

Acid-base Equilibria and Calculations

A Chem1 Reference Text

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Acid-base reactions, in which protons are exchanged between donor molecules (acids) and acceptors (bases), form the basis of the most common kinds of equilibrium problems which you will encounter in almost any application of chemistry.

This document provides a reasonably thorough treatment of aquatic-solution acid-base equilibria. Although it has been used as the principal text for part of a university-level General Chemistry course, it can also serve as a reference for teachers and advanced students who seek a more comprehensive treatment of the subject than is likely to be found in conventional textbooks.

As background, we will assume that you already have some understanding of the following topics:

- The Arrhenius concept of acids and bases
- the Brønsted-Lowry concept, conjugate acids and bases
- titration
- definition of pH and the pH scale
- strong *vs.* weak acids and bases
- the names of the common acids and bases

1 Proton donor-acceptor equilibria

In order to describe acid-base equilibria in the most general way, we will often represent an acid by the formula HA and its conjugate base as A⁻. The actual electric charges of the species will of course depend on the particular nature of A, but the base will always have one more negative charge than the acid HA. This pair of species constitutes an *acid-base system* whose two members are related by the reaction



The most fundamental property of a given acid-base system is the extent of the above reaction. If the concentration of undissociated HA is negligible when the reaction is at equilibrium, the acid is said to be *strong*. Only a very small number of acids fall into this category; most acids are *weak*.

There are two complications that immediately confront us when we attempt to treat acid-base equilibria in a quantitative way:

1. Since protons cannot exist in solution as independent species, the tendency of an acid or a base to donate or accept a proton (as in Eq 1) cannot be measured for individual acid or base species separately; the best we can do is compare two different acid-base systems, and determine the extent to which the bases are able to compete against each other for the proton.
2. Water itself can act both as an acid and a base, and most of the practical applications of acid-base chemistry are those involving aqueous solutions. This means that whenever we are studying an aqueous solution of an acid HA, we must also contend with the conjugate acid and base of H₂O.

We can make use of (2) to help us out with (1) by using water as a reference standard for proton-donating and -accepting power. Thus the strength of an acid HA can be defined by the equilibrium



Similarly, the strength of the base A⁻ is defined by



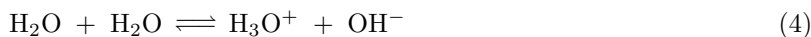
Note carefully that reaction (3) is *not* the reverse of (2).

1.1 The ion product of water

In pure water, about one H₂O molecule out of 10⁹ is “dissociated”:



The actual reaction, of course, is the proton transfer



for which the equilibrium constant

$$K_w = [\text{H}_3\text{O}^+][\text{OH}^-] \quad (5)$$

is known as the *ion product* of water. The value of K_w at room temperature is 1.008×10^{-14} .

In pure water, the concentrations of H₃O⁺ and OH⁻ must of course be the same:

$$[\text{H}_3\text{O}^+] = [\text{OH}^-] = \sqrt{K_w} \approx 10^{-7}$$

a solution in which $[\text{H}_3\text{O}^+] = [\text{OH}^-]$ is said to be *neutral*.

As with any equilibrium constant, the value of K_w is affected by the *temperature* (K_w undergoes a 10-fold increase between 0 °C and 60 °C), by the *pressure* (K_w is about doubled at 1000 atm), and by the presence of *ionic species* in the solution. Because most practical calculations involving K_w refer to ionic solutions rather than to pure water, the common practice of using 10^{-14} as if it were a universal constant is unwise; under the conditions commonly encountered in the laboratory, pK_w can vary from about 11 to almost 15¹. In seawater, K_w is 6.3×10^{-12} .

Notice that under conditions when K_w differs significantly from 1.0×10^{-14} , the pH of a neutral solution will not be 7.0. For example, at a pressure of 93 kbar and 527 °C, $K_w = 10^{-3.05}$, the pH of pure water would be 1.5. Such conditions might conceivably apply to deposits of water in geological formations and in undersea vents.

Problem Example 1

At 60 °C, the ion product of water is 9.6E-14. What is the pH of a neutral solution at this temperature?

Solution: Under these conditions, $[H^+][OH^-] = 9.6E-14$. If the solution is neutral, $[H^+] = [OH^-] = \sqrt{9.6E-14}$, corresponding to pH = 6.5.

¹See Stephen J. Hawkes: “ pK_w is almost never 14.0”, J. Chem. Education 1995: 72(9) 799-802

1.2 Acid and base strengths

The equilibrium constants that define the strengths of an acid and of a base are

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{OH}^-]}{[\text{HA}]} \quad (6)$$

and

$$K_b = \frac{[\text{HA}][\text{OH}^-]}{[\text{A}^-]} \quad (7)$$

How are K_a and K_b related? The answer can be found by adding Equations 2 and 3:



Since the sum of the first two equations represents the dissociation of water (we are using H^+ instead of H_3O^+ for simplicity), the equilibrium constant for the third reaction must be the product of the first two equilibrium constants:

$$\boxed{K_a K_b = K_w} \quad (11)$$

Clearly, as the strength of a series of acids increases, the strengths of their conjugate bases will decrease, hence the inverse relation between K_a and K_b .

pK values You will recall that the pH scale serves as a convenient means of compressing a wide range of $[\text{H}^+]$ -values into a small range of numbers. Just as we defined the pH as the negative logarithm of the hydrogen ion concentration, we can define

$$\text{p}K = -\log K$$

for any equilibrium constant. Acid and base strengths are very frequently expressed in terms of $\text{p}K_a$ and $\text{p}K_b$. From Eq 11 it should be apparent that

$$\text{p}K_a + \text{p}K_b = \text{p}K_w \quad (= 14.0 \text{ at } 25^\circ\text{C})$$

Table 1 on the next page gives the $\text{p}K$ values for a number of commonly-encountered acid-base systems which are listed in order of decreasing acid strength. Take a moment to locate the $\text{H}_3\text{O}^+/\text{H}_2\text{O}$ system in this table. Notice the value of $\text{p}K_a$ for the hydronium ion; its value of 0 corresponds to $K_a = 1$. Any acid whose K_a exceeds that of the hydronium ion is by definition a strong acid. You will also notice that the $\text{p}K$'s of the strongest acids and bases are given only approximate values; this is because these species are so strongly dissociated that the interactions between the resulting ions make it difficult to accurately define their concentrations in these solutions.

| acid | | pK_a | base | pK_b |
|--|--|--------|--|--------|
| HClO ₄ | perchloric acid | ~ -7 | ClO ₄ ⁻ | ~ 21 |
| HCl | hydrogen chloride | ~ -3 | Cl ⁻ | ~ 17 |
| H ₂ SO ₄ | sulfuric acid | ~ -3 | HSO ₄ ⁻ | ~ 17 |
| HNO ₃ | nitric acid | -1 | NO ₃ ⁻ | 15 |
| H ₃ O ⁺ | hydronium ion | 0 | H ₂ O | 14 |
| H ₂ SO ₃ | sulfurous acid | 1.8 | HSO ₃ ⁻ | 12.2 |
| HSO ₄ ⁻ | bisulfate | 1.9 | SO ₄ ²⁻ | 12.1 |
| H ₃ PO ₄ | phosphoric acid | 2.12 | H ₂ PO ₄ ⁻ | 11.88 |
| [Fe(H ₂ O) ₆] ³⁺ | aquo ferric ion | 2.10 | [Fe(H ₂ O) ₅ OH] ²⁺ | 11.90 |
| HF | hydrofluoric acid | 3.2 | F ⁻ | 10.8 |
| CH ₃ COOH | acetic acid | 4.7 | CH ₃ COO ⁻ | 9.3 |
| [Al(H ₂ O) ₆] ³⁺ | aquo aluminum ion | 4.9 | [Al(H ₂ O) ₅ OH] ²⁺ | 9.1 |
| H ₂ CO ₃ | total dissolved CO ₂ ^a | 6.3 | HCO ₃ ⁻ | 7.7 |
| H ₂ S | hydrogen sulfide | 7.04 | HS ⁻ | 6.96 |
| H ₂ PO ₄ ⁻ | dihydrogen phosphate | 7.2 | H ₂ PO ₄ ²⁻ | 6.8 |
| HSO ₃ ⁻ | bisulfite ion | 7.21 | SO ₃ ²⁻ | 6.79 |
| HOCl | hypochlorous acid | 8.0 | OCl ⁻ | 6.0 |
| HCN | hydrogen cyanide | 9.2 | CN ⁻ | 4.8 |
| H ₃ BO ₄ | boric acid | 9.30 | B(OH) ₄ ⁻ | 4.70 |
| NH ₄ ⁺ | ammonium ion | 9.25 | NH ₃ | 4.75 |
| Si(OH) ₄ | <i>o</i> -silicic acid | 9.50 | SiO(OH) ₃ ⁻ | 4.50 |
| HCO ₃ ⁻ | bicarbonate | 10.33 | CO ₃ ²⁻ | 3.67 |
| HPO ₄ ²⁻ | hydrogen phosphate | 12.32 | PO ₄ ³⁻ | 1.67 |
| SiO(OH) ₃ ⁻ | silicate | 12.6 | SiO ₂ (OH) ₂ ²⁻ | 1.4 |
| H ₂ O | water ^b | 14 | OH ⁻ | 0 |
| HS ⁻ | bisulfide ^c | ~ 19 | S ²⁻ | ~ -5 |
| NH ₃ | ammonia | ~ 23 | NH ₂ ⁻ | ~ -9 |
| OH ⁻ | hydroxide ion | ~ 24 | O ²⁻ | ~ -10 |

^aThe acid H₂CO₃ is only a minority species in aqueous carbon dioxide solutions, which contain mainly CO_{2(aq)}. The pK_a of 6.3 that is commonly given is calculated on the basis of the total CO₂ in the solution. The true pK_a of H₂CO₃ is about 3.5.

^bIf water is acting as a *solute*, as it must if the acid strength of H₂O is being compared with that of other very weak acids, then $pK_a \approx 16$ should be used. See *J. Chem. Education* 1990: 67(5) 386-388.

^cMany tables still give 14 as pK_2 for H₂S; this is now known to be incorrect.

Table 1: pK values of acids and bases in aqueous solutions at 25 °C

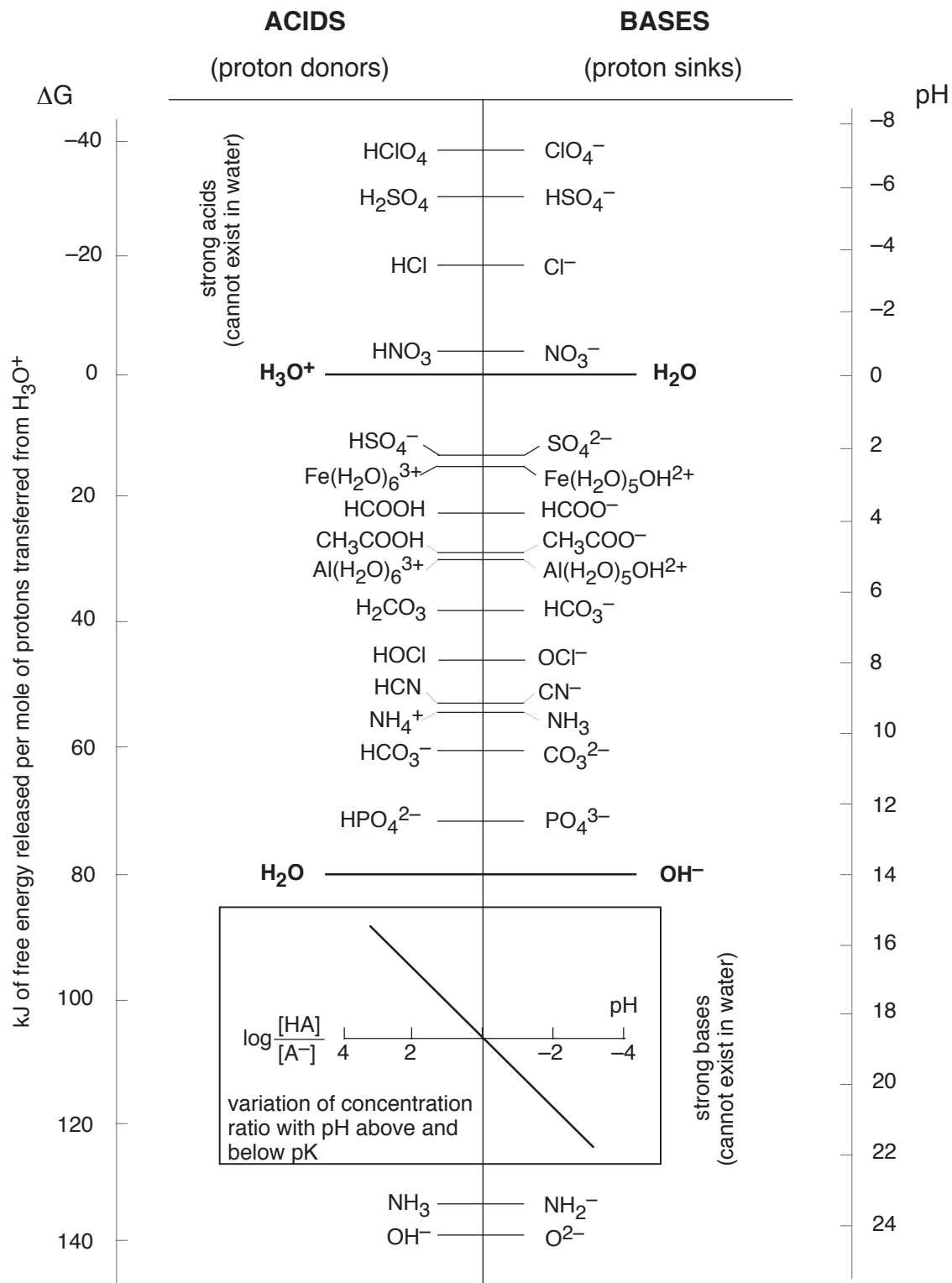


Table 2: Free energy diagram for acids and bases in aqueous solution.

2 The fall of the proton

An acid, being a proton donor, can only *act* as an acid if there is a suitable base present to accept the proton. What do we mean by “suitable” in this context? Simply that a base, in order to accept a proton, must provide a lower-free energy ² resting place for the proton than does the acid. Thus you can view an acid-base reaction as the “fall” of the proton from a higher free energy to a lower free energy.

2.1 Proton sources and sinks

Viewed in this way, an acid is a proton *source*, a base is a proton *sink*. The tendency for a proton to move from source to sink depends on how far the proton can fall in energy, and this in turn depends on the energy difference between the source and the sink. This is entirely analogous to measuring the tendency of water to flow down from a high elevation to a lower one; this tendency (which is related to the amount of energy that can be extracted in the form of electrical *work* if the water flows through a power station at the bottom of the dam) will be directly proportional to the difference in elevation (difference in potential energy) between the source (top of the dam) and the sink (bottom of the dam).

Now look at Table 2 on the following page and study it carefully. In the center columns of the diagram, you see a list of acids and their conjugate bases. These acid-base pairs are plotted on an energy scale which is shown at the left side of the diagram. This scale measures the free energy released when one mole of protons is transferred from a given acid to H₂O. Thus if one mole of HCl is added to water, it dissociates completely and heat is released as the protons fall from the source (HCl) to the lower free energy that they possess in the H₃O⁺ ions that are formed when the protons combine with H₂O.

Any acid shown on the left side of the vertical line running down the center of the diagram can donate protons to any base (on the right side of the line) that appears below it. The greater the vertical separation, the greater will be the fall in free energy of the proton, and the more complete will be the proton transfer at equilibrium.

Notice the H₃O⁺/H₂O pair shown at zero kJ on the free energy scale. This zero value of free energy corresponds to the proton transfer process



which is really no reaction at all, hence the zero fall in free energy of the proton. Since the proton is equally likely to attach itself to either of two identical H₂O molecules, the equilibrium constant is unity.

Now look at the acid/base pairs shown at the top of the table, above the H₃O⁺-H₂O line. All of these acids can act as proton sources to those sinks (bases) that appear below them. Since H₂O is a suitable sink for these acids, all such acids will lose protons to H₂O in aqueous solutions. These are therefore all *strong* acids that are 100% dissociated in aqueous solution; this total dissociation reflects the very large equilibrium constants that are associated with any reaction that undergoes a fall in free energy of more than a few kilojoules per mole.

2.2 Leveling effect

Because H₂O serves as a proton sink to any acid in which the proton free energy level is greater than zero, the strong acids such as HCl and H₂SO₄ cannot “exist” (as acids) in aqueous solution; they exist as their conjugate bases instead, and the only proton donor present will be H₃O⁺. This is the basis of the *leveling effect*, which states that *the strongest acid that can exist in aqueous solution is H₃O⁺*.

²You don’t know what *free energy* is? Don’t worry about it for the time being; just think of it as you would any other form of potential energy: something that falls when chemical reactions take place. This topic will be covered later in the course.

Now consider a weak acid, such as HCN at about 40 kJ mol^{-1} on the scale. This positive free energy means that in order for a mole of HCN to dissociate (transfer its proton to H_2O), the proton must *gain* 40 kJ of free energy per mole. In the absence of a source of energy, the reaction will simply not go; HCN is dissociated only to a minute extent in water.

2.3 Dissociation of weak acids

Why is a weak acid such as HCN dissociated at all? The molecules in solution are continually being struck and bounced around by the thermal motions of neighboring molecules. Every once in a while, a series of fortuitous collisions will provide enough kinetic energy to a HCN molecule to knock off the proton, effectively boosting it to the level required to attach itself to water. This process is called *thermal excitation*, and its probability falls off very rapidly as the distance (in kJ mol^{-1}) that the proton must rise increases. The protons on a “stronger” weak acid such as HSO_4^- or CH_3COOH will be thermally excited to the H_3O^+ level much more frequently than will the protons on HCN or HCO_3^- , hence the difference in the dissociation constants of these acids.

2.4 Titration

Although a weak acid such as HCN will not react with water to a significant extent, you are well aware that such an acid can still be titrated with strong base to yield a solution of NaCN at the equivalence point. To understand this process, find the $\text{H}_2\text{O}/\text{OH}^-$ pair at about 80 kJ mol^{-1} on the free energy scale. Because the OH^- ion can act as a proton sink to just about every acid shown on the diagram, the addition of strong base in the form of NaOH solution allows the protons at any acid above this level to fall to the OH^- level according to the reaction



Titration, in other words, consists simply in introducing a low free energy sink that can drain off the protons from the acids initially present, converting them all into their conjugate base forms.

2.5 Strong bases

There are two other aspects of the $\text{H}_2\text{O}-\text{H}_3\text{O}^+$ pair that have great chemical significance. First, its location at 80 kJ mol^{-1} tells us that for a H_2O molecule to transfer its proton to another H_2O molecule (which then becomes a H_3O^+ ion whose relative free energy is zero), a whopping 80 kJ/mol of free energy must be supplied by thermal excitation. This is so improbable that only one out of about 10 million H_2O molecules will have its proton elevated to the H_3O^+ level at a given time; this corresponds to the small value of the ion product of water, about 10^{-14} .

The other aspect of the $\text{H}_2\text{O}-\text{OH}^-$ pair is that its location defines the hydroxide ion as the strongest base that can exist in water. On our diagram only two stronger bases (lower proton free energy sinks) are shown: the amide ion NH_2^- , and the oxide ion O^{2-} . What happens if you add a soluble oxide such as Na_2O to water? Since O^{2-} is a proton sink to H_2O , it will react with the solvent, leaving OH^- as the strongest base present:



This again is the leveling effect; all bases stronger than OH^- appear equally strong in water, simply because they are all converted to OH^- .

2.6 Proton free energy and pH

The pH of a solution is more than a means of expressing its hydrogen ion concentration on a convenient logarithmic scale³. The pH as we commonly use it nowadays indicates the *availability* of protons in the solution; that is, the ability of the solution to supply protons to a base such as H₂O. This is the same as the hydrogen ion *concentration* [H⁺] only in rather dilute solutions; at ionic concentrations (whether of H⁺ or other ions) greater than about 0.01 M, electrostatic interactions between the ions cause the relation between the pH (as measured by direct independent means) and [H⁺] to break down. Thus we would *not* expect the pH of a 0.100 M solution of HCl to be exactly 1.00.

On the right side of Figure Table 2 is a pH scale. At the pH value corresponding to a given acid-base pair, the acid and base forms will be present at equal concentrations. For example, if you dissolve some solid sodium sulfate in pure water and then adjust the pH to 2.0, about half of the SO₄²⁻ will be converted into HSO₄⁻. Similarly, a solution of Na₂CO₃ in water will not contain a very large fraction of CO₃²⁻ unless the pH is kept above 10.

Suppose we have a mixture of many different weak acid-base systems, such as exists in most biological fluids or natural waters, including the ocean. The available protons will fall to the lowest free energy levels possible, first filling the lowest-energy sink, then the next, and so on until there are no more proton-vacant bases below the highest proton-filled (acid) level. Some of the highest protonated species will donate protons to H₂O through thermal excitation, giving rise to a concentration of H₃O⁺ that will depend on the concentrations of the various species. The equilibrium pH of the solution is a measure of this H₃O⁺ concentration, but this in turn reflects the relative free energy of protons required to keep the highest protonated species in its acid form; it is in this sense that pH is a direct measure of proton free energy.

In order to predict the actual pH of any given solution, we must of course know something about the nominal concentrations (C_a) of the various acid-base species, since this will strongly affect the distribution of protons. Thus if one proton-vacant level is present at twice the concentration of another, it will cause twice as many acid species from a higher level to become deprotonated. In spite of this limitation, the proton free energy diagram provides a clear picture of the relationships between the various acid and base species in a complex solution.

³The concept of pH was suggested by the Swedish chemist Sørensen in 1909 as a means of compressing the wide range of [H⁺] values encountered in aqueous solutions into a convenient range. The modern definition of pH replaces [H⁺] with {H⁺} in which the curly brackets signify the *effective* concentration of the hydrogen ion, which chemists refer to as the hydrogen ion *activity*:

$$\text{pH} = -\log\{\text{H}^+\}$$

3 Quantitative treatment of acid-base equilibria

3.1 Strong acids and bases

The usual definition of a “strong” acid or base is one that is completely dissociated in aqueous solution. Hydrochloric acid is a common example of a strong acid. When HCl gas is dissolved in water, the resulting solution contains the ions H_3O^+ , OH^- , and Cl^- , but except in very concentrated solutions, the concentration of HCl is negligible; for all practical purposes, molecules of “hydrochloric acid”, HCl, do not exist in dilute aqueous solutions.

In order to specify the concentrations of the three species present in an aqueous solution of HCl, we need three independent relations between them. These relations are obtained by observing that certain conditions must always be true in any solution of HCl. These are:

1. The *dissociation equilibrium of water* must always be satisfied:

$$[\text{H}_3\text{O}^+][\text{OH}^-] = K_w \quad (12)$$

2. For any acid-base system, one can write a *mass balance* equation that relates the concentrations of the various dissociation products of the substance to its “nominal concentration”, which we designate here as C_a . For a solution of HCl, this equation would be

$$[\text{HCl}] + [\text{Cl}^-] = C_a$$

but since HCl is a strong acid, we can neglect the first term and write the trivial mass balance equation

$$[\text{Cl}^-] = C_a \quad (13)$$

3. In any ionic solution, the sum of the positive and negative electric charges must be zero; in other words, all solutions are electrically neutral. This is known as the *electroneutrality principle*.

$$[\text{H}_3\text{O}^+] = [\text{OH}^-] + [\text{Cl}^-] \quad (14)$$

The next step is to combine these three equations into a single expression that relates the hydronium ion concentration to C_a . This is best done by starting with an equation that relates several quantities, such as Eq 14, and substituting the terms that we want to eliminate. Thus we can get rid of the $[\text{Cl}^-]$ term by substituting Eq 13 into Eq 14 :

$$[\text{H}_3\text{O}^+] = [\text{OH}^-] + C_a \quad (15)$$

A $[\text{OH}^-]$ -term can always be eliminated by use of Eq 12 :

$$[\text{H}_3\text{O}^+] = C_a + \frac{K_w}{[\text{H}_3\text{O}^+]} \quad (16)$$

This equation tells us that the hydronium ion concentration will be the same as the nominal concentration of a strong acid as long as the solution is not very dilute. As the acid concentration falls below about $10^{-6} M$, however, the second term predominates; $[\text{H}_3\text{O}^+]$ approaches $\sqrt{K_w}$, or $10^{-7} M$. The hydronium ion concentration can of course never fall below this value; no amount of dilution can make the solution alkaline!

Notice that Eq 16 is a quadratic equation; in regular polynomial form it would be

$$[\text{H}_3\text{O}^+]^2 - C_a[\text{H}_3\text{O}^+] - K_w = 0 \quad (17)$$

Most practical problems involving strong acids are concerned with more concentrated solutions in which the second term of Eq 16 can be dropped, yielding the simple relation $\text{H}_3\text{O}^+ = [\text{A}^-]$.

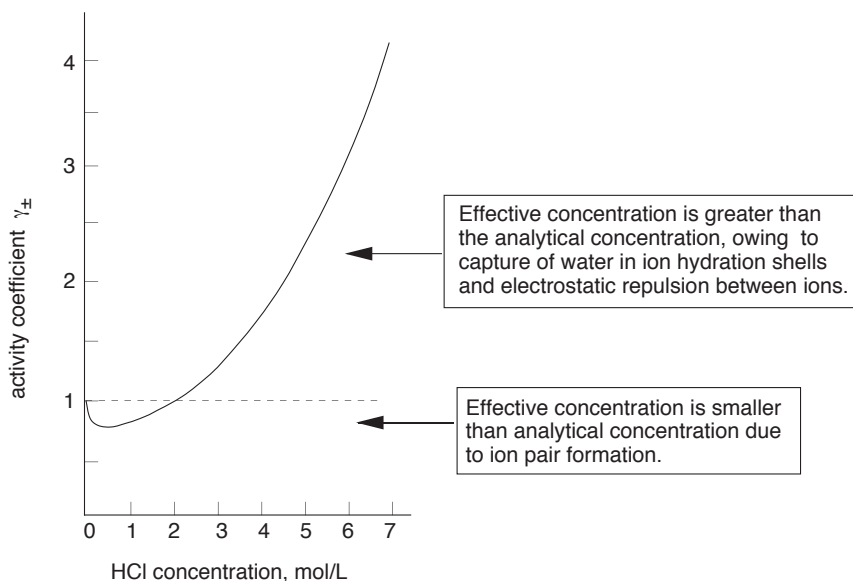


Figure 1: Mean ionic activity coefficient in HCl as a function of concentration

3.2 Concentrated solutions of strong acids

In more concentrated solutions, interactions between ions cause their “effective” concentrations, known as their *activities*, to deviate from their “analytical” concentrations.

Thus in a solution prepared by adding 0.5 mole of the very strong acid HClO_4 to sufficient water to make the volume 1 litre, freezing-point depression measurements indicate that the concentrations of hydronium and perchlorate ions are only about 0.4 *M*. This does not mean that the acid is only 80% dissociated; there is no evidence of HClO_4 molecules in the solution. What has happened is that about 20% of the H_3O^+ and ClO_4^- ions have formed *ion-pair complexes* in which the oppositely-charged species are loosely bound by electrostatic forces. Similarly, in a 0.10 *M* solution of hydrochloric acid, the activity of H^+ is 0.081, or only 81% of its concentration.

Activities are important because only these work properly in equilibrium calculations. Also, pH is defined as the negative logarithm of the hydrogen ion activity, not its concentration. The relation between the concentration of a species and its activity is expressed by the *activity coefficient* γ :

$$a = \gamma C \quad (18)$$

As a solution becomes more dilute, γ approaches unity. At ionic concentrations below about 0.001 *M*, concentrations can generally be used in place of activities with negligible error.

At very high concentrations, activities can depart wildly from concentrations. This is a practical consideration when dealing with strong mineral acids which are available at concentrations of 10 *M* or greater. In a 12 *M* solution of hydrochloric acid, for example, the mean ionic activity coefficient⁴ is 207. This means that under these conditions with $[\text{H}^+] = 12$, the activity $\{\text{H}^+\} = 2500$, corresponding to a pH of about -3.4 , instead of -1.1 as might be predicted if concentrations were being used.

These very high activity coefficients also explain another phenomenon: why you can detect the odor of HCl over a concentrated hydrochloric acid solution even though this acid is supposedly 100% dissociated.

⁴Activities of single ions cannot be determined, so activity coefficients in ionic solutions are always the average, or *mean*, of those for the ionic species present. This quantity is denoted as γ_{\pm} .

With such high effective concentrations, the “dissociated” ions come into such close contact that the term begins to lose its meaning; in effect, dissociation is no longer complete. Although the concentration of $\text{HCl}(aq)$ is never very high, its own activity coefficient can be as great as 2000, which means that its escaping tendency from the solution is extremely high, so that the presence of even a tiny amount is very noticeable.

3.3 Weak monoprotic acids

Most acids are weak; there are hundreds of thousands of them, whereas there are no more than a few dozen strong acids. We can treat weak acid solutions in exactly the same general way as we did for strong acids. The only difference is that we must now include the equilibrium expression for the acid. We will start with the simple case of the pure acid in water, and then go from there to the more general one in which strong cations are present. In this exposition, we will refer to “hydrogen ions” and $[\text{H}^+]$ for brevity, and will assume that the acid HA dissociates into H^+ and its conjugate base A^- .

3.4 Pure acid in water

In addition to the species H^+ , OH^- , and A^- which we had in the strong-acid case, we now have the undissociated acid HA ; four variables, four equations.

1. *Equilibria.* We now have two equilibrium relations:

$$[\text{H}^+][\text{OH}^-] = K_w \quad (19)$$

$$\frac{[\text{H}^+][\text{A}^-]}{[\text{HA}]} = K_a \quad (20)$$

2. *Mass balance.* The mass balance relation expresses the nominal concentration of the acid in terms of its two conjugate forms:

$$C_a = [\text{HA}] + [\text{A}^-] \quad (21)$$

3. *Electroneutrality.*

$$[\text{H}^+] = [\text{A}^-] + [\text{OH}^-] \quad (22)$$

We can use Eq 21 to get an expression for $[\text{HA}]$, and this can be solved for $[\text{A}^-]$; these are substituted into Eq 20 to yield

$$K_a = \frac{[\text{H}^+]([\text{H}^+] - [\text{OH}^-])}{C_a - ([\text{H}^+] - [\text{OH}^-])} \quad (23)$$

This equation is cubic in $[\text{H}^+]$ when $[\text{OH}^-]$ is expressed as $K_w/[\text{H}^+]$; in standard polynomial form it becomes

$$[\text{H}^+]^3 + K_a[\text{H}^+]^2 - (K_w + C_a K_a)[\text{H}^+] - K_w K_a = 0 \quad (24)$$

For most practical applications, we can make approximations that eliminate the need to solve a cubic equation.

1. Unless the acid is extremely weak or the solution is very dilute, the concentration of OH^- can be neglected in comparison to that of $[\text{H}^+]$. If we assume that $[\text{OH}^-] \ll [\text{H}^+]$, then Eq 23 can be simplified to

$$K_a = \frac{[\text{H}^+]^2}{C_a - [\text{H}^+]} \quad (25)$$

which is a quadratic equation:

$$[\text{H}^+]^2 + K_a[\text{H}^+] - K_a C_a = 0 \quad (26)$$

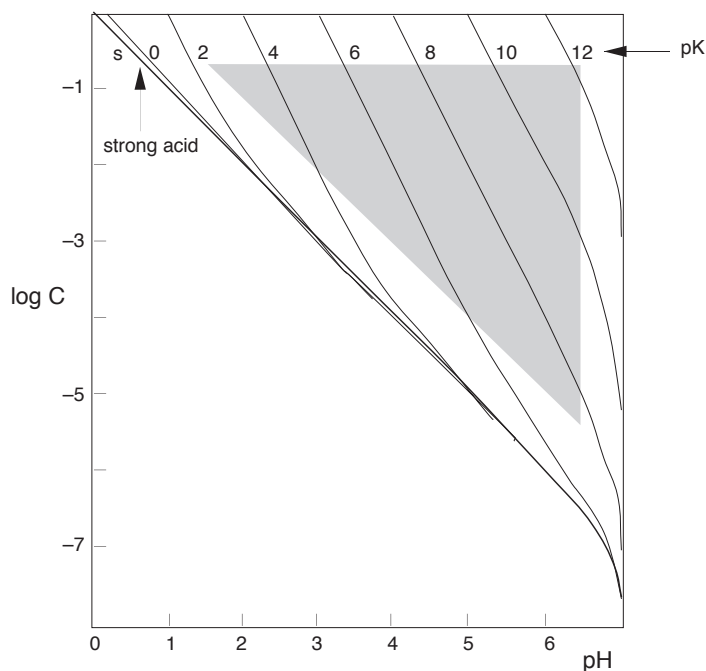


Figure 2: pH as a function of concentration for acids of various strengths

The shaded area indicates the range of acid strengths and concentrations for which the approximation Eq 28 is generally valid.

- If the acid is fairly concentrated (usually more than $10^{-3} M$), a further simplification can frequently be achieved by making the assumption that $[H^+] \ll C_a$. This is justified when most of the acid remains in its protonated form $[HA]$, so that relatively little H^+ is produced. In this event, Eq 25 reduces to

$$K_a = \frac{[H^+]^2}{C_a} \quad (27)$$

or

$$[H^+] \approx (K_a C_a)^{\frac{1}{2}} \quad (28)$$

3.5 Weak bases

The weak bases most commonly encountered are NH_3 , amines such as CH_3NH_2 , and anions A^- of weak acids. Using the latter as an example, we can write the base constant

$$K_b = \frac{[HA][OH^-]}{[A^-]}$$

For a $C_b M$ solution of NaA in water, the charge balance is

$$[Na^+] + [H^+] = [A^-] + [OH^-]$$

Replacing the $[\text{Na}^+]$ term by C_b and combining with K_w and the mass balance $C_b = [\text{HA}] + [\text{A}^-]$, a relation is obtained that is analogous to that of Eq 23 for weak acids:

$$K_b = \frac{[\text{OH}^-]([\text{OH}^-] - [\text{H}^+])}{C_b - ([\text{OH}^-] - [\text{H}^+])} \quad (29)$$

The approximations

$$K_b = \frac{[\text{OH}^-]^2}{C_b - [\text{OH}^-]} \quad (30)$$

and

$$[\text{OH}^-] \approx (K_b C_b)^{\frac{1}{2}} \quad (31)$$

can be derived in a similar manner.

3.6 Carrying out acid-base calculations

Acid-base calculations fall into two categories: those that are done as part of a course in which your aim is to obtain a good grade, and those done for real-world applications in which the goal is to obtain a useful answer with a minimum of effort. For the latter, there is almost never any need to do anything other than a graphical estimate as described in Section 6. Unless values of K_w and K_a 's that pertain to the actual conditions of temperature and ionic strength are available, carrying out a calculation to a precision of more than two significant figures while using $K_w = 10^{-14}$ and the K_w values commonly seen in textbooks (which apply only to pure water, which is rarely the subject of our interest) is a waste of time.

Even so, the algebraic approach that is taught in most General Chemistry courses is important in two respects: the quantitative treatment required to derive the equations provides a clearer view of the equilibria involved and serves as a model for the treatment of generalized equilibria, and the approximations commonly applied to simplify the relations serve as good models of the kinds of judgements that must be made very commonly in applied mathematics. It is important to bear in mind, however, that the results are only as valid as the data, and the latter are almost never good enough to yield correct answers for any but extremely dilute solutions.

Selecting the approximation.

Eq 25 serves as the starting point for most practical calculations on solutions of weak monoprotic acids. *Don't memorize this equation*; you should be able to *derive* it (as well as the analogous equation for weak bases) from the definition of the equilibrium constant. If you know that the system parameters fall into the shaded region of Fig. 2, then the approximation Eq 28 is usually satisfactory. However, if the acid is very dilute or very weak, the exact calculation Eq 23 will be required.

As an example, consider a $10^{-6} M$ solution of hypochlorous acid, $\text{p}K_a = 8.0$. (HOCl is a decomposition product of chlorine in water and is largely responsible for its bactericidal properties.) In this case, the approximation Eq 23 leads to a quadratic equation whose non-negative root is $9.50\text{E}-8$, clearly an absurd value for a solution of any acid, no matter how dilute or weak. Substitution into Eq 24 and plotting reveals a root at $[\text{H}^+] = 1.30\text{E}-7$.

For acids having $\text{p}K_a$ s of 10 or greater, even solutions as concentrated as $.001 M$ will yield incorrect pH values unless the exact calculation is used. The same is true of comparably weak *bases*, which are most commonly encountered in the form of anions which are conjugate to the stronger of the weak acids. Thus for a $0.0010 M$ solution of Na_2SO_4 (and using $K_a = .012$ for HSO_4^-), Eq 30 predicts a pH of 6.46 (an *acidic* solution!), while Eq 29 yields the more reasonable value of 7.02.

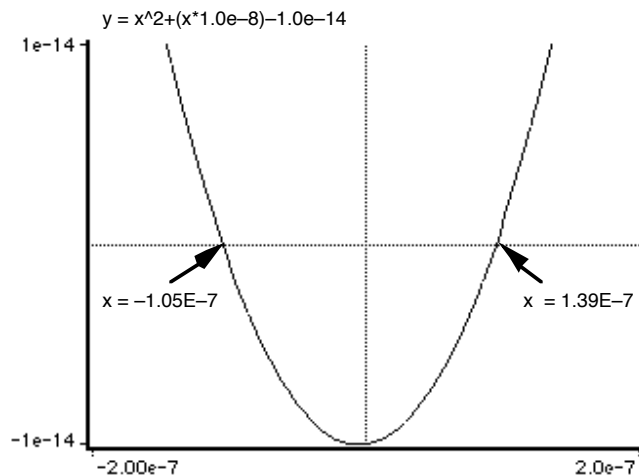


Figure 3: Plot of Eq 26 for $10^{-6} M$ HOCl

This was done with NumberCrunch, a widely-available free utility for the Macintosh computer. Several tries were required to set the limits of the axes so that both roots are revealed. The physically meaningful root is the one on the right, where the plot crosses the zero line at $x = +1.39E-7$.

Solving quadratic and higher-order polynomials

The roots of quadratic equations such as Eq 25 can of course be found by casting the equation into standard polynomial form and using the quadratic formula⁵. Deciding which of the roots corresponds to $[H^+]$ is almost never a problem, since you know it can't be negative and for an acid solution must be within the range 10^{-7} to C_a .

If Eq 28 gives a reasonable value of $[H^+]$, this can be substituted into the denominator of Eq 25 which then yields a revised version of Eq 28 to solve. Two or three iterations usually yield an unchanging value of $[H^+]$. This procedure is easily carried out on a hand-held calculator. However, it is not foolproof; successive answers do not always converge, especially if the initial guess is too far off.

For dealing with cubic and higher-order equations (and even for quadratics in some cases), the most practical methods are *trial-and-error* and *plotting*. The first of these involves making a series of guesses which are modified according to the value they give when substituted into the equation. If you have a plotting calculator or a computer equipped with a suitable utility, the easiest method of all is to simply plot the function within a suitable range of x -values Fig. 3.

Computer utilities such as MathCad and Mathematica are especially convenient for solving equilibrium problems and for comparing the results obtained by approximate and exact solutions.

⁵If you do this on a computer or programmable calculator, it is better to avoid calculating $x = (-b) \pm \sqrt{(b^2 - 4ac)}/2a$ directly. The reason is that if $b^2 \gg |4ac|$, one of the roots will involve the subtraction of two terms of similar value; this can lead to considerable error when carried out on hardware having finite precision. The recommended way is to calculate the quantity

$$Q = -(b + \text{sgn}(b) * \text{sqrt}(b^2 - 4ac))/2$$

from which the roots are $x_1 = Q/a$ and $x_2 = c/Q$. See any textbook on numerical computing methods for more information and other methods.

3.7 Calculations on mixtures of acids

Many practical problems relating to environmental and physiological chemistry involve solutions containing more than one acid. Several methods have been published for calculating the hydrogen ion concentration in solutions containing an arbitrary number of acids and bases⁶. These generally involve iterative calculations carried out by a computer.

In this section, we will restrict ourselves to a much simpler case of two acids, with a view toward showing the general method of approaching such problems by starting with charge- and mass-balance equations and making simplifying assumptions when justified.

In general, the hydrogen ions produced by the stronger acid will tend to suppress dissociation of the weaker one, and both will tend to suppress the dissociation of water, thus reducing the sources of H^+ that must be dealt with.

Consider a mixture of two weak acids HX and HY; their respective nominal concentrations and equilibrium constants are denoted by C_x , C_y , K_x and K_y . Starting with the charge balance expression

$$[H^+] = [X^-] + [Y^-] + [OH^-]$$

We use the equilibrium constants to replace the conjugate base concentrations with expressions of the form

$$[X^-] = K_x \frac{[HX]}{[H^+]}$$

to yield

$$[H^+] = \frac{[HX]}{K_x} + \frac{[HY]}{K_y} + K_w$$

Multiplying both sides by $[H^+]$ allows us to eliminate $[OH^-]$:

$$[H^+]^2 = K_x[HX] + K_y[HY]$$

If neither acid is very strong nor very dilute, we can replace equilibrium concentrations with nominal concentrations:

$$[H^+] \approx \sqrt{C_x K_x + C_y K_y + K_w}$$

For a solution containing 0.10 M acetic acid ($K_a = 1.75E-5$) and 0.20 M phenol ($K_a = 1.00E-10$) this yields a reasonable answer. But if 0.001 M chloroacetic acid ($K_a = .0014$) is used in place of phenol, the above expression becomes

$$[H^+] = \sqrt{1.40E-6 + 1.75E-8 + 10^{-14}} = 0.00118$$

which exceeds the concentration of the stronger acid; because the acetic acid makes a negligible contribution to $[H^+]$ here, the simple approximation given above is clearly invalid.

We now use the mass balance expression for the stronger acid

$$[HX] + [X^-] = C_x$$

to solve for $[X^-]$ which is combined with the expression for K_x to yield

$$[X^-] = C_x - \frac{[H^+][X^-]}{K_x}$$

⁶See, for example, *J. Chem. Education* 67(6) 501-503 (1990) and 67(12) 1036-1037 (1990).

Solving this for $[X^-]$ gives

$$[X^-] = \frac{C_x K_x}{K_x + [H^+]}$$

The approximation for the weaker acetic acid (HY) is still valid, so we retain it in the substituted electronegativity expression:

$$[H^+] = \frac{C_x K_x}{K_x + [H^+]} + \frac{C_y K_y}{[H^+]}$$

which is a cubic equation that can be solved by approximation.

3.8 Mixture of an acid and its conjugate base: buffers

If we add some sodium hydroxide to a solution of an acid, then an equivalent amount of the acid will be converted into its base form, resulting in a “partly neutralized” solution in which both the acid and its conjugate base are present in significant amounts. Solutions of this kind are far more common than those of a pure acid or a pure base, and it is very important that you have a thorough understanding of them.

For example, suppose that we have a solution containing 0.010 mole of acetic acid. To this we add 0.002 mole of sodium hydroxide, which consumes this same amount of acid and produces 0.002 mole of acetate ion. If the volume of the final solution is 100 ml, then the nominal acid and base concentrations are

$$C_a = \frac{.010 - .002 \text{ mol}}{.100 \text{ L}} = .080 \text{ M} \quad \text{and} \quad C_b = \frac{.002}{.100} = .020 \text{ M}$$

Note that this solution would be indistinguishable from one prepared by combining $C_a = .080$ mole of acetic acid with $C_b = 0.020$ mole of sodium acetate and adjusting the volume to 100 ml.

The equilibrium expressions for such a solution are just the ones for the pure-acid case: Eq 19 and Eq 20. The mass balance for the acid now contains the additional term C_b ; note that in the preceding example, this sum will have the value 0.100 M:

$$[HA] + [A^-] = C_a + C_b \tag{32}$$

There is a new mass balance equation for the cation, but it is trivial:

$$[Na^+] = C_b \tag{33}$$

The charge balance equation must also include $[Na^+]$:

$$[Na^+] + [H^+] = [OH^-] + [A^-] \tag{34}$$

Substituting Eq 33 into the above expression yields an equation for $[A^-]$:

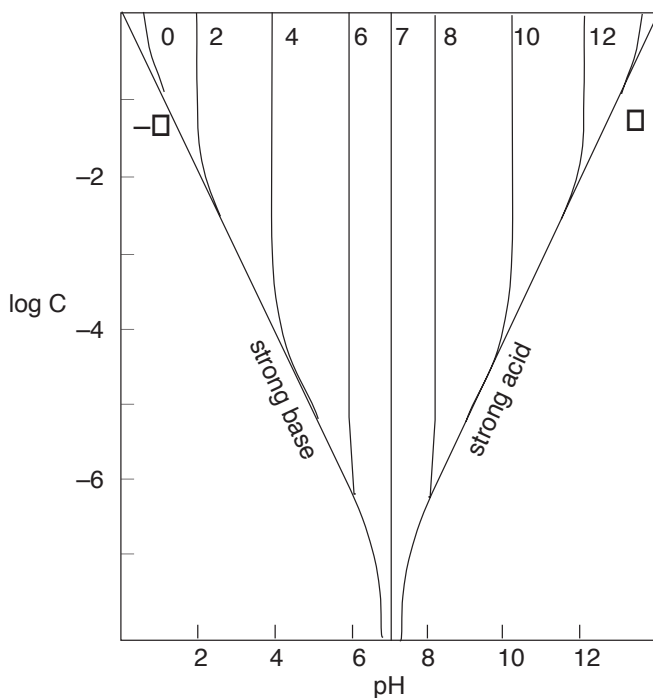
$$[A^-] = C_b + [H^+] - [OH^-] \tag{35}$$

Inserting this into Eq 32 and solving for $[HA]$,

$$[HA] = C_a - ([H^+] - [OH^-]) \tag{36}$$

Finally we substitute these last two expressions into the equilibrium constant Eq 20 :

$$[H^+] = K_a \frac{C_a - [H^+] + [OH^-]}{C_b + [H^+] - [OH^-]} \tag{37}$$



How dilute can a solution with $[A^-] = C_b$ be and still exhibit useful buffering action? As you can see from these plots, the answer depends very much on the pK_a of the particular acid-base system. (The pK_a values are indicated near the top of the figure.) The lines marked strong base and strong acid correspond to the limiting cases of $pK_a = \pm\infty$. The vertical part of each plot corresponds to the concentration range in which the approximation Eq 40 is valid.

Figure 4: Buffering action as a function of buffer concentration

which is cubic in $[H^+]$ when $[OH^-]$ is replaced by $K_w/[H^+]$:

$$[H^+]^3 + (C_b + 1)[H^+]^2 - (K_w + C_a K_a)[H^+] - K_w = 0 \quad (38)$$

In almost all practical cases it is possible to make simplifying assumptions. Thus if the solution is known to be acidic or alkaline, then the $[OH^-]$ or $[H^+]$ terms in Eq 37 can be neglected. In acidic solutions, for example, Eq 37 becomes

$$[H^+] \approx K_a \frac{C_a - [H^+]}{C_b + [H^+]} \quad (39)$$

If the concentrations C_a and C_b are sufficiently large, it may be possible to neglect the $[H^+]$ terms entirely, leading to the commonly-seen expression

$$[H^+] \approx K_a \frac{C_a}{C_b} \quad (40)$$

This relation is an extremely important one which you must know; it is sometimes referred to as the *Henderson-Hasselbalch equation*⁷.

Pitfalls of the Henderson-Hasselbalch equation The above equation will be found in virtually all textbooks and is widely used in practical calculations. What most books do not tell you is that Eq 40 is no more than an “approximation of an approximation” which can give incorrect and misleading results

⁷The first studies on buffer action were published by Lawrence Henderson (USA, 1908 and by Karl Hasselbalch (Denmark, 1916). See JACS 1908: 30 pg 959.

when applied to situations in which the simplifying assumptions are not valid. Unless you know what you are doing, your starting point should normally be Eq 39 for solutions that are expected to be acidic, or an analogous relation which can easily be derived for alkaline solutions.

Problem Example 2

Calculate the pH of a solution prepared by adding 0.10 mole of NaOH to a solution containing 0.20 mole/litre of iodic acid, HIO_3 , $K_a = 0.2$.

Solution: Eq 40 predicts a hydrogen ion concentration of

$$[\text{H}^+] = K_a \frac{C_a}{C_b} = 0.2 \frac{0.10}{0.10} = 0.2$$

or a pH of 0.70, but this is wrong. The problem is that HIO_3 is a rather “strong” weak acid, so the value of $[\text{H}^+]$ will be comparable in magnitude to those of C_a and C_b in Eq 39. Placing this equation in standard polynomial form yields

$$[\text{H}^+]^2 + (C_a + K_a)[\text{H}^+] - K_a C_a = 0 \quad (41)$$

Solving this for $[\text{H}^+]$ using the values in the problem gives a hydrogen ion concentration of 0.056 M and a pH of 1.2; notice that these results are quite different from what Eq 40 would predict.

Be careful about confusing the two relations

$$[\text{H}^+] = K_a \frac{[\text{HA}]}{[\text{A}^-]} \quad \text{and} \quad [\text{H}^+] \approx K_a \frac{C_a}{C_b}$$

The one on the left is simply a re-writing of the equilibrium constant expression, and is therefore *always true*. Of course, without knowing the actual equilibrium values of $[\text{HA}]$ and $[\text{A}^-]$, this relation is of little direct use in pH calculations. The equation on the right is *never true*, but will yield good results if the acid is sufficiently weak in relation to its concentration to keep the $[\text{H}^+]$ from being too high. Otherwise, the high $[\text{H}^+]$ will convert a significant fraction of the A^- into the acid form HA, so that the ratio $[\text{HA}]/[\text{A}^-]$ will differ from C_a/C_b in the above two equations. Consumption of H^+ by the base will also raise the pH above the value predicted by Eq 40 as we saw in the preceding problem example.

Finally, notice that Eq 40 can give absurd values of hydrogen ion concentration if one of C_a or C_b is extremely small.

Buffer solutions The important feature of Eq 37 or of its approximation Eq 40 is that they give the pH of the solution in terms of the *nominal concentrations* of the conjugate acid and base; in most practical cases these values are known or can easily be calculated. Furthermore, if C_a and C_b are quite large, any reactions that tend to produce or withdraw H_3O^+ or OH^- ions will have only a small effect on their *ratio*, and thus on the pH of the solution. Such a solution is said to be *buffered*.

One of the most important conjugate pairs involved in buffering is $\text{CO}_2/\text{HCO}_3^-$. These two species are largely responsible for maintaining the pH of the ocean and also of blood at a constant value. Many of the reactions that take place in organisms involve the uptake or release of hydrogen ions, and the media in which they occur must be buffered in order to keep the pH within the rather narrow bounds that the organism can tolerate.

3.9 Ionization fractions

It is important to be able to express the relative amounts of a conjugate acid-base system present in the protonated and deprotonated forms. The simple ratio $[\text{HA}]/[\text{A}^-]$ (or its inverse) is often used, but this

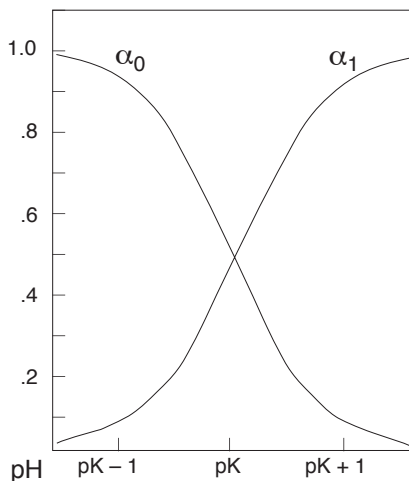


Figure 5: Ionization fraction diagram for a monoprotic acid.

suffers from the disadvantage of being indeterminate when the concentration in the denominator is zero. For many purposes it is more convenient to use the *ionization fractions*

$$\alpha_0 \equiv \alpha_{\text{HA}} = \frac{[\text{HA}]}{[\text{HA}] + [\text{A}^-]}; \quad \alpha_1 \equiv \alpha_{\text{A}^-} = \frac{[\text{A}^-]}{[\text{HA}] + [\text{A}^-]} \quad (42)$$

The fraction α_1 is also known as the *degree of dissociation* of the acid. By making appropriate substitutions using the relation

$$[\text{H}^+] = K_a \frac{[\text{HA}]}{[\text{A}^-]} \quad (43)$$

. we can express the ionization fractions as a function of the pH:

$$\alpha_0 \equiv \alpha_{\text{HA}} = \frac{[\text{H}^+]}{K_a + [\text{H}^+]}; \quad \alpha_1 \equiv \alpha_{\text{A}^-} = \frac{K_a}{K_a + [\text{H}^+]} \quad (44)$$

In the plot of these two functions shown in Fig. 5, notice the crossing point where $[\text{HA}] = [\text{A}^-]$ when $[\text{H}^+] = K_a$. This corresponds to unit value of the quotient in Eq 43.

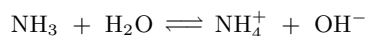
3.10 Calculations involving mixtures of acids and bases

Solutions containing significant concentrations of an acid and its conjugate base, or of a salt of a weak acid and a weak base, are encountered very frequently in many practical applications of chemistry and biochemistry. Exact calculations on such mixtures that take into account charge balance, all equilibria and all mass balances tend to be rather complicated and are almost never necessary. In most cases you can simplify the problem by identifying the major equilibrium species and neglecting minor ones. Doing so requires some chemical intuition which is best developed by carefully following examples of the kind presented in this section.

Problem Example 3

Calculate the pH of a solution containing 0.0100 mole of ammonium chloride and 0.0200 mole of ammonia in 100 ml of solution.

Solution: The equilibrium here is



For NH_4^+ , $K_a = 10^{-9.3}$ and thus $K_b = 10^{-(14-(-9.3))} = 10^{-4.7}$:

$$\frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_3]} = 10^{-4.7}$$

The nominal concentrations of the acid and conjugate base are respectively $C_a = 0.100\text{ M}$ and $C_b = 0.200\text{ M}$. The mass balance expressions are

$$[\text{NH}_4^+] + [\text{NH}_3] = C_a + C_b = 0.30 \quad \text{and} \quad [\text{Cl}^-] = C_a$$

and the charge balance is given by

$$[\text{Cl}^-] + [\text{OH}^-] = [\text{H}^+] + [\text{NH}_4^+] \approx [\text{NH}_4^+]$$

in which the approximation shown above is justified by our knowledge that the solution will be weakly alkaline. The equilibrium concentrations of the conjugate species are then

$$[\text{NH}_4^+] = 0.100 + [\text{OH}^-] \quad \text{and} \quad [\text{NH}_3] = 0.200 - [\text{OH}^-]$$

Because C_a and C_b are large compared to $[\text{OH}^-]$ (the solution is not expected to be strongly alkaline), the $[\text{OH}^-]$ terms in the above expressions can be dropped and the equilibrium expression becomes

$$\frac{(0.100)[\text{OH}^-]}{0.200} = 2.0\text{E-}5$$

from which we find $[\text{OH}^-] = 4.0\text{E-}5$, $\text{pOH} = 4.4$ and $\text{pH} = 9.6$.

Problem Example 4

What will be the change in the pH if 10 ml of 0.100 M HCl is added to 100 ml of the above solution?

Solution: We can continue using the approximations for the concentrations of the conjugate species that we developed in the preceding example. Addition of the strong acid (1.0 mmol) converts this amount of NH_3 into NH_4^+ and also increases the total volume of the solution. The values of C_b and C_a are now

$$C_b = \frac{(20\text{ mmol} - 1\text{ mmol})}{110\text{ ml}} = 0.173\text{ M} \approx [\text{NH}_3]$$

and

$$C_a = \frac{(10\text{ mmol} + 1\text{ mmol})}{110\text{ ml}} = 0.100\text{ M} \approx [\text{NH}_4^+]$$

Substituting these into the equilibrium constant expression yields

$$[\text{OH}^-] = \frac{[\text{NH}_3]}{[\text{NH}_4^+]} K_b = 1.73 \times 2.0 \times 10^{-5} = 3.46\text{E-}5$$

The new pOH is 4.5, so addition of the acid has changed the pH to 9.5, a decrease of only 0.1 pH unit.

Problem Example 5

Calculate the pH of a 0.01 M solution of ammonium chloride in pure water.

Solution: From the charge balance expression

$$[\text{NH}_4^+] + [\text{H}^+] = [\text{OH}^-] + [\text{Cl}^-]$$

we can drop the $[\text{OH}^-]$ term since we know that the solution will be weakly acidic. Using this approximation and the mass balance on the conjugate species, we have

$$[\text{NH}_4^+] = 0.01 - [\text{H}^+] \quad \text{and} \quad [\text{NH}_3] = [\text{H}^+]$$

Substituting these into the K_a expression for $[\text{NH}_4^+]$, we obtain (compare with Eq 37)

$$[\text{H}^+] = \frac{[\text{NH}_4^+]}{[\text{NH}_3]} K_a = \frac{0.01 - [\text{H}^+]}{[\text{H}^+]} \times 5.0 \times 10^{-10}$$

Can we drop the $[\text{H}^+]$ term in the numerator? Doing so yields

$$[\text{H}^+] = \sqrt{0.01 \times 5 \times 10^{-10}} = 2.2\text{E-}6$$

Because this value is small compared to 0.01, this approximation is acceptable and the pH is 5.6.

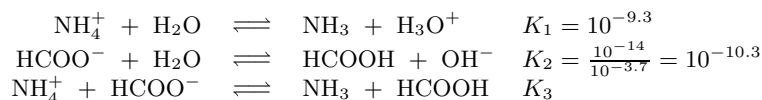
Comment: Because the concentrations were not extremely small, this turns out to be a typical buffer solution problem in which Eq 37 is simplified to Eq 40. However, instead of blindly substituting into the latter equation, we followed the much safer route of examining the effects of the various approximations as we made them. Only through this approach can you have any confidence that your result is a valid one.

A salt of a weak acid gives an alkaline solution, while that of a weak base yields an acidic solution. What happens if we dissolve a salt of a weak acid *and* a weak base in water? The following example is typical of a variety of problems that arise in applications as diverse as physiological chemistry and geochemistry:

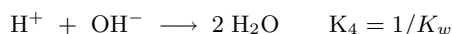
Problem Example 6

Estimate the pH of a 0.0100 M solution of ammonium formate in water. Formic acid, HCOOH, is the simplest organic acid and has $K_a = 10^{-3.7} = 1.76\text{E-}4$. For NH_4^+ , $K_a = 10^{-9.3}$.

Solution: Three equilibria are possible here; the reaction of the ammonium and formate ions with water, and their reaction with each other:



Inspection reveals that the last equation is the sum of the first two, plus the reaction



The value of K_3 is therefore

$$K_3 = \frac{10^{-9.3} \times 10^{-10.3}}{K_w} = 10^{-5.6}$$

A rigorous treatment of this system would require that we solve these equations simultaneously with the charge balance and the two mass balance equations. However, because K_3 is several orders of magnitude greater than K_1 or K_2 , we can greatly simplify things by neglecting the other equilibria and considering only the reaction between the ammonium and formate ions. Notice that the products of this reaction will tend to suppress the extent of the first two equilibria, reducing their importance even more than the relative values of the equilibrium constants would indicate.

From the stoichiometry of ammonium formate we can write

$$[\text{NH}_4^+] = [\text{HCOO}^-] \quad \text{and} \quad [\text{NH}_3] = [\text{HCOOH}]$$

Then

$$K_3 = \frac{[\text{NH}_3][\text{HCOOH}]}{[\text{NH}_4^+][\text{HCOO}^-]} = \frac{[\text{HCOOH}]^2}{[\text{HCOO}^-]^2} = \frac{K_w}{K_a K_b}$$

in which K_b is the base constant of ammonia, $K_w/10^{-9.3}$.

From the formic acid dissociation equilibrium we have

$$\frac{[\text{HCOOH}]}{[\text{HCOO}^-]} = \frac{[\text{H}^+]}{K_a}$$

Rewriting the expression for K_3 ,

$$K_3 = \frac{[\text{HCOOH}]^2}{[\text{HCOO}^-]^2} = \frac{[\text{H}^+]^2}{K_a^2} = \frac{K_w}{K_a K_b}$$

Which yields

$$[\text{H}^+] = \sqrt{\frac{K_w K_a}{K_b}} = 10^{-6.5}$$

Comment: This problem involved two subproblems: finding a value for K_3 , and then finding a relation that joins this quantity to the hydrogen ion concentration. Since the dissociation of HCOOH is the most important one involving H^+ , this brings in K_a .

What is interesting about this last example is that the pH of the solution is apparently *independent of the concentration* of the salt. If $K_a = K_b$ then this is *always* true and the solution will be neutral (neglecting activity effects in solutions of high ionic strength). Otherwise, it is only an approximation that remains valid as long as the salt concentration is substantially larger than the magnitude of either equilibrium constant. Clearly, the pH of any solution must approach that of pure water as the solution becomes more dilute (Fig. 2).

3.11 Zwitterions

Amino acids, the building blocks of proteins, contain amino groups $-\text{NH}_2$ that can accept protons, and carboxyl groups $-\text{COOH}$ that can lose protons. Under certain conditions both of these events can occur, so that the resulting molecule becomes a “double ion” which goes by its German name *Zwitterion*. The simplest of the twenty amino acids that occur in proteins is glycine, $\text{H}_2\text{N}-\text{CH}_2-\text{COOH}$ whose solutions are distributed between the acidic-, zwitterion-, and basic- species



which we denote by the abbreviations H_2Gly^+ (glycinium), HGly , and Gly^- (glycinate) respectively. The two acidity constants are

$$K_1 = 10^{-2.35} = \frac{[\text{H}^+][\text{HGly}]}{[\text{H}_2\text{Gly}^+]}, \quad K_2 = 10^{-9.78} = \frac{[\text{H}^+][\text{Gly}^-]}{[\text{HGly}]}$$

If glycine is dissolved in water, charge balance requires that

$$[\text{H}_2\text{Gly}^+] + [\text{H}^+] = [\text{Gly}^-] + [\text{OH}^-]$$

Substituting the equilibrium constant expressions (including that for the autoprotolysis of water) into the above relation yields

$$\frac{[\text{H}^+][\text{HGly}]}{K_1} + [\text{H}^+] = \frac{K_2[\text{HGly}]}{[\text{H}^+]} + \frac{K_w}{[\text{H}^+]}$$

whose solution is

$$[\text{H}^+] = \sqrt{\frac{K_2[\text{HGly}] + K_w}{[\text{HGly}]/K_1 + 1}}$$

Problem Example 7

Calculate the pH and the concentrations of the various species in a 0.100 M solution of glycine.

Solution: Substitution into the equation for $[H^+]$ developed above yields

$$[H^+] = \sqrt{\frac{10^{-9.78}(0.10) + 10^{-14}}{0.1/10^{-2.35} + 1}} = 10^{-6.08}$$

The concentrations of the acid and base forms can be found in the usual way:

$$[H_2Gly^+] = \frac{[H^+](0.10)}{10^{-2.35}} = 10^{-4.73}$$

$$[Gly^-] = \frac{10^{-9.78}(0.10)}{[H^+]} = 10^{-4.70}$$

From these values it is apparent that the zwitterion is the only significant glycine species present in the solution.

3.12 Diprotic acids

A diprotic acid such as H_2SO_4 can donate its protons in two steps, yielding first a monoprotonated species HSO_4^- and then the completely deprotonated form SO_4^{2-} . Since there are five unknowns (the concentrations of the acid, of the two conjugate bases and of H_3O^+ and OH^-), we need five equations to define the relations between these quantities. These are

- *Equilibria:*

$$[H^+][OH^-] = K_w \tag{45}$$

$$\frac{[H^+][HA^-]}{[H_2A]} = K_{a1} \tag{46}$$

$$\frac{[H^+][A^{2-}]}{[HA^-]} = K_{a2} \tag{47}$$

- *Material balance:* When we start with C_a moles per litre of the acid H_2A , the concentrations of those species containing the species A must add up to the amount initially present.

$$C_a = [H_2A] + [HA^-] + [A^{2-}] \tag{48}$$

The full equation (which we show only to impress you) is

$$K_2 = \frac{[H^+] \left([H^+] - [OH^-] - \frac{2K_2([H^+] - [OH^-])}{[H^+] + 2K_2} \right)}{C_a - \left([H^+] - [OH^-] - \frac{2K_2([H^+] - [OH^-])}{[H^+] + 2K_2} \right)} \tag{49}$$

which can be expressed as the quartic polynomial

$$[H^+]^4 + [H^+]^3([A^-] + K_1) = [H^+]^2(K_1K_2 - K_w) - [H^+](K_1([A^-]K_2 + K_w)) - K_1K_2K_w = 0 \tag{50}$$

There are very few, if any practical situations in which this exact relation needs to be used. If the solution is at all acidic then $[OH^-]$ is negligible compared to $[H^+]$ and the first equation reduces to

$$K_1 = \frac{[\text{H}^+] \left([\text{H}^+] - \frac{2K_2[\text{H}^+]}{[\text{H}^+] + 2K_2} \right)}{C_a - \left([\text{H}^+] - \frac{K_2[\text{H}^+]}{[\text{H}^+] + 2K_2} \right)} \quad (51)$$

For many polyprotic acids the second acid constant K_2 is small. If the solution is sufficiently acidic so that $K_2 \ll [\text{H}^+]$, then the preceding expression can be greatly simplified:

$$K_1 = \frac{[\text{H}^+]^2}{C_a - [\text{H}^+]} \quad (52)$$

This is the usual starting point for most practical calculations. Finally, if the solution is sufficiently concentrated (and K_a is sufficiently small) so that $[\text{H}^+] \ll C_a$, we can obtain

$$[\text{H}^+] = (K_a C_a)^{\frac{1}{2}} \quad (53)$$

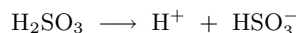
Notice that the K_2 term does not appear in these last two equations. This is tantamount to assuming that the first ionization step is the only significant source of hydrogen ions. This is true of many weak polyprotic acids, but there are some (mostly organic ones) in which the K_a s have similar orders of magnitude and for which these approximations may not be valid.

You are *not* expected to memorize the above relations or their derivations. You should, however, understand the assumptions of charge- and material- balance on which they are based, and you should be able to follow the algebra involved in simplifying the exact equations to the more useful approximate forms.

Problem Example 8

Estimate the concentrations of conjugate species present in a 0.010 M solution of sulfurous acid in pure water. $K_{a1} = 0.017$, $K_{a2} = 10^{-7.19}$.

Solution. Because the first K_a is much larger than the second, we may, as a first approximation, consider that the equilibrium concentrations of H_2SO_3 and of HSO_3^- are controlled solely by the equilibrium



Letting $[\text{H}^+] \approx [\text{HSO}_3^-] = x$, we have

$$\frac{x^2}{0.010 - x} = 0.017$$

which must be solved quadratically:

$$x^2 + 0.017x - 0.00017 = 0$$

The positive root is $x = 0.00706$, so this is the approximate concentration of H^+ and of HSO_3^- .

To estimate $[\text{SO}_3^{2-}]$, note that

$$\frac{[\text{H}^+][\text{HSO}_3^-]}{[\text{H}_2\text{SO}_3]} \times \frac{[\text{H}^+][\text{SO}_3^{2-}]}{[\text{HSO}_3^-]} = \frac{[\text{H}^+]^2[\text{SO}_3^{2-}]}{[\text{H}_2\text{SO}_3]} = K_{a1}K_{a2}$$

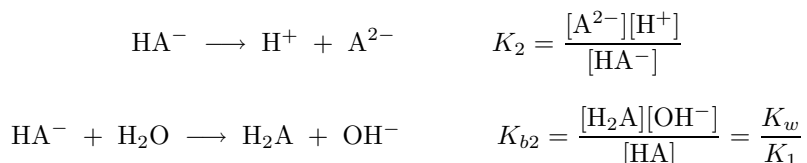
so

$$[\text{SO}_3^{2-}] = K_{a1}K_{a2} \frac{[\text{H}^+]^2}{[\text{HSO}_3^-]} = 8.5 \times 10^{-8} \times \frac{(.00706)^2}{(.00706)} = 6.0 \times 10^{-10} M$$

Note the very small value of $[\text{SO}_3^{2-}]$, which clearly justifies our approximation that $[\text{H}^+] = [\text{HSO}_3^-] = 0.00706$.

Solution of an ampholyte salt

Bisulfate and bicarbonate salts are among the more common examples of this class of substances. A solution of a salt NaHA can act both as an acid and a base:



The exact treatment of this system is best written in terms of the *proton balance* expression for HA^- which expresses the simple fact that for every H^+ that appears in solution, a species more basic than HA^- or H_2O is formed:

$$[\text{H}^+] = [\text{OH}^-] + [\text{A}^{2-}] - [\text{H}_2\text{A}] \quad (54)$$

The terms on the right can be replaced by expressions containing equilibrium constants:

$$[\text{H}^+] + \frac{K_w}{[\text{H}^+]} + \frac{K_2[\text{HA}^-]}{[\text{H}^+]} - \frac{[\text{H}^+][\text{HA}^-]}{K_1}$$

We then multiply both sides by $[\text{H}^+]$ and rearrange:

$$\begin{aligned} [\text{H}^+]^2 \left(1 + \frac{[\text{HA}^-]}{K_1} \right) &= K_2[\text{HA}^-] + K_w \\ [\text{H}^+] &= \frac{\sqrt{K_2[\text{HA}^-] + K_w}}{1 + ([\text{HA}^-]/K_1)} \end{aligned}$$

An exact solution would require that we eliminate $[\text{HA}^-]$ and would lead to some complicated algebra. In most practical cases we can assume that $[\text{HA}^-] = C_t$, which gives

$$[\text{H}^+] = \frac{\sqrt{K_2 C_t + K_w}}{1 + (C_t/K_1)} \quad (55)$$

In most practical cases K_w is sufficiently small in relation to $K_2 C_t$ that it can be dropped, leading to the very simple relation

$$[\text{H}^+] = \sqrt{K_1 K_2} \quad (56)$$

4 Acid-base titration

The objective of an acid-base titration is to determine C_a , the nominal concentration of acid in the solution. The operation is carried out by measuring the volume of the solution of strong base required to complete the reaction



in which n is the number of replaceable hydrogens in the acid. The point at which this reaction is just complete is known as the *equivalence point*. This is to be distinguished from the *end point*, which is the value we observe experimentally.

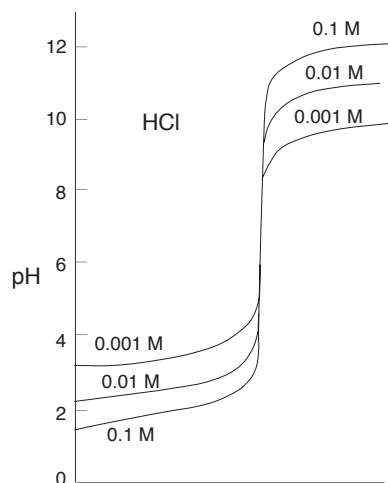


Figure 6: Titration curves for HCl at different concentrations

4.1 Titration curves

A plot showing the pH of the solution as a function of the volume of base added is known as a *titration curve*. These plots can be constructed from Eq 37 (but *not* from Eq 40!) by calculating the values of $[A^-]$ and C_b for each volume increment of base. A nearly identical (and more easily constructed) curve can be obtained from Eq 43 by plotting the pH as a function of the *equivalent fraction* f , which is simply the number of moles of base added per mole of acid present in the solution.

At the equivalence point of the titration of a solution initially containing $[A^-]$ moles of a monoprotic acid HA, the solution will be identical to one containing the same number of moles of the conjugate base A^- . Such a solution will neutral if the acid is a strong one; otherwise it will be alkaline. In the latter case the pH can be calculated from C_b and K_b in a manner exactly analogous to that used for calculating the pH of a solution of a weak acid in water.

As illustrated in Fig. 6, amount of base that must be added to reach the equivalence point is independent of the strength of the acid and of its concentration in the solution. The whole utility of titration as a means of quantitative analysis rests on this independence; we are in all cases measuring only the total number of moles of “acidic” hydrogens in the sample undergoing titration.

Although the strength of an acid has no effect on the location of the equivalence point, it does affect the shape of the titration curve and can be estimated on a plot of the curve.

The equivalence point represents the point at which the reaction



is stoichiometrically complete. Recalling that the pH is controlled by the ratio of conjugate species concentrations

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

it will be apparent that when the titration is *half* complete (that is, when $[HA] = [A^-]$), the pH of the solution will be identical to the pK of the acid. Thus once the titration curve has been plotted, the pK of the acid can be estimated by inspection.

The following two principles govern the detailed shape of a titration curve:

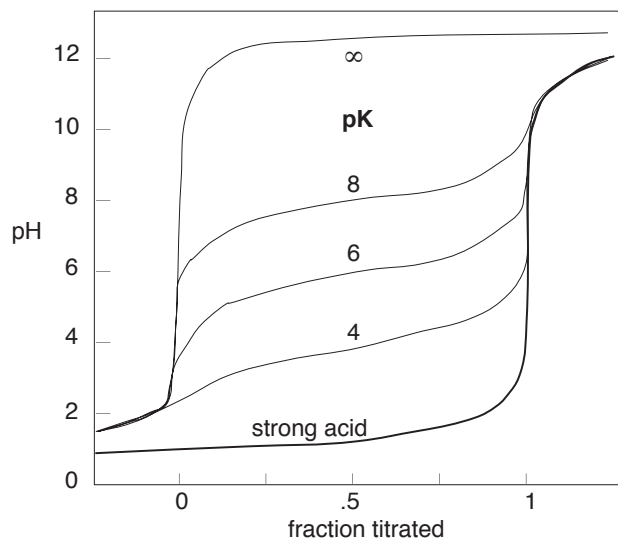


Figure 7: Titration curves of acids of various strengths

- The *stronger* the acid or base, the greater will be the slope of the curve near the equivalence point;
- The *weaker* the acid or base, the greater will the deviation of the pH from neutrality at the equivalence point.

It is important to understand the reasons for these two relations. The second is the simplest to explain. Titration of an acid HA results in a solution of NaA; that is, a solution of the conjugate base A^- . Being a base (albeit a weak one), it will react with water to yield an excess of hydroxide ions, leaving a slightly alkaline solution. Titration of a weak base with an acid will have exactly the opposite effect.

The extent of the jump in the pH at the equivalence point is determined by a combination of effects. In the case of a weak acid, for example, the initial pH is likely to be higher, so the titration curve starts higher. Further, the weaker the acid, the stronger will be its conjugate base, so the higher will be the pH at the equivalence point. These two factors raise the bottom part of the titration curve. The upper extent of the curve is of course limited by the concentration and strength of the titrant.

4.2 Observation of equivalence points

There will be as many equivalence points as there are replaceable hydrogens in an acid, but some may not correspond to a noticeable rise in the pH. In general, there are two requirements for a jump in the pH to occur:

1. The successive K_a s must differ by several orders of magnitude;
2. The pH of the equivalence point must not be very high or very low.

Polyprotic acids The effect of the first point is seen by comparing the titration curves of two diprotic acids, sulfurous and succinic. The appearance of only one equivalence point in the latter is a consequence of the closeness of the first and second acid dissociation constants. The pK_a s of sulfurous acid are sufficiently far apart that its titration curve can be regarded as the superposition of those for two independent

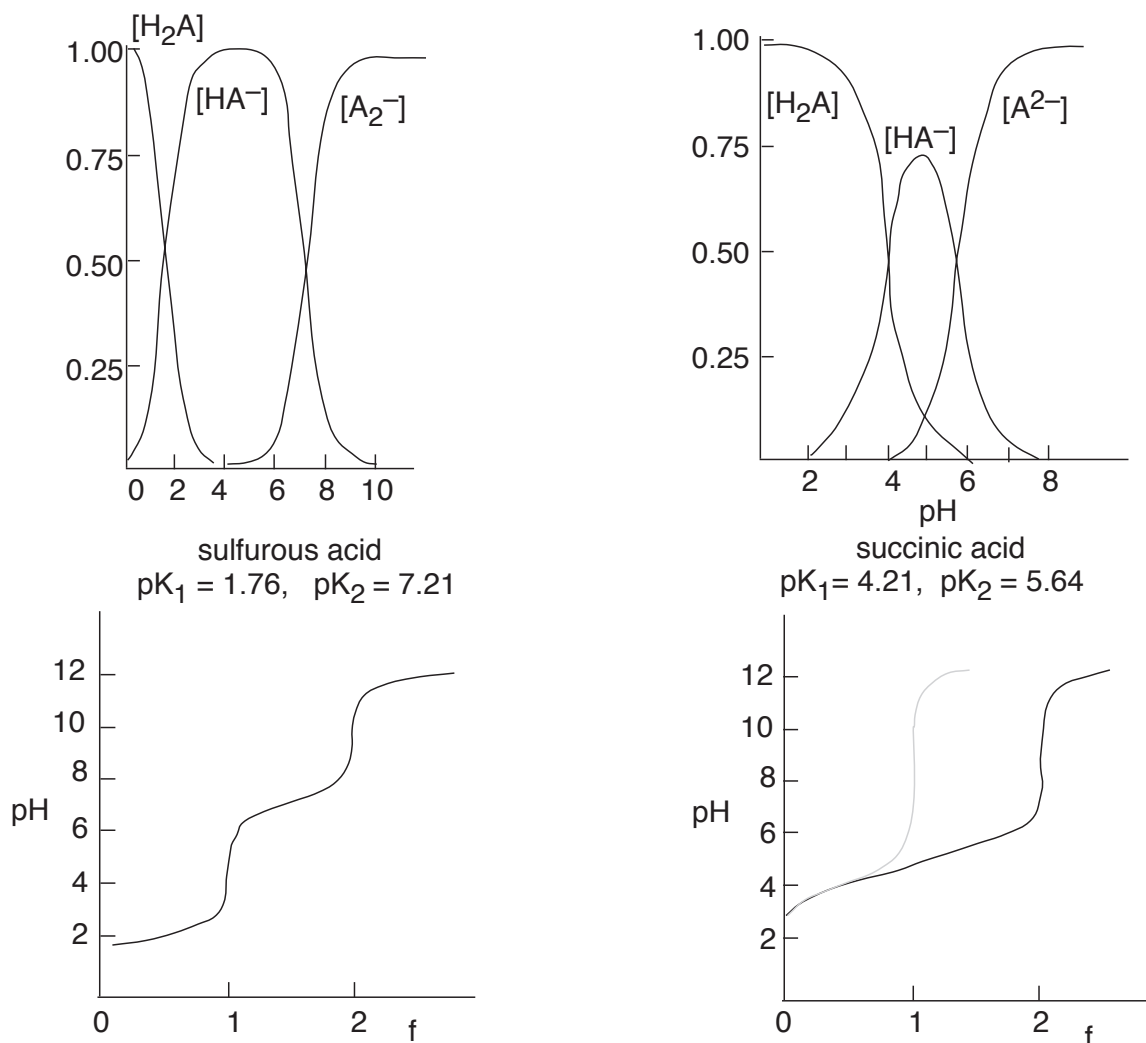


Figure 8: Distribution and titration curves for sulfurous and succinic acids

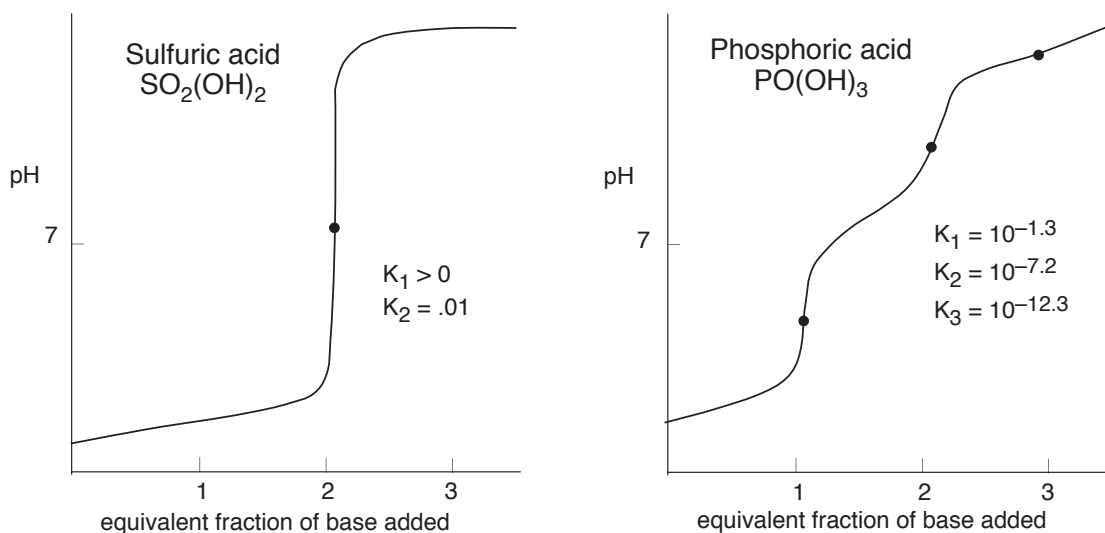


Figure 9: Titration curves with end points missing

monoprotic acids having the corresponding K_a s. This reflects the fact that the two acidic $-\text{OH}$ groups are connected to the same central atom, so that the local negative charge that remains when HSO_3^- is formed acts to suppress the second dissociation step.

In succinic acid, the two $-\text{COOH}$ groups are physically more separated and thus tend to dissociate independently⁸. Inspection of the species distribution curves for succinic acid in Fig. 8 reveals that the fraction of the ampholyte HA^- can never exceed 75 percent. That is, there is no pH at which the reaction $\text{H}_2\text{A} \rightarrow \text{HA}^-$ can be said to be “complete” while at the same time the second step $\text{HA}^- \rightarrow \text{A}^{2-}$ has occurred to only a negligible extent. Thus the rise in the pH that would normally be expected as HA^- is produced will be prevented by consumption of OH^- in the second step which will be well underway at that point; only when all steps are completed and hydroxide ion is no longer being consumed will the pH rise.

Two other examples of polyprotic acids whose titration curves whose shapes do not reveal all of the equivalence points are sulfuric and phosphoric acids (Fig. 9). Owing to the leveling effect, the apparent K_{a1} of H_2SO_4 is so close to $K_{a2} = 0.01$ that the effect is the same as in succinic acid, so only the second equivalence point is detected. In phosphoric acid, the third equivalence point is obscured because of low acid strength of the HPO_4^- ion for the reasons described below.

Very weak acids Notice, in Fig. 7, that the titration curve for $\text{p}K_a = 8$ has almost no steep part; extrapolation to $\text{p}K_a = 10$ would yield a curve having no inflection point at all in the equivalence region. Thus it is not possible to detect the equivalence point in the titration of boric acid ($\text{p}K_a = 9.3$) or of other similarly weak acids from the shape of the titration curve. The problem here is that aqueous solutions are buffered against pH change at very low and very high pH ranges, as is clearly evident from the topmost plot of Fig. 7 which refers to a solution of an “infinitely weak” acid; that is, essentially of pure water. At these extremes of pH the concentrations of H_3O^+ and of OH^- are sufficiently great that a competing buffer system (either $\text{H}_3\text{O}^+/\text{H}_2\text{O}$ or $\text{H}_2\text{O}/\text{OH}^-$, depending on whether the solution is highly acidic or highly alkaline) comes into play.

⁸It can be shown that in the limit of large n , the ratio of K_1/K_2 for a symmetrical dicarboxylic acid $\text{HOOC}-(\text{CH}_2)_n-\text{COOH}$ converges to a value of 4.

| indicator | acid color | alkaline color | pH color change range |
|-----------------|------------|----------------|-----------------------|
| methyl violet | yellow | violet | 0 - 2 |
| methyl orange | red | yellow | 3.1 - 4.4 |
| methyl red | red | yellow | 4.2 - 6.2 |
| bromthymol blue | yellow | blue | 6.0 - 7.6 |
| phenolphthalein | colorless | red | 8.0 - 9.8 |

Table 3: Some common acid-base indicators

4.3 Detection of the equivalence point

Whether or not the equivalence point is revealed by a distinct “break” in the titration curve, it will correspond to a unique hydrogen ion concentration which can be calculated in advance. The pH of a solution can be measured directly by means of a *pH meter*⁹. In modern analytical technique the pH meter is connected to a computer which also controls the addition of base. The computer plots the titration curve and differentiates it; when $d^2\text{pH}/d(\text{volume of titrant})^2 = 0$, the equivalence point has been reached and the titration is stopped.

For less exacting determinations one can employ an *indicator* dye, which is a second acid-base system in which the protonated and deprotonated forms have different colors and whose $\text{p}K_a$ is close to the pH expected at the equivalence point. If the acid being titrated is not a strong one, it is important to keep the indicator concentration as low as possible in order to prevent its own consumption of OH^- from distorting the titration curve.

The observed color change of an indicator does not take place sharply, but occurs over a range of about 1.5 to 2 pH units. Indicators are therefore only useful in the titration of acids and bases that are sufficiently strong to show a definite break in the titration curve.

⁹The pH meter detects the voltage produced when the H^+ ions in the solution displace Na^+ ions from a thin glass membrane that is dipped into the solution.

5 Acid- and base neutralizing capacity

Suppose you are given two unlabeled solutions: a $10^{-4} M$ solution of KOH whose pH is 11, and a solution made by acidifying a $.01 M$ solution of Na_2CO_3 until its pH is 11. How would you tell which is which? One way would be to titrate each solution with a strong acid such as HCl; you would compare the amount of HCl required to bring the pH of each solution to some arbitrary reference value, not necessarily 7. If you think about it, it should be apparent that considerably more HCl would be required to titrate the carbonate solution.

This example illustrates an important principle of acid-base chemistry: the pH does not tell the whole story. As a measure of the effective proton concentration, the pH expresses only the *intensity* aspect of acidity; as such, pH is not conserved when the temperature, density, or ionic strength of a solution is changed, or when the concentration is altered.

The corresponding *capacity* factor would be conserved under the above changes, and represents the number of moles per litre of strong acid or base required to bring the system to some arbitrary proton activity— that is, to a given pH— usually one corresponding to the equivalence point in a titration. In its simplest form, this capacity factor is known as the *acid neutralizing capacity*, denoted [ANC].

In order to employ this concept for a solution of an acid or base in water, it is necessary to identify all species containing more protons and all containing fewer protons than the initial components, and then take the difference between them. As an example, consider a solution of the acid HA in water. The two proton-deficient species possible in such a solution are the conjugate base A^- and OH^- . These two species are capable of accepting protons and are therefore the source of acid neutralizing capacity. However, any H_3O^+ ions already present in the solution will detract from the [ANC], so we need to subtract this quantity:

$$[\text{ANC}] = [\text{A}^-] + [\text{OH}^-] - [\text{H}^+] = C_a\alpha_1 + [\text{OH}^-] - [\text{H}^+] \quad (57)$$

[ANC] expresses the net deficiency of protons with respect to the reference level of HA and H_2O . In other words, [ANC] is the number of moles per litre of protons that must be added to fill all the proton-empty levels up to HA.

Although [ANC] can assume negative values, it is customary to use another quantity, [BNC] in this region. Base-neutralizing capacity is also known as the *acidity*. [BNC] measures the quantity of protons that must be removed (by reaction with strong base) in order to empty all proton levels down to and including HA, thus restoring the system to A^- and H_3O^+ .

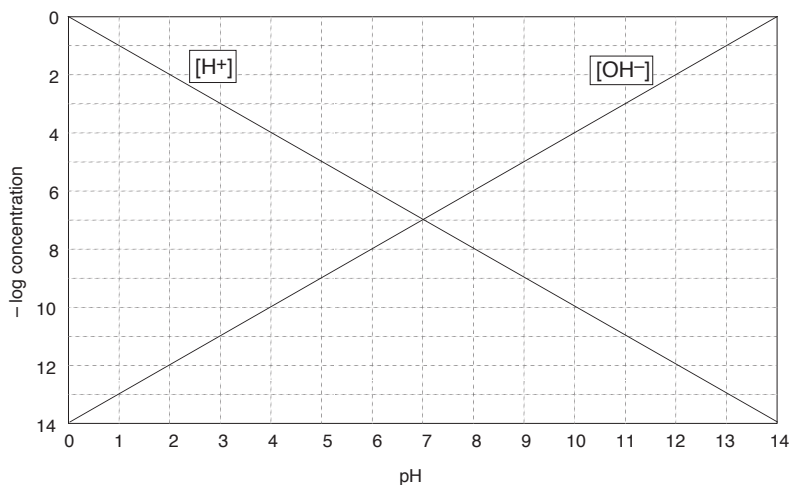
$$[\text{BNC}] = [\text{HA}] + [\text{H}^+] - [\text{OH}^-] = [\text{A}^-]\alpha_0 + [\text{H}^+] - [\text{OH}^-] \quad (58)$$

Problem Example 9

Find the [ANC] of a solution of

1. $0.01 M$ HCl: $[\text{A}^-]\alpha_1 + [\text{OH}^-] - [\text{H}^+] = (.01)(1) - .01 = \underline{0.0 M}$
2. $.01 M$ NaOH: $(.01)(0) + .01 - 0 = \underline{.01 M}$
3. $.01 M$ acetic acid at $\text{pH} = \text{p}K_a = 4.7$; $(.01)(.5) - 2 \times 10^{-5} \approx \underline{.005 M}$

Comment: Notice that whereas *acidic* and *alkaline* are mutually exclusive attributes, there is nothing illogical about a solution simultaneously possessing *acidity* and *alkalinity*, as illustrated in the third example above.

Figure 10: Basic log C vs pH plot showing $[\text{H}_3\text{O}^+]$ and $[\text{OH}^-]$

6 Graphical treatment of acid-base problems

In principle, the concentrations of all species in a monoprotic acid-base system can be found by solving the appropriate cubic equation. Although simplifications are often possible that reduce this to a quadratic or sometimes only a first-order equation, there is still an element of mathematical complexity that tends to get in the way of a real understanding of what is going on in such a solution.

6.1 Log- C vs pH plots

There is an alternative method that, while lacking precision, affords one a far clearer view of the relationships between the various species related to a given acid-base system. This starts out with the graph shown in Fig. 10. This graph is no more than a definition of pH and pOH; for example, when the pH is 4, $-\log[\text{H}_3\text{O}^+] = 4$. (Notice that the ordinate is the *negative* of the log concentration, so the smaller numbers near the top of the scale refer to larger concentrations.)

You should be able to construct this kind of graph from memory; all you need for the two straight lines are three points: the two at the top (0,0) and (14,0), and the other at (7,7) where the two lines intersect; let us hope that you understand the significance of this third point!

The graph of Fig. 10 is of no use by itself, but it forms the basis for the construction of other graphs specific to a given acid-base system. For example, suppose that we want to see how the species concentrations vary with pH in a 0.001 M solution of acetic acid, $K_a = 10^{-4.74}$. The graph in the top part of Fig. 11 describes this system. The H_3O^+ and OH^- log concentration lines are the same ones that we saw earlier. The other two lines show how the concentrations of CH_3COOH ("HAc") and of the acetate ion vary with the pH of the solution.

Locating the lines on the graph

How can we construct the plots for $[\text{HAc}]$ and $[\text{Ac}^-]$? It is easier than you might think. If you look carefully at Fig. 11a, you will observe that each line is horizontal at the top, and then bends to become diagonal. There are thus three parameters that define these two lines: the location of their top, horizontal parts, their crossing points with the other lines, and the slopes of their diagonal parts.

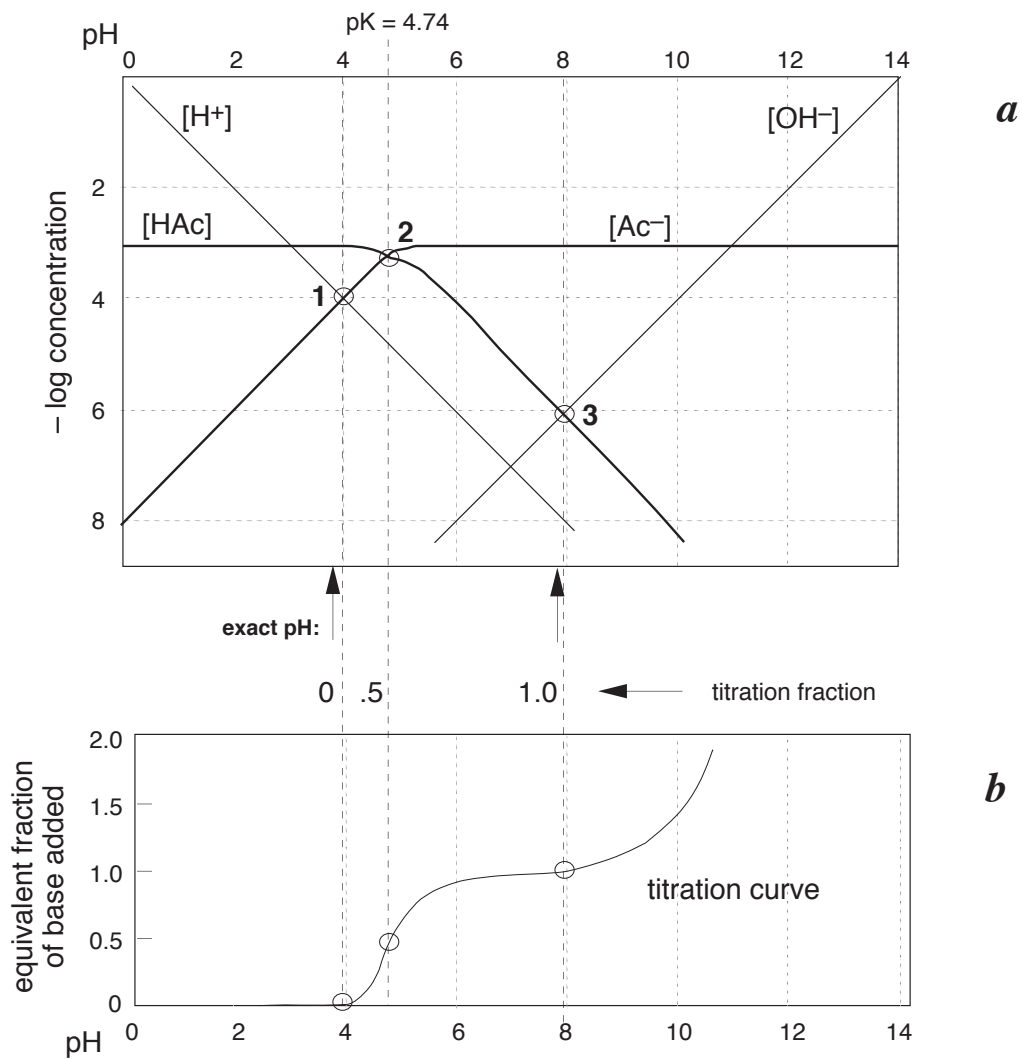


Figure 11: $\log C$ vs pH and titration curve for a $10^{-3} M$ solution of acetic acid

The horizontal sections of these lines are placed at 3 on the ordinate scale, corresponding to the nominal acid concentration of $10^{-3} M$. This value corresponds to

$$C_a = [\text{HAc}] + [\text{Ac}^-]$$

which you will recognize as the mass balance condition; $[\text{A}^-]$ is the nominal “acid concentration” of the solution, and is to be distinguished from the concentration of the actual acidic species HAc.

At low pH values (strongly acidic solution) the acetate species is completely protonated, so $[\text{HAc}] = 10^{-3}$ and $[\text{Ac}^-] = 0$. Similarly, at high pH, $-\log[\text{Ac}^-] = 3$ and $[\text{HAc}] = 0$. If the solution had some other nominal concentration, such as $0.1 M$ or $10^{-5} M$, we would simply move the pair of lines up or down.

The diagonal parts of the lines have slopes of equal magnitude but opposite sign. It can easily be shown that these slopes $d\log[\text{HAc}]/d\text{pH}$ etc. are ± 1 , corresponding to the slopes of the $[\text{OH}^-]$ and $[\text{H}_3\text{O}^+]$ lines. Using the latter as a guide, the diagonal portions of lines 3 and 4 can easily be drawn.

The crossing point of the plots for the acid and base forms corresponds to the condition $[\text{HAc}] = [\text{Ac}^-]$. You already know that this condition holds when the pH is the same as the $\text{p}K_a$ of the acid, so the pH coordinate of the crossing point must be 4.75 for acetic acid. The vertical location of the crossing point is found as follows: When $[\text{HAc}] = [\text{Ac}^-]$, the concentration of each species must be $\frac{1}{2}[\text{A}^-]$, or in this case $0.0005 M$. The logarithm of $\frac{1}{2}$ is 0.3, so a 50% reduction in the concentration of a species (from an initial value of $[\text{A}^-]$) will shift its location down on the log concentration scale by 0.3 unit. The crossing point therefore falls at a $\log-C$ value of $(-3) - .3 = -3.3$,

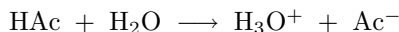
By following this example, you should be able to construct a similar diagram for any monoprotic acid, weak or strong; the only numbers you need are the $\text{p}K_a$ of the acid, and its nominal concentration $[\text{A}^-]$. The resulting graph will provide a reasonably precise indication of the concentrations of all four related species in the solution over the entire pH range. The only major uncertainty occurs within about one pH unit of the $\text{p}K_a$, where the lines undergo changes of slope from 0 (horizontal) to ± 1 .

6.2 Estimating the pH on $-\log C$ vs pH diagrams

Of special interest in acid-base chemistry are the pH values of a solution of an acid and of its conjugate base in pure water; as you know, these correspond to the beginning and equivalence points in the titration of an acid with a strong base.

pH of an acid in pure water

Except for the special cases of extremely dilute solutions or very weak acids in which the autoprotolysis of water is a major contributor to the $[\text{H}_3\text{O}^+]$, the pH of a solution of an acid in pure water will be determined largely by the extent of the reaction

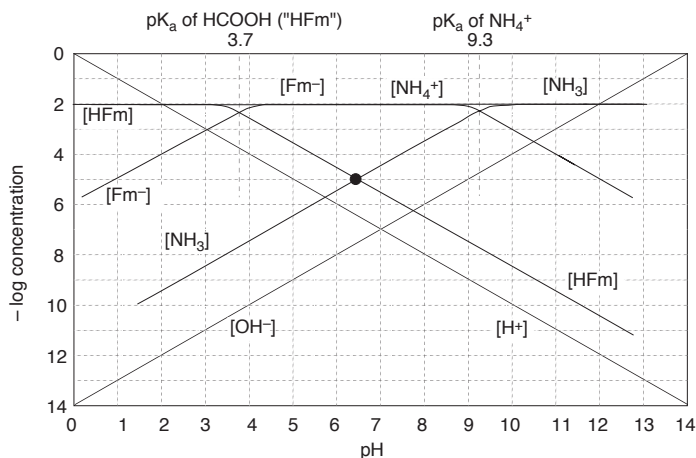


so that at equilibrium, the approximate relation $[\text{H}_3\text{O}^+] = [\text{Ac}^-]$ will hold. The equivalence of these two concentrations corresponds to the point labeled **1** in Fig. 11a; this occurs at a pH of about 3.7, and this is the pH of a $0.001 M$ solution of acetic acid in pure water.

pH of a solution of the conjugate base

Now consider a 0.001 molar solution of sodium acetate in pure water. This, you will recall, corresponds to the composition of a solution of acetic acid that has been titrated to its equivalence point with sodium hydroxide. The acetate ion, being the conjugate base of a weak acid, will undergo hydrolysis according to





This diagram is just the superposition of the separate diagrams for the ammonia and formic acid systems. In a solution of ammonium formate, stoichiometry requires that



This condition corresponds to the point indicated on the graph. Compare the pH of this crossing point with the result in the Problem Example on page 24.

Figure 12: Log- C diagram for 0.01 M ammonium formate

As long as we can neglect the contribution of OH^- from the autoprotolysis of the solvent, we can expect the relation $[\text{HAc}] = [\text{OH}^-]$ to be valid in such a solution. The equivalence of these two concentrations corresponds to the intersection point **3** in Fig. 11a; a 0.001 molar solution of sodium or potassium acetate should have a pH of about 8.

Titration curves

If you have carried out similar calculations mathematically, you will appreciate the simplicity and utility of this graphical approach. Even without graph paper and a ruler, you should be able to sketch out a graph of this kind on the back of an envelope, and without recourse to any calculations at all make estimates of the pH of a solution of any pure acid and its conjugate base to an accuracy of about one pH unit.

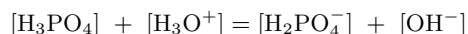
Besides being a useful tool for rough estimations of pH, the log- C plot provides considerable insight into the factors that determine the shape of the titration curve. As shown in the lower part of Fig. 11, you can use the log- C vs pH diagram to construct an approximate titration curve.

Polyprotic acids

Whereas pH calculations for solutions of polyprotic acids become quite complex, the log- C plots for such systems simply contain a few more lines but are no more difficult to construct than those for monoprotic acids. Phosphoric acid H_3PO_4 is a triprotic system that is widely used as a buffering agent. Each of the pK_a 's in Fig. 13 corresponds to a crossing point of the lines depicting the concentrations of a pair of conjugate species.

The only really new feature is that the slopes of plots change from ± 1 to ± 2 and then to ± 3 as they cross pK_a values successively more removed from the pH range at which the particular species predominates. When the slopes reach ± 3 the species concentrations are generally insignificant.

The pH of solutions of the individual phosphate species can be estimated by simplifying the appropriate proton balance expressions. For H_3PO_4 the relation



yields $[\text{H}_2\text{PO}_4^{2-}] = [\text{OH}^-]$ which corresponds to point **1** in Fig. 13. Similarly, for a solution of $\text{Na}_2\text{H}_2\text{PO}_4$ we have



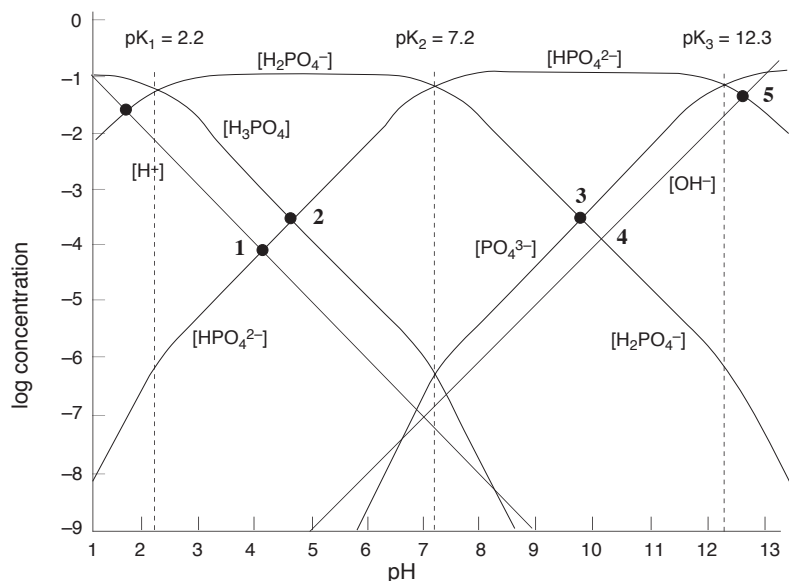
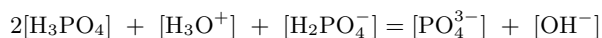


Figure 13: Log- C diagram for the phosphate system

which gives $[H_3PO_4] = [HPO_4^{2-}]$ after smaller terms are eliminated (2). Na_3PO_4 is treated straightforwardly and corresponds to point 5. The case of Na_2HPO_4 is not quite so simple, however; the proton-balance expression



cannot be so greatly simplified because the two terms on the right will be comparable. The approximation



does not correspond to any crossing point in Fig. 13 but falls at a pH slightly to the left of 3.

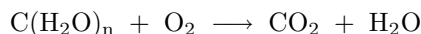
7 Acid-base chemistry in physiology

Acid-base chemistry plays a crucial role in physiology, both at the level of the individual cell and of the total organism. The reasons for this are twofold:

- Many of the major chemical components of an organism can themselves act as acids and/or bases. Thus *proteins* contain both acidic and basic groups, so that their shapes and their functional activities are highly dependent on the pH.
- Virtually all important metabolic processes involve the uptake or release of hydrogen ions. The very act of being alive tends to change the surrounding pH (usually reducing it); this will eventually kill the organism in the absence of buffering mechanisms.

About two-thirds of the weight of an adult human consists of water. About two-thirds of this water is located within cells, while the remaining third consists of extracellular water, mostly interstitial fluid that bathes the cells, and the blood plasma. The latter, amounting to about 5% of body weight (about 5 L in the adult), serves as a supporting fluid for the blood cells and acts as a means of transporting chemicals between cells and the external environment. It is basically a 0.15 M solution of NaCl containing smaller amounts of other electrolytes, the most important of which are HCO_3^- and protein anions.

Respiration, the most important physiological activity of a cell, is an acid-producing process. Carbohydrate substances are broken down into carbon dioxide, and thus carbonic acid:



Interestingly, ingestion of “acidic” foods can make the body more alkaline. This comes about because the weak organic acids in such foods are partly in the form of sodium or potassium salts K^+A^- . In order to maintain charge balance, some of the CO_2 produced by normal metabolism of these food acids must be converted to bicarbonate (that is, K^+HCO_3^-) which is a weak base.

7.1 Maintenance of acid-base balance

It is remarkable that the pH of most cellular fluids can be kept within such a narrow range, given the large number of processes that tend to upset it. This is due to the exquisite balance between a large number of interlinked processes operating at many different levels.

Acid-base balance in the body is maintained by two general mechanisms: selective *excretion* of acids or bases, and by the *buffering* action of weak acid-base systems in body fluids.

- Over a 24-hour period, the adult human eliminates the equivalent of about 20-40 moles of H^+ by way of the lungs in the form of CO_2 . In addition, the kidneys excrete perhaps 5% of this amount of acid, mostly in the form of H_2PO_4^- and NH_4^+ . Owing to their electric charges, these two species are closely linked to salt balance with ions such as Na^+ or K^+ and Cl^- .
- The major buffering system in the body is the carbonate system, which exists mainly in the form of HCO_3^- at normal physiological pH. Secondary buffering action comes from phosphate, from proteins and other weak organic acids, and (within blood cells), the hemoglobin.

7.2 Disturbances of acid-base balance

Deviations of the blood plasma pH from its normal value of 7.4 by more than about ± 0.1 can be very serious. These conditions are known medically as *acidosis* and *alkalosis*. They can be caused by metabolic disturbances such as diabetes and by kidney failure (in which excretion of H_2PO_4^- , for example, is inhibited).

[From J. Zobrist and W. Stumm, Forschung und Technik, Neue Zürcher Zeitung, June 1979.]

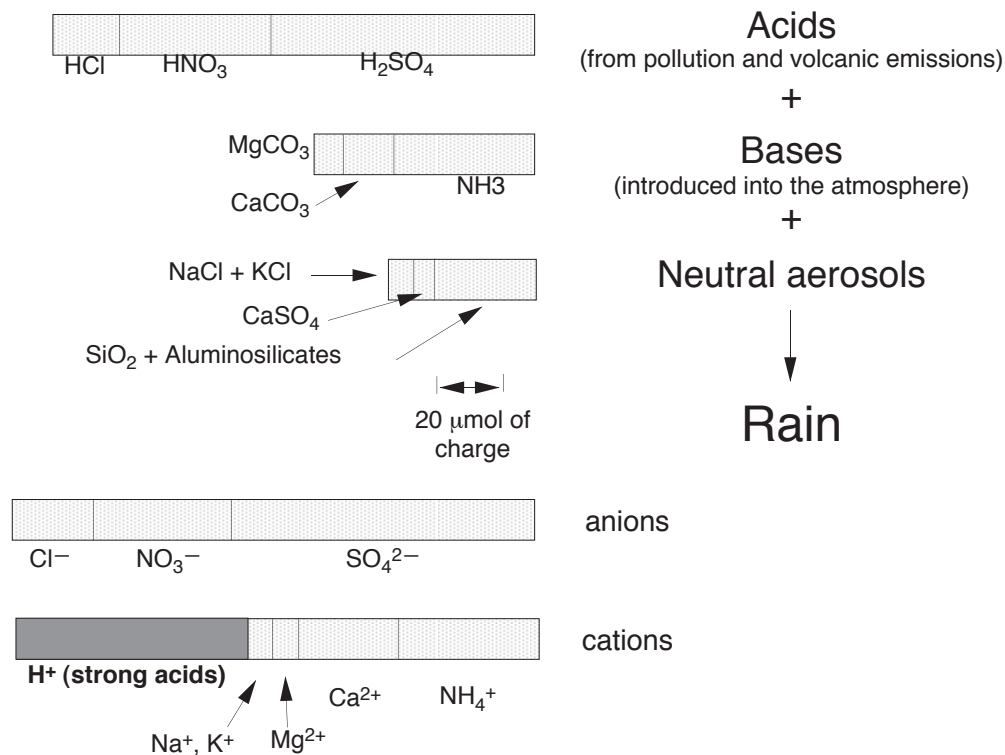


Figure 14: Origin of acid rain

Numerous other processes lead to temporary unbalances. Thus *hyperventilation*, which can result from emotional upset, leads to above-normal loss of CO₂, and thus to alkalosis. Similarly, *hypoventilation* can act as a compensatory mechanism for acidosis. On the other hand, retention of CO₂ caused by bronchopneumonia, for example, can give rise to acidosis. Acidosis can also result from diarrhea (loss of alkaline fluid from the intestine), while loss of gastric contents by vomiting promotes alkalosis.

8 Acid rain

As will be explained in the next section on the carbonate system, *all* rain is “acidic” in the sense that exposure of water to atmospheric carbon dioxide results in the formation of carbonic acid H₂CO₃ which will eventually reduce the pH to 5.7.

The term *acid rain* is therefore taken to mean rain whose pH is controlled by substances other than CO₂ and which can lower the pH into the range of 3-4. The major culprits are sulfuric, nitric, and hydrochloric acids. Most of the H₂SO₄ comes from the photooxidation of SO₂ released from the burning of fossil fuels and from industrial operations such as smelting.

As shown in Fig. 14, the atmosphere receives both acidic and basic substances from natural sources (volcanic emissions, salt spray, windblown dust and microbial metabolism) as well as from pollution. These react in a kind of gigantic acid-base titration to give a solution in which hydrogen ions must predominate in order to maintain charge balance.

| <i>source</i> | <i>moles C × 10¹⁸</i> | <i>relative to atmosphere</i> |
|--|----------------------------------|-------------------------------|
| sediments | | |
| carbonate | 1530 | 28,500 |
| organic carbon | 572 | 10,600 |
| land | | |
| organic carbon | .065 | 1.22 |
| ocean | | |
| CO ₂ + H ₂ CO ₃ | .018 | 0.3 |
| HCO ₃ ⁻ | 2.6 | 48.7 |
| CO ₃ ²⁻ | .33 | 6.0 |
| dead organic | .23 | 4.4 |
| living organic | .0007 | .01 |
| atmosphere | | |
| CO ₂ | .0535 | 1.0 |

Table 4: Distribution of carbon on the Earth.

9 The carbonate system

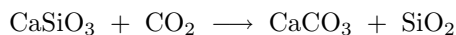
Of all the acid-base systems, none is more universally important than the one encompassing CO₂, HCO₃⁻, and CO₃²⁻. Interconversions between these species cover a huge scale of nature, from the operation of the global carbon cycle to the pH balance of blood and cellular fluids.

9.1 The geochemical carbon cycle

The carbonate system encompasses virtually all of the environmental compartments— the atmosphere, hydrosphere, biosphere, and major parts of the lithosphere. The complementary processes of photosynthesis and respiration drive a global cycle in which carbon passes slowly between the atmosphere and the lithosphere, and more rapidly between the atmosphere and the oceans.

9.2 Carbon dioxide in the atmosphere

CO₂ has probably always been present in the atmosphere in the relatively small absolute amounts now observed. Precambrian limestones, possibly formed by reactions with rock-forming silicates, e.g.



have likely had a moderating influence on the CO₂ abundance throughout geological time.

The volume-percent of CO₂ in dry air is .032%, leading to a partial pressure of 3×10^{-4} ($10^{-3.5}$) atm. In a crowded and poorly-ventilated room, P_{CO_2} can be as high as 100×10^{-4} atm.

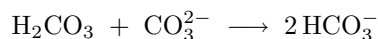
About 54E14 moles per year of CO₂ is taken from the atmosphere by photosynthesis, divided about equally between land and sea. Of this, all except .05% is returned by respiration (mostly by microorganisms); the remainder leaks into the slow, sedimentary part of the geochemical cycle where it can remain for thousands to millions of years.

Since the advent of large-scale industrialization around 1860, the amount of CO₂ in the atmosphere has been increasing. Most of this has been due to fossil-fuel combustion; in 1966, about 3.6E15 g of C was released to the atmosphere; this is about 12 times greater than the estimated natural removal of

carbon into sediments. The large-scale destruction of tropical forests, which has accelerated greatly in recent years, is believed to exacerbate this effect by removing a temporary sink for CO₂.

About 30-50% of the CO₂ released into the atmosphere by combustion remains there; the remainder enters the hydrosphere and biosphere. The oceans have a large absorptive capacity for CO₂ by virtue of its transformation into bicarbonate and carbonate in a slightly alkaline aqueous medium, and they contain about 60 times as much inorganic carbon as is in the atmosphere. However, efficient transfer takes place only into the topmost (100 m) wind-mixed layer, which contains only about one atmosphere equivalent of CO₂; mixing time into the deeper parts of the ocean is of the order of 1000 years. For this reason, only about ten percent of added CO₂ is taken up by the oceans.

Most of the carbon in the oceans is in the form of bicarbonate, as would be expected from the pH which ranges between 7.8 and 8.2. In addition to atmospheric CO₂, there is a carbon input to the ocean from streams. This is in the form of CO₃²⁻ which derives from the weathering of rocks and terrestrial carbonate sediments, and gives rise to the acid-base reaction



which can be considered to be the source of bicarbonate in seawater. In this sense, the ocean can be considered the site of a gigantic acid-base titration in which atmospheric acids (mainly CO₂ but also SO₂, HCl, and other acids of volcanic origin) react with bases that originate from rocks and are introduced through carbonate-bearing streams or in windblown dust.

9.3 Dissolution of CO₂ in water

Carbon dioxide is slightly soluble in water:

| | | | | |
|------|------|-------|-------|-----------|
| 0 °C | 4 °C | 10 °C | 20 °C | |
| .077 | .066 | .054 | .039 | mol/litre |

Henry's law is followed up to a CO₂ pressure of about 5 atm:

$$[\text{CO}_2] = .032 P_{\text{CO}_2} \quad (59)$$

“Dissolved carbon dioxide” consists mostly of the hydrated oxide CO₂(aq) together with a small proportion of carbonic acid:

$$[\text{CO}_2(\text{aq})] = 650 [\text{H}_2\text{CO}_3] \quad (60)$$

The acid dissociation constant K_1 that is commonly quoted for “H₂CO₃” is really a *composite* equilibrium constant that includes the above equilibrium.

9.4 Distribution of carbonate species in aqueous solutions

Water exposed to the atmosphere with $P_{\text{CO}_2} = 10^{-3.5}$ atm will take up carbon dioxide until, from Eq 59,

$$[\text{H}_2\text{CO}_3] = 10^{-1.5} \times 10^{-3.5} = 10^{-5} M \quad (61)$$

The carbon will be distributed between CO₂, HCO₃⁻ and CO₃²⁻ in proportions that depend on K_1 and K_2 and on the pH. The “total dissolved carbon” C_T is given by the mass balance

$$C_T = [\text{H}_2\text{CO}_3] + [\text{HCO}_3^-] + [\text{CO}_3^{2-}] \quad (62)$$

The distribution of these species as a function of pH can best be seen in the log C -pH diagram of Fig. 15. This diagram is constructed for a solution in which $C_T = 10^{-5} M$.

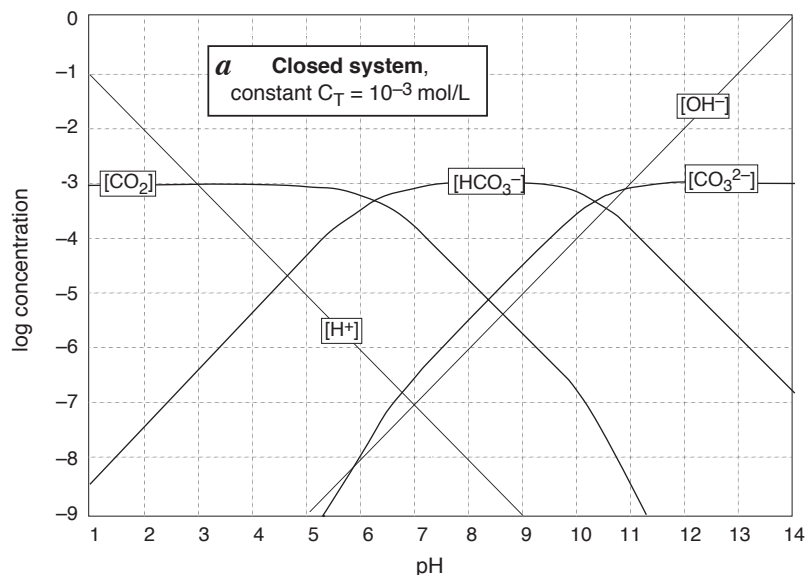


Figure 15: log C -pH diagram for a $10^{-5} M$ carbonate solution at $25^\circ C$.

It is important to note that this diagram applies only to a system in which C_T is constant. In a solution that is open to the atmosphere, this will not be the case at high pH values where the concentration of CO_3^{2-} is appreciable. Under these conditions this ion will react with H_2CO_3 and the solution will absorb CO_2 from the atmosphere, eventually resulting in the formation of a solid carbonate precipitate.

The plots of Fig. 15 can be used to predict the pH of $10^{-5} M$ solutions of carbon dioxide, sodium bicarbonate, and sodium carbonate in pure water. The pH values are estimated by using the proton balance conditions for each solution as noted below.

Solution of CO_2 or H_2CO_3

$$[H^+] = [OH^-] + [HCO_3^-] + 2[CO_3^{2-}] \quad (63)$$

which, since the solution will be acidic, is approximated by

$$[H^+] = [HCO_3^-] \quad (\text{point A}) \quad (64)$$

Solution of $NaHCO_3$

$$[H^+] + [H_2CO_3] = [CO_3^{2-}] + [OH^-] \quad (65)$$

or

$$[H_2CO_3] = [OH^-] \quad (\text{point B}) \quad (66)$$

Solution of Na_2CO_3

$$[H^+] + 2[H_2CO_3] + [HCO_3^-] = [OH^-] \quad (\text{point C}) \quad (67)$$

or

$$[HCO_3^-] = [OH^-] \quad (68)$$

(Point C)

Fig. 16 shows how the pH of solutions of pure H_2CO_3 , $NaHCO_3$ and Na_2CO_3 vary with the concentrations of these species. These pH values are of interest because they correspond to the equivalence points of the acidimetric or alkalimetric titration of carbonate-containing waters; for a natural water in equilibrium with atmospheric $[CO_2 + H_2CO_3] = 10^{-2.5} M$.

• Distribution of carbonate species in aqueous solutions

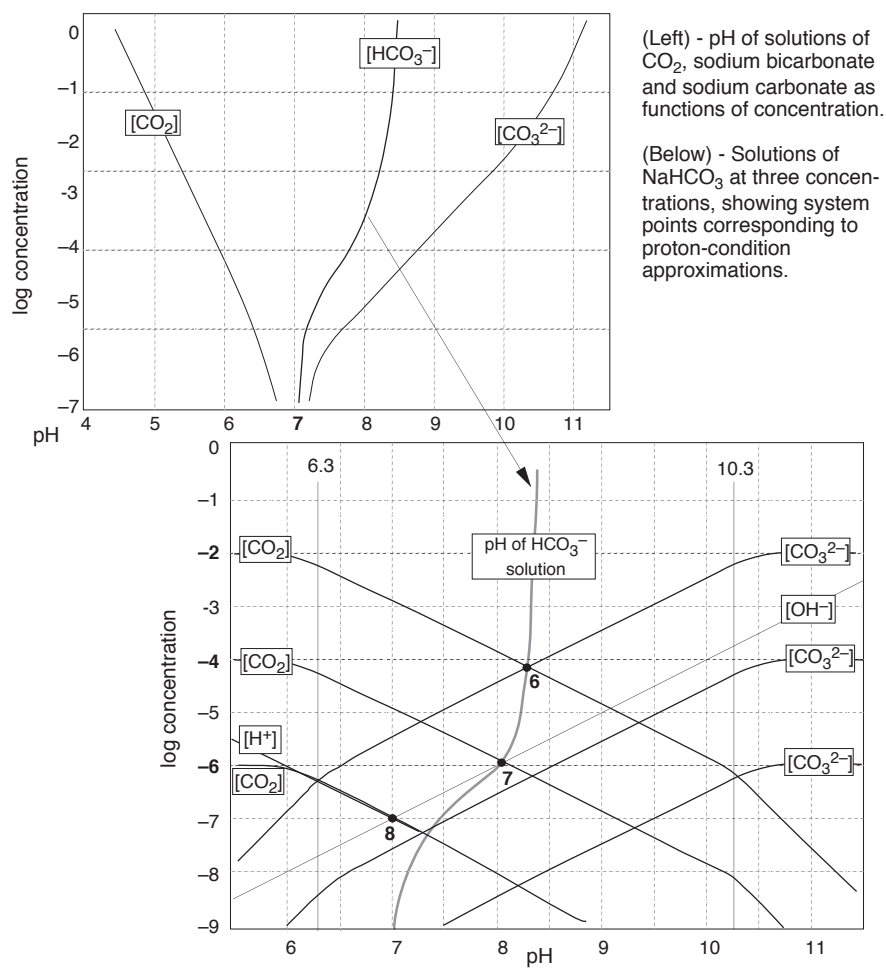


Figure 16: pH of pure solutions of carbonate species at various dilutions

9.5 Calculations on carbonate solutions

Problem Example 10

Calculate the pH of a 0.0250 M solution of CO₂ in water.

Solution: This is the same as a solution of H₂CO₃ of the same concentration. Because the first acid dissociation constant is much greater than either K_2 or K_w , we can usually treat carbonic acid solutions as if H₂CO₃ were monoprotic, so this becomes a standard monoprotic weak acid problem.

$$\frac{[\text{H}^+][\text{HCO}_3^-]}{[\text{H}_2\text{CO}_3]} = K_1 = 4.47\text{E-}7$$

Applying the usual approximation $[\text{H}^+] = [\text{HCO}_3^-]$ (i.e., neglecting the H⁺ produced by the autoprotolysis of water), the equilibrium expression becomes

$$\frac{[\text{H}^+]^2}{0.0250 - [\text{H}^+]} = 4.47\text{E-}7$$

The large initial concentration of H₂CO₃ relative to the value of K_1 justifies the further approximation of dropping the $[\text{H}^+]$ term in the denominator.

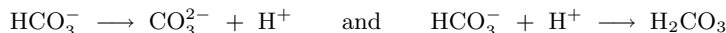
$$\frac{[\text{H}^+]^2}{0.0250} = 4.47\text{E-}7$$

$$[\text{H}^+] = 1.06\text{E-}4; \quad \text{pH} = 3.97$$

Problem Example 11

Calculate the pH of a 0.0500 M solution of sodium bicarbonate.

Solution: The bicarbonate ion HCO₃⁻, being amphiprotic, can *produce* protons and it can *consume* protons:



The total concentration of protons in the water due to the addition of NaHCO₃ will be equal to the number produced, minus the number lost; this quantity is expressed by the *proton balance*

$$[\text{H}^+] = [\text{CO}_3^{2-}] + [\text{OH}^-] - [\text{H}_2\text{CO}_3]$$

By making the appropriate substitutions (see the derivation of Eq 55) we can rewrite this in terms of $[\text{H}^+]$, the bicarbonate ion concentration and the various equilibrium constants:

$$[\text{H}^+] = \frac{K_2[\text{CO}_3^{2-}]}{[\text{H}^+]} + \frac{K_w}{[\text{H}^+]} - \frac{[\text{OH}^-][\text{HCO}_3^-]}{K_1}$$

which we rearrange to

$$[\text{H}^+]^2 = K_2[\text{HCO}_3^-] + K_w - \frac{[\text{H}^+]^2[\text{HCO}_3^-]}{K_1}$$

We solve this for $[\text{H}^+]$ by collecting terms

$$[\text{H}^+]^2 \left(1 + \frac{[\text{HCO}_3^-]}{K_1} \right) = K_2[\text{HCO}_3^-] + K_w$$

$$[\text{H}^+] = \sqrt{\frac{K_2[\text{HCO}_3^-] + K_w}{1 + \frac{[\text{HCO}_3^-]}{K_1}}}$$

This expression can be simplified in more concentrated solutions. If $[\text{HCO}_3^-]$ is greater than K_1 , then the fraction in the demoninator may be sufficiently greater than unity that the 1 can be neglected.

Similarly, recalling that $K_2 = 10^{-10.3}$, it will be apparent that K_w in the numerator will be small compared to $K_2[\text{HCO}_3^-]$ when $[\text{HCO}_3^-]$ is not extremely small. Making these approximations, we obtain the greatly simplified relation

$$[\text{H}^+] = \sqrt{K_1 K_2}$$

so that the pH is given by

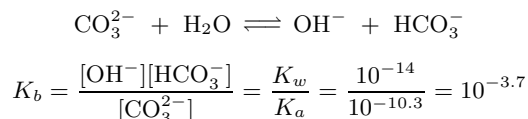
$$\text{pH} = \frac{1}{2}(\text{p}K_1 + \text{p}K_2) = \frac{1}{2}(6.3 + 10.3) = 8.3$$

Notice that under the conditions at which these approximations are valid, the pH of the solution is independent of the bicarbonate concentration.

Problem Example 12

Calculate the pH of a 0.0012 M solution of Na_2CO_3 .

Solution: The carbonate ion is the conjugate base of the weak acid HCO_3^- ($K = 10^{-10.7}$), so this solution will be alkaline. Given the concentration of this solution, the pH should be sufficiently high to preclude the formation of any significant amount of H_2CO_3 , so we can treat this problem as a solution of a monoprotic weak base:



Neglecting the OH^- produced by the autoprotolysis of water, we make the usual assumption that $[\text{OH}^-] = [\text{HCO}_3^-]$, and thus

$$K_b = \frac{[\text{OH}^-]^2}{0.0012 - [\text{OH}^-]} = 2.00\text{E-}4$$

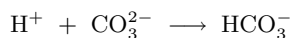
In this case the approximation $[\text{OH}^-] \approx \sqrt{K_b C_b}$ is not valid, owing to the magnitude of the equilibrium constant in relation to the carbonate ion concentration. The equilibrium expression must be solved as a quadratic and yields the root $[\text{OH}^-] = 4.0\text{E-}4$ which corresponds to $\text{pOH} = 3.4$ or $\text{pH} = 10.6$.

From the preceding example we see that soluble carbonate salts are among the stronger of the weak bases. Sodium carbonate was once known as “washing soda”, reflecting the ability of alkaline solutions to interact with and solubilize oily substances.

Problem Example 13

Calculate the pH of the solution resulting from the addition of 15.00 ml of 0.100 M hydrochloric acid to 25.00 ml of 0.0500 M sodium carbonate solution.

Solution: We are adding 1.50 millimoles of HCl to 1.25 millimoles of CO_3^{2-} , which being a base, will be completely converted into bicarbonate:

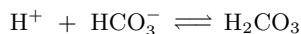


In addition, the extra 0.25 mmol of acid will convert an equivalent amount of the bicarbonate into H_2CO_3 , so the problem becomes one of determining the pH of a solution with

$$[\text{H}_2\text{CO}_3] = \frac{0.250 \text{ mmol}}{40 \text{ ml}} = 0.00625 \text{ M}$$

$$[\text{HCO}_3^-] = \frac{1.00 \text{ mmol}}{40 \text{ ml}} = 0.0250 \text{ M}$$

in which the principal equilibrium is



$$\frac{[\text{H}^+][\text{HCO}_3^-]}{[\text{H}_2\text{CO}_3]} = K_1 = 4.47\text{E-}7$$

The solution is not expected to be strongly acidic, so we can assume that the equilibrium concentration of H_2CO_3 remains at about 0.00625 M . Thus

$$\frac{[\text{H}^+](.0250)}{(.00625)} = 4.47\text{E-}7$$

from which we obtain

$$[\text{H}^+] = \frac{.00625}{.0250} \times 4.47\text{E-}7 = 1.12\text{E-}7$$

which corresponds to a pH of 6.95.
