

On Acid and Basic Reaction

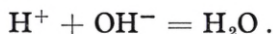
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The following short article aims at giving a survey of recent views on acid and basic reaction. We shall see how a rational method for measuring the reaction of a solution has been found by introducing the so-called "*hydrogen-ion exponent*", how the *reaction in solutions* of acids, bases, and salts can be computed, when the strength of the acids and bases is known, and how solutions with well-defined reaction (*buffer mixtures*) can be made. The theory of *dye-stuff indicators* will likewise be discussed, and we shall finally demonstrate, how *the error in an acid or alkali titration* depends on the strength of the acid or base, as well as on the properties of the indicator.

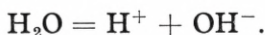
1. THE REACTION SCALE

According to the theory of electrolytic dissociation, the acid reaction of a solution depends on its content of hydrogen ions, and the basic reaction on its content of hydroxyl ions. It is customary to say that a solution cannot at the same time show both acid and basic reaction; this is correct in so far as it is impossible for hydrogen ions and hydroxyl ions to be simultaneously present in appreciable quantities in a solution without combining with each other to form water according to the equation:



This process takes place when acid and basic solutions are mixed and causes the acid or the basic reaction to disappear. When the two solutions are mixed in a definite proportion, both reactions disappear and the solution becomes *neutral*.

Accurate investigations have revealed, however, that hydrogen ions and hydroxyl ions do not combine completely; every aqueous solution, in fact, contains both kinds of ions, but one of them is always present in extremely small quantity. If one of them is totally absent in an aqueous solution, some water molecules will immediately dissociate according to the equation:



The reaction of hydrogen ions and hydroxyl ions to form water is therefore reversible and mobile at room temperature. Hence, it follows from the law of mass action that the product of the hydrogen-ion and hydroxyl-ion concentrations in all dilute aqueous solutions must have one and the same value. This value is called the *dissociation constant of water*. We shall designate it as $K_{\text{H}_2\text{O}}$. If the molar concentration of a substance is designated as C with the formula for the substance as suffix, we may write

$$C_{\text{H}^+} \cdot C_{\text{OH}^-} = K_{\text{H}_2\text{O}}$$

The dissociation equation for water.

At 20° C the numerical value of the dissociation constant of water is about 10^{-14} ; the constant increases about 7 per cent per degree centigrade, and at 100° C it is about 60 times as large as at 20° C. In what follows we shall use the value 10^{-14} .

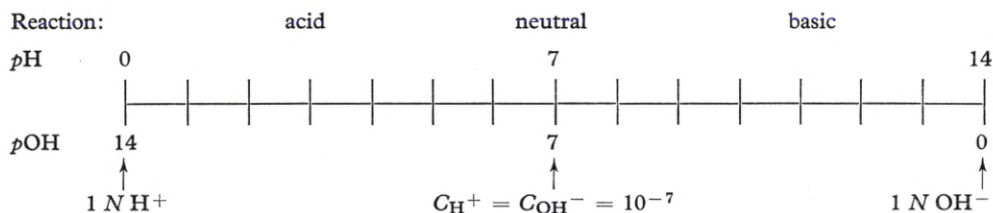
As a result of the connection between the hydrogen-ion and the hydroxyl-ion concentrations, the hydroxyl-ion concentration in a 1 molar hydrogen-ion solution has the very small value 10^{-14} . With decreasing hydrogen-ion concentration, the hydroxyl-ion concentration increases. When the hydrogen-ion concentration has decreased to 10^{-7} the two concentrations are equal, and when the hydrogen-ion concentration becomes even smaller, the hydroxyl-ion concentration is the larger. We find then, that in strongly acid solutions the hydroxyl-ion content is very small, and in strongly alkaline solutions the reverse is true and the content of hydrogen ions is very small.

As suggested by Friedenthal, the reaction of all solutions may be expressed by their hydrogen-ion concentration. If a solution shows basic reaction, it is easy from the hydrogen-ion concentration by means of the equation for the dissociation of water to compute the hydroxyl-ion concentration, and *vice versa*. This suggestion of Friedenthal makes it possible to measure the reaction in all solutions by the same scale.

It is often unpractical to express the reaction of a solution by means of the hydrogen-ion concentration, especially in graphical representations, for it varies over a very great interval, from about 1 to about 10^{-14} . A great improvement was therefore introduced when Professor S. P. L. Sørensen suggested substituting for the hydrogen-ion concentration, the negative value of its logarithm. Sørensen calls this value the *hydrogen-ion exponent* and designates it as $p\text{H}$. The relation between $p\text{H}$ and C_{H^+} may be expressed by one of the two following equations:

$$C_{\text{H}^+} = 10^{-p\text{H}}; \quad p\text{H} = -\log C_{\text{H}^+}$$

The first of the two equations explains the name hydrogen-ion exponent.



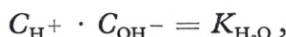
When the hydrogen-ion exponent decreases with 1, the hydrogen-ion concentration is correspondingly multiplied by 10 ($\log 10 = 1$), and a decrease in the hydrogen-ion exponent of 0.3 corresponds very nearly to doubling the hydrogen-ion concentration ($\log 2 = 0.301$) etc.

At ordinary temperature, the pH scale extends from about 0 to about 14. The value 0 corresponds to a 1 molar hydrogen-ion solution. The figures 0 to 7 represent acid solutions. The figure 7 indicates a completely neutral solution, in which hydrogen-ion and hydroxyl-ion concentrations are equal. The figures 7 to 14 represent alkaline solutions. The closer the hydrogen-ion exponent approaches 7, the closer the solution approaches neutrality. (This is only true at room temperature; at other temperatures, instead of 7, $-\frac{1}{2} \log K_{H_2O}$ should be inserted).

Under certain conditions it is practical to indicate the reaction by a *hydroxyl-ion exponent* pOH . Its definition is quite analogous to that of the hydrogen-ion exponent. Hence, we have

$$C_{OH^-} = 10^{-pOH}; \quad pOH = -\log C_{OH^-}.$$

From the dissociation equation of water



the following simple relation between pH and pOH may be deduced by taking the logarithms:

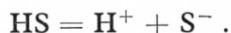
$$pH + pOH = 14.$$

The following diagram gives a survey of the relation between the pH scale and the pOH scale.

2. THE STRENGTH OF ACIDS AND BASES

Strong acids and bases like most salts are highly dissociated in solution. In computing hydrogen-ion exponents of solutions of strong acids and bases we may with good approximation assume that these compounds are completely split into ions. Throughout this paper we will therefore assume that strong acids and bases and all salts are completely dissociated into their ions. The inaccuracy thereby introduced, is irrelevant in presenting the main features of the phenomena.

In the case of weak acids and bases, the conditions are totally different. Let us consider a weak monobasic acid HS. In solution, it is but slightly split into ions, according to the equation:



The more an acid splits into ions, the more acid is the solution, and therefore the stronger the acid. Yet the degree of dissociation is not a good measure of the strength of an acid, because it changes with the concentration. The best measure of the *strength of an acid* is to be found in the so-called *dissociation constant*.

For any solution containing the acid radical S in one or the other form, we have according to the mass-action law that the expression

$$\frac{C_{\text{H}^+} \cdot C_{\text{S}^-}}{C_{\text{HS}}} = K_{\text{S}}$$

The dissociation equation for the acid HS

has the same constant value K_{S} which we call the dissociation constant of the acid.

This important equation is the basis for almost all that follows. It is perhaps not superfluous to emphasize the fact, that the validity of the above equation in no way depends on whether the hydrogen ions or the anions of the acid have been formed by the dissociation of one compound or another. The validity of the equation is totally independent of the past history of the ions.

If we wish to determine the dissociation constant of an acid, it is only necessary to determine its degree of dissociation at a single concentration. This can be done by measuring the electrical conductance of the solution of the acid. From the corresponding values of degree of dissociation and concentration, the dissociation constant may be calculated as follows.

In a solution of the acid, of which the molar concentration is C , and in which the degree of dissociation is γ , the ions and undissociated acid molecules have the following molar concentrations:

$$C_{\text{H}^+} = C_{\text{S}^-} = \gamma C, \quad C_{\text{HS}} = (1 - \gamma) C$$

The dissociation equation of the acid may then be transformed to read

$$C \cdot \frac{\gamma^2}{1 - \gamma} = K_{\text{S}} \text{ (Ostwald's law of dilution)}$$

This equation enables us, from the corresponding values of C and γ , to compute the dissociation constant. Table 1 shows some values of the dissociation constant of acetic acid calculated by this method.

Table 1. Dissociation of acetic acid at 18° C.

C	100 γ	K_s
1/8	1.19 per cent	0.0000179
1/16	1.68 - -	179
1/32	2.38 - -	181
1/64	3.33 - -	179
1/128	4.68 - -	179
1/1024	12.66 - -	179

The uniformity of the values of the dissociation constant in the last column prove experimentally the correctness of our dissociation equation.

The larger the dissociation constant of the acid, the larger the degree of dissociation of the acid at a given concentration, and therefore, the stronger the acid reaction at the concentration considered. The dissociation constant of the acid is therefore a measure of the strength of the acid.

Analogously, the *strength of a base* may be measured by its dissociation constant.

A tabulation of the dissociation constants of a large number of acids is found in *Landolt-Börnstein-Roth's Tables* 4th Edition (1912).

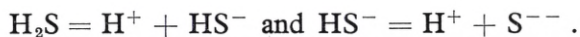
Table 2 shows dissociation constants of a selected series of acids and bases. I have endeavoured to select acids and bases with chemical properties with which one is familiar and of whose strength one already has a notion.

This table should enable us to obtain an idea of the strength of an acid (base) when its dissociation constant is known; for, using the table, the acid (base) in question can be placed between two acids (bases) of whose strengths one already has a definite notion.

In the table, the dissociation constants are expressed as powers of 10. This is convenient when the reaction is expressed by the hydrogen-ion exponent. In this case the strength of an acid is simply given by naming the numerical value of the exponent, the strength exponent of the acid in question, using the symbol pS (for bases pB).

$$K_s = 10^{-pS}$$

We note, that in the table, more than one dissociation constant is given for the polybasic acids. Each of these corresponds to one special hydrogen atom in the acid. With a dibasic acid account must be taken of two reversible dissociation processes



The corresponding mass-action equations are:

$$\frac{C_{H^+} \cdot C_{HS^-}}{C_{H_2S}} = K_1 \text{ and } \frac{C_{H^+} \cdot C_{S^{--}}}{C_{HS^-}} = K_2.$$

Table 2. Dissociation constants for selected acids and bases at room temperature about 18° C.*

	K_1	K_2	K_3		K_1
Strong acids	about 1			Strong bases	about 1
Sulphurous acid	$10^{-1.78}$	$10^{-5.3}$		Piperidine	$10^{-2.82}$
Phosphoric acid	$10^{-1.92}$	$10^{-6.7}$	$10^{-12.44}$	Methylamine	$10^{-3.3}$
Monochloro acetic acid	$10^{-2.82}$			Ammonia	$10^{-4.75}$
Formic acid	$10^{-3.67}$			Hydrazine	$10^{-5.52}$
Acetic acid	$10^{-4.75}$			Pyridine	$10^{-8.8}$
Carbonic acid	$10^{-6.52}$	$10^{-10.22}$		Aniline	$10^{-9.4}$
Hydrogen sulphide	$10^{-7.0}$			<i>p</i> -Nitroaniline	10^{-12}
Boric acid	$10^{-8.77}$			Urea	$10^{-13.92}$
Hydrocyanic acid	$10^{-9.3}$				
Phenol	10^{-10}				
Hydrogen peroxide	$10^{-11.7}$				

* Dissociation constants are in general not very accurately known; therefore too much reliance should not be placed on the decimals.

These two equations show the significance of the two dissociation constants K_1 and K_2 for a dibasic acid.

3. THE REACTION IN SOLUTIONS OF ACIDS, BASES, AND SALTS

Having shown how the dissociation constant and the strength exponent are measures of the strength of an acid or a base, we shall proceed to show how these figures make it possible to calculate the reaction not only of solutions of the free acid but also of solutions containing salts of the acid, and of mixtures containing the free acid and its salts.

a) *The reaction of a mixture of an acid and its salt.* In a mixture of a weak acid and one of its salts, the dissociation of the acid is very small and the dissociation of the salt large. The concentration of the undissociated acid molecules HS is therefore approximately equal to the concentration of the acid in the mixture, and the concentration of the anion S^- is approximately equal to the salt concentration in the mixture:

$$C_{HS} = C_{acid} \text{ and } C_{S^-} = C_{salt}$$

According to the dissociation equation of the acid, the hydrogen-ion concentration is determined by the concentration of undissociated acid molecules and the concentration of anions of the acid:

$$C_{H^+} = K_S \cdot \frac{C_{HS}}{C_{S^-}}$$

From the above equations we obtain:

$$C_{H^+} = K_S \cdot \frac{C_{acid}}{C_{salt}}$$

In a mixture of equivalent quantities of acid and salt, the hydrogen-ion concentration therefore equals the dissociation constant of the acid.

By taking logarithms we come to the following equation

$$pH = pS + \log \frac{C_{\text{salt}}}{C_{\text{acid}}}$$

It follows from this equation, that the hydrogen-ion exponent is equal to the strength exponent of the acid when acid and salt are present in equivalent amounts. When acid and salt are not present in equivalent amounts, but in amounts of the same order of magnitude, the last term of the equation, though not zero, is yet very small, and therefore the hydrogen-ion exponent in such a mixture, must always come close to the strength exponent of the acid. Each time the salt to acid ratio increases 10 times, the hydrogen-ion exponent increases one unit.

Example: The strength exponent of acetic acid is 4.75. Therefore a mixture of acetic acid and sodium acetate has a hydrogen-ion exponent close to 4.75. If the solution contains 10 times as many molecules of acetic acid as of sodium acetate, $pH = 3.75$. If, on the other hand, the acetate concentration is 10 times larger than the acetic acid concentration, $pH = 5.75$. By adding acetic acid and sodium acetate to a solution, a weakly acid reaction of the solution may be obtained with a pH value close to 4.75. This procedure is used in inorganic analysis to produce a very weakly acid reaction, at which ferric and aluminium phosphate precipitate completely, while phosphates of zinc, manganese, calcium and magnesium remain in solution.

b) *The reaction in a solution of an acid.* We shall now compute the reaction in a pure aqueous solution of a weak acid. As the acid is but slightly dissociated, we may consider the concentration of the undissociated acid molecules to be equal to the total concentration of the acid: $C_{\text{HS}} = C_{\text{acid}}$. Moreover as the two ions, by dissociation, are formed in equally large quantities the equation: $C_{\text{H}^+} = C_{\text{S}^-}$ holds. By introducing these values into the dissociation equation for the acid

$$\frac{C_{\text{H}^+} C_{\text{S}^-}}{C_{\text{HS}}} = K_{\text{S}},$$

we find the following expression for the hydrogen-ion concentration of the solution of the acid:

$$C_{\text{H}^+} = \sqrt{K_{\text{S}} \cdot C_{\text{acid}}}$$

Hence, on taking the logarithms,

$$pH = \frac{1}{2} pS - \frac{1}{2} \log C_{\text{acid}}.$$

In a 1 molar solution of an acid we see that the hydrogen-ion exponent is equal to half the acid-strength exponent, and as the hydrogen-ion exponent only changes

one half unit each time the concentration of the acid becomes ten times smaller, we may say that the value of the hydrogen-ion exponent in a non-dilute solution, is always close to half the value of the acid-strength exponent.

Example : In a 1 molar solution of acetic acid, the hydrogen-ion exponent will be $\frac{1}{2} \cdot 4.75 = 2.375$, i.e. the hydrogen-ion concentration will be $10^{-2.375} = 0.0042$. In a 0.1 molar solution of acetic acid, the hydrogen-ion exponent will be $\frac{1}{2} \cdot 4.75 + \frac{1}{2} = 2.875$, i.e. the hydrogen-ion concentration will be $10^{-2.875} = 0.0013$.

In a mixture of a free acid and one of its salts, the reaction may well be alkaline, even if the free acid is present in great quantities. According to the above, this anomaly may be shown by all the acids, whose strength exponents are close to 7 or even have higher values, f. inst. boric acid, hydrocyanic acid, phenol. On the other hand, the reaction of a pure solution of an acid in which no salt of the acid is present, is always acid, however weak the acid may be, for a hydrogen compound with a dissociation constant smaller than 10^{-14} would hardly be called an acid.

c) *The reaction in a salt solution. Hydrolysis.* When salts are dissolved in water, they split to a larger or lesser degree into free acids and bases, i.e. they *hydrolyze*. The extent of the hydrolysis process is determined by the fact that the hydrogen ions from the acid formed, and the hydroxyl ions from the base formed, must perforce possess concentrations whose product equals the dissociation constant of water. The less the acid and the base dissociate, the greater must be the extent of the hydrolysis in order to fulfill this requirement.

Let us calculate the *pH* and *pOH* for a solution of the salt of a weak acid HS with a strong base BOH. We take the following equations:

$$C_{H^+} \cdot C_{OH^-} = K_{H_2O} \text{ (the dissociation equation for water)}$$

$$\frac{C_{H^+} \cdot C_{S^-}}{C_{HS}} = K_S \text{ (the dissociation equation for the acid).}$$

Since the quantities of acid and base formed by hydrolysis must be equivalent, and since the strong base formed is completely dissociated, while the weak acid formed dissociates only to a small degree, we have further:

$$C_{HS} = C_{OH^-} \text{ (equivalence of acid and base).}$$

If we assume that the salt is completely ionized, but only slightly hydrolyzed, which is approximately true in most cases, we may set the concentration of the ion S^- equal to the concentration of the salt solution:

$$C_{S^-} = C_{\text{salt}}.$$

From the above four equations we derive:

$$C_{\text{OH}^-} = \sqrt{\frac{K_{\text{H}_2\text{O}}}{K_{\text{S}}} C_{\text{salt}}}$$

By taking the logarithms and substituting for $K_{\text{H}_2\text{O}}$ the value 10^{-14} we find:

$$p\text{OH} = -\frac{1}{2} pS + 7 - \frac{1}{2} \log C_{\text{salt}}, \text{ or}$$

$$p\text{H} = \frac{1}{2} pS + 7 + \frac{1}{2} \log C_{\text{salt}}$$

In a 1 molar salt solution the hydrogen-ion exponent will therefore be 7 units larger than half the value of the acid-strength exponent, and the hydrogen-ion exponent varies with only $\frac{1}{2}$ unit each time the concentration of the salt solution decreases ten times.

Example: In a 1 molar solution of sodium acetate the hydrogen-ion exponent is $\frac{1}{2} 4.75 + 7 = 9.375$, and in a 0.1 molar solution of the same substance it is $\frac{1}{2}$ unit smaller, i.e. 8.875. Since both of these hydrogen-ion exponents are larger than 7, both solutions show an alkaline reaction, but the hydroxyl-ion concentrations in the solutions are only small:

$$C_{\text{OH}^-} = 10^{-(14-9.375)} = 0.000024$$

$$C_{\text{OH}^-} = 10^{-(14-8.875)} = 0.0000075$$

All salts in which the acid is weaker than the base, show an alkaline reaction in solution.

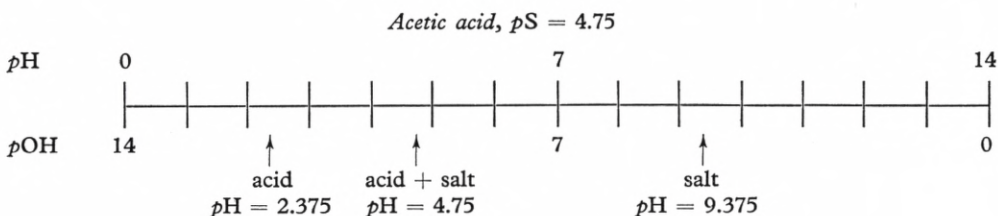
In the case of a dibasic acid the first strength exponent determines the reaction in solution of the free acid, while the second strength exponent determines the basic reaction of its salt. Therefore a polybasic acid may well, as free acid be stronger than a monobasic acid, and still, judged by the hydrolysis of its sodium salt, be weaker than the same monobasic acid. This is true in the case of sulphurous acid (first $pS = 1.78$, second $pS = 5.3$) and acetic acid ($pS = 4.75$).

Graphic representation. If we, in a $p\text{H}$ scale, plot the reactions

- a) of a mixture of equivalent amounts of acid and salt
- b) of a 1 molar acid solution
- c) of a 1 molar salt solution

we obtain a comprehensive survey of the system.

To find the point representing the reaction of the acid-salt mixture, we have only to introduce the strength exponent of the acid in the hydrogen-ion exponent scale. Halving the distance between this acid-salt-point and the point $p\text{H} = 0$ gives the reaction point for the solution of the acid; halving the distance between the acid-salt-point and the point $p\text{H} = 14$ (or more generally $p\text{OH} = 0$), gives the reaction point for the salt solution. In the following reaction scale, these 3 points are shown for acetic acid:



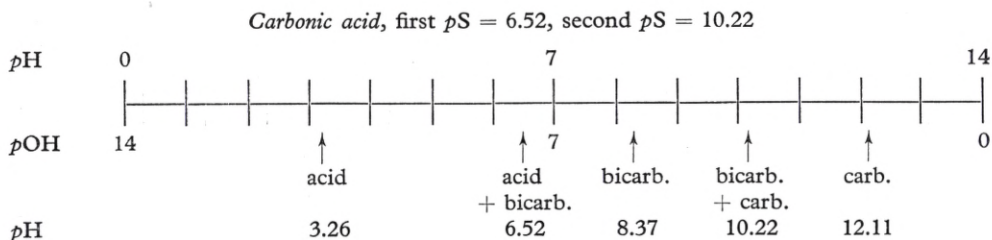
The *acid-point* moves $\frac{1}{2}$ unit to the right each time the solution becomes 10 times weaker. The *salt-point* moves $\frac{1}{2}$ unit to the left each time the solution becomes 10 times weaker, and the *salt-acid-point* moves one full unit to the right, each time the acid to salt ratio decreases 10 times.

In the case of a weak base an analogous procedure can be followed to find the reaction points for the base, for its salt with a strong acid, and for a mixture of base and salt; however, instead of the hydrogen-ion exponent scale the hydroxyl-ion exponent scale should be used.

This graphic method may be extended to polybasic acids. It is sufficient to show how to proceed for a dibasic acid as carbonic acid. It is easy to extend the method to acids of still higher basicity.

Carbonic acid has 2 strength exponents, 6.52 and 10.22. The first value represents ionization of the first hydrogen atom by which a bicarbonate ion is formed from undissociated carbonic acid. The second exponent represents ionization of the second hydrogen atom, by which a carbonate ion is formed from a bicarbonate ion. A mixture of free carbonic acid and bicarbonate has a hydrogen-ion exponent close to the first strength exponent, and a mixture of bicarbonate and carbonate has a hydrogen-ion exponent close to the second strength exponent. When the mixtures contain equivalent amounts, the reactions (pH values) will exactly equal the strength exponents. In other cases they will be displaced from these points according to the above rules, valid for an acetic acid-acetate mixture. By halving the distance between the point $pH = 0$ and the acid-bicarbonate point, the reaction point for the pure carbonic acid is found; by halving the distance between the acid-bicarbonate point and the bicarbonate-carbonate point the reaction point for a pure bicarbonate solution is found; and halving the distance between the bicarbonate-carbonate point and $pH = 14$ (or more generally $pOH = 0$) we finally obtain the reaction point for a soda solution. All these points are marked in the following reaction scale.

The reaction in the solution of free carbonic acid and in the solution of soda varies with dilution according to the rules governing a monobasic acid, and the points shown are exactly valid only for 1 molar solutions. The reaction of a bicarbonate solution, on the other hand, is independent of the concentration. In this case the point marked applies to all concentrations.



At this juncture let us remember that in all the discussions and results in this paper, complete dissociation of the salts has been taken for granted. This causes a slight inaccuracy in the results obtained. However, when the degree of dissociation of the salts is known, the inaccuracy may easily be corrected in each case by considering the incomplete dissociation. This correction, indeed, slightly changes the figures in the results, but the main features of the phenomena here described are not changed.

4. BUFFER MIXTURES

When hydrochloric acid is added drop by drop to a mixture of acetic acid and sodium acetate, the reaction in the mixture will, at first, hardly change at all. This is because the hydrochloric acid is consumed by the sodium acetate in forming acetic acid. Since the hydrogen-ion exponent of the mixture is determined by the ratio of free acetic acid to sodium acetate according to the equation mentioned earlier:

$$pH = pS + \log \frac{C_{\text{salt}}}{C_{\text{acid}}},$$

the reaction of the solution will change but little as long as the quantity of hydrochloric acid added is small compared with the quantities present of acetic acid and acetate. Not until the acetic acid is completely released does the solution become strongly acid. The addition of bases will likewise change the reaction but only little at first. The mixture of acetic acid and sodium acetate acts as a kind of "buffer" against change in reaction from the addition of strong acids and bases. How pronounced this buffer effect is, may be seen from the following example. If 1 per cent of 1 normal hydrochloric acid is added to pure water, the solution becomes 0.01 normal hydrochloric acid and the hydrogen-ion exponent drops from 7 to 2 — i.e. 5 units. If, on the other hand, 1 per cent of 1 normal hydrochloric acid is added to a solution which is 0.1 normal with respect to both acetic acid and sodium acetate, the hydrogen-ion exponent only falls from 4.75 to 4.66 — not even 0.1 unit.

Any mixture of a weak acid and one of its salts will act as a buffer, the same is true of mixtures of weak bases and their salts. In a mixture of ammonia and

ammonium chloride, the reaction lies close to $pH = 9.25$. The strength exponent of the ammonia base is 4.75, consequently the hydroxyl-ion exponent of the solution lies close to 4.75. From this the hydrogen-ion exponent is calculated by subtraction from 14.

$$pH = 14 - pOH = 14 - 4.75 = 9.25.$$

Since the reaction of a solution is of decisive importance to numerous properties of the solution and to many of the processes taking place within the solution, it is in many investigations necessary to ensure that the solution one investigates has a definite and well-defined reaction. Such a reaction may be obtained by adding a suitable buffer mixture. By this addition the solution attains a known hydrogen-ion exponent not appreciably influenced by accidental small quantities of impurities or by eventual new substances formed in the solution. A solution of the purest potassium chloride in ordinary distilled water has no well-defined reaction. The reaction is of course close to the neutral point $pH = 7$, but accidental impurities such as carbonic acid from the atmosphere, or alkali from the glass, may alter the hydrogen-ion exponent to 6 or 8, or even to 5 or 9 although the solutions have been prepared with great care. In many investigations results are only reproducible when the reaction of the solutions in question are fixed by means of buffer mixtures. This is true, for instance, in many enzymatic investigations, in solubility determinations of many so-called insoluble substances, and in investigations on reaction velocity of chemical processes. In living organisms the reaction of fluids is regulated by phosphate- and especially carbonate- containing buffer mixtures. The reaction of blood, for example, is regulated by a carbonic acid-bicarbonate buffer.

In a good buffer mixture both components must be present in not too small concentrations. Therefore, a definite pair of components, such as acetic acid and sodium acetate, cover only a rather small interval, generally not more than 2 units on the pH scale. It is therefore important to have recourse to a series of different component pairs to cover the entire reaction interval.

We are indebted to S. P. L. Sørensen for the most detailed and accurate directions for the preparation of good buffer mixtures. Following his directions, it is easy to produce any hydrogen-ion concentration with an accuracy of one or two per cent. Table 3 gives the composition of a series of solutions with round values of the hydrogen-ion exponent computed from the statements of S. P. L. Sørensen.

The standard solutions used in preparing these solutions are: 1) "*Hydrochloric acid*", a 0.1 *N* HCl, 2) "*Sodium hydroxide*", a 0.1 *N* (carbon-dioxide-free) solution of NaOH, 3) "*Glycine*", a 0.1 *M* glycine, which is also 0.1 *M* with respect to NaCl, 4) "*Secondary phosphate*", a $\frac{1}{15}$ *M* Na₂HPO₄, 5) "*Primary phosphate*", a

Table 3. Solutions with well-defined hydrogen-ion exponents

pH	Hydrochloric acid	Citrate	pH	Hydrochloric acid	Borate
1.04	10.00 cc.	0.00 cc.	8	4.43 cc.	5.57 cc.
1.5	7.77 -	2.23 -	8.5	3.51 -	6.49 -
2	6.93 -	3.07 -	9	1.49 -	8.51 -
2.5	6.45 -	3.55 -			
3	5.96 -	4.04 -		Sodium hydroxide	Borate
3.5	5.31 -	4.69 -			
4	4.38 -	5.62 -	9.5	2.03 cc.	7.97 cc.
4.5	2.79 -	7.21 -	10	4.06 -	5.94 -
			10.5	4.69 -	5.31 -
	Sodium hydroxide	Citrate	11	4.98 -	5.02 -
5	0.39 cc.	9.61 cc.		Sodium hydroxide	Glycine
5.5	2.78 -	7.22 -			
6	4.06 -	5.94 -	11.5	5.07 cc.	4.93 cc.
(6.5)	4.65 -	5.35 -	12	5.39 -	4.61 -
			12.5	6.32 -	3.68 -
	Primary phosphate	Secondary phosphate	13	9.23 -	0.77 -
(6)	8.77 cc.	1.23 cc.			
6.5	6.86 -	3.14 -			
7	3.90 -	6.10 -			
7.5	1.60 -	8.40 -			
(8)	0.54 -	9.46 -			

$\frac{1}{15}$ M KH_2PO_4 , 6) "Borate", a $\frac{1}{20}$ M borax, $\text{Na}_2\text{B}_4\text{O}_7$, prepared from 1 N sodium hydroxide and boric acid, 7) "Citrate", a 0.1 M solution of secondary sodium citrate, prepared from 1 N sodium hydroxide and citric acid. The solutions should be prepared from pure reagents and great care taken to prevent contamination by carbon dioxide.

5. THE DYE-STUFF INDICATORS

According to W. Ostwald dye-stuff indicators such as litmus and phenolphthalein are weak acids or bases which show different colours in undissociated and in ionized state. The free indicators are only little ionized and show the colours of the undissociated molecules, but when neutralized and transformed into salts, their colours change to those of their ions.

According to this theory, indicators may be divided into acid and basic indicators. This classification has, however, nothing to do with their sphere of applicability, their sensitivity, or their quality. In the following the indicator theory will be discussed for an acid indicator. A corresponding theory may be developed for a basic indicator with exactly corresponding results.

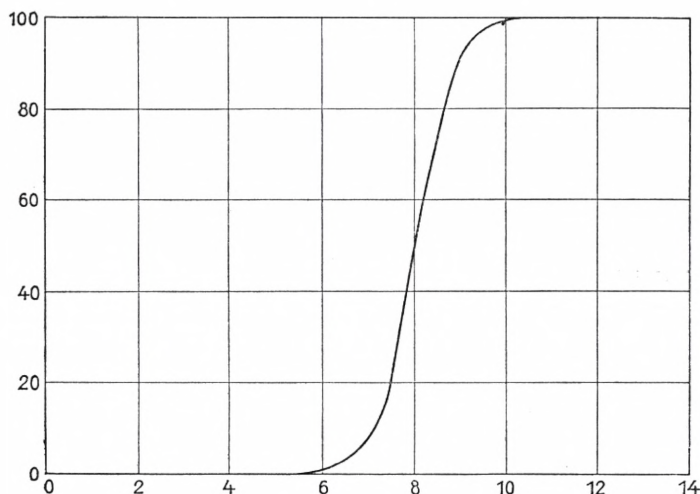


Fig. 1.

An indicator acting as a monobasic acid may be written HI; in solution it will be present, either as free indicator acid HI with "acid" colour, or as indicator-ion I^- , with "alkaline" colour. The ratio between the concentrations of the two differently coloured indicator forms is determined by the hydrogen-ion concentration in the solution, and the dissociation constant, K_I , of the indicator; this follows from the dissociation equation of the indicator acid:

$$C_{H^+} \cdot \frac{C_{I^-}}{C_{HI}} = K_I.$$

On taking logarithms, and designating the strength exponent of the indicator acid as pI :

$$\log \frac{C_{I^-}}{C_{HI}} = pH - pI.$$

It appears from these equations that the colour shown by an indicator depends only on the reaction of the solution. When the hydrogen-ion concentration in the solution is equal to the dissociation constant of the indicator-acid, the indicator is half-way transformed; when the hydrogen-ion concentration is larger, the indicator is mainly present with acid colour, and when smaller, the alkaline colour predominates. The curve drawn, fig. 1, shows how the dissociation of the indicator changes with the reaction. As abscissa is used the hydrogen-ion exponent and as ordinate the quantity of the basic form of the indicator, expressed in per cent of the total quantity of indicator present: $100 C_{I^-}/(C_{HI} + C_{I^-})$.

The curve is drawn for an indicator with strength exponent 8. For an indicator with another strength exponent the curve will be congruent with the one drawn,

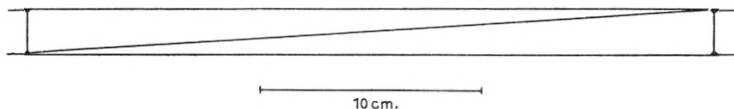


Fig. 2.

only displaced the proper distance parallel to the abscissa axis. The colour-transformation interval, expressed in pH units, is the same for all indicators.

When both indicator forms are coloured, as in the case of litmus, it will hardly be possible with the naked eye to distinguish the presence of $\frac{1}{20}$ of the one colour in $\frac{19}{20}$ of the other colour. In other words, as soon as the hydrogen-ion exponent

in the solution is $\log \frac{20}{1} = 1.28$ larger or smaller than the strength exponent of

the indicator, the indicator will be outside the interval within which its colour markedly changes with reaction. The entire change-interval will then only comprise 2.6 pH units, i.e. 1.3 units on each side of the strength exponent of the indicator.

Demonstration of the theory. To prove the correctness of the formulae for indicator change given here, colorimetric measurements are used to determine the ratio between the two indicator forms in solutions with known hydrogen-ion exponents. Such a measurement may be made, for instance as follows:

Using thin glass plates joined together with pitch, a cuvette, 30 cm long, 10 cm high, and 2 cm wide, is made. In this a long vertically placed glass plate is fastened diagonally. Fig. 2 shows the cuvette seen from above. The diagonal plate divides the cuvette into two wedge-shaped containers. One of these is filled with a solution of the indicator, so acid that it shows the pure acid colour of the indicator, the other container is filled with an alkaline solution of the indicator which shows the pure alkaline colour. The concentration of the indicator in both these solutions must equal the concentration of the indicator in the solution to be tested. Looking through the cuvette in different places, we always look through the same quantity of indicator, but the ratio between the quantities of the two forms is different. It is a simple matter to place a small graduated scale so that this ratio can be directly read. The indicator solution in which the ratio between the two indicator forms is to be determined is poured into a small cuvette, whose width equals the combined widths of the two sections of the large cuvette. In moving this small cuvette along the top of the large one, a point may be found where the large cuvette shows the same colour tone as the small cuvette. This is easily done by shading off and comparing the colour

of a narrow section in the large cuvette with the colour in the small cuvette standing on top of it.

This arrangement is well-suited for demonstration in a small lecture room. Using it in a lecture, I was able to find the results given in table 4 and from those to calculate the strength exponents pI for methyl orange according to the formula

$$pI = pH + \log \frac{a}{1-a}.$$

In this formula a denotes the fraction of the indicator present with red colour. The agreement between the strength exponent values listed in the last column proves the correctness of the formula used.

Table 4. State of methyl orange in solution

pH	C_{H^+}	Percentage of yellow colour	Percentage of red colour	pI
3	10^{-3}	20	80	3.60
3.5	$10^{-3.5}$	45	55	3.59
4	10^{-4}	70	30	3.64

Table 5 shows the transformation intervals of 22 indicators. S. P. L. Sørensen determined these transformation intervals by adding the indicator in question to different solutions with known hydrogen exponents and compared the colour of the indicators in these solutions with each other. The pH intervals given comprise the hydrogen-ion exponents within which the colour of the indicator is so sensitive to changes in the reaction, that, by comparing the colour tone of the indicator in the solution with the colour tone in the standard solutions with known hydrogen-ion exponents, it is possible to determine the unknown hydrogen-ion exponent in the solution with an accuracy of 0.02—0.05 units (*colorimetric reaction determination*). Outside the intervals stated here, the colour of the indicator only shows that the reaction of the solution is more acid or more alkaline than corresponding to the transformation interval, without permitting quantitative statements.

Table 6 contains transformation intervals according to Salm for some indicators not found in S. P. L. Sørensen's table.

The titration exponent. The indicators are chiefly used in titrating acids and bases. If an indicator is always used with the same concentration and titrated to the same colour tone, the titrated solutions will also have the same reaction, i.e. they have been titrated to a definite hydrogen-ion exponent. This exponent we call the *titration exponent* of the indicator and designate as pT . For an acid

Table 5. Transformation intervals for indicators according to Sørensen

Indicator	pH	Amount of indicator to 10 cc.
Methyl violet	0.1 - 1.5	8 — 3 drops 0.05 per cent
— —	1.5 - 3.2	10 — 4 — 0.01 — —
Mauveine	0.1 - 1.5	8 — 3 — 0.05 — —
—	1.5 - 2.9	10 — 4 — 0.01 — —
Benzene-azo-diphenylamine	1.2 - 2.1	15 — 6 — 0.01 — —
<i>m</i> -Benzenesulphonic acid-azo-diphenyl-amine	1.2 - 2.3	5 — 3 — 0.01 — —
<i>p</i> -Benzenesulphonic acid-azo-diphenyl-amine	1.4 - 2.6	5 — 3 — 0.01 — —
<i>p</i> -Benzenesulphonic acid-azo-benzyl-amine	1.9 - 3.3	6 — 3 — 0.01 — —
Benzene-azo-benzyl-aniline	2.3 - 3.3	10 — 5 — 0.02 — —
<i>p</i> -Benzenesulphonic acid-azo- <i>m</i> -chlorodiethylaniline	2.6 - 4.0	5 — 3 — 0.01 — —
Benzene-azo-dimethylaniline	2.9 - 4.0	10 — 5 — 0.01 — —
Methyl orange	3.1 - 4.4	5 — 3 — 0.01 — —
Benzene-azo- α -naphthylamine	3.7 - 5.0	20 — 10 — 0.01 — —
<i>p</i> -Benzenesulphonic acid-azo- α -naphthylamine	3.5 - 5.7	12 — 8 — 0.01 — —
Methyl red	4.2 - 6.3	4 — 2 — 0.02 — —
<i>p</i> -Nitrophenol	5.0 - 7.0	20 — 3 — 0.04 — —
Neutral red	6.8 - 8.0	20 — 10 — 0.01 — —
Rosolic acid	6.9 - 8.0	15 — 6 — 0.04 — —
<i>p</i> -Benzenesulphonic acid-azo- α -naphthol	7.6 - 8.9	10 — 4 — 0.01 — —
α -Naphtholphthalein	7.3 - 8.7	12 — 4 — 0.04 — —
Phenolphthalein	8.3 - 10.0	20 — 3 — 0.05 — —
Thymolphthalein	9.3 - 10.5	10 — 3 — 0.04 — —
<i>p</i> -Nitrobenzene-azo-salicylic acid	10.1 - 12.1	10 — 5 — 0.01 — —
<i>p</i> -Benzenesulphonic acid-azo-resorcinol	11.1 - 12.7	10 — 5 — 0.01 — —

Table 6. Transformation intervals for indicators according to Salm

Indicator	pH	Indicator	pH
Congo red	4	α -Naphthol benzoïn	10
Sodium alizarine sulphonate	5	Tropaeolin O	12
Cochineal	5.5	Trinitrobenzene	13.5
Lacmoid	6	Benzopurpurin B	13.5
Litmus	7	Safranin	15.5
Cyanin	7.5		

indicator the titration exponent will always be close to the strength exponent of the indicator but in certain cases it may deviate more than 1 unit from it. In table 7 the approximate titration exponents for some of the most important indicators are shown.

Table 7. Approximate values for the titration exponents of the most important indicators

Indicator	pT	Colour tone to which is titrated	Amount of indicator per 100 cc.		
Methyl orange	4	yellow with reddish tone	0.1 cc. 0.1 per cent		
Methyl red	5.5	— — — —	0.1 — 0.1 — —		
Rosolic acid	6.5	pale brown with rosa tone	1 — 0.1 — —		
Litmus	{	6	red with bluish tone	{ 1 cc. of 2 per cent solution of Kahlbaum's extract	
		7	blue with reddish tone		
Phenolphthalein	{	8	weakly red		0.7 cc. 1 per cent
		9	— —		0.04 — 0.1 — —

In titration analysis the titration exponents of the indicators are of fundamental interest. It is their values which determine the *useful ranges* of the indicators. On the other hand, the value of the titration exponent does not determine the general usefulness of an indicator. The usefulness of an indicator which, judged from its titration exponent, seems suitable for the titration in question, depends upon the accuracy with which a definite hydrogen-ion exponent may be fixed by means of the indicator. The more abrupt and contrasting the colour change, the better is the indicator. Under ordinary conditions we cannot expect to hit the pH value with a greater accuracy than 0.3 pH units, even when a good indicator is used.

6. THEORY OF TITRATION

When the amount of an acid is to be determined by titration it is natural to ask: *To what reaction is it best to titrate?* The answer must be: titrate to the reaction characteristic for the salt of the acid in question. We are, however, not told whether it is also necessary to use an indicator which changes colour at just that reaction, or whether other indicators can be used as well. We are led somewhat further by asking: *How great is the error when titrating with a definite indicator?* When this question is answered for the different indicators it is easy enough to decide which indicators are suitable and which are unsuitable for our purpose.

The titration error and formulae for computing it. We assume that we are to titrate an acid HS with strength exponent pS using an indicator with titration exponent pT . When titrating a weak acid a strong base should always be used, sodium hydroxide for instance. We will therefore compute the error under this assumption. The source of error in a titration is due to the fact that the solution, when completely titrated, should only contain the salt, but actually, contains some acid or base or both. Free acid may be present in our solution both as hydrogen ions and as undissociated acid molecules, free base must chiefly be

present as hydroxyl ion, since sodium hydroxide is strongly ionized. Therefore there are three kinds of error to take into account:

1. Hydrogen-ion error (H^+ - error)
2. Hydroxyl-ion error (OH^- - error)
3. Acid error (HS - error)

A closer consideration will show that each of the three errors must be small if the titration shall be exact. Even though some of the errors are positive and others negative we cannot be sure that they compensate each other to any great extent.

We will first write the formulae for these three kinds of error. In the case of the *hydrogen-ion error*, when the total volume at the close of the titration is designated v and the standard solution is n normal:

$$H^+ \text{ - error} = C_{H^+} \cdot \frac{v}{n} = 10^{-pT} \cdot \frac{v}{n} \text{ cc. standard solution.}$$

This expression is found by computing the amount of n normal solution, corresponding to v cc. of normality C_{H^+} . Analogously the hydroxyl-ion error may be expressed:

$$OH^- \text{ - error} = C_{OH^-} \cdot \frac{v}{n} = 10^{-(14-pT)} \cdot \frac{v}{n} \text{ cc. standard solution.}$$

In dealing with the *acid error* it is easiest to give its relative value, i.e. its value in relation to the total amount of acid to be titrated. Since the main part of the acid at the end of the titration is present in the solution as S^- -ions, the relative value of the acid error is found by computing the ratio between the number of undissociated molecules and anions, in the completely titrated solution. This is found from the dissociation equation of the acid:

$$\frac{C_{HS}}{C_{S^-}} = \frac{C_{H^+}}{K_S} = \frac{10^{-pT}}{10^{-pS}} = 10^{pS-pT}.$$

Hence, the relative acid error = $\frac{C_{H^+}}{K_S} = 10^{pS-pT}$.

Examples. Let us compute these three kinds of error in certain definite cases using the formulae found.

Example 1. Titration of acetic acid ($pS = 4.75$) with phenolphthalein in small quantities ($pT = 9$) in a total volume of 100 cc. ($v = 100$) with 0.1 normal sodium hydroxide ($n = 0.1$).

H^+ - error: negligible, since the reaction at the end point of the titration is alkaline.

$$\text{OH}^- - \text{error: } 10^{-(14-9)} \cdot \frac{100}{0.1} = 0.01 \text{ cc.}$$

$$\text{relative HS} - \text{error: } 10^{4.75-9} = 10^{-4.25} = \frac{1}{18000} = \frac{1}{180} \text{ per cent.}$$

From this we conclude that the titration of the acid with phenolphthalein as indicator, is extremely exact.

Example 2. Same titration with litmus as indicator to distinct blue colour ($pT = 7$).

$$\text{H}^+ - \text{error} = 10^{-7} \cdot \frac{100}{0.1} = 10^{-4} \text{ cc.}$$

$$\text{OH}^- - \text{error} = 10^{-7} \cdot \frac{100}{0.1} = 10^{-4} \text{ cc.}$$

$$\text{relative HS} - \text{error} = 10^{4.75-7} = 10^{-2.25} = \frac{1}{180}.$$

Titrating acetic acid with litmus as indicator, by which one titrates very close to the true neutral point, the acid error is 1/180 of the entire amount of acid. At the close of titration this fraction of the acid is present in the solution as free acid. Titrating acetic acid with litmus indicator is not as exact as titrating it with phenolphthalein.

Example 3. The same titration using methyl orange ($pT = 4$) as indicator.

$$\text{H}^+ - \text{error} = 10^{-4} \cdot \frac{100}{0.1} = 0.1 \text{ cc.}$$

$\text{OH}^- - \text{error: negligible.}$

$$\text{relative HS} - \text{error} = 10^{4.75-4} = 10^{0.75} = \text{about } 6.$$

With methyl orange as indicator, the acid error is very large and the hydrogen-ion error is appreciable. Methyl orange is of no use at all for the titration of acetic acid. The value 6 for the acid error indicates that methyl orange changes from red to yellow when only 1/7 of the acetic acid is changed to acetate, i.e. when 6/7 of the total acetic acid is still in solution as free acid.

The factors determining the value and influence of titration errors. The values of hydrogen-ion and hydroxyl-ion errors are quite independent of the strength of the acid. The errors are constant, as long as the same indicator is used, whether one titrates hydrochloric acid, acetic acid or boric acid. To keep these errors under 0.01 cc. in titrations with 0.1 normal sodium hydroxide in 100 cc. solution ("normal titration"), the titration exponent of the indicator must lie between 5 and 9. Methyl red, litmus, and phenolphthalein fulfill these requirements. If the titra-

tion exponent of the indicator lies outside the interval 5 to 9, as does that of methyl orange, it is necessary either to titrate in a smaller volume than 100 cc., or titrate with a solution stronger than 0.1 normal. Otherwise we must expect a larger error than 0.01 cc.

It is characteristic of the *acid error* that it does *not* depend on the volume of the solution, but depends solely on the strength of the acid and the transition point of the indicator. If the acid error must be less than 0.1 per cent, the titration exponent of the indicator must be 3 units larger than the strength exponent of the acid; we have the equation:

$$\text{relative HS-error} = 10^{pS-pT}$$

This result may be expressed as follows: *At the end of the titration, the reaction must lie at least 3 units in the pH scale to the right of the strength exponent of the acid.* If an accuracy of 1 per cent is sufficient, the titration exponent may lie only 2 units to the right of the strength exponent of the acid etc.

When titrating weak acids, it is accordingly best to select an indicator with a transition point so far beyond on the alkaline side of the neutral point as is compatible with a small hydroxyl-ion error. In accord with this condition we prefer an indicator with titration exponent 9 when titrating weak acids. Since phenolphthalein has just this titration exponent, it is particularly well-adapted to the titration of weak acids. Using phenolphthalein as indicator, it is possible, in 100 cc. solution with 0.1 N sodium hydroxide to titrate acids with dissociation constants down to 10^{-6} with an accuracy of 0.1 per cent. In titrating weaker acids we must either tolerate an error above 0.1 per cent, or use stronger titration solutions in smaller volumes with an indicator whose titration exponent is larger than 9. As yet, no indicator with titration exponent 9.5–10, and well adapted to this use, seems to have been found.

When titrating *weak bases* a strong acid should be used as titrating solution. The errors to be expected in titrating weak bases with strong acids are subject to the same rules as the errors in titrating strong acids with weak bases. There is nothing new to be said in regard to the hydrogen-ion error and hydroxyl-ion error. Instead of an acid error, in this case a *base error* occurs, dependent on the hydroxyl-ion exponent and the strength exponent of the base, in the same way as the acid error depends on the hydrogen-ion exponent and the strength exponent of the acid. If titration is to be accurate to 0.1 per cent the hydroxyl-ion exponent must, at the end point of titration, be at least 3 units larger than the strength exponent of the base i.e. *the reaction at the end point of the titration, must lie at least 3 units in the hydroxyl-ion exponent scale to the right of the strength exponent for the base.*

Titration of ammonia, with $pB = 4.75$, requires the use of an indicator, for

which, at the transition point the hydroxyl-ion exponent is larger than $4.75 + 3 = 7.75$. Its titration exponent must consequently be less than $14 - 7.75 = 6.25$. When titrating with litmus to clear red, the titration exponent will be about 6 and thus fulfill the requirement, consequently litmus may be used in ammonia titration.

The smaller the titration exponent of the indicator, the smaller the "base error" in titrations of weak bases. The smallest titration exponent which should be used in ordinary titration is $pT = 5$. If the titration exponent is smaller the hydrogen-ion error will be too large. The end point of titration $pH = 5$ is obtained using methyl red; this indicator is just as advantageous in titrating weak bases as is phenolphthalein in titrating weak acids. With no difficulty whatsoever, methyl red can be used to titrate bases with strength exponents up to 6. Ammonia ($pB = 4.75$) is very satisfactorily titrated with this indicator, and hydrazine ($pB = 5.5$) as well, but we are here close to the limit. For even weaker bases, methyl orange, with titration exponent 4, can be used. If by using a sufficiently small volume, and sufficiently strong titration solution, the hydrogen-ion error is kept sufficiently small, methyl orange may be used with an accuracy of 0.1 per cent for titrating bases with dissociation constants down to 10^{-7} , and even weaker bases with an accuracy of 1 per cent.

Example. The strength exponent of the base pyridine is 8.8. To keep the base error in a titration of pyridine below 1 per cent the hydroxyl-ion exponent must, at the end point of titration, be equal to, or larger than 10.8. Consequently, the titration exponent must be equal to, or smaller than 3.2. When we titrate with methyl orange to so strong red colour, that more than one half of the methyl orange is changed to the red form, we are approximately working with this titration exponent. When we furthermore titrate with $1/5$ normal hydrochloric acid and keep the volume below 50 cc. the hydrogen-ion error may be expressed:

$$H^+ - \text{error} = 10^{-3.2} \cdot \frac{50}{0.2} = \frac{1}{16} \text{ cc.}$$

This estimate shows the accuracy which may be expected in titrations of pyridine. The simplest way to determine the colour tone at which titration should end, is to make a solution of the pyridine salt formed in the titration, and then titrate to the colour of methyl orange in that solution.

Insensitivity of indicators to very weak acids. The use of methyl orange in titrating alkali hydroxydes which contain carbonates is important and interesting from a theoretical point of view. This use depends on the insensitivity of methyl orange to carbonic acid. When hydrochloric acid is added to sodium carbonate, methyl orange first changes to red when all the carbonate has been transformed to chloride.

We shall consider how weak an acid must be, in order that it should not be

affected by the titration. The requirement is that, at the end point of the titration, the acid must mainly be present as an undissociated hydrogen compound. The fraction present as ion causes an acid error.

If we designate an acid, which we wish should not be affected, as H_s , the relative value of the acid error is C_s-/C_{H_s} .

On introducing the dissociation equation for the acid, we find:

$$\text{relative } H_s - \text{error} = \frac{C_s}{C_{H_s}} = \frac{K_s}{C_H} = 10^{pT-ps}$$

If this error is to be small, the dissociation constant of the acid must be less than the hydrogen-ion concentration at the end point of the titration, or, as it may otherwise be expressed: the strength exponent of the acid must be larger than the titration exponent of the indicator. If the strength exponent is 2 units larger than the titration exponent, the acid error may be estimated to 1 per cent, if it is 3 units larger the value of the error is reduced to 0.1 per cent.

Example. The titration exponent of methyl orange is 4; the smaller of the two strength exponents of carbonic acid is 6.52. To the difference 2.52, corresponds a relative acid error of $10^{-2.52} = 0.003$, i.e. when a titration with methyl orange as indicator is made, 0.003 part = 0.3 per cent of the carbonic acid present is titrated as monobasic acid, the rest of the carbonic acid remains as free acid at the end of the titration. If the titration of acid is continued until methyl orange shows an orange colour, the titration is carried to $pT = 3.5$ instead of $pT = 4$, and in that case only $10^{3.5-6.5} = 0.001$ part of the amount of carbonic acid is affected by the titration. The greater accuracy attained in this way will, however, in many instances be lost by an increase of the hydrogen-ion error.

The following little table shows the carbonic-acid sensitivity of the most important indicators. The figures indicate how many equivalents base each carbonic-acid molecule present binds.

Methyl orange	$\left\{ \begin{array}{l} pT = 3.5 \\ pT = 4 \end{array} \right.$	$\begin{array}{l} 0.001 \\ 0.003 \end{array}$
Methyl red	$\left\{ \begin{array}{l} pT = 5 \\ pT = 5.5 \end{array} \right.$	$\begin{array}{l} 0.03 \\ 0.1 \end{array}$
Litmus	$\left\{ \begin{array}{l} pT = 6 \\ pT = 7 \end{array} \right.$	$\begin{array}{l} 0.3 \\ 1 \end{array}$
Phenolphthalein	$\left\{ \begin{array}{l} pT = 8 \\ pT = 9 \end{array} \right.$	$\begin{array}{l} 1 \\ 1.5 \end{array}$

As seen from the table *methyl red* is but slightly sensitive to carbonic acid in comparison with litmus and phenolphthalein. When this indicator is used, the

amounts of carbonic acid present in ordinary distilled water and in acid solutions made from it, are, as a rule, no cause for error; this is not the case with litmus and phenolphthalein. When these two indicators are used, it is necessary to boil away the carbonic acid. *Methyl orange* is even less sensitive to carbonic acid than methyl red.

Titration of mixtures. When a mixture of several acids and bases is to be titrated, it is necessary to take into account not only the hydrogen-ion error and hydroxyl-ion error but also a base and acid error for each base and acid present in the mixture. Therefore, for the sake of accuracy in the titration, the hydrogen-ion exponent, at the end of titration must not lie near to the strength exponent of anyone of the acids present in the solution, (nor must the hydroxyl-ion exponent at the end of titration lie close to the strength exponent of any of the bases present in the solution). The problem is to locate a point on the reaction scale, sufficiently removed from the strength exponents of the acids and bases present, and to select an indicator which changes at this point. It is hardly necessary to state that the smaller the quantity of acid present, the closer may the hydrogen-ion exponent be to the strength exponent of the acid, and it is evident that only those acids (bases) whose strength points on the reaction scale lie to the left (right) of the end point of the titration are included in the titration, whereas the acids (bases) whose strength points lie to the right (left) of the end point of the titration are not affected by the titration.

A *polybasic acid* behaves during titration almost like a mixture of monobasic acids with the same strength exponents as the polybasic acid. In a titration in which the titration exponent is less than all the strength exponents of the polybasic acid, the acid is not included in the titration; if the titration exponent lies between the first and second strength exponent, preferably just in the middle, the acid is titrated as a monobasic acid; if the titration exponent lies between the second and third strength exponent, the acid is titrated as dibasic; if the titration exponent is larger than all the strength exponents of the acid, the acid is titrated with its complete basicity.

1. *Example.* The strength exponents of carbonic acid are 6.52 and 10.22. If a titration exponent is selected half-way between these two figures, i.e. about 8.4, the carbonic acid is titrated as a monobasic acid. To the end point $pT = 8.4$, phenolphthalein can be used as indicator, and carbonic acid will react with this indicator as a *monobasic acid*. As the interval between 8.4 and the two strength exponents of the carbonic acid 6.52 and 10.22 hardly equals 2, the accuracy to be expected from titrating carbonic acid with phenolphthalein is not very great, less than 1 per cent.

2. *Example.* The strength exponents of phosphoric acid are 1.96, 6.7 and 12.44. When titration is performed with methyl orange as indicator ($pT = 4$) the ti-

titration exponent lies between the 1st and 2nd strength exponent, and the phosphoric acid is titrated as a *monobasic acid*. In this titration, the distance of the titration exponent from the strength exponents is larger than 2, and the accuracy obtainable is somewhat greater than 1 per cent. If phosphoric acid is titrated with phenolphthalein, the titration exponent is about 9, and it lies between the 2nd and 3rd strength exponent of phosphoric acid; phosphoric acid, then, is titrated as a *dibasic acid*. It is best to titrate to a hydrogen-ion exponent located exactly half-way between the two strength exponents, that is to 9.6. Titration must therefore continue to strong red colour. With this titration it is possible to obtain an accuracy of nearly 0.1 per cent, for the distance between 9.6 and each of the two strength exponents (6.7 and 12.44) is here almost 3. However, we must remember, that when working with a titration exponent larger than 9, the hydroxyl-ion error may easily decrease the accuracy of the titration.

The important subject whose main points are outlined in this little paper, has been more thoroughly discussed in several larger articles. The hydrogen-ion exponent, its experimental determination and importance especially in the field of biology is described by S. P. L. Sørensen (in *Compt. rend. trav. lab. Carlsberg* **8** (1909) and in *Asher-Spiros Ergeb. Physiol.* **12** (1912) 393) and by L. Michaelis (in *Die Wasserstoffionenkonzentration*, Verlag Springer, Berlin). Titration analysis and the theory of indicators are discussed in a paper by A. A. Noyes (*J. Am. Chem. Soc.* **32** (1910) 815). The author of the present article has written a monograph on the subject which may be consulted by those who wish a more comprehensive treatment of the subject along the same lines as those followed in the present paper (*Die Theorie der alkalimetrischen and acidimetrischen Titrierungen. Sammlung chemischer und chemisch-technischer Vorträge.* **21** (1914)).