

COLE'S  
PRACTICAL  
PHYSIOLOGICAL  
CHEMISTRY

TENTH EDITION

REVISED AND RE-WRITTEN

BY

ERNEST BALDWIN

AND

DAVID JAMES BELL

HEFFER

— CAMBRIDGE

# COLE'S Practical Physiological Chemistry

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TENTH EDITION

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1955

TO THE EVERGREEN MEMORY OF  
SYDNEY WILLIAM COLE  
THIS 10TH EDITION OF HIS "PRACTICAL PHYSIOLOGICAL  
CHEMISTRY" IS AFFECTIONATELY DEDICATED BY TWO OF  
HIS FRIENDS AND FORMER COLLEAGUES

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## PREFACE

Our former colleague and mentor, Sydney William Cole, M.A. of Trinity College, Cambridge, died on 18th December 1951 at the age of 75. It is no exaggeration to say that as the author of "Practical Physiological Chemistry," as one of the earliest collaborators of F. Gowland Hopkins, and as one of the original members of the Cambridge School of Biochemistry, his fame is world-wide.

During his years of retirement from his University Lectureship Mr. Cole deputed us to re-write his book, the last edition of which, the ninth, appeared 20 odd years ago. Since then the chemical investigation of biological mechanisms as well as the methods employed in these investigations have advanced our knowledge to a degree that was scarcely even dreamed of 20 years ago.

We have endeavoured to retain the familiar plan of Cole, a plan to which we have long been accustomed, formerly as students and later as teachers. We have retained the outlook on human physiology knowing that most students of that subject, if they wish to learn about organisms other than man, must be prepared to study the wider field of comparative biochemistry and leave the conventional courts of medical study.

All the experiments detailed here we have been accustomed to find successful in the hands of students. The more knowledgeable may criticise some of the quantitative procedures as being "old-fashioned" or as "not used in the hospital." We would answer that, over a period of many years' teaching by Mr. Cole and later by ourselves the methods described are in our collective experience the most suitable for the student of physiology; they require simple apparatus, are not time-consuming and, in the hands of the average student, give satisfactory results.

Excellent manuals of clinical chemistry exist for those who require them; "Cole" has always been a students' textbook and we hope that the present-day students will find the 10th edition as useful as the nine earlier editions were to their predecessors.

ERNEST BALDWIN.  
D. J. BELL.

*Easter, 1955.*

# CONTENTS

---

	PAGE
DEDICATION .. .. .	iv
PREFACE .. .. .	v

## CHAPTER I

### HYDROGEN ION CONCENTRATION

A. The Dissociation of Water .. .. .	1
B. Acids and Bases; The pH Scale .. .. .	3
C. The Dissociation of Acids and Bases .. .. .	5
D. Mixtures of a Weak Acid with its Salt .. .. .	7
E. Titration Curves of Weak Acids .. .. .	10
F. Buffer Solutions .. .. .	11
G. The Hydrolysis of Salts .. .. .	13
H. The Preparation of Standard Buffer Solutions .. .. .	14
I. Indicators .. .. .	18
J. Choice of Indicators for Acidimetric Titrations .. .. .	24
K. Determination of pH by Indicators, with the Use of Standard Buffers .. .. .	26
L. Determination of pH by Gillespie's Drop Method .. .. .	29
M. Determination of pH by the Hydrogen Electrode.. .. .	32
N. Determination of pH by the Quinhydrone Electrode .. .. .	42

## CHAPTER II

### SOME PHYSICAL PROPERTIES OF SOLUTIONS

A. Colloids .. .. .	45
B. Ampholytes and the Isoelectric pH .. .. .	49
C. Osmotic Pressure, Diffusion and Dialysis.. .. .	52
D. Freezing Point Depression .. .. .	56
E. Surface Tension and Adsorption .. .. .	58

## CHAPTER III

### REACTIONS OF THE CARBOHYDRATES

A. Classification and Structure .. .. .	60
B. Summary of the Principal Reactions of Carbo- hydrates .. .. .	63
C. Digestive Hydrolysis of Di- and Polysaccharides.. .. .	64
D. Reactions of Carbohydrates in Acid Solution .. .. .	64
E. Reactions of Carbohydrates in Alkaline Solutions .. .. .	66
F. Identification of some Reducing Sugars as their Phenylosazones .. .. .	68
G. Disaccharides .. .. .	69
H. Polysaccharides .. .. .	70

## CHAPTER IV

## PROTEINS

PAGE

A.	General Chemical Properties	..	..	..	75
B.	The "R" groups of Proteins	..	..	..	78
C.	Classification of the Proteins	..	..	..	81
D.	Precipitation of Proteins by Heavy Metals	..	..	..	83
E.	Precipitation of Proteins by Acidic or "Alkaloidal"				
	Reagents	..	..	..	83
F.	Precipitation of Proteins by Ethanol	..	..	..	84
G.	Heat Coagulation of Albumins and Globulins	..	..	..	85
H.	"Derived" Proteins	..	..	..	87
I.	Scleroproteins and their Derivatives	..	..	..	88
J.	Phosphoproteins; Casein	..	..	..	91
K.	Glycoproteins (Mucoproteins)	..	..	..	93

## CHAPTER V

## LIPIDS: FATS AND ASSOCIATED SUBSTANCES: BILE

A.	Composition and General Properties	..	..	95
B.	Emulsification of Fats	..	..	97
C.	Saponification	..	..	98
D.	Unsaturation: the Iodine Number	..	..	100
E.	Properties of Sterols (Cholesterol)	..	..	101
F.	Bile Salts	..	..	102

## CHAPTER VI

## THE CHEMISTRY OF SOME FOODS

A.	Milk	..	..	..	..	..	105
B.	Cheese	..	..	..	..	..	108
C.	Potatoes	..	..	..	..	..	109
D.	Flour	..	..	..	..	..	110
E.	Bread	..	..	..	..	..	111
F.	Meat	..	..	..	..	..	112
G.	Vitamins	..	..	..	..	..	116

## CHAPTER VII

## DIGESTION AND THE DIGESTIVE ENZYMES

A.	Enzymes	..	..	..	..	..	120
B.	Saliva	..	..	..	..	..	126
C.	Gastric Juice	..	..	..	..	..	131
D.	Pepsin	..	..	..	..	..	135
E.	Rennin	..	..	..	..	..	140
F.	Trypsin and Erepsin	..	..	..	..	..	142
G.	Intestinal Peptidases ("Erepsin")	..	..	..	..	..	148
H.	Pancreatic Amylase ("Amylopsin")	..	..	..	..	..	149
I.	Autolysis: Kathepsins	..	..	..	..	..	150



# CONTENTS

ix

## CHAPTER VIII

THE RED BLOOD CORPUSCLES: PIGMENTS OF BLOOD AND BILE	PAGE
A. The Laking of Blood: Haemolysis.. ..	152
B. Haemoglobin and its Derivatives .. ..	154
C. The Absorption Spectra of Haemoglobin and its Derivatives .. ..	158
D. Spectroscopic Examination of the Blood Pigments	161
E. Bile Pigments .. ..	166

## CHAPTER IX

### URINE: QUALITATIVE ANALYSIS

A. Formation and General Properties.. ..	168
B. Constituents of Normal Urine and their Origins ..	171
C. Properties and Reactions of Constituents of Normal Urine .. ..	172
D. Properties and Reactions of Abnormal or Pathological Constituents of Urine .. ..	184

## CHAPTER X

### QUANTITATIVE ANALYSIS: GENERAL TECHNIQUE

A. Introductory .. ..	194
B. Some General Notes on Microchemical Analysis ..	195
C. Removal of Proteins and other Interfering Substances from Blood and Tissue Extracts ..	196
D. Method for obtaining small Samples of Blood from the Finger .. ..	198

## CHAPTER XI

### QUANTITATIVE ANALYSIS OF BLOOD

A. General Aspects .. ..	199
B. Some Non-protein Constituents of Blood ..	200
C. Some Organic Constituents of Blood .. ..	203

## CHAPTER XII

### QUANTITATIVE ANALYSIS OF URINE

A. General Aspects .. ..	216
B. Nitrogenous Constituents of Urine.. ..	217
C. Reducing Sugar .. ..	226
D. Inorganic Constituents .. ..	228
E. Some Metabolic Experiments .. ..	231

## CHAPTER XIII

### DETECTION OF SUBSTANCES OF PHYSIOLOGICAL INTEREST

A. Fluids .. ..	234
B. Solids .. ..	242

## APPENDICES

PAGE

Weights and Measures .. .. .	244
Tension of Aqueous Vapour .. .. .	245
International Atomic Weights .. .. .	245
Specific Gravities Tables .. .. .	245
Boiling Points .. .. .	247
Standard Acids and Alkalis .. .. .	248
Pipettes, etc. .. .. .	249
Use of the Centrifuge .. .. .	250
Use of the Hand Spectroscope .. .. .	251
Use of Colorimeters .. .. .	252
Routine Clinical Examination of Urine .. .. .	254
Index .. .. .	256
Logarithm Tables .. .. .	<i>end of book</i>

## ILLUSTRATIONS AND FIGURES

FIG.

PAGE

1. Titration curve of a weak acid .. .. .	10
2. Paraffined bottle for standard alkali .. .. .	15
3. Dissociation curves of indicators .. .. .	20
4. Indicator chart .. .. .	21
5. Dropping pipette .. .. .	23
6. Cole and Onslow's Comparator .. .. .	28
7. Arrangement of tubes in comparator .. .. .	29
8. Comparator for 4 tubes .. .. .	30
9. Comparator for Gillespie's method .. .. .	30
10. Arrangement of tubes for Gillespie's method .. .. .	31
11. Concentration cell with two hydrogen electrodes .. .. .	33
12. Diagram of compensation method .. .. .	35
13. The Cole potentiometer .. .. .	36
14. Wiring diagram of the Cole potentiometer .. .. .	36
15. Cole's hydrogen electrodes .. .. .	37
16. Water bath for electrodes .. .. .	38
17. Determination of Osmotic pressure .. .. .	53
18. Beckmann's freezing point apparatus .. .. .	57
19. Beckmann's thermometer .. .. .	58
20. Absorption spectra of reduced and oxyhaemoglobin .. .. .	160
21. Method of drawing blood .. .. .	198
22. Estimation of urea by hypobromite .. .. .	220
23. Estimation of ammonia, using suction pump .. .. .	224

## CHAPTER ONE

# HYDROGEN ION CONCENTRATION

### A. The Dissociation of Water

BIOCHEMICAL processes are profoundly affected by the acidity or alkalinity, i.e. by the "reaction," of the dilute aqueous media in which they take place. It is therefore necessary to become familiar with the factors that determine this "reaction," with the mode of its expression and with methods for its estimation.

Pure water itself is very slightly dissociated into hydrogen ions and hydroxyl ions, the extent of this dissociation increasing with rising temperature:



By determinations of electrical conductivity and other physical measurements it has been found that at 22° C. the concentration of hydrogen ions in pure water is only one ten-millionth ( $10^{-7}$ ) of a gram per litre. The number of hydroxyl ions is equal to that of the hydrogen ions but, because the hydroxyl ion is 17 times heavier, the concentration of hydroxyl ions in pure water at this temperature is  $17 \times 10^{-7}$  g. per litre. However, it is usual for theoretical reasons to express concentrations in terms not of g. per litre but of g. ions per litre, i.e. in terms of *molarity*. This is indicated by putting the symbol for the ion or molecule in square brackets. Thus, in pure water at 22° C. we can write:

$$[\text{H}^+] = [\text{OH}^-] = 10^{-7} \text{ g. ions/litre.}$$

The relationship between the concentrations of the two ions can be worked out by applying the Law of Mass Action. The fundamental principle expressed by this law is that, at a given temperature, *the velocity of a chemical reaction is proportional to the product of the molecular concentrations of the reacting substances.*

Suppose, for example, that substances *A* and *B* react together in solution forming *C* and *D* as products, and that *C* and *D* can also react together to form *A* and *B*; then:



The rate of reaction (a) depends upon the frequency of collisions between molecules of *A* and *B*. Similarly, the rate of the reverse reaction (reaction b) depends upon the frequency of molecular collisions between *C* and *D*. At first, only reaction (a) will take

place and its velocity will fall off as  $A$  and  $B$  are used up. At the same time, since  $C$  and  $D$  are being formed, the reverse reaction, which starts at zero velocity, increases in speed as more and more molecules of  $C$  and  $D$  are produced. Eventually a point will be reached at which the forward and backward reactions take place at the same rate, so that an equilibrium condition is reached and may be represented as follows:



According to the law of mass action the rate of the forward reaction is proportional to the *product* of the molar concentrations of  $A$  and  $B$ . Thus, if the concentration of  $A$  is increased, say, 3 times, the chances of molecular collisions between  $A$  and  $B$  are increased threefold and the reaction velocity is trebled. If now the concentration of  $B$  is also increased 3 times, the chances of molecular collisions between  $A$  and  $B$  are trebled once more and the reaction velocity is increased again by a factor of three, i.e. to 9 times its original velocity. Thus the rate of reaction is proportional to the *product* and not to the sum of the concentrations of  $A$  and  $B$ .

The rates or velocities of the two reactions taking place in the equilibrium system ( $v_a$  and  $v_b$  in the following equations) are proportional, then, to the *products of the molar concentrations of the reactants*, and may be expressed by multiplying these products by a constant which is characteristic of each particular reaction and, as a rule, increases with temperature for any given reaction. This constant is the *reaction velocity constant* for the particular reaction. Thus, for reactions (a) and (b) we can write:

$$\begin{aligned} v_a &= k_a [A][B] \\ v_b &= k_b [C][D] \end{aligned}$$

When equilibrium is attained,  $v_a = v_b$  and hence:

$$k_a [A][B] = k_b [C][D] \quad \text{or} \quad \frac{k_b}{k_a} = \frac{[A][B]}{[C][D]}.$$

Since the ratio of two constants is itself a constant we arrive at the following important equation:—

$$K = \frac{[A][B]}{[C][D]}$$

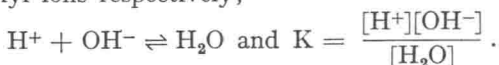
where  $K$  is the *equilibrium constant* of the reversible reaction,



For the simpler system  $A + B \rightleftharpoons C$  we can similarly arrive at the formula,

$$K = \frac{[A][B]}{[C]}.$$

It follows that, if  $C$  represents water and  $A$  and  $B$  the hydrogen and hydroxyl ions respectively;



Now the amount of water actually ionised is, as we have seen, extremely small, so that the concentration of unionised water,  $[H_2O]$ , is virtually constant at any given temperature. It follows that, in dilute solutions,

$$[H^+][OH^-] = K_w \quad \dots \quad (1)$$

$K_w$  is called the *ion product of water*.

This is a fundamental proposition. It means that *the product of the molar concentrations of the  $H^+$  and  $OH^-$  ions in dilute aqueous solutions is always the same at any given temperature, no matter what other substances may be present*. This is not necessarily true of concentrated solutions, but in dilute solutions the proposition holds, even if acids, alkalis or salts are present. In what follows it is assumed that we are dealing with dilute solutions.

The value of  $K_w$  has been determined in various ways and the mean results obtained at different temperatures are listed in Table I. It will be noticed that  $K_w$  increases appreciably with rising temperature and has a temperature coefficient of about 2, i.e. it is about doubled for a rise in temperature of  $10^\circ \text{C}$ .

TABLE I  
CHANGE OF  $K_w$  WITH TEMPERATURE

Temp. ( $^\circ \text{C}$ .)	$K_w \times 10^{-14}$	$-\log_{10} K_w$ ( $\text{p}K_w$ )	pH of neutral point
16	0.63	14.20	7.10
17	0.68	14.17	7.08
18	0.74	14.13	7.07
19	0.79	14.10	7.05
20	0.86	14.07	7.03
21	0.93	14.03	7.01
22	1.01	14.00	7.00
25	1.27	13.90	6.95
30	1.89	13.73	6.86
35	2.71	13.57	6.78
38	3.35	13.48	6.74
40	3.80	13.42	6.71

### B. Acids and Bases; The pH Scale

All acids have one property in common: they all dissociate in aqueous solution to yield hydrogen ions. Now "strong" acids, such as hydrochloric, are almost completely ionised in aqueous

solutions whereas "weak" acids, such as acetic, ionise to only a small extent. If we compare, say,  $N$  solutions of hydrochloric and acetic acids we find that, while the *molar concentrations* of the two acids are the same, the *acidities* of the solutions are very different. Hydrochloric acid ionises extensively and yields a strongly acid solution containing a large proportion of hydrogen ions. Acetic acid on the other hand ionises to a relatively small extent and yields only a weakly acid solution containing relatively few hydrogen ions. In short, the acidity of a solution depends, not upon the molarity of the acid but upon the concentration of the hydrogen ions,  $[H^+]$ , to which the acid gives rise. It follows that, if we know  $[H^+]$  for a given solution, we can express the acidity of that solution in quantitative terms.

It will be convenient to define first of all what we mean by the terms "acid," "neutral" and "alkaline." *Neutrality* is conveniently defined in terms of the properties of pure water, which has always been regarded as an ideally neutral substance. As we have seen, in pure water  $[H^+] = [OH^-] = 10^{-7}$ . Since  $[H^+][OH^-] = K_w$  it follows that, if the concentration of the one ion is known, that of the other can be calculated from the known values of the constant  $K_w$ ; generally speaking, however, we work in terms of  $[H^+]$ . By definition, then, a solution is:

*neutral* if  $[H^+] = 10^{-7}$ ,  
*acid* if  $[H^+]$  is greater than  $10^{-7}$ ,  
*alkaline* if  $[H^+]$  is less than  $10^{-7}$ .

Since it is possible to measure  $[H^+]$  with considerable accuracy by suitable methods, we can express acidity or alkalinity quantitatively in terms of hydrogen ion concentration,  $[H^+]$ . This is a great advance over the use of vague and purely qualitative terms such as "weakly acid," "strongly alkaline" and the like.

For reasons of practical convenience the acidity or alkalinity of a solution is not nowadays usually expressed in terms of hydrogen ion concentration itself, but in the logarithmic terms introduced in 1909 by Sørensen. Hydrogen ion concentrations of physiological importance can usually be expressed as  $[H^+] = 10^{-x}$ ; for example, the  $[H^+]$  of  $N/100\text{-HCl}$  is very nearly  $1/100$  or  $10^{-2}$ . Now if, to take a general case,  $[H^+] = 10^{-x}$ , it follows as a matter of definition that

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

The quantity  $x$  is known as the pH of the solution, i.e.

$$x = \text{pH}$$

and hence, by definition,

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

Thus we may define pH as the *logarithm of the hydrogen ion concentration with the sign reversed*.

We can now amplify our definitions in terms of the pH scale. A solution is

*neutral* if  $[H^+] = 10^{-7}$ , or  $pH = 7$ ,

*acid* if  $[H^+] > 10^{-7}$ , or  $pH < 7$ ,

*alkaline* if  $[H^+] < 10^{-7}$ , or  $pH > 7$ .

It cannot be too clearly realised that *the pH scale is a logarithmic and not an arithmetical one* and that as  $[H^+]$  increases, *pH decreases* because of the reversal of the sign. Thus a solution of pH 2 does not have one-half the  $[H^+]$  of a solution of pH 4, but its acidity is  $10^2 = 100$  times greater.

The conversion of  $[H^+]$  to pH is done by reference to a table of common (decadic) logarithms (see the last pages of this book).

Thus if  $[H^+] = 4 \times 10^{-7}$  then, since  $\log 4 = 0.602$ ,

$$[H^+] = 10^{0.602} \times 10^{-7} = 10^{-6.398} = 10^{-6.4} \text{ (approx.)},$$

and therefore

$$pH = 6.4 \text{ (approx.)}.$$

Conversely, we can convert pH into  $[H^+]$  as follows:—

If  $pH = 6.6$ , then

$$[H^+] = 10^{-6.6} = 10^{0.4-7.0} = 10^{0.4} \times 10^{-7}.$$

The antilog of 0.4 is 2.51 and hence

$$[H^+] = 2.51 \times 10^{-7}.$$

It is worth while to notice that, since  $\log 2 = 0.30$ , a decrease in pH of 0.3 corresponds to a two-fold increase of  $[H^+]$  and therefore of acidity.

### C. The Dissociation of Acids and Bases

An *acid* is an electrically neutral substance which, in solution, gives rise to  $H^+$  or combines with and thereby removes  $OH^-$ . Since  $[H^+][OH^-] = K_w$ , either the addition of  $H^+$  or the removal of  $OH^-$  results in an increase in acidity. A *base* is a substance which yields  $OH^-$  when dissolved in water, or which combines with and removes  $H^+$ . An *ampholyte* is a substance that possesses both these properties.

Ions which are negatively charged and can therefore combine with the positively charged hydrogen ions are called *anions*, since they migrate towards the anode if placed in an electric field. Examples are the acetate ion,  $CH_3COO^-$ , and the bicarbonate ion,  $HCO_3^-$ . Positively charged ions such as those of  $Na^+$  or  $K^+$ , which migrate towards the cathode, are called *cations* and can combine with the negatively charged hydroxyl ions.

A strong acid such as HCl is freely dissociated in aqueous solution, so that a high concentration of  $H^+$  results. The "strength" of an acid depends upon the concentration of  $H^+$  to which it gives

rise in aqueous solution. By contrast with HCl, acetic acid is very weak, since it dissociates only feebly in aqueous solution and gives rise to correspondingly low concentrations of hydrogen ions. Now, whether we consider a strong or a weak acid we can represent its condition in aqueous solution by the following equilibrium,



where  $\text{A}^-$  represents the anion. The essential difference between a strong acid such as HCl and a weak acid such as acetic lies in the extent to which the reverse reaction takes place. Free hydrogen ions show very little tendency to combine with chloride ions to re-form HCl. Acetate ions, on the other hand, combine readily with  $\text{H}^+$  to re-form the feebly ionising acetic acid so that, while the hydrogen ion concentration in a solution of HCl is very high, that in a solution of acetic acid of the same molar concentration is always low.

To make this clear we may take the following example. 0.1 N-HCl behaves as though it were about 83% dissociated at room temperature. Hence

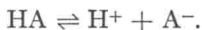
$$[\text{H}^+] = 0.83 \times 10^{-1} = 10^{0.92 - 2} = 10^{-1.08}$$

so that  $\text{pH} = 1.08$ . Similarly, 0.1 N-acetic acid behaves as though it were 1.35% dissociated at room temperature, so that

$$[\text{H}^+] = 0.0135 \times 10^{-1} = 10^{-0.13 - 3} = 10^{-2.87}$$

so that  $\text{pH} = 2.87$ . Thus a decinormal solution of HCl is about 6 times as strongly acid as a decinormal solution of acetic acid (a difference of 1.8 pH units).

Let us now consider the dissociation of some arbitrary weak acid such as acetic or lactic acid, writing  $\text{A}^-$  as before to represent the anion. In aqueous solution an acid of this kind is ionised to a small extent, depending upon temperature and dilution:



By applying the law of mass action we can derive the following equation:

$$\frac{[\text{H}^+][\text{A}^-]}{[\text{HA}]} = K \quad \dots \quad (2)$$

Here  $[\text{HA}]$  is the concentration of the undissociated acid and  $[\text{A}^-]$  that of the anion, e.g. acetate.  $K$  is the characteristic *dissociation constant* of the particular acid. Transposing and taking logarithms we get

$$[\text{H}^+] = K \frac{[\text{HA}]}{[\text{A}^-]}$$

$$\therefore \log \text{H}^+ = \log K + \log \frac{[\text{HA}]}{[\text{A}^-]}.$$



Expressing this relationship in terms of pH we get

$$- \text{pH} = \log K + \log \frac{[\text{HA}]}{[\text{A}^-]}$$

or

$$\text{pH} = -\log K - \log \frac{[\text{HA}]}{[\text{A}^-]} = -\log K + \log \frac{[\text{A}^-]}{[\text{HA}]}$$

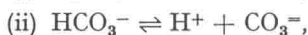
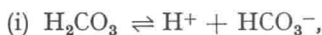
Here  $K$ , the dissociation constant of  $\text{HA}$ , is an important quantity. It will be observed that  $-\log K$  corresponds to that pH at which  $[\text{A}^-] = [\text{HA}]$ , i.e. when  $\log \frac{[\text{A}^-]}{[\text{HA}]} = \log 1 = 0$ ; in other words,  *$-\log K$  is that pH at which exactly one-half of  $\text{HA}$  is dissociated.*

Since, therefore,  $-\log K$  has the dimensions of pH, it is usually written in comparable terms and expressed as  $\text{pK}$ . Our equation can therefore be rewritten thus:

$$\text{pH} = \text{pK} + \log \frac{[\text{A}^-]}{[\text{HA}]} \quad \dots \quad \dots \quad (3)$$

where  $\text{pK}$  is that pH at which the acid is half dissociated.

Similar considerations show that dibasic acids, e.g. oxalic and succinic, have two dissociation constants, one corresponding to the ionisation of each of the two acidic radicals. A particularly important dibasic acid in biological systems is carbonic acid, which ionises thus:



and the following equations can be written to correspond to the two stages of its dissociation:—

$$K_1 = \frac{[\text{H}^+][\text{HCO}_3^-]}{[\text{H}_2\text{CO}_3]} \text{ and } K_2 = \frac{[\text{H}^+][\text{CO}_3^{2-}]}{[\text{HCO}_3^-]}.$$

Tribasic acids such as phosphoric and citric have three dissociation constants, and so on. Values for the dissociation constants and  $\text{pK}$  values of a number of weak acids are given in Table II.

#### D. Mixtures of a Weak Acid with its Salt

Although weak acids are only feebly ionised in aqueous solution, the salts they form with alkali metals are strongly dissociated and are strong electrolytes. Thus, whereas 0.1 N-acetic acid behaves as if only 1.35% is dissociated, 0.1 N-sodium acetate behaves as if no less than 79% dissociates. Similarly, while ammonia, a weak