human body is normally about 60% water. In a standard 70-kg male adult, therefore, there must be about 42 liters of aqueous solutions whose acid–base properties we need to understand. That means understanding why the hydrogen ion concentration has the values it does in these fluids and how and why it changes as it does. We shall begin to do that in the next chapter. First, in this chapter we present a summary picture of those 42 liters of solutions.

The body is not, of course, simply a 42-liter tank. It is organized into organs, tissues, and cells, so that there are many different little solutions, and we might expect each of them to have its own peculiar acid–base behavior. Fortunately, we find that they may be lumped together conveniently into a surprisingly small number of representative solutions, so that a satisfactory analysis of body-fluid acid–base behavior is indeed practical. Two obvious major subdivisions of the 42 liters are the intracellular solution, about 25 liters, and the extracellular solution, about 17 liters.

In the body, solutions are separated from one another by membranes, and the properties of these membranes can also be expected to affect acid-base behavior by controlling the kinds of interactions that can occur between the solutions that they separate. We shall therefore first develop the theory and techniques needed to understand the behavior of solutions in isolation (Chapters 2 through 7) before turning to the complications introduced by these membranes (Chapter 8). We shall then be well prepared to understand acid-base phenomena in the whole body, so-called "acid-base balance," and its regulation by the lungs and kidneys (Chapter 9).

1.2. INTRACELLULAR SOLUTIONS

Though intracellular solutions form the largest aggregate fluid compartment in the body, they occur as at least 10^{14} tiny separate individual solutions, one inside each cell. Because different cell types are chemically different, there is no reason to expect their internal solutions to be identical. In fact, we know that they are not. Fortunately, they all share a few common differences from extracellular solutions, and it is really on this basis that we justify lumping them all together as intracellular fluid. Intracellular solutions are always high in potassium and magnesium ions and low in sodium and chloride; extracellular solutions are just the reverse. Intracellular solutions contain high concentrations of organic acids; extracellular solutions almost never do.

We shall therefore find it useful to discuss an idealized intracellular fluid whose chemical composition is our best estimate of what we would have if we could put all 10^{14} of those tiny drops of real intracellular fluids together. We shall use ICF as the symbol for this fluid. In view of its ideal or virtual nature, numerical values for its composition must always be understood to be representative rather than strictly factual, except in those rare cases in which specific chemical measurements have somehow been made. To keep this representative quality of ICF always in sight, we shall refer to it frequently as "standard" ICF.

1.3. INTERSTITIAL SOLUTIONS (TISSUE FLUIDS)

Extracellular fluids may be subdivided into interstitial solutions or tissue fluids, blood plasma, and "others." We shall devote a brief section here to each one. The largest by far (13.5 liters) is the interstitial fluid that bathes most of the cells in the body and constitutes the "internal environment" whose regulation by several organs of the body gives rise to the physiologists' concept of homeostasis. Its major chemical features are

low potassium and magnesium ion concentrations, high sodium and chloride concentrations, and very low or negligible concentrations of proteins or other organic acids.

Like intracellular fluid, interstitial fluid occurs in innumerable tiny pockets of solution in the interstices of all body tissues. These are mostly in the form of very thin layers, on the order of 1 μ thick or less, and virtually impossible to sample for chemical analysis. Each one is somewhat different from its neighbors, although probably not as different as the corresponding intracellular samples would be. What we mean by interstitial fluid is the whole 13.5 liters of solution we would have if we could somehow instantaneously remove all those little pockets from the tissues, mix them together, and store them at 37 C under appropriate partial pressures of oxygen and carbon dioxide. It is therefore an ideal or virtual fluid also. We shall use the symbol ISF for it and refer to it often as "standard" ISF to remind us that it too is representative rather than "real."

A special subset of ISF is the lymphatic fluid, or lymph. Physiologically, lymph can be thought of as the overflow fluid from the tissues, en route back to the bloodstream by way of the lymphatic vessels. It arises because reabsorption of fluid at the venous ends of capillaries seldom precisely balances filtration out at the arterial ends, and also because of leakage of protein out of the capillaries. These proteins, along with the excess fluid, are constantly removed from the tissues and returned to the circulating blood plasma as lymph. Because lymph is in vessels, it is possible to sample it, so that measurements of lymph composition are often cited as approximations of the composition of ISF. In most cases, they are all that we have, but they may be rather poor approximations.

1.4. BLOOD PLASMA

The third largest fluid entity in the body is blood plasma. It is a single fluid, confined to the interior of the cardiovascular system, so it is not such an idealized or "lumped" fluid as ISF and ICF. It is certainly the most frequently analyzed fluid in all of biology and medicine, because samples are so easy to obtain by simple venipuncture.

Plasma volume is about 4% of body weight, or 3 liters. Seventy percent of it, about 2 liters, is normally contained in the veins. It circulates rapidly throughout the body and is in effective diffusion equilibrium with the ISF for most solutes except macromolecules. Plasma therefore differs in composition from ISF mainly in its protein content, and this difference has some acid-base consequences.

In the body, plasma has a large content of suspended red blood cells, normally 40 to 45% of the total blood volume. The presence of these suspended cells has to be taken into account when analyzing the behavior

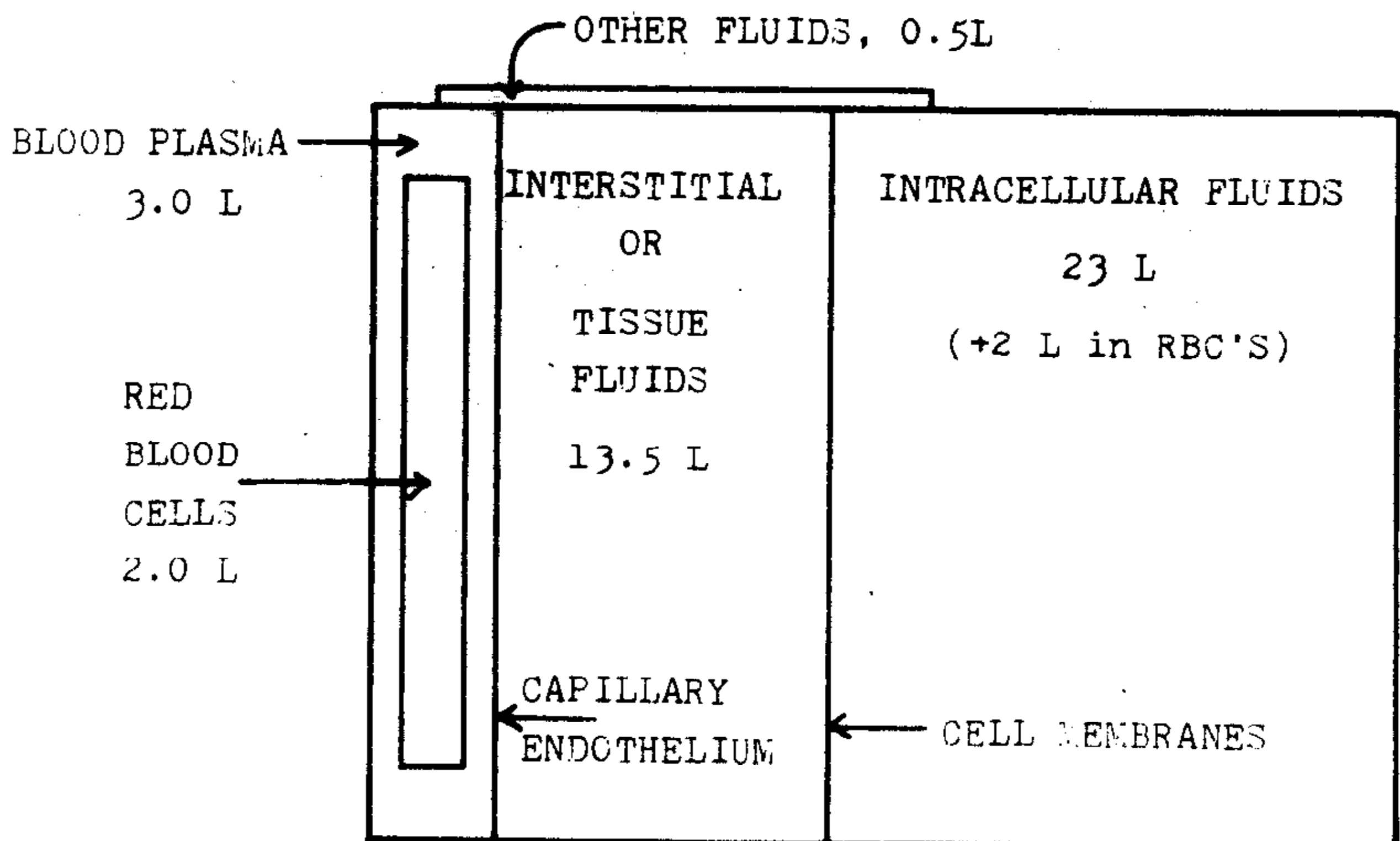
of plasma, and complicates that analysis somewhat. We shall therefore analyze blood plasma twice, first in isolation, without blood cells, in Chapter 7, and then, with its normal complement of red blood cells, as whole blood, in Chapter 8. It is useful, in this context, to think of blood plasma as the interstitial fluid of a very special (liquid) tissue, namely, whole blood.

1.5. OTHER BODY FLUIDS

This category includes a variety of small volumes of special, usually rather small and localized, solutions such as aqueous humor, synovial and bursal fluids, bile, saliva, and many others. These are sometimes referred to as "transcellular" fluids. Each one is extremely important in its own local situation, but they are not of much quantitative significance for whole-body acid-base behavior because they only total about 0.5 liter on the average.

Two of these special fluids, however, are of acid-base importance, gastric "acid" and pancreatic secretion. Gastric acid can be as much as 0.1N HCl, and pancreatic "juice" contains high concentrations of sodium but almost no chloride. We shall examine in Chapters 4 and 6 how such solutions can be produced from (alkaline) blood plasma and how they

Figure 1.1. Diagrammatic representation of major body fluid volumes and relationships in a standard 70-kg human body.



$$\begin{aligned} \text{TOTAL BODY WATER} &= 23 + 13.5 + 3.0 + 2.0 + 0.5 \text{ L} \\ &= 42 \text{ L} \end{aligned}$$

interact in the duodenum. Otherwise, we shall generally ignore the “other” body fluids.

1.6. SUMMARY

The volumes, membranes separating, and topological relationships between the major body fluids just discussed are summarized diagrammatically in Fig. 1.1. All these solutions are generally considered to be in osmotic equilibrium because all the membranes are freely permeable to water. Body-fluid osmolarity is normally maintained by the hypothalamus–pituitary–kidney team at a value close to 0.285 osmole/liter.

The solutions involved in major body fluids are (70 kg man):

- 1. Intracellular Fluid (ICF)
25 liters The sum of all the solutions inside all the cells of the body.
- 2. Interstitial Fluid (ISF)
13.5 liters The sum of all the little pockets of tissue fluid in the interstices between cells throughout the body.
- 3. Blood Plasma
3 liters The interstitial fluid of blood.
- 4. Other Fluids
0.5 liter

Total Body Water = 42 liters = 25 + 13.5 + 3 + 0.5 liters.

CHAPTER TWO

GOALS, DEFINITIONS, AND BASIC PRINCIPLES

2.1. RATIONALE AND GOALS

Hydrogen ion concentration in body fluids is extremely low, on the order of one ten-millionth to one hundred-millionth of an equivalent per liter. Why are we so interested in the behavior of such a rare species? One reason is that as protons, hydrogen ions are very small, and therefore have a very high charge density. This in turn results in very large electric field gradients in their neighborhoods. They may therefore have important effects on other molecules in the solution around them, even at very low concentrations. In particular, hydrogen bonds are important in the determination of macromolecular structure and configuration, and their strengths should be particularly sensitive to local hydrogen ion concentrations. Partly for these reasons, enzyme activities are often significantly dependent on local hydrogen ion concentration.

Changes in hydrogen ion concentration may also have important effects on biochemical reaction rates simply because hydrogen ions are involved in so many biochemical reactions. This multiple involvement also contributes to the complexities of understanding the dynamics of hydrogen ion concentration changes. In particular, hydrogen ions can be formed from water or can be destroyed by the formation of water. Because water is by orders of magnitude the most concentrated substance in living systems (55.3M), it provides an effectively inexhaustible source, or unfillable sink, for hydrogen ions as well as for hydroxyl ions. These two ions therefore behave quite differently from other kinds of ions that do not have such resources available to them.

Clinically, hydrogen ion concentration, ($[H^+]$), in body fluids is important as a useful indicator of several different kinds of pathology. $[H^+]$ is most easily measured in blood, via a small venipuncture sample and a pH meter. The $[H^+]$ of a mixed venous blood sample is usually near 4.5×10^{-8} Eq/liter (pH 7.35), while arterial blood $[H^+]$ is near 4.0×10^{-8} Eq/liter (pH 7.40). Values above about 1.2×10^{-7} Eq/liter (pH 6.9) or below about 1.6×10^{-8} Eq/liter (pH 7.8) indicate life-threatening situations and demand immediate intervention. Between these limits, wide variations can occur, sometimes very rapidly. It is important to understand how such variations arise, how blood $[H^+]$ is related to $[H^+]$ in other body fluids, and how the body may be helped to restore normal conditions.

The general goal of this book is quantitative explanation and understanding of hydrogen ion concentration and its changes in any biological solution. Quantitative understanding requires precise knowledge of the significant variables in the system and the physically necessary quantitative relationships between them. Our specific goal may therefore be stated in these terms:

In any given solution, under any specified conditions, we want to establish the quantitative relationships between hydrogen ion concentration in that solution and all the other variables in the solution that determine that hydrogen ion concentration. We shall then be able to understand, and explain, the value of the hydrogen ion concentration in terms of those determining variables.

Armed with this quantitative understanding, we shall be able to answer precisely and confidently any questions about how and why the hydrogen ion concentration changes as it does, and to design rational and effective therapy, on a quantitative basis, for situations involving abnormal $[H^+]$ values (acid–base disorders).

To achieve this goal, we must first spend some time and effort to make sure that we agree on definitions and then, in the rest of this chapter, formulate clearly the basic physical and chemical principles that will be our major tools for analysis and quantitative understanding of hydrogen ion behavior in body fluids.

2.2. DEFINITIONS: NEUTRAL, ACIDIC, ALKALINE, ACID, BASE

The concept of an acid or a base has a long folk history, but a rather short scientific history, and emotional arguments have often centered on the meanings of these words. For the purposes of this book, we shall adopt the very simple but practical and useful definitions given below. They are very close to current common usage in biology and medicine, and they

will serve very well our goal of understanding quantitatively how biological acid-base systems behave.

Definition: A solution is said to be acid-base neutral if its hydrogen ion concentration is equal to its hydroxyl ion concentration.

Acid-base neutrality is a very special, rarely achieved condition. It must be carefully distinguished from electrical neutrality, a very different, and completely general, requirement that all solutions must satisfy (Section 2.4).

Definition: A solution is said to be acidic, or acid, if its hydrogen ion concentration is greater than its hydroxyl ion concentration.

Definition: A solution is said to be alkaline, or basic, if its hydrogen ion concentration is less than its hydroxyl ion concentration.

Hydrogen ion concentration, by itself, is clearly not a reliable measure of acidity, alkalinity, or neutrality, nor is its negative logarithm, pH. In pure water, for example, hydrogen and hydroxyl ion concentrations are always equal, so pure water is always acid-base neutral, but its hydrogen ion concentration varies significantly with temperature, from 3.4×10^{-8} Eq/liter (pH 7.5) at 0 C to 8.8×10^{-7} Eq/liter (pH 6.1) at 100 C. The common textbook statement that neutrality is at pH 7.0, corresponding to hydrogen ion concentration of 1.0×10^{-7} Eq/liter, is only true in pure water at 25 C. In particular, it is not true at body temperature, 37 C, for which the pH of pure water is 6.8.

Definition: A substance is an acid if, when added to a solution, it brings about an increase in the hydrogen ion concentration of the solution, all other independent variables in the solution remaining constant.

Definition: A substance is a base if, when added to a solution, it brings about a decrease in the hydrogen ion concentration of the solution, all other independent variables in the solution remaining constant.

Acids achieve their effect either by dissociating in solution to yield an anion plus a hydrogen ion or by associating with a hydroxyl ion and thereby increasing the dissociation of water. Bases act either by dissociation to form a cation plus a hydroxyl ion or by associating with a hydrogen ion. In all cases, water dissociation equilibrium (Chapter 3) readjusts, with the final result specified in the definition.

These definitions may appear old-fashioned and very simpleminded, particularly to the advanced student of physical chemistry. It is much